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Mitchell

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[45] **Date of Patent:** **Mar. 17, 1987**

[54] THIN FILM CADMIUM TELLURIDE SOLAR CELL

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[73] Assignee: **Atlantic Richfield Company,** Los Angeles, Calif.

[21] Appl. No.: **790,709**

[22] Filed: **Oct. 24, 1985**

[51] **Int. Cl.⁴** **H01L 31/06**
[52] **U.S. Cl.** **136/258;** 136/256; 136/260; 136/264; 357/16; 357/30; 357/59; 357/65
[58] **Field of Search** .... 136/256, 258 PC, 260, 136/264; 357/16, 30, 59 D, 65

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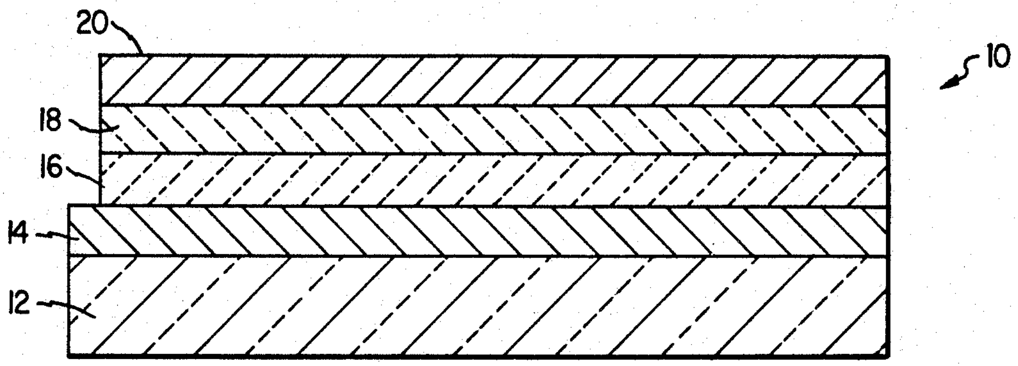
Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Robert D. Lott

[57] ABSTRACT

A phosphorous doped layer of cadmium telluride is deposited onto a conductive window layer to form a thin film cadmium telluride solar cell. Back contacts to the solar cell are made by first depositing a layer of p conductivity type lead telluride upon the cadmium telluride and then depositing the metallic back contacts onto the lead telluride.

5 Claims, 5 Drawing Figures



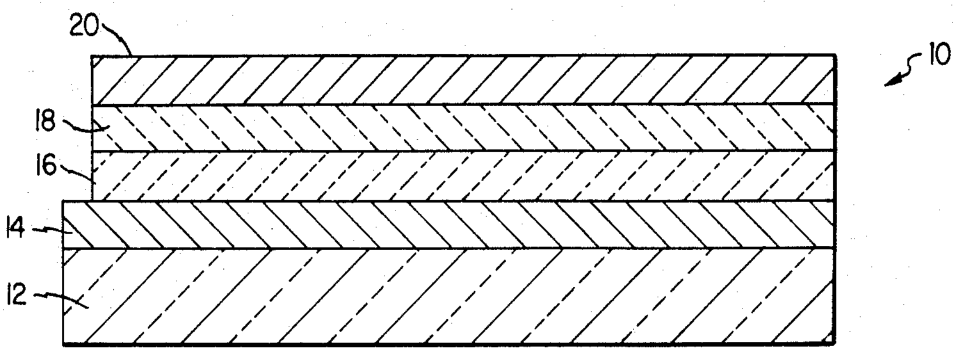


FIG. 1

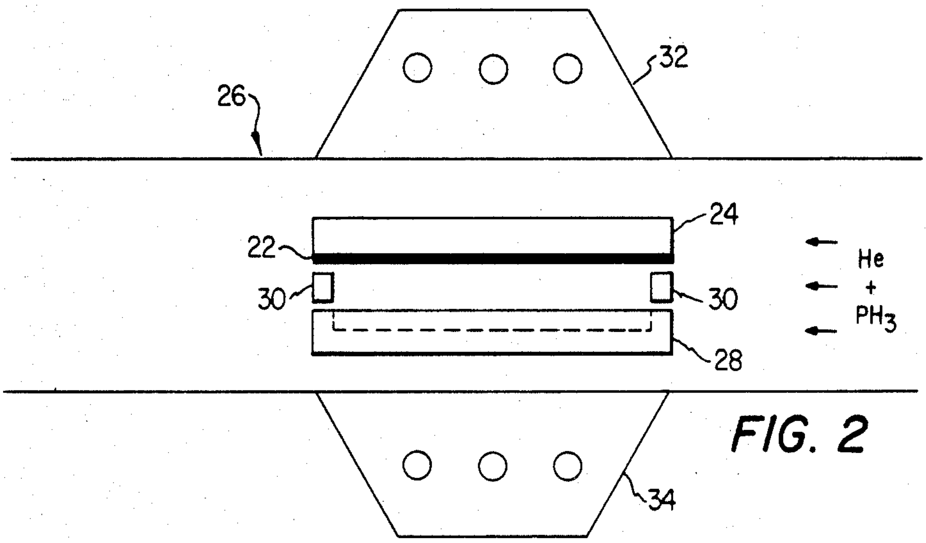


FIG. 2

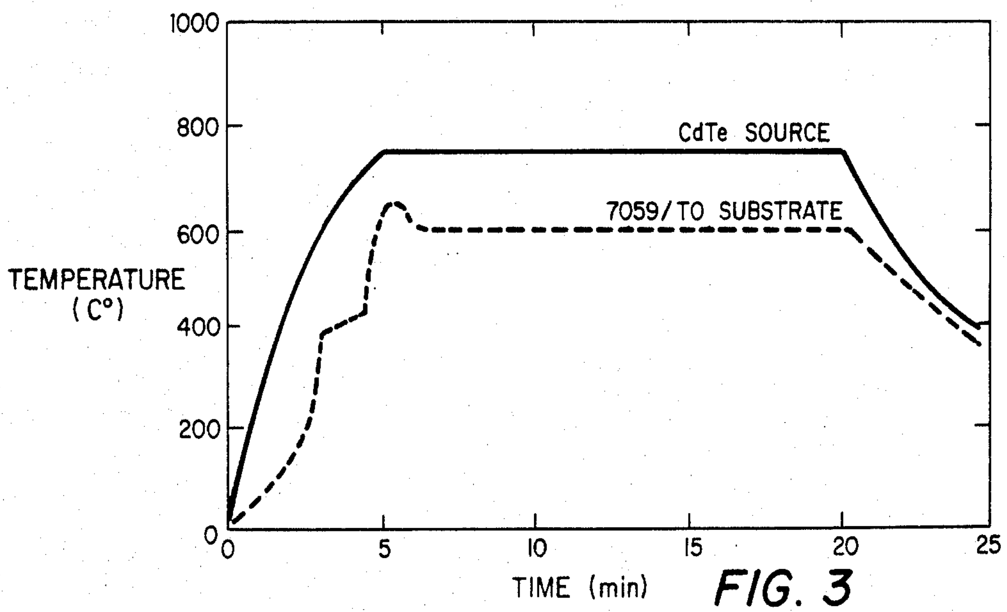
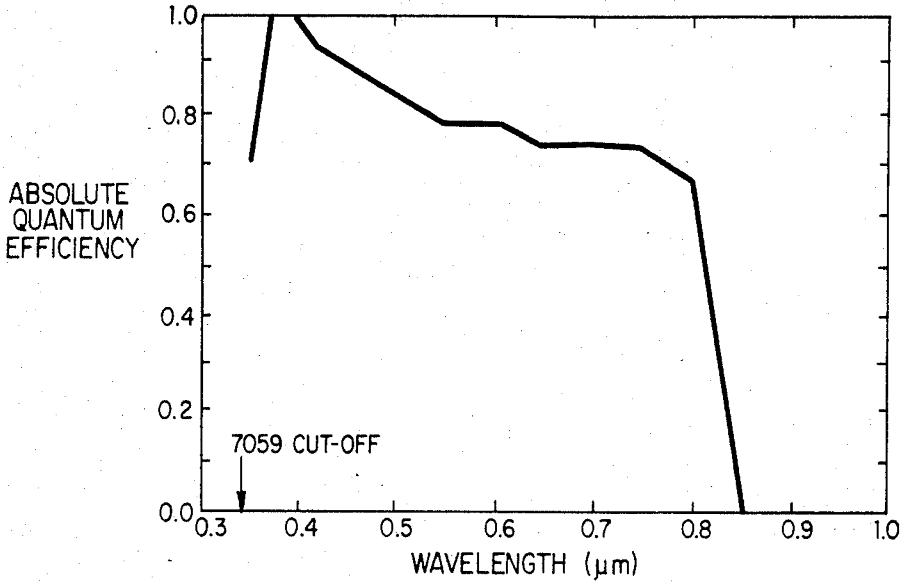


FIG. 3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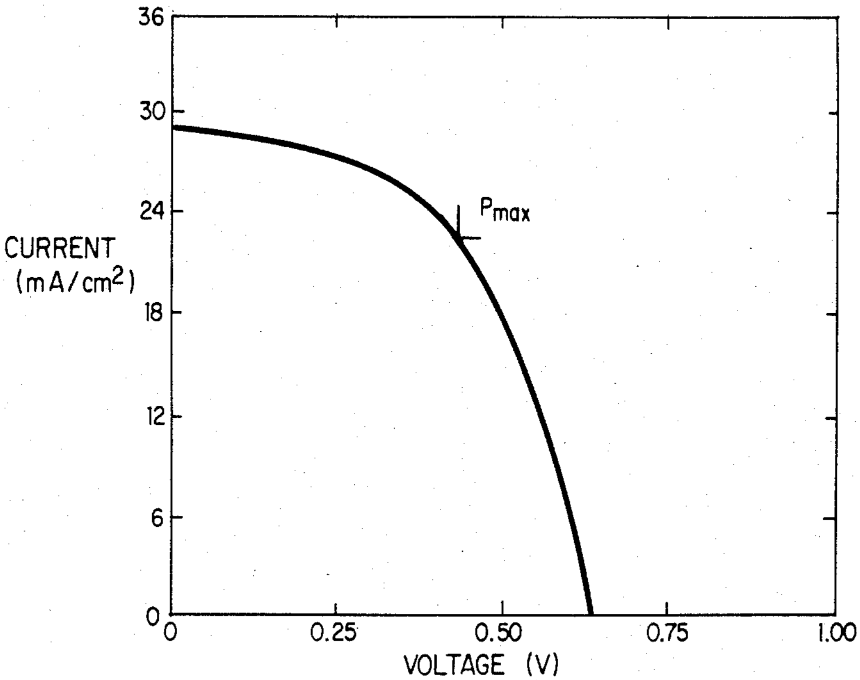
0.9
1.0
WAVELENGTH (μm)

FIG. 4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18
12
6
0
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0.50
0.75
1.00
VOLTAGE (V)

FIG. 5

THIN FILM CADMIUM TELLURIDE SOLAR CELL

BACKGROUND OF THE INVENTION

This invention relates to p-n tin oxide-cadmium telluride photovoltaic cells.

Cadmium telluride has long been identified as a strong candidate for low cost, thin film, photovoltaic applications because of its direct band gap and its ability to be doped n and p type permitting formation of a variety of junction structures, and to be deposited by a variety of techniques ranging from vacuum evaporation and chemical vapor deposition to electrodeposition and screen printing.

Photovoltaic cells using polycrystalline cadmium sulfide and cadmium telluride have been described in the past. For example U.S. Pat. No. 4,207,119 to Yuan-Sheng Tyan, which is hereby incorporated by reference, describes a cadmium sulfide/cadmium telluride solar cell in which oxygen atoms are present in the cadmium sulfide and/or cadmium telluride to improve the efficiency of the cell. A disadvantage of the examples shown in the Tyan patent is the use of low pressure conditions while depositing the cadmium telluride layers. It has also been found that the addition of oxygen must be kept low during the deposition process because the oxygen can result in substantial oxidation of the cadmium telluride source thereby suppressing the deposition process.

A problem in the past in fabricating photovoltaic cells containing cadmium telluride is the formation of low resistance, electrical contacts to the cadmium telluride layer. One prior art technique is to chemically etch the cadmium telluride to form a telluride rich P+ conductivity region at the surface, then to deposit back metallization usually using high work function metals such as gold or nickel. However, contacts made by this method have not proven to be altogether satisfactory for several reasons including the sensitivity of the contact to excessive heat treatment causing chemical rections to form metal tellurides, and the present of surface oxides which tend to give rise to high contact resistances.

Therefore, it can be appreciated that a photovoltaic junction which can be formed at atmospheric pressure and under other conditions which lend themselves well to high throughput production, and a photovoltaic cell which has low resistance electrical contacts to the back conductor is highly desirable.

SUMMARY OF THE INVENTION

In accordance with the present invention, a thin film photovoltaic cell having a layer of cadmium telluride is manufactured in a process in which the cadmium telluride is deposited directly onto a conductive window layer.

Further in accordance with the present invention, a thin film photovoltaic cell having a layer of cadmium telluride is manufactured in a process in which the cadmium telluride can be deposited under atmospheric pressure conditions.

In accordance with a related aspect of the invention a photovoltaic cell is prepared which has conversion efficiencies which are improved as compared to a similar cell previously produced.

In a further aspect of the invention a cadmium telluride photovoltaic cell is produced which has a means for providing a low resistance electrical contact to a back contact of the photovoltaic cell.

As shown in an illustrated embodiment of the invention a photovoltaic cell is produced in which a conductive window layer, preferably tin oxide, is deposited upon a substrate and a cadmium telluride layer, preferably of a p conductivity type, is further deposited upon the tin oxide layer to form a p-n junction. A lead telluride layer is deposited upon the cadmium telluride layer and a metallic back contact is positioned on top of the lead telluride layer either by deposition or screen printing.

In accordance with another aspect of the invention the cadmium telluride is deposited upon the window layer in the presence of phosphine to thereby produce phosphorus atoms in the cadmium telluride layer to advantageously enhance the efficiency of the photovoltaic cell.

In accordance with a related aspect of the invention, the deposition of the cadmium telluride onto the tin oxide window layer is carried out in a reactor in which the temperature of the cadmium telluride source and the tin oxide is controlled in a manner to keep the temperature of the tin oxide at about 400° C. until the temperature of the cadmium telluride source is greater than about 600° C. thereby inhibiting the tin oxide from reducing to elemental tin and yet allowing the temperature of the tin oxide to rise above about 600° C. in order to significantly increase the transmission qualities through the tin oxide layer.

Also shown in a preferred embodiment of the invention is a structure for providing electrical contacts to the cadmium telluride layer by placing a layer of lead telluride between the cadmium telluride and the metallization back contacts.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features of this invention may be more fully understood from the following detailed description taken together with the accompanying drawing in which:

FIG. 1 is a fragmentary vertical sectional view of a photovoltaic cell according to the present invention;

FIG. 2 is a partial schematic vertical sectional view of a chamber suitable for depositing cadmium telluride onto tin oxide;

FIG. 3 is a plot of the temperatures of the cadmium telluride source and the glass-tin oxide substrate during the deposition of the cadmium telluride;

FIG. 4 is a plot of the absolute quantum efficiency versus wavelength of a photovoltaic cell having a tin oxide/cadmium telluride photovoltaic junction formed according to the present invention; and

FIG. 5 is a plot of the voltage/current characteristics of a photovoltaic cell in which a tin oxide/cadmium telluride photovoltaic junction is formed according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings, **FIG. 1** shows, in partial schematic sectional view, a cell **10** prepared in accordance with the present invention. The cell **10** consists of a substrate layer **12** which in the preferred embodiment is made from 7059 glass. Deposited onto the substrate **12** is a tin oxide layer **14**. However, it will be appreciated that other materials such as cadmium stannate, can also be used for the conductive window layer **14**. For a photovoltaic cell the sheet resistivity of the tin oxide is preferably less than ten ohms per square, but may be higher if the cell is to used as a photodetector. The tin oxide layer **14** is advantageously transparent and forms both the conductive window layer and the n conductivity type constituent of the photovoltaic p-n junction. Deposited on top of the tin oxide is a layer **16** of cadmium telluride which in the preferred embodiment is a polycrystalline p conductivity type material, although it is also within the scope of the present invention for the cadmium telluride to be n-type, or intrinsic, in conductivity. The preferred thickness of the cadmium telluride layer **16** is in the range of five to fifteen microns, although the thickness may be as thin as one micron for certain devices. On top of the cadmium telluride is another layer **18** consisting of lead telluride which forms a P+ conductivity type layer between the cadmium telluride layer **16** and a top conductor layer **20**. The top layer **20** can be composed of any of several metals including nickel, aluminum, gold, solder, and graphite-copper, but in the preferred embodiment graphite-silver (C-Ag) is used.

A critical element in carrying out one aspect of the present invention is the deposition of the cadmium telluride layer **16**. FIG. **2** depicts a sectional view of a chamber suitable for depositing the cadmium telluride layer **16**. The substrate **12** and tin oxide layer **14**, together shown as element **22** in FIG. **2**, are mounted against a substrate block **24** and placed inside a quartz reactor **26**. A source crucible **28** is placed inside the reactor **26** and spaced away from the substrate window layer structure **22** by spacers shown as elements **30**. Mounted on either side of the quartz reactor **26** are a pair of heat lamps **32** and **34**. Heat lamp **32** is positioned to heat substrate block **24** and is hereinafter referred to as the substrate lamp **32**. The heat lamp **34** is positioned to heat the source crucible **28** and is hereinafter referred to the source lamp **34**. In the preferred procedure for carrying out the present invention the cadmium telluride source is ground cadmium telluride powder (Alpha Ultapure #87821) held in the source crucible **28** which is heated by the source lamp **34** to vaporize and become deposited upon the tin oxide through the process of close-space vapor transport (CSVT). The spacers **30** are less than one centimeter in width and the substrate structure **22** is typically ten centimeters by ten centimeters in size. Although not shown in FIG. **2**, additional elements which may be used including a mask placed in front of the substrate structure **22** for patterning the cadmium telluride deposited onto the structure **22**, and shutters mounted on crucible **28** which can be remotely activated to contain the cadmium telluride vapors until the temperature of the cadmium telluride source is at a desired temperature. During the cadmium telluride growth, the atmosphere inside the reactor **26** is helium with 200 PPM of phosphine (PH_3). The PH_3provides phosphorus atoms for the cadmium telluride layer **16**. Phosphorus is a well known acceptor dopant. The pressure inside the quartz reactor **26** may be atmospheric pressure thereby reducing the amount of time and equipment required during the manufacturing process as compared to a low pressure process. On the other hand, it has been found that the deposition of cadmium telluride occurs faster during CSVT when the atmospheric pressure is reduced to about 1 TORR.

The apparatus shown in FIG. **2** allows precise control of deposition parameters. Using instrumentation not shown in FIG. **2**, independent control of gas flows, chamber pressure, and source and substrate temperatures can be achieved.

In order for the photovoltaic cell to be efficient, the window layer, in this case tin oxide, must be compatible with the layer disposed upon it, in this case cadmium telluride, and with other subsequent processing. Experiments were made in which the optical transmission and x-ray diffraction were measured for different heat treatment conditions of the tin oxide. It was found that for an ambient condition of one atmosphere of hydrogen the tin oxide should not be exposed to temperatures above 450° C., otherwise the reduction of the tin oxide to elemental tin occurs with the consequent loss in optical transmission. Unfortunately, experiments with cadmium telluride grown on tin oxide previously deposited onto 7059 glass and then heated to 450° C. produced a low quality cadmium telluride crystalline structure which had less than 5% optical transmission below the cadmium telluride band gap, and that temperatures of about 600° C. were necessary for high quality cadmium telluridge indicated by below band optical transmissions of about 67 percent, which, considering reflection losses, is considered ideal.

Advantageously, it was discovered that it is possible to raise the temperature of the tin oxide layer to about 600° C. without causing a degradation or reducing of the tin oxide to elemental tin. The solution involves heating the source crucible and then heating the substrate in a defined manner as shown in FIG. **3** so that the temperature of the substrate was kept below 450° C. until the temperature of the source crucible reached 600° C., then the substrate was quickly heated to 650° C. to improve initial film growth and cooled to 509° C. to complete the film growth. The resultant cadmium telluride layer was 10.3 microns thick.

In order to form the photovoltaic junction between the tin oxide and cadmium telluride, it is necessary that one of the layers be of p conductivity type, generally the cadmium telluride layer, and the other layer be of n conductivity type, generally the tin oxide layer. Advantageously, the deposition technique described above produces a tin oxide layer which is inherently n conductivity type and a cadmium telluride layer which is doped with acceptor type atoms to become p conductivity type.

It was also found that the use of phosphorus in the form of PH_3 mixed with the helium in the quartz reactor tube **26** improves the efficiency of the resulting photovoltaic cell by producing a p conductivity type layer to promote a relatively high voltage pn junction.

A photovoltaic cell was fabricated in the manner described above with the spectral response shown FIG. **4** and the voltage current characteristics of the cell shown in FIG. **5**. The quantum efficiencies shown in FIG. **5** are above unity near the tin oxide cutoff and are not understood. But these characteristics have also been seen in other devices and it is theorized that the efficiency shown may be due to avalanche effects or to current densities which are light dependent. As shown in FIG. **5**, the short circuit current for this example was 28.8 milliamperes per square centimeter, with an open circuit voltage of 0.642 volts and a fill factor of 0.524. The efficiency of the 4 square centimeter cell was 9.7 percent. In this experimental cell the back surface of the cadmium telluride was etched for ten seconds with an etch of 1.25 ml HNO_3: 100 ml H_3PO_4 and graphite-silver was then screen printed onto the etched cadmium telluride to form the back contact.

However, the back contact can also be formed by first depositing a layer of tellurium rich lead telluride onto the cadmium telluride using vacuum evaporation of lead telluride. The lead telluride is evaporated at 600° C. to 800° C., and the lead telluride must be raised to this temperature rapidly in order to keep the lead telluride tellurium rich to preserve the p conductivity type characteristics of the lead telluride. It is theorized that if the lead telluride is allowed to heat up slowly, the tellurium tends to separate from the lead, causing the resultant layer to be of less p conductivity type. After the lead telluride film is deposited, a suitable metal such as graphite-silver, gold, nickel, aluminum, solder, or graphite-copper, may be deposited onto the lead telluride to form the back contact. Analysis of back contacts formed in this manner show a ohmic junction of relatively low resistivity which are stable.

An alternative method using close-space vapor transport has also been used to deposit the layer of lead telluride. This method of deposition combined with the process described above has the advantage of permitting the production of photovoltaic cell entirely at atmospheric pressure.

As can be seen from this description, several major advantages arise from this invention. A photovoltaic cell has been described which is formed by the junction of tin oxide and cadmium telluride without an intervening cadmium sulfide layer in which phosphorus has been used to increase the efficiency of the cell, and a method to provide good ohmic contacts to the cadmium telluride layer has been described. Moreover, the process described is suited for an industrial mass production of photovoltaic cells which does not not require special crystal growing equipment, in which the fabrication of a photovoltaic cell can be carried out in atmospheric pressure conditions.

Although the invention has been described in detail with particular reference to a preferred embodiments, it will be understood by those skilled in the art that modifications and variations can be made to the described embodiments without departing from the spirit and scope of the invention.

I claim:

1. A photovoltaic cell comprising:
(a) a substrate layer consisting of a transparent or semi-transparent material;
(b) an n conductivity type layer of tin oxide contiguous to said substrate layer;
(c) a p conductivity type layer of polycrystalline cadmium telluride contiguous to said layer of tin oxide thereby forming a pn junction, said layer of cadmium telluride containing atoms of phosphorus; and
(d) a layer of lead telluride contiguous to said layer of said cadmium telluride.

2. A photovoltaic cell as set forth in claim 1 further including a conductive layer contiguous to said lead telluride layer whereby said conductive layer and said tin oxide layer form electrodes for said photovoltaic cell.

3. In a photovoltaic cell having a layer of cadmium telluride and an electrode in nonrectifying electrical contact with said cadmium telluride layer, the improvement comprising a layer of lead telluride interposed between said cadmium telluride layer and said electrode.

4. A cell as set forth in claim 3 wherein said cadmium telluride layer and said lead telluride layer are of p conductivity type.

5. A cell in set forth in claim 3 wherein said electrode is composed of one of the metal containing materials chosen from the group of graphite-silver, nickel, aluminum, gold, solder, and graphite-copper.

* * * * *

US005304499A

United States Patent [19]
Bonnet et al.

[11] **Patent Number: 5,304,499**
[45] **Date of Patent: Apr. 19, 1994**

[54] **METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS**

[75] Inventors: **Dieter Bonnet**, Friedrichsdorf; **Beate Henrichs**, Eschborn; **Karlheinz Jager**, Kronberg; **Hilmar Richter**, Frankfurt am Main, all of Fed. Rep. of Germany

[73] Assignee: **Battelle-Institut e.V.**, Frankfurt am Main, Fed. Rep. of Germany

[21] Appl. No.: **929,514**

[22] Filed: **Sep. 28, 1992**

[30] **Foreign Application Priority Data**

Oct. 3, 1991 [DE] Fed. Rep. of Germany 4132882

[51] **Int. Cl.**^{5} **H01L 31/18**; H01L 31/072
[52] **U.S. Cl.** **437/5**; 136/260; 136/264; 437/102; 437/234; 427/76
[58] **Field of Search** 437/4-5, 437/81, 87, 103, 139, 234; 427/74, 76; 136/260, 264

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Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Lane, Aitken & McCann

[57] **ABSTRACT**

A method of making pn CdTe/CdS thin film solar cells, in which a transparent TCO layer is deposited as a front contact on a transparent substrate in the form of inexpensive soda-lime glass, and is preferably provided with an ultra-thin indium layer, which is in turn coated with the CdS layer, wherein the thus coated substrate is brought to the CdTe coating at a temperature between 480° C. and 520° C., which is maintained during the ensuing rapid CdTe deposition using the close-spaced sublimation method with a preferred rate of deposition of 5 to 15 μm/min in an inert atmosphere. The indium layer dissolves during this deposition and effects the necessary n-doping of the CdS layer, without an additional method step. Solar cells can be made in this way with high efficiency in an inexpensive method, suitable for mass production.

10 Claims, 2 Drawing Sheets

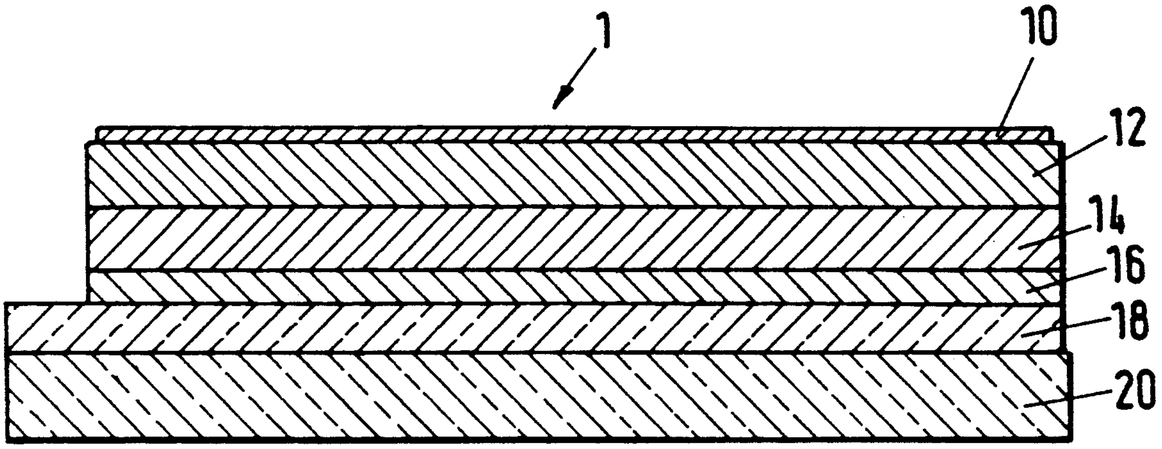


Fig.1

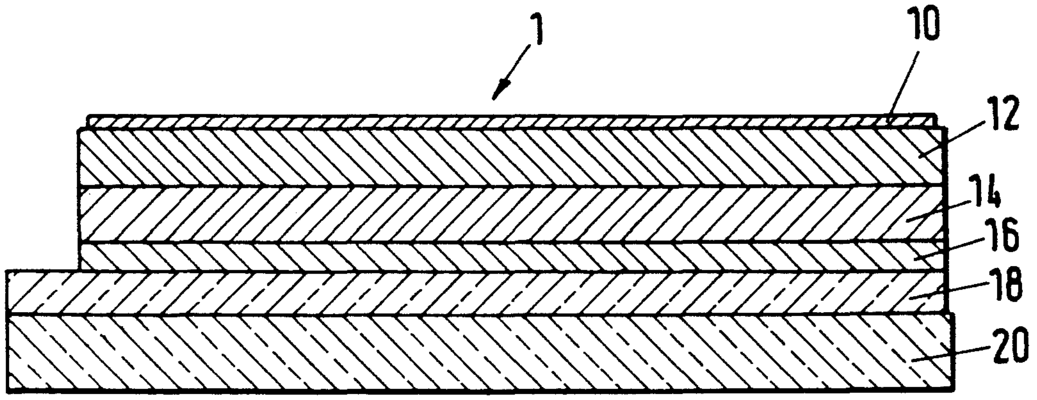


Fig.2

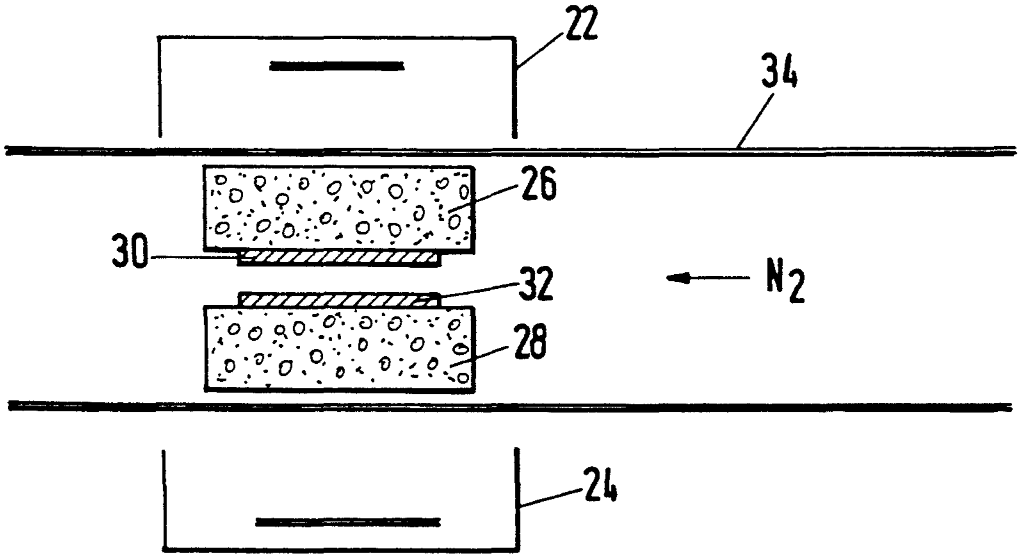
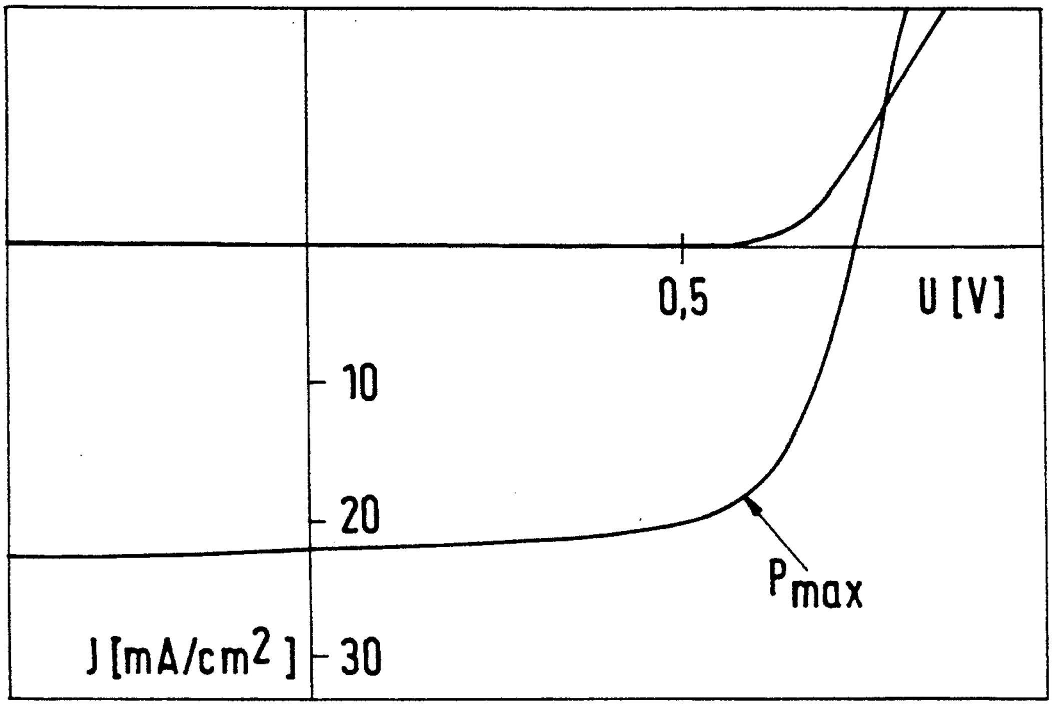


Fig.3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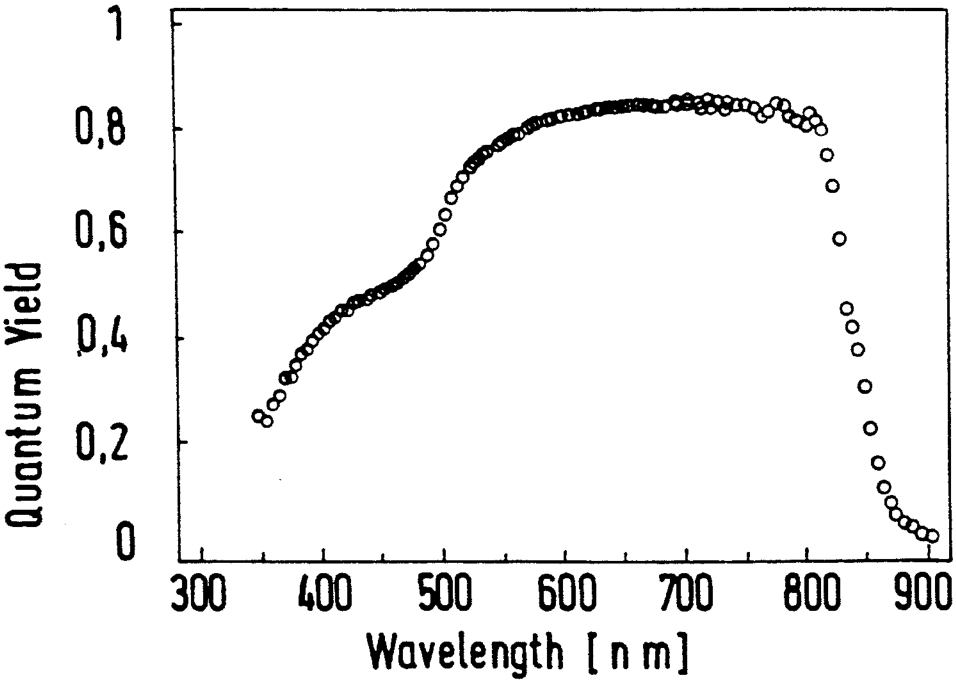
Pmax

Fig.4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METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

The present invention relates to methods of making polycrystalline pn CdTe/CdS thin film solar cells and especially such methods which make inexpensive mass production possible.

Because of its favorable energy gap of 1.45 eV, CdTe is ideally suited as photo-active material for solar cells. Moreover, polycrystalline layers of a few μm thickness can be made by various methods (physical or chemical evaporation/sublimation in a vacuum, electrolytic deposition, screen printing, spray methods), which in general are subjected to a chemical-thermal post-treatment to improve their electronic properties (R. W. Birkmire et al, Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84). These two characteristics make CdTe one of the most interesting candidates for inexpensive thin film solar cells.

CdTe came into use in thin film solar cells for the first time around 1960. At the end of the 70's efficiencies for such solar cells of around 9% were reported. For example, U.S. Pat. No. 4,207,119 (Yuan-Sheng Tyan, 1980) describes a CdS/CdTe solar cell with oxygen as the dopant in both semiconductor layers CdS and CdTe of the cells. There is a disadvantage in the use of oxygen during the manufacture of the layers, since oxidation of the CdTe source can occur easily at too high an oxygen concentration in the deposition chamber, whereby the process of deposition is adversely affected or even interrupted. Moreover, the temperature of the substrate on which the polycrystalline CdTe layer was deposited is at least 575° C. and expensive temperature resistant glass substrates are used (with softening temperatures of 650° to 700° C.). Below a substrate temperature of 575° C. a significant fall-off in the attainable efficiency is observed. Thus, the CdTe layer was deposited experimentally at low temperatures in an atmosphere containing oxygen down to 500° C., when, however, an efficiency of less than 4% resulted. The possibility of increasing the efficiency by 1 to 2% by additional subsequent oxygen post-treatment was also proposed, whereby only values of 6% maximum resulted at 500° C. Attempts were also made to deposit the CdS layer free from oxygen, in contrast to the CdTe layer. The attempts showed, however, that the CdS layer also had to be deposited in an atmosphere containing oxygen, in order to be able to attain an efficiency of up to 8.9% at substrate temperatures above 575° C. In the experiments performed, CdTe layers 0.5 μm thick were deposited in 2 min. With a minimum thickness of around 2 to 3 μm needed for physical reasons, approximately 10 min. is already needed for the deposition.

In U.S. Pat. No. 4,650,921 (Kim W. Mitchell, 1987) there is described a pn CdTe/SnO_2 thin film solar cell, in which the polycrystalline CdTe layer is also deposited at high substrate temperatures (600°-650° C.), whereby the usual expensive temperature resistant glass substrates are also used. The CdTe source is first heated to 600° C. and, on attaining this temperature, the substrate previously heated to 450° C. is rapidly heated up to 650° C. The CdTe deposition rates to obtain a CdTe layer about 10 μm thick in the CSVT (closed space vapor transport) methods are very small, and deposition must take place for approximately 20 minutes.

As well as these vacuum-assisted deposition methods, electrolytic methods were described in the 80's (e.g. B. M. Basol, *Solar Cells,* 23, (1988) pp. 69-88; V. Ramanathan et al. *Proc. 20th IEEE Photovoltaic Specialists Conf.,* Las Vegas, (1988) pp. 1417-1421), as well as screen printing (e.g., S. Ikegami, *Solar Cells,* 23, (1988) pp. 89-105) or spray methods (e.g. J. F. Jordan, *Solar Cells,* 23, (1988) pp. 107-113), for making polycrystalline CdTe layers.

The electrolytic deposition takes place in an aqueous solution of $CdSO_4$ and Te_2O_3 at temperatures of about 90° C. In order to avoid fluctuations in the stoichiometric composition of the growing CdTe layer, it is necessary to adhere to very small and hence uneconomic rates of deposition of only about 1 μm/hour.

In the screen printing method, suspensions of Cd and Te powders are applied to a substrate and sintered with high usage of material into relatively thick layers of around 30 μm, whereby Cd and Te react to form CdTe. High temperatures of more than 700° C. are also required here, which necessitates the use of expensive substrates.

In the spray method, an aqueous solution of compounds containing Cd and Te in the form of a fine droplet aerosol is sprayed onto a substrate heated to about 400° C. The growing CdTe layer is markedly inclined to porosity, so that relatively thick layers have to be made in order to ensure the necessary impermeability of the layers. An uneconomic high usage of materials is again involved. Furthermore, a significant loss of the sprayed solution is inherent in the method, in that this fills the whole reaction chamber as a fine aerosol and is lost on the walls and through the exhaust air, whereby only a moderate material yield of the compounds of the Cd and Te compounds can be achieved. The chemical-thermal post treatment proves to be particularly critical in the spray method.

The invention is thus based on the problem of providing an improved method for making pn CdTe thin film solar cells which is especially suitable for inexpensive mass production and makes the production of satisfactory solar cells possible.

The solution to this problem according to the invention involves a complete departure from the high substrate temperatures hitherto regarded as necessary in order to be able to make solar cells with efficiencies around and above all in excess of 10%. Thus, the inventor has surprisingly ascertained that it is possible to make satisfactory solar cells with high efficiency if care is taken that the temperature of the transparent substrate provided with the TCO layer and the CdS layer is brought to a temperature below about 520° C. and above about 480° C. before the CdTe coating and this temperature is maintained also during the following coating. During this time the CdTe layer is deposited steadily in an inert gas atmosphere. In the oxygen-free processes in the state of the art, substrate temperatures of 600° C. and more were universally employed.

It has furthermore been found that inexpensive soda-lime glass (window glass) can be used as the substrate material and resulted in solar cells with a high efficiency of more than 10% in all embodiments tested. This represents a significant technical advance, since the substantial reduction in cost widens the scope for use of the mass-produced product. Hitherto, it has not been considered or even thought possible for solar cells of this kind to be made with window glass and be not merely functional but seriously capable of use.

Furthermore, it has been found that, with such temperature control of the substrate, it is possible to work

with a high CdTe deposition rate of between 5 and 15 μm/min, so that the growth of the CdTe layer takes place from the very start at a temperature favoring the attainment of the required (photo)electronic characteristics, so that a good efficiency of the cells is likewise obtainable. Such high rates of deposition have not been possible hitherto, either in oxygen or in inert gases.

Preferably, one proceeds in accordance with the invention as follows. Inexpensive, ordinary soda-lime glass ("window glass") is used as the transparent substrate and is coated with a transparent, electrically conductive TCO (transparent conducting oxide) layer. This consists, for example, of a suitably doped tin oxide layer, for example of ITO or a modified ITO layer. The TCO layer also forms the electrical front contact of the solar cell. A thin CdS layer (thickness approximately 80 to 120 nm, preferably 100 nm) is then evaporated on in a high vacuum, with doping preferably achieved in the manner indicated below.

The deposition of the photo-active CdTe layer then takes place directly on the CdS layer, according to the close-space (CSS) method (close-spaced sublimation). The substrate carrying the CdS layer is brought for this to a temperature, of 480° to 520° C., preferably 500° C., in a steady heating process, preferably in approximately 3 min. The TCO layer suffers no adverse effects in the course of this short heating phase, since it is protected by the CdS layer. During this time the CdTe source attains a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the substrate temperature has reached (after e.g. the 3 minutes) 480° to 520° C., preferably 500° C., is the CdTe source brought in approximately 1 minute to such a temperature (e.g., in the range from 700° to about 770° C., preferably about 740° C.), that a CdTe deposition rate of 5 to 15 μm/min., preferably about 10 μm/min., is attained, so that the required CdTe layer 5 to 10 μm thick can be created in the short time of approximately 1 minute.

During the CdTe deposition a pressure of about 0.1 mbar nitrogen (or similar inert gases such as helium, argon or hydrogen) is preferably so maintained in the reaction chamber (quartz tube) that the same amount of gas is fed in as is pumped out, in the nature of a dynamic balance through the various connections of the reaction chamber.

The CdTe source from which the material to be deposited on the CdS layer sublimes is preferably located at a small distance of only about 2 to 3 mm from the substrate surface. On account of the small distance between the substrate and the CdTe source, as well as their direct opposition, there is nearly 100% usage of the CdTe starting material. Furthermore, the small thickness of the CdTe layer possible according to the invention contributes to inexpensive handling of the valuable semiconductor material. The short deposition time also acts inexpensively in the course of this method.

During the described operation of the CdTe deposition, the substrate and CdTe source are preferably held in opposed graphite blocks, which are heated by heating elements (e.g. halogen lamps), in order to create the required temperatures. The latter are adjusted by suitable manual or computer-controlled regulation of the heating load of the heating element. The $CdCl_2$ tempering which is carried out at the end of the CdTe deposition is known per se.

The further development of the method in accordance with the present invention contributes significantly to mass-production, in that the method of doping of the CdS layer is substantially facilitated. It is also possible to increase the efficiency of the finished solar cell by this measure.

Finally, in contrast to the known critical oxygen doping, it is possible to operate without endangering the CdTe source by oxidation during the CdTe coating at high pressure.

It is beneficial for obtaining a good efficiency of the pn CdTe/CdS thin film solar cell to use an n-type CdS with high conductivity, of the order of magnitude of 0.1 S/cm. While a CdS layer made at about 150° C. fulfills this condition well, a CdS layer subjected to a thermal process, as in the CdTe deposition, only exhibits a very small conductivity of $<10^{-5}$ S/cm. In order to obtain a desirable order of magnitude of 0.1 S/cm for the conductivity of the CdS even after the thermal stress of the CdTe deposition, an ultra-thin indium layer with a thickness of approximately 0.1 to 0.5 nm, preferably 0.2 nm, is applied in a high vacuum to the TCO layer at approximately 25° C., before the CdS layer is applied preferably in the manner given above. The thickness of the indium layer is so selected that the diffusion of the indium into the CdS layer during the CdTe deposition at the predetermined substrate temperature, which preferably lies between 480° and 520° C., creates such n-type doping in the CdS that the conductivity value stays in the required order of magnitude of 0.1 S/cm. The required and desirable n-type doping of the CdS layer is thus effected inexpensively without additional expense during the CdTe deposition. It should further be noted that, even without the indium doping of the CdS layer, efficiencies of around and in excess of 10% are obtained.

After the customary $CdCl_2$ tempering (R. W. Birkmire et al., Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84), a gold layer approximately 5 to 10 μm thick is evaporated onto the CdTe layer as the back contact. In order to avoid series resistance, the gold layer preferably has an evaporated inexpensive metal layer (e.g. aluminum) (about 100-200 nm) or is painted with a conductive paste and so brought up to the conductivity necessary for the flow of the photocurrent.

The illumination of the solar cell takes place through the transparent glass substrate.

The features of the special doping of the CdS layer according to the invention are preferably combined with the other features according to the invention. Thus, with the substrate temperatures controlled in accordance with the invention, the mixing of the CdS layer and the indium layer can be well achieved. In combination with the likewise possible high rate of deposition, the efficiency of the method and its suitability for mass production are further improved.

The features according to the invention, taken alone and in their combination, thus promote inexpensive mass production of pn CdTe/CdS thin film solar cells with a type of construction previously known. Inexpensive substrate materials can be used and high yields of the expensive substrate materials with high rates of deposition for the semiconductor layers are possible. The doping step which was previously frequently critical is markedly improved and rationalized. In addition, the features referred to contribute to high efficiency. The inventive features thus contribute an important step towards an alternative energy source through solar

cells, which arises both from the mass production and from a high efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further explained below with reference to the drawings, in which:

FIG. **1** shows a section, in a schematic view, through a pn CdTe/CdS thin film solar cell made according to a preferred embodiment of the method according to the invention,

FIG. **2** shows a section, in a schematic view, through an apparatus suitable for carrying out the method according to the invention,

FIG. **3** shows the current/voltage characteristic of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. **1**, and

FIG. **4** shows the graph of the (external) absolute quantum yield as a function of wavelength of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. **1**.

FIG. **1** shows a schematic section through a pn CdTe/CdS thin film solar cell **1**, which has been made by a preferred embodiment of the method according to the invention. The transparent substrate **20** consists of soda-lime glass ("window glass") and is coated with a transparent, electrically conductive TCO layer **18**. There follow an ultra-thin indium layer **16** and a CdS layer **14** (e.g. 0.10 μm thick). The photo-active CdTe layer **12** (preferably around 5 μm thick but not critical in thickness for the cell as a whole so long as it stays above 2 to 3 μm) is deposited on the CdS layer according to the foregoing techniques. As has further been indicated, the layers **16** and **14** mix so tht the indium layer **16** dissolves in the layer **14** because of the diffusion of the indium atoms and is no longer identifiable as such in the finished solar cell **1**. The CdS layer thus contains the indium atoms of the indium layer **16** in dispersed form after manufacture, as the desired and necessary n-type doping.

This n-type doping of the CdS layer taking place at the same time as the deposition of the CdTe layer **12** represents a further advance both in relation to improving the suitability of the method to inexpensive mass production, as well as to the creation of a solar cell with high efficiency. The indium layer **16**, preferably 0.1 to 0.5 nm thick and preferably evaporated in a high vacuum at about 25° C., is therefore only identifiable as such up to the method step preceding the CdTe deposition.

After completion of the CdTe deposition, there follows after the $CdCl_2$ tempering the application of an electrically conductive metal contact **10** on the CdTe layer **12**, serving as the back contact of the solar cell **1**. The TCO layer **18** functions as the front contact of the solar cell **1**. The illumination of the solar cell **1** takes place through the glass substrate **20** and the TCO layer **18**.

The CdTe deposition method is also especially important. In FIG. **2** there is shown a reaction chamber which is preferably used, likewise in schematic cross-section. This consists of a quartz reactor **34** and graphite blocks **26** and **28**, as well as heating elements **22** and **24** (e.g. halogen lamps), with which the graphite blocks **26** and **28** are heated. The glass substrate **20** with the TCO layer **18** as well as the indium layer **16** and the CdS layer **14**, shown as element **30** in FIG. **2**, is so attached to the upper graphite block **26** that the glass substrate lies against the graphite block **26** and the CdS layer **24** is directed towards the CdTe source. The CdTe source **32**, e.g. in the form of a polycrystalline disc, is located on the lower graphite block **28**. Instead of a polycrystalline disc, a pressed blank of CdTe powder or a device with CdTe powder can obviously be used as the CdTe source **32**.

The CdTe deposition is effected in the reaction chamber **33** according to a procedure in which, as already particularly explained above, it is crucial that the variation with time of the temperature of the element **30** and of the CdTe source **32** is such that the element **30** including the CdS layer is brought up to a temperature of 480°-520° C., preferably 500° C., in a steady heating process (without interruption) in e.g., 3 min., whereby the TCO layer **18** does not suffer any adverse effects in the course of this short heating phase, since it is protected by the CdS layer **24**. During this time the CdTe source **32** reaches a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the temperature of the element **30** has reached 480°-520° C., preferably 500° C., is the CdTe source **32** brought up in about 1 min. to such a temperature that a CdTe deposition rate onto the CdS layer **14** of 5 to 15 μm/min, preferably about 10 μm/min, is obtained and the required CdTe layer **12** of 5 to 10 μm thickness can be created in the short time of about 1 minute. This procedure results in the growth of the CdTe layer **12** taking place from the start at a temperature favoring the required (photo) electronic characteristics. The temperature of the element **30** is so selected that cheap soda-lime glass can be used as the material for the substrate **20**. The pressure in the reaction chamber **34** amounts during the CdTe deposition to about 0.1 mbar and is maintained by inflow or pumping out nitrogen (or helium, argon or hydrogen).

The heating load of the heating elements **22** and **24** can be optionally varied manually or by computer control.

In FIGS. **3** and **4** there are shown the current/voltage characteristic and the (external) absolute quantum yield as a function of the wavelength respectively of a pn CdTe/CdS thin film solar cell made in accordance with the above method. As can be seen from FIG. **3**, the short-circuit current density of the manufactured solar cell amounts to 22.8 mA/cm^2 with a no-load voltage of 0.750 V and a space factor of 65%. The active surface of the solar cell of the embodiment set forth amounts to 0.388 cm^2. This gives an efficiency of 11.0% (relative to illumination with 100 mW/cm^2, 1.5 AM overall).

The (external) absolute quantum yield according to FIG. **4** exhibits a constant value over the substantial part of the spectrum (about 820–520 nm) with a value around 85%. The fall off at 520 μm is caused by the absorption of the CdS layer **14**.

We claim:

1. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO layer and an n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere free of oxygen according to the close-spaced sublimation method from a CdTe source and is provided with an electrically conducting back contact,

characterized in that,

a substrate of soda-lime glass is used, the substrate is provided with the TCO layer, and the CdS layer is brought to a temperature between approximately 480° C. and 520° C. before coating with the CdTe

layer, said temperature being maintained during the CdTe coating.

2. A method according to claim 1, characterized in that a $CdCl_2$ tempering step is employed after the CdTe coating.

3. A method according to claim 1, characterized in that the substrate with the TCO layer and the CdS layer is brought to a temperature of about 500° C. before the CdTe coating, which temperature is maintained during the CdTe coating.

4. A method according to claim 1, characterized in that the heating of the substrate provided with the TCO layer and the CdS layer is effected in a steady heating process over between approximately 1 and 5 min.

5. A method according to claim 4, characterized in that the heating is effected in approximately 3 min.

6. A method according to claim 1, characterized in that the deposition rate of the CdTe on the CdS layer is approximately 5 to 15 μm/min.

7. A method according to claim 6, characterized in that the CdTe layer is deposited in approximately 1 min.

8. A method according to claim 6, characterized in that the CdTe deposition rate is adjusted to 10 μm/min.

9. A method according to claim 1, characterized in that the variation with time of the temperature of the substrate provided with the TCO layer and the CdS layer and of the CdTe source is so controlled that the substrate is brought in a steady heating process to a temperature of 480° to 520° C. in approximately 1 to 5 min. and, during this time, the CdTe source is brought to a temperature at which there is no appreciable sublimation of the CdTe, and in that, only when the temperature of the substrate with the TCO and CdS layers has attained the desired temperature between 480° and 520° C., the CdTe source is brought in approximately 1 min. to a temperature at which a deposition rate on to the CdS layer is obtained such that the required CdTe layer can be applied in approximately 1 min.

10. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO front contact layer and an overlying n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere according to the close-spaced sublimation method and is provided with an electrically conducting back contact, characterized in that indium is used for the n-doping of the CdS layer and in that, before the deposition of the CdS layer, an ultra-thin indium layer less than 0.5 nm thick is applied to the TCO layer and in that the In and CdS layers so mix during the deposition of the CdTe layer that the indium layer is dissolved by diffusion of the indium atoms into the CdS layer and is no longer identifiable as such in the finished solar cell and the CdS layer includes the indium atoms of the indium layer in dispersed form as n-doping.

* * * * *

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United States Patent [19]

Bonnet et al.

[11] **Patent Number:** **5,304,499**

[45] **Date of Patent:** **Apr. 19, 1994**

[54] METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

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[21] Appl. No.: **929,514**

[22] Filed: **Sep. 28, 1992**

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**^{5} **H01L 31/18**; H01L 31/072

[52] **U.S. Cl.** **437/5**; 136/260; 136/264; 437/102; 437/234; 427/76

[58] **Field of Search** 437/4-5, 437/81, 87, 103, 139, 234; 427/74, 76; 136/260, 264

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Primary Examiner—Aaron Weisstuch

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[57] ABSTRACT

A method of making pn CdTe/CdS thin film solar cells, in which a transparent TCO layer is deposited as a front contact on a transparent substrate in the form of inexpensive soda-lime glass, and is preferably provided with an ultra-thin indium layer, which is in turn coated with the CdS layer, wherein the thus coated substrate is brought to the CdTe coating at a temperature between 480° C. and 520° C., which is maintained during the ensuing rapid CdTe deposition using the close-spaced sublimation method with a preferred rate of deposition of 5 to 15 µm/min in an inert atmosphere. The indium layer dissolves during this deposition and effects the necessary n-doping of the CdS layer, without an additional method step. Solar cells can be made in this way with high efficiency in an inexpensive method, suitable for mass production.

10 Claims, 2 Drawing Sheets

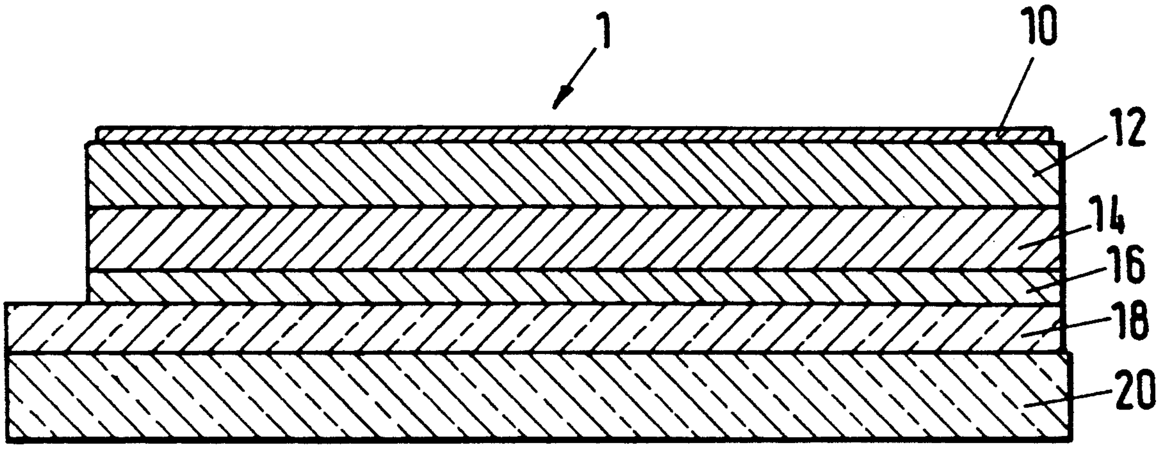


Fig.1

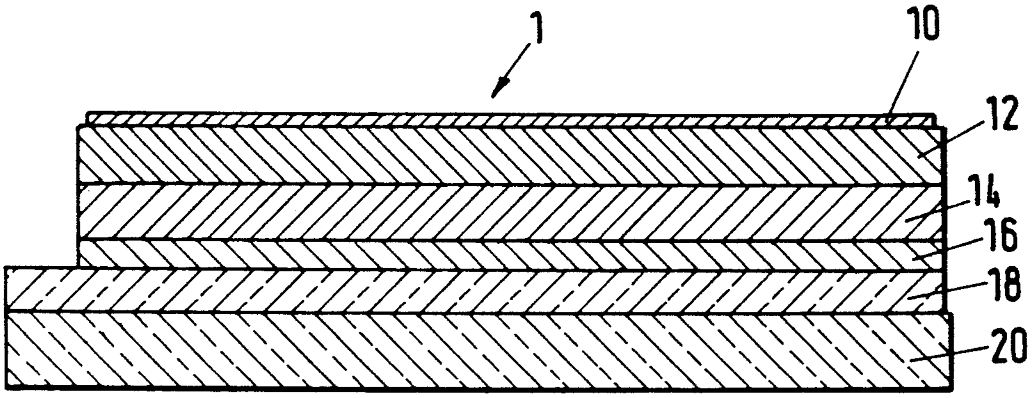


Fig.2

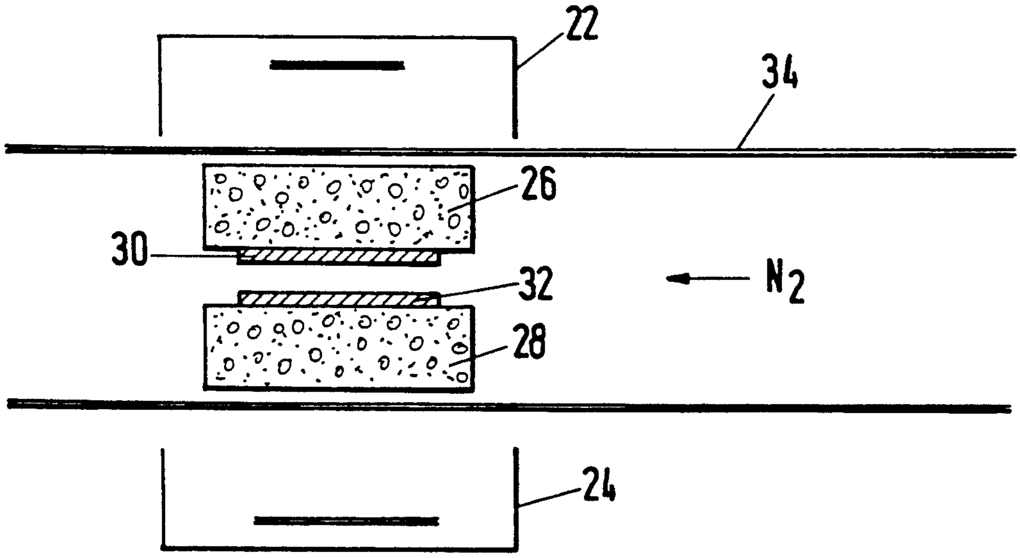
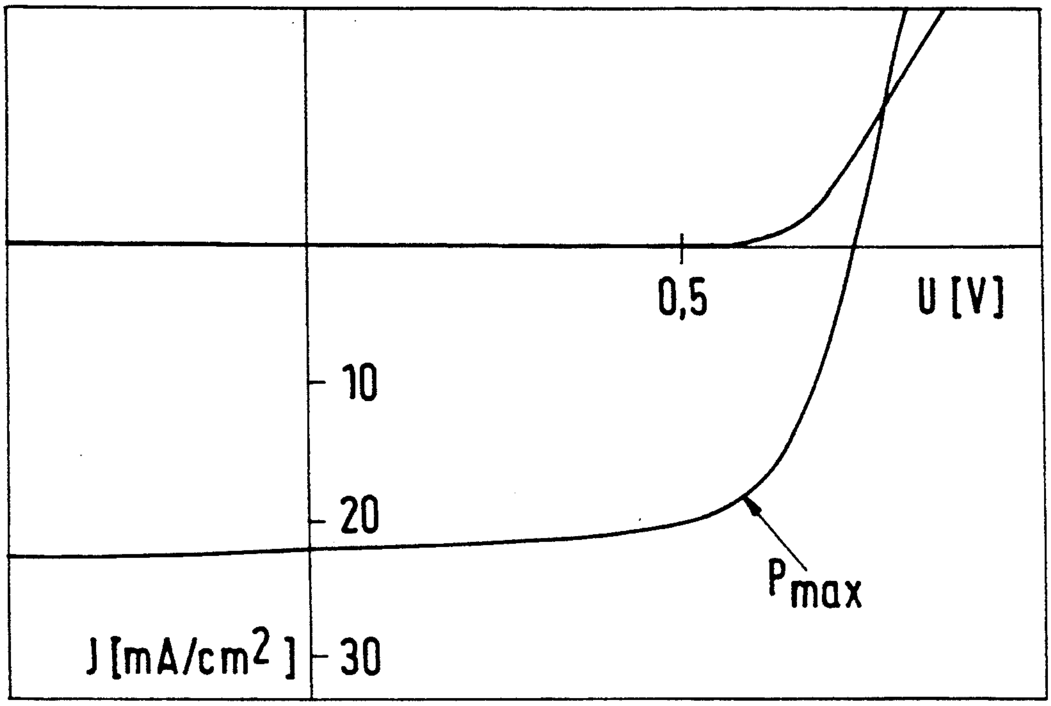


Fig.3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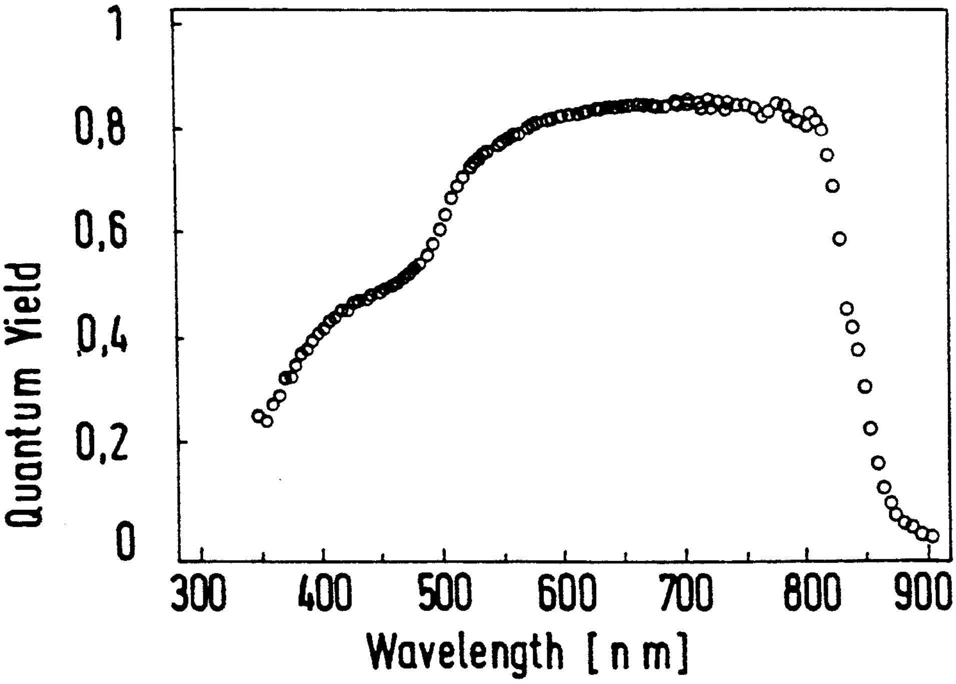
10
20
30
J [mA/cm²]
P_{max}

Fig.4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0,2
0
Quantum Yield
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400
500
600
700
800
900
Wavelength [n m]

METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

The present invention relates to methods of making polycrystalline pn CdTe/CdS thin film solar cells and especially such methods which make inexpensive mass production possible.

Because of its favorable energy gap of 1.45 eV, CdTe is ideally suited as photo-active material for solar cells. Moreover, polycrystalline layers of a few μm thickness can be made by various methods (physical or chemical evaporation/sublimation in a vacuum, electrolytic deposition, screen printing, spray methods), which in general are subjected to a chemical-thermal post-treatment to improve their electronic properties (R. W. Birkmire et al, Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77–84). These two characteristics make CdTe one of the most interesting candidates for inexpensive thin film solar cells.

CdTe came into use in thin film solar cells for the first time around 1960. At the end of the 70's efficiencies for such solar cells of around 9% were reported. For example, U.S. Pat. No. 4,207,119 (Yuan-Sheng Tyan, 1980) describes a CdS/CdTe solar cell with oxygen as the dopant in both semiconductor layers CdS and CdTe of the cells. There is a disadvantage in the use of oxygen during the manufacture of the layers, since oxidation of the CdTe source can occur easily at too high an oxygen concentration in the deposition chamber, whereby the process of deposition is adversely affected or even interrupted. Moreover, the temperature of the substrate on which the polycrystalline CdTe layer was deposited is at least 575° C. and expensive temperature resistant glass substrates are used (with softening temperatures of 650° to 700° C.). Below a substrate temperature of 575° C. a significant fall-off in the attainable efficiency is observed. Thus, the CdTe layer was deposited experimentally at low temperatures in an atmosphere containing oxygen down to 500° C., when, however, an efficiency of less than 4% resulted. The possibility of increasing the efficiency by 1 to 2% by additional subsequent oxygen post-treatment was also proposed, whereby only values of 6% maximum resulted at 500° C. Attempts were also made to deposit the CdS layer free from oxygen, in contrast to the CdTe layer. The attempts showed, however, that the CdS layer also had to be deposited in an atmosphere containing oxygen, in order to be able to attain an efficiency of up to 8.9% at substrate temperatures above 575° C. In the experiments performed, CdTe layers 0.5 μm thick were deposited in 2 min. With a minimum thickness of around 2 to 3 μm needed for physical reasons, approximately 10 min. is already needed for the deposition.

In U.S. Pat. No. 4,650,921 (Kim W. Mitchell, 1987) there is described a pn CdTe/SnO_2 thin film solar cell, in which the polycrystalline CdTe layer is also deposited at high substrate temperatures (600°–650° C.), whereby the usual expensive temperature resistant glass substrates are also used. The CdTe source is first heated to 600° C. and, on attaining this temperature, the substrate previously heated to 450° C. is rapidly heated up to 650° C. The CdTe deposition rates to obtain a CdTe layer about 10 μm thick in the CSVT (closed space vapor transport) methods are very small, and deposition must take place for approximately 20 minutes.

As well as these vacuum-assisted deposition methods, electrolytic methods were described in the 80's (e.g. B. M. Basol, *Solar Cells,* 23, (1988) pp. 69–88; V. Ramanathan et al. *Proc. 20th IEEE Photovoltaic Specialists Conf.,* Las Vegas, (1988) pp. 1417–1421), as well as screen printing (e.g., S. Ikegami, *Solar Cells,* 23, (1988) pp. 89–105) or spray methods (e.g. J. F. Jordan, *Solar Cells,* 23, (1988) pp. 107–113), for making polycrystalline CdTe layers.

The electrolytic deposition takes place in an aqueous solution of $CdSO_4$ and Te_2O_3 at temperatures of about 90° C. In order to avoid fluctuations in the stoichiometric composition of the growing CdTe layer, it is necessary to adhere to very small and hence uneconomic rates of deposition of only about 1 μm/hour.

In the screen printing method, suspensions of Cd and Te powders are applied to a substrate and sintered with high usage of material into relatively thick layers of around 30 μm, whereby Cd and Te react to form CdTe. High temperatures of more than 700° C. are also required here, which necessitates the use of expensive substrates.

In the spray method, an aqueous solution of compounds containing Cd and Te in the form of a fine droplet aerosol is sprayed onto a substrate heated to about 400° C. The growing CdTe layer is markedly inclined to porosity, so that relatively thick layers have to be made in order to ensure the necessary impermeability of the layers. An uneconomic high usage of materials is again involved. Furthermore, a significant loss of the sprayed solution is inherent in the method, in that this fills the whole reaction chamber as a fine aerosol and is lost on the walls and through the exhaust air, whereby only a moderate material yield of the compounds of the Cd and Te compounds can be achieved. The chemical-thermal post treatment proves to be particularly critical in the spray method.

The invention is thus based on the problem of providing an improved method for making pn CdTe thin film solar cells which is especially suitable for inexpensive mass production and makes the production of satisfactory solar cells possible.

The solution to this problem according to the invention involves a complete departure from the high substrate temperatures hitherto regarded as necessary in order to be able to make solar cells with efficiencies around and above all in excess of 10%. Thus, the inventor has surprisingly ascertained that it is possible to make satisfactory solar cells with high efficiency if care is taken that the temperature of the transparent substrate provided with the TCO layer and the CdS layer is brought to a temperature below about 520° C. and above about 480° C. before the CdTe coating and this temperature is maintained also during the following coating. During this time the CdTe layer is deposited steadily in an inert gas atmosphere. In the oxygen-free processes in the state of the art, substrate temperatures of 600° C. and more were universally employed.

It has furthermore been found that inexpensive soda-lime glass (window glass) can be used as the substrate material and resulted in solar cells with a high efficiency of more than 10% in all embodiments tested. This represents a significant technical advance, since the substantial reduction in cost widens the scope for use of the mass-produced product. Hitherto, it has not been considered or even thought possible for solar cells of this kind to be made with window glass and be not merely functional but seriously capable of use.

Furthermore, it has been found that, with such temperature control of the substrate, it is possible to work

with a high CdTe deposition rate of between 5 and 15 μm/min, so that the growth of the CdTe layer takes place from the very start at a temperature favoring the attainment of the required (photo)electronic characteristics, so that a good efficiency of the cells is likewise obtainable. Such high rates of deposition have not been possible hitherto, either in oxygen or in inert gases.

Preferably, one proceeds in accordance with the invention as follows. Inexpensive, ordinary soda-lime glass ("window glass") is used as the transparent substrate and is coated with a transparent, electrically conductive TCO (transparent conducting oxide) layer. This consists, for example, of a suitably doped tin oxide layer, for example of ITO or a modified ITO layer. The TCO layer also forms the electrical front contact of the solar cell. A thin CdS layer (thickness approximately 80 to 120 nm, preferably 100 nm) is then evaporated on in a high vacuum, with doping preferably achieved in the manner indicated below.

The deposition of the photo-active CdTe layer then takes place directly on the CdS layer, according to the close-space (CSS) method (close-spaced sublimation). The substrate carrying the CdS layer is brought for this to a temperature, of 480° to 520° C., preferably 500° C., in a steady heating process, preferably in approximately 3 min. The TCO layer suffers no adverse effects in the course of this short heating phase, since it is protected by the CdS layer. During this time the CdTe source attains a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the substrate temperature has reached (after e.g. the 3 minutes) 480° to 520° C., preferably 500° C., is the CdTe source brought in approximately 1 minute to such a temperature (e.g., in the range from 700° to about 770° C., preferably about 740° C.), that a CdTe deposition rate of 5 to 15 μm/min., preferably about 10 μm/min., is attained, so that the required CdTe layer 5 to 10 μm thick can be created in the short time of approximately 1 minute.

During the CdTe deposition a pressure of about 0.1 mbar nitrogen (or similar inert gases such as helium, argon or hydrogen) is preferably so maintained in the reaction chamber (quartz tube) that the same amount of gas is fed in as is pumped out, in the nature of a dynamic balance through the various connections of the reaction chamber.

The CdTe source from which the material to be deposited on the CdS layer sublimes is preferably located at a small distance of only about 2 to 3 mm from the substrate surface. On account of the small distance between the substrate and the CdTe source, as well as their direct opposition, there is nearly 100% usage of the CdTe starting material. Furthermore, the small thickness of the CdTe layer possible according to the invention contributes to inexpensive handling of the valuable semiconductor material. The short deposition time also acts inexpensively in the course of this method.

During the described operation of the CdTe deposition, the substrate and CdTe source are preferably held in opposed graphite blocks, which are heated by heating elements (e.g. halogen lamps), in order to create the required temperatures. The latter are adjusted by suitable manual or computer-controlled regulation of the heating load of the heating element. The $CdCl_2$ tempering which is carried out at the end of the CdTe deposition is known per se.

The further development of the method in accordance with the present invention contributes significantly to mass-production, in that the method of doping of the CdS layer is substantially facilitated. It is also possible to increase the efficiency of the finished solar cell by this measure.

Finally, in contrast to the known critical oxygen doping, it is possible to operate without endangering the CdTe source by oxidation during the CdTe coating at high pressure.

It is beneficial for obtaining a good efficiency of the pn CdTe/CdS thin film solar cell to use an n-type CdS with high conductivity, of the order of magnitude of 0.1 S/cm. While a CdS layer made at about 150° C. fulfills this condition well, a CdS layer subjected to a thermal process, as in the CdTe deposition, only exhibits a very small conductivity of $<10^{-5}$ S/cm. In order to obtain a desirable order of magnitude of 0.1 S/cm for the conductivity of the CdS even after the thermal stress of the CdTe deposition, an ultra-thin indium layer with a thickness of approximately 0.1 to 0.5 nm, preferably 0.2 nm, is applied in a high vacuum to the TCO layer at approximately 25° C., before the CdS layer is applied preferably in the manner given above. The thickness of the indium layer is so selected that the diffusion of the indium into the CdS layer during the CdTe deposition at the predetermined substrate temperature, which preferably lies between 480° and 520° C., creates such n-type doping in the CdS that the conductivity value stays in the required order of magnitude of 0.1 S/cm. The required and desirable n-type doping of the CdS layer is thus effected inexpensively without additional expense during the CdTe deposition. It should further be noted that, even without the indium doping of the CdS layer, efficiencies of around and in excess of 10% are obtained.

After the customary $CdCl_2$ tempering (R. W. Birkmire et al., Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84), a gold layer approximately 5 to 10 μm thick is evaporated onto the CdTe layer as the back contact. In order to avoid series resistance, the gold layer preferably has an evaporated inexpensive metal layer (e.g. aluminum) (about 100-200 nm) or is painted with a conductive paste and so brought up to the conductivity necessary for the flow of the photocurrent.

The illumination of the solar cell takes place through the transparent glass substrate.

The features of the special doping of the CdS layer according to the invention are preferably combined with the other features according to the invention. Thus, with the substrate temperatures controlled in accordance with the invention, the mixing of the CdS layer and the indium layer can be well achieved. In combination with the likewise possible high rate of deposition, the efficiency of the method and its suitability for mass production are further improved.

The features according to the invention, taken alone and in their combination, thus promote inexpensive mass production of pn CdTe/CdS thin film solar cells with a type of construction previously known. Inexpensive substrate materials can be used and high yields of the expensive substrate materials with high rates of deposition for the semiconductor layers are possible. The doping step which was previously frequently critical is markedly improved and rationalized. In addition, the features referred to contribute to high efficiency. The inventive features thus contribute an important step towards an alternative energy source through solar

cells, which arises both from the mass production and from a high efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further explained below with reference to the drawings, in which:

FIG. 1 shows a section, in a schematic view, through a pn CdTe/CdS thin film solar cell made according to a preferred embodiment of the method according to the invention,

FIG. 2 shows a section, in a schematic view, through an apparatus suitable for carrying out the method according to the invention,

FIG. 3 shows the current/voltage characteristic of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1, and

FIG. 4 shows the graph of the (external) absolute quantum yield as a function of wavelength of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1.

FIG. 1 shows a schematic section through a pn CdTe/CdS thin film solar cell **1**, which has been made by a preferred embodiment of the method according to the invention. The transparent substrate **20** consists of soda-lime glass ("window glass") and is coated with a transparent, electrically conductive TCO layer **18**. There follow an ultra-thin indium layer **16** and a CdS layer **14** (e.g. 0.10 μm thick). The photo-active CdTe layer **12** (preferably around 5 μm thick but not critical in thickness for the cell as a whole so long as it stays above 2 to 3 μm) is deposited on the CdS layer according to the foregoing techniques. As has further been indicated, the layers **16** and **14** mix so tht the indium layer **16** dissolves in the layer **14** because of the diffusion of the indium atoms and is no longer identifiable as such in the finished solar cell **1**. The CdS layer thus contains the indium atoms of the indium layer **16** in dispersed form after manufacture, as the desired and necessary n-type doping.

This n-type doping of the CdS layer taking place at the same time as the deposition of the CdTe layer **12** represents a further advance both in relation to improving the suitability of the method to inexpensive mass production, as well as to the creation of a solar cell with high efficiency. The indium layer **16**, preferably 0.1 to 0.5 nm thick and preferably evaporated in a high vacuum at about 25° C., is therefore only identifiable as such up to the method step preceding the CdTe deposition.

After completion of the CdTe deposition, there follows after the $CdCl_2$ tempering the application of an electrically conductive metal contact **10** on the CdTe layer **12**, serving as the back contact of the solar cell **1**. The TCO layer **18** functions as the front contact of the solar cell **1**. The illumination of the solar cell **1** takes place through the glass substrate **20** and the TCO layer **18**.

The CdTe deposition method is also especially important. In FIG. 2 there is shown a reaction chamber which is preferably used, likewise in schematic cross-section. This consists of a quartz reactor **34** and graphite blocks **26** and **28**, as well as heating elements **22** and **24** (e.g. halogen lamps), with which the graphite blocks **26** and **28** are heated. The glass substrate **20** with the TCO layer **18** as well as the indium layer **16** and the CdS layer **14**, shown as element **30** in FIG. 2, is so attached to the upper graphite block **26** that the glass substrate lies against the graphite block **26** and the CdS layer **24** is directed towards the CdTe source. The CdTe source **32**, e.g. in the form of a polycrystalline disc, is located on the lower graphite block **28**. Instead of a polycrystalline disc, a pressed blank of CdTe powder or a device with CdTe powder can obviously be used as the CdTe source **32**.

The CdTe deposition is effected in the reaction chamber **33** according to a procedure in which, as already particularly explained above, it is crucial that the variation with time of the temperature of the element **30** and of the CdTe source **32** is such that the element **30** including the CdS layer is brought up to a temperature of 480°-520° C., preferably 500° C., in a steady heating process (without interruption) in e.g., 3 min., whereby the TCO layer **18** does not suffer any adverse effects in the course of this short heating phase, since it is protected by the CdS layer **24**. During this time the CdTe source **32** reaches a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the temperature of the element **30** has reached 480°-520° C., preferably 500° C., is the CdTe source **32** brought up in about 1 min. to such a temperature that a CdTe deposition rate onto the CdS layer **14** of 5 to 15 μm/min, preferably about 10 μm/min, is obtained and the required CdTe layer **12** of 5 to 10 μm thickness can be created in the short time of about 1 minute. This procedure results in the growth of the CdTe layer **12** taking place from the start at a temperature favoring the required (photo) electronic characteristics. The temperature of the element **30** is so selected that cheap soda-lime glass can be used as the material for the substrate **20**. The pressure in the reaction chamber **34** amounts during the CdTe deposition to about 0.1 mbar and is maintained by inflow or pumping out nitrogen (or helium, argon or hydrogen).

The heating load of the heating elements **22** and **24** can be optionally varied manually or by computer control.

In FIGS. 3 and 4 there are shown the current/voltage characteristic and the (external) absolute quantum yield as a function of the wavelength respectively of a pn CdTe/CdS thin film solar cell made in accordance with the above method. As can be seen from FIG. 3, the short-circuit current density of the manufactured solar cell amounts to 22.8 mA/cm^2 with a no-load voltage of 0.750 V and a space factor of 65%. The active surface of the solar cell of the embodiment set forth amounts to 0.388 cm^2. This gives an efficiency of 11.0% (relative to illumination with 100 mW/cm^2, 1.5 AM overall).

The (external) absolute quantum yield according to FIG. 4 exhibits a constant value over the substantial part of the spectrum (about 820–520 nm) with a value around 85%. The fall off at 520 μm is caused by the absorption of the CdS layer **14**.

We claim:

1. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO layer and an n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere free of oxygen according to the close-spaced sublimation method from a CdTe source and is provided with an electrically conducting back contact,

characterized in that,

a substrate of soda-lime glass is used, the substrate is provided with the TCO layer, and the CdS layer is brought to a temperature between approximately 480° C. and 520° C. before coating with the CdTe

layer, said temperature being maintained during the CdTe coating.

2. A method according to claim **1**, characterized in that a $CdCl_2$ tempering step is employed after the CdTe coating.

3. A method according to claim **1**, characterized in that the substrate with the TCO layer and the CdS layer is brought to a temperature of about 500° C. before the CdTe coating, which temperature is maintained during the CdTe coating.

4. A method according to claim **1**, characterized in that the heating of the substrate provided with the TCO layer and the CdS layer is effected in a steady heating process over between approximately 1 and 5 min.

5. A method according to claim **4**, characterized in that the heating is effected in approximately 3 min.

6. A method according to claim **1**, characterized in that the deposition rate of the CdTe on the CdS layer is approximately 5 to 15 μm/min.

7. A method according to claim **6**, characterized in that the CdTe layer is deposited in approximately 1 min.

8. A method according to claim **6**, characterized in that the CdTe deposition rate is adjusted to 10 μm/min.

9. A method according to claim **1**, characterized in that the variation with time of the temperature of the substrate provided with the TCO layer and the CdS layer and of the CdTe source is so controlled that the substrate is brought in a steady heating process to a temperature of 480° to 520° C. in approximately 1 to 5 min. and, during this time, the CdTe source is brought to a temperature at which there is no appreciable sublimation of the CdTe, and in that, only when the temperature of the substrate with the TCO and CdS layers has attained the desired temperature between 480° and 520° C., the CdTe source is brought in approximately 1 min. to a temperature at which a deposition rate on to the CdS layer is obtained such that the required CdTe layer can be applied in approximately 1 min.

10. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO front contact layer and an overlying n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere according to the close-spaced sublimation method and is provided with an electrically conducting back contact, characterized in that indium is used for the n-doping of the CdS layer and in that, before the deposition of the CdS layer, an ultra-thin indium layer less than 0.5 nm thick is applied to the TCO layer and in that the In and CdS layers so mix during the deposition of the CdTe layer that the indium layer is dissolved by diffusion of the indium atoms into the CdS layer and is no longer identifiable as such in the finished solar cell and the CdS layer includes the indium atoms of the indium layer in dispersed form as n-doping.

* * * * *

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United States Patent [19]
Higuchi et al.

[11] **Patent Number: 5,994,642**
[45] **Date of Patent: Nov. 30, 1999**

[54] METHOD FOR PREPARING CDTE FILM AND SOLAR CELL USING THE SAME

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[86] PCT No.: **PCT/JP97/01791**
§ 371 Date: **Mar. 13, 1998**
§ 102(e) Date: **Mar. 13, 1998**
[87] PCT Pub. No.: **WO97/45880**
PCT Pub. Date: **Dec. 4, 1997**

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Apr. 28, 1997	[JP]	Japan	9-110727
Apr. 28, 1997	[JP]	Japan	9-110728

[51] **Int. Cl.**^{6} **H01L 31/00**
[52] **U.S. Cl.** **136/260**; 136/264; 427/74; 427/76; 427/255.2; 438/761; 438/763
[58] **Field of Search** 136/260, 264; 427/74, 76, 255.2; 438/761, 763

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Primary Examiner—Mark Chapman
Attorney, Agent, or Firm—Akin, Gump, Strauss, Hauer & Feld, L.L.P.

[57] ABSTRACT

A method for forming a CdTe film of good quality by an improved close-spaced sublimation process is disclosed. This method comprises: a step of applying a paste which contains material for CdTe semiconductor on a supporting member, thereby to form a coating film which contains the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, and causing the material for the semiconductor in the coating film to evaporate.

16 Claims, 5 Drawing Sheets

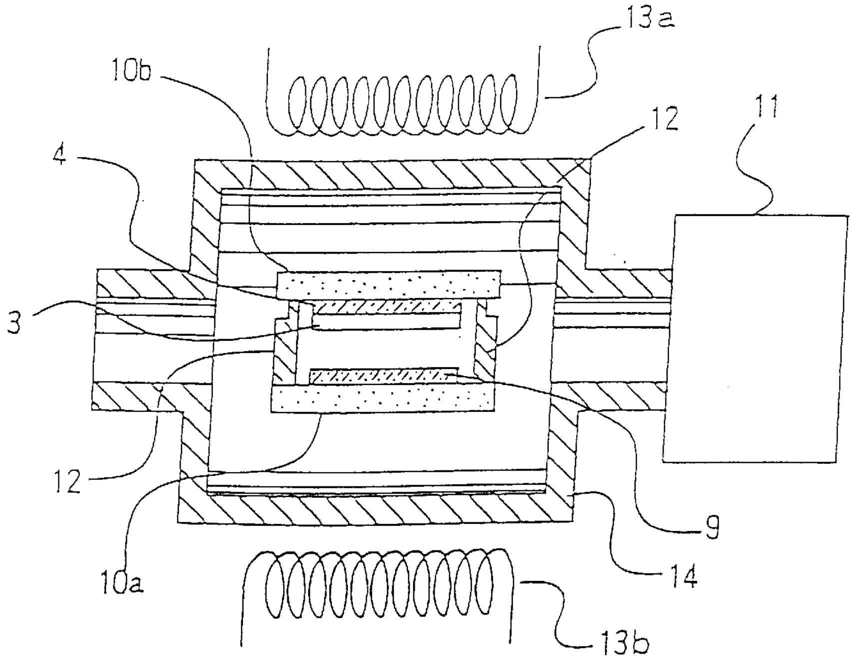


FIG. 1

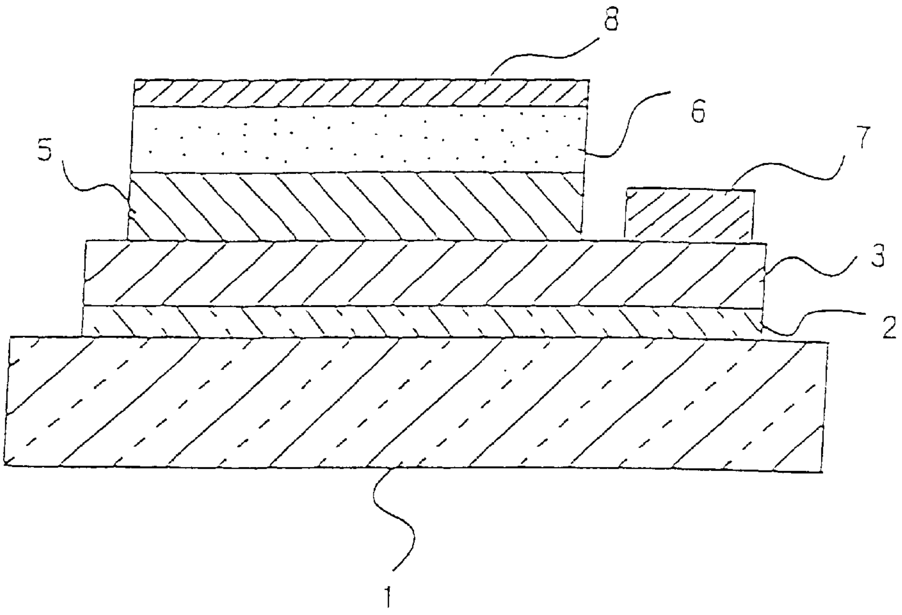
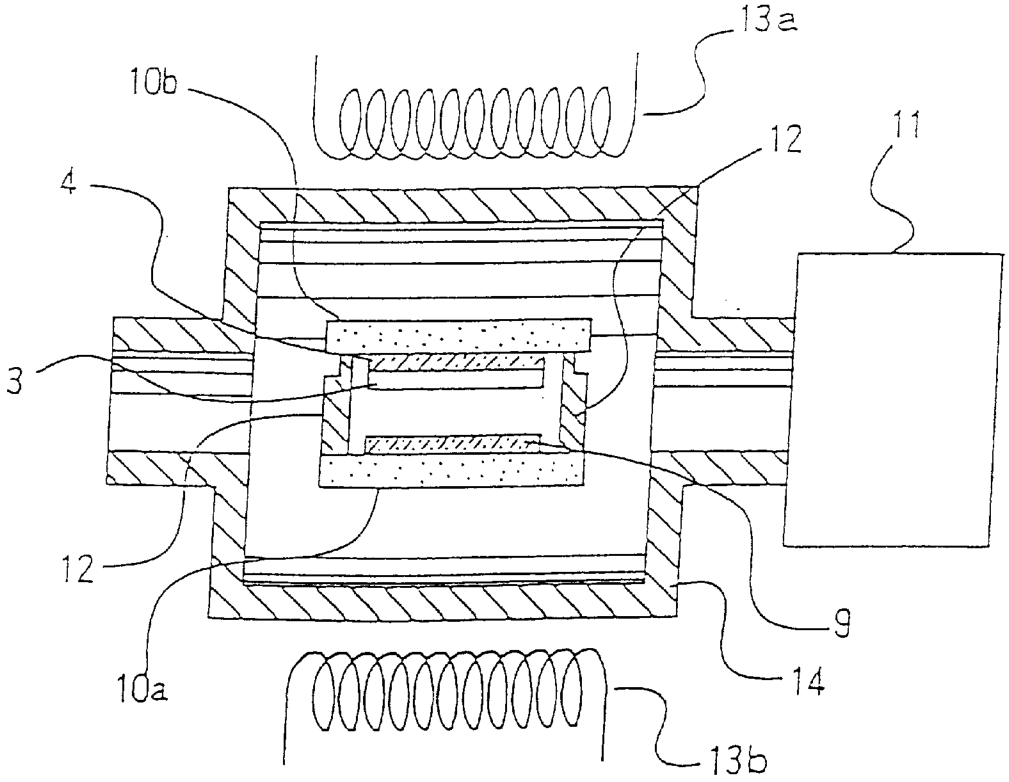
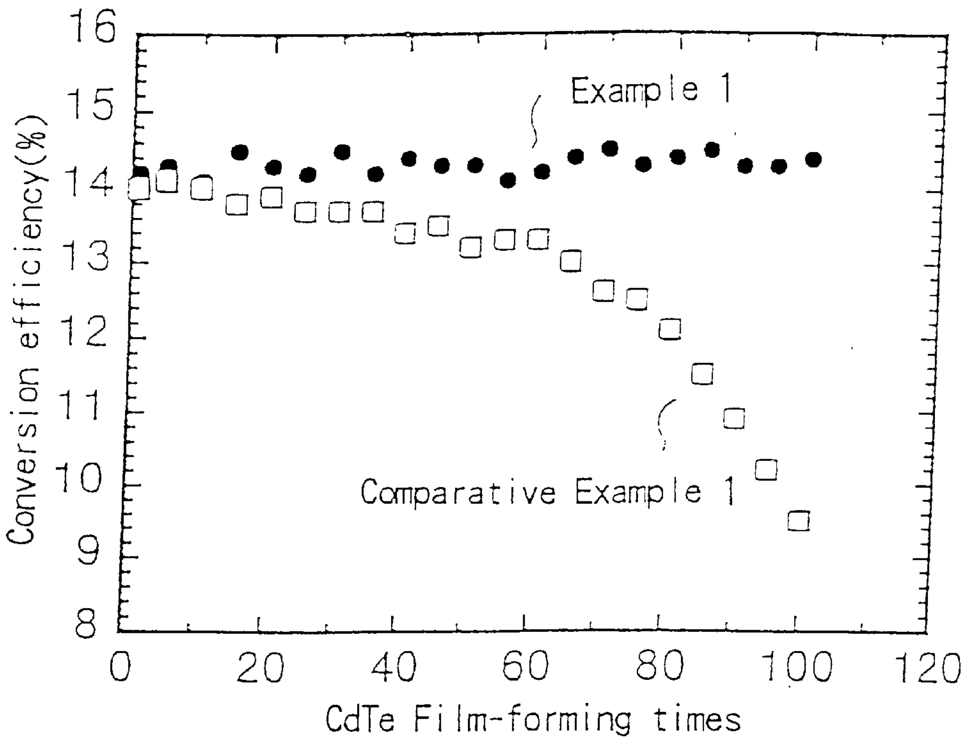


FIG. 2



F I G. 3


16
15
14
13
12
11
10
9
8
Conversion efficiency(%)
0
20
40
60
80
100
120
CdTe Film-forming times
Example 1
Comparative Example 1

F I G. 4

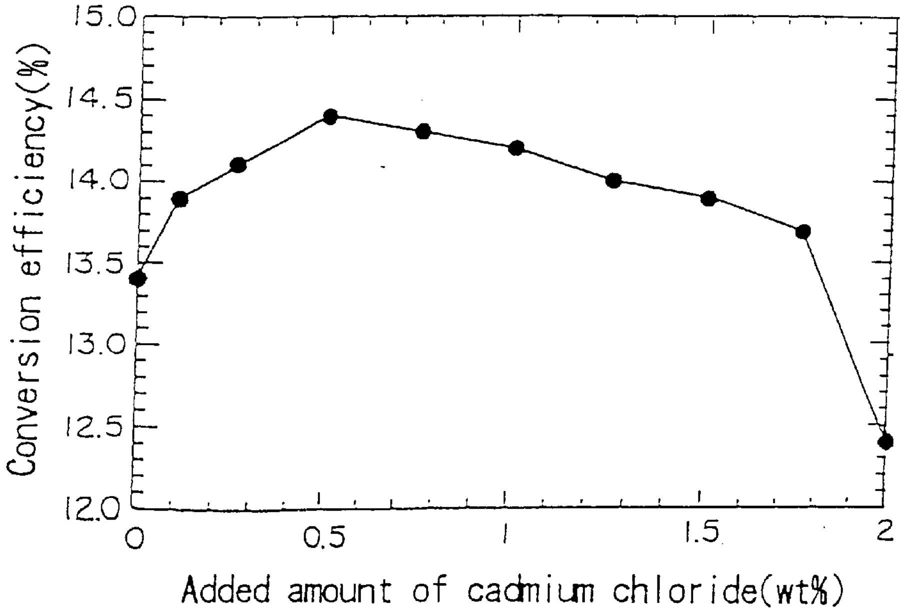

15.0
14.5
14.0
13.5
13.0
12.5
12.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 5

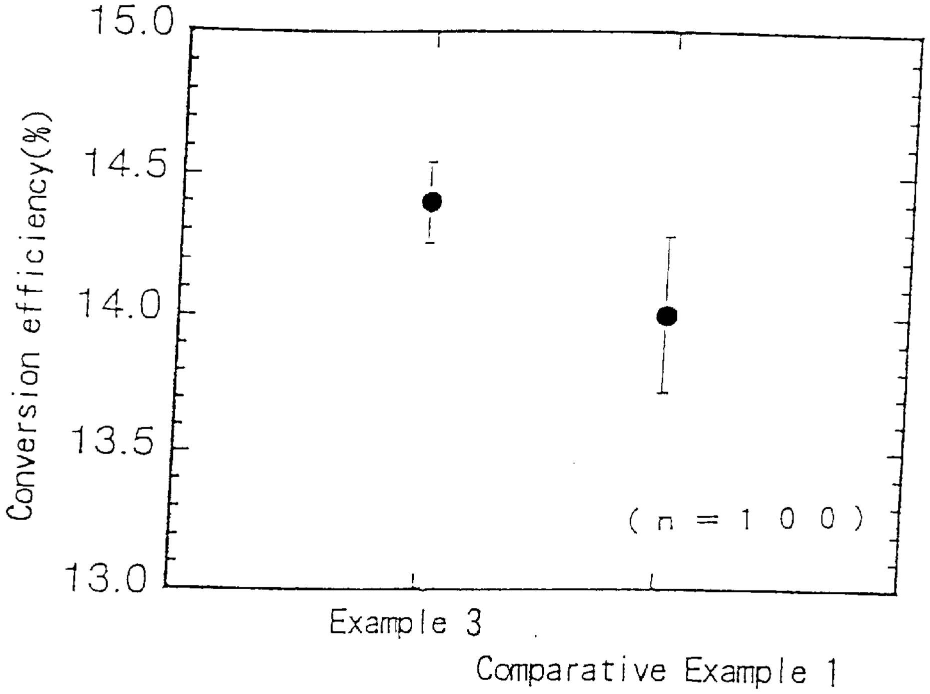

15.0
14.5
14.0
13.5
13.0
Conversion efficiency(%)
(n = 100)
Example 3
Comparative Example 1

FIG. 6

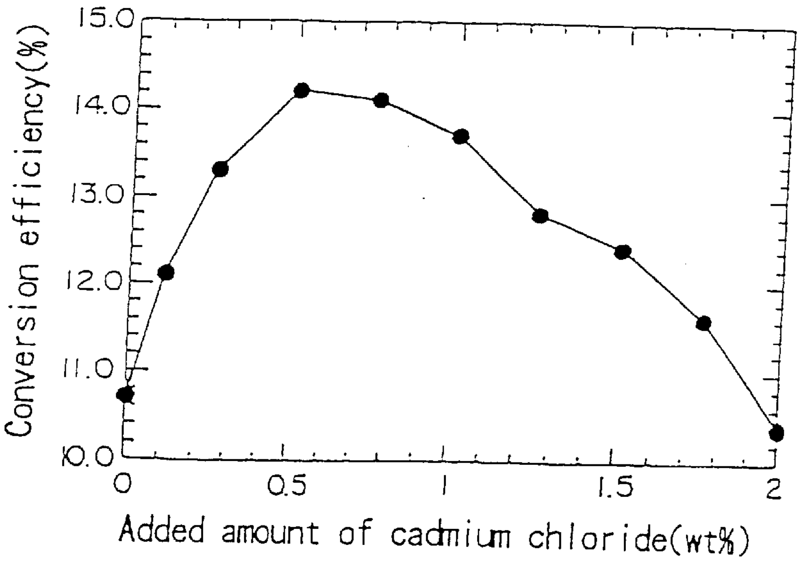

15.0
14.0
13.0
12.0
11.0
10.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 7

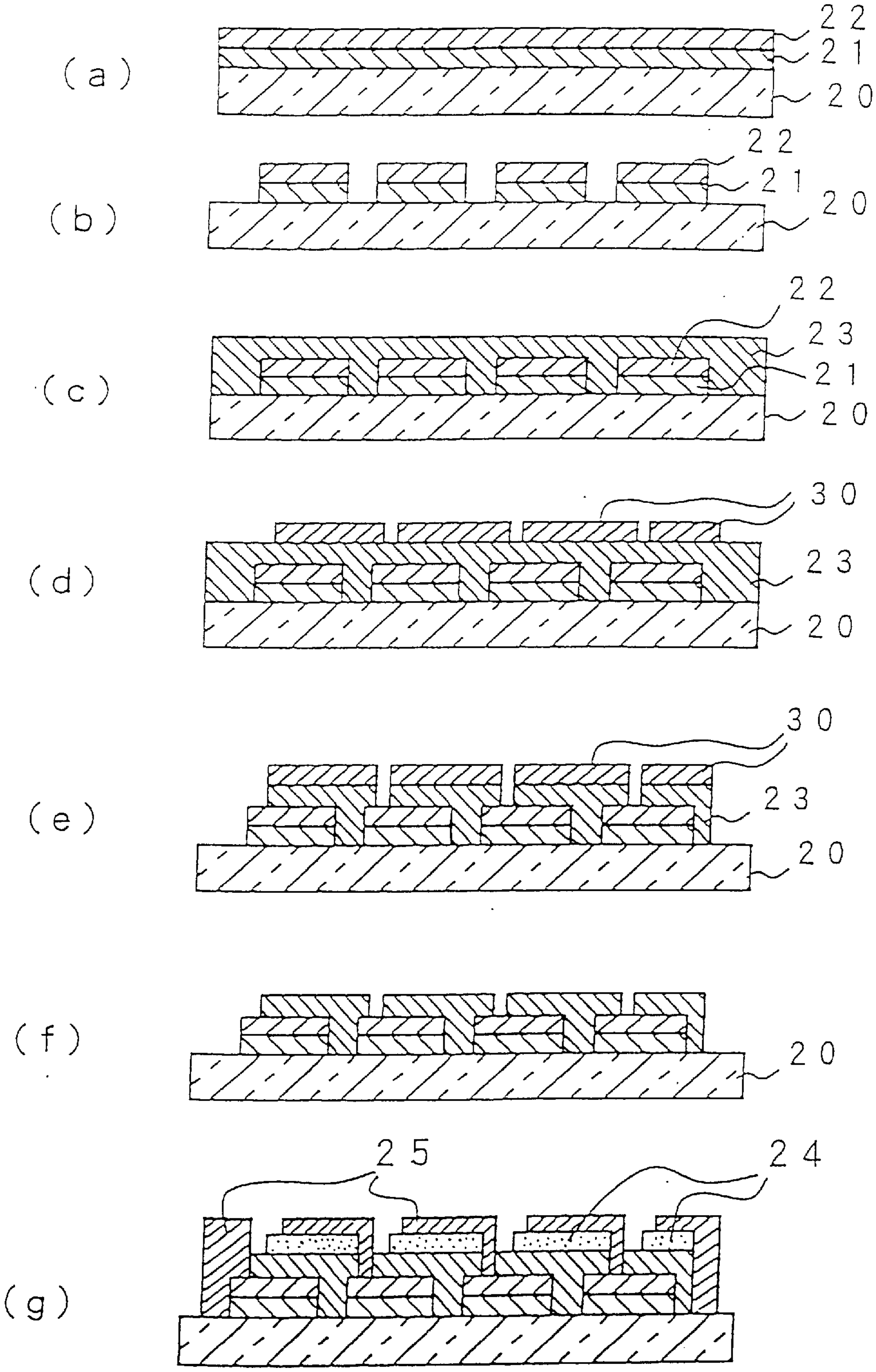
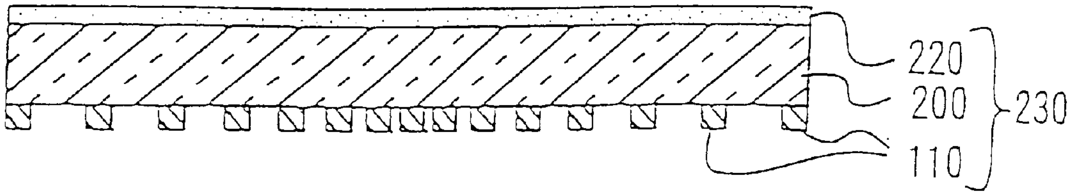


FIG. 8



METHOD FOR PREPARING CDTE FILM AND SOLAR CELL USING THE SAME

TECHNICAL FIELD

The present invention relates to a method for preparing a CdTe semiconductor film which is used mainly for solar cells, in particular, to a method for preparing the CdTe film by a close-spaced sublimation process.

BACKGROUND ART

In recent years, global environmental problems such as global warming due to carbon dioxide, depletion of the ozone layer, and the like have been highlighted. For that reason, expectation for development of new energy, in particular, that for solar cells have become glowingly great. However, for popularization of the solar cells, there are a number of problems which must be solved. In particular, an improvement in conversion efficiency of the solar cells and a reduction in price are desired.

A CdS/CdTe solar cell uses CdTe which has an forbidden band gap (=1.44 eV) being suitable for a light absorption layer, and thus it is one of the solar cells which are expected to yield a high conversion efficiency.

In the manufacturing process of the CdS/CdTe solar cell, a cadmium telluride (CdTe) film is formed on a surface of a cadmium sulfide (CdS) film in general. As a method for forming the CdTe film, the close-spaced sublimation process which can produce the CdTe film of high quality is attracting attention. The close-spaced sublimation process is a kind of the vapor deposition process. A CdTe solar cell which has a conversion efficiency of the world highest level (15.8%) at present is obtained by this process. The close-spaced sublimation process is disclosed in, for instance, "HIGH EFFICIENCY CdS/CdTe SOLAR CELLS FROM SOLUTION-GROWN CdS FILMS" (The Conference Record of the 22nd IEEE Photovoltaic Specialists Conference (1991) Vol. 2, p.952) by T. L. Chu et. al., or the like. According to this process, a material for forming the CdTe film (hereinafter referred to as a source) and a substrate are so placed as to face each other, with a gap of about 0.5–5 mm, and heated under a reduced pressure. In this manner, the source is caused to sublime and then deposit on the substrate.

According to this process, since the sublimed source is rearranged and crystallized on the substrate placed at a short distance as long as the mean free path level, a CdTe film which has a high crystallinity is obtained. Further, since the treatment is performed under the reduced pressure, the film-forming speed is high.

However, the above-mentioned conventional close-spaced sublimation process has the following problems.

In general, in the close-spaced sublimation process, as a source, a CdTe powder placed on a dish-shaped container so as to cover over it is used. In the above-mentioned literature for instance, a commercially-available polycrystal of CdTe with a purity of 5N, or a powder produced by pulverizing a polycrystal ingot of CdTe obtained by directly implanting a dopant as one of the constituting element, is used as the source.

In addition to the fact that this process uses an expensive CdTe powder, it has a low utilization efficiency. In this process, it is difficult to evenly place as much amount of the source for forming the film just once for covering over the container. For that reason, the same source is repeatedly used for forming the CdTe films. It is difficult to control the CdTe powder or the source since it changes in particle size, powder density, stoichiometric ratio and the like by the sublimation, and hence, with the repetition of the film-forming, dispersions in thickness and in quality of the CdTe film increases gradually. Therefore, the obtained solar cell has a large dispersion in performance. For that reason, in order to make the dispersion in performance of the solar cell small, of the source placed for covering, only about 10% is actually consumed for the film-forming, and the rest is discarded without being used.

Further, according to this process, since the film is formed under the reduced pressure, an equipment must once be stopped when the source is exchanged. Therefore, the production efficiency is also low.

When a CdTe film is formed by this process, on a substrate which has a large area, a central part of the obtained CdTe film is made thicker than that of a peripheral part because the central part of the source is liable to trap a heat flowed from circumference, as opposed to the peripheral part where the heat is liable to escape. Therefore, the variation in thickness within the same film is large.

Moreover, according to this process, when the source is used repeatedly, the particle diameter of the material decreases gradually and the surface area of the material increases, and in addition, the surface temperature of the source rises because the particles combine together by sintering. Therefore, the thermal conductivity increases and the film-forming speed increases gradually. When the same source is used repeatedly still more and the remaining amount of the source decreases accordingly, pores are produced between and among the particles and the thermal conductivity of the source is gradually lowered, thereby to decrease the film-forming speed conversely. For that reason, even when the manufacturing is performed under the same conditions, the thickness of the obtained CdTe film varies for every film-forming processes.

As previously described, according to the conventional close-spaced sublimation process, it is difficult to obtain CdTe film having uniform quality and thickness within the same film and between a plurality of the films. For that reason, although the CdTe film theoretically has the forbidden band gap which is the most ideal for converting the solar light as a compound semiconductor, a CdTe film as an ideal p-type semiconductor has not actually been obtained by the conventional close-spaced sublimation process.

In order to improve the conversion efficiency of the CdTe solar cells, means of making the CdTe film a weak p-type one by diffusing copper or the like into the CdTe film from the electrode side has widely been used, as reported, for instance, by B. E. Mccandless et. al., in "A treatment to allow contacting CdTe with different conductors" (Conference record of the 24th IEEE photovoltaic specialists conference 1994 volume II, p. 107–110). However, according to this method, a solar cell having a satisfactory conversion efficiency has not been obtained.

DISCLOSURE OF THE INVENTION

The present invention intends to solve the above-mentioned conventional problems, and has, as its object, a provision of a method for preparing a CdTe film of good quality simply.

The method for preparing the CdTe film in accordance with the present invention comprises: a step of coating a paste containing a material for CdTe semiconductor on a supporting member thereby to form a coating film containing the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, thereby to cause the semiconductor material in the coating film to evaporate.

According to this method, it is possible to greatly improve the utilization rate of the material as compared with the case of using the above-mentioned conventional source. That is, since a thin coating film can be formed by coating, the utilization rate of the source which has conventionally been about 10% can be improved to about 50%. For that reason, it is not necessary to use the source for the formation of the film repeatedly. That is, since the source can be made disposable and a new source can constantly be used for the film-forming, it is possible to suppress the dispersion in characteristics of the CdTe film due to the repeated use of the source. Further, since the thin source can be obtained, it is possible to form the CdTe film without giving an excessive thermal damage to the previously formed CdS film.

Moreover, it is preferable to use a mixture of a cadmium powder and a tellurium powder as the semiconductor material. By using the mixture of the cadmium powder and the tellurium powder or, preferably, the pulverized powder, which is very inexpensive as compared with the CdTe powder thereof, the material cost can be reduced in great deal. In particular, by pulverizing Cd and Te in a mixed state, a mixed power can be obtained in a short time period. Further, with an energy for the pulverization, a part of the mixture can be synthesized into CdTe.

Moreover, by adding cadmium chloride into the paste, the crystallinity of the formed CdTe film is improved and the grain size of CdTe increases. In this manner, it is possible to obtain a solar cell of a high conversion efficiency. It is believed that the improvement in the crystallinity of the CdTe film is due to the fact that position of lattice defect of tellurium is substituted by chlorine, thereby to improve the crystallinity of the CdTe film. Moreover, since cadmium chloride is mixed into a paste and then coated, it is possible to constantly use the new source wherein cadmium chloride is uniformly dispersed. Therefore, it is possible to repeatedly and stably manufacture a CdTe film of high quality. If the added amount of cadmium chloride is smaller than 0.1 wt %, great effect cannot be obtained for the improvement in the performance of the solar cell. In contrast, if it is larger than 1.75 wt %, the performance is deteriorated conversely. For that reason, the added amount of cadmium chloride is preferably 0.1–1.75 wt %, and particularly 0.3–1.0 wt %.

In addition, it is preferable that the paste is one with a Group I element or a Group V element incorporated therein. By incorporating an impurity which acts as a carrier into the paste, it is possible to control the carrier concentration of the CdTe film in simple means. Incidentally, use of the Group I element or the Group V element in the conventional process employing a source prepared by placing the semiconductor material of powder state in a container so as to cover over it causes a variation in composition of the source, if such films are formed for plural times by using the same source, due to the differences in the sublimation speeds of the semiconductor material and the impurities. Therefore, a semiconductor film of stable composition cannot be obtained. On the other hand, according to the present invention, since the coating film of the semiconductor material formed on the surface of a heat-resistant supporting member is used as the source, it is possible to use a very small amount of the semiconductor material as the source. Therefore, a semiconductor film which has a constant concentration of the impurity can be formed. It is preferable that the Group I element to be mixed is lithium, potassium, sodium, rubidium, copper, silver or gold. Further, it is preferable that the Group V element to be mixed is arsenic, antimony, bismuth, phosphor or nitrogen. These can be used singly or plurally.

Moreover, by adding to the paste a substance which is stable in composition against the heat applied at the time of forming the semiconductor film and remains on the supporting member after the heating, it is possible to place the semiconductor material of an amount which is exactly necessary for one time film-forming on the supporting member in a stable state with a small dispersion. By causing all semiconductor materials to sublime, it is possible to manufacture a CdTe film of large area which is stable in thickness and quality. For instance, according to a screen-printing, it is difficult to form a coating film of a uniform thickness unless the thickness of the coating film to be formed is not less than 50 μm. However, in a case of adding no additive to the paste, when a coating film with the thickness of 50 μm is entirely sublimed, a CdTe film with a thickness of about 20 μm is obtained. If such a thick CdTe film is used in the solar cell, resistance of the CdTe film in the thickness direction is large and thus the characteristics of the obtained solar cell are poor. That is, a thinner CdTe film is desired for employing it in the solar cell. The most suitable thickness is about 6 μm. That is, if no additive is added to the paste, it is necessary to stop the film formation halfway while the source remains. On the other hand, by adding an additive to the paste as in this example, the amount of the semiconductor material in the coating film can easily be adjusted and thus it becomes possible to form a semiconductor film which has a preferable thickness. Since to control the thickness of the coating film becomes so easy, it is possible to use only a necessary amount of the semiconductor material for one film formation as the source. As the substance to be added, carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride or aluminum nitride is preferable. Further, these substances can be used by mixing them. Since the carbon and silicon carbide can absorb radiated infrared ray, the source can be heated efficiently by using them. Moreover, since they can protect the CdS film which has previously been formed from a thermal damage, it is possible to suppress an occurrence of micro-short-circuiting resulting from a thinning of the CdS film by the sublimation, and an excessive mutual diffusion at an interface between the CdS film and the CdTe film.

Further, at the time of painting the paste, by making more amount of the paste adhere to the peripheral part of the supporting member where its temperature at heating is relatively lower than the central part of the supporting member, some more amount of semiconductor material may be placed there.

The supporting member for holding the paste is preferably a plate-shaped carbon material which has a heat soaking property and a small heat capacity. A glass substrate is preferable in viewpoints of price and easiness in handling. As the glass, borosilicate glass, a low alkali glass, soda-lime glass and the like may be used. In a case of using the glass substrate, it is preferable to place at least one carbon plate beneath the glass substrate. Further, if an expansion of the supporting member due to the thermal treatment is taken into consideration, a ceramics which has a small linear expansion coefficient is preferable. These supporting member can be used repeatedly.

It is preferable that the supporting member is composed of a glass having a conductive oxide film on the surface thereof. By using a glass having the conductive oxide film of, for instance, indium oxide, indium tin oxide, stannic oxide, zinc oxide and the like, as the supporting member, it is possible to suppress a radiation heat which reaches the formed semiconductor film, after the evaporation of the source is completed, thereby to prevent the excessive mutual diffusion at the interface of the CdS film and the CdTe film. Further, by roughening a surface of the supporting member which is opposite to the side where the paste is painted, the radiation heat can similarly be suppressed. In this case, by scatter due to an unevenness of the surface of the supporting member and an improvement in the heat absorbing property due to the increase in the surface area, it is possible to reduce the amount of infrared ray which transmits through the supporting member and reaches the formed semiconductor film.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is a schematic longitudinal cross-sectional view of a solar cell which uses CdTe film in accordance with one embodiment of the present invention.

FIG. **2** is a schematic longitudinal cross-sectional view showing a structure of an equipment employed for forming the CdTe film in the same embodiment.

FIG. **3** is a characteristic diagram showing the relationship between the times of forming the CdTe film in the same embodiment and the conversion efficiency of a solar cell produced by using the CdTe film.

FIG. **4** is a characteristic diagram showing the relationship between added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in another embodiment of the present invention.

FIG. **5** is a characteristic diagram showing the dispersion in the conversion efficiency of a solar cell produced by using CdTe film obtained in a still other embodiment of the present invention.

FIG. **6** is a characteristic diagram showing the added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in a still other embodiment of the present invention.

FIG. **7**(*a*)–FIG. **7**(*g*), each is a longitudinal cross-sectional view showing the state of the respective step in manufacture of the solar cell in another embodiment of the present invention.

FIG. **8** is a schematic longitudinal cross-sectional view of source substrate plate used in another embodiment of the present invention.

THE BEST MODE FOR CARRYING OUT THE INVENTION

The method for preparing the CdTe film in accordance with the present invention will be described in detail with reference to the drawings.

In the following examples, a solar cell shown by FIG. **1** is produced by using the obtained CdTe film.

A transparent and insulating substrate **1** is made from borosilicate glass, low-alkaline glass, low-iron soda-lime glass, soda-lime glass and the like. On the surface of this substrate **1**, a transparent conductive film **2** with a thickness of 1,000–10,000 Å composed of tin oxide, indium tin oxide (ITO) and the like is formed by chemical vapor-phase growing process or sputtering. In this occasion, a silica film (SiO_2 film) may sometime be formed between the substrate **1** and the transparent conductive film **2**, in order to prevent an alkali component in the substrate **1** from diffusing into the transparent conductive film **2**. Then, by forming a CdS film **3** with a thickness of 500–2,000 Å on the transparent conductive film **2** as an n-type semiconductor, a substrate **4** for forming CdTe film is obtained. This CdS film **3** is formed by thermally decomposing such an organometallic complex compound as cadmium isopropyl xanthogenate on the transparent conductive film **2**.

In the followings, as examples of the method for preparing CdTe semiconductor film in accordance with the present invention, methods for forming a CdTe film **5** on the surface of the thus obtained CdS film **3** of the substrate **4** will be described.

EXAMPLE 1

By mixing a CdTe powder as a semiconductor material with propylene glycol as a viscosity improver, a paste was prepared. By printing the obtained paste on the glass substrate as the supporting member and drying, a film of the semiconductor material was formed on a glass substrate, thereby to obtain a source substrate **9**.

The obtained source substrate **9** and the substrate **4** were installed on a manufacturing equipment shown in FIG. **2**, and the CdTe film **5** was formed on the surface of the substrate **4** in the following manner.

A chamber **14** is made of quartz tube, inside of which susceptors **10***a* and **10***b* made of carbon with a thickness of 1 mm are arranged as heat-soaking members. On the mutually confronting surfaces of the susceptors **10***a* and **10***b*, the source substrate **9** and the substrate **4** are arranged so as to make the semiconductor material film to face the CdS film **3**, respectively. In that arrangement, a spacer **12** is disposed between the source substrate **9** and the substrate **4** so that the distance between the both is constant. The source substrate **9** and the substrate **4** may be disposed on the susceptors inversely, bottom to top.

By substituting the atmosphere inside the chamber **14** with an argon gas, and heating the source substrate **9** and the substrate **4** by lamp heaters **13***a* and **13***b* for 30 second to several minutes, while maintaining the pressure inside the chamber **14** to 1 Torr by aspirating with a rotary pump **11**, a CdTe film **5** was formed on the CdS film **3** of the substrate. In this step, the temperature of the substrate **4** was kept to 400–650° C. by heating, and the temperature of the source substrate **9** was kept to a temperature which was higher than the temperature of the substrate **4** by 5–100° C.

In the above-mentioned manner, 100 pieces of samples wherein the CdTe films **5** were formed on the CdS films **3** of the substrates **4** were prepared. In this preparation, the sources were replaced for every samples. Further, about half of the source was consumed for forming the film.

On the surfaces of the CdTe films **5** of the respective samples thus formed, a methanol or an aqueous saturated solution of cadmium chloride was applied and then the applied methanol or water was evaporated. Further, the substrate **4** for thin film forming was thermally treated at 400° C. for 30 minutes. By this thermal treatment, grains in the CdTe film were grown.

A carbon paste was prepared by mixing a carbon powder and a solution obtained by dissolving polyvinylbutyral as a viscosity improver in diethylene glycol monobutyl ether with kneading. After applying this carbon paste on the surface of the CdTe film **5** by screen printing, it was dried and sintered, thereby to form a carbon electrode layer **6** as a current collector. On the other hand, a paste was prepared by mixing and kneading a mixed powder of silver and indium, an epoxide and an alcohol solution consisting mainly of terpineol. By applying the obtained paste on the surface of the CdS film **3** and carbon electrode layer **6** by screen printing, drying and then sintering, a + side electrode **7** and a − side electrode **8** were formed, respectively.

COMPARATIVE EXAMPLE 1

As a comparative example, a CdTe film was formed by using one obtained by filling the CdTe powder similar to that used in Example 1 in a dish-shape container as the source. In that case, the CdTe films were formed with the same source for a plurality of times. By this process, about 90% of the source was left after the formation of the CdTe films for 100 times. By using the obtained CdTe films, solar cells similar to those in Example 1 were produced.

Each 100 pieces of the solar cells of Example 1 and of Comparative Example 1 obtained in the above-mentioned manner were investigated about their conversion efficiencies with a solar simulator at AM 1.5, 100 mW/cm^2. The results are shown in FIG. **3**. In this diagram, the abscissa represents the respective solar cells arranged in the orders of forming the CdTe films.

As clearly seen from FIG. **3**, according to the manufacturing method of Comparative Example 1, the composition of the source varies with the repetition of the manufacture of the film, thereby to change the quality and the thickness of the obtained CdTe film. Therefore, the characteristics of the cells prepared with these CdTe films deteriorated. In contrast, according to the manufacturing method of Example 1, it is possible to make a small amount of the source to be uniformly held on the glass substrate. By this method, the utilization rate of the material can greatly be improved as compared with the manufacturing method of Comparative Example 1, even if the source is replaced for every film formations. That is, by employing a source of the coating film obtained by making a semiconductor material a paste-state and painting this paste on a substrate, a constantly stable supply of the source is enabled. Therefore, a semiconductor film with a high quality can be manufactured stably at a low cost.

EXAMPLE 2

In this example, a description will be made in a case of adding cadmium chloride into the paste for forming the CdTe film beforehand.

A CdTe powder similar to that in Example 1 was used as a semiconductor material. Pastes were respectively prepared by adding cadmium chloride at a rate of from 0 to 2.0 parts by weight to 100 parts by weight of this CdTe powder.

By using the obtained pastes, CdTe films were formed and then, solar cells were prepared in a manner similar to that in Example 1.

The relationship between the incorporation ratios of cadmium chloride to the CdTe powder and the conversion efficiency of the obtained solar cells are shown in FIG. **4**.

As shown in FIG. **4**, it is appreciated that by adding not less than 0.1 wt % of cadmium chloride to the CdTe powder, the conversion efficiency of the obtained cell is improved. However, if it is added in excess over 1.75 wt %, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1–1.75 wt % to the CdTe powder. In particular, the improvement in the conversion efficiency is remarkable at 0.3–1.0 wt %, and vicinity of 0.5 wt % is the most desirable.

100 parts by weight of the CdTe powder was mixed with 0.5 parts by weight of cadmium chloride. By using the obtained mixture, a paste was prepared as mentioned above. By using a semiconductor film formed by painting this paste as the source, a CdTe film was formed. In this step, the source was replaced for every times of film forming in a similar manner to that in Example 1.

As a comparative example, a CdTe film was also formed by using the same mixture so placed in a dish-shape container as to cover over it at a high density. In this time, the source was used continuously for a plurality of times for the film formation without replacing.

Solar cells were produced by using the CdTe films obtained in the above-mentioned manner. The characteristics of the obtained solar cells were investigated in a similar manner. The results are shown in Table 1.

TABLE 1

Film forming	Conversion efficiency (%)	
times (time)	Example 2	Comparative Example
1	14.6	13.6
20	14.5	13.5
40	14.7	13.2
60	14.5	12.5
80	14.5	11.3
100	14.6	8.5

As shown in Table 1, in the case of using the semiconductor material of powder state covering over the container, the characteristics of the semiconductor film decrease with the repeated times of the film forming. This is due to the above-mentioned varying in the cadmium chloride concentration and its non-uniformity. According to this method, it is difficult to form a CdTe film of good quality by using a small amount of the semiconductor material. That is, in any other means than discarding the source while consuming only a part of the source and leaving the remaining semiconductor material in a considerable amount, it is impossible to stably manufacture the CdTe film.

In contrast, according to the manufacturing method in accordance with this example, whereby the semiconductor material is made to have a paste-state, and the coating film obtained by applying the paste on the substrate is used as the source, the unevenness in the characteristics of the solar cells produced by using the obtained semiconductor film is small because there is no need for using the source repeatedly. Therefore, it is possible to stably manufacture the semiconductor film of a high quality at a low cost.

As the atmospheric gas, a similar effect is obtained in a case of using an inert gas such as nitrogen, hydrogen or helium gas in place of argon used in the above-mentioned example. In addition, in a film formation under a pressure of not more than 2 atm, a similar effect is also obtained.

EXAMPLE 3

By using a source of the coating film of the CdTe obtained by printing it as in Example 1, a CdTe film with a good quality can be formed. However, due to the fact that the CdTe powder as the raw material is very expensive, the price of the product becomes high. The reason for this is that the single crystal of CdTe is manufactured by Bridgman process in general. According to this process, in addition to the fact that heating at a high temperature of not less than 1,000° C. is required, a long period of time is required for elevating the temperature and cooling for the safety in operation and the improvement in the crystallinity.

Therefore, a description will be made, in this example, on a method for forming the CdTe film of a good quality, by using a starting material of a Cd powder and a Te powder which are inexpensive as compared with the CdTe powder. The price of the commercially available CdTe powder is about 250 yen/g but, in contrast, the prices of the commercially available Cd powder and Te powder are about 20 yen/g, respectively. Therefore, according to the manufacturing method of this example, the material cost can be reduced in great deal.

The Cd powder, the Te powder and a liquid (for instance, water) were mixed together and stirred by using a medium of ring-shape or spherical shape. Subsequently, a paste was prepared by adding propylene glycol to the obtained mixture after being dried. By using the paste thus obtained, a CdTe film was formed and a solar cell was produced in a manner similar to that in Example 1.

The conversion efficiency of the obtained solar cell was measured in a manner similar to that in Example 1. The results thereof are shown in FIG. **5**. In this diagram, the ordinate represents mean value ± standard variance in the conversion efficiencies of the solar cells of Example 3 and of the solar cells of Comparative Example 1.

As clearly shown by FIG. **5**, according to the manufacturing method of this example, it is possible to obtain a solar cell of an excellent characteristic by using low-priced materials. As the reason for this, there are given the fact that the temperature distribution in the source can be made uniform since the particle diameters of Cd and Te can be made uniform by pulverizing, and the amount of the source can be made small by using the film obtained by applying the pulverized mixture as the source.

The Cd powder and the Te powder were mixed in an equimolar amount, and pulverized in water to give a particle diameter of not more than about 1 μm by using a medium stirring mill. After drying the pulverized powder thus obtained, propylene glycol as a viscosity improver was added to the pulverized powder and kneaded, thereby to prepare a paste. By printing this paste on a carbon plate with a thickness of 1 mm as the supporting member, and drying at 120° C. for 1 hour, a coating film was formed and a source substrate was obtained.

On investigating the composition of the formed coating film by X-ray diffraction, diffraction peaks of Cd single substance, Te single substance and CdTe were observed. It is believed that this CdTe is synthesized at the pulverization by the pulverizing energy.

This source substrate **9** and the substrate **4** were arranged so as to make the coating film to face the CdS film, with a gap of 2 mm. Thereafter, the atmosphere inside the chamber **14** was substituted by argon, the source substrate **9** and the substrate **4** were heated to temperatures of 600–630° C. and of 580–600° C., respectively, while maintaining the pressure to 1–5 Torr, and kept there for 1 minute. By this procedure, a CdTe film with a thickness of 6 μm was formed on the CdS film of the substrate **4**.

An aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the surface of the obtained CdTe film, and then the water was evaporated. Thereafter, by thermally treating the CdTe film at 400° C. for 30 minutes, the crystallinity of the CdTe film was improved. Subsequently, a carbon film and an AgIn film were formed as an electrode of the CdTe film side and an electrode of the CdS film side, respectively, thereby to produce a solar cell.

The measurement on the characteristics of the obtained solar cell conducted with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.5 mA/cm^2 and the open-circuit voltage was 0.813 V. Further, the fill factor was 0.696 and the conversion efficiency was 13.3%. These characteristics are about the same degree as the characteristics of the solar cell of Comparative Example 1 produced by using the CdTe film formed by using the CdTe powder placed in the dish-shape container so as to cover over it (short-circuit current of 23.4 mA/cm^2, open-circuit voltage of 0.815 V, fill factor of 0.701 and conversion efficiency of 13.4%).

Next, a paste was prepared by adding an appropriate amount of $CdCl_2$ as a melting point depression agent in addition to propylene glycol as the viscosity improver to the pulverized powder similar to the above-mentioned. After printing the obtained paste on a carbon plate with a thickness of 1 mm, the paste was dried by drying at 120° C. for 1 hour, thereby to form a coating film comprising a semiconductor material, and to obtain a source substrate **9**. In an X-ray diffraction pattern of the obtained coating film, a peak attributable to the $CdCl_2$ was observed in addition to the diffraction peaks of Cd single substance, Te single substance and CdTe, of course.

By heating the obtained source substrate **9** under a nitrogen atmosphere at a temperature of 600–700° C. for 1 hour, the coating film was sintered. In an X-ray diffraction pattern of the sintered film thus obtained, only the diffraction peak attributable to CdTe was observed.

Next, the source substrate **9** and the substrate **4** were so placed as to face each other, with a gap of 2 mm, and a CdTe film **5** was formed on the CdS film **3** in a procedure as shown above. After the formation of the CdTe film **5**, an aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the CdTe film **5** and water was evaporated, and then, it was thermally treated at 400° C. for 30 minutes. Thereafter, a solar cell was produced in a procedure as shown above and the characteristics of the solar cell were evaluated in a similar manner. Measurements on the characteristics of the solar cell with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.6 mA/cm^2, and the open-circuit voltage was 0.816 V. Further, the fill factor and the conversion efficiency were found to be 0.699 and 13.5%, respectively. These values are the same degree as those of the solar cell of Comparative Example 1.

A film formed by painting a fine powder obtained by pulverizing Cd and Te singly or a CdTe compound and drying it, or a sintered film thereof obtained in the above-mentioned manner was used as the source to obtain a good quality CdTe film.

Incidentally, a similar effect is obtained by using a commercially-available CdTe as the starting material.

EXAMPLE 4

In this example, a description will be made on a method which employs the Cd and Te similar to those in Example 3 as the starting material, wherein cadmium chloride is further added to this mixture.

A muddy mixture was prepared by pulverizing the Cd and Te similar to those used in Example 3 in a wet process. Next, by drying the mixture and adding cadmium chloride and propylene glycol as the viscosity improver to this mixture, a paste was prepared. A CdTe film was formed by using the obtained paste and a solar cell was produced in a manner similar to that in Example 1.

The characteristics of the obtained solar cell were evaluated in a manner similar to those in the above-mentioned examples.

The added amounts of cadmium chloride to the sources and the conversion efficiencies of the solar cells produced by using the respective sources are shown in FIG. **6**.

From FIG. **6**, it is appreciated that by adding cadmium chloride in an amount of not less than 0.1 wt % for a sum of the weights of Cd and Te to it, the conversion efficiency is improved as compared with a case of not adding cadmium chloride. However, if cadmium chloride is added in an amount of more than 1.75 wt % for a sum of the weights of Cd and Te, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1–1.75 wt %. In particular, the improvement in the conversion efficiency is remarkable in 0.3–1.0 wt %, and that in the vicinity of 0.5 wt % is the most desirable.

EXAMPLE 5

In this example, a description will be made on a method with an incorporation of a Group I element or a Group V element as a dopant into the source. According to this method, carrier concentration of the CdTe film can easily be controlled. The Group I element and/or the Group V element to be added is/are incorporated into it in a state of single substance or a compound such as organometallic compounds. These elements may be used singly or plurally.

On a surface of a substrate **1** with a thickness of 1.1 mm made from a borosilicate glass, a transparent conductive film **2** with a thickness of 500–5,000 Å composed of tin oxide was formed by a sputtering process. Next, a CdS film **3** with a thickness of 500–2,000 Å was formed by a CVD process. For the formation of the CdS film **3**, any other process, for instance, a solution deposition method, may be employed.

A source substrate **9** provided with the source added with an impurity was arranged on a susceptor **12***a* in the lower side of the equipment. On the other hand, on a susceptor **12***b* in the upper side, a substrate **4** was arranged with a gap of 0.1 mm to several mm to the surface of the source. After substituting the atmosphere inside the chamber **14** with argon gas or nitrogen gas, by heating the substrate **4** in a temperature range of 400–800° C. and the source substrate **9** at a temperature higher than that of the substrate **4** and keeping them there for a certain time period, a semiconductor film was formed on the surface of the substrate **4**.

In this step, although it is preferable to keep the pressure of argon gas or nitrogen gas to about 1–20 Torr, it is possible to form the film under 1 atm. In that case, it is preferable that the temperature difference between the substrate **4** and the source substrate **9** is not less than 50° C. In the case of forming the film under 1 atm, there is no need for making the chamber to have a pressure-resistant structure, and thus it is possible to simplify the equipment. Further, since a speeds in inlet and outlet of the substrate to and from the equipment can be made high, the productivity is greatly improved.

For the source, a paste is prepared by using the CdTe incorporated with antimony telluride at 0.01 wt %. By printing the obtained paste on a glass substrate and drying, the source substrate **9** was obtained.

By using the obtained source substrate **9**, a CdTe film **5** was formed under the atmosphere of argon with a pressure of 1 Torr. In this step, by maintaining the substrate **4** in a temperature range of 400–650° C. and the source substrate **9** at a temperature higher by 30° C. than that of the substrate **4** for 2 minutes, the CdTe film **5** was formed on the CdS film **3**.

Separately, a carbon paste was prepared by mixing and kneading a carbon powder with a solution of diethylene glycol monobutyl ether which dissolved polyvinyl butyral. The obtained carbon paste was applied on the CdTe film **5** by a screen printing process and sintered after being dried, to form a carbon electrode layer **6**.

By mixing a mixed powder of silver and indium, and an epoxide with an alcohol consisting mainly of terpineol, and kneading the mixture, a paste was prepared. The obtained paste was applied on the CdS film **3** and the carbon electrode layer **6** by the screen printing process, which was then dried and sintered to form a + electrode **7** and a − electrode **8**.

The CdTe films **5** were also formed in a similar manner by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the CdTe paste. By using the respective CdTe films **5** thus obtained, solar cells were produced.

Further, as a comparative example, a solar cell employing a CdTe film prepared by using a CdTe paste with no additional impurity was produced as shown above and was similarly evaluated.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentration of the CdTe films are shown in Table 2.

TABLE 2

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
Antimony telluride	9.5×10^{14}	14.1
Phosphor	8.4×10^{14}	14.5
Arsenic	8.2×10^{14}	14.0
Antimony	8.1×10^{14}	14.2
Bismuth	8.2×10^{14}	14.1
Lithium	5.4×10^{14}	13.2
Potassium	8.1×10^{14}	14.0
Sodium	5.0×10^{14}	13.5
Rubidium	6.3×10^{14}	13.8
Copper	8.7×10^{14}	14.2
Silver	8.3×10^{14}	13.9
Gold	8.4×10^{14}	14.0
Triphenylantimony	1.2×10^{15}	14.5
Antimony octylate	1.4×10^{15}	14.6
Triphenylbismuth	1.3×10^{15}	14.4
Triphenylphosphine	1.8×10^{15}	14.7
Triphenylphosphate	1.7×10^{15}	14.7
Triphenylphosphite	1.8×10^{15}	14.6
Triallylphosphine	1.8×10^{15}	14.5
Triallylamine	1.6×10^{15}	14.2
None	3.5×10^{14}	13.0

From Table 2, it is appreciated that in the case of incorporating a Group I element or a Group V element into the source, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 6

A CdTe film was formed by the similar method as that in Example 5 except for the use of nitrogen in place of argon as the atmospheric gas. The conditions employed for forming the CdTe film **5** were that the pressure inside the chamber **14** was 1 atm, the substrate **4** was kept in a temperature range of 400–650° C., and the source substrate **9** was kept at a temperature higher by about 100° C. than that of the substrate **4** for 10 minutes, thereby to form a CdTe film **5**. Further, a solar cell was similarly produced by using the obtained CdTe film **5**.

Moreover, the CdTe films **5** were also formed by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the paste, and by using the CdTe films **5** thus obtained, solar cells were produced.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentrations of the CdTe films are shown in Table 3.

As a comparative example, a relationship between the conversion efficiency of a solar cell employing a CdTe film produced by using a CdTe paste with no additional impurity, and the carrier concentration of the CdTe film is also shown in Table 3.

TABLE 3

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Antimony telluride	8.2×10^{14}	14.1
Phosphor	8.4×10^{14}	14.7
Arsenic	7.1×10^{14}	14.2
Antimony	7.9×10^{14}	14.4
Bismuth	6.1×10^{14}	14.1
Lithium	5.4×10^{14}	14.0
Potassium	5.2×10^{14}	14.0
Sodium	4.9×10^{14}	13.8
Rubidium	5.8×10^{14}	14.1
Copper	8.5×10^{14}	14.7
Silver	7.1×10^{14}	14.1
Gold	8.2×10^{14}	14.4
Triphenylantimony	1.0×10^{15}	14.9
Antimony octylate	1.1×10^{15}	14.9
Triphenylbismuth	9.8×10^{15}	14.8
Triphenylphosphine	1.3×10^{15}	15.1
Triphenylphosphate	1.2×10^{15}	15.0
Triphenylphosphite	1.3×10^{15}	15.1
Triallylphosphine	1.3×10^{15}	15.1
Triallylamine	1.2×10^{15}	15.0
None	3.2×10^{14}	13.2

From Table 3, it is appreciated that in either case of incorporating a Group I element or a Group V element into the source material, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 7

A solution was prepared by dissolving cadmium isopropyl xanthogenate, which is an organometallic compound with a sulfur bond, in 1-methyl-2-pyrrolidone.

Separately, on a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm shown in FIG. **7**(*a*), a stannic dioxide film **21** with a thickness of about 600 nm was formed.

The solution obtained in the above-mentioned manner was painted on the surface of the stannic dioxide film **21** and dried at 110° C., thereby to evaporate the solvent. Thereafter, it was subjected to a thermal treatment in the air at 450° C. for 3 minutes, thereby to decompose the cadmium isopropyl xanthogenate and to form the CdS film **22**. At this step, by adjusting the concentration of the solution thus used and the repeat times of the coating, the thickness of the CdS films **22** were set to 70 nm.

Thereafter, by a laser scribing process employing a YAG laser, a pattern for 42 cell series connection as shown by FIG. **7**(*b*) was formed.

Subsequently, a mixed powder was obtained by mixing 1 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, with 6 g of CdTe powder with a purity of 5N.

The mixed powder thus obtained was placed on a glass substrate (Corning #1737) with a width and a length of 35 cm so as to cover over it, thereby to form a particle layer and to obtain a source substrate. Then, the source substrate and the substrate **20** were placed so as to make the particle layer to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source at 630° C. under argon atmosphere with a pressure of 1 Torr for 2 minutes, CdTe films **23** with a thickness of about 6 μm were formed on the CdS films **22** as shown by FIG. **7**(*c*). Thereafter, as shown by FIG. **7**(*d*), etching resists **30** were applied on the surface of the substrate **20** by a screen printing process, and a thermal treatment was conducted in a dryer at 100° C. for 5 minutes.

Subsequently, after subjecting the substrate **20** to an etching process for 5 minutes by immersing it in nitric acid, the substrate **20** was immersed in a 10% solution of sodium hydroxide, thereby to fall the resist layer **30** off as shown by FIG. **7**(*f*). Thereafter, the substrate **20** was immersed in a methanol saturated solution of cadmium chloride and dried, and then subjected to a thermal treatment in the air at 400° C. for 20 minutes. Thereafter, residue of the cadmium chloride was removed by ultrasonic-wave washing in pure water.

Subsequently, after forming a carbon film **24** which was added with a trace amount of copper on the surface of the substrate **20** by the screen printing process, it was dried and heated at 390° C. for 30 minutes, thereby to diffuse the copper into the CdTe films **23**. Thereafter, silver-indium films **25** were formed by a similar screen printing process and thermal treatment, thereby to obtain a solar cell of 42 cells series connection as shown by FIG. **7**(*g*).

EXAMPLE 8

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **21** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **21**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 50 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate (Corning #1737) with a width and a length of the same 35 cm, and drying it in the air at 120° C. for 4 hours, a particle layer with a thickness of about 100 μm consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate **20** were placed so as to make the particle layer to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate at 630° C. under argon atmosphere with a pressure of 1 Torr for 2 minutes, the source in the particle layer was entirely sublimed, thereby to form a CdTe film **23** with a thickness of about 6 μm on the CdS films **22** as shown by FIG. **7**(*c*). Thereafter, as shown by FIG. **7**(*d*), etching resists **30** were painted on the substrate **20** by a screen printing process, and a thermal treatment was performed in a dryer at 100° C. for 5 minutes.

By using the obtained CdTe films **23**, a solar cell similar to that of Example 7 was produced.

Further, by using powders of carbon black, silicon carbide, silicon dioxide, silicon nitride, aluminum oxide, boron nitride, zirconia, silicon nitride, and aluminum nitride, each of which has a purity of 3N and a particle diameter of not more than 5 μm, in place of graphite, solar cells were similarly produced.

EXAMPLE 9

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **21** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **21**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate **100** (Corning #1737) with a width and a length of the same 35 cm, and drying it in the air at 120° C. for 4 hours, a particle layer consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate **20** were placed so as to make the particle layer **120** to face the CdS film, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate at 630° C. under argon atmosphere with a pressure of 1 Torr, and until the CdTe on the source substrate was entirely evaporated (for 5 minutes), thereby to form a CdTe film **23** with a thickness of about 6 μm on the surface of the substrate **20**.

By using the obtained CdTe film **23**, a solar cell similar to that of Example 7 was produced.

EXAMPLE 10

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **11** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **11**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

After forming an indium oxide film on one surface of a glass substrate **200** (Corning #1737) with a width and a length of the same 35 cm, the indium oxide film **110** was removed by etching excepting the specified portion as shown by FIG. **8**. In this step, a ratio occupied by the indium oxide films **110** in the central part of the surface was made higher than that in the peripheral part. On the surface of the other side of this glass substrate **200**, the above-mentioned paste was painted and dried in the air at 120° C. for 4 hours, thereby to form a particle layer **220** consisting mainly of CdTe and to obtain a source substrate **230**.

Then, the source substrate **230** and the substrate **20** which was similar to that used in Example 7 were placed so as to make the particle layer **220** to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate **230** at 630° C. under argon atmosphere with a pressure of 1 Torr, until all of the CdTe on the source substrate **230** was evaporated (for 5 minutes), thereby to form a CdTe film **23** with a thickness of about 6 μm.

By using the obtained CdTe film, a solar cell similar to that of Example 7 was produced. EXAMPLE 11

After roughening one surface of a glass substrate **200** (Corning #1737) with a length and a width of the same 35 cm by etching with hydrofluoric acid, a particle layer was formed on the other surface with the paste which was similar to that used in Example 10, thereby to obtain a source substrate.

By using the obtained source substrate, a CdTe film was formed, and a solar cell was produced in a manner similar to that in Example 8.

COMPARATIVE EXAMPLE 3

As a comparative example, a paste was prepared in a method similar to that in Example 8 excepting an addition of graphite. The obtained paste was applied in a manner similar to that in Example 8 in an amount just required for forming the CdTe film with a thickness of 6 nm. In that case, since it does not contain graphite, the amount of the paste to coat is required to be less as compared with Example 8 so as to adjust the thickness of the coating film to be formed to about 50 μm, but it is impossible to make the amount of the source and the thickness of the coating film uniform. Therefore, by applying the minimum amount for uniformly painting, a source substrate was produced. By using the source substrate, a CdTe film was formed in a manner similar to that in Example 8. In this step, although the thickness of the coating film was made uniform, the dispersion in the thickness of the obtained CdTe film was larger than that of the CdTe film obtained in Example 8. By using this CdTe film, a solar cell was produced in a manner similar to that of Example 8. This was named as the solar cell of Comparative Example 3.

On the solar cells of Example 7–11 and of Comparative Example 3, measurements of the open circuit voltage (V_{oc}) and fill factor (FF) which is a standard for the decision of good/bad of the output characteristic were conducted under condition of AM; 1.5, 100 mW/cm^2. The results thereof are shown in Table 4.

TABLE 4

	Additive	V_{cc} (V)	FF (%)	η (%)
Example 7	Graphite	31.8	57	9.6
Example 8	Carbon black	33.0	61	10.1
	Graphite	33.6	64	10.6
	Silicon dioxide	32.7	59	9.8
	Aluminum oxide	33.3	62	10.2
	Zirconium oxide	31.0	58	9.7
	Boron nitride	32.4	60	10.0
	Silicon nitride	32.6	60	9.9
	Aluminum nitride	32.0	57	9.7
	Silicon carbide	33.0	60	10.0
Example 9	Graphite	33.4	62	10.3
Example 10	Graphite	33.2	63	10.4
Example 11	Graphite	33.6	64	10.5
Comparative Example 3	None	24.2	52	6.8

From Table 4, it is appreciated that the solar cells of Examples 7–11 employing the CdTe films which have been formed by using, as the source, a CdTe material added with a material which remains after the heating are excellent in every respect of the characteristics, as compared with the solar cell of Comparative Example 3. It is believed that this is due to the fact that by adding these materials, thermal damage of the CdS film attributable to the radiation heat can be prevented.

In particular, in the case of using graphite, carbon or silicon carbide in Example 8, or in Examples 9–11, by using the coating film of an amount just required for the film forming of one time as the source, it is possible to suppress an occurrence of an excessive heating of the substrate for thin-film forming, directly by the radiation heat, after the completion of the vaporization of the source. Tellurium, cadmium and cadmium telluride have a low absorption rate for infrared ray and a low heat conductivity. Therefore, if the source consisting of these semiconductor material is thick, since the temperature of the source is hardly elevated at the heating, the film forming speed is low, the infrared ray transmitted through the source is incident on the CdS film which has previously been formed on the substrate. Since the CdS which is typical as the n-type semiconductor for the solar cells has a very high absorption rate for infrared ray, it is heated by the incident infrared ray and made to be liable to vaporize. Therefore, when the CdS film is made thinner than the suitable thickness and when the vaporization of the CdS film further proceeds, pinholes are produced, thereby to invite micro-short-circuitings. For that reason, by using the infrared-absorption materials being mixed with the source as in these examples, the excessive temperature rise of the substrate is suppressed. Therefore, the mutual diffusion at a joint between the CdS film and the CdTe film is suppressed, thereby to obtain a solar cell which has a high open-circuit voltage and fill factor.

In addition, according to the method of the examples, since the source can be used exhaustively, the utilization rate of the material can greatly be improved. Although the CdTe film of good quality can also be obtained in Example 7 wherein a mixture of the source and the additive is used by filling it in a container as described above, it is limited to the cases where the times of repeatedly using the same source for forming the CdTe film are small. That is, according to this method, the change in the source cannot be avoided if the source is used repeatedly. Therefore, by using the coating film as the source as described in Examples 1–9, it is possible to obtain the CdTe film of good quality more effectively.

Further, measurements were made on the thickness distributions in the CdTe film formed in accordance with Example 8 and the CdTe film formed in accordance with Comparative Example 3. The results thereof are shown in Table 5. In this table, distance indicates a distance from the central part of the substrate in the diagonal direction.

TABLE 5

Distance (mm)	Example 8 (μm)	Comparative Example 3 (μm)
0	6.5	10.4
25	6.5	10.2
50	6.4	10.0
75	6.3	9.5
100	6.4	8.8
125	6.4	8.5
150	6.3	7.0
175	6.3	6.0

TABLE 5-continued

Distance (mm)	Example 8 (μm)	Comparative Example 3 (μm)
200	6.2	4.9
212	6.0	3.0

Moreover, the solar cells which employ the CdTe film obtained in accordance with Example 8 and the solar cells obtained in accordance with Comparative Example 3 were produced in trial, for each five lots, each of which contains 10 pieces, and the measurements were made on the film thickness of CdTe and the solar cell characteristics The results thereof are shown in Table 6.

TABLE 6

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
1	6.5	6.8	6.4	6.7	6.0	6.0	8.5	5.0	9.9	6.2
	10.0	9.8	9.8	10.5	9.4	8.0	7.2	8.2	7.5	8.1
2	6.4	6.6	6.5	6.9	6.2	7.0	9.0	5.9	10.0	6.9
	9.9	9.9	10.0	9.5	9.1	8.5	6.9	8.8	7.3	8.2
3	6.7	6.7	6.3	6.2	6.8	6.5	7.6	6.5	9.1	6.5
	10.2	10.0	10.1	10.1	9.9	7.9	8.0	7.9	7.0	7.5
4	6.3	6.9	6.5	6.1	6.9	7.2	9.5	6.1	9.5	6.9
	10.1	9.8	9.9	9.7	9.6	6.9	7.0	5.9	6.9	8.5
5	6.6	6.7	6.7	6.9	6.2	5.3	8.7	5.1	8.7	6.8
	10.2	9.9	9.7	9.8	10.4	7.6	6.8	7.1	7.2	7.4
6	6.5	6.5	6.4	6.7	6.0	5.9	7.1	4.0	8.8	6.6
	9.9	10.1	9.5	9.7	10.2	9.2	5.9	6.9	6.1	7.8
7	6.7	6.9	6.5	6.5	6.9	7.8	6.6	4.9	7.9	6.0
	10.3	9.9	10.1	10.2	10.0	8.4	9.0	7.3	6.9	7.7
8	6.3	6.8	6.6	6.8	6.4	6.3	8.7	6.1	7.8	6.5
	10.0	10.0	9.8	10.5	9.3	8.6	6.4	7.5	7.0	6.3
9	6.6	6.7	6.7	6.7	6.8	6.9	7.5	5.9	10.0	6.8
	9.9	9.7	9.9	10.4	9.7	9.0	8.8	7.7	6.1	5.2
10	6.4	6.9	6.8	6.1	6.3	8.0	6.2	9.0	9.5	6.9
	10.3	9.8	9.6	10.1	9.5	7.1	6.5	8.1	6.8	8.1

Upper column: Thickness of CdTe film at central part of substrate (μm).
Lower column: Conversion efficiency (%).

The difference between the CdTe film of Example 8 and the CdTe film of Comparative Example 3 is only a presence/absence of the addition of graphite to the pastes. That is, as clearly shown from Table 5, by forming with a mixture of the source and the additive, a CdTe film with a stable thickness can be obtained.

Further, it is also appreciated from Table 6 that the CdTe film of Example 8 has a smaller dispersion in thickness within one lot and between the lots as compared with the CdTe film of Comparative Example 3. For that reason, according to Example 8, it is possible to stably obtain a solar cell of more excellent characteristics as compared with Comparative example 3.

As previously described, by using a source mixed with an additive, it is possible to suppress mutual diffusion at a joint between the CdS and the CdTe resulting from an excessive heating by a radiation, thereby to stably obtain a CdTe film of good quality.

As the additive, any stable substance which does not decompose or cause a chemical reaction on the supporting member at the time of heating can be used.

Further, by using a substrate which has an uneven structure on the surface opposite to the surface on which a particle layer is formed as in Example 11, it is possible to absorb the infrared ray by the uneven surface and a similar effect can be obtained.

On the other hand, according to Example 10, by lowering the proportion occupied by a transparent conductive film at the peripheral part of the substrate as compared with that of the central part, it is possible to make the temperature difference of the surface of the substrate small, by utilizing an action of the transparent conductive film to suppress the radiation of the infrared ray. According to this method, the dispersion in the thickness of the CdTe film formed on the surface of the substrate can be made small. A similar effect can also be obtained by directly piling a separate substrate which has a similar structure on a normal source substrate.

Further, in the above-mentioned examples, although CdS is employed as the n-type semiconductor for a solar cell, a similar effect can also be obtained in a case of using CdZnS. For forming these n-type semiconductors, a known method such as a process of thermally decomposing an organometallic compound, a liquid phase film-forming process, a close-spaced sublimation process, a vapor-deposition process, a sputtering process and the like can be employed.

As the transparent conductive film, indium tin oxide or zinc oxide can also be employed in place of tin oxide. For forming the transparent conductive film, a sputtering process, a chemical vapor-phase growing process, a vapor-deposition process or the like can be employed.

In the preciously-mentioned examples, although the glass substrate which has the transparent conductive film and the CdS film on the surface is used as a substrate for forming the CdTe, it is also possible to use, in place of this, any of semiconductor materials of cadmium zinc sulfide, gallium arsenide, indium gallium arsenide, indium gallium phosphor arsenide, zinc selenide, indium selenide, silicon, germanium, indium copper selenide, indium gallium copper selenide, gallium nitride and the like, and metals of iron, nickel, molybdenum and the like, as the substrate. As the substrate, a ceramic material can also be used in addition to the glass.

Further, although a description has exemplary been made on the method for forming the CdTe film, it can also be applied to a thin film formation of other semiconductors such as CdS, cadmium zinc sulfide, zinc selenide, indium selenide, indium copper selenide, indium gallium copper selenide, and the like.

As the viscosity improver used in preparing the paste, such another material as ethylene glycol, methyl cellulose or the like can also be employed, in addition to propylene glycol which was used in the above-mentioned examples.

POSSIBILITY OF INDUSTRIAL UTILIZATION

According to the present invention, it is possible to form a CdTe film of good quality in an inexpensive efficiently. The present invention can be embodied in the manufacture of semiconductor device such as a solar cell, an infrared ray receiving device, and an integrated circuit.

We claim:

1. A method for preparing a CdTe film comprising:

a step of applying a paste containing a material for CdTe semiconductor on a supporting member, thereby to form a coating film containing said material for CdTe semiconductor on the surface of said supporting member,

a step of closely arranging said supporting member and a substrate on which a CdTe film is to be formed, to make said coating film to face the surface of said substrate, and

a step of forming a CdTe film on said substrate, by heating said coating film and said substrate, and causing said material for the semiconductor in said coating film to evaporate.

2. The method for preparing a CdTe film in accordance with claim **1**, wherein said semiconductor material is a mixture of a cadmium powder and a tellurium powder.

3. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains cadmium chloride.

4. The method for preparing a CdTe film in accordance with claim **3**, wherein the added amount of said cadmium chloride is 0.1–1.75 wt % to said semiconductor material.

5. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains a Group I element or a Group V element incorporated therein.

6. The method for preparing the CdTe film in accordance with claim **5**, wherein said Group I element is at least one member selected from the group consisting of lithium, potassium, sodium, rubidium, copper, silver and gold.

7. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is at least one member selected from the group consisting of arsenic, antimony, bismuth, phosphor and nitrogen.

8. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is antimony, and is contained in said paste in a state of antimony telluride.

9. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is contained in said paste in a state of at least one member selected from the group consisting of triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine.

10. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains an additive of powder state which is stable in composition at the heating step.

11. The method for preparing a CdTe film in accordance with claim **10**, wherein said additive is at least one member selected from the group consisting of carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride, and aluminum nitride.

12. The method for preparing a CdTe film in accordance with claim **1**, wherein at the step of applying said paste, the painted amount of the paste in the peripheral part of said substrate is made to be larger than the painted amount of the paste in the central part of said substrate.

13. The method for preparing a CdTe film in accordance with claim **1**, wherein said supporting member is at least one member selected from the group consisting of glass, ceramic material and carbon.

14. The method for preparing a CdTe film in accordance with claim **1**, wherein said supporting member is glass having a conductive oxide film on the surface thereof.

15. The method for preparing a CdTe film in accordance with claim **1**, wherein one surface of said supporting member that is opposite to the surface on which said paste is painted is rough.

16. A solar cell comprising: an insulating and transparent substrate, a transparent conductive film formed on said substrate, an n-type semiconductor film formed on said transparent conductive film, a p-type semiconductor layer formed on said n-type semiconductor film as a light absorbing layer, a current collector formed on said p-type semiconductor layer, a + side electrode electrically connected to said current collector, and a − side electrode electrically connected to said n-type semiconductor layer, wherein said p-type semiconductor film is a CdTe film formed by the method in accordance with claim **1**.

* * * * *

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(12) **United States Patent**
Gegenwart et al.

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(45) **Date of Patent: Sep. 3, 2002**

(54) **APPARATUS FOR DEPOSITING CDS AND CDTE LAYERS ON SUBSTRATES BY MEANS OF A CSS PROCESS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(51) **Int. Cl.**^{7} **C23C 14/00**
(52) **U.S. Cl.** **118/726**; 392/389
(58) **Field of Search** 118/726; 392/389

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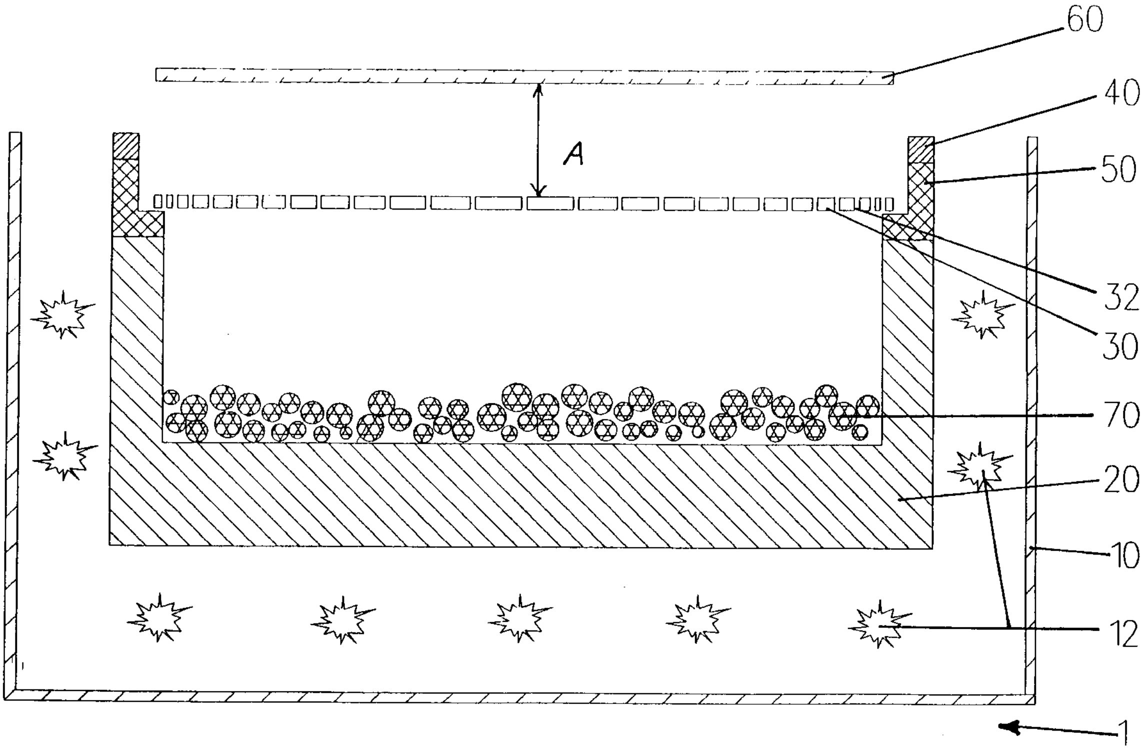
(57) **ABSTRACT**

Apparatus for depositing substrates by means of a CSS process comprising a heated receptacle (**20**) for a supply (**70**) of material to be deposited and carrier means for holding the substrate (**60**) with its side to be deposited towards an opening (**22**) of said receptacle, said receptacle opening (**22**) being provided with a cover (**30**) including a plurality of through-holes (**32**) for the sublimated material, said cover separating said material supply (**70**) from said substrate (**60**) and, due to being heated to a temperature higher than that of said receptacle (**20**), acting as sublimation source for said substrate.

16 Claims, 3 Drawing Sheets



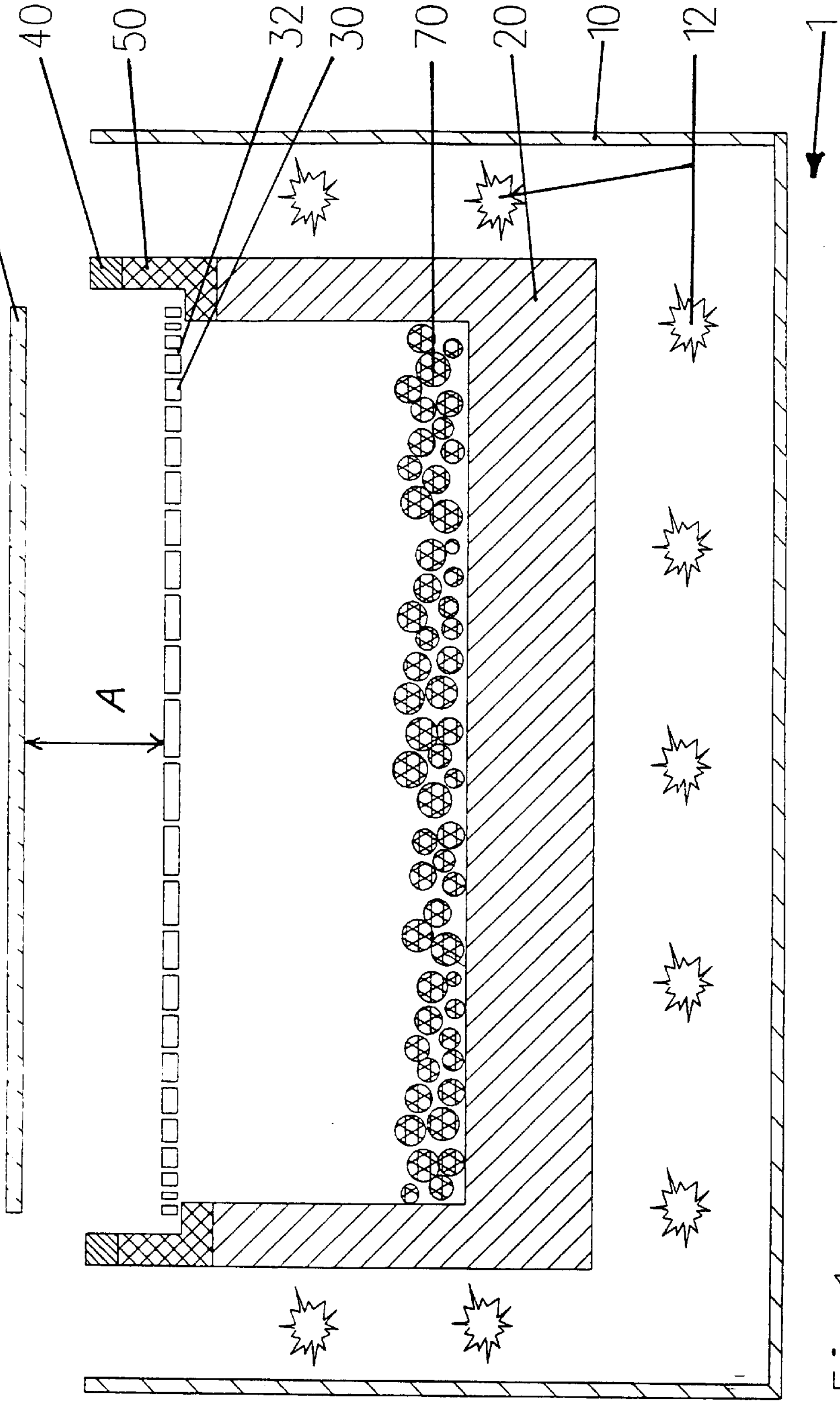


Fig. 1

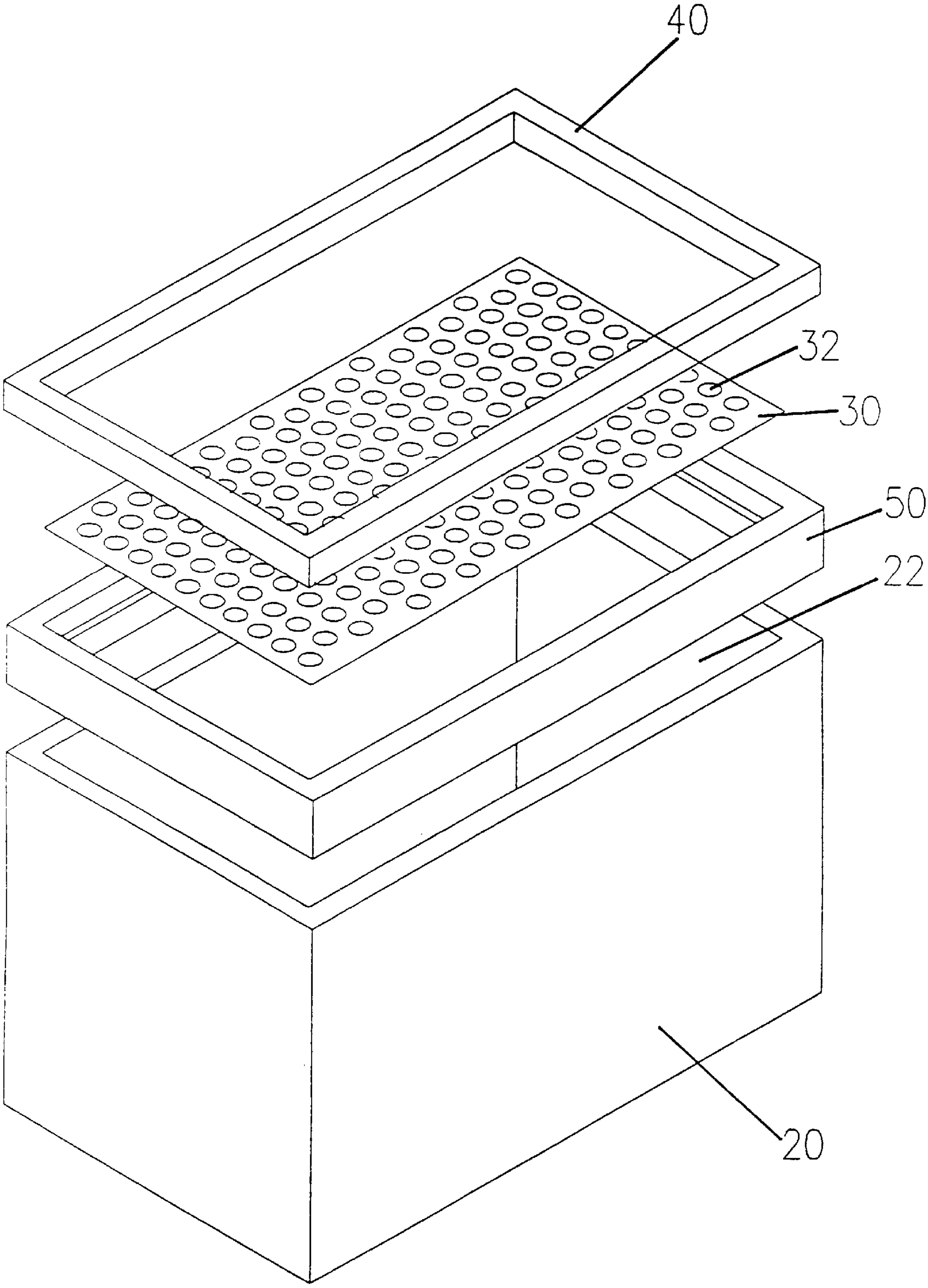


Fig.2

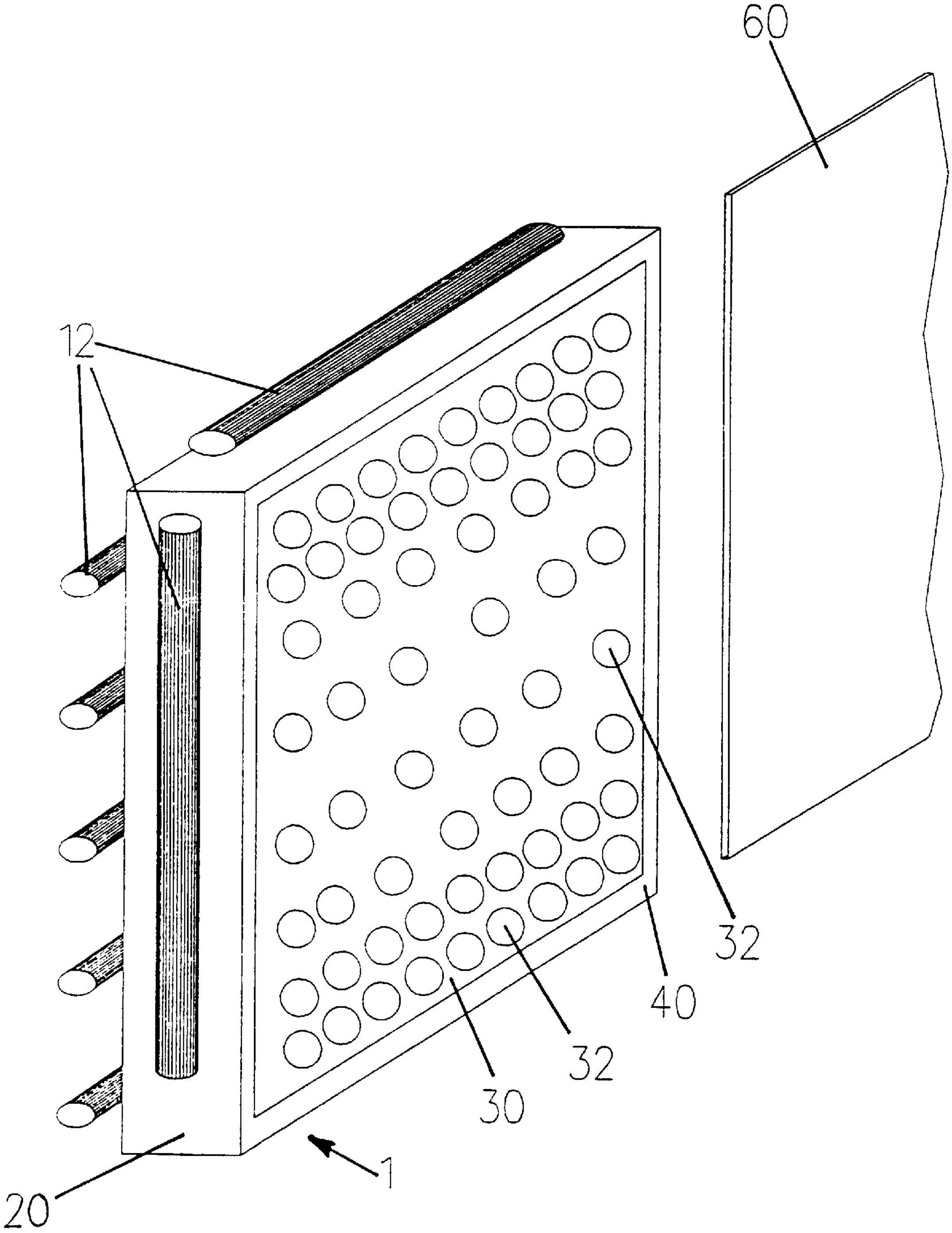


Fig.3

APPARATUS FOR DEPOSITING CDS AND CDTE LAYERS ON SUBSTRATES BY MEANS OF A CSS PROCESS

CROSS REFERENCES TO RELATED APPLICATIONS

Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

Not Applicable

BACKGROUND OF THE INVENTION

The present invention relates to an apparatus for depositing CdS and CdTe layers on substrates by means of a PVD process (Physical Vapor Deposition Process) in the form of a CSS (Close Spaced Sublimation) process. In particular, the invention is directed to a process for deposition of sublimated materials onto substrates for the production of CdS/CdTe solar cells.

In industrial semiconductor deposition processes and in those processes for manufacturing large-area electronic components CVD processes (Chemical Vapor deposition Processes) are employed for depositing, particularly silicon or dielectrics, such as SiO_2, Si_3N_4. Corresponding devices for mass production have been known. For the production of electronic and optical components, furthermore, selenium layers have been applied by CVD processes since a long time, as will be described in more detail in the following.

For the production of e.g. electroluminescence displays or certain solar or photovoltaic cells, such as CdS/CdTe solar cells, on the other hand, PVD processes are suited which provide thin layers or films by vapor deposition of material from a heated source. In addition to thermal evaporizers utilized, for instance, in the field of large area electronics (e.g. for the production of displays), particularly the CSS technology has been used during the last decades for CdS/CdTe solar cells. The devices hitherto known have not been suited for a continuous production of larger modules, neither with a view to their dimensions nor to their material sources.

The CSS technology as compared to CVE technology (Combination of Vapors of Elements) offers the advantage that, for instance, CdTe can be deposited with very high deposition rate. The microstructure, on the other hand, and the resulting electric properties of the CdTe layer-generated are suited for solar cell technology only if and when the close space or CSS distance between the sublimation material and the substrate is accurately adjusted and maintained and all the components of the source material, in the present case of the dissociated CdTe, are directly transported to the substrate surface for recombination thereon, independently from the remaining system parameters and the conditions elsewhere in the system. The close space distance is generally smaller than a few percent of the substrate dimensions. In order to ensure, moreover, that the condensation process remains limited to the small distance area between substrate and source material and that the desired temperature-depending dissociation pressure is obtained, pressure and temperature of source material and substrate should sensitively be adapted to each other.

When adapting a CSS apparatus to production scales including large deposition surfaces and high throughput, it should be ensured that the apparatus can be integrated in a continuous production line. The possibility of using a large number of adjacent evaporator sources was turned down because of the immense constructional efforts and the necessity of adjusting similar conditions of deposition at all sources. It was furthermore turned down to employ large-volume receptacles and to vary the temperatures thereof during the course of the deposition in order to adapt for deposition rate changes depending on the filling level of the material source or supply. Such temperature changes are hardly manageable the more so as layer formation on the substrate is considerably affected thereby.

BRIEF SUMMARY OF THE INVENTION

In view of long years of experience in connection with the critical deposition parameters for CdS/CdTe solar cells in CSS processes, the present inventors were indeed surprised that notwithstanding the problematic nature as outlined above it was possible to substantially uncouple the source material from the substrate in a spatial and physical manner and to locally displace the CSS distance between source material and substrate out of a source material receptacle in the area between the substrate and the cover provided at the opening of the receptacle of the inventional apparatus. Accordingly, the source material and substrate are actually separated by a multiple of the CSS distance from each other. Thereby, it became possible to operate with practically any receptacle and material supply.

An object of the present invention is to provide an apparatus for depositing CdS and CdTe layers on substrates by means of a PVD process in form of a CSS process, which is suited for a large-size deposition and a continuous deposition process. The object is solved by the subject matter of claim 1. Advantageous further developments are defined in the subclaims.

Based on the solution revealed in claim 1, it is possible to employ a large-surface sublimation source which allows sufficient material supply for a long uninterrupted production period without having to resort to corrective measures which depend on the actual filling level or having to refill the material supply. The cover provided according to the invention uncouples the deposition process from the material supply. Because of the higher temperature of the cover, the substrate does no longer "see" the material supply, as was the case in CSS apparatuses hitherto used, but, instead, the substrate rather "sees" the cover as sublimation source which thereby acts as physical deposition source and determines the thermal and kinetic behavior of the evaporated or sublimated materials, respectively. Consequently, the cover provides for spatial and physical separation of the material supply from the substrate. Contrary to disturbances and problems otherwise observed even in case of smallest interferences into the parameters of the deposition process, the deposition behavior, nevertheless, does not change. The inventors using the now completely differently dimensioned CSS deposition apparatus were able to successfully produce CdS/CdTe solar cells of high efficiency and output by applying temperature and pressure parameters which had proved of advantage in a typical conventional CSS device. According to the invention, changes of distribution and rate of deposition, otherwise occurring with decreasing filling level in the material receptacle, can successfully be avoided.

As described further above, substrates have been provided with selenium layers for a number of years using selenium which was evaporated in a material receptacle and impinged from the evaporation receptacle upon the material to be provided with the layer. Since as a rule evaporation and vapor exhaust from the receptacles are non-uniform, it has become, and still is, the practice to close the receptacles by a sieve or a perforated plate with through-holes (See, U.S. Pat. No. 5,532,102; DE 24 36 431 A; and WO 91 04 348 A). These holes plates provided a uniform deposition and vapor transport. Clogging of the holes is avoided in that the hole plate is heated in order to evaporize any condensing material. DE 24 36 431 A utilizes a hole plate the temperature of which is about 5 to 30° C. higher than the temperature of the material receptacle. A further advantage of the hole plate is that it blocks material spatters. According to U.S. Pat. No. 5,532,102, the hole plate is brought at the beginning of the deposition to a temperature significantly higher than the material receptacle and subsequently is lowered to that of the receptacle or somewhat higher. The holes in the cover are larger at the marginal zones of the plate in order to obtain a more uniform deposition of the vapor passing through the holes. WO 91 04 348 A employs heating means which are distributed over the complete height of an evaporation crucible in order to ensure highly uniform heat distribution. Uniform heat distribution is further promoted by a perforated cover arranged on the crucible, which is heated to a higher temperature relative to the crucible and should also block material spatters and the like. DE 26 53 909 A describes a thermal evaporization for large-surface substrates, which includes a perpendicularly disposed perforated cover. The surface area of the outlet openings of this vertical evaporization source should be less than 30%, preferably 15%, of the total cover surface. Condensations on the cover are avoided in that the cover material automatically heats up during the course of the deposition operation. In this way, reproducible vapor streams e.g. of evaporated silver, may be obtained.

The present invention, however, was not concerned with the problem to direct and distribute the evaporation cloud of a thermal evaporation source into a uniform and reproducible vapor stream onto a substrate using a perforated plate. The present invention, instead, had to solve the problem to precipitate elements having been dissociated by sublimation on a substrate such that the dissociated elements directly recombine on the substrate with a given micro structure of the resulting layer.

Preferred further developments of the present invention are defined in the subclaims. In this connection it is for instance possible to improve the deposition at the substrate edge zone by means of a particular hole pattern. A considerable improvement is, furthermore, accomplished by using a frame heated to a higher temperature than the temperature of the receptacle. Condensations of the sublimated material at the colder, outer upper edge of the material receptacle are thereby avoided, which otherwise would lead, in addition to material loss, also to transport problems. The material loss at the small gap between frame and substrate is, moreover, substantially reduced because this gap can be considerably smaller adjusted than the CSS distance between substrate and perforated cover. Hence, by means of that frame, considerably longer production periods can be obtained since precipitates at the upper edges of the receptacle which cannot be completely avoided anyway, grow more slowly because of the frame and need be removed less frequently. The frame may be a separate part arranged on the receptacle. It may also be integrated in a receptacle rim extending beyond the cover.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following, a preferred embodiment of the present invention is explained in more detail referring to the drawings wherein

FIG. **1** is a diagrammatic sectional view of a preferred embodiment of the apparatus of the invention for horizontal deposition;

FIG. **2** is a perspective exploded view of a material receptacle, a cover and a heated frame of FIG. **1**; and

FIG. **3** is a view on a material receptacle having a cover and a heated frame for vertical deposition according to a further embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The apparatus of the invention is used as a CSS apparatus particularly for the production of CdS/CdTe solar cells. The apparatus can, in principle, also be provided with different sublimation sources for alternative applications. It is also suited for the production of other photovoltaic elements such as CIS modules (Cu In Se_2 modules) for instance with a CdS deposition to be applied.

Apparatus **1** shown in FIG. **1** differs from prior art CSS deposition devices basically in that the close space distance for the deposition process is no longer defined between the material (CdS or CdTe, respectively) to be sublimated in the form of a granulate, of a polycrystalline disc or the like and the substrate (as shown for example EP 92 116 254.1 corresponding to EP 0,535,522 A2 and U.S. Pat. No. 5,304, 499). In a vacuum chamber, not shown, a plurality of apparatuses **1** are arranged in series. The vacuum chamber is held by means of mechanical pumps at a residual gas pressure of 10^{-4} to 10 mbar, preferably 10^{-2} mbar, and the substrate deposition of the present embodiment is made in this residual gas atmosphere. Optionally, flushing can be performed by means of inert gases such as nitrogen, helium, argon and the like. Substrates **60** are moved in a continuous passage via entrance and exit locks into the vacuum chamber and moved over apparatuses **1**. Rollers are provided between apparatuses **1** as carrier devices on which substrates **60** move on their passage over the apparatuses. The planar substrates **60** are directed with the deposition side downward. In FIG. **1**, substrates **60** are guided perpendicular to paper plane.

Apparatus **1** comprises a heated shield **10** rectangular in cross section made of graphite (for instance fiber-reinforced graphite) or other high-melting materials, such as tantalum or molybdenum, which are inert against the material to be evaporized. Within the heat shield, a rectangular receptacle **20** is provided. In the present embodiment, it is made of graphite.

Receptacle **20** having a large volume as compared to graphite crucibles formerly used includes a large-area top opening **22** and has a height which is sufficient to hold a material supply **70** (in the present case CdTe granulate) for a highest possible production period. In the present embodiment, rectangular opening **22** has dimensions of 250 mm by 700 mm and the receptacle can hold, at a depth of 200 mm, about 80 kg CdTe. With one receptacle filling, production periods of several days can be obtained. If a plurality of receptacles are successively arranged in the moving direction of the substrate, the production period can be extended without any difficulties up to one week.

According to FIG. **2**, a perforated hole plate **30** made of graphite (SIGRA-BOND (registered trade mark) by SGL Carbon Group) is embedded into the upper receptacle edge. Plate **30** may however also include other materials as mentioned above which are inert against the deposition material. Plate **30** is not placed directly on the receptacle edge but rather in an insulating ceramic holder **50**. In the present embodiment, the latter is L-shaped in cross section and is fastened in the receptacle edge by means of pins, not shown. In the shown example, plate **30** rests in the ceramic holder **50** consisting for instance of alumina. In the present embodiment, through-holes **32** of plate **30** have a medium diameter of about two mm. On one hand, through-holes **32** are so large that they do not significantly prevent the passage of the sublimation-evaporated material through plate **30**, and on the other hand, are small enough not to impair the desired uncoupling from the material supply. This is made possible in that, as shown, a plurality of holes having a diameter of about one to four mm are uniformly arranged at a small distance relative to each other, as can particularly be taken from FIG. **3**. In the present embodiment, holes **32** are arranged in a cubic face centered hole pattern having dimensions of 8 by 8 mm. Therefrom results an open surface area portion of 10% of the total surface of plate **30** passing the sublimated material. At the marginal zones of the substrate, the holes are provided larger and/or tighter in order to obtain a uniform deposition over the total plate width. (A substrate point is not only impacted by material passing through the hole disposed directly under it but also by the surrounding holes, and that is why in case of an unchanged hole structure deposition in marginal zones would be smaller.)

A plate as compared to wire-mesh shaped embodiments of electrically and thermally conductive material which in principle are possible is well, has the advantage that the percentage of the open passage area may be adjusted by one single plate to suitable values of between 5 and 25%. The passage through the hole pattern may, moreover, be locally changed. In the case of a wire mesh, the passage percentage, as a rule, is too large for the desired uncoupling so that two or more meshes arranged one above the other would have to be employed.

Graphite as the material for the plate offers the advantage of good electric conductivity and also thermal conductivity, and as corrosion proof material has the advantage of not reacting with the vapor particles. Graphite plate **30** can also be heated directly. To this end, the plate is directly connected to a separate ohmic heater.

Distance A (exaggeratedly represented in the Figure) between substrate **60** and hole plate **30** is adjusted by guiding and distance means, not shown, to 2 to 50 mm. In the present embodiment, the distance amounts to about 10 mm. It corresponds to the CSS distance normally to be adjusted between the substrate and the source material.

A heatable frame **40** also made of graphite is disposed at an elevated position relative to plate **30**. In this case the material alternatives described above in connection with plate **30** and shield **10** as well as with receptacle **20** are in principle possible too. Frame **40** is secured as shown to the upper side of ceramic holder **50** and can be heated, again by direct ohmic heating, independently from plate **30** and receptacle **20**. Rigid electric feed wires may be used for stabilizing the light frame **40**. In the present embodiment, ceramic holder **50** is so designed that it provides, as a one-piece part, both for electric insulation of receptacle **20** relative to plate **30** and of plate **30** relative to frame **40**, so that separate heating circuits are possible for frame **40** and plate **30**. Numerous further insulation measures can, however, be selected by those versed in the art. In the actual apparatus, the substrate is guided at smallest possible distance over frame **40** (e.g. 1 or 2 mm).

Receptacle **20** is also independently heated, in the present embodiment by means of heating lamps **12** in the form of halogen lamps or special infrared lamps with carbon filaments, so called “Carbonstrahler” (carbon radiators). For the deposition process, heating is generally effected so that hole plate **30** is hotter for a few degrees Celsius, preferably about 2 to 5° C., than receptacle **20** which in the present embodiment is heated to about 750° C. as compared to substrate **60** which is preheated to a temperature of about 500° C. When moved over apparatus **1**, the substrate retains its preheating temperature of about 500° C. because it is heated up by hot apparatus elements **12**, **20** and **30**. Frame **40** on the other hand, is again heated to a higher temperature than hole plate **30**, in the present case about preferably 2 to 5° C. higher. With the particular deposition parameters, the temperature ranges here specified have proved to be suitable. The temperature ranges for substrate (480° C. to 520° C.) and the receptacle or the CdTe source (700° C. to 770° C.), respectively, correspond to the data specified in EP 92,116,254.1 corresponding to EP 0,535,522 A2 and U.S. Pat. No. 5,304,499. The present inventors found out that the deposition parameters specified in that patent specification for the conventional small CSS apparatus (including pressures, deposition thickness, etc) can also be successfully applied in the large scale apparatus of the present invention. As to these parameters which are also considered preferred in the present invention, reference is explicitly made to that prior art patent.

It is not impossible that the above mentioned temperature differences may be smaller or higher. In general, however, a temperature difference of less than 2° C. between hole plate **30** and receptacle **20** as well as plate **30** and frame **40** will not be sufficient for the effects described in the following. Larger temperature differences above 10° C. are possible in principle, the respective deposition parameters should, however, not be changed by the temperature gradients which means that the temperature difference between hole plate **30** acting as physical deposition source and substrate **60** should fulfil the respective deposition parameters and that in the material supply, moreover, an optimum sublimation temperature can be adjusted.

As already described, the temperature difference between hole plate **30** and receptacle **20** ensures that the deposition parameters do not depend on the filling level of receptacle **20**. Furthermore, changes of the deposition rate distribution due to shadowing effects caused by the decreasing filling level need not be compensated. Uninterrupted production period of one week is possible by utilizing the apparatus described and adjusting a deposition rate of about 10 μm/minute and performing continuous deposition of about 0.7 m^2 large substrates. The local distribution of the deposition rate can be adjusted by the design of the hole pattern in hole plate **30** so that the deposition rate distribution can be selected by changing the plate. In other words, the deposition rate distribution is uncoupled from the source consisting of heated receptacle and material supply or material source.

The heating frame **40** offers the advantage that due to its increased temperature the material loss at the edge of receptacle **20** which is open on top may be reduced up to 80%. Undesired condensation effects in those otherwise colder edge zone are furthermore avoided that might also impede the quality of the deposition at the marginal zones of the substrate.

A further advantage offered by the apparatus of the present invention can be taken from FIG. **3** wherein hole plate **30** is perpendicularly disposed in front of opening **22** of receptacle **20** which has an open side. Thereby, a deposition process in continuously working vertical plants becomes possible. Within receptacle **20** moreover, fan-like divisions have been made and additional hole plates have been provided in order to obtain a uniform distribution of the deposition material. In view of the uncoupling effect according to the invention it is very well possible to provide in a perpendicularly disposed apparatus according to FIG. **3** a container for the material supply, the opening of which covered by hole plate **30** joins a container side wall in the area of which a larger material supply is provided on the bottom of the container. It is also possible to stack a plurality of such containers one upon the other to obtain a single large-surface deposition source.

In the present embodiment, a plate was inserted to cover the opening of receptacle **20**. Such plane structure is necessary for common deposition operations. If for instance different deposition parameters are to be adjusted over the substrate, it is, however, also conceivable to employ a curved structure provided with throughholes as cover. Neither need the substrate be always plane. In case of non-planar substrates, the different distance between hole plate and deposition surface can, moreover, be adjusted by varying the hole pattern of the hole plate or cover.

In the case of evaporation material tending to particle emission, it is possible to use e.g. two slightly spaced hole plates having hole patterns offset relative to each other instead of a single plate. In this way, it is avoided that particles chipping off from the evaporation material find their way as sputters through a hole in the plate and reach the substrate. By means of the two plates and by offsetting the hole pattern, optical shielding is ensured.

What is claimed is:

1. An apparatus for depositing CdS and CdTe layers on a substrate by means of a CSS process, said apparatus comprising:

a heated receptacle having an opening, said receptacle being heated to a first temperature;

an initially fixed volume of material supply disposed in said receptacle, and selected from a group consisting of CdS and CdTe, wherein said heated receptacle sublimates said material supply to form a sublimated material which exits said receptacle through said opening to decrease said initially fixed volume of material supply;

a heated plate covering said opening, and including a plurality of through-holes through which said sublimated material passes, said plate being heated to a second temperature which is higher than said first temperature to form a sublimation source;

a substrate disposed outside of said receptacle and having a face facing said plate for receiving said sublimated material, said face being spaced a distance between about 2 and about 50 mm from said plate.

2. Apparatus according to claim **1**, characterized in that said through-holes are perforations.

3. Apparatus according to claim **2**, characterized in that said through-holes define a pattern in said plate **(30)**, wherein said plate is more porous proximal edges of said plate than in a central portion of said plate.

4. Apparatus according to claim **1**, characterized in that said plate **(30)** consists of electrically conductive material.

5. Apparatus according to claim **4**, characterized in that said electrically conductive material is graphite.

6. Apparatus according to claim **1**, characterized in that a frame **(40)** extends past said plate toward said substrate and adjacent at least one edge of said plate, and that second means are provided for independently heating said frame **(40)** such that it is kept at a temperature higher than that of said plate.

7. Apparatus according to claim **6**, characterized in that said plate **(30)** and said frame **(40)** each are electrically insulated relative to each other and said plate **(30)** and said frame **(40)** each are connected to an ohmic heating means.

8. Apparatus according to claim **1**, characterized in that for perpendicular substrate deposition, said plate **(30)** is disposed in a side opening of said receptacle **(20)**.

9. Apparatus according to claim **8**, characterized in that in said receptacle **(20)** includes divisions subdividing the interior of the receptacle.

10. Apparatus according to claim **1**, characterized in that said receptacle is a graphite receptacle **(20)**.

11. Apparatus according to claim **1**, characterized in that said receptacle **(20)** consists of a high-melting point material.

12. Apparatus according to claim **1**, characterized in that said material supply is granular.

13. Apparatus according to claim **1**, characterized in that said plate **(30)** is flat.

14. Apparatus according to claim **1**, characterized in that said plate **(30)** is curved.

15. Apparatus according to claim **6**, characterized in that said frame **(40)** is a separate part attached to the upper edge of the receptacle at an elevated position relative to said plate **(30)**.

16. Apparatus according to claim **6**, characterized in that said frame **(40)** is formed as an integral part of said receptacle.

* * * * *

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(12) **United States Patent**
Romeo et al.

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(45) **Date of Patent: May 1, 2007**

(54) **PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS**

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(2), (4) Date: **Apr. 5, 2004**

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Oct. 17, 2001	(IT)	LU2001A0012
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(51) **Int. Cl.**
H01L 21/00 (2006.01)

(52) **U.S. Cl.** **438/95**; 438/93; 438/102; 438/57; 257/184

(58) **Field of Classification Search** 438/57, 438/93, 94, 95, 98, 102; 257/183, 184
See application file for complete search history.

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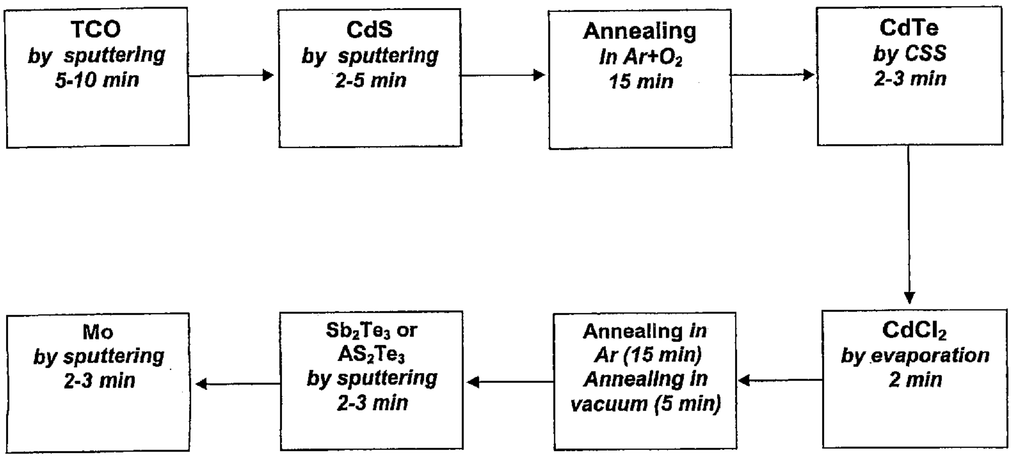
(57) **ABSTRACT**

A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; depositing a back-contact film on the treated CdTe film. Treatment of the CdTe film with $CdCl_2$ comprises the steps of: forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature; annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

19 Claims, 2 Drawing Sheets



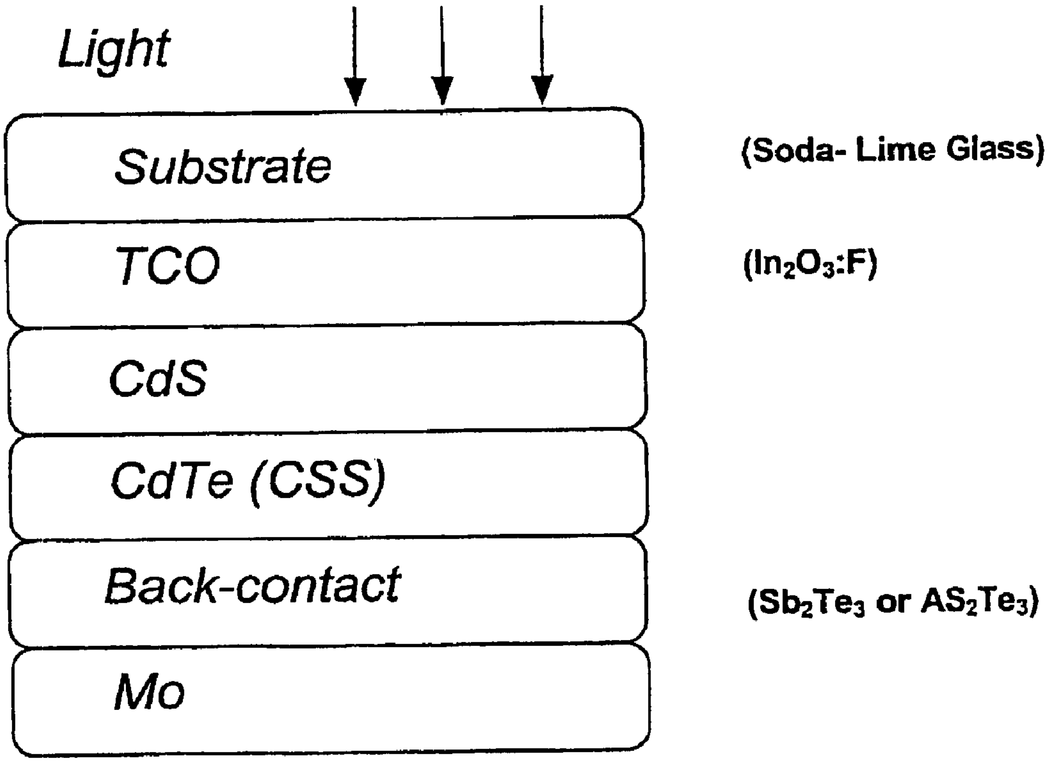

Light
Substrate
TCO
CdS
CdTe (CSS)
Back-contact
Mo
(Soda- Lime Glass)
(In_2O_3:F)
(Sb_2Te_3 or AS_2Te_3)

Fig. 1

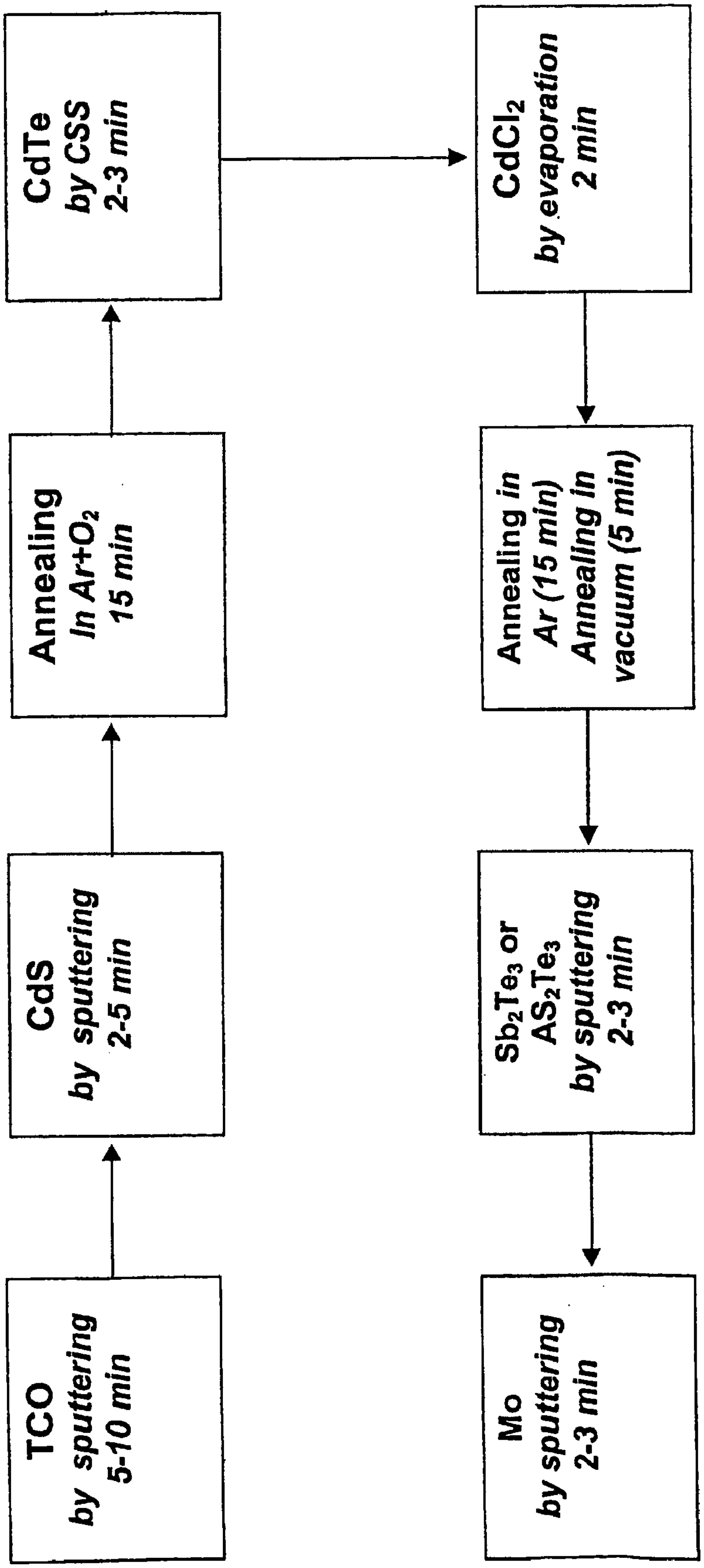

TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In Ar+O$_2$
15 min
CdTe
by CSS
2-3 min
CdCl$_2$
by evaporation
2 min
Annealing in
Ar (15 min)
Annealing in
vacuum (5 min)
Sb$_2$Te$_3$ or
AS$_2$Te$_3$
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

FIELD OF THE INVENTION

The present invention relates generally to alternative energy resources technology and, more particularly, to solar energy storage and the like.

BACKGROUND OF THE INVENTION

Conventional CdTe/CdS solar cells typically comprise a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film serving as the n-conductor, a CdTe film serving as the p-conductor and a metallic back-contact. A solar cell of this general description is disclosed, for example, in U.S. Pat. No. 5,304,499, which issued on Apr. 19, 1994.

While this “float” glass concept may be adapted for commercial use as a transparent substrate, frequent diffusion of Na into the TCO film has often resulted. Consequently, despite its relatively low cost, special glasses are often preferred over such a “float” glass arrangement.

Perhaps the most common TCO material is In_2O_3 which contains about 10% Sn (ITO). This material is usually characterized by a very low resistivity on the order of 3×10^{-4} Ωcm and a relatively high transparency (>85%) in the visible spectrum. While useful this material is made by sputtering and, after several runs, the ITO target forms noodles which contain excess In. In addition, a discharge may occur between noodles during sputtering which can damage the film.

Another material that is commonly used for the transparent conductive oxide film is fluorine doped SnO_2. Although helpful, this material exhibits a higher resistivity close to about 10^{-3} Ωcm. As a result, a 1 μm thick layer is necessary to keep the sheet resistance at about 10 $\Omega/_{square}$. Generally, a high TCO thickness decreases the transparency and, in turn, the photocurrent of the solar cell. In addition, a novel material, namely Cd_2SnO_4, developed by the NREL group (X. Wu et al., *Thin Solid Films,* 286 (1996) 274–276)) has been utilized. However, since the target is made up of a mixture of CdO and SnO_2, CdO being considered highly hygroscopic, the stability of the target has often been found unsatisfactory.

Generally speaking, the CdS film is deposited either by sputtering or Close-Spaced Sublimation (CSS) from a CdS granulate material. The latter technique allows thin films to be prepared at a substrate temperature considerably higher than that used in simple vacuum evaporation or sputtering. This is because the substrate and evaporation source are positioned very close to one another, i.e., at a distance of 2–6 mm, and deposition is performed in the presence of an inert gas such as Ar, He or N_2 at a pressure of about 10^{-1}–100 mbar. A higher substrate temperature usually allows growth of a better quality crystalline material. A significant characteristic of close-spaced sublimation is a very high growth rate up to about 10 μm/min, which is suitable for large-scale production.

Next, a CdTe film is deposited on the CdS film through close-spaced sublimation at a substrate temperature of 480–520° C. CdTe granulate is generally used as a source of CdTe which is vaporized from an open crucible.

An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$. Traditionally, most research groups would perform this step by depositing a layer of $CdCl_2$ on top of CdTe by simple evaporation or by dipping the CdTe in a methanol solution containing $CdCl_2$, and then annealing the material in air at about 400° C. for between about 15 and about 20 min. It is generally believed that $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of the small grains and removing defects in the material.

After $CdCl_2$ treatment, the CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ must be removed in order to provide for good back-contact onto the CdTe film. Also, it is believed that, since etching produces a Te-rich surface, formation of an ohmic contact when a metal is deposited on CdTe is facilitated.

The electric back-contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g., in graphite contacts, which, upon annealing, can diffuse in the CdTe film. Use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell is set forth by applicants in N. Romeo et al., *Solar Energy Materials & Solar Cells,* 58 (1999), 209–218).

Industrial interest in thin films solar cells has increased in recent years, especially in view of the relatively high conversion efficiency achieved. Recently, for instance, a record 16.5% conversion efficiency was reported (see X. Wu et al., 17*th* *European Photovoltaic Solar Energy Conversion Conference,* Munich, Germany, 22–26 Oct. 2001, II, 995–1000). Accordingly, a number of attempts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells. A state-of-the art report of these efforts may be found in D. Bonnet, *Thin Solid Films* 361–362 (2000), 547–552. While helpful, they include crucial steps that also affect either the stability and efficiency of CdTe/CdS thin film solar cells or their costs, thereby hindering achievement of a commercially viable process.

A significant problem of these processes is the etching step to which the CdTe surface must be submitted for removing CdO or $CdTeO_3$ oxides that form thereon. Although etching requires the steps of immersing substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for such continuous operation does not currently exist. Another difficulty that can negatively affect the stability of TCO films, as well as the cost of the final product, are the aforementioned disadvantages encountered using known TCOs. Moreover, known TCOs typically require the use of special glasses, such as borosilicate glass, to avoid Na diffusion and associated damage to the film that often occurs when soda-lime glass is used.

A further drawback of conventional processes relates to the source from which the CdS film and the CdTe film are produced through close-spaced sublimation. When relatively small pieces of these materials which contain dust, are used as a sublimation source, because of a different thermal contact, some micro-particles can overheat and, together with the vapor, split onto the substrate. In an attempt to avoid this inconvenience, complicated metallic masks are often used which make continuous operation problematic.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a process suitable for large-scale production of stable and efficient CdTe/CdS thin film solar cells using a low cost substrate.

Another object of the present invention is to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells in which the CdTe film is treated with $CdCl_2$ so as to eliminate the need for an etching step for removal of oxides that may form on the CdTe film.

It is a further object of the present invention to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells in which deposition of the TCO film is conducted such that a film of very low resistivity can be deposited without formation of metal noodles on the target, thereby enabling a relatively inexpensive substrate to be used.

Still another object of the present invention is to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells which allows formation of CdS and CdTe films that are entirely free of dust.

It is yet another object of the present invention to provide a CdTe/CdS thin film solar cell that is stable, efficient and relatively low-cost.

According to one aspect of the present invention, treatment of CdTe film with $CdCl_2$ is accomplished by first forming a layer of $CdCl_2$ having a thickness between about 100 and about 200 nm on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380 and 420° C. and a pressure between about 300 and about 1000 mbar under an inert gas atmosphere; and, finally, removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is maintained at a temperature generally within a range of 350 and 420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. As a result, etching treatment of the CdTe film is unnecessary and the process can be conducted continuously.

According to another aspect of the present invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing approximately 1–3 vol. % hydrogen and a gaseous fluoroalkyle compound, in particular, CHF_3. In this manner, the TCO is doped with fluorine.

According to a further aspect of the present invention, as a source material for formation of the CdS and CdTe films by sputtering or close-spaced sublimation, a CdS or CdTe material, respectively, is used in the form of a relatively compact block.

Further features of the process according to the invention are set forth in the dependent claims.

In accordance with still another aspect of the present invention, a process is provided for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; and depositing a back-contact film on the treated CdTe film. In treatment of the CdTe film with CdCl, initially a layer of $CdCl_2$ is formed on the CdTe film by evaporation, while maintaining the substrate at room temperature. Second, the $CdCl_2$ layer is annealed in a vacuum chamber at a temperature, generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere. Finally, the inert gas is removed from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

According to yet another aspect of the present invention, a process is provided for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of (i) depositing a film of a transparent conductive oxide (TCO) on the substrate; (ii) depositing a film of CdS on the TCO film; (iii) depositing a film of CdTe on the CdS film; (iv) treating the CdTe film with $CDCl_2$; and (v) depositing a back-contact film on the treated CdTe film, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

In accordance with still a further aspect of the present invention, a process for large-scale production of CdTe/CdS thin film solar cells is provided. Films of the cells are deposited, in sequence, on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; and depositing a back-contact film on the treated CdTe film, wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or CdTe material, respectively, generally in the form of a compact block is used.

Yet a further aspect of the present invention is directed to a CdTe/CdS thin film solar cell comprising a transparent substrate on which a layer of a transparent conductive oxide (TCO) is deposited. A CdS layer is deposited on the TCO layer, a CdTe layer is deposited on the CdS layer and a back-contact layer on the CdTe layer, wherein the transparent conductive oxide is In_2O_3 doped with fluorine and the back-contact layer is formed by a layer of Sb_2Te_3 or As_2Te_3 covered by a layer of Mo.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and advantages of the process for large-scale production of CdTe/CdS thin film solar cells, according to the present invention, will become apparent from the following description of specific, illustrative embodiments thereof made with reference to the following drawings, in which:

FIG. **1** is a schematic diagram showing a film deposition sequence for producing CdTe/CdS thin film solar cells, according to one aspect of the present invention;

FIG. **2** is a flow diagram showing a process for producing CdTe/CdS thin film solar cells, according to another aspect of the present invention.

The same numerals are used throughout the drawing figures to designate similar elements. Still other objects and advantages of the present invention will become apparent from the following description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings and, more particularly, to FIGS. **1**–**2**, there is shown generally a specific, illustrative process for producing CdTe/CdS solar cells, according to the present invention. Such solar cells comprise five layers deposited in a selected sequence on a transparent base layer or substrate, the layers consisting of about a 300 nm to about a 500 nm thick layer of a transparent conducting oxide

(TCO), about an 80 nm to about a 200 nm thick layer of CdS deposited on the TCO layer, about a 4 μm to about a 12 μm thick layer of CdTe on the CdS layer and a back contact layer formed of at least about a 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate preferably comprises soda-lime glass and the transparent conducting oxide is desirably fluorine-doped (In_2O_3.F).

TCO layer consists of In_2O_3, which is doped with fluorine during growth. The In_2O_3 target, unlike ITO, does not form any noodles. A very low resistivity is obtained by introducing a relatively small amount of fluorine to the sputtering chamber in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a $Ar+H_2$ mixture, in which H_2 is around 20% in respect to Ar. A typical example is a generally 500 nm thick film of In_2O_3 deposited with a deposition rate generally higher than about 10 Å/sec at a substrate temperature of approximately 500° C., with an Ar flow-rate of about 200 sccm, a CHF_3 flow-rate of roughly 5 sccm and an $Ar+H_2$ flow-rate of around 20 sccm. Accordingly, the reactive sputtering gas comprises Ar in the amount of about 2.5 vol. % of CHF_3 and about 1.8 vol. % of H_2. This film exhibits a sheet resistance of approximately 5 $\Omega/_{square}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than about 85% in the wavelength generally within a range of 400 and 800 nm. Another characteristic of this film is its high degree of stability as well as its ability to prevent Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable, even if heated to about 180° C. when illuminated by "ten suns" for several hours.

After deposition of the CdS and CdTe films in the known way of sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ as follows.

First, 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. Annealing is then performed for about 15–20 min at approximately 400° C. in a vacuum chamber in which roughly 500 mbar of Ar is introduced. After annealing, the chamber evacuated while keeping the substrate at a temperature of about 400° C. for 5 min. Since $CdCl_2$ has a relatively high vapor pressure at about 400° C., any residual $CdCl_2$ re-evaporates from the CdTe surface. It is noted that CdO or CdTeO, are not formed since annealing is conducted in an inert atmosphere, which does not generally contain O_2.

According to various aspects of the present invention, a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing a thin layer of a relatively highly conducting p-type semiconductor, such as Sb_2Te_3 or As_2Te_3, on top of the CdTe film. Generally speaking, a good, non-rectifying contact is achieved on a clean CdTe surface if a layer of Sb_2Te_3 or As_2Te_3 at least about 100 mm thick is deposited by sputtering at a substrate temperature of between about 250 and about 300° C. and between about 200 and about 250° C., respectively. Sb_2Te_3 grows naturally as p-type with a resistivity of around 10^{-4} Ωcm, whereas As_2Te_3 also grows as p-type but with a resistivity of roughly 10^{-3} Ωcm. The contact procedure is then completed by covering the low resistivity p-type semiconductor with at least about 100 nm of Mo_2 as is considered common practice in the art. A relatively thin layer of Mo is necessary in order to have a relatively low sheet-resistance on the back-contact.

As a source of CdS and CdTe materials used to form the respective layers by sputtering or CSS, a granulate material can be used, as is common practice in the art. However, in view of the disadvantages indicated above, when operating in this way, according to a preferred embodiment of the present invention, a new sublimation source can be used which consists of a relatively compact block obtained by melting and solidifying the material in an oven capable of sustaining a temperature generally higher than the melting temperature of the material.

A procedure for preparing the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3), which is a low melting point material (450° C.) and exhibits a very low vapor pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over the CdS and covers the CdS completely upon cooling. In this way, CdS covered with B_2O_3, if it is placed in an oven containing an inert gas at a pressure higher than approximately 50 atm. does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of about 1750° C., the oven is heated up to a temperature of about 1800° C. or more, and then cooled down to room temperature. In this manner, a unique compact block of CdS is obtained that is particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared using this type of source resulted in a very smooth film that is completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically approximately 100 nm thick. The substrate temperature is preferably kept between about 200 and 300° C. when CdS is prepared by sputtering and generally within a range of 480 and 520° C. when it is prepared by close-spaced-sublimation. The sputtered CdS layer generally requires annealing at about 500° C. in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a relatively high efficiency. In the case where CdS is prepared by close-spaced sublimation, O_2 is introduced to the sublimation chamber during deposition. While the role of O_2 is not known, it is presumed to passivate the CdS grain boundaries.

In accordance with another embodiment of the present invention, the CdTe source too is a generally compact block obtained through melting and solidifying pieces of CdTe in an oven under high pressure, as described previously. Since CdTe melts at around 1120° C., the oven must be heated to about 1200° C. in order to have complete melting of the CdTe pieces. CdTe films are deposited on the CdS by close-spaced sublimation at a substrate temperature generally within a range of 480 and 520° C. Deposition rates during CdTe growth are typically about 4 μm/min. In this manner, about 8 μm of CdTe are deposited in approximately 2 minutes.

By following the procedure described above, several solar cells have been prepared using as a substrate a I inch square low-cost soda-lime glass. A typical area of these cells is 1 cm^2. The finished cells are generally put under 10–20 suns for several hours at a temperature of around 180° C. in the open-circuit-voltage (V_{oc}) conditions. Advantageously, an increase in efficiency of about 20% or more is, thereby, achieved and without any material degradation.

The efficiency of these cells is generally within a range of 12% and 14% with open-circuit-voltages (V_{oc}) larger than approximately 800 mV, short-circuit-currents (J_{ac}) of between about 22 and about 25 MA/cm^2 and fill-factors (ff) ranging from about 0.6 to about 0.66.

EXAMPLE

A cell exhibiting an efficiency of around 14% has been prepared in the following way: soda-lime glass is covered with 500 nm of In_2O_3.F (fluorine-doped) deposited at a substrate temperature of about 500° C. as described above. 100 nm of CdS are then deposited thereon by sputtering at approximately 300° C. substrate temperature and annealed for about 15 min. at approximately 500° C. in 500 mbar of Ar containing about 20% O_2. 8 μm of CdTe are deposited on top of the CdS by CSS at a substrate temperature of approximately 500° C. Both the CdS and CdTe films are produced from a relatively compact block source as described above. A treatment with 150 nm of $CdCl_2$ is then performed in an Ar atmosphere, as described above. Finally, a back-contact is created, without any etching, by depositing, in sequence, through sputtering about 150 nm of Sb_2Te_3 and 150 nm of Mo.

After one hour under 10 suns at a temperature of about 180° C. in open-circuit conditions, the solar cell prepared in this way exhibited the following characteristics:

V_{OC}	852 mv
J_{SC}	25 mA/cm^2
ff	0.66
efficiency	14%

The techniques used in this process, such as sputtering and close-spaced sublimitation, are fast, reproducible and easily scalable.

In general, sputtering systems capable of covering an area of around 1×0.5 m^2 of glass are already commercially available, while close-spaced sublimation, which at a laboratory scale can readily cover 20×20 cm^2 area glass, does not yield any problems in being scaled up to about 1.5×0.5 m^2. An in-line process can work well if a large area glass is moved slowly over the different sources, namely, TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3, and Mo. In order to connect the single cells in series, the in-line system desirably also includes three laser scribing processes, the first one after the TCO deposition, the second one before the back-contact deposition, and the third at the end of the process. An relatively important part of the process, according to the present invention, is that no acids or liquids are used and, as a consequence, the process can be conducted on a continuous basis without interruption as is often needed to for etching in acid or in a Br-methanol solution.

Various modifications and alterations to the invention may be appreciated based on a review of this disclosure. These changes and additions are intended to be within the scope and spirit of the invention as defined by the following claim.

What is claimed is:

1. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the treatment of the CdTe film with $CdCl_2$ comprises the steps of:

forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature;

annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; and

removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process set forth in claim **1**, wherein the $CdCl_2$ layer is between about 100 nm and about 200 nm thick.

3. The process set forth in claim **1**, wherein annealing of the $CdCl_2$ layer is carried out for about 15–20 minutes.

4. The process set forth in claim **1**, wherein the inert gas is Ar.

5. The process set forth in claim **1**, wherein the back-contact film is formed of a Sb_2Te_3 layer covered by a layer of Mo.

6. The process set forth in claim **5**, wherein the Sb_2Te_3 layer is formed by sputtering at a temperature between about 250° C. and about 300° C.

7. The process set forth in claim **1**, wherein the back-contact film is formed of a As_2Te_3 layer covered with a layer of Mo.

8. The process set forth in claim **7**, wherein the As_2Te_3 layer is formed by sputtering at a temperature between about 200° C. and about 250° C.

9. The process set forth in claim **1**, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process set forth in claim **9**, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

11. The process set forth in claim **10**, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume, and wherein the fluoroalkyle compound is CHF_3.

12. The process set forth in claim **1**, wherein, as a source material for formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

13. The process set forth in claim **12**, wherein the compact block CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

14. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

15. The process set forth in claim **14**, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

16. The process set forth in claim **15**, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume, and wherein the fluoroalkyle compound is CHF_3.

17. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

18. The process set forth in claim **17**, wherein the compact block of CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than about 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

19. The process set forth in claim **1**, wherein the transparent substrate is soda-lime glass.

* * * * *

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(12) United States Patent

Barth et al.

(10) **Patent No.: US 7,220,321 B2**

(45) **Date of Patent: May 22, 2007**

(54) **APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 465 days.

(21) Appl. No.: **10/808,050**

(22) Filed: **Mar. 24, 2004**

(65) **Prior Publication Data**

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Related U.S. Application Data

(62) Division of application No. 10/200,265, filed on Jul. 22, 2002, now abandoned, which is a division of application No. 09/583,381, filed on May 30, 2000, now Pat. No. 6,423,565.

(51) **Int. Cl.**
C23G 16/00 (2006.01)

(52) **U.S. Cl.** **118/729**; 117/109

(58) **Field of Classification Search** 438/542; 118/729, 50.1; 117/109
See application file for complete search history.

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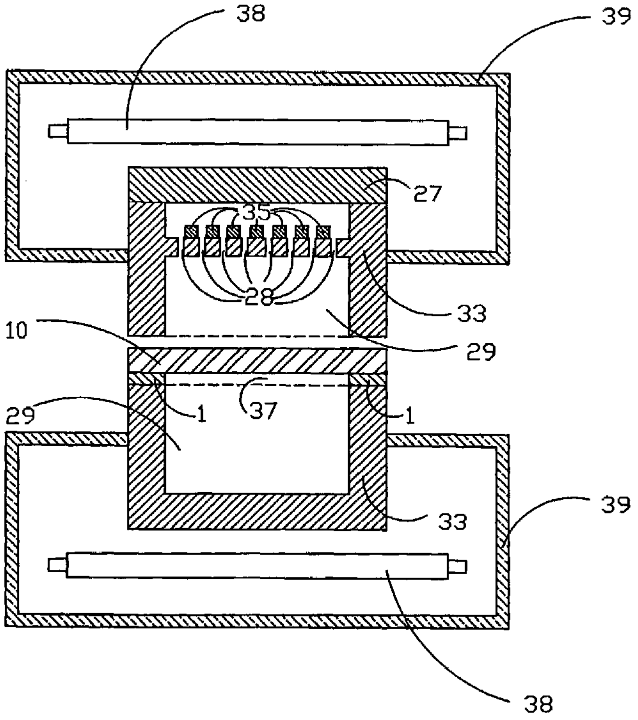
Primary Examiner—Caridad Everhart
(74) *Attorney, Agent, or Firm*—William E. Hein

(57) **ABSTRACT**

An apparatus and processes for large scale inline manufacturing of CdTe photovoltaic modules in which all steps, including rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation, are performed within a single vacuum boundary at modest vacuum pressures. A p+ ohmic contact region is formed by subliming a metal salt onto the CdTe layer. A back electrode is formed by way of a low cost spray process, and module scribing is performed by means of abrasive blasting or mechanical brushing through a mask. The vacuum process apparatus facilitates selective heating of substrates and films, exposure of substrates and films to vapor with minimal vapor leakage, deposition of thin films onto a substrate, and stripping thin films from a substrate. A substrate transport apparatus permits the movement of substrates into and out of vacuum during the thin film deposition processes, while preventing the collection of coatings on the substrate transport apparatus itself.

5 Claims, 14 Drawing Sheets



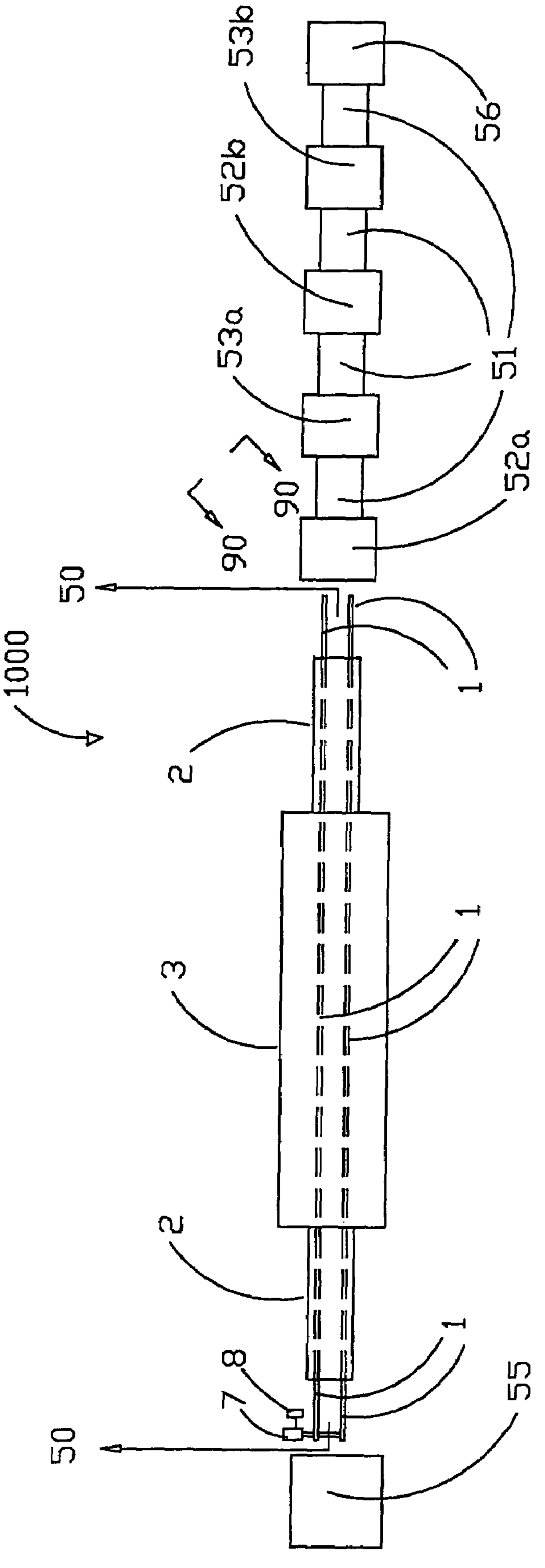


Fig. 1

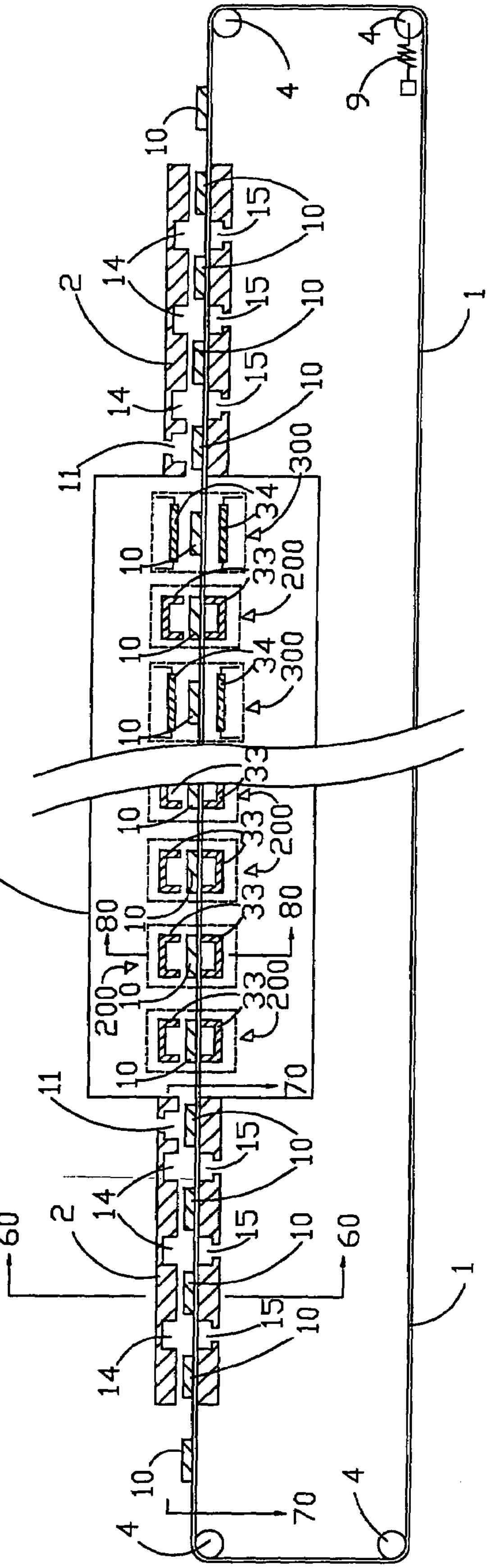


Fig. 2A

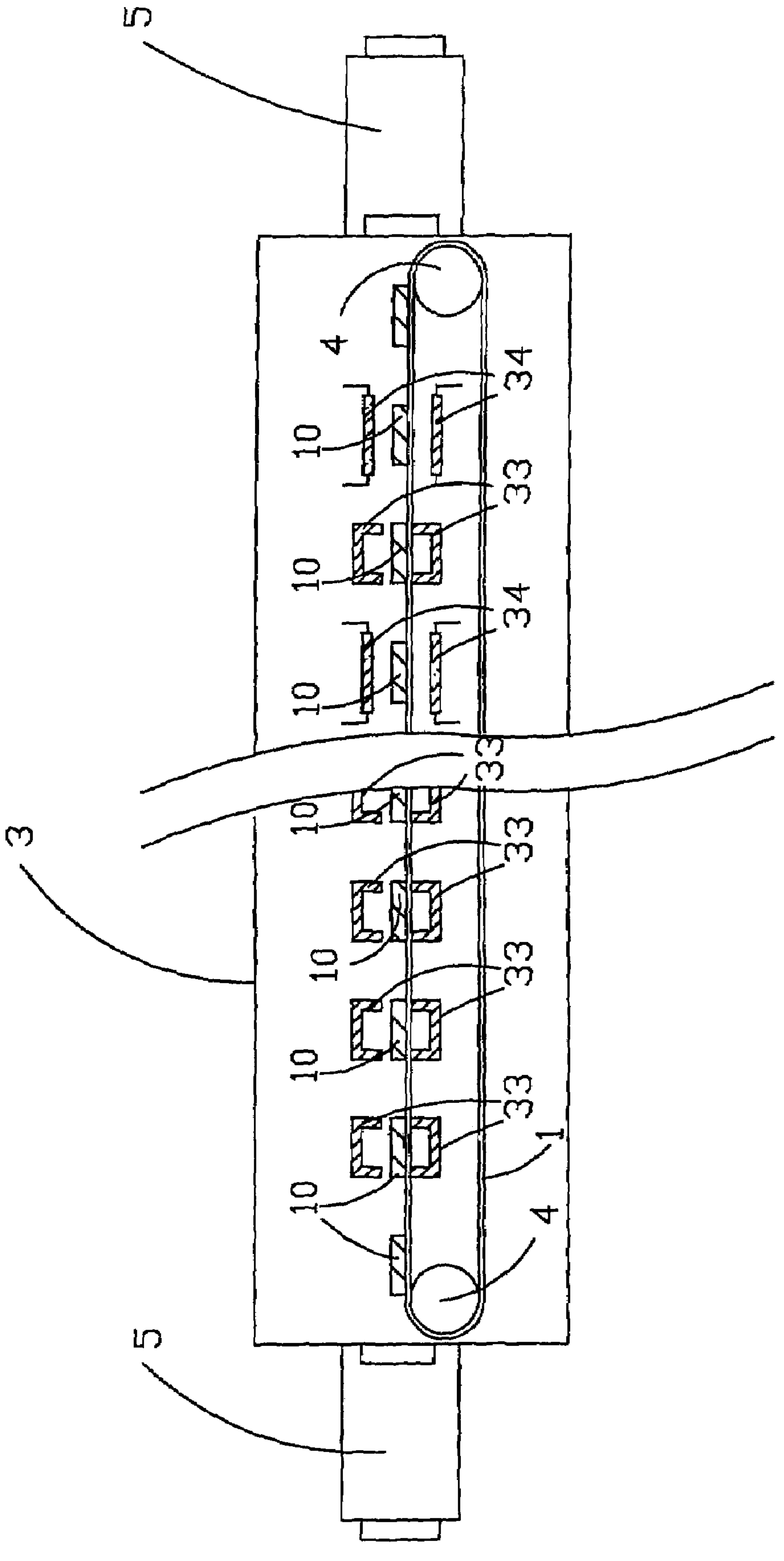


Fig. 2B

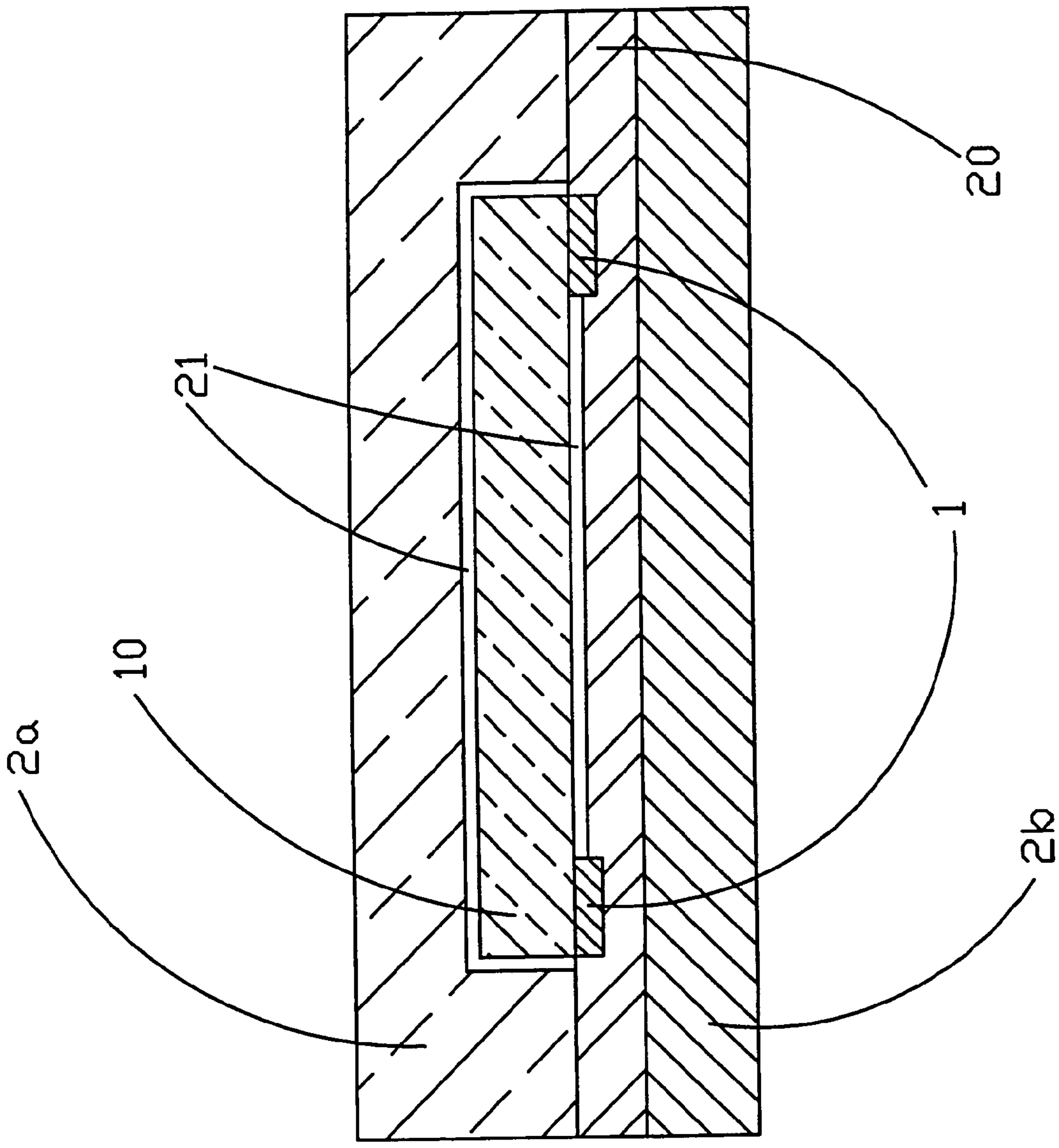


Fig. 3

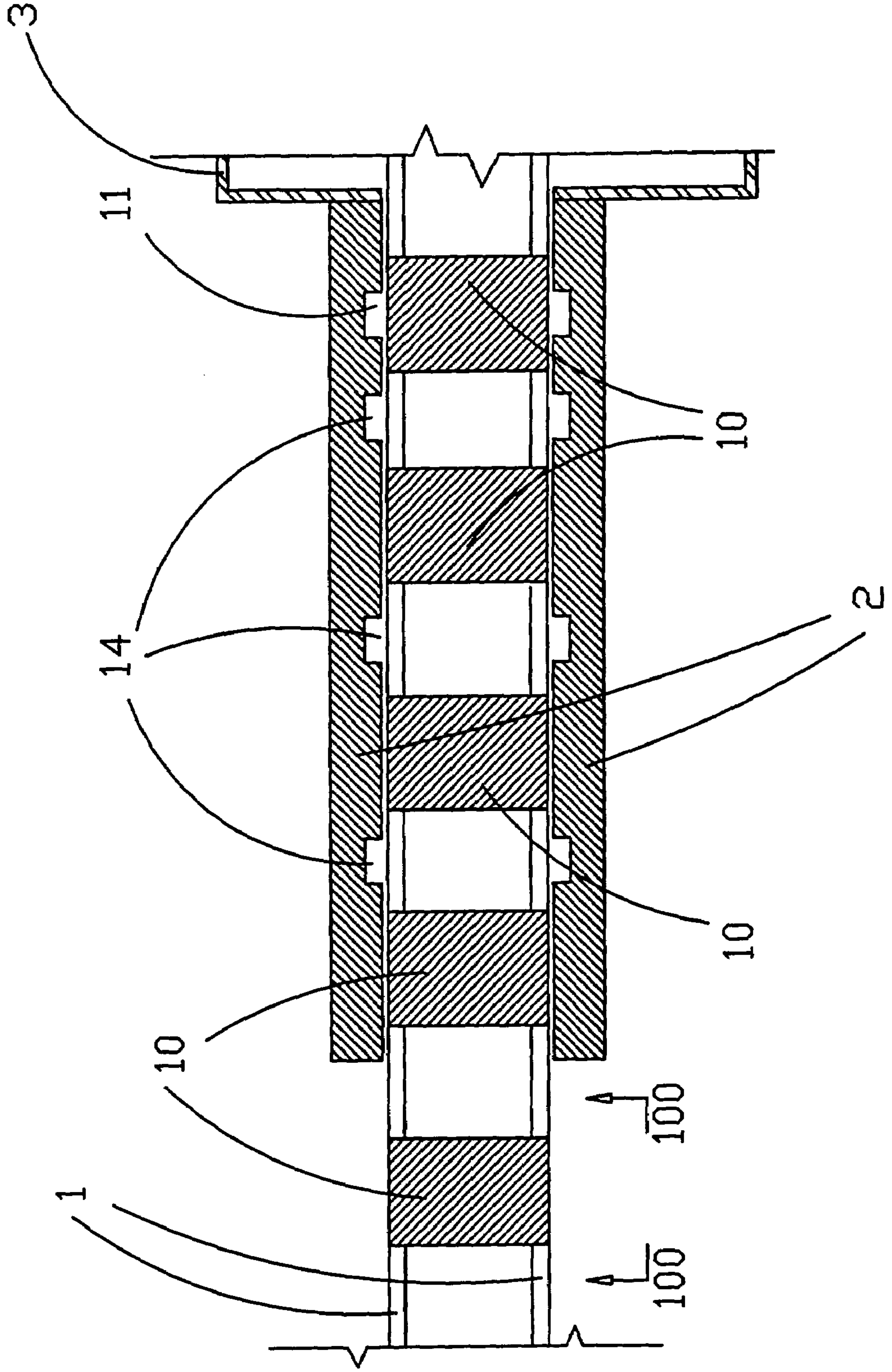


Fig. 4

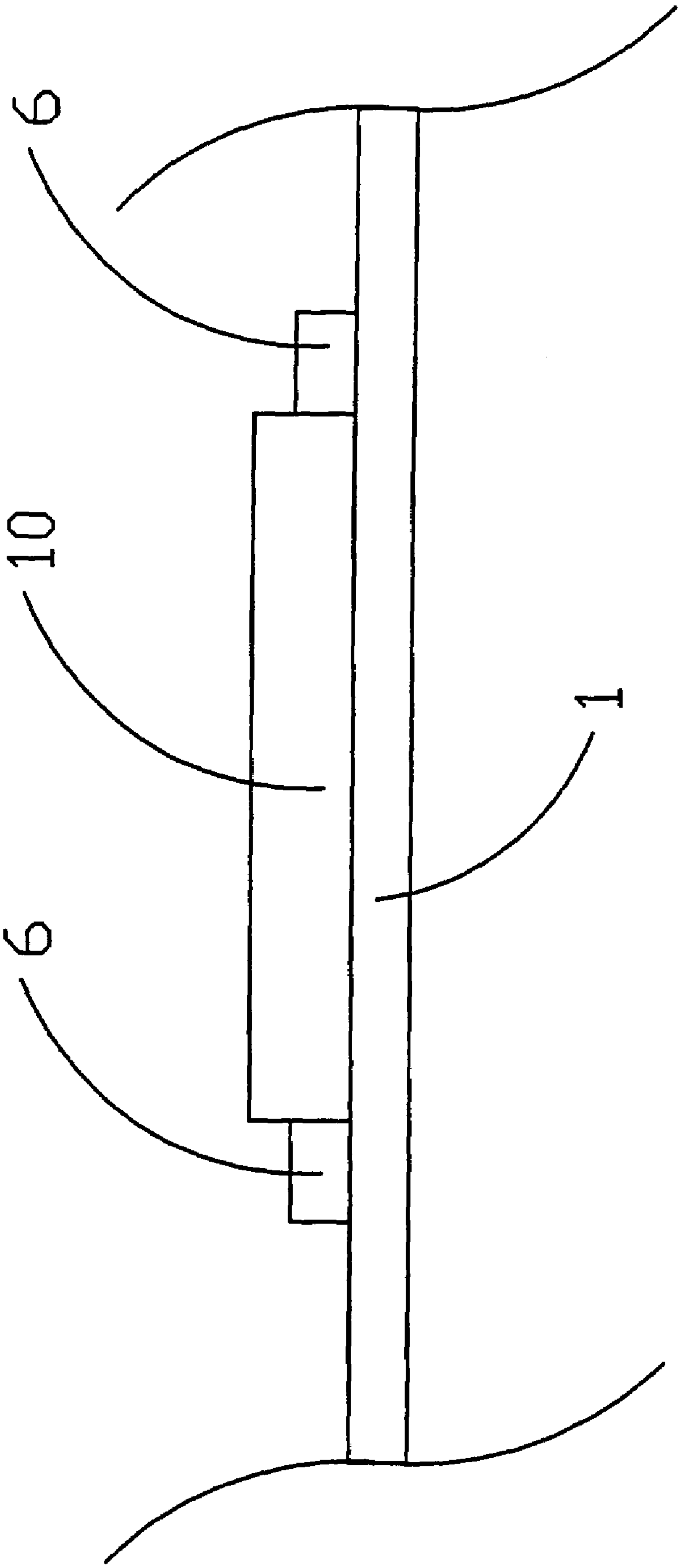


Fig. 5

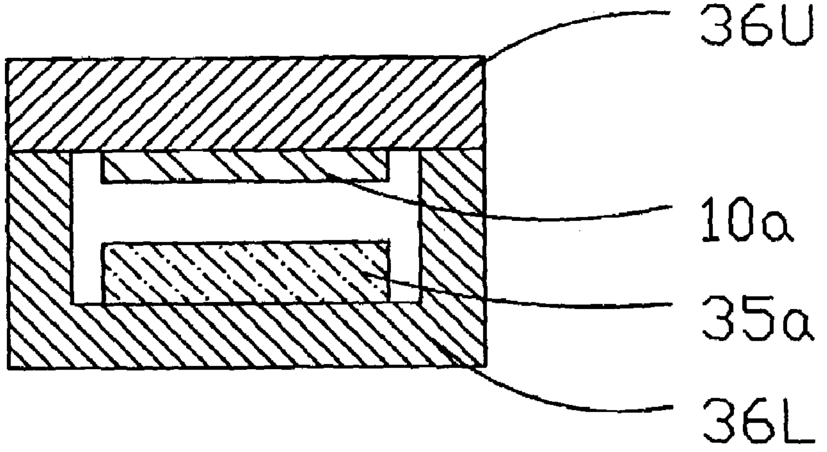


Fig. 6A (PRIOR ART)

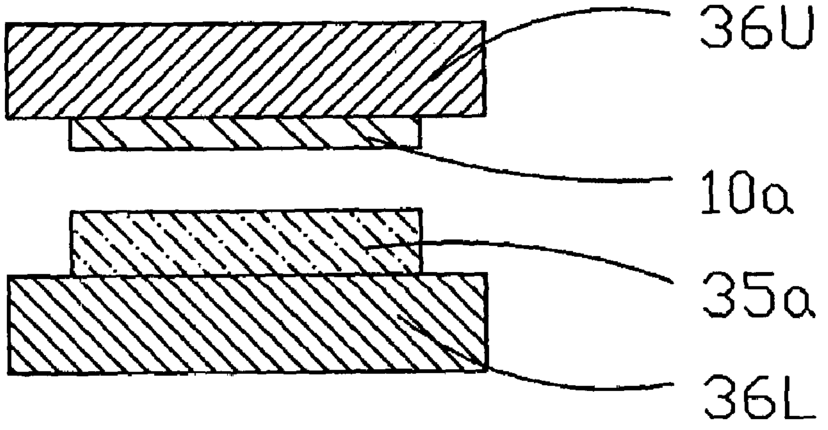


Fig. 6B (PRIOR ART)

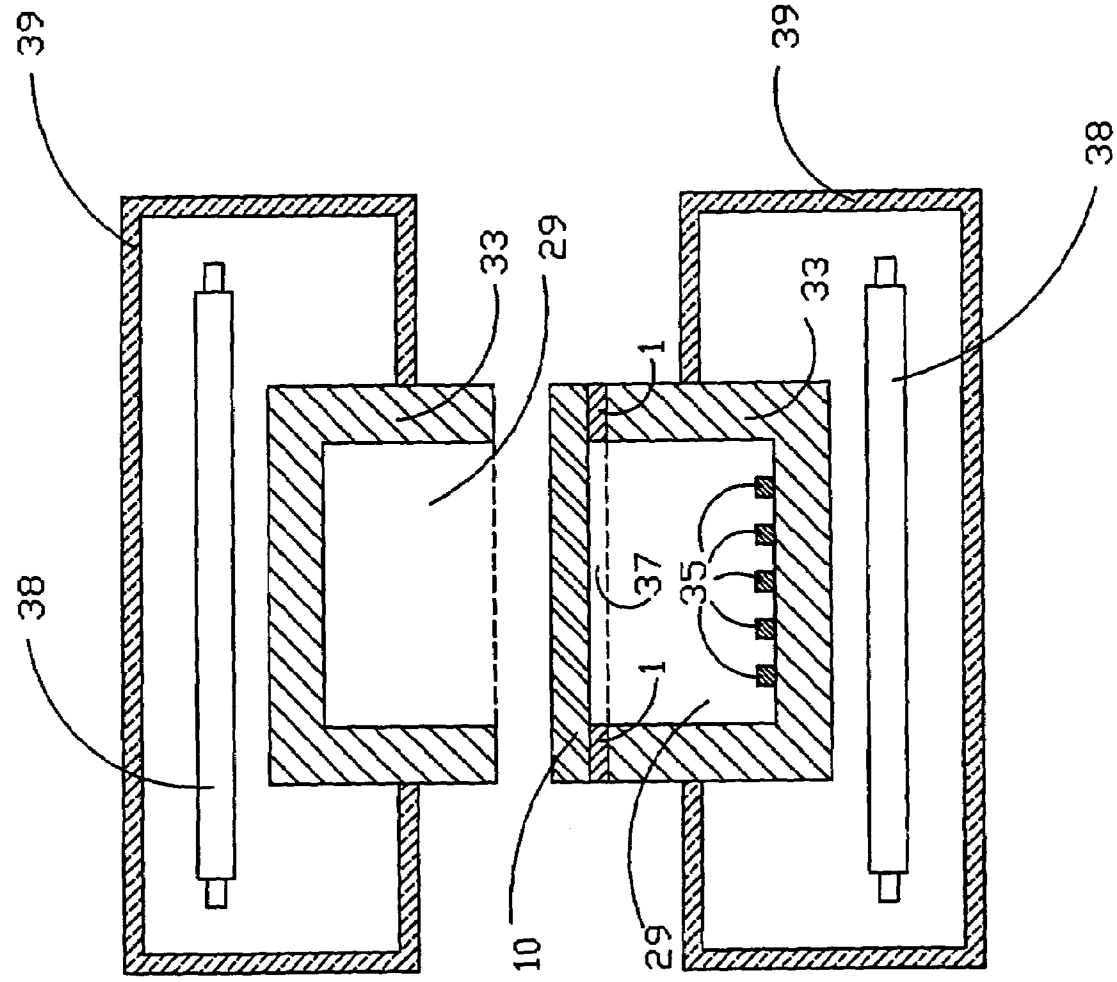


Fig. 7A

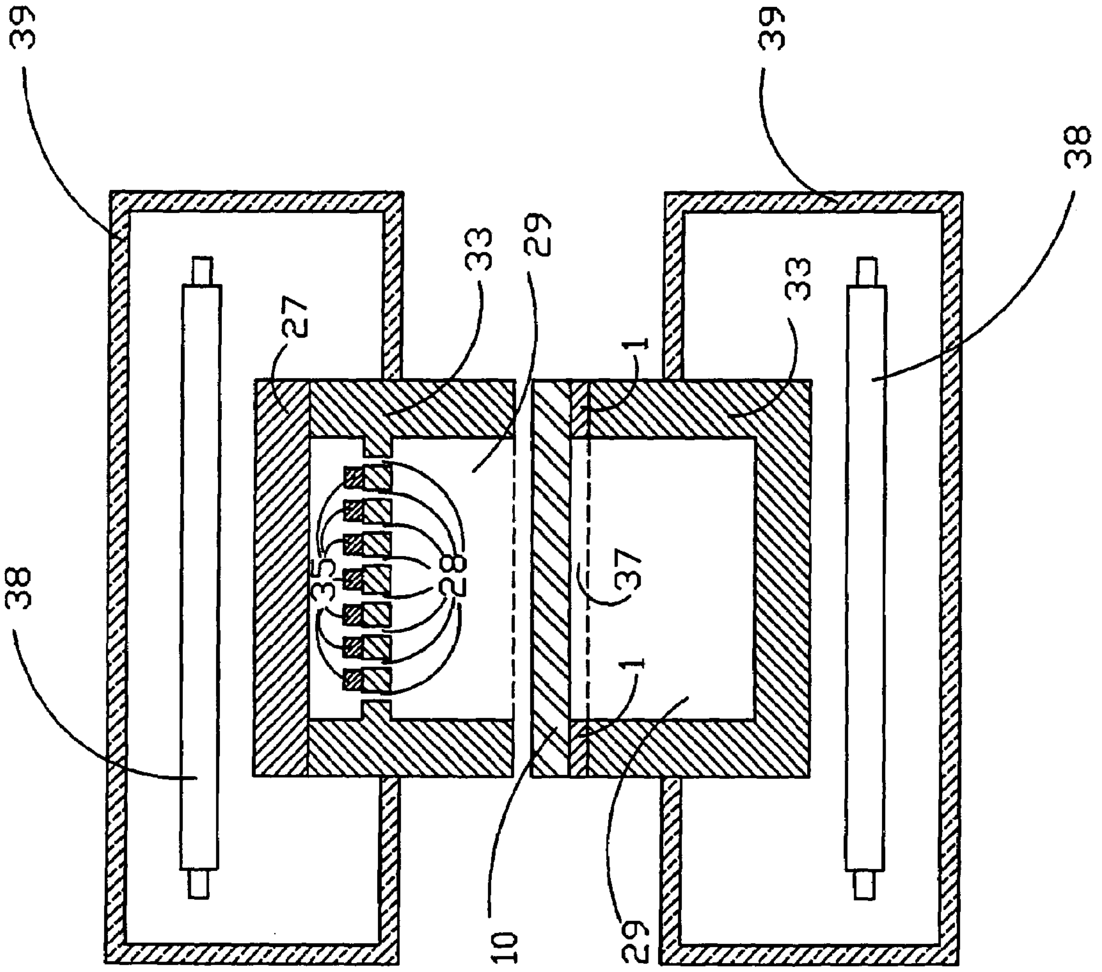


Fig. 7B

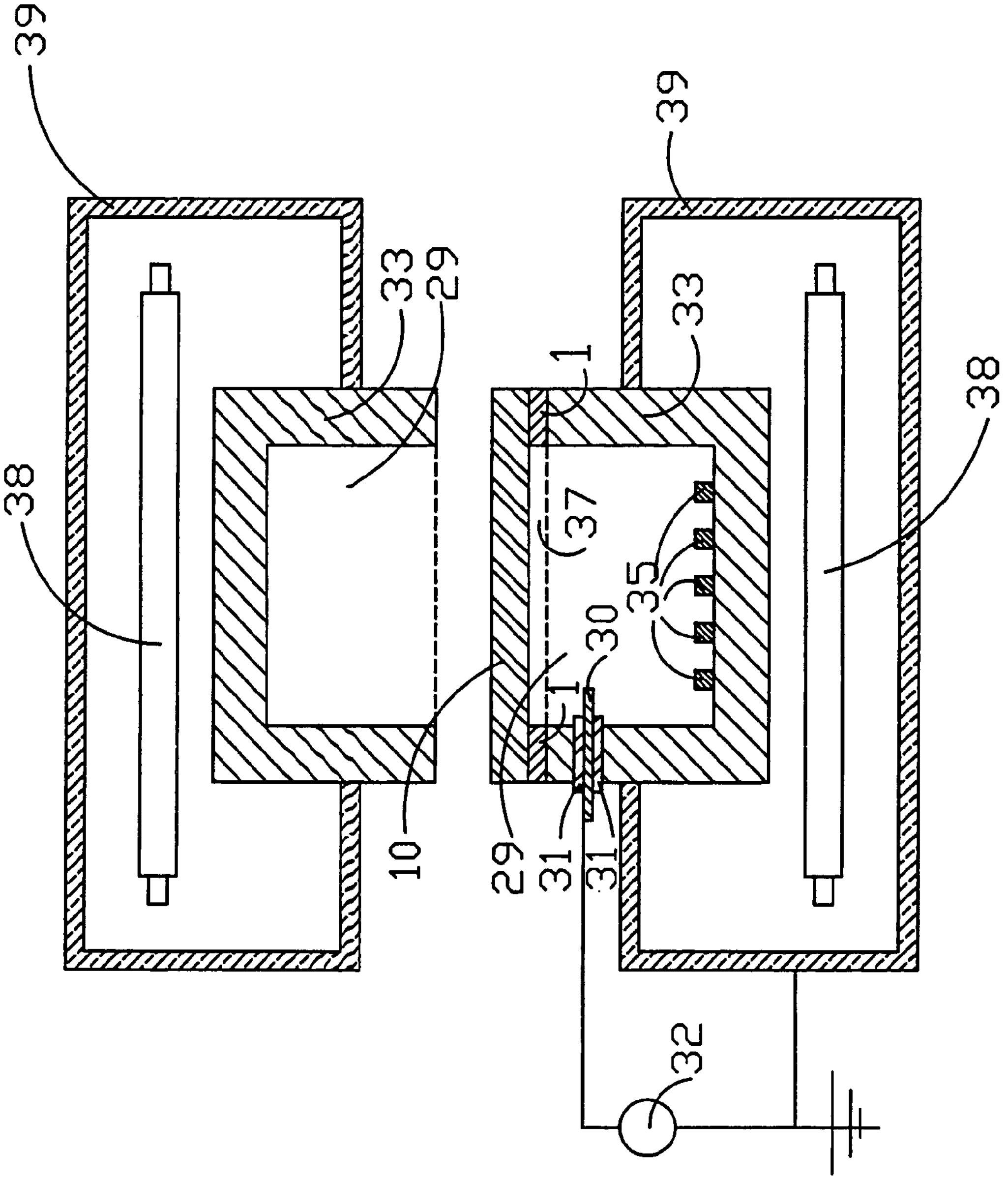


Fig. 8

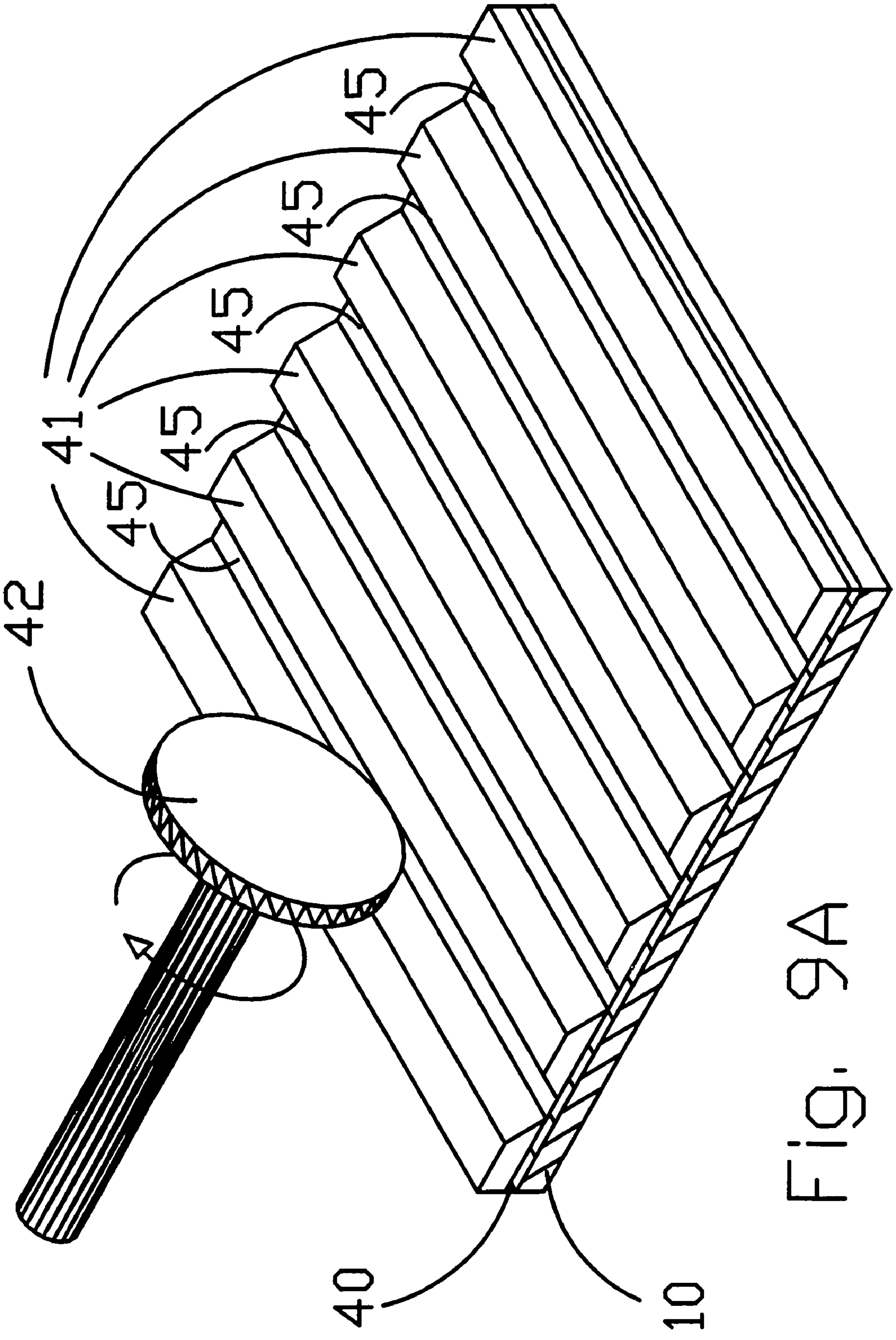


Fig. 9A

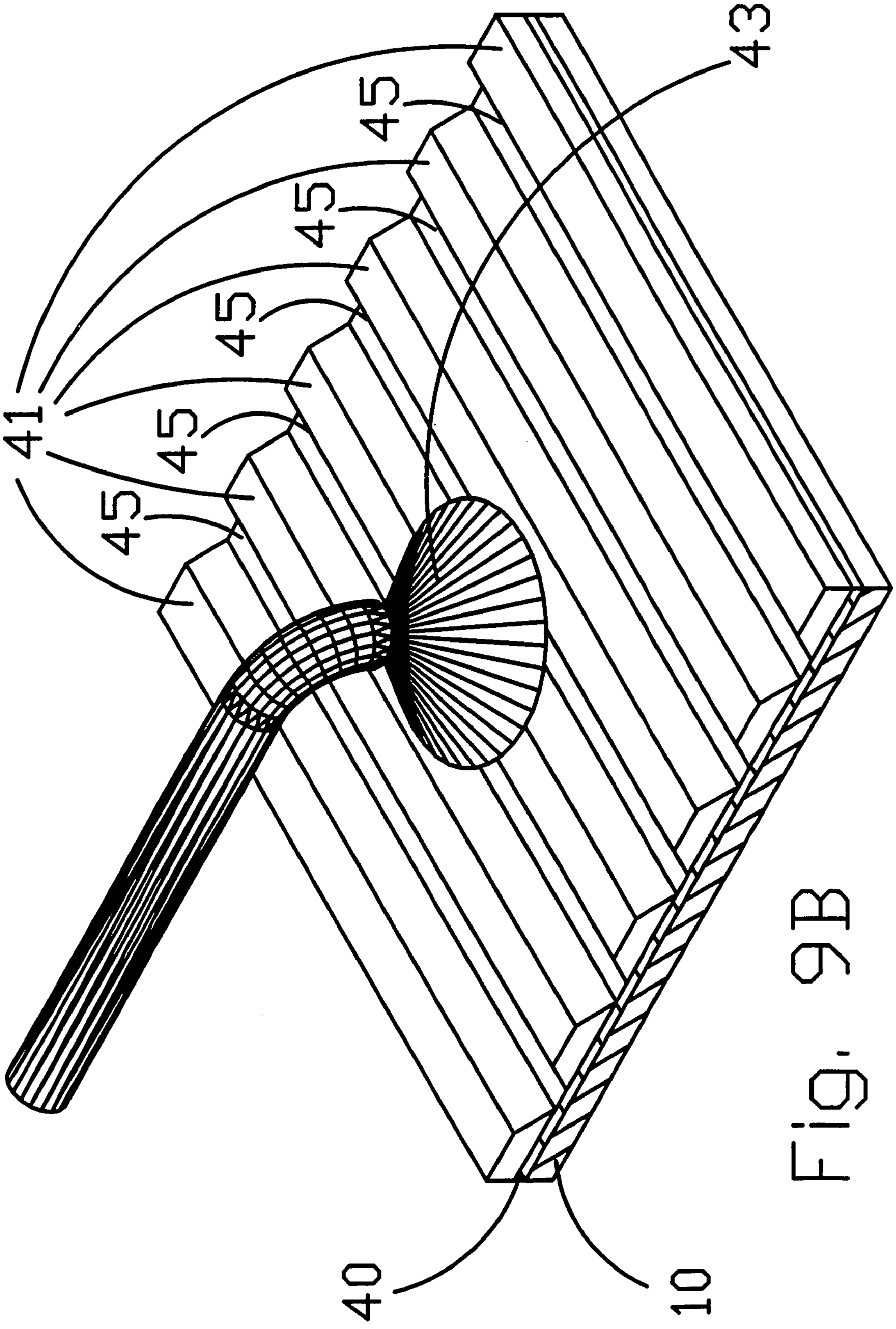


Fig. 9B

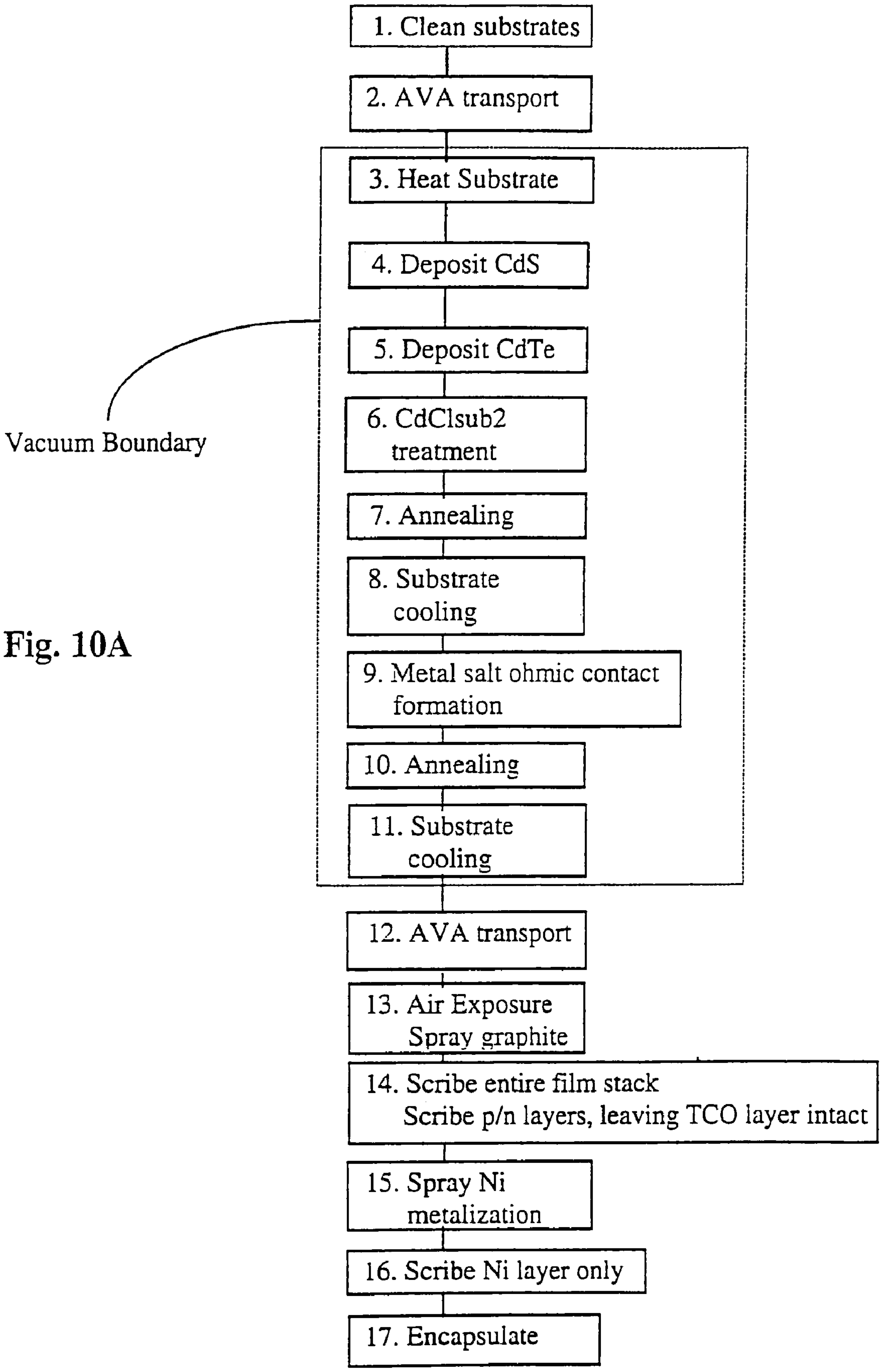

1. Clean substrates
2. AVA transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. CdClsub2 treatment
7. Annealing
8. Substrate cooling
9. Metal salt ohmic contact formation
10. Annealing
11. Substrate cooling
12. AVA transport
13. Air Exposure Spray graphite
14. Scribe entire film stack Scribe p/n layers, leaving TCO layer intact
15. Spray Ni metalization
16. Scribe Ni layer only
17. Encapsulate
Vacuum Boundary

Fig. 10A

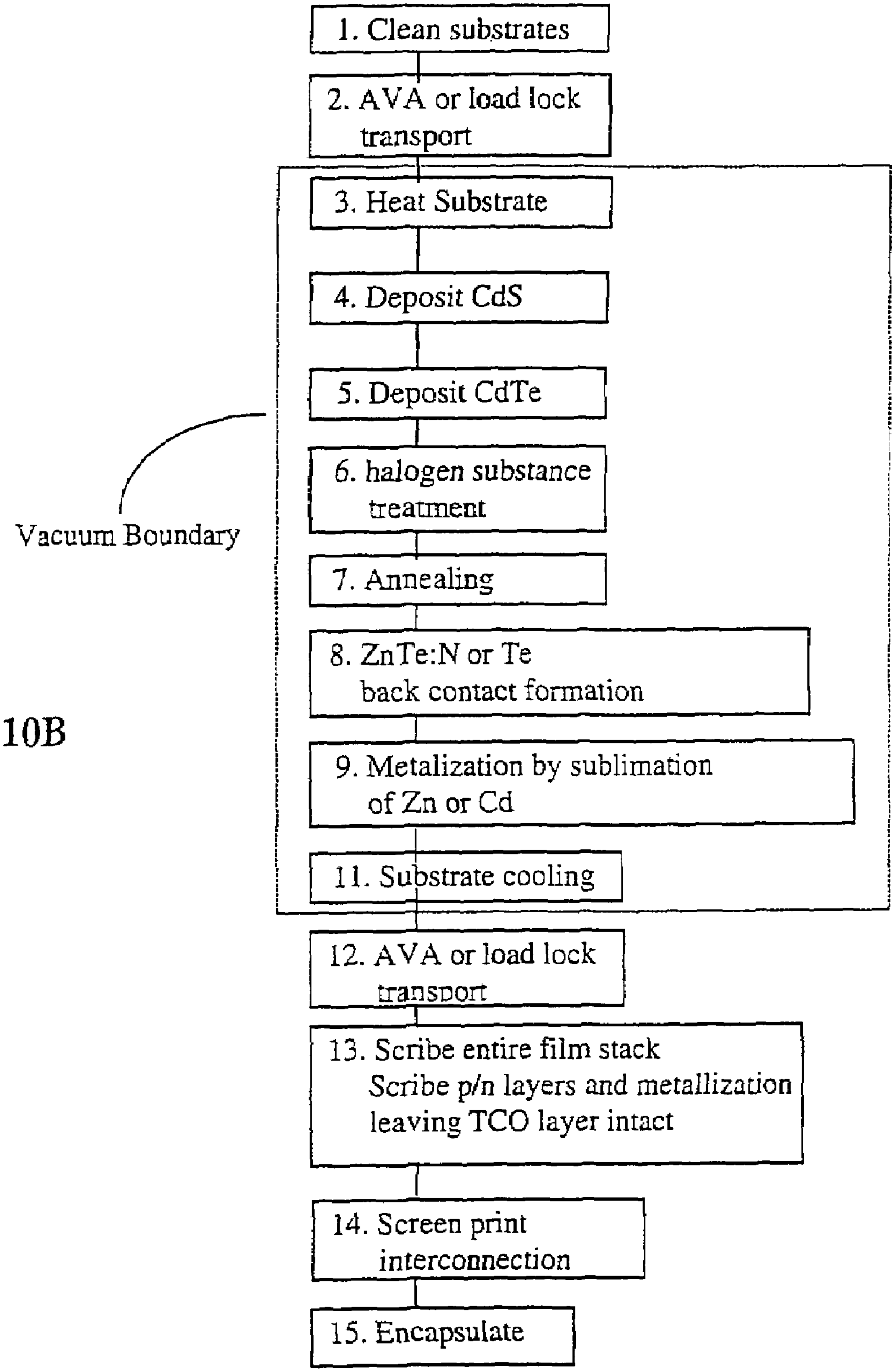

1. Clean substrates
2. AVA or load lock transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. halogen substance treatment
7. Annealing
8. ZnTe:N or Te back contact formation
9. Metalization by sublimation of Zn or Cd
11. Substrate cooling
12. AVA or load lock transport
13. Scribe entire film stack Scribe p/n layers and metallization leaving TCO layer intact
14. Screen print interconnection
15. Encapsulate
Vacuum Boundary

Fig. 10B

APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES

REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of application Ser. No. 10/200,265 filed on Jul. 22, 2002 now abandoned, which is in turn a divisional application of prior application Ser. No. 09/583,381 filed on May 30, 2000, now issued as U.S. Pat. No. 6,423,565.

GOVERNMENT SUPPORT

This invention was made with Government support under grants awarded by the National Science Foundation and the Department of Energy. The Government has certain rights in this invention.

FIELD OF THE INVENTION

The present invention relates to apparatus and processes for the mass production of low cost photovoltaic modules and, more specifically to an inline continuous vacuum apparatus and process for fabricating the critical semiconductor layers, which together with attendant non-vacuum processes, are all accomplished at high throughput.

BACKGROUND OF THE INVENTION

Photovoltaic (PV) modules are used to generate electricity from sunlight by the photovoltaic effect. It has been recognized for decades that if these modules could be mass produced at low cost, they could be used to meet a considerable portion of the world's energy needs. Major companies, such as Royal Dutch/Shell and BP-Amoco, have stated that PV modules have the potential to become a major energy source and that their use has significant benefits to the global environment. However, for these benefits to be realized, PV modules must be produced at many times the current volume and at costs below \$100/m^2, as discussed by Bonnet et. al. in "Cadmium-telluride material for thin film solar cells", J. Mater. Res., Vol. 13, No. 10 (1998). Currently, PV modules are manufactured in small quantities at costs of about \$500/m^2. About one hundred times the current yearly production is required to sustain a PV module manufacturing capacity that can contribute just 5% of the current electricity generated. Consequently, the manufacturing volume of PV modules needs to be greatly increased and costs significantly reduced.

To realize the required increases in production volume and decreases in manufacturing costs, PV modules must be produced as a commodity. Commodity level manufacturing requires innovation to develop highly automated production processes and equipment, which are designed to specifically fabricate the commodity product. Commodity manufacturing necessitates high production speeds (high throughput), minimal labor costs, and a continuous process flow. Low capital costs and ease of expanding production capacity also facilitate commodity manufacturing. There are a variety of known PV devices, but only the cadmium telluride (CdTe) thin film PV device has the potential to satisfy the requirements for commodity manufacturing.

Since 1974, there have been many industrial efforts to create technologies for CdTe PV module manufacturing. Most of these industrial efforts, as exemplified by the teachings of U.S. Pat. Nos. 4,319,069, 4,734,381, and 5,501,744, have been terminated because of fundamental inadequacies in their manufacturing technologies. To date, no technology suitable for commodity level manufacturing of CdTe PV modules has been developed, thus demonstrating the need for innovation in this area.

The most common CdTe PV cells are thin film polycrystalline devices, in which the CdTe layer is paired with a cadmium sulfide (CdS) layer to form a heterojunction. The thin films of a CdS/CdTe PV device can be produced through a variety of vacuum and non-vacuum processes. Of the many types of thin film deposition methods, sublimation in vacuum is most amenable to commodity manufacturing. This is because vacuum sublimation of CdS/CdTe PV modules exhibits deposition rates 10 to 100 times higher than any other PV module deposition method. Vacuum sublimation of the semiconductor layers for CdS/CdTe PV modules can also be performed in modest vacuum levels and does not require costly high vacuum equipment. Vacuum deposition methods for other thin film PV devices require costly, complex high vacuum equipment and results in low throughput.

Due to the high rate of deposition and low capital cost, the CdS/CdTe thin film cell fabricated by vacuum sublimation is the most suitable for commodity level manufacturing of PV modules. However, cadmium is a Group B carcinogen. According to U.S. government regulations, the quantity of this material which can be lawfully released into the environment or into an occupational setting is extremely small. The known prior art in CdS/CdTe vacuum sublimation requires process and hardware innovations to achieve occupational and environmental safety as required by federal regulations, as well as commodity scale manufacturing.

One known configuration for a CdTe device is the back wall configuration, in which the thin films are deposited onto a glass superstrate, hereinafter referred to as a substrate. The CdTe device is most often fabricated on a glass substrate coated with a transparent conductive oxide (TCO) film onto which other film layers are deposited in the following order: a) a CdS film, b) a CdTe film, c) an ohmic contact layer, and d) a metal film. Along with the deposition of these films, many heat treatments are also needed to enhance the device properties. The TCO and the metal films form the front and back electrodes, respectively. The CdS layer (n-type) and the CdTe layer (p-type) form the p/n junction of the device. The cells are deployed with the substrate facing the sun. Photons travel through the glass and TCO film before reaching the p/n junction of the device. A module is formed by interconnecting individual cells in series to produce a useful voltage.

Thus, a process for manufacturing CdS/CdTe modules includes the following steps: 1) cleaning the TCO coated glass substrates, 2) heating the substrates, 3) depositing an n-type CdS layer, 4) depositing a p-type CdTe layer, 5) performing a $CdCl_2$ treatment to improve CdTe grain structure and electrical properties, 6) forming a p+ ohmic low resistance contact layer to improve current collection from the CdTe, 7) depositing a metal layer (metallization) to form the back electrode, 8) scribing the film layers into individual cells, 9) interconnecting the cells in series and providing a means of electrical connection to the module, and 10) encapsulating the finished module.

All of the prior art methods for the production of CdTe modules have limitations that render them unsuitable for commodity level manufacturing. For example, prior art methods of $CdCl_2$ treatment are disconnected, low throughput batch operations, rather than continuous flow processes. These batch type processes are inefficient and involve extremely high costs in order to increase throughput to the commodity manufacturing level. Most of the known methods of $CdCl_2$ treatment also require rinsing, which generates liquid wastes that contain cadmium. Known methods of ohmic contact formation are also batch type processes that exhibit low throughput rates. Prior art metallization steps also exhibit low throughput and require costly process equipment. It is necessary to improve the current methods of $CdCl_2$ treatment, ohmic contact formation, and metallization in order to achieve high throughput continuous processes.

Prior art methods for scribing the layers to form a module include laser scribing, mechanical scribing, and abrasive blasting. Known laser scribing methods used in the PV industry are associated with low production speed and high capital cost. Laser scribing was abandoned recently in one industrial setting due to laser equipment failure as discussed by Borg in, "Commercial Production of Thin-Film CdTe Photovoltaic Modules", NREL/SR-520-23733, October 1997. Known mechanical and abrasive blast scribing methods have only been shown on a small scale as typified by U.S. Pat. No. 5,501,744 to Albright and require innovation and improvement to be suitable for commodity level manufacturing.

Specific examples of prior art relating to CdS deposition and CdTe deposition performed by vacuum sublimation are described in detail below. The other prior art steps that are necessary to form a complete CdTe PV module are also discussed below.

One known vacuum method of producing CdTe solar cells by vacuum sublimation is taught in U.S. Pat. No. 5,536,333 to Foote et. al. This method is further described by Sasala et. al. in "Technology Support for Initiation of High-Throughput Processing of Thin-Film CdTe PV Modules", NREL/SR-520-23542, pp. 1–2, (1997). These references discuss a technique known as vapor transport deposition (VTD), which involves heating of the semiconductor materials in a contained vessel in order to create vapor. An inert carrier gas, such as nitrogen, transports the vapor of the semiconductor to the substrate through heated conduits. The substrate is held horizontally in a heated environment and supported from beneath by ceramic rollers in the heated environment. The deposition of the semiconductor is made onto the top surface of the substrate. In accordance with this prior art method, the ceramic rollers prevent the glass substrate from sagging under its own weight due to the elevated temperatures involved.

The entire VTD method is very complex and costly. It is possible to deposit a complete CdTe solar cell in a very short time and at sufficiently low substrate temperatures to eliminate glass sagging completely or reduce it to a very small acceptable value. Thus, the expensive ceramic rollers of the VTD method are not needed. Reloading starting material may also be performed in a much simple manner than as shown in this prior art. Since the films are thin, only small amounts of material are required to form them. Consequently, only very small volumes of starting material are needed for many days of operation, thus eliminating the need for this complex reloading arrangement. The heated vessels of this method contain toxic vapors, which pose significant occupational safety problems when they are opened for reloading during processing. In the VTD method, vapors are transported through long distances in a carrier gas, an arrangement which will likely lead to the formation of very small nano-particles through condensation of the vapors. These nano-particles degrade the film qualities and lead to occupational hazards when the system is serviced. Furthermore, in the VTD method, the continuous flow of carrier gas has to be maintained along the substrate. Any CdS or CdTe vapors that are carried past the substrate will be wasted. Any deposits of waste material on the inner surface of the vacuum chamber, pumps, exhaust, etc. must be cleaned, thereby exposing maintenance workers to toxic materials and raising occupational safety issues. In order to prevent unwanted condensation of CdS and CdTe vapors, the VTD method also requires continued heating of large portions of the equipment, including the vaporization vessel itself, the conduits, the deposition chamber, etc. This wastes energy and increases the capital costs. The VTD method is only used for depositing the p/n junction layers. Other processing steps, such as the $CdCl_2$ treatment, ohmic contact formation, and metallization are inherently low throughput batch processes. Scribing is taught to be either laser scribing or photolithography, both of which are slow and costly processes.

In another prior art reference entitled "The CdTe Thin Film Solar Cell," International Journal of Solar Energy, vol. 12, 1992, Bonnet proposes an inline production method for fabricating CdS/CdTe layers using a close-spaced sublimation (CSS) type deposition process. This prior art reference describes inline deposition within one vacuum boundary for only the steps of substrate heating, CdS deposition, and CdTe deposition. The other steps of $CdCl_2$ treatment, ohmic contact formation, and metallization are not shown as part of a continuous inline vacuum process, and are presumably performed by previously known methods. As described above, known methods for performing these steps have limitations. The Bonnet method does allow multiple substrate processing of more than one film. However, it is not clear if long term operation and uniformity of deposition over time and across large substrates are achieved. Furthermore, the Bonnet method relies on CSS, which by definition, requires a space of 2–3 mm between the source and the substrate. This gap will allow a vapor leak at the edge of the substrate. As the source charge sublimes away over time the gap will increase. It is the present inventors' experience that this gap and the associated vapor leak causes non-uniform deposition on the substrates and also results in condensation of toxic materials on unwanted areas on the inner surfaces of the process chamber. This leak will be reduced if the background chamber pressure is held high enough to decrease the mean free path between gas molecules in the process chamber. However, higher pressures lead to lower deposition rates and greater nano-particle formation. An operating pressure of 750 millitorr is specified. At these pressures, nano-particles will be formed, since the vapor will homogeneously condense in the ambient gas near the edge of the deposition space. These very small particles degrade film quality and pose a health hazard to workers during routine maintenance inside the vacuum chamber.

Each of the individual prior art process steps required to produce a CdTe PV module exhibits limitations, as outlined above. In addition, nothing in the prior art describes an overall process to perform the series of steps of substrate heating, depositing an n-type CdS layer, depositing a p-type CdTe layer, performing a $CdCl_2$ treatment, and forming an ohmic contact inline, continuously, and in one vacuum boundary. In particular, the steps of $CdCl_2$ treatment and ohmic contact formation require significant innovation before they can be included in a continuous inline vacuum process. Such a continuous inline vacuum process would have significant advantages for commodity manufacturing of CdTe PV modules.

Any vacuum process for manufacturing CdTe PV modules would also require an apparatus to transport substrates through the process steps within vacuum and to transport the substrates into and out of vacuum rapidly. This apparatus should be robust, simple, and low cost. The apparatuses described in the prior art simply do not meet these requirements.

BRIEF SUMMARY OF THE INVENTION

The present invention is directed to commodity scale manufacturing of CdTe PV modules and involves innovations in both manufacturing processes and hardware.

One aspect of the present invention involves providing all of the processing steps for the critical semiconductor layers of a CdTe PV device inline, with all of those steps being completely performed within one vacuum boundary, at high throughput. They include rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation. These steps are performed at modest vacuum pressures without requiring costly high vacuum equipment. By utilizing inline vacuum processing to form all of the critical layers without breaking vacuum, an improvement in process throughput, film quality, device efficiency, and device stability is realized, while at the same time avoiding pinhole formation. All inline vacuum processing is also advantageous in that it limits the production of toxic waste and environmental and occupational exposure to toxic compounds.

Another aspect of the present invention is a novel $CdCl_2$ treatment step, which may be performed in the same vacuum boundary and inline with the other fabrication steps. Our $CdCl_2$ treatment process has the advantage of a high throughput rate while producing stable, high efficiency devices and, at the same time, limiting environmental and occupational exposure to toxic compounds.

Another aspect of the present invention is a novel vacuum process to produce a p+ ohmic contact region by subliming a metal salt onto a CdTe layer. Our ohmic contact formation process has the advantage of producing, at high throughput rates, a low resistance ohmic contact that is stable over time.

Another aspect of the present invention is a unique high throughput, low cost spray process to form the back electrode. This process has the advantage of producing a durable, high conductivity back electrode using known low cost industrial spray methods.

Another aspect of the present invention is to provide novel high throughput, low cost processes to perform module scribing using abrasive blasting or mechanical brushing through a mask. These novel scribing processes have the advantage of selectively scribing the semiconductor layers without scribing the TCO layer. In addition, the scribe process may be adjusted so that the TCO layer may be removed as well.

Another aspect of the present invention is a novel vacuum process station to selectively heat substrates and films, to expose substrates and films to vapor, to deposit thin films on a substrate, and to strip thin films off of a substrate. This vacuum process station allows substrates to be transported into and out of vacuum. When used as a deposition source, our vacuum process station has the advantage of very minimal vapor leakage, which significantly reduces occupational exposure to toxic materials. This unique deposition source deposits very uniform layers and is suitable for long term continuous operation.

Another aspect of the present invention is a novel substrate transport apparatus, which is employed to move substrates within vacuum or, in combination with a unique opening, to transport substrates rapidly into and out of vacuum. This substrate transport apparatus is robust, simple, and low cost and has the additional advantage of not collecting any coatings as it moves substrates through the thin film deposition processes.

Yet another aspect of the present invention is to provide substrate cleaning in a clean mini-environment at the entrance to the inline continuous vacuum process, which has the advantage of greatly reduced cost resulting from the elimination of a clean room to contain the entire process line.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic top plan view of a system for making photovoltaic modules in accordance with the present invention.

FIG. **2**A is a partially broken away schematic elevation view in longitudinal section along the line **50**—**50** of FIG. **1**, illustrating a substrate transport apparatus and a plurality of vacuum processing stations.

FIG. **2**B is a partially broken away schematic elevation view in longitudinal section, illustrating an alternate embodiment of the substrate transport apparatus of FIG. **2**A.

FIG. **3** is a schematic elevation view in cross section along the line **60**—**60** of FIG. **2**A illustrating the sealing arrangement by which the introduction of outside air into the vacuum chamber is minimized.

FIG. **4** is a partial schematic top plan view in longitudinal section along the line **70**—**70** of FIG. **2**A, further illustrating the sealing arrangement of FIG. **3**.

FIG. **5** is a schematic elevation view along the line **100**—**100** of FIG. **4**, further illustrating the substrate transport apparatus of FIG. **2**A.

FIGS. **6**A–B are schematic sectional elevation views illustrating enclosed and unenclosed substrates as they are positioned in prior art apparatuses.

FIG. **7**A is a schematic elevation view in cross section along the line **80**—**80** in FIG. **2**A, illustrating details of a vacuum process station of the substrate transport apparatus of FIG. **2**A.

FIG. **7**B is a schematic elevation view in cross section to illustrate an alternative embodiment of the vacuum process station of FIG. **7**A.

FIG. **8** is a schematic elevation view in cross section to illustrate a second alternate embodiment of the vacuum process station of FIG. **7**A.

FIG. **9**A is a schematic perspective view along the line **90**—**90** of FIG. **1**, illustrating the way in which photovoltaic modules are scribed.

FIG. **9**B is a schematic perspective view along the line **90**—**90** of FIG. **1**, illustrating an alternative way to scribe photovoltaic modules.

FIG. **10**A is a flow chart illustrating the process steps of the present invention.

FIG. **10**B is a flow chart of some of the alternate embodiments of the process steps of FIG. **10**A.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIG. **1**, there is shown an overview of the preferred embodiment of an apparatus **1000** for producing photovoltaic modules in accordance with the present invention. A substrate cleaning station **55** cleans the commercially available substrates that typically comprise low cost soda lime glass coated with transparent conducting oxide (TCO). After cleaning, a pair of metal strip belts **1** transport the substrates through the next portion of the apparatus **1000**. The belts may be moved bidirectionally by means of a known stepper motor **7**. Precise indexing of the position of the pair of belts **1** is accomplished by the use of a commercially available stepper motor controller **8**. The pair of metal strip belts **1** pass through a pair of openings **2** and a vacuum chamber **3**. A plurality of process stations for the processing of the critical semiconductor layers are contained within the vacuum chamber **3**, and are described in detail below. Another series of process stations are linked by a plurality of conveyor belts **51**. These process stations do not require vacuum. A first spray process station **52***a* is followed by a first film scribing process station **53***a*. These process stations are followed by a second spray process station **52***b* and a second film scribing process station **53***b*. The final process station in the apparatus **1000** is an encapsulation station **56**. The description of the apparatus and processes of the instant invention is presented in the following order: the substrate transport apparatus and openings, the vacuum process stations, the metallization method, the film scribing method, and the process steps to produce a photovoltaic module. Following the description of the preferred embodiment is a description of alternate embodiments.

FIGS. **2**A, **3**, **4**, and **5** in combination illustrate the complete assembly of the preferred embodiment of a pair of air-to-vacuum-to-air (AVA) openings and the substrate transport system of the present invention. The pair of AVA openings **2** facilitate the rapid transport of substrates from air into vacuum and then back into air. FIG. **2**A illustrates vacuum chamber **3**, which is pumped to a suitable vacuum by known techniques. A pair of AVA openings **2** is shown on either side of the vacuum chamber **3**. A pair of continuous metal strip belts **1** pass through both of the AVA openings **2** and also through the entire length of the vacuum chamber **3**. A plurality of substrates **10**, which are carried on the twin metal belts **1**, are also shown. The AVA openings **2** are shown with a plurality of pockets **14** and a plurality of vacuum pump ports **15** for vacuum pumping. A pair of injection ports **11** are shown for the injection of process gas. A plurality of pulleys **4** are provided for moving the belts **1**. A belt tensioner **9** maintains the belts **1** at a predetermined tension.

FIG. **3** shows the details of the AVA openings **2** in cross section. A top channel **2***a* and a bottom plate **2***b* are split by a belt bearing plate **20**. In total, parts **2***a*, **2***b*, and **20** form the cross section of the opening **2** of FIGS. **2**A, **3**, and **4**. A clearance distance **21** on the order of 0.005 in. ±0.002 in. is formed around the substrate **10**. This clearance distance **21** is formed between the substrate **10** and the top channel **2***a* and between the substrate **10** and the belt bearing plate **20**. The clearance distance **21** is large enough so that the substrate **10** may move freely, but is small enough to provide resistance to fluid flow through the clearance distance **21**. This resistance to fluid flow allows the vacuum chamber **3** to be maintained at a desired vacuum level. The pair of continuous metal strip belts **1** provide a substrate carrier to convey the plurality of substrates **10**.

FIG. **5** is a detailed view of a pair of tabs **6** which are attached to the metal strip belt **1**. The tabs **6**, a plurality of which are placed periodically along the belt **1**, provide a means of locating the substrate **10**.

The pair of continuous metal strip belts **1** provide a substrate carrier that will not be coated by the vacuum deposition processes. The elimination of coating on the belt **1** is a significant improvement over the prior art. As exemplified by Charschan in U.S. Pat. No. 3,294,670 (1966), the prior art utilized substrate carriers which enclosed the perimeter of the substrate in a "picture frame" type arrangement. The picture frame type substrate carriers are necessarily coated during deposition. These coatings lead to jamming in the close tolerance seals during motion, present occupational safety issues due to particle generation, and result in cross contamination between the processes. In the present invention, these problems have been addressed by exposing only the substrates **10** to coating during a vacuum deposition. In addition, unlike all of the prior art, the clearance distance **21** is not formed between the substrate carrier and the openings. Rather, the clearance distance **21** is formed between the precisely cut substrate **10** and the AVA openings **2**. The clearance **21** is formed specifically between the substrate **10** and the top channel **2***a* and between the substrate **10** and the linear bearing plate **20**.

The use of the pair of metal strip belts **1** as the substrate carrier in accordance with the present invention has many other advantages. The fact that the belts **1** have a low mass will create less wear on any bearing surface used. The low mass will also greatly decrease the inertia of the substrate carrier, thus allowing the substrate to be moved quickly between processing stations.

Continuous metal strip belts **1** also have advantages in situations calling for a series of vacuum processes to be carried out in one vacuum chamber **3**. Continuous metal strip belts **1** of 200 feet in length can be fabricated by known methods. This allows a large number of process steps to be carried out in one vacuum chamber **3**.

Another advantage is the cost of fabrication of this type of substrate carrier, which is considerably less than the cost of machining close tolerance picture frame type substrate carriers of the prior art. The present substrate carriers also facilitate scaling up the process. For larger substrates **10**, the openings **2** must be increased in size. However, the strip belts **1** may be simply spaced further apart.

The continuous metal strip belts **1** are preferably formed of metal alloys that have high resistance to corrosion and that retain high strength at elevated temperatures. These belts may be coated with other materials to alter the surface properties further, if needed. Many different attachments or tabs **6** for retaining the substrate **10** may be welded or fixed to the metal strip belts **1** at relatively low cost.

A cut tolerance of ±0.003 inch is required for the glass substrates **10** which are carried on the continuous metal strip belts **1**. High throughput, low cost equipment is commercially available for cutting the substrates **10** to the required tolerances. The precision glass cutting required for this invention is not an additional processing step, since the substrates **10** must be cut to size in any method.

The continuous metal strip belts **1** are also relatively small in cross section. The small cross section decreases the thermal expansion as the belts pass through high temperature vacuum processes, which will decrease any tendency to jam in the AVA openings **2** due to thermal expansion.

The relatively low mass of the metal strip belts **1** also allows the substrate carrier to cool and heat more rapidly than the prior art picture frame type substrate carrier. The low mass of the metal strip belts **1** allows the belt temperature to match the glass temperature during processing, thereby reducing thermal gradients in the glass substrates **10** which could otherwise lead to stresses that may crack the glass.

Referring now to FIG. **2**A, the vacuum chamber **3** and a plurality of vacuum processing stations, generally indicated by **200** and **300**, are illustrated in a partial schematic elevation view in section. The metal strip belts **1** carry the plurality of substrates **10** through the plurality of vacuum processing stations **200** and **300**. The process stations **300** provide for cooling of substrates **10** by radiation to a pair of water cooled plates **34**.

Each of the process stations **200** of FIG. **2**A contain a pair of heated pockets **33**. These heated pockets **33** provide a flux of heat or vapor and are suitably shaped blocks of a material with a high thermal conductivity. In FIG. **7**A the pair of heated pockets **33** are shown with details of the pair of continuous metal strip belts **1** in cross section. Both upper and lower heated pockets **33** have a machined pocket **29**. A deposition material **35** is shown in the pocket **29** of the lower heated pocket **33**. Only the substrate **10** spans the pocket **29**. No part of the belts **1** crosses the pocket **29**, thus avoiding deposition anywhere but on the substrate **10**. The upper heated pocket **33** serves as a heater for the substrate **10**.

Heated pocket **33** may be fabricated using any material which has an acceptable level of thermal conductivity. Further, that material should have a low level of porosity to prevent adsorption of air and water vapor and a low level of impurities. One material which has proven useful is purified pyrolitic grade graphite. However, metals and metals coated with ceramics, as well as other suitable materials, may be chosen.

In the preferred embodiment of the invention, the heated pockets **33** are heated by a plurality of quartz halogen lamps **38**, which are not damaged when used in vacuum at high temperatures. The temperature control of the heated pocket **33** may be accomplished by placing a thermocouple in the wall of the heated pocket **33** and using well known proportional with integral and derivative (PID) temperature control of the power to the lamps **38**. Lamps **38** are contained in boxes **39** for protection. Boxes **39** also serve as support structure for the lamps **38** and the heated pocket **33**. The boxes **39** also provide electrical isolation for safety, prevent arcing from the lamps **38**, and also serve as radiation shields to reduce the loss of energy. Other means of heating the heated pocket **33**, including resistive heating and inductive heating, for example, may be used as well.

Each of the process stations **200** may perform a variety of processes on a substrate **10**. These processes include: i) rapidly heating a substrate, ii) annealing a substrate and films, iii) thermally stripping a film from a substrate, iv) exposing a substrate and films to a vapor treatment, or v) depositing a thin film on a substrate. The chosen processes performed by station **200** depend on three parameters: a) the temperature of the lower heated pocket **33**, b) the temperature of the upper heated pocket **33**, and c) the presence or absence of the deposition material **35**. For processes i) through iii) described above, no deposition material **35** is loaded into the pocket **29**. For process i) the upper and lower heated pockets **33** are maintained at temperatures such that the rapid heating of glass substrates **10** may be done in a short cycle time, on the order of one minute. The uniformity of heating prevents cracking of the substrates **10**. For process ii), the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature which will not resublime thin films off of the substrate **10**. For process iii) the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature that is high enough to cause films on the substrate **10** to sublime away.

For processes iv) and v) described above, deposition material **35** is loaded into the pocket **29**. For process iv), the upper heated pocket **33** and substrate **10** are maintained at a higher temperature than the lower heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33** and expose the lower surface of the substrate **10** to vapor, but the vapor will not be deposited as a film on the substrate **10**. For process v), the lower heated pocket **33** is maintained at a relatively higher temperature than the substrate **10** and the upper heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33**, and the vapor will condense and be deposited as a film on the lower surface of the substrate **10**. All of these processes are robust, may be performed at high throughput, are occupationally and environmentally safe, and involve low capital cost.

In accordance with the present invention, the pair of metal belts **1** transports the substrates **10** through the plurality of process stations **200** or **300**. The metal belts **1** and the substrates **10** may be moved continuously. However, the preferred embodiment of the present invention provides for intermittent motion of the metal belt **1** and the substrates **10**. This motion is accomplished using a conventional stepper motor **7** and a stepper motor motion controller **8**. The substrates **10** are placed at equal pitch distances on the belts **1**, and the process stations **200** or **300** are placed one pitch distance apart. The intermittent motion consists of pauses in the motion of the belts **1** for processing and brief periods of motion of the belts **1** to advance the plurality of substrates **10** through the series of process steps. In this manner, an individual substrate **10** will pause at each process station **200** or **300** for an equal amount of time. A useful period of time, hereinafter defined as the cycle time, consists of the total period of time for one pause and one movement of the belts **1**. One substrate **10** will complete the series of inline vacuum process steps for each period of cycle time.

Since the process stations **200** or **300** are modular, a plurality of one type of process may be placed in series. If a given process step requires a processing time which exceeds the cycle time, then the given process step may be carried out over a series of similar processing stations **200** or **300**. For example, an annealing step, which requires a longer period of time to complete than the cycle time, may be carried out over a series of annealing process stations **200**.

The deposition of thin films onto substrates **10** is a critical processing step of the present invention. A detailed description of the deposition apparatus is given below.

The intermittent motion of the belts **1** allows a pause for deposition. During the pause, as shown in FIG. **2**A, the individual substrates **10**, which are spaced at regular pitch intervals on the metal strip belts **1**, will be in a sealing relationship with individual heated pockets **33**. During this pause, the individual heated pockets **33** will deposit a film onto the substrates **10**. For a given pause time, the thickness of the films can be varied by varying the temperature of each individual heated pocket **33**. Closed loop control of film thickness may be achieved by measuring film thickness with known thickness monitors and adjusting the heated pocket **33** temperature as needed. Very precise control may be achieved since the deposition rate is a function of the temperature of the heated pocket **33**.

The present invention is specifically designed to produce very uniform film deposition across the surface of the substrate **10** at high throughput so that in a mass manufacturing environment the reproducibility of the film uniformity from one substrate **10** to another substrate **10** is tightly controlled over long periods of time. In order to accomplish this desired aspect of the present invention, the substrate **10** is held in a novel sealing relationship with the pocket **29**.

The novel sealing relationship is unique and is not shown or suggested in the prior art. FIG. **6**A and FIG. **6**B show an elevation view of two prior art devices used for film deposition by vacuum sublimation. In FIG. **6**A, the known method of Bozler in U.S. Pat. No. 3,636,919 (1972) shows the source deposition material **35***a* and substrate **10***a* in an enclosed space. The enclosed space is formed by an upper heater **36** U and a lower heater **36** L. Because the substrate **10***a* is sealed in the enclosed space, the substrate **10***a* could not be moved and only one film could be deposited for each pump down of the vacuum chamber. FIG. **6**B details another known method according to Bonnet in U.S. Pat. No. 5,304,499 (1994) which is commonly known as close spaced sublimation (CSS). In this known method, the deposition material **35***a* is placed on a flat heated plate **36** L and the substrate is held at a typical distance of 2 to 3 mm from the deposition material **35***a*. The disadvantage of this known method is that the clearance between the deposition material **35***a* and the substrate **10***a* forms a leak path for the vapor. This leak will lead to non-uniform deposition and the formation of toxic nano particles in the process space.

The heated pocket deposition apparatus of the present invention overcomes the limitations of the prior art. With reference to FIG. **7**A, there is a clearance distance **37** on the order of 0.001 in. to 0.018 in. between the substrate **10** and the top surface of the heated pocket **33** block. Clearance distance **37** is formed on the two sides of the substrate **10** where the substrate **10** spans the belts **1**. The clearance distance **37** is necessary to prevent the substrates **10** from touching the heated pocket **33** and damaging the deposited films. The clearance distance **37** is formed in such a manner as to provide a close tolerance slip fit seal between the top of the heated pocket **33** and the bottom of each of the substrates **10**. Any vapor leak through the clearance distance **37** will be in the molecular flow regime and will be very small. This effectively eliminates vapor leaks through the clearance distance **37** and allows the substrates **10** to act as a shutter across the source pocket **29**.

Furthermore, the walls of the pocket **29** will collimate the vapor flux from the subliming material **35**. Since the clearance distance **37** is at the top of the pocket **29** and at a right angle to the collimated vapor flux, nearly all of the vapor flux will pass the entry of the clearance distance **37** without directly entering it. Any vapor which does enter the clearance distance **37** due to gas scattering will be readily deposited on the surface of the substrate **10**. The design of the clearance distance **37** allows for movement of multiple substrates **10** while maintaining a vapor seal. This design has advantages over the prior art since it will maintain the deposition uniformity across the substrate **10**. In the present invention, the use of the substrates **10** to act as a shutter virtually eliminates cross contamination between heated pockets **33**. The elimination of cross contamination allows the use of one vacuum boundary for the multiple processing steps and reduces the capital cost of the system. In most vacuum processes for processing PV devices, load locks or load locks in combination with intermediate chambers are used to prevent cross contamination between processing steps.

As shown in FIG. **7**A, the deposition material **35** must be distributed in an evenly spaced pattern across the floor of the pocket **29**. The deposition material **35** may be in the form of powder, pellets pressed from powder, or random chunks. All of these forms of material for the fabrication of CdTe PV are commercially available. Also, the distance between the deposition material **35** and the lower surface of the substrate **10**, which is provided by the depth of the pocket **29** in the lower heated pocket **33**, must be sufficient to allow for gas scattering of the sublimed species.

Gas scattering is the result of collisions among the sublimed species or between the sublimed species and the molecules of the ambient background gas. These collisions deflect and scatter the sublimed species from following a straight line path from the deposition material **35** to the substrate **10**. This scattering of the sublimed species results in a uniform deposition on the substrate **10** The Knudsen number is a known dimensionless parameter which is used to quantify the amount of gas scattering present. The Knudsen number is the ratio of the mean free path in the pocket **29**, at a given temperature and pressure, divided by the distance between the deposition material **35** and the substrate **10**. If the Knudsen number is less than 0.01, then the species within the pocket **29** are in viscous flow and gas scattering will be significant In this viscous flow regime, the gas scattering may lead to such a loss of energy from the sublimed species that they condense to form nano-particles. For Knudsen numbers greater than 1, the species will be in a molecular flow regime with very little gas scattering. In this molecular flow regime, the sublimed species will travel in straight lines to the substrate. This line of sight deposition causes non-uniform film thickness across the substrate **10**. For Knudsen numbers between 0.01 and 1, the species will be in transition flow with some gas scattering. In the transition regime, the vapor flux is randomized by gas scattering. However, the number of collisions are few enough that the sublimed species retain most of their energy and therefore do not condense into nano-particles before striking the substrate **10**. In the present invention, deposition has been done with Knudsen numbers in the transition regime from 0.07 to 0.44, which has led to uniform film thickness across the substrate **10**.

An additional advantage of the present invention is the heating of the process gas in the pocket **29**. Since the substrates **10** act as a shutter for the heated pocket **33**, the process gas in the source pocket **29** comes to a uniform high temperature. The high temperature of the process gas in the heated pocket **33** is another factor which prevents the formation of nano-particles due to the gas scattering collisions described above.

The preferred embodiment of the present invention provides a means of forming a back electrode layer at high throughput and using equipment that is low capital cost. This layer is adherent to the other layers in the film stack and has a very low electrical resistivity. As shown in FIG. **1**, the back electrode is fabricated by a novel spray process at atmospheric pressure in process stations **52***a* and **52***b*. A layer of conductive graphite coating followed by a layer of conductive Ni coating are applied by known industrial spray methods to form the back electrode for carrying current. Sprays containing other metals besides Ni are known and may also be used. A metal conductive coating layer may also be applied by spray directly to the ohmic contact layer without an intervening carbon layer. In this description, carbon is not considered a metal. To limit the inclusion of oxygen and water vapor into the metallization layer, the gas used as a propellant in the spray process may be a dry inert gas such as N_2 or Ar, and the process may be performed in a controlled environment.

The thick film of the back electrode contains a polymer binder, which provides a level of encapsulation and protection for the completed device. The spray is performed at room temperatures and does not harm or introduce defects into the previously fabricated semiconductor layers. The spray method has the advantage of low capital cost. Other known methods of metallization for PV devices, such as sputtering, require expensive high vacuum equipment.

The preferred embodiment of the present invention also provides a means of scribing that exhibits high throughput and low cost. As shown in FIG. **1**, a scribing step may be performed at the film scribing station **53***a* after the graphite layer is formed by the spray process at the process station **52***a*. The scribing is performed after the application of the graphite layer to prevent any damage to the semiconductor layers by handling.

FIG. **9**A illustrates the details of the preferred embodiment of the film scribing method. A rotating wire brush **42** is brought into contact through openings **45** in a mask **41** to remove portions of the film **40** from the substrate **10**. The openings **45** in the mask **41** are tapered in cross section and are narrower near the contact of the mask **41** and the film layers **40**. This facilitates the entry of the rotating brush **42** into the openings **45**. The mask **41** may be coated with a hard coating, such as titanium nitride, to reduce wear.

The preferred embodiment of the film scribing method shown in FIG. **9**A does not require a precisely defined rotating brush **42** since the openings **45** in the mask **41** define the area of the film **40** which will be removed. The rotating wire brush **42** is passed axially along the openings **45** in the mask **41** over the substrate **10** to perform a scribe. A plurality of rotating metal brushes **42** may also be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes on an entire substrate **10**. This film scribing method has the ability to scribe layers selectively. By using an abrasive powder with the rotating brush **42**, the TCO layer may be scribed. By using the rotating brush **42** alone, all of the layers except the TCO layer may be removed.

The process steps of the preferred embodiment of the present invention are shown in the flow chart of FIG. **10**A. The overall system **1000** required to perform the process is shown in FIG. **1**. The apparatus required to perform the vacuum portion of the process, from step **2**) of FIG. **10**A through step **12**) of FIG. **10**A, is illustrated in FIG. **2**A. With reference to FIG. **2**A, the substrates **10** are transported through the vacuum process stations **200** and **300** on the metal strip belts **1**. As shown in FIG. **10**A, these process steps may be performed by a single one or a series of the vacuum process stations **200** or **300** illustrated in FIG. **2**A. The total time required for processing at each process station **200** or **300** and the transport of the substrate **10** to the next process station **200** or **300** is a unit of cycle time as defined above. The cycle time in the process description below is in the range of 30 seconds to 2 minutes.

With reference to FIG. **10**A, a description of the process steps performed on each individual substrate **10** as the plurality of substrates **10** pass through the process is given below.

In step (**1**) the substrate **10**, which may have a TCO layer on one surface, is ultrasonically cleaned, rinsed, dipped in isopropyl alcohol to remove water from the surface, and dried in a clean room type mini-environment.

In step (**2**) the substrate **10** is transported into the vacuum chamber **3** through the AVA opening **2** using the metal strip belts **1**.

In step (**3**) the substrate **10** is heated to a temperature in the range of 500° C. to 560° C. and transported to the next process.

In step (**4**) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdS film is deposited onto the TCO layer on the substrate **10** and the substrate **10** is transported to the next process.

In step (**5**) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdTe film is deposited onto the CdS layer on the substrate **10** and the substrate **10** is transported to the next process.

In step (**6**) and step (**7**) a $CdCl_2$ treatment is performed on the CdS/CdTe layers. In step (**6**) with the temperature of the substrate **10** in the range of 300° C. to 500° C., the CdS/CdTe layers on the substrate **10** are exposed to $CdCl_2$ and the substrate **10** is transported to the next process. The $CdCl_2$ exposure of the CdS/CdTe layers on the substrate **10** may be to a $CdCl_2$ vapor or a $CdCl_2$ film may be deposited on the CdTe layer. Either method of $CdCl_2$ exposure will produce high efficiency CdTe PV devices. For this process step, a series of $CdCl_2$ treatment stations may be required.

In step (**7**) with the temperature of the substrate **10** in the range of 400° C. to 450° C., the $CdCl_2$ treated layers on the substrate **10** are annealed, any $CdCl_2$ film is removed, and the substrate **10** is transported to the next process. For this process step, a series of annealing stations may be required. In combination, step (**6**) and step (**7**) provide the $CdCl_2$ treatment of the CdS/CdTe layers. The $CdCl_2$ treatment of CdTe PV devices in vacuum is known. However, no prior art shows the $CdCl_2$ treatment step performed inline between the deposition of the CdTe layer and the formation of the ohmic contact layer and without the substrate leaving vacuum. Also, no prior art shows directly transporting substrates from CdTe deposition to $CdCl_2$ treatment.

In step (**8**) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

In step (**9**) and step (**10**) an ohmic low resistance contact is formed on the CdTe layer. In step (**9**) with the substrate **10** temperature in a range of 150° C. to 300° C., a metal salt is deposited onto the CdTe layer on the substrate **10**, and the substrate **10** is transported to the next process. One metal salt which has been used for this process step is CuCl. In step (**10**) with the temperature of the substrate **10** in a range of 150° C. to 250° C., the CdS/CdTe/metal salt layers on the substrate **10** are annealed, and the substrate **10** is transported to the next process. For this process step a series of annealing stations may be required. In combination, step (**9**) and step (**10**) produce a reaction between the metal salt and the surface of the CdTe layer and this reaction produces a thin p+ semiconductor layer on the CdTe surface to form the ohmic contact. In the case of a Cu salt, a copper telluride such as $CuTe_X$ or Cu doped CdTe:Cu or both may be formed. The thin p+ layer provides a low resistance ohmic contact on the surface of the CdTe layer and is stable. The prior art does not show the formation of an ohmic contact layer on CdTe by deposition of a metal salt onto the CdTe layer in vacuum.

In step (**11**) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

In step (**12**) the substrate **10** is transported out of the vacuum chamber **3** through the AVA opening **2** on the metal strip belts **1**.

In step (**13**) the ohmic contact layer is exposed to air for an optimum time in the range of 4 to 16 hours before a layer of conductive coating containing carbon is applied onto the ohmic contact layer by a spray process. The air exposure has led to PV devices with increased long term stability.

As described in the prior art, a series of scribes in selected film layers on the substrate **10** are required to isolate individual PV cells on the substrate and to interconnect the individual cells on the substrate **10** to form a completed module.

In step (**14**) a plurality of first scribes through the all of the film layers on the substrate **10** including the transparent conductive oxide are performed. A second plurality of scribes through the carbon and the p/n layers without removing the TCO are performed parallel to the first set of scribes. Both of these sets of scribes are performed by the novel film scribing method described above with reference to FIG. **9**A.

In step (**15**) a layer of conductive coating containing Ni is applied by spray onto the layer of conductive coating containing carbon. Since the Ni metalization layer is formed after the second set of scribes, the Ni layer will fill the cuts in the semiconductor layers from the second scribe. This will cause an electrical connection of the back electrode of one cell to the front electrode of another cell. This step in combination with the following step of the final scribe of the metalization layer will complete the interconnection of the PV cells in series to form the PV module.

In step (**16**) a plurality of third scribes through only the metallization layers are performed. This third set of scribes is performed by the novel film scribing method described above with reference to FIG. **9**A.

In step (**17**) electrical connections are made and the finished module is encapsulated.

In any of the film deposition steps, including the steps **4**), **5**), **6**), or **9**) of FIG. **10**A, more than one layer of a particular material may be deposited. These multiple layers may be deposited by a series of heated pocket deposition apparatuses. If one layer of material is deposited in a given cycle time, to a given thickness, then this single layer may be replaced by many thinner layers built up to the thickness of the single layer of material by using many depositions at shorter cycle times. Multiple depositions are advantageous since for every decrease in cycle time there is a corresponding increase in production rate. Multiple processing stations can also be used to decrease the cycle time for the other steps including annealing, vapor treatment, cooling, etc.

It would also be possible to create a multijunction solar cell in accordance with the teachings of the present invention. In this case, a monolithic multijunction structure could be fabricated on the substrate. In this structure, two or more solar cells would be stacked on one substrate in such a way that solar radiation passes through the larger band gap material first, and residual radiation passes through the stack to a smaller band gap material. The band gap of the materials needed could be tailored by using semiconductors formed by the combination of any of the elements Zn, Cd, Hg, S, Se, or Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may be in the form of alloys containing three or more elements. The multiple layers may be deposited by a series of heated pocket deposition apparatuses. Also, by varying the composition of the deposition material in the multiple heated pockets, a graded band gap photovoltaic device may be fabricated.

Many devices were fabricated by following the process steps (**1**) through (**13**) and step (**15**) of FIG. **10**A described above. CuCl was used as the metal salt in step (**9**). Individual PV devices with an area of 0.3 sq. cm. were formed on many substrates **10**. These devices were defined by masking certain areas and removing the rest of the films on the substrates **10** with an abrasive blast. The best device had a conversion efficiency of 11.8% and was produced on a commercially available low cost SnO_X:F coated soda lime glass substrate **10**. Such high efficiency devices have also proven to be stable. Accelerated stress testing by light soaking at 1000 W/m^2 and 65° C. at open circuit condition was performed on many devices. Over a time period of hundreds of hours, measured device efficiencies were at least 98% of the original efficiencies.

A description of the preferred embodiment of the present invention was given above. Other alternate embodiments of the present invention are described below. These specific alternate embodiments are best described with reference to FIG. **10**A, which is a flow chart of the process steps of the preferred embodiment of the invention.

In alternate embodiments of step **9**) in FIG. **10**A, the deposition of the metal compound may include compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb. These compounds may be metal salts as described in the preferred embodiment or organometallic compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb may also be used. These compounds may be deposited onto CdTe in vacuum to form an ohmic low resistance contact layer by reaction with the CdTe layer. This ohmic low resistance contact may be formed by tellurides of Cu, Ag, Au, Hg, Sn, Sb, and Pb, or the ohmic contact may be highly doped CdTe. An alternative embodiment to step **10**) of FIG. **10**A is to anneal the ohmic contact layer in air, inert gas or other atmospheres outside the vacuum chamber.

In other embodiments of the process steps **4**) and **5**) of FIG. **10**A other semiconductors may be used instead of CdS and CdTe. These semiconductors are formed by the combination of any of the elements Zn, Cd, Hg, S, Se or, Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may also be in the form of alloys containing three or more elements. These compound semiconductors are known to be useful in the formation of PV devices, are readily sublimable, and may be deposited in vacuum by the present invention. A series of stations may be used to deposit the n-type and p-type semiconductors. Thus, more than one layer may be used to form the n-type and p-type regions of the device This allows a faster cycle time while still maintaining adequate semiconductor film thickness. Also, the different stations may deposit different IIB-VIB compound semiconductors made up of the elements Zn, Cd, Hg, S, Se or, Te.

In alternate embodiments of step **6**) of FIG. **10**A, halogen containing substances such as HCl or Cl_2 gas may be used in place of or in addition to $CdCl_2$. In this case, a controlled amount of the gas can be introduced into the heated pocket **33**. Other halogen containing substances which are known to have effects similar to $CdCl_2$ may also be used. Some known examples of these compounds are $CdBr_2$ and CdI_2.

In another alternate embodiment of the process steps of FIGS. **10**A, a CdTe PV device may be fabricated without the deposition of CdS shown in step **4**) of FIG. **10**A. In this embodiment, the p/n junction is formed between the n-type TCO and the p-type CdTe or other IIB-VIB compounds.

In another embodiment of the process steps of FIG. **10**A, a CdTe device may be fabricated by depositing the CdS layer on the substrate **10** outside of the vacuum chamber **3** by known methods, including chemical bath deposition. In this embodiment, the substrate **10** with the CdS layer would be brought into the vacuum chamber **3** and steps **3**) through step **11**) of FIG. **10**A would be performed in vacuum.

In another embodiment of the process steps of FIG. **10**A, a $CdCl_2$ treatment may be performed after step **4**) CdS deposition and before step **5**) CdTe deposition. This $CdCl_2$ treatment is in addition to the step **6**) $CdCl_2$ treatment as shown in FIG. **10**A. The additional $CdCl_2$ treatment is known to further increase the device performance.

In other alternative embodiments of FIG. **10**A, the HPD deposition heated pocket **33** may be used to apply other film layers which would improve the performance of a CdS/CdTe PV device. One such layer is an anti-reflection (AR) coating which would be deposited on the glass substrate **10** on the opposite side of the substrate **10** from the TCO. The AR coating would face the sun and reduce the amount of incoming sunlight which is reflected off of the glass surface. This would increase the current that the device could produce. One such AR coating is a thin film of MgF_2. Since MgF_2 is sublimable, this film may be applied with the heated pocket **33** deposition. The AR coating can be done at a suitable location in the vacuum chamber **3**. Another layer which is known to increase the efficiency of a CdS/CdTe device is a layer of high resistivity intrinsic tin oxide (i-SnO_X). This layer would be applied between the TCO layer and the CdS layer or a layer of SnO_X of the desired resistivity could be deposited directly on the glass substrate **10**. This intrinsic layer has a much higher electrical resistivity than the TCO layer and has been shown to increase device efficiency. This resistive layer would allow the CdS layer to be thinner. The thinner CdS layer would allow more light to pass into the CdTe layer and increase the current the device would produce. The heated pocket **33** could be used to sublime i-SnO_X. The i-SnO_X deposition would be performed before the CdS deposition of step **4**) of FIG. **10**A.

An alternate embodiment to step **15**) of FIG. **10**A is that the graphite and Ni may be sprayed through a mask to form a patterned deposition. This patterned back electrode would eliminate the need for the second and third set of scribes shown in steps **14**) and **16**) of FIG. **10**A. In another embodiment, a spray through a mask may also be used to fill the cut of the first scribe with an insulating compound before the spraying of the Ni conductive coating. The insulating compound eliminates electrical shunts between the Ni layer and the TCO.

Other alternate embodiments of the present invention are described below. The figures which show these alternative embodiments are FIGS. **2**B, **7**B, **8**, **9**B, and **10**B. These alternative embodiments are described with reference to these figures.

FIG. **2**B shows an alternate embodiment of the present invention in which the pair of continuous metal strip belts **1** are entirely contained within the vacuum chamber **3**. A pair of known load locks **5** on either side of the chamber **3** provide a means of transporting the substrates **10** into and out of vacuum.

FIG. **7**B illustrates an alternate embodiment of the vacuum process station of FIG. **7**A involving a different arrangement for the upper heated pocket **33**. This alternate embodiment involves the addition of a baffle having a plurality of holes **28**. The deposition material **35** is placed above the baffle in a confined space. The confined space has a lid **27**, which may be removed to reload the deposition material **35**. As the upper heated pocket **33** is heated, the deposition material **35** will sublime, and vapor will pass through the holes **28** into the source pocket **29** of the upper heated pocket **33**. This alternative embodiment of the vacuum process station **200** may be used as the heated pocket **33** to deposit films on the upper surface of the substrate **10**. When the deposition is on the upper surface of the substrates **10**, the substrates **10** can be transported by arrangements such as rollers, robotic arms, etc., which are well known. This would be especially useful for the deposition of the AR coating.

FIG. **8** illustrates an alternative to the heated pocket **33**. This embodiment can be used to generate plasma in the pocket **29**. This arrangement is called plasma enhanced heated pocket deposition (PEHPD). The alternate embodiment of the heated pocket **33** provides a high voltage pin **30** for the generation of plasma, the pin **30** may be made from graphite. The pin **30** is electrically isolated by insulation **31** which may be a quartz tube. The high voltage from the DC power supply **32** generates the plasma. The heated pocket-to-substrate distance in the PEHPD heated pocket must be large enough to produce ions within the pocket **29**. If the pocket **29** is too shallow it will not produce a glow discharge at desirable pressures, when the substrate **10** is sealing the pocket **29** during deposition. In alternate embodiments of the present invention, both the CdS and CdTe heated pocket may optionally be of the PEHPD type so that the advantages of plasma enhanced deposition may be incorporated. These advantages of plasma enhanced deposition, which serve to improve the device efficiency, include: (i) doping of CdTe with nitrogen, (ii) passivation of the defects in CdTe, (iii) alteration of the morphology of CdS, (iv) doping of CdS, and (v) mixing of the CdS/CdTe interface. In addition, ZnTe may be doped with nitrogen by PEHPD to form ZnTe:N, a p+ semiconductor layer which may be used as an ohmic contact to CdTe.

FIG. **10**B is a flow chart of the process steps of some of the alternate embodiments of the invention. The processing steps as shown schematically in that figure include (**1**) cleaning the substrate by known means in a clean room type mini-environment, (**2**) transporting the substrate into the vacuum chamber using AVA or load lock transport, (**3**) heating the substrate, (**4**) depositing a CdS film on the substrate using heated pockets with or without plasma, (**5**) depositing a CdTe film onto the CdS film using heated pockets with or without plasma, (**6**) performing a treatment, with a halogen containing substance, on the CdS/CdTe films using a heated pocket, (**7**) annealing the substrate and films, (**8**) forming an ohmic contact on the CdTe layer by heated pocket deposition of a Te layer on the CdTe layer or by heated pocket deposition with plasma of a ZnTe:N layer on the CdTe layer, (**9**) depositing a metallization layer onto the ohmic contact layer by heated pocket deposition of a sublimable metal layer such as Zn or Cd, (**10**) annealing the substrate and films, (**11**) cooling the substrate and films, (**12**) transporting the substrate and films from the vacuum chamber using AVA or load lock transport, (**13**) performing a first scribe through the entire film stack including the metallization and the transparent conductive oxide, (**14**) screen printing the electrical connection of the back electrode of one cell to the front electrode of the next cell by known screen printing methods, and (**15**) encapsulating the furnished module. Step (**13**) involves a first scribe that may be performed in accordance with the teachings of the present invention or by one of several known means including mechanical or laser scribing and a second scribe through the carbon and the p/n layers without removing the TCO.

Step **8**) in FIG. **10**B illustrates another alternative embodiment of the present invention in which Te is used as an ohmic contact layer Te is easily sublimed and is known to form an ohmic contact material for CdTe devices. After the $CdCl_2$ treatment and annealing steps, Te could be deposited inline by heated pocket deposition with or without a cooling step. A metal back electrode can be applied to the Te ohmic contact by either a vacuum deposition step or by the spray process of the present invention.

Step **9**) of FIG. **10**B illustrates an alternate embodiment of the present invention in which the back electrode metallization may be accomplished inline in vacuum. In this embodiment, the back electrode metallization may be applied by a heated pocket deposition of metals including, but not limited to, Zn or Cd, which are readily sublimable and electrically conductive.

FIG. **9**B illustrates an alternative embodiment of the scribing method of the present invention involving the use of an abrasive blast **43** which is provided by known methods.

The abrasive blast **43** is performed through openings **45** in the mask **41** to remove portions of the film **40** from the substrate **10**. This embodiment of the scribing method does not require a precisely defined abrasive blast **43** since the mask **41** defines the area of the film **40** which will be removed. The abrasive blast **43** is passed over the substrate **10** to perform a scribe. Each abrasive blast **43** may enter more than one opening **45** in the mask **41** so that one abrasive blast **43** may perform more than one scribe for each pass over the substrate **10**. A plurality of abrasive blasts **43** may be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes of an entire substrate **10**. Different abrasive media with different hardness and size may be provided so that various layers in the film stack **40** may be scribed selectively. This allows the scribing method of the present invention to: **1**) scribe all the way through the film stack including the relatively hard TCO layer, and **2**) selectively scribe through all of the layers above the TCO layer without removing the TCO.

We claim:

1. Apparatus for transporting substrates within a vacuum chamber, the apparatus comprising:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert; and

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts.

2. Apparatus for transporting substrates within a vacuum chamber as in claim **1**, wherein the vacuum chamber includes front and rear openings through which the pair of metal belts and the substrates pass, extending outside said front and rear openings, the apparatus further comprising:

a clearance distance between each of the substrates and the front and rear openings so as to permit motion of the substrates while at the same time restricting air leaks, to thereby maintain a desired level of vacuum in the chamber.

3. Apparatus for transporting and processing a plurality of substrates by exposing them to heating, film deposition or vapor treatment within a vacuum chamber, the apparatus comprising:

a plurality of heated pockets positioned in proximity to and in correspondence with each of the plurality of substrates such that a clearance distance between a surface of each of the substrates and the corresponding one of the heated pockets is minimized so as to permit motion of the substrates while restricting vapor leaks from the heated pockets; and

a transporter for moving the substrates from one heated pocket to the next.

4. Apparatus as in claim **3**, wherein the transporter comprises:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert;

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts; and

a controller, coupled to said translator, for indexing the belts incrementally to move each of the substrates from one heated pocket to another.

5. Apparatus as in claim **3**, wherein a selected one or more of the heated pockets includes a high voltage pin coupled to a source of D.C. voltage for creating a plasma within a selected one or more of the heated pockets.

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(54) **APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES**

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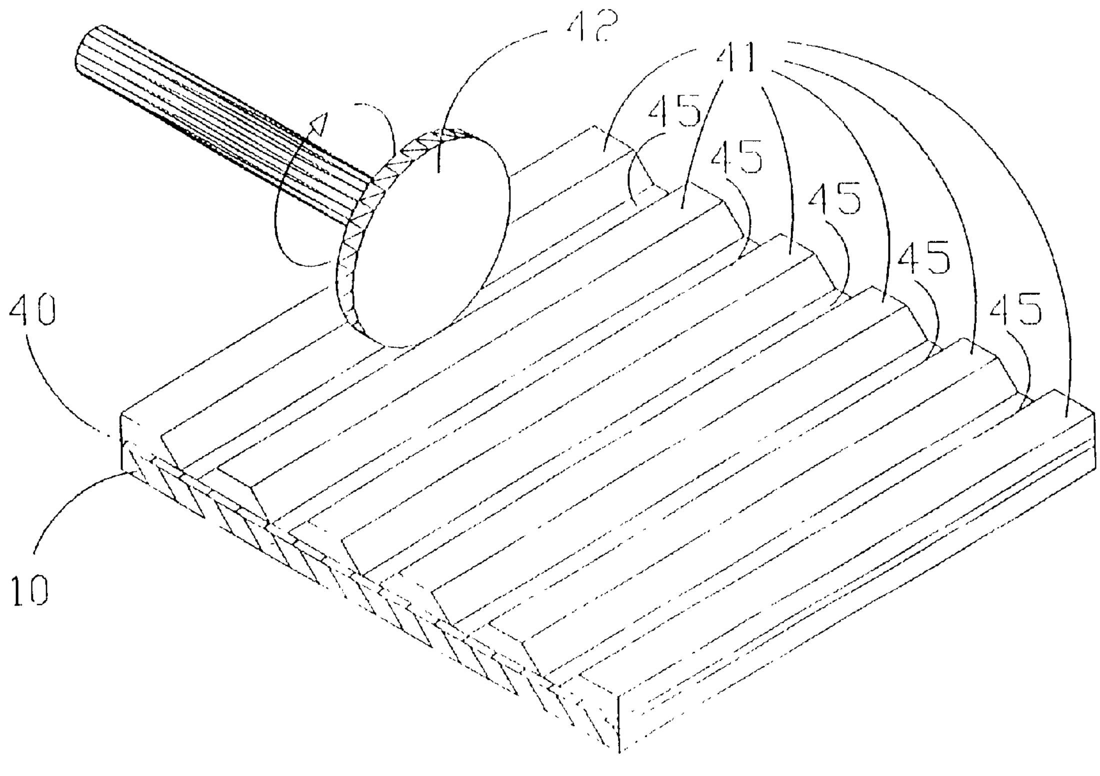
(52) **U.S. Cl.** **438/462**

(57) **ABSTRACT**

An apparatus and processes for large scale inline manufacturing of CdTe photovoltaic modules in which all steps, including rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation, are performed within a single vacuum boundary at modest vacuum pressures. A p+ ohmic contact region is formed by subliming a metal salt onto the CdTe layer. A back electrode is formed by way of a low cost spray process, and module scribing is performed by means of abrasive blasting or mechanical brushing through a mask. The vacuum process apparatus facilitates selective heating of substrates and films, exposure of substrates and films to vapor with minimal vapor leakage, deposition of thin films onto a substrate, and stripping thin films from a substrate. A substrate transport apparatus permits the movement of substrates into and out of vacuum during the thin film deposition processes, while preventing the collection of coatings on the substrate transport apparatus itself.



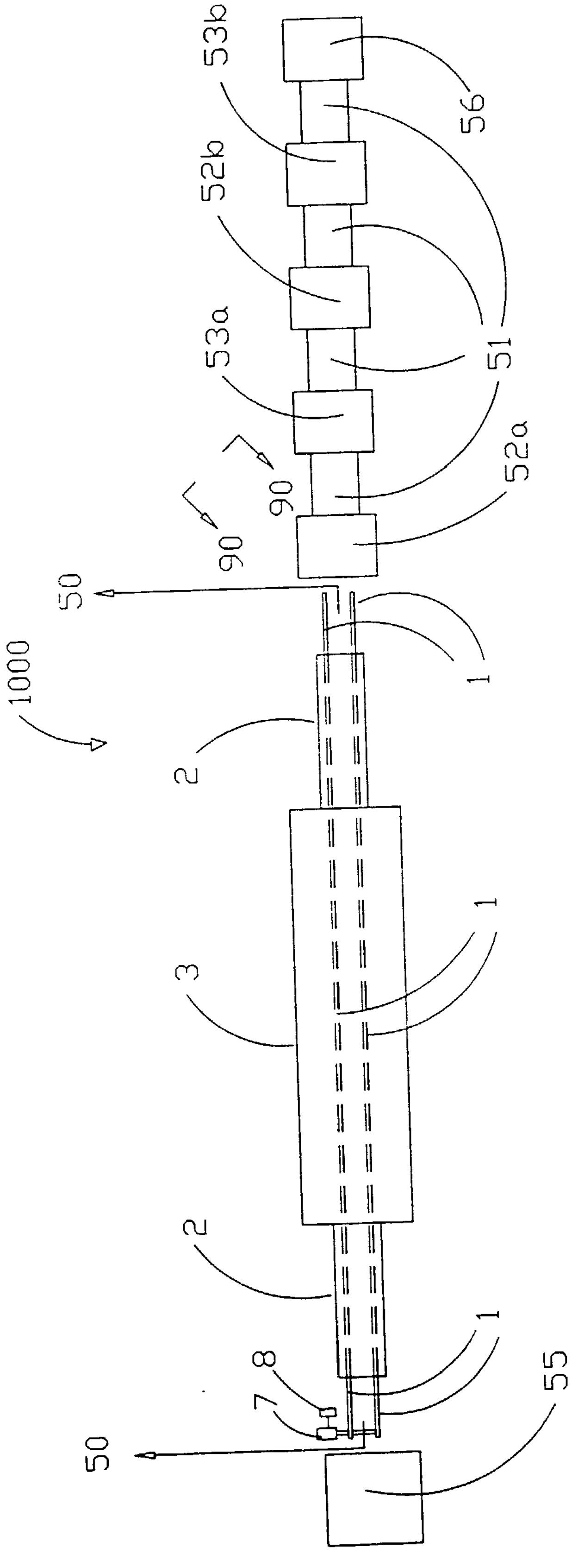


Fig. 1

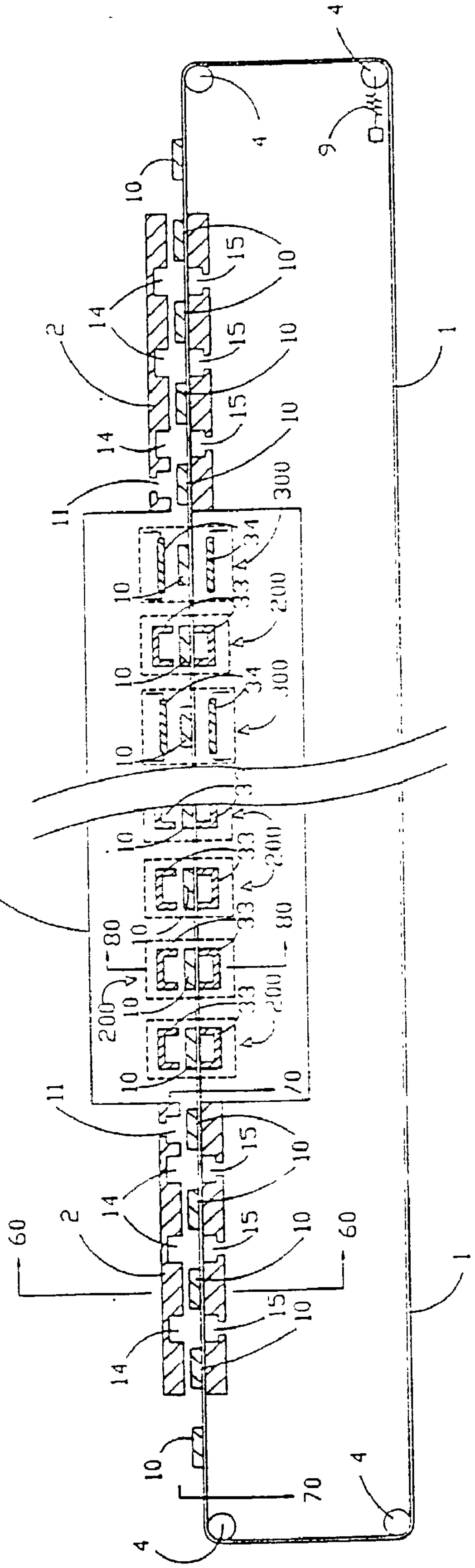

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Fig. 2A

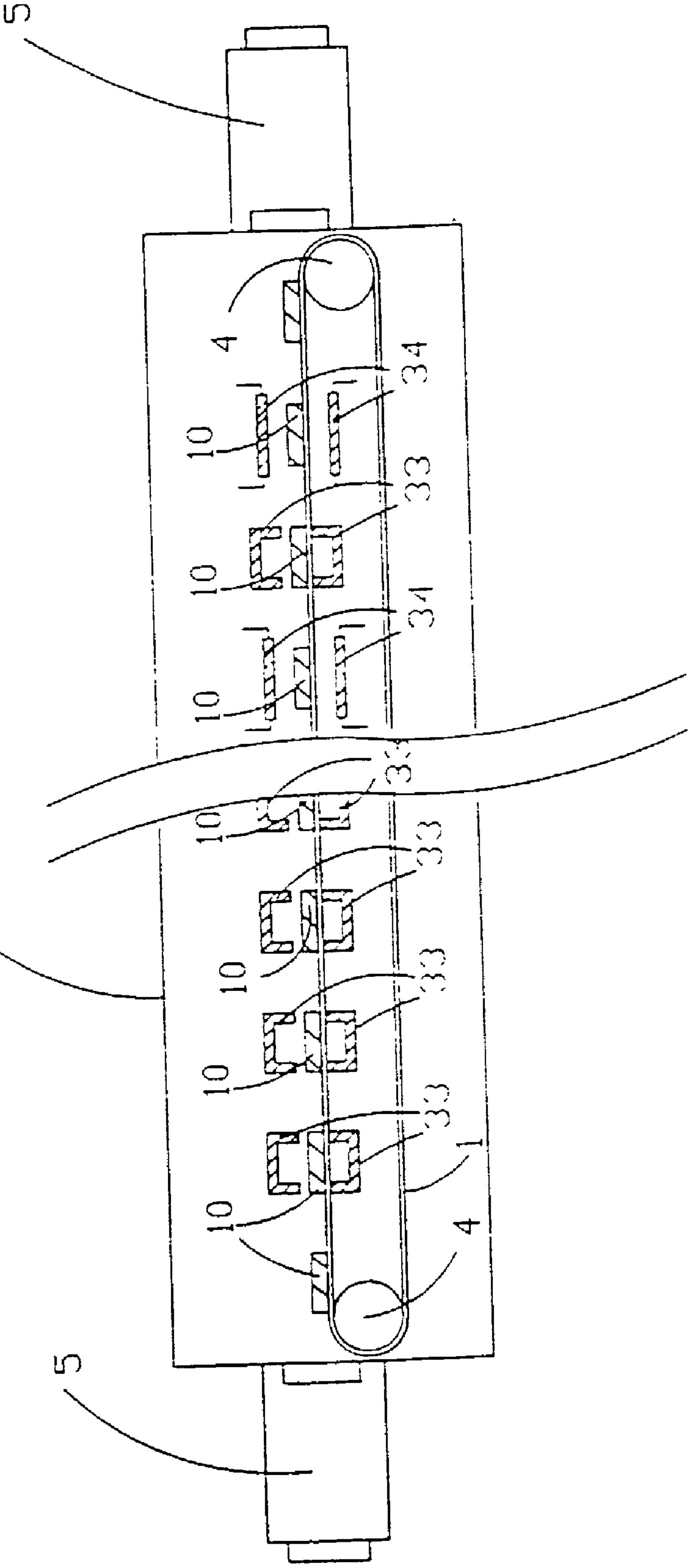

Fig. 2B

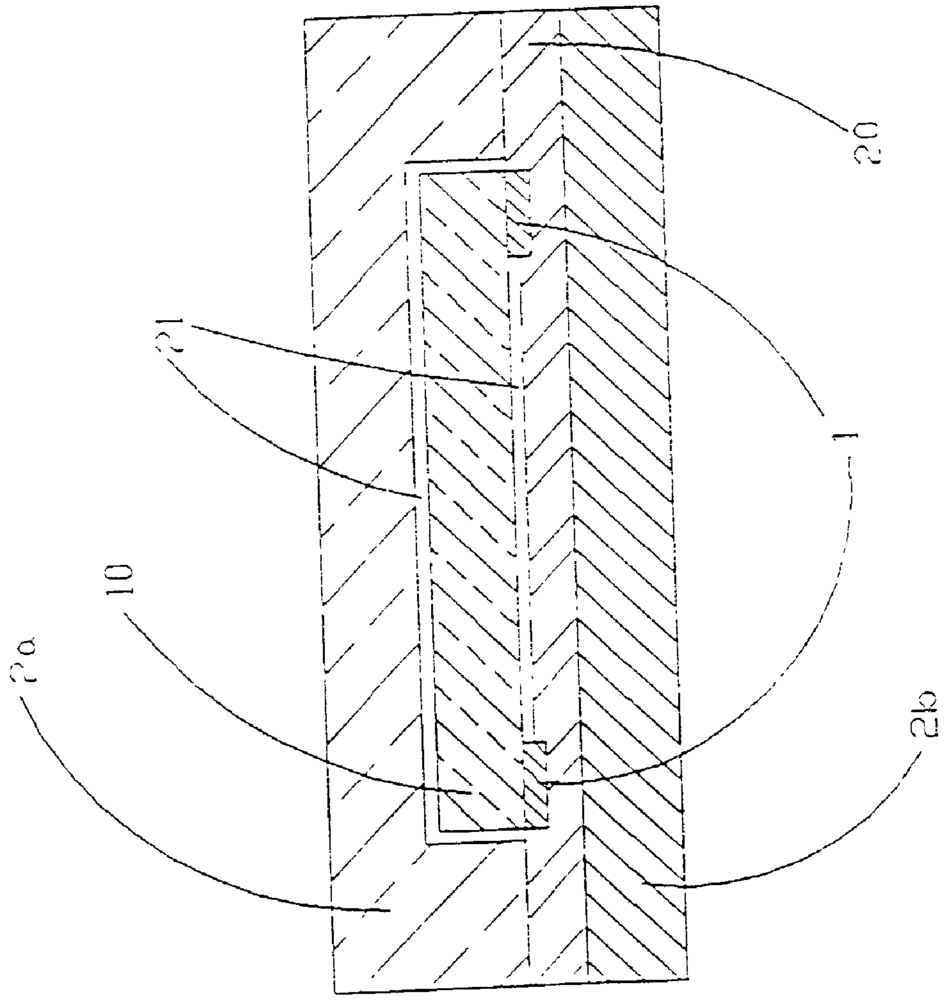

Fig. 3

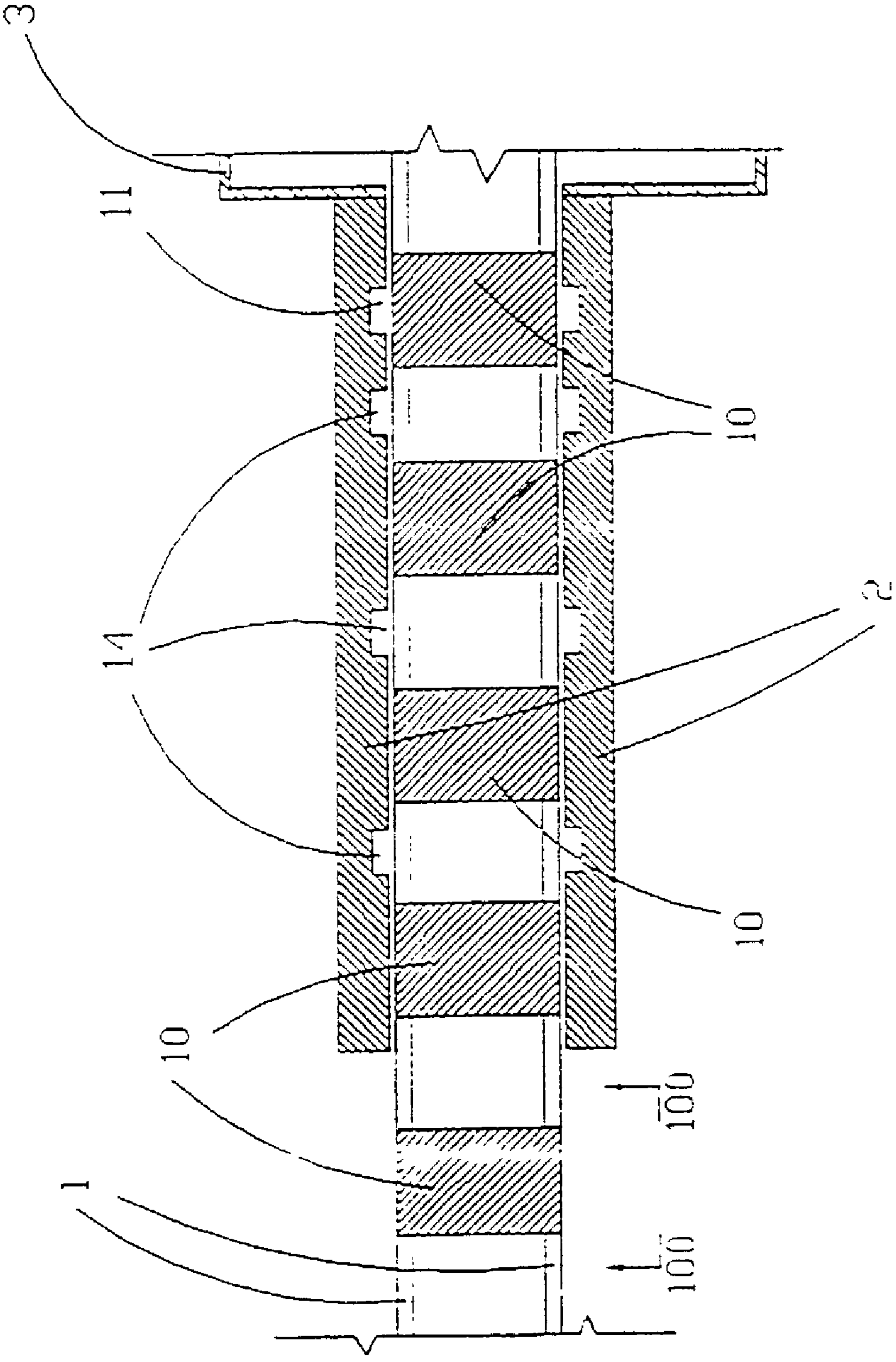

Fig. 4

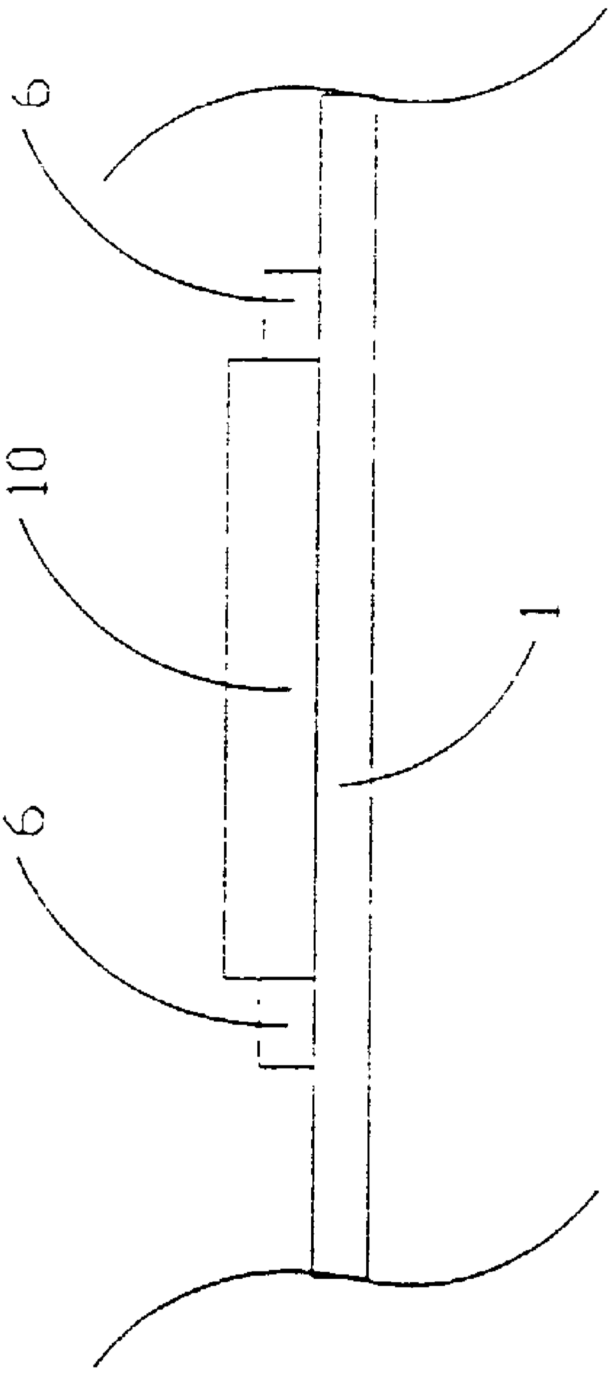

Fig. 5

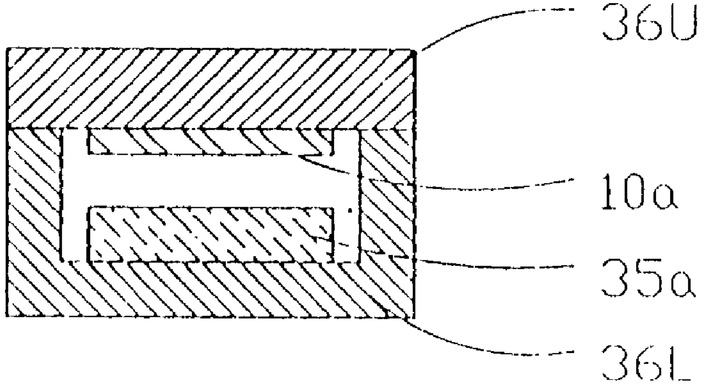

Fig. 6A (PRIOR ART)

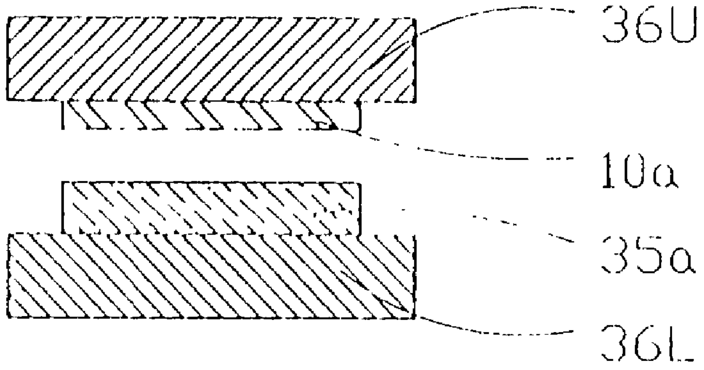

Fig. 6B (PRIOR ART)

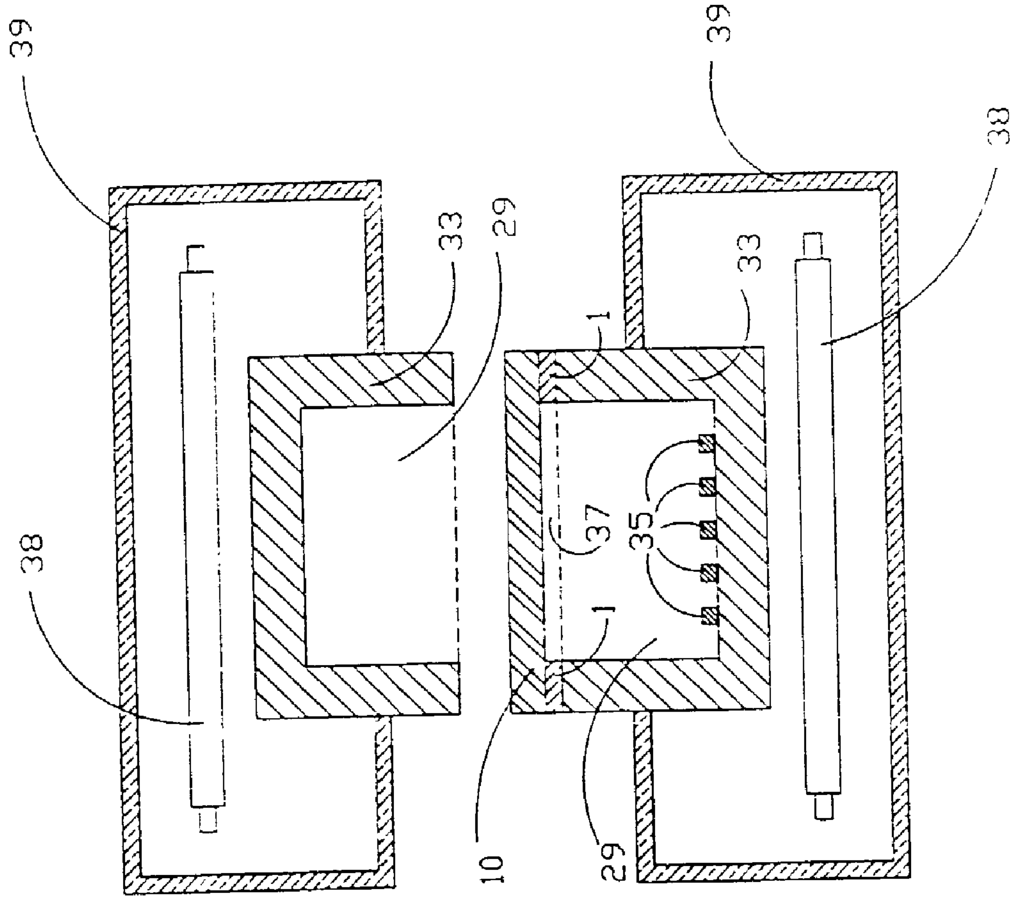

Fig. 7A

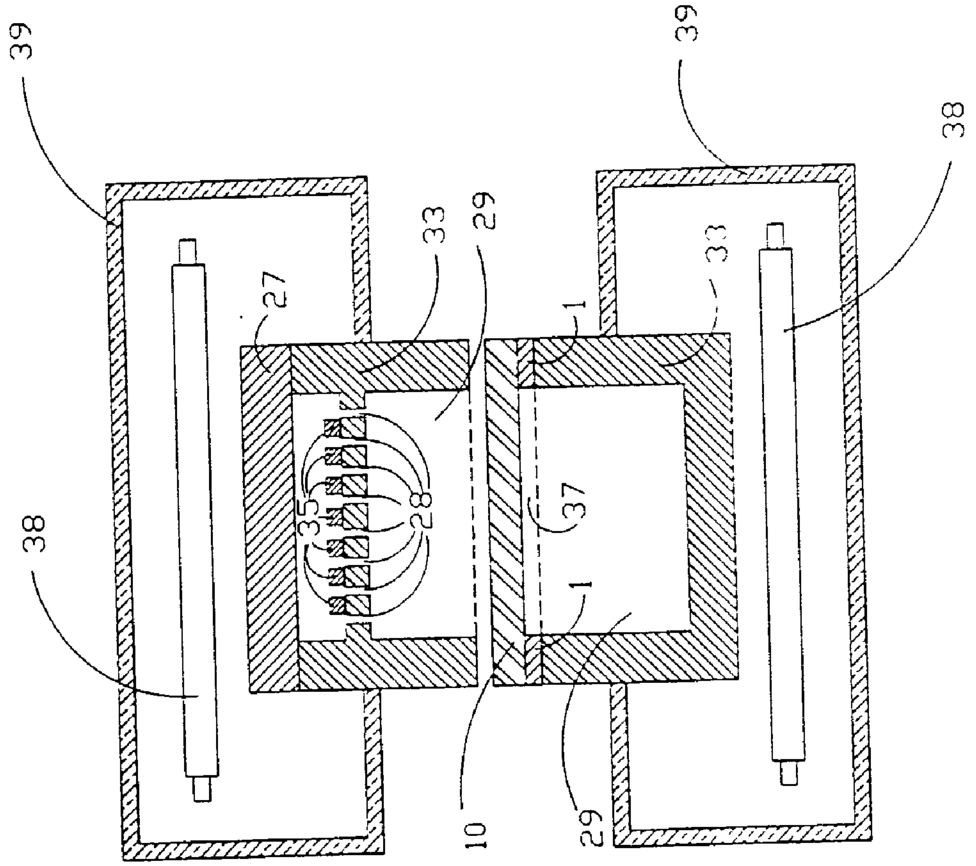

Fig. 7B

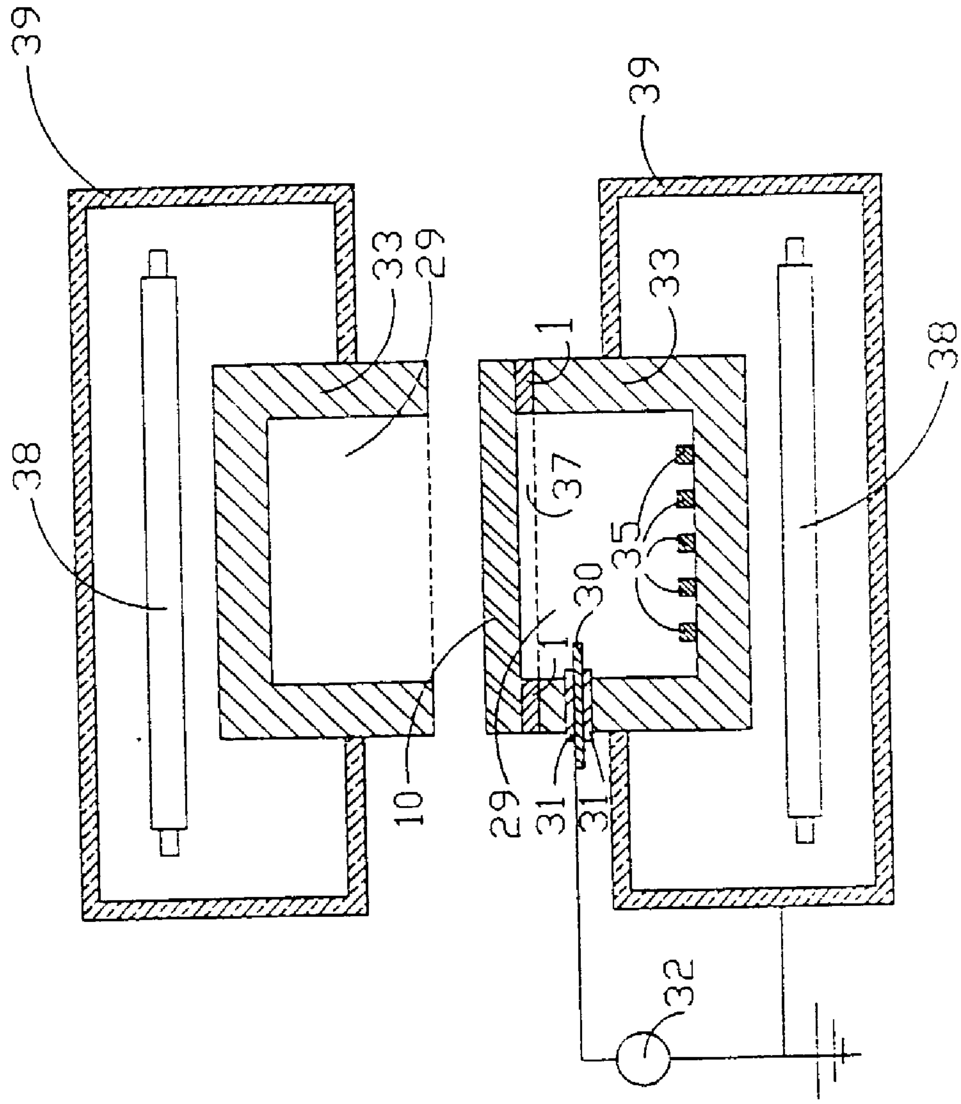

Fig. 8

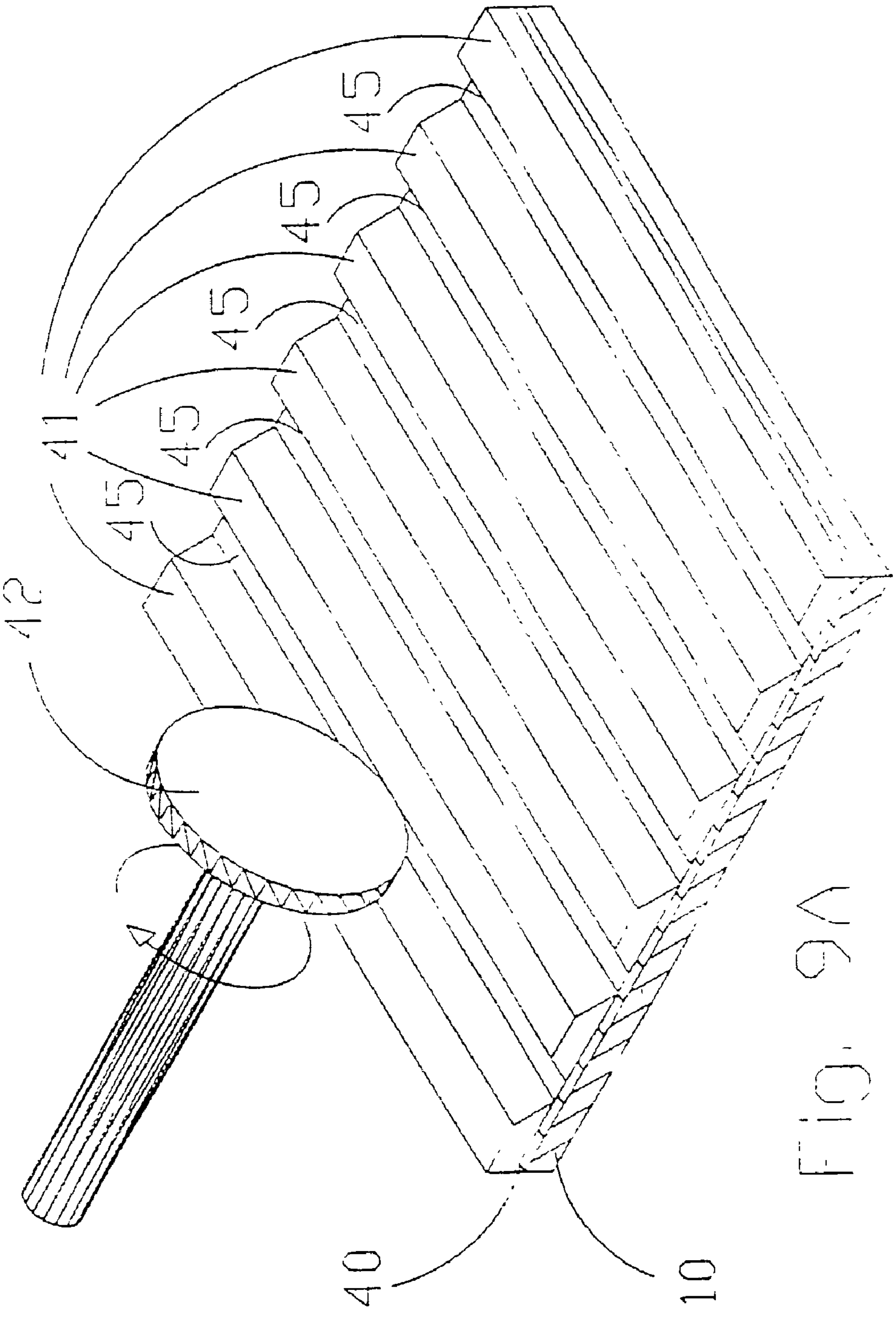

Fig. 9A

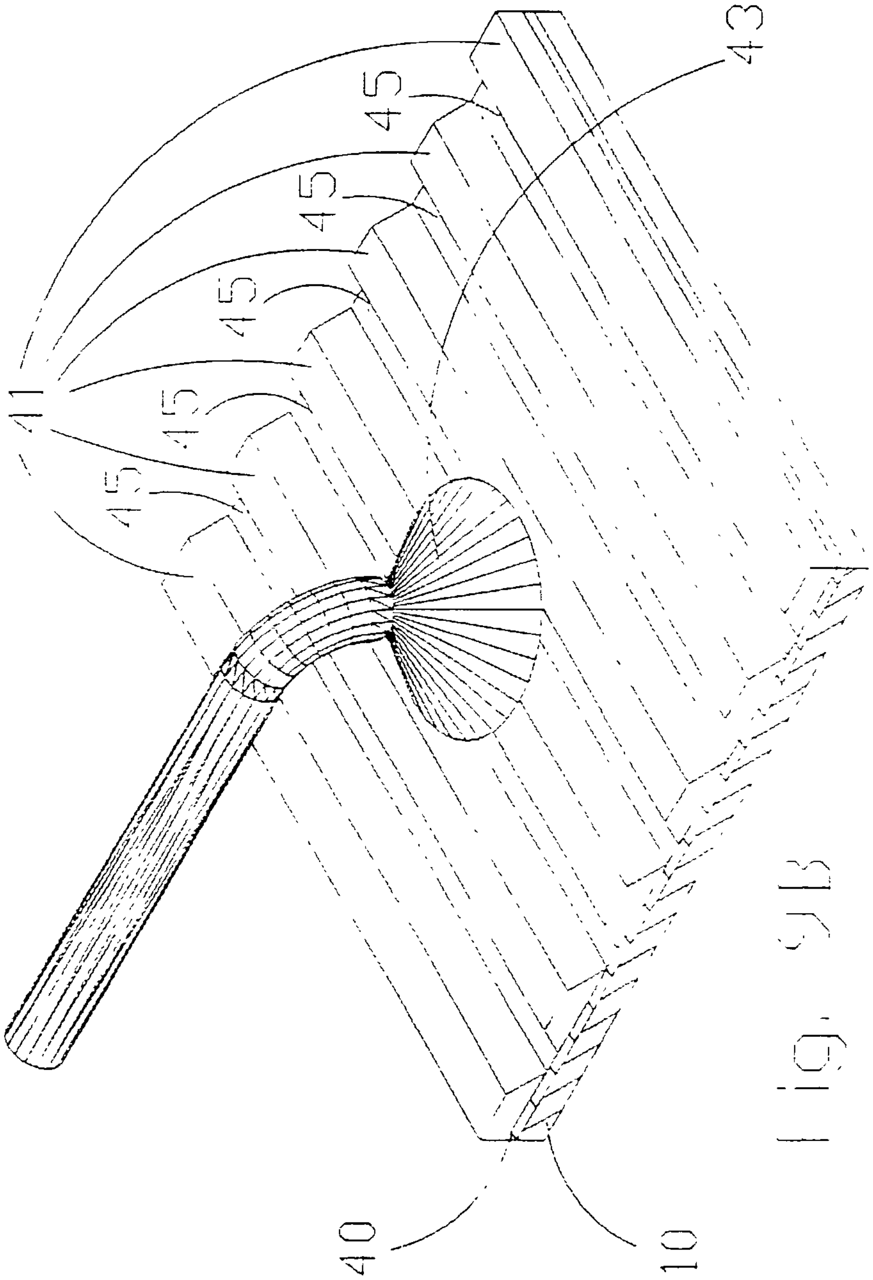

Fig. 9B

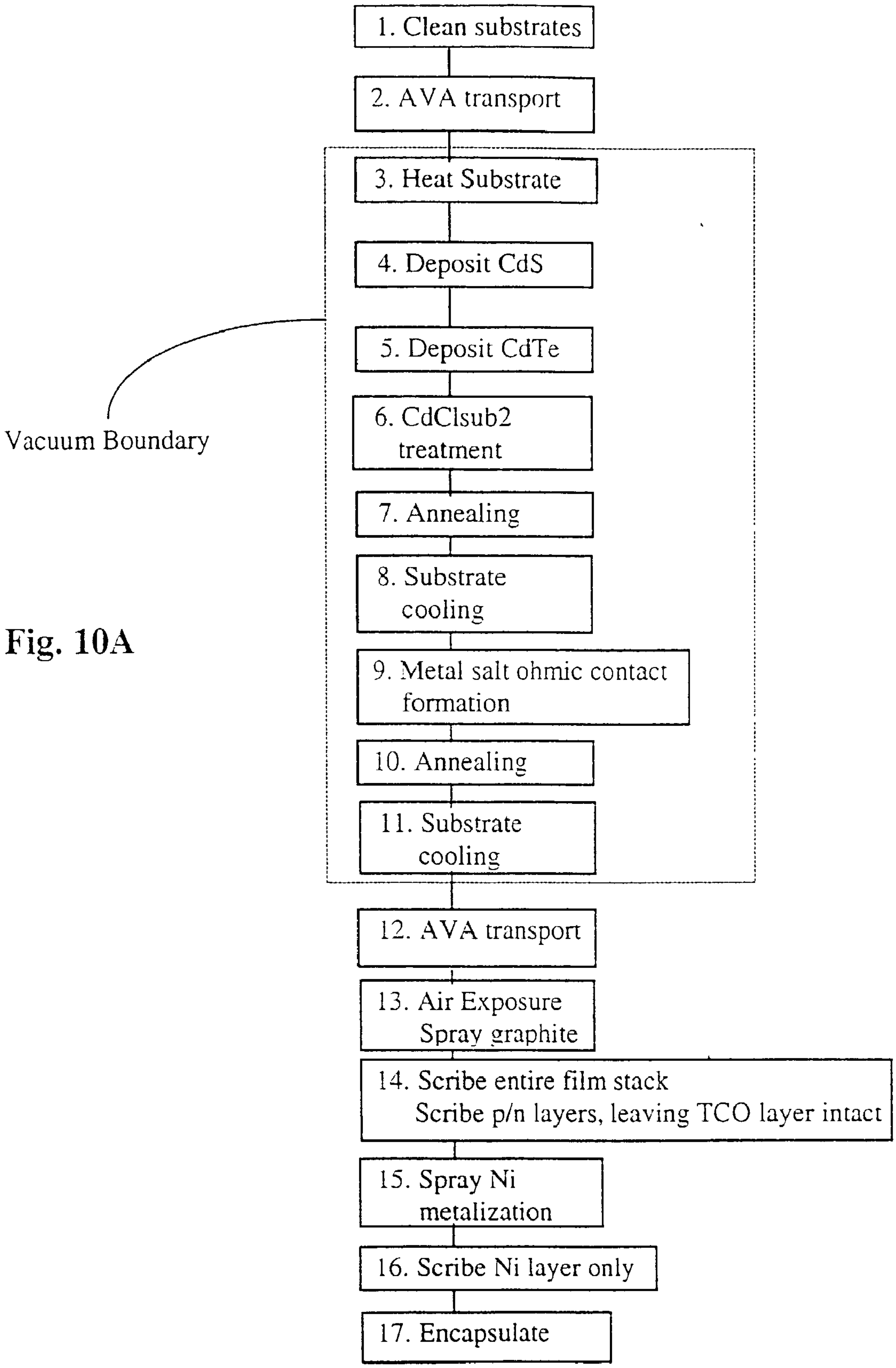
1. Clean substrates
2. AVA transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. CdClsub2 treatment
7. Annealing
8. Substrate cooling
9. Metal salt ohmic contact formation
10. Annealing
11. Substrate cooling
12. AVA transport
13. Air Exposure Spray graphite
14. Scribe entire film stack Scribe p/n layers, leaving TCO layer intact
15. Spray Ni metalization
16. Scribe Ni layer only
17. Encapsulate
Vacuum Boundary

Fig. 10A

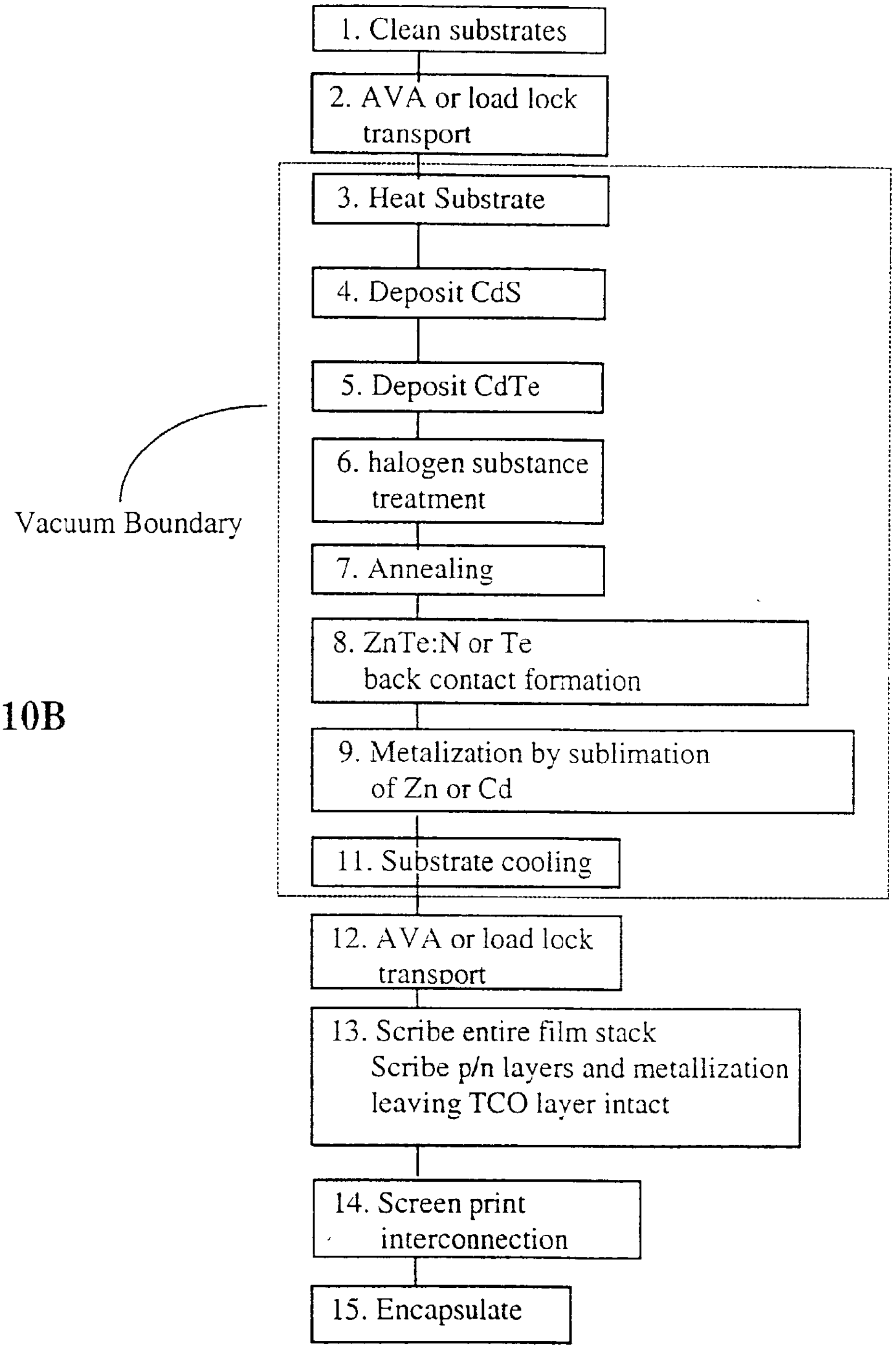
1. Clean substrates
2. AVA or load lock transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. halogen substance treatment
7. Annealing
8. ZnTe:N or Te back contact formation
9. Metalization by sublimation of Zn or Cd
11. Substrate cooling
12. AVA or load lock transport
13. Scribe entire film stack Scribe p/n layers and metallization leaving TCO layer intact
14. Screen print interconnection
15. Encapsulate
Vacuum Boundary

Fig. 10B

APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES

[0001] Government Support

[0002] This invention was made with Government support under grants awarded by the National Science Foundation and the Department of Energy. The Government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to apparatus and processes for the mass production of low cost photovoltaic modules and, more specifically to an inline continuous vacuum apparatus and process for fabricating the critical semiconductor layers, which together with attendant non-vacuum processes, are all accomplished at high throughput.

BACKGROUND OF THE INVENTION

[0004] Photovoltaic (PV) modules are used to generate electricity from sunlight by the photovoltaic effect. It has been recognized for decades that if these modules could be mass produced at low cost, they could be used to meet a considerable portion of the world's energy needs. Major companies, such as Royal Dutch/Shell and BP-Amoco, have stated that PV modules have the potential to become a major energy source and that their use has significant benefits to the global environment. However, for these benefits to be realized, PV modules must be produced at many times the current volume and at costs below \$100/m^2, as discussed by Bonnet et. al. in "Cadmium-telluride material for thin film solar cells", J. Mater. Res., Vol. 13, No. 10 (1998). Currently, PV modules are manufactured in small quantities at costs of about \$500/m^2. About one hundred times the current yearly production is required to sustain a PV module manufacturing capacity that can contribute just 5% of the current electricity generated. Consequently, the manufacturing volume of PV modules needs to be greatly increased and costs significantly reduced.

[0005] To realize the required increases in production volume and decreases in manufacturing costs, PV modules must be produced as a commodity. Commodity level manufacturing requires innovation to develop highly automated production processes and equipment, which are designed to specifically fabricate the commodity product. Commodity manufacturing necessitates high production speeds (high throughput), minimal labor costs, and a continuous process flow. Low capital costs and ease of expanding production capacity also facilitate commodity manufacturing. There are a variety of known PV devices, but only the cadmium telluride (CdTe) thin film PV device has the potential to satisfy the requirements for commodity manufacturing.

[0006] Since 1974, there have been many industrial efforts to create technologies for CdTe PV module manufacturing. Most of these industrial efforts, as exemplified by the teachings of U.S. Pat. Nos. 4,319,069, 4,734,381, and 5,501,744, have been terminated because of fundamental inadequacies in their manufacturing technologies. To date, no technology suitable for commodity level manufacturing of CdTe PV modules has been developed, thus demonstrating the need for innovation in this area.

[0007] The most common CdTe PV cells are thin film polycrystalline devices, in which the CdTe layer is paired with a cadmium sulfide (CdS) layer to form a heterojunction. The thin films of a CdS/CdTe PV device can be produced through a variety of vacuum and non-vacuum processes. Of the many types of thin film deposition methods, sublimation in vacuum is most amenable to commodity manufacturing. This is because vacuum sublimation of CdS/CdTe PV modules exhibits deposition rates 10 to 100 times higher than any other PV module deposition method. Vacuum sublimation of the semiconductor layers for CdS/CdTe PV modules can also be performed in modest vacuum levels and does not require costly high vacuum equipment. Vacuum deposition methods for other thin film PV devices require costly, complex high vacuum equipment and results in low throughput.

[0008] Due to the high rate of deposition and low capital cost, the CdS/CdTe thin film cell fabricated by vacuum sublimation is the most suitable for commodity level manufacturing of PV modules. However, cadmium is a Group B carcinogen. According to U.S. government regulations, the quantity of this material which can be lawfully released into the environment or into an occupational setting is extremely small. The known prior art in CdS/CdTe vacuum sublimation requires process and hardware innovations to achieve occupational and environmental safety as required by federal regulations, as well as commodity scale manufacturing.

[0009] One known configuration for a CdTe device is the back wall configuration, in which the thin films are deposited onto a glass superstrate, hereinafter referred to as a substrate. The CdTe device is most often fabricated on a glass substrate coated with a transparent conductive oxide (TCO) film onto which other film layers are deposited in the following order: a) a CdS film, b) a CdTe film, c) an ohmic contact layer, and d) a metal film. Along with the deposition of these films, many heat treatments are also needed to enhance the device properties. The TCO and the metal films form the front and back electrodes, respectively. The CdS layer (n-type) and the CdTe layer (p-type) form the p/n junction of the device. The cells are deployed with the substrate facing the sun. Photons travel through the glass and TCO film before reaching the p/n junction of the device. A module is formed by interconnecting individual cells in series to produce a useful voltage.

[0010] Thus, a process for manufacturing CdS/CdTe modules includes the following steps: 1) cleaning the TCO coated glass substrates, 2) heating the substrates, 3) depositing an n-type CdS layer, 4) depositing a p-type CdTe layer, 5) performing a $CdCl_2$ treatment to improve CdTe grain structure and electrical properties, 6) forming a p+ohmic low resistance contact layer to improve current collection from the CdTe, 7) depositing a metal layer (metallization) to form the back electrode, 8) scribing the film layers into individual cells, 9) interconnecting the cells in series and providing a means of electrical connection to the module, and 10) encapsulating the finished module.

[0011] All of the prior art methods for the production of CdTe modules have limitations that render them unsuitable for commodity level manufacturing. For example, prior art methods of $CdCl_2$ treatment are disconnected, low throughput batch operations, rather than continuous flow processes. These batch type processes are inefficient and involve extremely high costs in order to increase throughput to the commodity manufacturing level. Most of the known methods of $CdCl_2$ treatment also require rinsing, which generates liquid wastes that contain cadmium. Known methods of ohmic contact formation are also batch type processes that exhibit low throughput rates. Prior art metallization steps also exhibit low throughput and require costly process equipment. It is necessary to improve the current methods of $CdCl_2$ treatment, ohmic contact formation, and metallization in order to achieve high throughput continuous processes.

[**0012**] Prior art methods for scribing the layers to form a module include laser scribing, mechanical scribing, and abrasive blasting. Known laser scribing methods used in the PV industry are associated with low production speed and high capital cost. Laser scribing was abandoned recently in one industrial setting due to laser equipment failure as discussed by Borg in, "Commercial Production of Thin-Film CdTe Photovoltaic Modules", NREL/SR-520-23733, October 1997. Known mechanical and abrasive blast scribing methods have only been shown on a small scale as typified by U.S. Pat. No. 5,501,744 to Albright and require innovation and improvement to be suitable for commodity level manufacturing.

[**0013**] Specific examples of prior art relating to CdS deposition and CdTe deposition performed by vacuum sublimation are described in detail below. The other prior art steps that are necessary to form a complete CdTe PV module are also discussed below.

[**0014**] One known vacuum method of producing CdTe solar cells by vacuum sublimation is taught in U.S. Pat. No. 5,536,333 to Foote et. al. This method is further described by Sasala et. al. in "Technology Support for Initiation of High-Throughput Processing of Thin-Film CdTe PV Modules", NREL/SR-520-23542, pp. 1-2, (1997). These references discuss a technique known as vapor transport deposition (VTD), which involves heating of the semiconductor materials in a contained vessel in order to create vapor. An inert carrier gas, such as nitrogen, transports the vapor of the semiconductor to the substrate through heated conduits. The substrate is held horizontally in a heated environment and supported from beneath by ceramic rollers in the heated environment. The deposition of the semiconductor is made onto the top surface of the substrate. In accordance with this prior art method, the ceramic rollers prevent the glass substrate from sagging under its own weight due to the elevated temperatures involved.

[**0015**] The entire VTD method is very complex and costly. It is possible to deposit a complete CdTe solar cell in a very short time and at sufficiently low substrate temperatures to eliminate glass sagging completely or reduce it to a very small acceptable value. Thus, the expensive ceramic rollers of the VTD method are not needed. Reloading starting material may also be performed in a much simple manner than as shown in this prior art. Since the films are thin, only small amounts of material are required to form them. Consequently, only very small volumes of starting material are needed for many days of operation, thus eliminating the need for this complex reloading arrangement. The heated vessels of this method contain toxic vapors, which pose significant occupational safety problems when they are opened for reloading during processing. In the VTD method, vapors are transported through long distances in a carrier gas, an arrangement which will likely lead to the formation of very small nano-particles through condensation of the vapors. These nano-particles degrade the film qualities and lead to occupational hazards when the system is serviced. Furthermore, in the VTD method, the continuous flow of carrier gas has to be maintained along the substrate. Any CdS or CdTe vapors that are carried past the substrate will be wasted. Any deposits of waste material on the inner surface of the vacuum chamber, pumps, exhaust, etc. must be cleaned, thereby exposing maintenance workers to toxic materials and raising occupational safety issues. In order to prevent unwanted condensation of CdS and CdTe vapors, the VTD method also requires continued heating of large portions of the equipment, including the vaporization vessel itself, the conduits, the deposition chamber, etc. This wastes energy and increases the capital costs. The VTD method is only used for depositing the p/n junction layers. Other processing steps, such as the $CdCl_2$ treatment, ohmic contact formation, and metallization are inherently low throughput batch processes. Scribing is taught to be either laser scribing or photolithography both of which are slow and costly processes.

[**0016**] In another prior art reference entitled "The CdTe Thin Film Solar Cell" International Journal of Solar Energy, vol. 12, 1992, Bonnet proposes an inline production method for fabricating CdS/CdTe layers using a close-spaced sublimation (CSS) type deposition process. This prior art reference describes inline deposition within one vacuum boundary for only the steps of substrate heating, CdS deposition, and CdTe deposition. The other steps of $CdCl_2$ treatment. ohmic contact formation, and metallization are not shown as part of a continuous inline vacuum process, and are presumably performed by previously known methods. As described above, known methods for performing these steps have limitations. The Bonnet method does allow multiple substrate processing of more than one film. However, it is not clear if long term operation and uniformity of deposition over time and across large substrates are achieved. Furthermore, the Bonnet method relies on CSS, which by definition, requires a space of 2-3 mm between the source and the substrate. This gap will allow a vapor leak at the edge of the substrate. As the source charge sublimes away over time the gap will increase. It is the present inventors' experience that this gap and the associated vapor leak causes non-uniform deposition on the substrates and also results in condensation of toxic materials on unwanted areas on the inner surfaces of the process chamber. This leak will be reduced if the background chamber pressure is held high enough to decrease the mean free path between gas molecules in the process chamber. However, higher pressures lead to lower deposition rates and greater nano-particle formation. An operating pressure of 750 millitorr is specified. At these pressures, nano-particles will be formed, since the vapor will homogeneously condense in the ambient gas near the edge of the deposition space. These very small particles degrade film quality and pose a health hazard to workers during routine maintenance inside the vacuum chamber.

[**0017**] Each of the individual prior art process steps required to produce a CdTe PV module exhibits limitations, as outlined above. In addition, nothing in the prior art describes an overall process to perform the series of steps of substrate heating, depositing an n-type CdS layer, depositing a p-type CdTe layer, performing a $CdCl_2$ treatment, and forming an ohmic contact inline, continuously, and in one vacuum boundary. In particular, the steps of $CdCl_2$ treatment and ohmic contact formation require significant innovation before they can be included in a continuous inline vacuum process. Such a continuous inline vacuum process would have significant advantages for commodity manufacturing of CdTe PV modules.

[0018] Any vacuum process for manufacturing CdTe PV modules would also require an apparatus to transport substrates through the process steps within vacuum and to transport the substrates into and out of vacuum rapidly. This apparatus should be robust, simple, and low cost. The apparatuses described in the prior art simply do not meet these requirements.

BRIEF SUMMARY OF THE INVENTION

[0019] The present invention is directed to commodity scale manufacturing of CdTe PV modules and involves innovations in both manufacturing processes and hardware.

[0020] One aspect of the present invention involves providing all of the processing steps for the critical semiconductor layers of a CdTe PV device inline, with all of those steps being completely performed within one vacuum boundary, at high throughput. They include rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation. These steps are performed at modest vacuum pressures without requiring costly high vacuum equipment. By utilizing inline vacuum processing to form all of the critical layers without breaking vacuum, an improvement in process throughput, film quality, device efficiency, and device stability is realized, while at the same time avoiding pinhole formation. All inline vacuum processing is also advantageous in that it limits the production of toxic waste and environmental and occupational exposure to toxic compounds.

[0021] Another aspect of the present invention is a novel $CdCl_2$ treatment step, which may be performed in the same vacuum boundary and inline with the other fabrication steps. Our $CdCl_2$ treatment process has the advantage of a high throughput rate while producing stable, high efficiency devices and, at the same time, limiting environmental and occupational exposure to toxic compounds.

[0022] Another aspect of the present invention is a novel vacuum process to produce a p+ ohmic contact region by subliming a metal salt onto a CdTe layer. Our ohmic contact formation process has the advantage of producing, at high throughput rates, a low resistance ohmic contact that is stable over time.

[0023] Another aspect of the present invention is a unique high throughput, low cost spray process to form the back electrode. This process has the advantage of producing a durable, high conductivity back electrode using known low cost industrial spray methods.

[0024] Another aspect of the present invention is to provide novel high throughput, low cost processes to perform module scribing using abrasive blasting or mechanical brushing through a mask. These novel scribing processes have the advantage of selectively scribing the semiconductor layers without scribing the TCO layer. In addition, the scribe process may be adjusted so that the TCO layer may be removed as well.

[0025] Another aspect of the present invention is a novel vacuum process station to selectively heat substrates and films, to expose substrates and films to vapor, to deposit thin films on a substrate, and to strip thin films off of a substrate. This vacuum process station allows substrates to be transported into and out of vacuum. When used as a deposition source, our vacuum process station has the advantage of very minimal vapor leakage, which significantly reduces occupational exposure to toxic materials. This unique deposition source deposits very uniform layers and is suitable for long term continuous operation.

[0026] Another aspect of the present invention is a novel substrate transport apparatus, which is employed to move substrates within vacuum or, in combination with a unique opening, to transport substrates rapidly into and out of vacuum. This substrate transport apparatus is robust, simple, and low cost and has the additional advantage of not collecting any coatings as it moves substrates through the thin film deposition processes.

[0027] Yet another aspect of the present invention is to provide substrate cleaning in a clean mini-environment at the entrance to the inline continuous vacuum process, which has the advantage of greatly reduced cost resulting from the elimination of a clean room to contain the entire process line.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] **FIG. 1** is a schematic top plan view of a system for making photovoltaic modules in accordance with the present invention.

[0029] **FIG. 2A** is a partially broken away schematic elevation view in longitudinal section along the line **50-50** of **FIG. 1**, illustrating a substrate transport apparatus and a plurality of vacuum processing stations.

[0030] **FIG. 2B** is a partially broken away schematic elevation view in longitudinal section, illustrating an alternate embodiment of the substrate transport apparatus of **FIG. 2A**.

[0031] **FIG. 3** is a schematic elevation view in cross section along the line **60-60** of **FIG. 2A** illustrating the sealing arrangement by which the introduction of outside air into the vacuum chamber is minimized.

[0032] **FIG. 4** is a partial schematic top plan view in longitudinal section along the line **70-70** of **FIG. 2A**, further illustrating the sealing arrangement of **FIG. 3**.

[0033] **FIG. 5** is a schematic elevation view along the line **100-100** of **FIG. 4**, further illustrating the substrate transport apparatus of **FIG. 2A**.

[0034] FIGS. 6A-B are schematic sectional elevation views illustrating enclosed and unenclosed substrates as they are positioned in prior art apparatuses.

[0035] **FIG. 7A** is a schematic elevation view in cross section along the line **80-80** in **FIG. 2A**, illustrating details of a vacuum process station of the substrate transport apparatus of **FIG. 2A**.

[0036] **FIG. 7B** is a schematic elevation view in cross section to illustrate an alternative embodiment of the vacuum process station of **FIG. 7A**.

[0037] **FIG. 8** is a schematic elevation view in cross section to illustrate a second alternate embodiment of the vacuum process station of **FIG. 7A**.

[0038] **FIG. 9A** is a schematic perspective view along the line **90-90** of **FIG. 1**, illustrating the way in which photovoltaic modules are scribed.

[0039] **FIG. 9B** is a schematic perspective view along the line **90-90** of **FIG. 1**, illustrating an alternative way to scribe photovoltaic modules.

[0040] **FIG. 10A** is a flow chart illustrating the process steps of the present invention.

[0041] **FIG. 10B** is a flow chart of some of the alternate embodiments of the process steps of **FIG. 10A**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0042] Referring now to **FIG. 1**, there is shown an overview of the preferred embodiment of an apparatus **1000** for producing photovoltaic modules in accordance with the present invention. A substrate cleaning station **55** cleans the commercially available substrates that typically comprise low cost soda lime glass coated with transparent conducting oxide (TCO). After cleaning, a pair of metal strip belts **1** transport the substrates through the next portion of the apparatus **1000**. The belts may be moved bidirectionally by means of a known stepper motor **7**. Precise indexing of the position of the pair of belts **1** is accomplished by the use of a commercially available stepper motor controller **8**. The pair of metal strip belts **1** pass through a pair of openings **2** and a vacuum chamber **3**. A plurality of process stations for the processing of the critical semiconductor layers are contained within the vacuum chamber **3**, and are described in detail below. Another series of process stations are linked by a plurality of conveyor belts **51**. These process stations do not require vacuum. A first spray process station **52***a* is followed by a first film scribing process station **53***a*. These process stations are followed by a second spray process station **52***b* and a second film scribing process station **53***b*. The final process station in the apparatus **1000** is an encapsulation station **56**. The description of the apparatus and processes of the instant invention is presented in the following order: the substrate transport apparatus and openings, the vacuum process stations, the metallization method, the film scribing method, and the process steps to produce a photovoltaic module. Following the description of the preferred embodiment is a description of alternate embodiments.

[0043] **FIGS. 2A, 3, 4**, and **5** in combination illustrate the complete assembly of the preferred embodiment of a pair of air-to-vacuum-to-air (AVA) openings and the substrate transport system of the present invention. The pair of AVA openings **2** facilitate the rapid transport of substrates from air into vacuum and then back into air. **FIG. 2A** illustrates vacuum chamber **3**, which is pumped to a suitable vacuum by known techniques. A pair of AVA openings **2** is shown on either side of the vacuum chamber **3**. A pair of continuous metal strip belts **1** pass through both of the AVA openings **2** and also through the entire length of the vacuum chamber **3**. A plurality of substrates **10**, which are carried on the twin metal belts **1**, are also shown. The AVA openings **2** are shown with a plurality of pockets **14** and a plurality of vacuum pump ports **15** for vacuum pumping. A pair of injection ports **11** are shown for the injection of process gas. A plurality of pulleys **4** are provided for moving the belts **1**. A belt tensioner **9** maintains the belts **1** at a predetermined tension.

[0044] **FIG. 3** shows the details of the AVA openings **2** in cross section. A top channel **2***a* and a bottom plate **2***b* are split by a belt bearing plate **20**. In total, parts **2***a*, **2***b*, and **20** form the cross section of the opening **2** of **FIGS. 2A, 3**, and **4**. A clearance distance **21** on the order of 0.005 in.±0.002 in. is formed around the substrate **10**. This clearance distance **21** is formed between the substrate **10** and the top channel **2***a* and between the substrate **10** and the belt bearing plate **20**. The clearance distance **21** is large enough so that the substrate **10** may move freely, but is small enough to provide resistance to fluid flow through the clearance distance **21**. This resistance to fluid flow allows the vacuum chamber **3** to be maintained at a desired vacuum level. The pair of continuous metal strip belts **1** provide a substrate carrier to convey the plurality of substrates **10**.

[0045] **FIG. 5** is a detailed view of a pair of tabs **6** which are attached to the metal strip belt **1**. The tabs **6**, a plurality of which are placed periodically along the belt **1**, provide a means of locating the substrate **10**.

[0046] The pair of continuous metal strip belts **1** provide a substrate carrier that will not be coated by the vacuum deposition processes. The elimination of coating on the belt **1** is a significant improvement over the prior art. As exemplified by Charschan in U.S. Pat. No. 3,294,670 (1966), the prior art utilized substrate carriers which enclosed the perimeter of the substrate in a "picture frame" type arrangement. The picture frame type substrate carriers are necessarily coated during deposition. These coatings lead to jamming in the close tolerance seals during motion, present occupational safety issues due to particle generation, and result in cross contamination between the processes. In the present invention, these problems have been addressed by exposing only the substrates **10** to coating during a vacuum deposition. In addition, unlike all of the prior art, the clearance distance **21** is not formed between the substrate carrier and the openings. Rather, the clearance distance **21** is formed between the precisely cut substrate **10** and the AVA openings **2**. The clearance **21** is formed specifically between the substrate **10** and the top channel **2***a* and between the substrate **10** and the linear bearing plate **20**.

[0047] The use of the pair of metal strip belts **1** as the substrate carrier in accordance with the present invention has many other advantages. The fact that the belts **1** have a low mass will create less wear on any bearing surface used. The low mass will also greatly decrease the inertia of the substrate carrier, thus allowing the substrate to be moved quickly between processing stations.

[0048] Continuous metal strip belts **1** also have advantages in situations calling for a series of vacuum processes to be carried out in one vacuum chamber **3**. Continuous metal strip belts **1** of 200 feet in length can be fabricated by known methods. This allows a large number of process steps to be carried out in one vacuum chamber **3**.

[0049] Another advantage is the cost of fabrication of this type of substrate carrier, which is considerably less than the cost of machining close tolerance picture frame type substrate carriers of the prior art. The present substrate carriers also facilitate scaling up the process. For larger substrates **10**, the openings **2** must be increased in size. However, the strip belts **1** may be simply spaced further apart.

[0050] The continuous metal strip belts **1** are preferably formed of metal alloys that have high resistance to corrosion and that retain high strength at elevated temperatures. These belts may be coated with other materials to alter the surface properties further, if needed. Many different attachments or tabs **6** for retaining the substrate **10** may be welded or fixed to the metal strip belts **1** at relatively low cost.

[**0051**] A cut tolerance of ±0.003 inch is required for the glass substrates **10** which are carried on the continuous metal strip belts **1**. High throughput, low cost equipment is commercially available for cutting the substrates **10** to the required tolerances. The precision glass cutting required for this invention is not an additional processing step, since the substrates **10** must be cut to size in any method.

[**0052**] The continuous metal strip belts **1** are also relatively small in cross section. The small cross section decreases the thermal expansion as the belts pass through high temperature vacuum processes, which will decrease any tendency to jam in the AVA openings **2** due to thermal expansion.

[**0053**] The relatively low mass of the metal strip belts **1** also allows the substrate carrier to cool and heat more rapidly than the prior art picture frame type substrate carrier. The low mass of the metal strip belts **1** allows the belt temperature to match the glass temperature during processing, thereby reducing thermal gradients in the glass substrates **10** which could otherwise lead to stresses that may crack the glass.

[**0054**] Referring now to **FIG. 2**A, the vacuum chamber **3** and a plurality of vacuum processing stations, generally indicated by **200** and **300**, are illustrated in a partial schematic elevation view in section. The metal strip belts **1** carry the plurality of substrates **10** through the plurality of vacuum processing stations **200** and **300**. The process stations **300** provide for cooling of substrates **10** by radiation to a pair of water cooled plates **34**.

[**0055**] Each of the process stations **200** of **FIG. 2A** contain a pair of heated pockets **33**. These heated pockets **33** provide a flux of heat or vapor and are suitably shaped blocks of a material with a high thermal conductivity. In **FIG. 7A** the pair of heated pockets **33** are shown with details of the pair of continuous metal strip belts **1** in cross section. Both upper and lower heated pockets **33** have a machined pocket **29**. A deposition material **35** is shown in the pocket **29** of the lower heated pocket **33**. Only the substrate **10** spans the pocket **29**. No part of the belts **1** crosses the pocket **29**, thus avoiding deposition anywhere but on the substrate **10**. The upper heated pocket **33** serves as a heater for the substrate **10**.

[**0056**] Heated pocket **33** may be fabricated using any material which has an acceptable level of thermal conductivity. Further, that material should have a low level of porosity to prevent adsorption of air and water vapor and a low level of impurities. One material which has proven useful is purified pyrolitic grade graphite. However, metals and metals coated with ceramics, as well as other suitable materials, may be chosen.

[**0057**] In the preferred embodiment of the invention, the heated pockets **33** are heated by a plurality of quartz halogen lamps **38**, which are not damaged when used in vacuum at high temperatures. The temperature control of the heated pocket **33** may be accomplished by placing a thermocouple in the wall of the heated pocket **33** and using well known proportional with integral and derivative (PID) temperature control of the power to the lamps **38**. Lamps **38** are contained in boxes **39** for protection. Boxes **39** also serve as support structure for the lamps **38** and the heated pocket **33**. The boxes **39** also provide electrical isolation for safety, prevent arcing from the lamps **38**, and also serve as radiation shields to reduce the loss of energy. Other means of heating the heated pocket **33**, including resistive heating and inductive heating, for example, may be used as well.

[**0058**] Each of the process stations **200** may perform a variety of processes on a substrate **10**. These processes include: i) rapidly heating a substrate, ii) annealing a substrate and films, iii) thermally stripping a film from a substrate, iv) exposing a substrate and films to a vapor treatment, or v) depositing a thin film on a substrate. The chosen processes performed by station **200** depend on three parameters: a) the temperature of the lower heated pocket **33**, b) the temperature of the upper heated pocket **33**, and c) the presence or absence of the deposition material **35**. For processes i) through iii) described above, no deposition material **35** is loaded into the pocket **29**. For process i) the upper and lower heated pockets **33** are maintained at temperatures such that the rapid heating of glass substrates **10** may be done in a short cycle time, on the order of one minute. The uniformity of heating prevents cracking of the substrates **10**. For process ii), the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature which will not resublime thin films off of the substrate **10**. For process iii) the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature that is high enough to cause films on the substrate **10** to sublime away.

[**0059**] For processes iv) and v) described above, deposition material **35** is loaded into the pocket **29**. For process iv), the upper heated pocket **33** and substrate **10** are maintained at a higher temperature than the lower heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33** and expose the lower surface of the substrate **10** to vapor, but the vapor will not be deposited as a film on the substrate **10**. For process v), the lower heated pocket **33** is maintained at a relatively higher temperature than the substrate **10** and the upper heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33**, and the vapor will condense and be deposited as a film on the lower surface of the substrate **10**. All of these processes are robust, may be performed at high throughput, are occupationally and environmentally safe, and involve low capital cost.

[**0060**] In accordance with the present invention, the pair of metal belts **1** transports the substrates **10** through the plurality of process stations **200** or **300**. The metal belts **1** and the substrates **10** may be moved continuously. However, the preferred embodiment of the present invention provides for intermittent motion of the metal belt **1** and the substrates **10**. This motion is accomplished using a conventional stepper motor **7** and a stepper motor motion controller **8**. The substrates **10** are placed at equal pitch distances on the belts **1**, and the process stations **200** or **300** are placed one pitch distance apart. The intermittent motion consists of pauses in the motion of the belts **1** for processing and brief periods of motion of the belts **1** to advance the plurality of substrates **10** through the series of process steps. In this manner, an individual substrate **10** will pause at each process station **200** or **300** for an equal amount of time. A useful period of time, hereinafter defined as the cycle time, consists of the total period of time for one pause and one movement of the belts **1**. One substrate **10** will complete the series of inline vacuum process steps for each period of cycle time.

[0061] Since the process stations **200** or **300** are modular, a plurality of one type of process may be placed in series. If a given process step requires a processing time which exceeds the cycle time, then the given process step may be carried out over a series of similar processing stations **200** or **300**. For example, an annealing step, which requires a longer period of time to complete than the cycle time, may be carried out over a series of annealing process stations **200**.

[0062] The deposition of thin films onto substrates **10** is a critical processing step of the present invention. A detailed description of the deposition apparatus is given below.

[0063] The intermittent motion of the belts **1** allows a pause for deposition. During the pause, as shown in **FIG.** 2A, the individual substrates **10**, which are spaced at regular pitch intervals on the metal strip belts **1**, will be in a sealing relationship with individual heated pockets **33**. During this pause, the individual heated pockets **33** will deposit a film onto the substrates **10**. For a given pause time, the thickness of the films can be varied by varying the temperature of each individual heated pocket **33**. Closed loop control of film thickness may be achieved by measuring film thickness with known thickness monitors and adjusting the heated pocket **33** temperature as needed. Very precise control may be achieved since the deposition rate is a function of the temperature of the heated pocket **33**.

[0064] The present invention is specifically designed to produce very uniform film deposition across the surface of the substrate **10** at high throughput so that in a mass manufacturing environment the reproducibility of the film uniformity from one substrate **10** to another substrate **10** is tightly controlled over long periods of time. In order to accomplish this desired aspect of the present invention, the substrate **10** is held in a novel sealing relationship with the pocket **29**.

[0065] The novel sealing relationship is unique and is not shown or suggested in the prior art. **FIG. 6**A and **FIG. 6B** show an elevation view of two prior art devices used for film deposition by vacuum sublimation. In **FIG. 6**A, the known method of Bozler in U.S. Pat. No. 3,636,919 (1972) shows the source deposition material **35***a* and substrate **10***a* in an enclosed space. The enclosed space is formed by an upper heater **36** U and a lower heater **36** L. Because the substrate **10***a* is sealed in the enclosed space, the substrate **10***a* could not be moved and only one film could be deposited for each pump down of the vacuum chamber. **FIG. 6B** details another known method according to Bonnet in U.S. Pat. No. 5,304, 499 (1994) which is commonly known as close spaced sublimation (CSS). In this known method, the deposition material **35***a* is placed on a flat heated plate **36** L and the substrate is held at a typical distance of 2 to 3 mm from the deposition material **35***a*. The disadvantage of this known method is that the clearance between the deposition material **35***a* and the substrate **10***a* forms a leak path for the vapor. This leak will lead to non-uniform deposition and the formation of toxic nano particles in the process space.

[0066] The heated pocket deposition apparatus of the present invention overcomes the limitations of the prior art. With reference to **FIG. 7**A, there is a clearance distance **37** on the order of 0.001 in. to 0.018 in. between the substrate **10** and the top surface of the heated pocket **33** block. Clearance distance **37** is formed on the two sides of the substrate **10** where the substrate **10** spans the belts **1**. The clearance distance **37** is necessary to prevent the substrates **10** from touching the heated pocket **33** and damaging the deposited films. The clearance distance **37** is formed in such a manner as to provide a close tolerance slip fit seal between the top of the heated pocket **33** and the bottom of each of the substrates **10**. Any vapor leak through the clearance distance **37** will be in the molecular flow regime and will be very small. This effectively eliminates vapor leaks through the clearance distance **37** and allows the substrates **10** to act as a shutter across the source pocket **29**.

[0067] Furthermore, the walls of the pocket **29** will collimate the vapor flux from the subliming material **35**. Since the clearance distance **37** is at the top of the pocket **29** and at a right angle to the collimated vapor flux, nearly all of the vapor flux will pass the entry of the clearance distance **37** without directly entering it. Any vapor which does enter the clearance distance **37** due to gas scattering will be readily deposited on the surface of the substrate **10**. The design of the clearance distance **37** allows for movement of multiple substrates **10** while maintaining a vapor seal. This design has advantages over the prior art since it will maintain the deposition uniformity across the substrate **10**. In the present invention, the use of the substrates **10** to act as a shutter virtually eliminates cross contamination between heated pockets **33**. The elimination of cross contamination allows the use of one vacuum boundary for the multiple processing steps and reduces the capital cost of the system. In most vacuum processes for processing PV devices, load locks or load locks in combination with intermediate chambers are used to prevent cross contamination between processing steps.

[0068] As shown in **FIG. 7**A, the deposition material **35** must be distributed in an evenly spaced pattern across the floor of the pocket **29**. The deposition material **35** may be in the form of powder, pellets pressed from powder, or random chunks. All of these forms of material for the fabrication of CdTe PV are commercially available. Also, the distance between the deposition material **35** and the lower surface of the substrate **10**, which is provided by the depth of the pocket **29** in the lower heated pocket **33**, must be sufficient to allow for gas scattering of the sublimed species.

[0069] Gas scattering is the result of collisions among the sublimed species or between the sublimed species and the molecules of the ambient background gas. These collisions deflect and scatter the sublimed species from following a straight line path from the deposition material **35** to the substrate **10**. This scattering of the sublimed species results in a uniform deposition on the substrate **10** The Knudsen number is a known dimensionless parameter which is used to quantify the amount of gas scattering present. The Knudsen number is the ratio of the mean free path in the pocket **29**, at a given temperature and pressure, divided by the distance between the deposition material **35** and the substrate **10**. If the Knudsen number is less than 0.01, then the species within the pocket **29** are in viscous flow and gas scattering will be significant In this viscous flow regime, the gas scattering may lead to such a loss of energy from the sublimed species that they condense to form nano-particles.

For Knudsen numbers greater than 1, the species will be in a molecular flow regime with very little gas scattering. In this molecular flow regime, the sublimed species will travel in straight lines to the substrate. This line of sight deposition causes non-uniform film thickness across the substrate **10**. For Knudsen numbers between 0.01 and 1, the species will be in transition flow with some gas scattering. In the transition regime, the vapor flux is randomized by gas scattering. However, the number of collisions are few enough that the sublimed species retain most of their energy and therefore do not condense into nano-particles before striking the substrate **10**. In the present invention, deposition has been done with Knudsen numbers in the transition regime from 0.07 to 0.44, which has led to uniform film thickness across the substrate **10**.

[**0070**] An additional advantage of the present invention is the heating of the process gas in the pocket **29**. Since the substrates **10** act as a shutter for the heated pocket **33**, the process gas in the source pocket **29** comes to a uniform high temperature. The high temperature of the process gas in the heated pocket **33** is another factor which prevents the formation of nano-particles due to the gas scattering collisions described above.

[**0071**] The preferred embodiment of the present invention provides a means of forming a back electrode layer at high throughput and using equipment that is low capital cost. This layer is adherent to the other layers in the film stack and has a very low electrical resistivity. As shown in **FIG. 1**, the back electrode is fabricated by a novel spray process at atmospheric pressure in process stations **52***a* and **52***b*. A layer of conductive graphite coating followed by a layer of conductive Ni coating are applied by known industrial spray methods to form the back electrode for carrying current. Sprays containing other metals besides Ni are known and may also be used. A metal conductive coating layer may also be applied by spray directly to the ohmic contact layer without an intervening carbon layer. In this description, carbon is not considered a metal. To limit the inclusion of oxygen and water vapor into the metallization layer, the gas used as a propellant in the spray process may be a dry inert gas such as N_2 or Ar, and the process may be performed in a controlled environment.

[**0072**] The thick film of the back electrode contains a polymer binder, which provides a level of encapsulation and protection for the completed device. The spray is performed at room temperatures and does not harm or introduce defects into the previously fabricated semiconductor layers. The spray method has the advantage of low capital cost. Other known methods of metallization for PV devices, such as sputtering, require expensive high vacuum equipment.

[**0073**] The preferred embodiment of the present invention also provides a means of scribing that exhibits high throughput and low cost. As shown in **FIG. 1, a** scribing step may be performed at the film scribing station **53***a* after the graphite layer is formed by the spray process at the process station **52***a*. The scribing is performed after the application of the graphite layer to prevent any damage to the semiconductor layers by handling.

[**0074**] **FIG. 9A** illustrates the details of the preferred embodiment of the film scribing method. A rotating wire brush **42** is brought into contact through openings **45** in a mask **41** to remove portions of the film **40** from the substrate **10**. The openings **45** in the mask **41** are tapered in cross section and are narrower near the contact of the mask **41** and the film layers **40**. This facilitates the entry of the rotating brush **42** into the openings **45**. The mask **41** may be coated with a hard coating, such as titanium nitride, to reduce wear.

[**0075**] The preferred embodiment of the film scribing method shown in **FIG. 9A** does not require a precisely defined rotating brush **42** since the openings **45** in the mask **41** define the area of the film **40** which will be removed. The rotating wire brush **42** is passed axially along the openings **45** in the mask **41** over the substrate **10** to perform a scribe. A plurality of rotating metal brushes **42** may also be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes on an entire substrate **10**. This film scribing method has the ability to scribe layers selectively. By using an abrasive powder with the rotating brush **42**, the TCO layer may be scribed. By using the rotating brush **42** alone, all of the layers except the TCO layer may be removed.

[**0076**] The process steps of the preferred embodiment of the present invention are shown in the flow chart of **FIG. 10A**. The overall system **1000** required to perform the process is shown in **FIG. 1**. The apparatus required to perform the vacuum portion of the process, from step **2**) of **FIG. 10A** through step **12**) of **FIG. 10A**, is illustrated in **FIG. 2A**. With reference to **FIG. 2A**, the substrates **10** are transported through the vacuum process stations **200** and **300** on the metal strip belts **1**. As shown in **FIG. 10A**, these process steps may be performed by a single one or a series of the vacuum process stations **200** or **300** illustrated in **FIG. 2A**. The total time required for processing at each process station **200** or **300** and the transport of the substrate **10** to the next process station **200** or **300** is a unit of cycle time as defined above. The cycle time in the process description below is in the range of 30 seconds to 2 minutes.

[**0077**] With reference to **FIG. 10A, a** description of the process steps performed on each individual substrate **10** as the plurality of substrates **10** pass through the process is given below.

[**0078**] In step (1) the substrate **10**, which may have a TCO layer on one surface, is ultrasonically cleaned, rinsed, dipped in isopropyl alcohol to remove water from the surface, and dried in a clean room type mini-environment.

[**0079**] In step (2) the substrate **10** is transported into the vacuum chamber **3** through the AVA opening **2** using the metal strip belts **1**.

[**0080**] In step (3) the substrate **10** is heated to a temperature in the range of 500° C. to 560° C. and transported to the next process.

[**0081**] In step (4) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdS film is deposited onto the TCO layer on the substrate **10** and the substrate **10** is transported to the next process.

[**0082**] In step (5) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdTe film is deposited onto the CdS layer on the substrate **10** and the substrate **10** is transported to the next process.

[**0083**] In step (6) and step (7) a $CdCl_2$ treatment is performed on the CdS/CdTe layers. In step (6) with the temperature of the substrate **10** in the range of 300° C. to

500° C., the CdS/CdTe layers on the substrate **10** are exposed to $CdCl_2$ and the substrate **10** is transported to the next process. The $CdCl_2$ exposure of the CdS/CdTe layers on the substrate **10** may be to a $CdCl_2$ vapor or a $CdCl_2$ film may be deposited on the CdTe layer. Either method of $CdCl_2$ exposure will produce high efficiency CdTe PV devices. For this process step, a series of $CdCl_2$ treatment stations may be required.

[**0084**] In step (7) with the temperature of the substrate **10** in the range of 400° C. to 450° C., the $CdCl_2$ treated layers on the substrate **10** are annealed, any $CdCl_2$ film is removed, and the substrate **10** is transported to the next process. For this process step, a series of annealing stations may be required. In combination, step (6) and step (7) provide the $CdCl_2$ treatment of the CdS/CdTe layers. The $CdCl_2$ treatment of CdTe PV devices in vacuum is known. However, no prior art shows the $CdCl_2$ treatment step performed inline between the deposition of the CdTe layer and the formation of the ohmic contact layer and without the substrate leaving vacuum. Also, no prior art shows directly transporting substrates from CdTe deposition to $CdCl_2$ treatment.

[**0085**] In step (8) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

[**0086**] In step (9) and step (10) an ohmic low resistance contact is formed on the CdTe layer. In step (9) with the substrate **10** temperature in a range of 150° C. to 300° C., a metal salt is deposited onto the CdTe layer on the substrate **10**, and the substrate **10** is transported to the next process. One metal salt which has been used for this process step is CuCl. In step (10) with the temperature of the substrate **10** in a range of 150° C. to 250° C., the CdS/CdTe/metal salt layers on the substrate **10** are annealed, and the substrate **10** is transported to the next process. For this process step a series of annealing stations may be required. In combination, step (9) and step (10) produce a reaction between the metal salt and the surface of the CdTe layer and this reaction produces a thin p+ semiconductor layer on the CdTe surface to form the ohmic contact. In the case of a Cu salt, a copper telluride such as $CuTe_x$ or Cu doped CdTe:Cu or both may be formed. The thin p+ layer provides a low resistance ohmic contact on the surface of the CdTe layer and is stable. The prior art does not show the formation of an ohmic contact layer on CdTe by deposition of a metal salt onto the CdTe layer in vacuum.

[**0087**] In step (11) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

[**0088**] In step (12) the substrate **10** is transported out of the vacuum chamber **3** through the AVA opening **2** on the metal strip belts **1**.

[**0089**] In step (13) the ohmic contact layer is exposed to air for an optimum time in the range of 4 to 16 hours before a layer of conductive coating containing carbon is applied onto the ohmic contact layer by a spray process. The air exposure has led to PV devices with increased long term stability.

[**0090**] As described in the prior art, a series of scribes in selected film layers on the substrate **10** are required to isolate individual PV cells on the substrate and to interconnect the individual cells on the substrate **10** to form a completed module.

[**0091**] In step (14) a plurality of first scribes through the all of the film layers on the substrate **10** including the transparent conductive oxide are performed. A second plurality of scribes through the carbon and the p/n layers without removing the TCO are performed parallel to the first set of scribes. Both of these sets of scribes are performed by the novel film scribing method described above with reference to **FIG. 9A**.

[**0092**] In step (15) a layer of conductive coating containing Ni is applied by spray onto the layer of conductive coating containing carbon. Since the Ni metalization layer is formed after the second set of scribes, the Ni layer will fill the cuts in the semiconductor layers from the second scribe. This will cause an electrical connection of the back electrode of one cell to the front electrode of another cell. This step in combination with the following step of the final scribe of the metalization layer will complete the interconnection of the PV cells in series to form the PV module.

[**0093**] In step (16) a plurality of third scribes through only the metallization layers are performed. This third set of scribes is performed by the novel film scribing method described above with reference to **FIG. 9A**.

[**0094**] In step (17) electrical connections are made and the finished module is encapsulated.

[**0095**] In any of the film deposition steps, including the steps 4), 5), 6), or 9) of **FIG. 10A**, more than one layer of a particular material may be deposited. These multiple layers may be deposited by a series of heated pocket deposition apparatuses. If one layer of material is deposited in a given cycle time, to a given thickness, then this single layer may be replaced by many thinner layers built up to the thickness of the single layer of material by using many depositions at shorter cycle times. Multiple depositions are advantageous since for every decrease in cycle time there is a corresponding increase in production rate. Multiple processing stations can also be used to decrease the cycle time for the other steps including annealing, vapor treatment, cooling, etc.

[**0096**] It would also be possible to create a multifunction solar cell in accordance with the teachings of the present invention. In this case, a monolithic multifunction structure could be fabricated on the substrate. In this structure, two or more solar cells would be stacked on one substrate in such a way that solar radiation passes through the larger band gap material first, and residual radiation passes through the stack to a smaller band gap material. The band gap of the materials needed could be tailored by using semiconductors formed by the combination of any of the elements Zn, Cd, Hg, S, Se, or Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may be in the form of alloys containing three or more elements. The multiple layers may be deposited by a series of heated pocket deposition apparatuses. Also, by varying the composition of the deposition material in the multiple heated pockets, a graded band gap photovoltaic device may be fabricated.

[**0097**] Many devices were fabricated by following the process steps (1) through (13) and step (15) of **FIG. 10A** described above. CuCl was used as the metal salt in step (9). Individual PV devices with an area of 0.3 sq. cm. were formed on many substrates **10**. These devices were defined by masking certain areas and removing the rest of the films on the substrates **10** with an abrasive blast. The best device had a conversion efficiency of 11.8% and was produced on a commercially available low cost SnO_x:F coated soda lime glass substrate **10**. Such high efficiency devices have also proven to be stable. Accelerated stress testing by light soaking at 1000 W/m^2 and 65° C. at open circuit condition was performed on many devices. Over a time period of hundreds of hours, measured device efficiencies were at least 98% of the original efficiencies.

[**0098**] A description of the preferred embodiment of the present invention was given above. Other alternate embodiments of the present invention are described below. These specific alternate embodiments are best described with reference to **FIG. 10**A, which is a flow chart of the process steps of the preferred embodiment of the invention.

[**0099**] In alternate embodiments of step 9) in **FIG. 10**A, the deposition of the metal compound may include compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb. These compounds may be metal salts as described in the preferred embodiment or organometallic compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb may also be used. These compounds may be deposited onto CdTe in vacuum to form an ohmic low resistance contact layer by reaction with the CdTe layer. This ohmic low resistance contact may be formed by tellurides of Cu, Ag, Au, Hg, Sn, Sb, and Pb, or the ohmic contact may be highly doped CdTe. An alternative embodiment to step 10) of **FIG. 10A** is to anneal the ohmic contact layer in air, inert gas or other atmospheres outside the vacuum chamber.

[**0100**] In other embodiments of the process steps 4) and 5) of **FIG. 10A** other semiconductors may be used instead of CdS and CdTe. These semiconductors are formed by the combination of any of the elements Zn, Cd, Hg, S, Se or, Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may also be in the form of alloys containing three or more elements. These compound semiconductors are known to be useful in the formation of PV devices, are readily sublimable, and may be deposited in vacuum by the present invention. A series of stations may be used to deposit the n-type and p-type semiconductors. Thus, more than one layer may be used to form the n-type and p-type regions of the device This allows a faster cycle time while still maintaining adequate semiconductor film thickness. Also, the different stations may deposit different IIB-VIB compound semiconductors made up of the elements Zn, Cd, Hg, S, Se or, Te.

[**0101**] In alternate embodiments of step 6) of **FIG. 10**A, halogen containing substances such as HCl or Cl_2 gas may be used in place of or in addition to $CdCl_2$. In this case, a controlled amount of the gas can be introduced into the heated pocket **33**. Other halogen containing substances which are known to have effects similar to $CdCl_2$ may also be used. Some known examples of these compounds are $CdBr_2$ and CdI_2.

[**0102**] In another alternate embodiment of the process steps of **FIG. 10A, a** CdTe PV device may be fabricated without the deposition of CdS shown in step 4) of **FIG. 10A**. In this embodiment, the p/n junction is formed between the n-type TCO and the p-type CdTe or other IIB-VIB compounds.

[**0103**] In another embodiment of the process steps of **FIG. 10A, a** CdTe device may be fabricated by depositing the CdS layer on the substrate **10** outside of the vacuum chamber **3** by known methods, including chemical bath deposition. In this embodiment, the substrate **10** with the CdS layer would be brought into the vacuum chamber **3** and steps 3) through step 11) of **FIG. 10A** would be performed in vacuum.

[**0104**] In another embodiment of the process steps of **FIG. 10A, a** $CdCl_2$ treatment may be performed after step 4) CdS deposition and before step 5) CdTe deposition. This $CdCl_2$ treatment is in addition to the step 6) $CdCl_2$ treatment as shown in **FIG. 10A**. The additional $CdCl_2$ treatment is known to further increase the device performance.

[**0105**] In other alternative embodiments of **FIG. 10**A, the HPD deposition heated pocket **33** may be used to apply other film layers which would improve the performance of a CdS/CdTe PV device. One such layer is an anti-reflection (AR) coating which would be deposited on the glass substrate **10** on the opposite side of the substrate **10** from the TCO. The AR coating would face the sun and reduce the amount of incoming sunlight which is reflected off of the glass surface. This would increase the current that the device could produce. One such AR coating is a thin film of MgF_2. Since MgF_2 is sublimable, this film may be applied with the heated pocket **33** deposition. The AR coating can be done at a suitable location in the vacuum chamber **3**. Another layer which is known to increase the efficiency of a CdS/CdTe device is a layer of high resistivity intrinsic tin oxide (i-SnO_x). This layer would be applied between the TCO layer and the CdS layer or a layer of SnO_x of the desired resistivity could be deposited directly on the glass substrate **10**. This intrinsic layer has a much higher electrical resistivity than the TCO layer and has been shown to increase device efficiency. This resistive layer would allow the CdS layer to be thinner. The thinner CdS layer would allow more light to pass into the CdTe layer and increase the current the device would produce. The heated pocket **33** could be used to sublime i-SnO_x. The i-SnO_x deposition would be performed before the CdS deposition of step 4) of **FIG. 10A**.

[**0106**] An alternate embodiment to step 15) of **FIG. 10A** is that the graphite and Ni may be sprayed through a mask to form a patterned deposition. This patterned back electrode would eliminate the need for the second and third set of scribes shown in steps 14) and 16) of **FIG. 10A**. In another embodiment, a spray through a mask may also be used to fill the cut of the first scribe with an insulating compound before the spraying of the Ni conductive coating. The insulating compound eliminates electrical shunts between the Ni layer and the TCO.

[**0107**] Other alternate embodiments of the present invention are described below. The figures which show these alternative embodiments are **FIGS. 2B, 7B, 8, 9**B, and **10**B. These alternative embodiments are described with reference to these figures.

[**0108**] **FIG. 2B** shows an alternate embodiment of the present invention in which the pair of continuous metal strip belts **1** are entirely contained within the vacuum chamber **3**. A pair of known load locks **5** on either side of the chamber **3** provide a means of transporting the substrates **10** into and out of vacuum.

[**0109**] **FIG. 7B** illustrates an alternate embodiment of the vacuum process station of **FIG. 7A** involving a different arrangement for the upper heated pocket **33**. This alternate embodiment involves the addition of a baffle having a plurality of holes **28**. The deposition material **35** is placed above the baffle in a confined space. The confined space has a lid **27**, which may be removed to reload the deposition material **35**. As the upper heated pocket **33** is heated, the deposition material **35** will sublime, and vapor will pass through the holes **28** into the source pocket **29** of the upper heated pocket **33**. This alternative embodiment of the vacuum process station **200** may be used as the heated pocket **33** to deposit films on the upper surface of the substrate **10**. When the deposition is on the upper surface of the substrates **10**, the substrates **10** can be transported by arrangements such as rollers, robotic arms, etc., which are well known. This would be especially useful for the deposition of the AR coating.

[0110] **FIG. 8** illustrates an alternative to the heated pocket **33**. This embodiment can be used to generate plasma in the pocket **29**. This arrangement is called plasma enhanced heated pocket deposition (PEHPD). The alternate embodiment of the heated pocket **33** provides a high voltage pin **30** for the generation of plasma, the pin **30** may be made from graphite. The pin **30** is electrically isolated by insulation **31** which may be a quartz tube. The high voltage from the DC power supply **32** generates the plasma. The heated pocket-to-substrate distance in the PEHPD heated pocket must be large enough to produce ions within the pocket **29**. If the pocket **29** is too shallow it will not produce a glow discharge at desirable pressures, when the substrate **10** is sealing the pocket **29** during deposition. In alternate embodiments of the present invention, both the CdS and CdTe heated pocket may optionally be of the PEHPD type so that the advantages of plasma enhanced deposition may be incorporated. These advantages of plasma enhanced deposition, which serve to improve the device efficiency, include: (i) doping of CdTe with nitrogen, (ii) passivation of the defects in CdTe, (iii) alteration of the morphology of CdS, (iv) doping of CdS, and (v) mixing of the CdS/CdTe interface. In addition, ZnTe may be doped with nitrogen by PEHPD to form ZnTe:N, a p+ semiconductor layer which may be used as an ohmic contact to CdTe.

[0111] **FIG. 10B** is a flow chart of the process steps of some of the alternate embodiments of the invention. The processing steps as shown schematically in that figure include (1) cleaning the substrate by known means in a clean room type mini-environment, (2) transporting the substrate into the vacuum chamber using AVA or load lock transport, (3) heating the substrate, (4) depositing a CdS film on the substrate using heated pockets with or without plasma, (5) depositing a CdTe film onto the CdS film using heated pockets with or without plasma, (6) performing a treatment, with a halogen containing substance, on the CdS/CdTe films using a heated pocket, (7) annealing the substrate and films, (8) forming an ohmic contact on the CdTe layer by heated pocket deposition of a Te layer on the CdTe layer or by heated pocket deposition with plasma of a ZnTe:N layer on the CdTe layer, (9) depositing a metallization layer onto the ohmic contact layer by heated pocket deposition of a sublimable metal layer such as Zn or Cd, (10) annealing the substrate and films, (11) cooling the substrate and films, (12) transporting the substrate and films from the vacuum chamber using AVA or load lock transport, (13) performing a first scribe through the entire film stack including the metallization and the transparent conductive oxide, (14) screen printing the electrical connection of the back electrode of one cell to the front electrode of the next cell by known screen printing methods, and (15) encapsulating the finished module. Step (13) involves a first scribe that may be performed in accordance with the teachings of the present invention or by one of several known means including mechanical or laser scribing and a second scribe through the carbon and the p/n layers without removing the TCO.

[0112] Step 8) in **FIG. 10B** illustrates another alternative embodiment of the present invention in which Te is used as an ohmic contact layer Te is easily sublimed and is known to form an ohmic contact material for CdTe devices. After the $CdCl_2$ treatment and annealing steps, Te could be deposited inline by heated pocket deposition with or without a cooling step. A metal back electrode can be applied to the Te ohmic contact by either a vacuum deposition step or by the spray process of the present invention.

[0113] Step 9) of **FIG. 10B** illustrates an alternate embodiment of the present invention in which the back electrode metallization may be accomplished inline in vacuum. In this embodiment, the back electrode metallization may be applied by a heated pocket deposition of metals including, but not limited to, Zn or Cd, which are readily sublimable and electrically conductive.

[0114] **FIG. 9B** illustrates an alternative embodiment of the scribing method of the present invention involving the use of an abrasive blast **43** which is provided by known methods. The abrasive blast **43** is performed through openings **45** in the mask **41** to remove portions of the film **40** from the substrate **10**. This embodiment of the scribing method does not require a precisely defined abrasive blast **43** since the mask **41** defines the area of the film **40** which will be removed. The abrasive blast **43** is passed over the substrate **10** to perform a scribe. Each abrasive blast **43** may enter more than one opening **45** in the mask **41** so that one abrasive blast **43** may perform more than one scribe for each pass over the substrate **10**. A plurality of abrasive blasts **43** may be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes of an entire substrate **10**. Different abrasive media with different hardness and size may be provided so that various layers in the film stack **40** may be scribed selectively. This allows the scribing method of the present invention to: 1) scribe all the way through the film stack including the relatively hard TCO layer, and 2) selectively scribe through all of the layers above the TCO layer without removing the TCO.

We claim:

1. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level, the method comprising the steps of:

providing, in the vacuum chamber, a substrate upon which the photovoltaic cell is to be fabricated;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of n-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto the one or more layers of n-type IIB/VIB semiconductor material in the vacuum chamber;

treating the one or more layers of n-type IIB/VIB and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber by depositing a metal compound onto the treated one or more layers of p-type IIB/VIB semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

2. A method as in claim 1, wherein the n-type semiconductor material comprises cadmium sulfide.

3. A method as in claim 1, wherein the p-type semiconductor material comprises cadmium telluride.

4. A method as in claim 1, wherein the halogen containing substance comprises cadmium chloride.

5. A method as in claim 1, further comprising the step of depositing in the vacuum chamber a layer of a transparent conductive oxide onto the substrate prior to the step of depositing the one or more layers of n-type IIB/VIB semiconductor onto the substrate.

6. A method as in claim 1, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

7. A method as in claim 1, further comprising the step of treating the one or more layers of n-type IIB/VIB semiconductor material with the halogen containing substance prior to depositing the one or more layers of p-type IIB/VIB semiconductor material.

8. A method as in claim 7, wherein the halogen containing substance comprises cadmium chloride.

9. A method as in claim 7, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material with the halogen containing substance comprises:

exposing the one, or more layers of n-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material previously exposed to the vapor of the halogen containing substance.

10. A method as in claim 9, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material is exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of n-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and removing the previously deposited film of the halogen containing substance.

11. A method as in claim 1, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material that have been exposed to the vapor of the halogen containing substance.

12. A method as in claim 11, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material and removing the previously deposited film of the halogen containing substance.

13. A method as in claim 1, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

14. A method as in claim 1, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

15. A method for forming an ohmic contact on one or more layers of p-type IIB/VIB semiconductor material, the method comprising the steps of:

depositing a metal compound onto the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber; and

annealing the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

16. A method as in claim 15, wherein the step of annealing the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber comprises heating said one or more layers of p-type IIB/VIB semiconductor material in a suitable gas.

17. A method as in claim 15, wherein the one or more layers of p-type IIB/VIB semiconductor material comprises cadmium telluride.

18. A method as in claim 15, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

19. A method as in claim 15, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

20. A method for forming a conductive electrode on a desired surface of a semiconductor device, the method comprising the steps of:

spraying a conductive graphite coating onto the desired surface; and spraying a conductive metal coating onto the conductive graphite coating.

21. A method as in claim 20, wherein the conductive metal coating comprises nickel.

22. A method for forming a conductive electrode on a desired surface of a semiconductor device, the method comprising the steps of:

spraying a conductive metal coating onto the desired surface; and

drying the sprayed conductive metal coating.

23. A method for scribing one or more selected layers of a photovoltaic device, the method comprising the steps of:

positioning a contact mask over the one or more selected layers, the contact mask having openings defining areas of the one or more layers to be removed; and

impacting the one or more selected layers through the openings in the contact mask to remove the defined areas of one or more selected layers.

24. A method as in claim 23, wherein the step of impacting the one or more selected layers through the openings in the contact mask comprises abrasive blasting with a selected medium.

25. A method as in claim 23, wherein the step of impacting the one or more selected layers through the openings in the contact mask comprises applying a rotating abrasive device to the one or more selected layers through the openings in the contact mask.

26. Apparatus for transporting substrates within a vacuum chamber, the apparatus comprising:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert; and

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts.

27. Apparatus for transporting substrates within a vacuum chamber as in claim 26, wherein the vacuum chamber includes front and rear openings through which the pair of metal belts and the substrates pass, extending outside said front and rear openings, the apparatus further comprising:

a clearance distance between each of the substrates and the front and rear openings so as to permit motion of the substrates while at the same time restricting air leaks, to thereby maintain a desired level of vacuum in the chamber.

28. Apparatus for transporting and processing a plurality of substrates by exposing them to heating, film deposition or vapor treatment within a vacuum chamber, the apparatus comprising:

a plurality of heated pockets positioned in proximity to and in correspondence with each of the plurality of substrates such that a clearance distance between a surface of each of the substrates and the corresponding one of the heated pockets is minimized so as to permit motion of the substrates while restricting vapor leaks from the heated pockets; and

a transporter for moving the substrates from one heated pocket to the next.

29. Apparatus as in claim 28, wherein the transporter comprises:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert;

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts; and

a controller, coupled to said translator for indexing the belts incrementally to move each of the substrates from one heated pocket to another.

30. Apparatus as in claim 28, wherein a selected one or more of the heated pockets includes a high voltage pin coupled to a source of D.C. voltage for creating a plasma within the selected one or more of the heated pockets.

31. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level the method comprising the steps of:

providing, in the vacuum chamber, a substrate having one or more layers of an n-type transparent conductive oxide upon which the photovoltaic cell is to be fabricated;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

32. A method as in claim 31, wherein the p-type IIB/VIB semiconductor material comprises cadmium telluride.

33. A method as in claim 31, wherein the halogen containing substance comprises cadmium chloride.

34. A method as in claim 31, wherein the step of treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material that have been previously exposed to the vapor of the halogen containing substance.

35. A method as in claim 34, wherein:

the temperature at which the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semidconductor material and removing the film of the previously deposited halogen containing substance.

36. A method as in claim 31, wherein the step of forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material comprises depositing a metal compound onto the treated one or more layers of p-type semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

37. A method as in **36**, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony and mercury.

38. A method as in claim 36, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

39. A method as in claim 31, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

40. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level, the method comprising the steps of:

providing, in the vacuum chamber, a substrate upon which the photovoltaic cell is to be fabricated, the substrate having one or more layers of n-type transparent conductive oxide thereon and one or more layers of n-type IIB/VIB semiconductor material on top of the one or more layers of n-type transparent conductive oxide;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

41. A method as in claim 40, wherein the n-type IIB/VIB semiconductor material comprises cadmium sulfide.

42. A method as in claim 40, wherein the p-type IIB/VIB semiconductor material comprises cadmium telluride.

43. A method as in claim 40, wherein the halogen containing substance comprises cadmium chloride.

44. A method as in claim 40, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material that have been previously exposed to the vapor of the halogen containing substance.

45. A method as in claim 44, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance upon the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material and removing the film of the previously deposited halogen containing substance.

46. A method as in claim 40, wherein the step of forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material comprises depositing a metal compound onto the treated one or more layers of p-type IIB/VIB semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

47. A method as in claim 46, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

48. A method as in claim 46, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

49. A method as in claim 40, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

50. A method as in claim 40, further comprising the step of treating the one or more layers of n-type IIB/VIB semiconductor material with a halogen containing substance prior to depositing the one or more layers of p-type IIB/VIB semiconductor material.

51. A method as in claim 50, wherein the halogen containing substance comprises cadmium chloride.

52. A method as in claim 50, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material that has been previously exposed to the vapor of the halogen containing substance.

53. A method as in claim 50, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material is exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of n-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and removing the film of the previously deposited halogen containing substance.

* * * * *

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(54) PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

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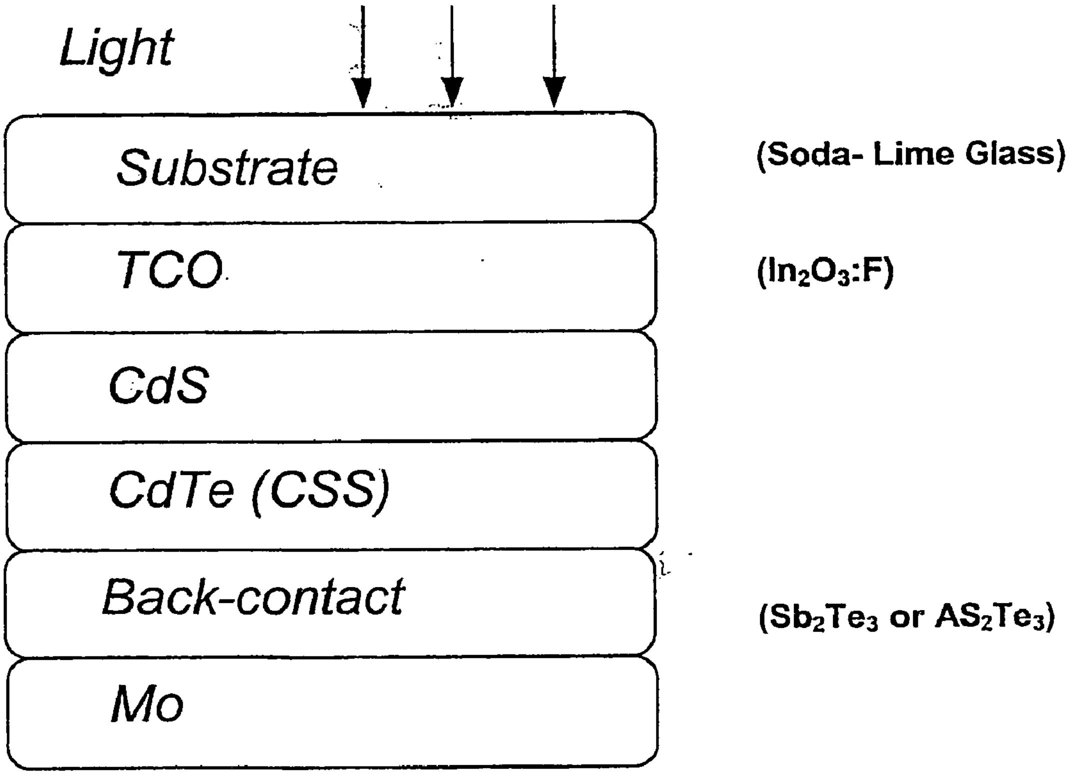
(57) ABSTRACT

A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequences on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; depositing a back-contact film on the treated CdTe film. Treatment of the CdTe film with $CdCl_2$ comprises the steps of: forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature; annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.



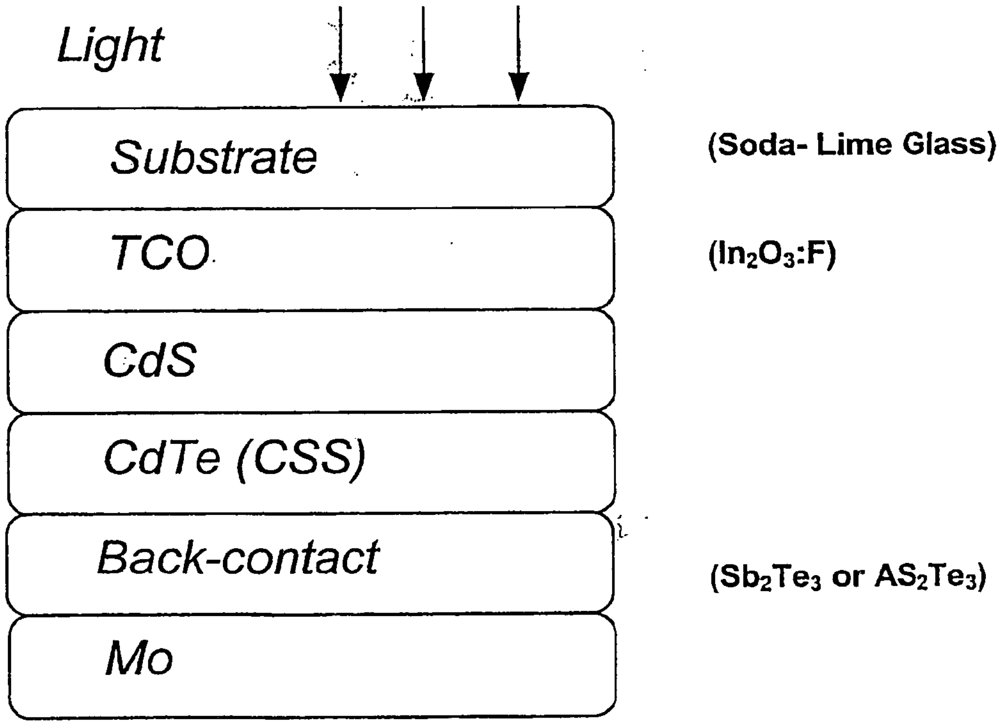

Light
Substrate
TCO
CdS
CdTe (CSS)
Back-contact
Mo
(Soda- Lime Glass)
(In_2O_3:F)
(Sb_2Te_3 or AS_2Te_3)

Fig. 1

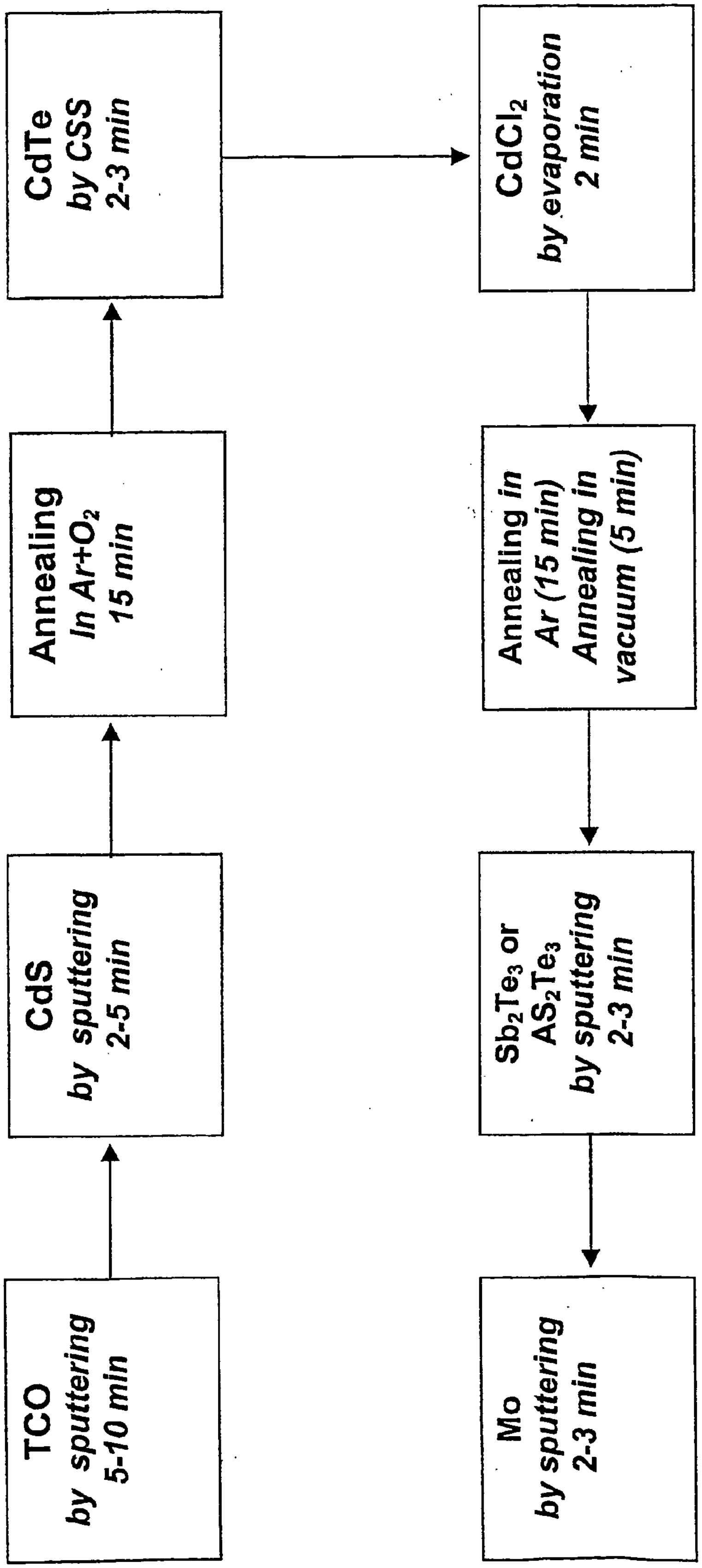

TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In Ar+O2
15 min
CdTe
by CSS
2-3 min
CdCl2
by evaporation
2 min
Annealing in
Ar (15 min)
Annealing in
vacuum (5 min)
Sb2Te3 or
AS2Te3
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

FIELD OF THE INVENTION

[0001] The present invention relates to the field of the solar cells technology and more particularly concerns a process for the large-scale production of CdTe/CdS thin film solar cells.

BACKGROUND ART OF THE INVENTION

[0002] As is known, a typical configuration of a CdTe/CdS solar cell has a film sequence of the multi-layer arrangement comprising a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film representing the n-conductor, a CdTe film representing the p-conductor and a metallic back-contact. A solar cell with a layer arrangement and structure of this type is disclosed, for example, in U.S. Pat. No. 5,304,499.

[0003] The commercial float glass may be used as a transparent substrate, but, in spite of its low cost, special glasses are often preferred to avoid drawbacks of the float glass, in particular Na diffusion into TCO film.

[0004] The most common TCO is In_2O_3 containing 10% of Sn (ITO). This material has a very low resistivity on the order of 3×10^{-4} Ωcm and high transparency (>85%) in the visible spectrum. However, this material is made by sputtering and the ITO target after several runs forms some noodles which contain an In excess and a discharge between noodles can happen during sputtering which can damage the film. Another material which is commonly used is fluorine doped SnO_2 which however exhibits a higher resistivity close to 10^{-3} Ωcm and as a consequence a 1 μm thick layer is needed in order for the sheet resistance to be around 10 $\Omega/_{\text{square}}$. A high TCO thickness decreases the transparency and then the photocurrent of the solar cell. Finally a novel materia+03–1, namely Cd_2SnO_4 has been developed by the NREL group (X. Wu et al., *Thin Solid Films,* 286 (1996) 274-276)). Also this material has some drawbacks since the target is made up of a mixture of CdO and SnO_2 and, being CdO highly hygroscopic, the stability of the target may result to be unsatisfactory.

[0005] The CdS film is deposited by sputtering or Close-Spaced Sublimation (CSS) from CdS granulate material. This last technique allows the preparation of thin films at a substrate temperature much higher than that used in simple vacuum evaporation or sputtering, because substrate and evaporation source are put very close to each other at a distance of 2-6 mm and the deposition is done in the presence of an inert gas such as Ar, He or N_2 at a pressure of 10^{-1}-100 mbar. A higher substrate temperature allows the growth of a better crystalline quality material. An important characteristic of the close-spaced sublimation is a very high growth rate up to 10 μm/min, which is suitable for large-scale production.

[0006] CdTe film is deposited on top of CdS film by close-spaced sublimation (CSS) at a substrate temperature of 480-520° C. CdTe granulate is generally used as a source of CdTe which is vaporised from an open crucible.

[0007] An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$. Most research groups use to carry out this step by depositing on top of CdTe a layer of $CdCl_2$ by simple evaporation or by dipping CdTe in a methanol solution containing $CdCl_2$ and then anneal the material in air at 400° C. for 15-20 min. It is generally believed that the $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of small grains and by removing several defects in the material.

[0008] After $CdCl_2$ treatment, CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ have to be removed in order to make a good back contact onto CdTe. Besides it is believed that, since etching produces a Te-rich surface, the formation of an ohmic contact when a metal is deposited on top of CdTe is facilitated.

[0009] The electric back contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g. in graphite contacts, which, upon annealing, can diffuse in the CdTe film. The use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell has been disclosed by the same applicants (N. Romeo et al., *Solar Energy Materials & Solar Cells,* 58 (1999), 209-218)

[0010] Industrial interest towards thin films solar cells is increased in recent years also in view of the high conversion efficiency reached so far. A record 16,5% conversion efficiency has been recently reported (see X.Wu et al., 17th *European Photovoltaic Solar Energy Conversion Conference*, Munich, Germany, 22-26 Oct. 2001, II, 995-1000). Therefore several efforts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells.

[0011] A state-of-the-art report concerning this issue may be found in D. Bonnet, *Thin Solid Films* 361-362 (2000), 547-552. However, a number of problems still hinder the achievement of this result, in particular concerning some crucial steps which affect either stability and efficiency of CdTe/CdS thin film solar cells or their costs.

[0012] A major problem of the known processes is the etching step to which the CdTe surface must be submitted to remove CdO or $CdTeO_3$ oxides formed thereon. Since etching requires the immersion of substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for a continuous operation presently does not exist. Another significant problem which negatively affects the stability of the TCO films, as well as the cost of the final product are the drawbacks presently encountered with the use of known TCOs, as previously mentioned. In addition to these drawbacks, known TCOs require the use of special glasses, such as borosilicate glass, to avoid the problem of Na diffusion, occurring if a soda-lime glass is used, which would damage the film.

[0013] A further problem concerns the source from which the CdS film and the CdTe film are produced by close-spaced sublimation. When small pieces of these materials containing dust are used as a sublimation source, due to a different thermal contact, some micro-particles can be overheated and then split on to the substrate together with the vapour. In order to avoid this inconvenience, complicated metallic masks are used in some cases, which make a continuous operation problematic.

OBJECT AND SUMMARY OF THE INVENTION

[0014] It is the main object of the present invention to provide a process suitable for a large-scale production of stable and efficient CdTe/CdS thin film solar cells on a low cost substrate.

[0015] A particular object of the present invention is to provide a process of the above mentioned type in which the treatment of the CdTe film with $CdCl_2$ is conducted in such a way as not to require an etching treatment to remove the oxides possibly formed on the CdTe film.

[0016] A further object of the present invention is to provide a process of the above mentioned type, in which the deposition of the TCO film is conducted in such a way that a film of very low resistivity can be deposited without formation of any metal noodles on the target and allowing the use of a inexpensive substrate.

[0017] Still another object of the invention is to provide a process of the above-mentioned type, which allows the formation of CdS and CdTe films completely free of dusts.

[0018] A further object of the present invention is to provide a stable, efficient and relatively low-cost CdTe/CdS thin film solar cell.

[0019] The above object are achieved with the process for the large scale production of CdTe/CdS thin film solar cells, the main features of which are set forth in claim **1**.

[0020] According to an important aspect of the invention, the treatment of the CdTe film with $CdCl_2$ is carried out by first forming a 100-200 nm thick layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at 380-420° C. and 300-1000 mbar under inert gas atmosphere; and finally removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. In this way, there is no need for the etching treatment of the CdTe film and the process can be conducted in a continuous way.

[0021] According to another aspect of the invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing 1-3 vol. % hydrogen and a gaseous fluoroalkyle compound, in particular CHF_3. In this way the TCO is doped whit fluorine

[0022] According to another important aspect of the invention, as a source material for the formation of the CdS and the CdTe films by sputtering or close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

[0023] Further features of the process according to the invention are set forth in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Further features and advantages of the process for large-scale production of CdTe/CdS thin film solar cells according to the present invention will be apparent from the following description of a preferred embodiment made with reference to the attached drawings, wherein:

[0025] **FIG. 1** is a schematic representation of the film sequence of the CdTe/CdS thin film solar cells according to the invention;

[0026] **FIG. 2** is a schematic diagram of the process according to the invention.

DESCRIPTION OF AN EMBODIMENT OF THE INVENTION

[0027] With reference to the figures+, the CdTe/CdS solar cells produced with the process according to the invention comprise five layers deposited in a sequence on a transparent base layer or substrate and consisting of a 300-500 nm thick layer of a transparent conducting oxide (TCO), a 80-200 nm thick layer of CdS deposited on top of the TCO layer, a 4-12 μm thick layer of CdTe on top of the CdS layer and a back contact layer formed by at least 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate consists of soda-lime glass and the transparent conducting oxide is fluorine-doped (In_2O_3:F).

[0028] TCO layer consists of In_2O_3, which is doped with fluorine during the growth. The In_2O_3 target, differently from ITO, does not form any noodle. A very low resistivity is obtained by introducing in the sputtering chamber a small amount of fluorine in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a Ar+H_2 mixture, in which H_2 is 20% in respect to Ar. A typical example is a 500 nm film of In_2O_3 deposited with a deposition rate higher than 10 Å/sec at a substrate temperature of 500° C., with an Ar flow-rate of 200 sccm, a CHF_3 flow-rate of 5 sccm and an Ar+H_2 flow-rate of 20 sccm. In this way, the reactive sputtering gas is composed by Ar containing 2.5 vol. % of CHF_3 and 1.8 vol. % of H_2. This film exhibits a sheet resistance of $5\ \Omega/_{square}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than 85% in the wavelength range of 400-800 nm. Another characteristic of this film is its good stability and the ability to stop Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable even if heated up to 180° C. when illuminated by "ten suns" for several hours.

[0029] After deposition of the CdS film and CdTe film in the known way by sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ in the following way.

[0030] 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. An annealing of 15-20 min is done at 400° C. in a vacuum chamber in which 500 mbar of Ar are introduced. After the annealing the chamber is evacuated keeping the substrate at 400° C. for 5 min. and, since $CdCl_2$ has a high vapour pressure at 400° C., any residual $CdCl_2$ re-evaporates from the CdTe surface.

[0031] CdO or $CdTeO_3$ are not formed since the annealing is conducted in an inert atmosphere, which does not contain O_2.

[0032] According to the present invention a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing on top of CdTe film a thin layer of a highly conducting p-type semiconductors such as Sb_2Te_3 or As_2Te_3. A good not rectifying contact is obtained on a clean CdTe surface if at least 100 nm thick layer of Sb_2Te_3 or As_2Te_3 is deposited by sputtering at a substrate temperature respectively of 250-300° C. and 200-250° C.

Sb_2Te_3 grows naturally p-type with a resistivity of 10^{-4} Ωcm, while As_2Te_3 grows p-type with a resistivity of 10^{-3} Ωcm. The contact procedure is completed by covering the low resistivity p-type semiconductor with at least 100 nm of Mo, as common practice in the art. A thin layer of Mo is needed in order to have a low sheet-resistance on the back-contact.

[**0033**] As a source for the CdS and CdTe materials used to form the respective layers by sputtering or CSS a granulate material can be used, as common practice in this field. However, in view of the drawbacks mentioned above when operating in this way, according to a particularly preferred aspect of the invention a new sublimation source can be used which consists of a compact block obtained by melting and solidifying the material in an oven able to sustain a temperature higher than the melting temperature of the material. The procedure to prepare the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3), which is a low melting point material (450° C.) and exhibits a very low vapour pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over CdS and covers CdS completely upon cooling. In this way, CdS covered by B_2O_3, if it is put into an oven containing an inert gas at pressure higher than 50 atm, does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of 1750° C., the oven is heated up to a temperature of 1800° C. or more and then cooled down to room temperature. In this way, a unique compact block of CdS is obtained which results to be particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared with this type of source resulted to be very smooth and completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically 100 nm thick. The substrate temperature is kept at 200-300° C. when CdS is prepared by sputtering and at 480-520° C. when it is prepared by close-spaced-sublimation. The sputtered CdS layer needs an annealing at 500° C. in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a high efficiency. In the case CdS is prepared by close-spaced sublimation, O_2 is introduced in the sublimation chamber during the deposition. The role of O_2 is not known, but it is presumed to passivate the CdS grain boundaries.

[**0034**] In a preferred embodiment of the invention, the CdTe source too is a compact block obtained by melting and solidifying pieces of CdTe in an oven under high pressure as described previously. Since CdTe melts at 1120° C., the oven needs to be heated up to 1200° C. in order to have a complete melting of the CdTe pieces. CdTe films are deposited on top of CdS by close-spaced sublimation at a substrate temperature of 480-520° C. Deposition rates during the CdTe growth are typically 4 μm/min. In this way 8 μm of CdTe are deposited in 2 min.

[**0035**] By following the procedure described above several solar cells have been prepared by using as a substrate a 1 inch square low-cost soda-lime glass.

[**0036**] A typical area of these cells is 1 cm^2. The finished cells are generally put under 10-20 suns for several hours at a temperature of 180° C. in the open-circuit-voltage (V_{oc}) conditions. No degradation has been notified but rather a 20% or more increase in the efficiency has been found.

[**0037**] The efficiency of these cells are in the range 12%-14% with open-circuit-voltages (V_{oc}) larger than 800 mV, short-circuit-currents (J_{sc}) of 22-25 mA/cm^2 and fill-factors (ff) ranging from 0.6 to 0.66.

EXAMPLE

[**0038**] A cell exhibiting a 14% efficiency has been prepared in the following way: a soda-lime glass has been covered by 500 nm of In_2O_3:F (fluorine-doped) deposited at 500° C. substrate temperature as described above. 100 nm of CdS have been deposited by sputtering at 300° C. substrate temperature and annealed for 15 min at 500° C. in 500 mbar of Ar containing 20% of O_2. 8 μm of CdTe have been deposited on top of CdS by CSS at a substrate temperature of 500° C. Both CdS and CdTe films are produced from a compact block source as described above. A treatment with 150 nm of $CdCl_2$ has been done in an Ar atmosphere as described above. Finally a back contact has been created, without any etching, by depositing in sequence by sputtering 150 nm of Sb_2Te_3 and 150 nm of Mo.

[**0039**] After one hour under 10 suns at a temperature of 180° C. in open-circuit conditions the solar cell prepared in this way exhibited the following parameters:

V_{oc}	852 mv
J_{sc}	25 mA/cm^2
ff	0.66
efficiency	14%

[**0040**] The techniques used in this process such as sputtering and close-spaced sublimation are both fast, reproducible and easily scalable.

[**0041**] Sputtering systems capable to cover 1×0.5 m^2 area glass are already commercial, while close-spaced sublimation, which at a laboratory scale can cover easily 20×20 cm^2 area glass, does not give any problem in being scaled up to 1×0.5 m^2. An in-line process can work well if a large area glass is made to move slowly over the different sources namely TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3 and Mo. In order to make a series connection between the single cells the in-line system should also contain three laser scribing processes, the first after the TCO deposition, the second one before the back-contact deposition and the third one at the end of the process. An important part of the process according to the present invention is that no use is made of acids or liquids and, as a consequence, the process can operate on a continuous basis without the interruption which is needed to make the etching in acid or in a Br-methanol solution.

1. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the treatment of the CdTe film with $CdCl_2$ comprises the steps of

forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature;

annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; and

removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process set forth in claim 1, wherein the $CdCl_2$ layer is between about 100 nm and about 200 nm thick.

3. The process set forth in claim 1, wherein annealing of the $CdCl_2$ layer is carried out for about 15-20 minutes.

4. The process set forth in claim 1, wherein the inert gas is Ar.

5. The process set forth in claim 1, wherein the back-contact film is formed of a Sb_2Te_3 layer covered by a layer of Mo.

6. The process set forth in claim 5, wherein the Sb_2Te_3 layer is formed by sputtering at a temperature between about 250° C. and about 300° C.

7. The process set forth in claim 1, wherein the back-contact film is formed of a As_2Te_3 layer covered with a layer of Mo.

8. The process set forth in claim 7, wherein the As_2Te_3 layer is formed by sputtering at a temperature between about 200° C. and about 250° C.

9. The process set forth in claim 1, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process set forth in claim 9, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

11. The process set forth in claim 10, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen bv volume, and wherein the fluoroalkyle compound is CHF_3.

12. The process set forth in claim 1, wherein, as a source material for formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

13. The process set forth in claim 12, wherein the compact block CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

14. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

15. The process set forth in claim 14, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

16. The process set forth in claim 15, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume and wherein the fluoroalkyle compound is CHF_3.

17. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

18. The process set forth in claim 17, wherein the compact block of CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than about 50 atm. and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

19. The process set forth in claim 1, wherein the transparent substrate is soda-lime glass.

20. A CdTe/CdS thin film solar cell product of the process set forth in claim 14.

* * * * *

US005304499A

United States Patent [19]

Bonnet et al.

[11] **Patent Number: 5,304,499**

[45] **Date of Patent: Apr. 19, 1994**

[54] METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

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[73] Assignee: **Battelle-Institut e.V.**, Frankfurt am Main, Fed. Rep. of Germany

[21] Appl. No.: **929,514**

[22] Filed: **Sep. 28, 1992**

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.**^{5} **H01L 31/18**; H01L 31/072

[52] **U.S. Cl.** **437/5**; 136/260; 136/264; 437/102; 437/234; 427/76

[58] **Field of Search** 437/4-5, 437/81, 87, 103, 139, 234; 427/74, 76; 136/260, 264

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Primary Examiner—Aaron Weisstuch

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[57] ABSTRACT

A method of making pn CdTe/CdS thin film solar cells, in which a transparent TCO layer is deposited as a front contact on a transparent substrate in the form of inexpensive soda-lime glass, and is preferably provided with an ultra-thin indium layer, which is in turn coated with the CdS layer, wherein the thus coated substrate is brought to the CdTe coating at a temperature between 480° C. and 520° C., which is maintained during the ensuing rapid CdTe deposition using the close-spaced sublimation method with a preferred rate of deposition of 5 to 15 μm/min in an inert atmosphere. The indium layer dissolves during this deposition and effects the necessary n-doping of the CdS layer, without an additional method step. Solar cells can be made in this way with high efficiency in an inexpensive method, suitable for mass production.

10 Claims, 2 Drawing Sheets

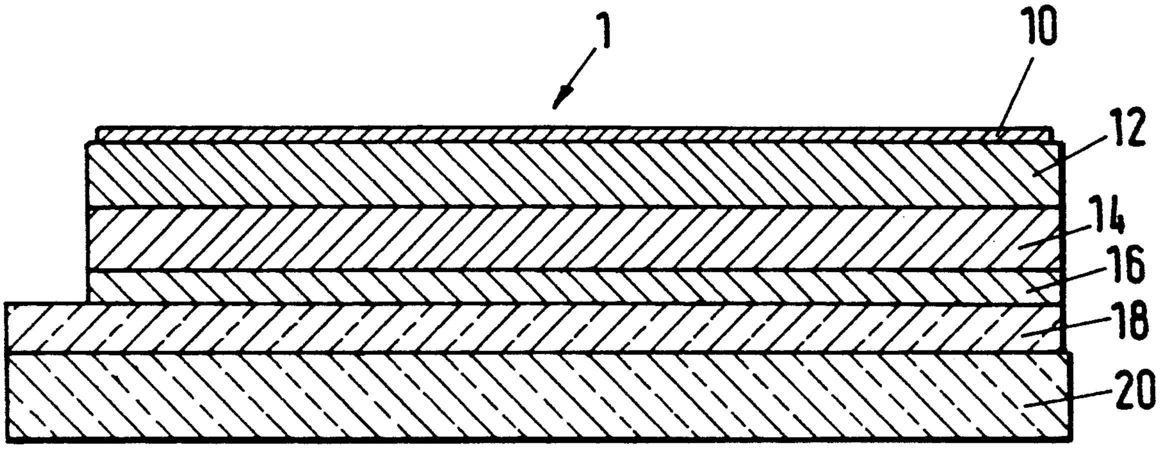


Fig.1

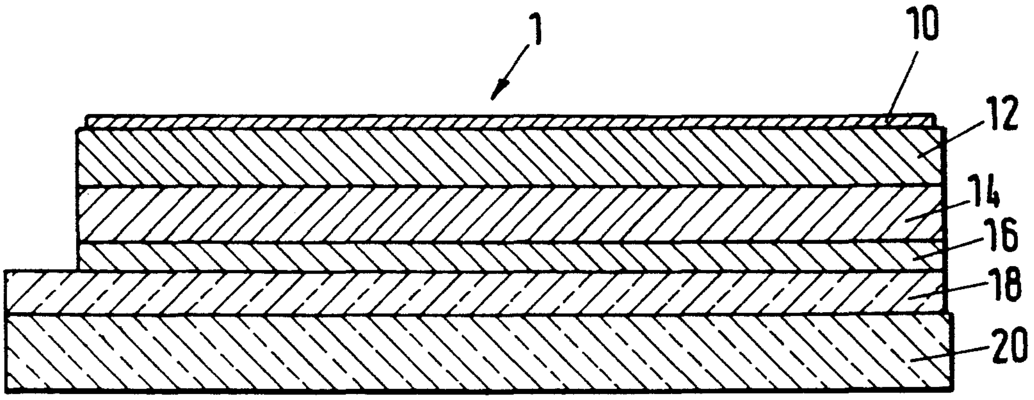


Fig.2

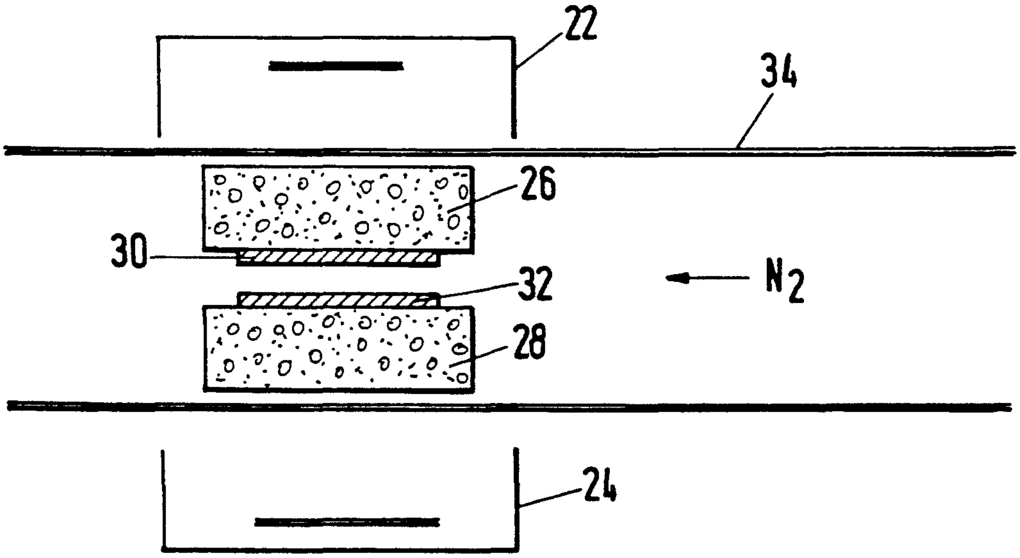
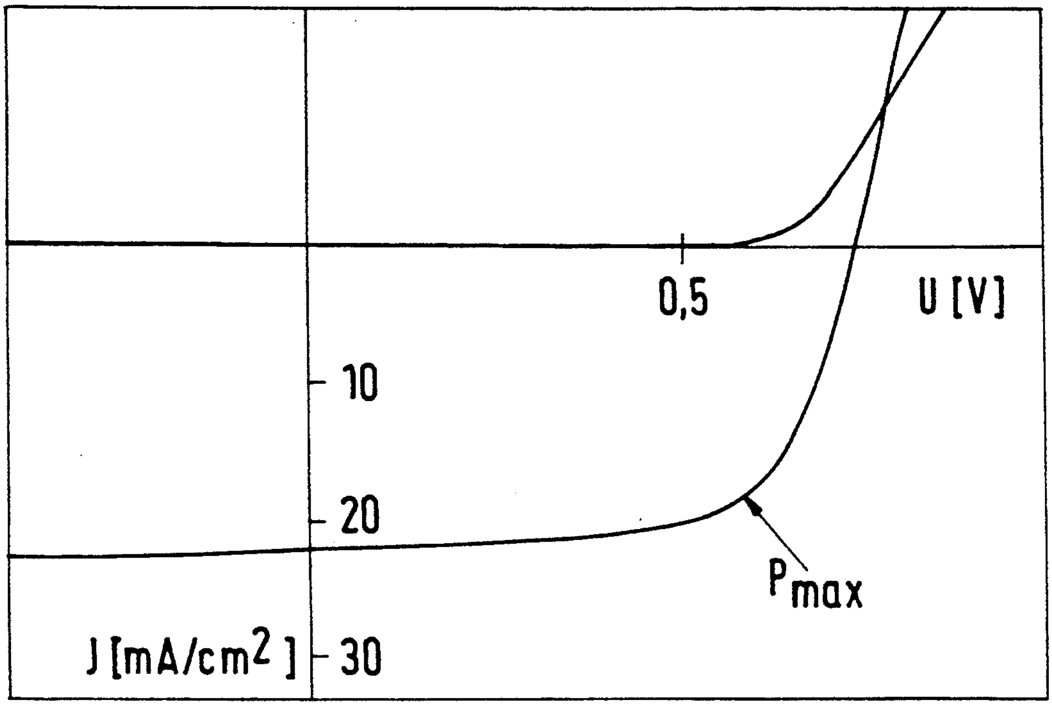


Fig.3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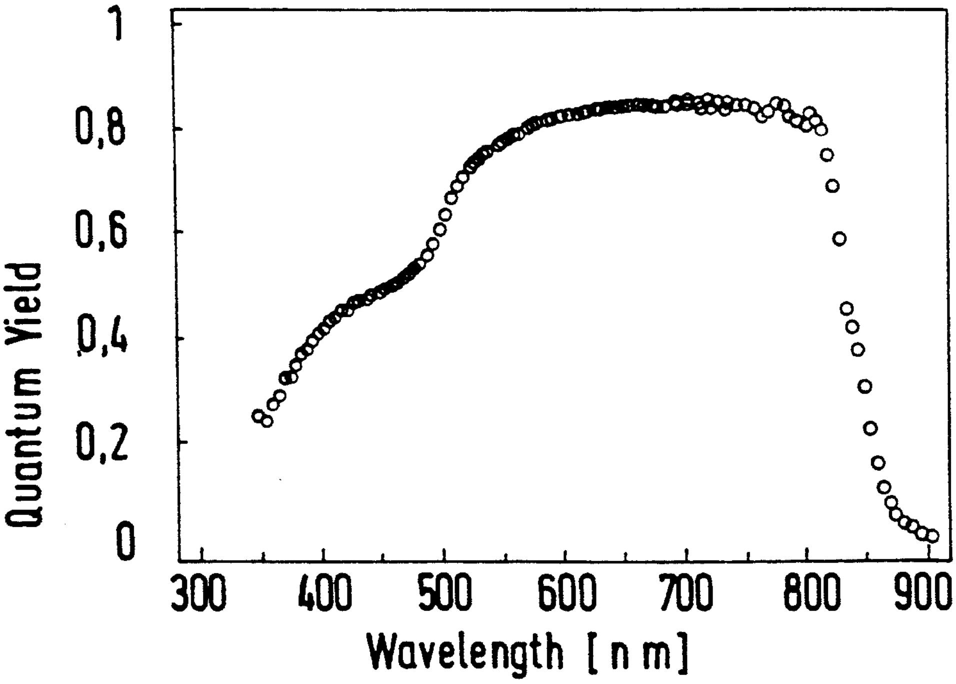
30
P_{max}

Fig.4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Quantum Yield
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700
800
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Wavelength [n m]

METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

The present invention relates to methods of making polycrystalline pn CdTe/CdS thin film solar cells and especially such methods which make inexpensive mass production possible.

Because of its favorable energy gap of 1.45 eV, CdTe is ideally suited as photo-active material for solar cells. Moreover, polycrystalline layers of a few μm thickness can be made by various methods (physical or chemical evaporation/sublimation in a vacuum, electrolytic deposition, screen printing, spray methods), which in general are subjected to a chemical-thermal post-treatment to improve their electronic properties (R. W. Birkmire et al, Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84). These two characteristics make CdTe one of the most interesting candidates for inexpensive thin film solar cells.

CdTe came into use in thin film solar cells for the first time around 1960. At the end of the 70's efficiencies for such solar cells of around 9% were reported. For example, U.S. Pat. No. 4,207,119 (Yuan-Sheng Tyan, 1980) describes a CdS/CdTe solar cell with oxygen as the dopant in both semiconductor layers CdS and CdTe of the cells. There is a disadvantage in the use of oxygen during the manufacture of the layers, since oxidation of the CdTe source can occur easily at too high an oxygen concentration in the deposition chamber, whereby the process of deposition is adversely affected or even interrupted. Moreover, the temperature of the substrate on which the polycrystalline CdTe layer was deposited is at least 575° C. and expensive temperature resistant glass substrates are used (with softening temperatures of 650° to 700° C.). Below a substrate temperature of 575° C. a significant fall-off in the attainable efficiency is observed. Thus, the CdTe layer was deposited experimentally at low temperatures in an atmosphere containing oxygen down to 500° C., when, however, an efficiency of less than 4% resulted. The possibility of increasing the efficiency by 1 to 2% by additional subsequent oxygen post-treatment was also proposed, whereby only values of 6% maximum resulted at 500° C. Attempts were also made to deposit the CdS layer free from oxygen, in contrast to the CdTe layer. The attempts showed, however, that the CdS layer also had to be deposited in an atmosphere containing oxygen, in order to be able to attain an efficiency of up to 8.9% at substrate temperatures above 575° C. In the experiments performed, CdTe layers 0.5 μm thick were deposited in 2 min. With a minimum thickness of around 2 to 3 μm needed for physical reasons, approximately 10 min. is already needed for the deposition.

In U.S. Pat. No. 4,650,921 (Kim W. Mitchell, 1987) there is described a pn CdTe/SnO_2 thin film solar cell, in which the polycrystalline CdTe layer is also deposited at high substrate temperatures (600°-650° C.), whereby the usual expensive temperature resistant glass substrates are also used. The CdTe source is first heated to 600° C. and, on attaining this temperature, the substrate previously heated to 450° C. is rapidly heated up to 650° C. The CdTe deposition rates to obtain a CdTe layer about 10 μm thick in the CSVT (closed space vapor transport) methods are very small, and deposition must take place for approximately 20 minutes.

As well as these vacuum-assisted deposition methods, electrolytic methods were described in the 80's (e.g. B. M. Basol, *Solar Cells,* 23, (1988) pp. 69-88; V. Ramanathan et al. *Proc. 20th IEEE Photovoltaic Specialists Conf.,* Las Vegas, (1988) pp. 1417-1421), as well as screen printing (e.g., S. Ikegami, *Solar Cells,* 23, (1988) pp. 89-105) or spray methods (e.g. J. F. Jordan, *Solar Cells,* 23, (1988) pp. 107-113), for making polycrystalline CdTe layers.

The electrolytic deposition takes place in an aqueous solution of $CdSO_4$ and Te_2O_3 at temperatures of about 90° C. In order to avoid fluctuations in the stoichiometric composition of the growing CdTe layer, it is necessary to adhere to very small and hence uneconomic rates of deposition of only about 1 μm/hour.

In the screen printing method, suspensions of Cd and Te powders are applied to a substrate and sintered with high usage of material into relatively thick layers of around 30 μm, whereby Cd and Te react to form CdTe. High temperatures of more than 700° C. are also required here, which necessitates the use of expensive substrates.

In the spray method, an aqueous solution of compounds containing Cd and Te in the form of a fine droplet aerosol is sprayed onto a substrate heated to about 400° C. The growing CdTe layer is markedly inclined to porosity, so that relatively thick layers have to be made in order to ensure the necessary impermeability of the layers. An uneconomic high usage of materials is again involved. Furthermore, a significant loss of the sprayed solution is inherent in the method, in that this fills the whole reaction chamber as a fine aerosol and is lost on the walls and through the exhaust air, whereby only a moderate material yield of the compounds of the Cd and Te compounds can be achieved. The chemical-thermal post treatment proves to be particularly critical in the spray method.

The invention is thus based on the problem of providing an improved method for making pn CdTe thin film solar cells which is especially suitable for inexpensive mass production and makes the production of satisfactory solar cells possible.

The solution to this problem according to the invention involves a complete departure from the high substrate temperatures hitherto regarded as necessary in order to be able to make solar cells with efficiencies around and above all in excess of 10%. Thus, the inventor has surprisingly ascertained that it is possible to make satisfactory solar cells with high efficiency if care is taken that the temperature of the transparent substrate provided with the TCO layer and the CdS layer is brought to a temperature below about 520° C. and above about 480° C. before the CdTe coating and this temperature is maintained also during the following coating. During this time the CdTe layer is deposited steadily in an inert gas atmosphere. In the oxygen-free processes in the state of the art, substrate temperatures of 600° C. and more were universally employed.

It has furthermore been found that inexpensive soda-lime glass (window glass) can be used as the substrate material and resulted in solar cells with a high efficiency of more than 10% in all embodiments tested. This represents a significant technical advance, since the substantial reduction in cost widens the scope for use of the mass-produced product. Hitherto, it has not been considered or even thought possible for solar cells of this kind to be made with window glass and be not merely functional but seriously capable of use.

Furthermore, it has been found that, with such temperature control of the substrate, it is possible to work

with a high CdTe deposition rate of between 5 and 15 μm/min, so that the growth of the CdTe layer takes place from the very start at a temperature favoring the attainment of the required (photo)electronic characteristics, so that a good efficiency of the cells is likewise obtainable. Such high rates of deposition have not been possible hitherto, either in oxygen or in inert gases.

Preferably, one proceeds in accordance with the invention as follows. Inexpensive, ordinary soda-lime glass ("window glass") is used as the transparent substrate and is coated with a transparent, electrically conductive TCO (transparent conducting oxide) layer. This consists, for example, of a suitably doped tin oxide layer, for example of ITO or a modified ITO layer. The TCO layer also forms the electrical front contact of the solar cell. A thin CdS layer (thickness approximately 80 to 120 nm, preferably 100 nm) is then evaporated on in a high vacuum, with doping preferably achieved in the manner indicated below.

The deposition of the photo-active CdTe layer then takes place directly on the CdS layer, according to the close-space (CSS) method (close-spaced sublimation). The substrate carrying the CdS layer is brought for this to a temperature, of 480° to 520° C., preferably 500° C., in a steady heating process, preferably in approximately 3 min. The TCO layer suffers no adverse effects in the course of this short heating phase, since it is protected by the CdS layer. During this time the CdTe source attains a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the substrate temperature has reached (after e.g. the 3 minutes) 480° to 520° C., preferably 500° C., is the CdTe source brought in approximately 1 minute to such a temperature (e.g., in the range from 700° to about 770° C., preferably about 740° C.), that a CdTe deposition rate of 5 to 15 μm/min., preferably about 10 μm/min., is attained, so that the required CdTe layer 5 to 10 μm thick can be created in the short time of approximately 1 minute.

During the CdTe deposition a pressure of about 0.1 mbar nitrogen (or similar inert gases such as helium, argon or hydrogen) is preferably so maintained in the reaction chamber (quartz tube) that the same amount of gas is fed in as is pumped out, in the nature of a dynamic balance through the various connections of the reaction chamber.

The CdTe source from which the material to be deposited on the CdS layer sublimes is preferably located at a small distance of only about 2 to 3 mm from the substrate surface. On account of the small distance between the substrate and the CdTe source, as well as their direct opposition, there is nearly 100% usage of the CdTe starting material. Furthermore, the small thickness of the CdTe layer possible according to the invention contributes to inexpensive handling of the valuable semiconductor material. The short deposition time also acts inexpensively in the course of this method.

During the described operation of the CdTe deposition, the substrate and CdTe source are preferably held in opposed graphite blocks, which are heated by heating elements (e.g. halogen lamps), in order to create the required temperatures. The latter are adjusted by suitable manual or computer-controlled regulation of the heating load of the heating element. The $CdCl_2$ tempering which is carried out at the end of the CdTe deposition is known per se.

The further development of the method in accordance with the present invention contributes significantly to mass-production, in that the method of doping of the CdS layer is substantially facilitated. It is also possible to increase the efficiency of the finished solar cell by this measure.

Finally, in contrast to the known critical oxygen doping, it is possible to operate without endangering the CdTe source by oxidation during the CdTe coating at high pressure.

It is beneficial for obtaining a good efficiency of the pn CdTe/CdS thin film solar cell to use an n-type CdS with high conductivity, of the order of magnitude of 0.1 S/cm. While a CdS layer made at about 150° C. fulfills this condition well, a CdS layer subjected to a thermal process, as in the CdTe deposition, only exhibits a very small conductivity of $<10^{-5}$ S/cm. In order to obtain a desirable order of magnitude of 0.1 S/cm for the conductivity of the CdS even after the thermal stress of the CdTe deposition, an ultra-thin indium layer with a thickness of approximately 0.1 to 0.5 nm, preferably 0.2 nm, is applied in a high vacuum to the TCO layer at approximately 25° C., before the CdS layer is applied preferably in the manner given above. The thickness of the indium layer is so selected that the diffusion of the indium into the CdS layer during the CdTe deposition at the predetermined substrate temperature, which preferably lies between 480° and 520° C., creates such n-type doping in the CdS that the conductivity value stays in the required order of magnitude of 0.1 S/cm. The required and desirable n-type doping of the CdS layer is thus effected inexpensively without additional expense during the CdTe deposition. It should further be noted that, even without the indium doping of the CdS layer, efficiencies of around and in excess of 10% are obtained.

After the customary $CdCl_2$ tempering (R. W. Birkmire et al., Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84), a gold layer approximately 5 to 10 μm thick is evaporated onto the CdTe layer as the back contact. In order to avoid series resistance, the gold layer preferably has an evaporated inexpensive metal layer (e.g. aluminum) (about 100-200 nm) or is painted with a conductive paste and so brought up to the conductivity necessary for the flow of the photocurrent.

The illumination of the solar cell takes place through the transparent glass substrate.

The features of the special doping of the CdS layer according to the invention are preferably combined with the other features according to the invention. Thus, with the substrate temperatures controlled in accordance with the invention, the mixing of the CdS layer and the indium layer can be well achieved. In combination with the likewise possible high rate of deposition, the efficiency of the method and its suitability for mass production are further improved.

The features according to the invention, taken alone and in their combination, thus promote inexpensive mass production of pn CdTe/CdS thin film solar cells with a type of construction previously known. Inexpensive substrate materials can be used and high yields of the expensive substrate materials with high rates of deposition for the semiconductor layers are possible. The doping step which was previously frequently critical is markedly improved and rationalized. In addition, the features referred to contribute to high efficiency. The inventive features thus contribute an important step towards an alternative energy source through solar

cells, which arises both from the mass production and from a high efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further explained below with reference to the drawings, in which:

FIG. 1 shows a section, in a schematic view, through a pn CdTe/CdS thin film solar cell made according to a preferred embodiment of the method according to the invention,

FIG. 2 shows a section, in a schematic view, through an apparatus suitable for carrying out the method according to the invention,

FIG. 3 shows the current/voltage characteristic of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1, and

FIG. 4 shows the graph of the (external) absolute quantum yield as a function of wavelength of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1.

FIG. 1 shows a schematic section through a pn CdTe/CdS thin film solar cell **1**, which has been made by a preferred embodiment of the method according to the invention. The transparent substrate **20** consists of soda-lime glass ("window glass") and is coated with a transparent, electrically conductive TCO layer **18**. There follow an ultra-thin indium layer **16** and a CdS layer **14** (e.g. 0.10 μm thick). The photo-active CdTe layer **12** (preferably around 5 μm thick but not critical in thickness for the cell as a whole so long as it stays above 2 to 3 μm) is deposited on the CdS layer according to the foregoing techniques. As has further been indicated, the layers **16** and **14** mix so tht the indium layer **16** dissolves in the layer **14** because of the diffusion of the indium atoms and is no longer identifiable as such in the finished solar cell **1**. The CdS layer thus contains the indium atoms of the indium layer **16** in dispersed form after manufacture, as the desired and necessary n-type doping.

This n-type doping of the CdS layer taking place at the same time as the deposition of the CdTe layer **12** represents a further advance both in relation to improving the suitability of the method to inexpensive mass production, as well as to the creation of a solar cell with high efficiency. The indium layer **16**, preferably 0.1 to 0.5 nm thick and preferably evaporated in a high vacuum at about 25° C., is therefore only identifiable as such up to the method step preceding the CdTe deposition.

After completion of the CdTe deposition, there follows after the $CdCl_2$ tempering the application of an electrically conductive metal contact **10** on the CdTe layer **12**, serving as the back contact of the solar cell **1**. The TCO layer **18** functions as the front contact of the solar cell **1**. The illumination of the solar cell **1** takes place through the glass substrate **20** and the TCO layer **18**.

The CdTe deposition method is also especially important. In FIG. 2 there is shown a reaction chamber which is preferably used, likewise in schematic cross-section. This consists of a quartz reactor **34** and graphite blocks **26** and **28**, as well as heating elements **22** and **24** (e.g. halogen lamps), with which the graphite blocks **26** and **28** are heated. The glass substrate **20** with the TCO layer **18** as well as the indium layer **16** and the CdS layer **14**, shown as element **30** in FIG. 2, is so attached to the upper graphite block **26** that the glass substrate lies against the graphite block **26** and the CdS layer **24** is directed towards the CdTe source. The CdTe source **32**, e.g. in the form of a polycrystalline disc, is located on the lower graphite block **28**. Instead of a polycrystalline disc, a pressed blank of CdTe powder or a device with CdTe powder can obviously be used as the CdTe source **32**.

The CdTe deposition is effected in the reaction chamber **33** according to a procedure in which, as already particularly explained above, it is crucial that the variation with time of the temperature of the element **30** and of the CdTe source **32** is such that the element **30** including the CdS layer is brought up to a temperature of 480°-520° C., preferably 500° C., in a steady heating process (without interruption) in e.g., 3 min., whereby the TCO layer **18** does not suffer any adverse effects in the course of this short heating phase, since it is protected by the CdS layer **24**. During this time the CdTe source **32** reaches a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the temperature of the element **30** has reached 480°-520° C., preferably 500° C., is the CdTe source **32** brought up in about 1 min. to such a temperature that a CdTe deposition rate onto the CdS layer **14** of 5 to 15 μm/min, preferably about 10 μm/min, is obtained and the required CdTe layer **12** of 5 to 10 μm thickness can be created in the short time of about 1 minute. This procedure results in the growth of the CdTe layer **12** taking place from the start at a temperature favoring the required (photo) electronic characteristics. The temperature of the element **30** is so selected that cheap soda-lime glass can be used as the material for the substrate **20**. The pressure in the reaction chamber **34** amounts during the CdTe deposition to about 0.1 mbar and is maintained by inflow or pumping out nitrogen (or helium, argon or hydrogen).

The heating load of the heating elements **22** and **24** can be optionally varied manually or by computer control.

In FIGS. 3 and 4 there are shown the current/voltage characteristic and the (external) absolute quantum yield as a function of the wavelength respectively of a pn CdTe/CdS thin film solar cell made in accordance with the above method. As can be seen from FIG. 3, the short-circuit current density of the manufactured solar cell amounts to 22.8 mA/cm^2 with a no-load voltage of 0.750 V and a space factor of 65%. The active surface of the solar cell of the embodiment set forth amounts to 0.388 cm^2. This gives an efficiency of 11.0% (relative to illumination with 100 mW/cm^2, 1.5 AM overall).

The (external) absolute quantum yield according to FIG. 4 exhibits a constant value over the substantial part of the spectrum (about 820–520 nm) with a value around 85%. The fall off at 520 μm is caused by the absorption of the CdS layer **14**.

We claim:

1. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO layer and an n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere free of oxygen according to the close-spaced sublimation method from a CdTe source and is provided with an electrically conducting back contact,

characterized in that,

a substrate of soda-lime glass is used, the substrate is provided with the TCO layer, and the CdS layer is brought to a temperature between approximately 480° C. and 520° C. before coating with the CdTe

layer, said temperature being maintained during the CdTe coating.

2. A method according to claim 1, characterized in that a $CdCl_2$ tempering step is employed after the CdTe coating.

3. A method according to claim 1, characterized in that the substrate with the TCO layer and the CdS layer is brought to a temperature of about 500° C. before the CdTe coating, which temperature is maintained during the CdTe coating.

4. A method according to claim 1, characterized in that the heating of the substrate provided with the TCO layer and the CdS layer is effected in a steady heating process over between approximately 1 and 5 min.

5. A method according to claim 4, characterized in that the heating is effected in approximately 3 min.

6. A method according to claim 1, characterized in that the deposition rate of the CdTe on the CdS layer is approximately 5 to 15 μm/min.

7. A method according to claim 6, characterized in that the CdTe layer is deposited in approximately 1 min.

8. A method according to claim 6, characterized in that the CdTe deposition rate is adjusted to 10 μm/min.

9. A method according to claim 1, characterized in that the variation with time of the temperature of the substrate provided with the TCO layer and the CdS layer and of the CdTe source is so controlled that the substrate is brought in a steady heating process to a temperature of 480° to 520° C. in approximately 1 to 5 min. and, during this time, the CdTe source is brought to a temperature at which there is no appreciable sublimation of the CdTe, and in that, only when the temperature of the substrate with the TCO and CdS layers has attained the desired temperature between 480° and 520° C., the CdTe source is brought in approximately 1 min. to a temperature at which a deposition rate on to the CdS layer is obtained such that the required CdTe layer can be applied in approximately 1 min.

10. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO front contact layer and an overlying n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere according to the close-spaced sublimation method and is provided with an electrically conducting back contact, characterized in that indium is used for the n-doping of the CdS layer and in that, before the deposition of the CdS layer, an ultra-thin indium layer less than 0.5 nm thick is applied to the TCO layer and in that the In and CdS layers so mix during the deposition of the CdTe layer that the indium layer is dissolved by diffusion of the indium atoms into the CdS layer and is no longer identifiable as such in the finished solar cell and the CdS layer includes the indium atoms of the indium layer in dispersed form as n-doping.

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United States Patent [19]
Mitchell

[11] **Patent Number: 4,650,921**
[45] **Date of Patent: Mar. 17, 1987**

[54] **THIN FILM CADMIUM TELLURIDE SOLAR CELL**

[75] Inventor: **Kim W. Mitchell,** Granada Hills, Calif.

[73] Assignee: **Atlantic Richfield Company,** Los Angeles, Calif.

[21] Appl. No.: **790,709**

[22] Filed: **Oct. 24, 1985**

[51] **Int. Cl.**⁴ **H01L 31/06**
[52] **U.S. Cl.** **136/258;** 136/256; 136/260; 136/264; 357/16; 357/30; 357/59; 357/65
[58] **Field of Search** .... 136/256, 258 PC, 260, 136/264; 357/16, 30, 59 D, 65

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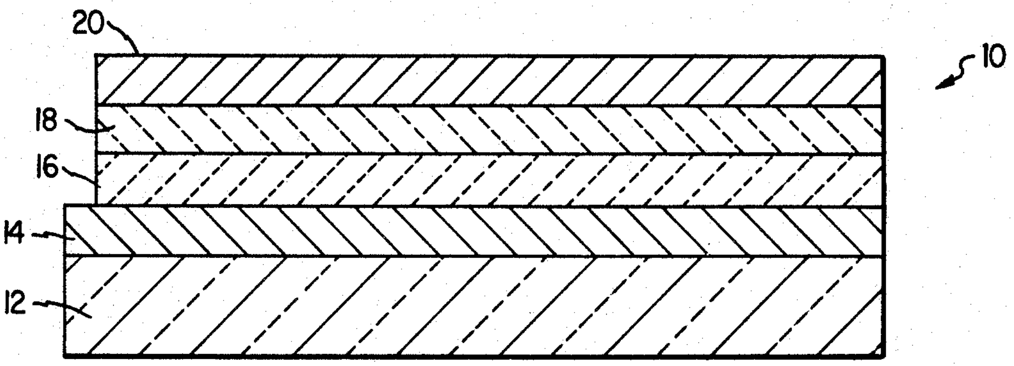
Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Robert D. Lott

[57] **ABSTRACT**

A phosphorous doped layer of cadmium telluride is deposited onto a conductive window layer to form a thin film cadmium telluride solar cell. Back contacts to the solar cell are made by first depositing a layer of p conductivity type lead telluride upon the cadmium telluride and then depositing the metallic back contacts onto the lead telluride.

5 Claims, 5 Drawing Figures



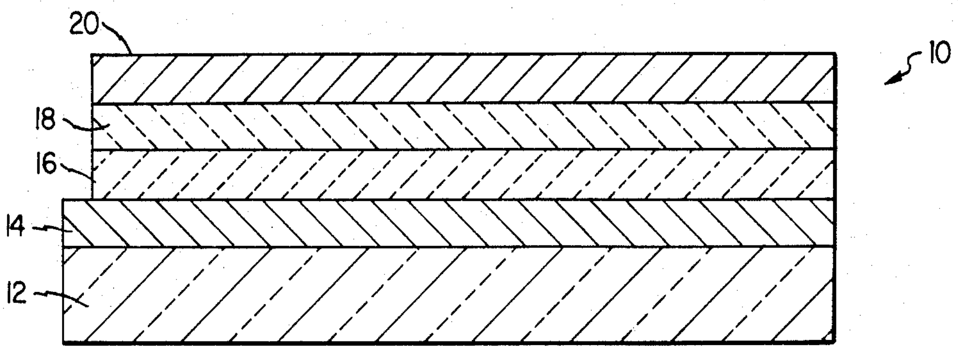


FIG. 1

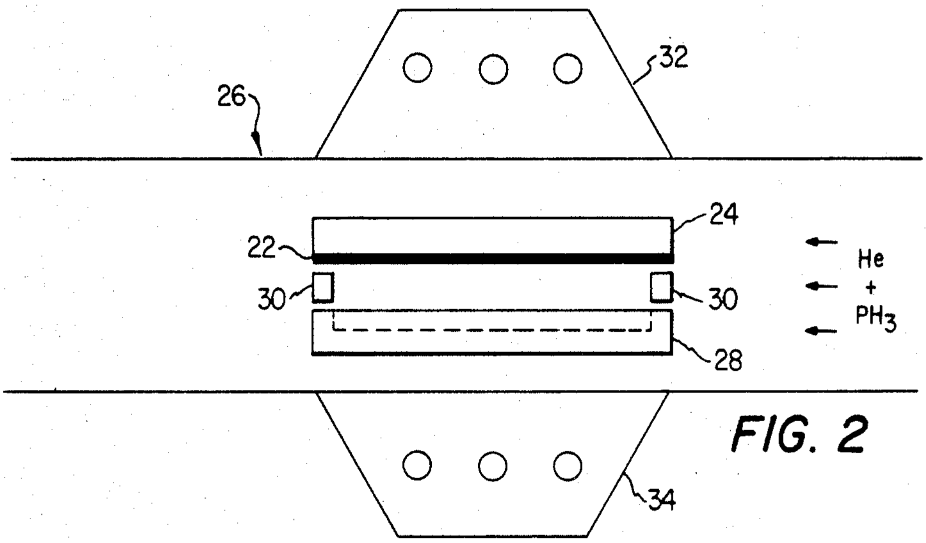


FIG. 2

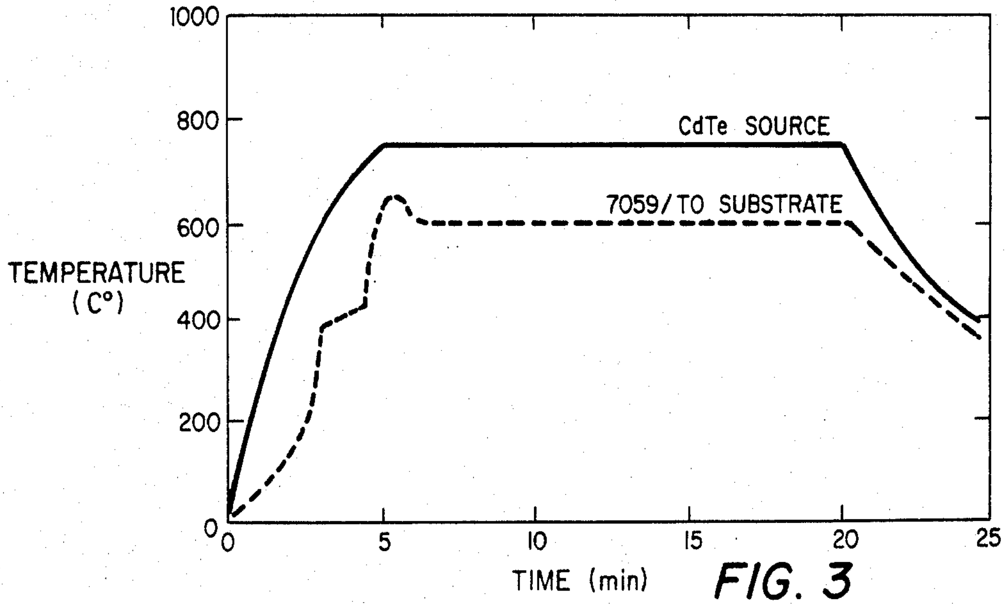
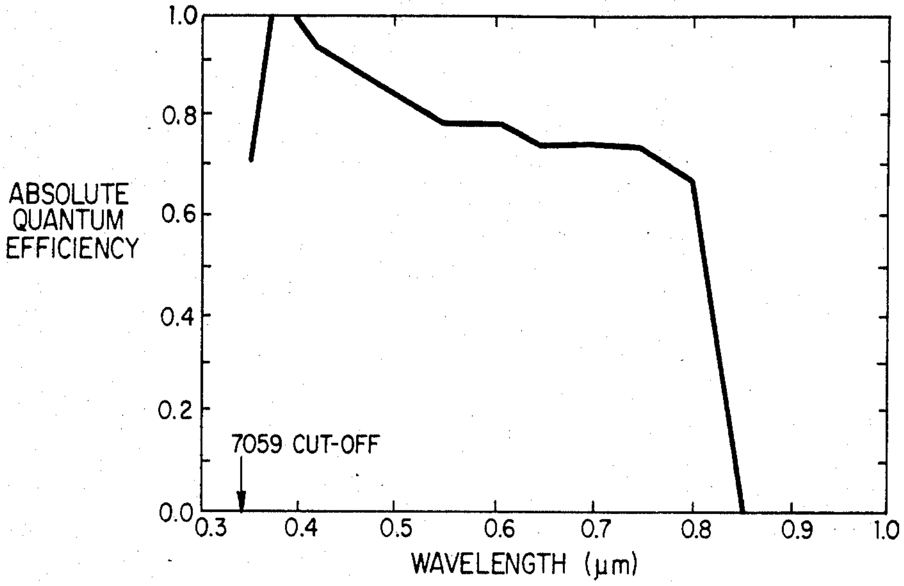


FIG. 3


1.0
0.8
0.6
0.4
0.2
0.0
ABSOLUTE QUANTUM EFFICIENCY
7059 CUT-OFF
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0.4
0.5
0.6
0.7
0.8
0.9
1.0
WAVELENGTH (μm)

FIG. 4

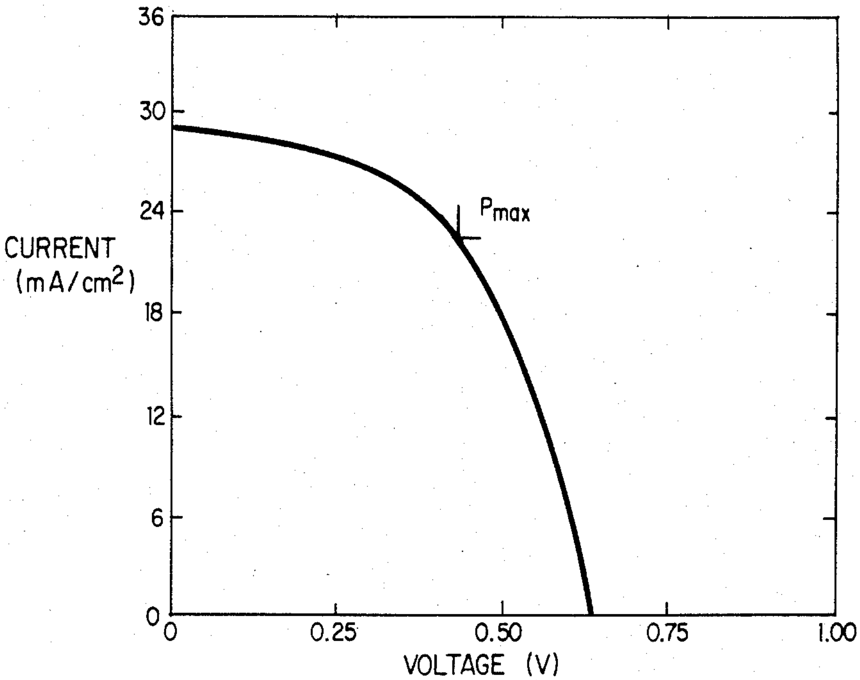
36
30
24
18
12
6
0
CURRENT (mA/cm2)
Pmax
0
0.25
0.50
0.75
1.00
VOLTAGE (V)

FIG. 5

THIN FILM CADMIUM TELLURIDE SOLAR CELL

BACKGROUND OF THE INVENTION

This invention relates to p-n tin oxide-cadmium telluride photovoltaic cells.

Cadmium telluride has long been identified as a strong candidate for low cost, thin film, photovoltaic applications because of its direct band gap and its ability to be doped n and p type permitting formation of a variety of junction structures, and to be deposited by a variety of techniques ranging from vacuum evaporation and chemical vapor deposition to electrodeposition and screen printing.

Photovoltaic cells using polycrystalline cadmium sulfide and cadmium telluride have been described in the past. For example U.S. Pat. No. 4,207,119 to Yuan-Sheng Tyan, which is hereby incorporated by reference, describes a cadmium sulfide/cadmium telluride solar cell in which oxygen atoms are present in the cadmium sulfide and/or cadmium telluride to improve the efficiency of the cell. A disadvantage of the examples shown in the Tyan patent is the use of low pressure conditions while depositing the cadmium telluride layers. It has also been found that the addition of oxygen must be kept low during the deposition process because the oxygen can result in substantial oxidation of the cadmium telluride source thereby suppressing the deposition process.

A problem in the past in fabricating photovoltaic cells containing cadmium telluride is the formation of low resistance, electrical contacts to the cadmium telluride layer. One prior art technique is to chemically etch the cadmium telluride to form a telluride rich P+ conductivity region at the surface, then to deposit back metallization usually using high work function metals such as gold or nickel. However, contacts made by this method have not proven to be altogether satisfactory for several reasons including the sensitivity of the contact to excessive heat treatment causing chemical rections to form metal tellurides, and the present of surface oxides which tend to give rise to high contact resistances.

Therefore, it can be appreciated that a photovoltaic junction which can be formed at atmospheric pressure and under other conditions which lend themselves well to high throughput production, and a photovoltaic cell which has low resistance electrical contacts to the back conductor is highly desirable.

SUMMARY OF THE INVENTION

In accordance with the present invention, a thin film photovoltaic cell having a layer of cadmium telluride is manufactured in a process in which the cadmium telluride is deposited directly onto a conductive window layer.

Further in accordance with the present invention, a thin film photovoltaic cell having a layer of cadmium telluride is manufactured in a process in which the cadmium telluride can be deposited under atmospheric pressure conditions.

In accordance with a related aspect of the invention a photovoltaic cell is prepared which has conversion efficiencies which are improved as compared to a similar cell previously produced.

In a further aspect of the invention a cadmium telluride photovoltaic cell is produced which has a means for providing a low resistance electrical contact to a back contact of the photovoltaic cell.

As shown in an illustrated embodiment of the invention a photovoltaic cell is produced in which a conductive window layer, preferably tin oxide, is deposited upon a substrate and a cadmium telluride layer, preferably of a p conductivity type, is further deposited upon the tin oxide layer to form a p-n junction. A lead telluride layer is deposited upon the cadmium telluride layer and a metallic back contact is positioned on top of the lead telluride layer either by deposition or screen printing.

In accordance with another aspect of the invention the cadmium telluride is deposited upon the window layer in the presence of phosphine to thereby produce phosphorus atoms in the cadmium telluride layer to advantageously enhance the efficiency of the photovoltaic cell.

In accordance with a related aspect of the invention, the deposition of the cadmium telluride onto the tin oxide window layer is carried out in a reactor in which the temperature of the cadmium telluride source and the tin oxide is controlled in a manner to keep the temperature of the tin oxide at about 400° C. until the temperature of the cadmium telluride source is greater than about 600° C. thereby inhibiting the tin oxide from reducing to elemental tin and yet allowing the temperature of the tin oxide to rise above about 600° C. in order to significantly increase the transmission qualities through the tin oxide layer.

Also shown in a preferred embodiment of the invention is a structure for providing electrical contacts to the cadmium telluride layer by placing a layer of lead telluride between the cadmium telluride and the metallization back contacts.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features of this invention may be more fully understood from the following detailed description taken together with the accompanying drawing in which:

FIG. **1** is a fragmentary vertical sectional view of a photovoltaic cell according to the present invention;

FIG. **2** is a partial schematic vertical sectional view of a chamber suitable for depositing cadmium telluride onto tin oxide;

FIG. **3** is a plot of the temperatures of the cadmium telluride source and the glass-tin oxide substrate during the deposition of the cadmium telluride;

FIG. **4** is a plot of the absolute quantum efficiency versus wavelength of a photovoltaic cell having a tin oxide/cadmium telluride photovoltaic junction formed according to the present invention; and

FIG. **5** is a plot of the voltage/current characteristics of a photovoltaic cell in which a tin oxide/cadmium telluride photovoltaic junction is formed according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings, FIG. **1** shows, in partial schematic sectional view, a cell **10** prepared in accordance with the present invention. The cell **10** consists of a substrate layer **12** which in the preferred embodiment is made from 7059 glass. Deposited onto the substrate **12** is a tin oxide layer **14**. However, it will be appreciated that other materials such as cadmium stannate, can also be used for the conductive window layer **14**. For a photovoltaic cell the sheet resistivity of the tin oxide is preferably less than ten ohms per square, but may be higher if the cell is to used as a photodetector. The tin oxide layer **14** is advantageously transparent and forms both the conductive window layer and the n conductivity type constituent of the photovoltaic p-n junction. Deposited on top of the tin oxide is a layer **16** of cadmium telluride which in the preferred embodiment is a polycrystalline p conductivity type material, although it is also within the scope of the present invention for the cadmium telluride to be n-type, or intrinsic, in conductivity. The preferred thickness of the cadmium telluride layer **16** is in the range of five to fifteen microns, although the thickness may be as thin as one micron for certain devices. On top of the cadmium telluride is another layer **18** consisting of lead telluride which forms a P+ conductivity type layer between the cadmium telluride layer **16** and a top conductor layer **20**. The top layer **20** can be composed of any of several metals including nickel, aluminum, gold, solder, and graphite-copper, but in the preferred embodiment graphite-silver (C-Ag) is used.

A critical element in carrying out one aspect of the present invention is the deposition of the cadmium telluride layer **16**. FIG. **2** depicts a sectional view of a chamber suitable for depositing the cadmium telluride layer **16**. The substrate **12** and tin oxide layer **14**, together shown as element **22** in FIG. **2**, are mounted against a substrate block **24** and placed inside a quartz reactor **26**. A source crucible **28** is placed inside the reactor **26** and spaced away from the substrate window layer structure **22** by spacers shown as elements **30**. Mounted on either side of the quartz reactor **26** are a pair of heat lamps **32** and **34**. Heat lamp **32** is positioned to heat substrate block **24** and is hereinafter referred to as the substrate lamp **32**. The heat lamp **34** is positioned to heat the source crucible **28** and is hereinafter referred to the source lamp **34**. In the preferred procedure for carrying out the present invention the cadmium telluride source is ground cadmium telluride powder (Alpha Ultapure #87821) held in the source crucible **28** which is heated by the source lamp **34** to vaporize and become deposited upon the tin oxide through the process of close-space vapor transport (CSVT). The spacers **30** are less than one centimeter in width and the substrate structure **22** is typically ten centimeters by ten centimeters in size. Although not shown in FIG. **2**, additional elements which may be used including a mask placed in front of the substrate structure **22** for patterning the cadmium telluride deposited onto the structure **22**, and shutters mounted on crucible **28** which can be remotely activated to contain the cadmium telluride vapors until the temperature of the cadmium telluride source is at a desired temperature. During the cadmium telluride growth, the atmosphere inside the reactor **26** is helium with 200 PPM of phosphine (PH_3). The PH_3provides phosphorus atoms for the cadmium telluride layer **16**. Phosphorus is a well known acceptor dopant. The pressure inside the quartz reactor **26** may be atmospheric pressure thereby reducing the amount of time and equipment required during the manufacturing process as compared to a low pressure process. On the other hand, it has been found that the deposition of cadmium telluride occurs faster during CSVT when the atmospheric pressure is reduced to about 1 TORR.

The apparatus shown in FIG. **2** allows precise control of deposition parameters. Using instrumentation not shown in FIG. **2**, independent control of gas flows, chamber pressure, and source and substrate temperatures can be achieved.

In order for the photovoltaic cell to be efficient, the window layer, in this case tin oxide, must be compatible with the layer disposed upon it, in this case cadmium telluride, and with other subsequent processing. Experiments were made in which the optical transmission and x-ray diffraction were measured for different heat treatment conditions of the tin oxide. It was found that for an ambient condition of one atmosphere of hydrogen the tin oxide should not be exposed to temperatures above 450° C., otherwise the reduction of the tin oxide to elemental tin occurs with the consequent loss in optical transmission. Unfortunately, experiments with cadmium telluride grown on tin oxide previously deposited onto 7059 glass and then heated to 450° C. produced a low quality cadmium telluride crystalline structure which had less than 5% optical transmission below the cadmium telluride band gap, and that temperatures of about 600° C. were necessary for high quality cadmium telluridge indicated by below band optical transmissions of about 67 percent, which, considering reflection losses, is considered ideal.

Advantageously, it was discovered that it is possible to raise the temperature of the tin oxide layer to about 600° C. without causing a degradation or reducing of the tin oxide to elemental tin. The solution involves heating the source crucible and then heating the substrate in a defined manner as shown in FIG. **3** so that the temperature of the substrate was kept below 450° C. until the temperature of the source crucible reached 600° C., then the substrate was quickly heated to 650° C. to improve initial film growth and cooled to 509° C. to complete the film growth. The resultant cadmium telluride layer was 10.3 microns thick.

In order to form the photovoltaic junction between the tin oxide and cadmium telluride, it is necessary that one of the layers be of p conductivity type, generally the cadmium telluride layer, and the other layer be of n conductivity type, generally the tin oxide layer. Advantageously, the deposition technique described above produces a tin oxide layer which is inherently n conductivity type and a cadmium telluride layer which is doped with acceptor type atoms to become p conductivity type.

It was also found that the use of phosphorus in the form of PH_3 mixed with the helium in the quartz reactor tube **26** improves the efficiency of the resulting photovoltaic cell by producing a p conductivity type layer to promote a relatively high voltage pn junction.

A photovoltaic cell was fabricated in the manner described above with the spectral response shown FIG. **4** and the voltage current characteristics of the cell shown in FIG. **5**. The quantum efficiencies shown in FIG. **5** are above unity near the tin oxide cutoff and are not understood. But these characteristics have also been seen in other devices and it is theorized that the efficiency shown may be due to avalanche effects or to current densities which are light dependent. As shown in FIG. **5**, the short circuit current for this example was 28.8 milliamperes per square centimeter, with an open circuit voltage of 0.642 volts and a fill factor of 0.524. The efficiency of the 4 square centimeter cell was 9.7 percent. In this experimental cell the back surface of the cadmium telluride was etched for ten seconds with an etch of 1.25 ml HNO_3: 100 ml H_3PO_4 and graphite-silver was then screen printed onto the etched cadmium telluride to form the back contact.

However, the back contact can also be formed by first depositing a layer of tellurium rich lead telluride onto the cadmium telluride using vacuum evaporation of lead telluride. The lead telluride is evaporated at 600° C. to 800° C., and the lead telluride must be raised to this temperature rapidly in order to keep the lead telluride tellurium rich to preserve the p conductivity type characteristics of the lead telluride. It is theorized that if the lead telluride is allowed to heat up slowly, the tellurium tends to separate from the lead, causing the resultant layer to be of less p conductivity type. After the lead telluride film is deposited, a suitable metal such as graphite-silver, gold, nickel, aluminum, solder, or graphite-copper, may be deposited onto the lead telluride to form the back contact. Analysis of back contacts formed in this manner show a ohmic junction of relatively low resistivity which are stable.

An alternative method using close-space vapor transport has also been used to deposit the layer of lead telluride. This method of deposition combined with the process described above has the advantage of permitting the production of photovoltaic cell entirely at atmospheric pressure.

As can be seen from this description, several major advantages arise from this invention. A photovoltaic cell has been described which is formed by the junction of tin oxide and cadmium telluride without an intervening cadmium sulfide layer in which phosphorus has been used to increase the efficiency of the cell, and a method to provide good ohmic contacts to the cadmium telluride layer has been described. Moreover, the process described is suited for an industrial mass production of photovoltaic cells which does not not require special crystal growing equipment, in which the fabrication of a photovoltaic cell can be carried out in atmospheric pressure conditions.

Although the invention has been described in detail with particular reference to a preferred embodiments, it will be understood by those skilled in the art that modifications and variations can be made to the described embodiments without departing from the spirit and scope of the invention.

I claim:

1. A photovoltaic cell comprising:
   - (a) a substrate layer consisting of a transparent or semi-transparent material;
   - (b) an n conductivity type layer of tin oxide contiguous to said substrate layer;
   - (c) a p conductivity type layer of polycrystalline cadmium telluride contiguous to said layer of tin oxide thereby forming a pn junction, said layer of cadmium telluride containing atoms of phosphorus; and
   - (d) a layer of lead telluride contiguous to said layer of said cadmium telluride.

2. A photovoltaic cell as set forth in claim 1 further including a conductive layer contiguous to said lead telluride layer whereby said conductive layer and said tin oxide layer form electrodes for said photovoltaic cell.

3. In a photovoltaic cell having a layer of cadmium telluride and an electrode in nonrectifying electrical contact with said cadmium telluride layer, the improvement comprising a layer of lead telluride interposed between said cadmium telluride layer and said electrode.

4. A cell as set forth in claim 3 wherein said cadmium telluride layer and said lead telluride layer are of p conductivity type.

5. A cell in set forth in claim 3 wherein said electrode is composed of one of the metal containing materials chosen from the group of graphite-silver, nickel, aluminum, gold, solder, and graphite-copper.

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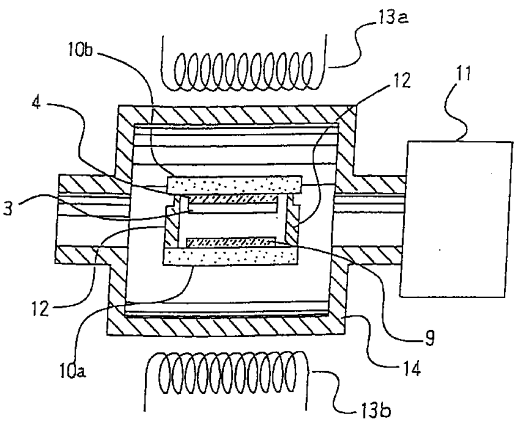
(54) METHOD FOR FORMING CdTe FILM AND SOLAR BATTERY USING THE FILM

(57) A method for forming a CdTe film of good quality by an improved close-spaced sublimation process is disclosed. This method comprises: a step of applying a paste which contains material for CdTe semiconductor on a supporting member, thereby to form a coating film which contains the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, and causing the material for the semiconductor in the coating film to evaporate.

F I G. 2



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Description

TECHNICAL FIELD

The present invention relates to a method for preparing a CdTe semiconductor film which is used mainly for solar cells, in particular, to a method for preparing the CdTe film by a close-spaced sublimation process.

BACKGROUND ART

In recent years, global environmental problems such as global warming due to carbon dioxide, depletion of the ozone layer, and the like have been highlighted. For that reason, expectation for development of new energy, in particular, that for solar cells have become glowingly great. However, for popularization of the solar cells, there are a number of problems which must be solved. In particular, an improvement in conversion efficiency of the solar cells and a reduction in price are desired.

A CdS/CdTe solar cell uses CdTe which has an forbidden band gap (=1.44 eV) being suitable for a light absorption layer, and thus it is one of the solar cells which are expected to yield a high conversion efficiency.

In the manufacturing process of the CdS/CdTe solar cell, a cadmium telluride (CdTe) film is formed on a surface of a cadmium sulfide (CdS) film in general. As a method for forming the CdTe film, the close-spaced sublimation process which can produce the CdTe film of high quality is attracting attention. The close-spaced sublimation process is a kind of the vapor deposition process. A CdTe solar cell which has a conversion efficiency of the world highest level (15.8%) at present is obtained by this process. The close-spaced sublimation process is disclosed in, for instance, "HIGH EFFICIENCY CdS/CdTe SOLAR CELLS FROM SOLUTION-GROWN CdS FILMS" (The Conference Record of the 22nd IEEE Photovoltaic Specialists Conference (1991) Vol. 2, p.952) by T. L. Chu et. al., or the like. According to this process, a material for forming the CdTe film (hereinafter referred to as a source) and a substrate are so placed as to face each other, with a gap of about 0.5 - 5 mm, and heated under a reduced pressure. In this manner, the source is caused to sublime and then deposit on the substrate. According to this process, since the sublimed source is rearranged and crystallized on the substrate placed at a short distance as long as the mean free path level, a CdTe film which has a high crystallinity is obtained. Further, since the treatment is performed under the reduced pressure, the film-forming speed is high.

However, the above-mentioned conventional close-spaced sublimation process has the following problems.

In general, in the close-spaced sublimation process, as a source, a CdTe powder placed on a dish-shaped container so as to cover over it is used. In the above-mentioned literature for instance, a commercially-available polycrystal of CdTe with a purity of 5N, or a powder produced by pulverizing a polycrystal ingot of CdTe obtained by directly implanting a dopant as one of the constituting element, is used as the source.

In addition to the fact that this process uses an expensive CdTe powder, it has a low utilization efficiency. In this process, it is difficult to evenly place as much amount of the source for forming the film just once for covering over the container. For that reason, the same source is repeatedly used for forming the CdTe films. It is difficult to control the CdTe powder or the source since it changes in particle size, powder density, stoichiometric ratio and the like by the sublimation, and hence, with the repetition of the film-forming, dispersions in thickness and in quality of the CdTe film increases gradually. Therefore, the obtained solar cell has a large dispersion in performance. For that reason, in order to make the dispersion in performance of the solar cell small, of the source placed for covering, only about 10% is actually consumed for the film-forming, and the rest is discarded without being used.

Further, according to this process, since the film is formed under the reduced pressure, an equipment must once be stopped when the source is exchanged. Therefore, the production efficiency is also low.

When a CdTe film is formed by this process, on a substrate which has a large area, a central part of the obtained CdTe film is made thicker than that of a peripheral part because the central part of the source is liable to trap a heat flowed from circumference, as opposed to the peripheral part where the heat is liable to escape. Therefore, the variation in thickness within the same film is large.

Moreover, according to this process, when the source is used repeatedly, the particle diameter of the material decreases gradually and the surface area of the material increases, and in addition, the surface temperature of the source rises because the particles combine together by sintering. Therefore, the thermal conductivity increases and the film-forming speed increases gradually. When the same source is used repeatedly still more and the remaining amount of the source decreases accordingly, pores are produced between and among the particles and the thermal conductivity of the source is gradually lowered, thereby to decrease the film-forming speed conversely. For that reason, even when the manufacturing is performed under the same conditions, the thickness of the obtained CdTe film varies for every film-forming processes.

As previously described, according to the conventional close-spaced sublimation process, it is difficult to obtain CdTe film having uniform quality and thickness within the same film and between a plurality of the films. For that reason, although the CdTe film theoretically has the forbidden band gap which is the most ideal for converting the solar light as a compound semiconductor, a CdTe film as an ideal p-type semiconductor has not actually been obtained by the conventional close-spaced sublimation process.

In order to improve the conversion efficiency of the CdTe solar cells, means of making the CdTe film a weak p-type one by diffusing copper or the like into the CdTe film from the electrode side has widely been used, as reported, for instance, by B. E. Mccandless et. al., in "A treatment to allow contacting CdTe with different conductors" (Conference record of the 24th IEEE photovoltaic specialists conference 1994 volume II, p. 107-110). However, according to this method, a solar cell having a satisfactory conversion efficiency has not been obtained.

DISCLOSURE OF THE INVENTION

The present invention intends to solve the above-mentioned conventional problems, and has, as its object, a provision of a method for preparing a CdTe film of good quality simply.

The method for preparing the CdTe film in accordance with the present invention comprises: a step of coating a paste containing a material for CdTe semiconductor on a supporting member thereby to form a coating film containing the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, thereby to cause the semiconductor material in the coating film to evaporate.

According to this method, it is possible to greatly improve the utilization rate of the material as compared with the case of using the above-mentioned conventional source. That is, since a thin coating film can be formed by coating, the utilization rate of the source which has conventionally been about 10% can be improved to about 50%. For that reason, it is not necessary to use the source for the formation of the film repeatedly. That is, since the source can be made disposable and a new source can constantly be used for the film-forming, it is possible to suppress the dispersion in characteristics of the CdTe film due to the repeated use of the source. Further, since the thin source can be obtained, it is possible to form the CdTe film without giving an excessive thermal damage to the previously formed CdS film.

Moreover, it is preferable to use a mixture of a cadmium powder and a tellurium powder as the semiconductor material. By using the mixture of the cadmium powder and the tellurium powder or, preferably, the pulverized powder, which is very inexpensive as compared with the CdTe powder thereof, the material cost can be reduced in great deal. In particular, by pulverizing Cd and Te in a mixed state, a mixed power can be obtained in a short time period. Further, with an energy for the pulverization, a part of the mixture can be synthesized into CdTe.

Moreover, by adding cadmium chloride into the paste, the crystallinity of the formed CdTe film is improved and the grain size of CdTe increases. In this manner, it is possible to obtain a solar cell of a high conversion efficiency. It is believed that the improvement in the crystallinity of the CdTe film is due to the fact that position of lattice defect of tellurium is substituted by chlorine, thereby to improve the crystallinity of the CdTe film. Moreover, since cadmium chloride is mixed into a paste and then coated, it is possible to constantly use the new source wherein cadmium chloride is uniformly dispersed. Therefore, it is possible to repeatedly and stably manufacture a CdTe film of high quality. If the added amount of cadmium chloride is smaller than 0.1 wt%, great effect cannot be obtained for the improvement in the performance of the solar cell. In contrast, if it is larger than 1.75 wt%, the performance is deteriorated conversely. For that reason, the added amount of cadmium chloride is preferably 0.1 - 1.75 wt%, and particularly 0.3 - 1.0 wt%.

In addition, it is preferable that the paste is one with a Group I element or a Group V element incorporated therein. By incorporating an impurity which acts as a carrier into the paste, it is possible to control the carrier concentration of the CdTe film in simple means. Incidentally, use of the Group I element or the Group V element in the conventional process employing a source prepared by placing the semiconductor material of powder state in a container so as to cover over it causes a variation in composition of the source, if such films are formed for plural times by using the same source, due to the differences in the sublimation speeds of the semiconductor material and the impurities. Therefore, a semiconductor film of stable composition cannot be obtained. On the other hand, according to the present invention, since the coating film of the semiconductor material formed on the surface of a heat-resistant supporting member is used as the source, it is possible to use a very small amount of the semiconductor material as the source. Therefore, a semiconductor film which has a constant concentration of the impurity can be formed. It is preferable that the Group I element to be mixed is lithium, potassium, sodium, rubidium, copper, silver or gold. Further, it is preferable that the Group V element to be mixed is arsenic, antimony, bismuth, phosphor or nitrogen. These can be used singly or plurally.

Moreover, by adding to the paste a substance which is stable in composition against the heat applied at the time of forming the semiconductor film and remains on the supporting member after the heating, it is possible to place the semiconductor material of an amount which is exactly necessary for one time film-forming on the supporting member in a stable state with a small dispersion. By causing all semiconductor materials to sublime, it is possible to manufacture a CdTe film of large area which is stable in thickness and quality. For instance, according to a screen-printing, it is difficult to form a coating film of a uniform thickness unless the thickness of the coating film to be formed is not less than 50 μm.

However, in a case of adding no additive to the paste, when a coating film with the thickness of 50 μm is entirely sublimed, a CdTe film with a thickness of about 20 μm is obtained. If such a thick CdTe film is used in the solar cell, resistance of the CdTe film in the thickness direction is large and thus the characteristics of the obtained solar cell are poor. That is, a thinner CdTe film is desired for employing it in the solar cell. The most suitable thickness is about 6 μm. That is, if no additive is added to the paste, it is necessary to stop the film formation halfway while the source remains. On the other hand, by adding an additive to the paste as in this example, the amount of the semiconductor material in the coating film can easily be adjusted and thus it becomes possible to form a semiconductor film which has a preferable thickness. Since to control the thickness of the coating film becomes so easy, it is possible to use only a necessary amount of the semiconductor material for one film formation as the source. As the substance to be added, carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride or aluminum nitride is preferable. Further, these substances can be used by mixing them. Since the carbon and silicon carbide can absorb radiated infrared ray, the source can be heated efficiently by using them. Moreover, since they can protect the CdS film which has previously been formed from a thermal damage, it is possible to suppress an occurrence of micro-short-circuiting resulting from a thinning of the CdS film by the sublimation, and an excessive mutual diffusion at an interface between the CdS film and the CdTe film.

Further, at the time of painting the paste, by making more amount of the paste adhere to the peripheral part of the supporting member where its temperature at heating is relatively lower than the central part of the supporting member, some more amount of semiconductor material may be placed there.

The supporting member for holding the paste is preferably a plate-shaped carbon material which has a heat soaking property and a small heat capacity. A glass substrate is preferable in viewpoints of price and easiness in handling. As the glass, borosilicate glass, a low alkali glass, soda-lime glass and the like may be used. In a case of using the glass substrate, it is preferable to place at least one carbon plate beneath the glass substrate. Further, if an expansion of the supporting member due to the thermal treatment is taken into consideration, a ceramics which has a small linear expansion coefficient is preferable. These supporting member can be used repeatedly.

It is preferable that the supporting member is composed of a glass having a conductive oxide film on the surface thereof. By using a glass having the conductive oxide film of, for instance, indium oxide, indium tin oxide, stannic oxide, zinc oxide and the like, as the supporting member, it is possible to suppress a radiation heat which reaches the formed semiconductor film, after the evaporation of the source is completed, thereby to prevent the excessive mutual diffusion at the interface of the CdS film and the CdTe film. Further, by roughening a surface of the supporting member which is opposite to the side where the paste is painted, the radiation heat can similarly be suppressed. In this case, by scatter due to an unevenness of the surface of the supporting member and an improvement in the heat absorbing property due to the increase in the surface area, it is possible to reduce the amount of infrared ray which transmits through the supporting member and reaches the formed semiconductor film.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic longitudinal cross-sectional view of a solar cell which uses CdTe film in accordance with one embodiment of the present invention.

FIG. 2 is a schematic longitudinal cross-sectional view showing a structure of an equipment employed for forming the CdTe film in the same embodiment.

FIG. 3 is a characteristic diagram showing the relationship between the times of forming the CdTe film in the same embodiment and the conversion efficiency of a solar cell produced by using the CdTe film.

FIG. 4 is a characteristic diagram showing the relationship between added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in another embodiment of the present invention.

FIG. 5 is a characteristic diagram showing the dispersion in the conversion efficiency of a solar cell produced by using CdTe film obtained in a still other embodiment of the present invention.

FIG. 6 is a characteristic diagram showing the added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in a still other embodiment of the present invention.

FIG. 7(a) - FIG. 7(g), each is a longitudinal cross-sectional view showing the state of the respective step in manufacture of the solar cell in another embodiment of the present invention.

FIG. 8 is a schematic longitudinal cross-sectional view of source substrate plate used in another embodiment of the present invention.

THE BEST MODE FOR CARRYING OUT THE INVENTION

The method for preparing the CdTe film in accordance with the present invention will be described in detail with reference to the drawings.

In the following examples, a solar cell shown by FIG. 1 is produced by using the obtained CdTe film.

A transparent and insulating substrate 1 is made from borosilicate glass, low-alkaline glass, low-iron soda-lime glass, soda-lime glass and the like. On the surface of this substrate 1, a transparent conductive film 2 with a thickness of 1,000 - 10,000 Å composed of tin oxide, indium tin oxide (ITO) and the like is formed by chemical vapor-phase growing process or sputtering. In this occasion, a silica film (SiO_2 film) may sometime be formed between the substrate 1 and the transparent conductive film 2, in order to prevent an alkali component in the substrate 1 from diffusing into the transparent conductive film 2. Then, by forming a CdS film 3 with a thickness of 500 - 2,000 Å on the transparent conductive film 2 as an n-type semiconductor, a substrate 4 for forming CdTe film is obtained. This CdS film 3 is formed by thermally decomposing such an organometallic complex compound as cadmium isopropyl xanthogenate on the transparent conductive film 2.

In the followings, as examples of the method for preparing CdTe semiconductor film in accordance with the present invention, methods for forming a CdTe film 5 on the surface of the thus obtained CdS film 3 of the substrate 4 will be described.

EXAMPLE 1

By mixing a CdTe powder as a semiconductor material with propylene glycol as a viscosity improver, a paste was prepared. By printing the obtained paste on the glass substrate as the supporting member and drying, a film of the semiconductor material was formed on a glass substrate, thereby to obtain a source substrate 9.

The obtained source substrate 9 and the substrate 4 were installed on a manufacturing equipment shown in FIG. 2, and the CdTe film 5 was formed on the surface of the substrate 4 in the following manner.

A chamber 14 is made of quartz tube, inside of which susceptors 10a and 10b made of carbon with a thickness of 1 mm are arranged as heat-soaking members. On the mutually confronting surfaces of the susceptors 10a and 10b, the source substrate 9 and the substrate 4 are arranged so as to make the semiconductor material film to face the CdS film 3, respectively. In that arrangement, a spacer 12 is disposed between the source substrate 9 and the substrate 4 so that the distance between the both is constant. The source substrate 9 and the substrate 4 may be disposed on the susceptors inversely, bottom to top.

By substituting the atmosphere inside the chamber 14 with an argon gas, and heating the source substrate 9 and the substrate 4 by lamp heaters 13a and 13b for 30 second to several minutes, while maintaining the pressure inside the chamber 14 to 1 Torr by aspirating with a rotary pump 11, a CdTe film 5 was formed on the CdS film 3 of the substrate. In this step, the temperature of the substrate 4 was kept to 400 - 650°C by heating, and the temperature of the source substrate 9 was kept to a temperature which was higher than the temperature of the substrate 4 by 5 - 100°C.

In the above-mentioned manner, 100 pieces of samples wherein the CdTe films 5 were formed on the CdS films 3 of the substrates 4 were prepared. In this preparation, the sources were replaced for every samples. Further, about half of the source was consumed for forming the film.

On the surfaces of the CdTe films 5 of the respective samples thus formed, a methanol or an aqueous saturated solution of cadmium chloride was applied and then the applied methanol or water was evaporated. Further, the substrate 4 for thin film forming was thermally treated at 400°C for 30 minutes. By this thermal treatment, grains in the CdTe film were grown.

A carbon paste was prepared by mixing a carbon powder and a solution obtained by dissolving polyvinylbutyral as a viscosity improver in diethylene glycol monobutyl ether with kneading. After applying this carbon paste on the surface of the CdTe film 5 by screen printing, it was dried and sintered, thereby to form a carbon electrode layer 6 as a current collector. On the other hand, a paste was prepared by mixing and kneading a mixed powder of silver and indium, an epoxide and an alcohol solution consisting mainly of terpineol. By applying the obtained paste on the surface of the CdS film 3 and carbon electrode layer 6 by screen printing, drying and then sintering, a + side electrode 7 and a - side electrode 8 were formed, respectively.

COMPARATIVE EXAMPLE 1

As a comparative example, a CdTe film was formed by using one obtained by filling the CdTe powder similar to that used in Example 1 in a dish-shape container as the source. In that case, the CdTe films were formed with the same source for a plurality of times. By this process, about 90% of the source was left after the formation of the CdTe films for 100 times. By using the obtained CdTe films, solar cells similar to those in Example 1 were produced.

Each 100 pieces of the solar cells of Example 1 and of Comparative Example 1 obtained in the above-mentioned manner were investigated about their conversion efficiencies with a solar simulator at AM 1.5, 100 mW/cm^2. The results are shown in FIG. 3. In this diagram, the abscissa represents the respective solar cells arranged in the orders of forming the CdTe films.

As clearly seen from FIG. 3, according to the manufacturing method of Comparative Example 1, the composition of the source varies with the repetition of the manufacture of the film, thereby to change the quality and the thickness of the obtained CdTe film. Therefore, the characteristics of the cells prepared with these CdTe films deteriorated. In contrast, according to the manufacturing method of Example 1, it is possible to make a small amount of the source to be uniformly held on the glass substrate. By this method, the utilization rate of the material can greatly be improved as compared with the manufacturing method of Comparative Example 1, even if the source is replaced for every film formations. That is, by employing a source of the coating film obtained by making a semiconductor material a paste-state and painting this paste on a substrate, a constantly stable supply of the source is enabled. Therefore, a semiconductor film with a high quality can be manufactured stably at a low cost.

EXAMPLE 2

In this example, a description will be made in a case of adding cadmium chloride into the paste for forming the CdTe film beforehand.

A CdTe powder similar to that in Example 1 was used as a semiconductor material. Pastes were respectively prepared by adding cadmium chloride at a rate of from 0 to 2.0 wt% to 100 parts by weight of this CdTe powder.

By using the obtained pastes, CdTe films were formed and then, solar cells were prepared in a manner similar to that in Example 1.

The relationship between the incorporation ratios of cadmium chloride to the CdTe powder and the conversion efficiency of the obtained solar cells are shown in FIG. 4.

As shown in FIG. 4, it is appreciated that by adding not less than 0.1 wt% of cadmium chloride to the CdTe powder, the conversion efficiency of the obtained cell is improved. However, if it is added in excess over 1.75 wt%, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1 - 1.75 wt% to the CdTe powder. In particular, the improvement in the conversion efficiency is remarkable at 0.3 - 1.0 wt%, and vicinity of 0.5 wt% is the most desirable.

100 parts by weight of the CdTe powder was mixed with 0.5 parts by weight of cadmium chloride. By using the obtained mixture, a paste was prepared as mentioned above. By using a semiconductor film formed by painting this paste as the source, a CdTe film was formed. In this step, the source was replaced for every times of film forming in a similar manner to that in Example 1.

As a comparative example, a CdTe film was also formed by using the same mixture so placed in a dish-shape container as to cover over it at a high density. In this time, the source was used continuously for a plurality of times for the film formation without replacing.

Solar cells were produced by using the CdTe films obtained in the above-mentioned manner. The characteristics of the obtained solar cells were investigated in a similar manner. The results are shown in Table 1.

Table 1

Film forming times (time)	Conversion efficiency (%)	
	Example 2	Comparative Example
1	14.6	13.6
20	14.5	13.5
40	14.7	13.2
60	14.5	12.5
80	14.5	11.3
100	14.6	8.5

As shown in Table 1, in the case of using the semiconductor material of powder state covering over the container, the characteristics of the semiconductor film decrease with the repeated times of the film forming. This is due to the above-mentioned varying in the cadmium chloride concentration and its non-uniformity. According to this method, it is difficult to form a CdTe film of good quality by using a small amount of the semiconductor material. That is, in any other means than discarding the source while consuming only a part of the source and leaving the remaining semiconductor material in a considerable amount, it is impossible to stably manufacture the CdTe film.

In contrast, according to the manufacturing method in accordance with this example, whereby the semiconductor material is made to have a paste-state, and the coating film obtained by applying the paste on the substrate is used as the source, the unevenness in the characteristics of the solar cells produced by using the obtained semiconductor film is small because there is no need for using the source repeatedly. Therefore, it is possible to stably manufacture the semiconductor film of a high quality at a low cost.

As the atmospheric gas, a similar effect is obtained in a case of using an inert gas such as nitrogen, hydrogen or helium gas in place of argon used in the above-mentioned example. In addition, in a film formation under a pressure of not more than 2 atm, a similar effect is also obtained.

EXAMPLE 3

By using a source of the coating film of the CdTe obtained by printing it as in Example 1, a CdTe film with a good quality can be formed. However, due to the fact that the CdTe powder as the raw material is very expensive, the price of the product becomes high. The reason for this is that the single crystal of CdTe is manufactured by Bridgman process in general. According to this process, in addition to the fact that heating at a high temperature of not less than 1,000 °C is required, a long period of time is required for elevating the temperature and cooling for the safety in operation and the improvement in the crystallinity.

Therefore, a description will be made, in this example, on a method for forming the CdTe film of a good quality, by using a starting material of a Cd powder and a Te powder which are inexpensive as compared with the CdTe powder. The price of the commercially available CdTe powder is about 250 yen/g but, in contrast, the prices of the commercially available Cd powder and Te powder are about 20 yen/g, respectively. Therefore, according to the manufacturing method of this example, the material cost can be reduced in great deal.

The Cd powder, the Te powder and a liquid (for instance, water) were mixed together and stirred by using a medium of ring-shape or spherical shape. Subsequently, a paste was prepared by adding propylene glycol to the obtained mixture after being dried. By using the paste thus obtained, a CdTe film was formed and a solar cell was produced in a manner similar to that in Example 1.

The conversion efficiency of the obtained solar cell was measured in a manner similar to that in Example 1. The results thereof are shown in FIG. 5. In this diagram, the ordinate represents mean value ± standard variance in the conversion efficiencies of the solar cells of Example 3 and of the solar cells of Comparative Example 1.

As clearly shown by FIG. 5, according to the manufacturing method of this example, it is possible to obtain a solar cell of an excellent characteristic by using low-priced materials. As the reason for this, there are given the fact that the temperature distribution in the source can be made uniform since the particle diameters of Cd and Te can be made uniform by pulverizing, and the amount of the source can be made small by using the film obtained by applying the pulverized mixture as the source.

The Cd powder and the Te powder were mixed in an equimolar amount, and pulverized in water to give a particle diameter of not more than about 1 μm by using a medium stirring mill. After drying the pulverized powder thus obtained, propylene glycol as a viscosity improver was added to the pulverized powder and kneaded, thereby to prepare a paste. By printing this paste on a carbon plate with a thickness of 1 mm as the supporting member, and drying at 120°C for 1 hour, a coating film was formed and a source substrate was obtained.

On investigating the composition of the formed coating film by X-ray diffraction, diffraction peaks of Cd single substance, Te single substance and CdTe were observed. It is believed that this CdTe is synthesized at the pulverization by the pulverizing energy.

This source substrate 9 and the substrate 4 were arranged so as to make the coating film to face the CdS film, with a gap of 2 mm. Thereafter, the atmosphere inside the chamber 14 was substituted by argon, the source substrate 9 and the substrate 4 were heated to temperatures of 600 - 630°C and of 580 - 600°C, respectively, while maintaining the pressure to 1 - 5 Torr, and kept there for 1 minute. By this procedure, a CdTe film with a thickness of 6 μm was formed on the CdS film of the substrate 4.

An aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the surface of the obtained CdTe film, and then the water was evaporated. Thereafter, by thermally treating the CdTe film at 400°C for 30 minutes, the crystallinity of the CdTe film was improved. Subsequently, a carbon film and an AgIn film were formed as an electrode of the CdTe film side and an electrode of the CdS film side, respectively, thereby to produce a solar cell.

The measurement on the characteristics of the obtained solar cell conducted with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.5 mA/cm^2 and the open-circuit voltage was 0.813 V. Further, the fill factor was 0.696 and the conversion efficiency was 13.3%. These characteristics are about the same degree as the characteristics of the solar cell of Comparative Example 1 produced by using the CdTe film formed by using the CdTe powder placed in the dish-shape container so as to cover over it (short-circuit current of 23.4 mA/cm^2, open-circuit voltage of 0.815 V, fill factor of 0.701 and conversion efficiency of 13.4%).

Next, a paste was prepared by adding an appropriate amount of $CdCl_2$ as a melting point depression agent in addition to propylene glycol as the viscosity improver to the pulverized powder similar to the above-mentioned. After printing the obtained paste on a carbon plate with a thickness of 1 mm, the paste was dried by drying at 120°C for 1 hour, thereby to form a coating film comprising a semiconductor material, and to obtain a source substrate 9. In an X-ray diffraction pattern of the obtained coating film, a peak attributable to the $CdCl_2$ was observed in addition to the diffraction peaks of Cd single substance, Te single substance and CdTe, of course.

By heating the obtained source substrate 9 under a nitrogen atmosphere at a temperature of 600 - 700°C for 1 hour, the coating film was sintered. In an X-ray diffraction pattern of the sintered film thus obtained, only the diffraction peak attributable to CdTe was observed.

Next, the source substrate 9 and the substrate 4 were so placed as to face each other, with a gap of 2 mm, and a CdTe film 5 was formed on the CdS film 3 in a procedure as shown above. After the formation of the CdTe film 5, an aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the CdTe film 5 and water was evaporated, and then, it was thermally treated at 400 °C for 30 minutes. Thereafter, a solar cell was produced in a procedure as shown above and the characteristics of the solar cell were evaluated in a similar manner. Measurements on the characteristics of the solar cell with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.6 mA/cm^2, and the open-circuit voltage was 0.816 V. Further, the fill factor and the conversion efficiency were found to be 0.699 and 13.5%, respectively. These values are the same degree as those of the solar cell of Comparative Example 1.

A film formed by painting a fine powder obtained by pulverizing Cd and Te singly or a CdTe compound and drying it, or a sintered film thereof obtained in the above-mentioned manner was used as the source to obtain a good quality CdTe film.

Incidentally, a similar effect is obtained by using a commercially-available CdTe as the starting material.

EXAMPLE 4

In this example, a description will be made on a method which employs the Cd and Te similar to those in Example 3 as the starting material, wherein cadmium chloride is further added to this mixture.

A muddy mixture was prepared by pulverizing the Cd and Te similar to those used in Example 3 in a wet process. Next, by drying the mixture and adding cadmium chloride and propylene glycol as the viscosity improver to this mixture, a paste was prepared. A CdTe film was formed by using the obtained paste and a solar cell was produced in a manner similar to that in Example 1.

The characteristics of the obtained solar cell were evaluated in a manner similar to those in the above-mentioned examples.

The added amounts of cadmium chloride to the sources and the conversion efficiencies of the solar cells produced by using the respective sources are shown in FIG. 6.

From FIG. 6, it is appreciated that by adding cadmium chloride in an amount of not less than 0.1 wt% for a sum of the weights of Cd and Te to it, the conversion efficiency is improved as compared with a case of not adding cadmium chloride. However, if cadmium chloride is added in an amount of more than 1.75 wt% for a sum of the weights of Cd and Te, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1 - 1.75 wt%. In particular, the improvement in the conversion efficiency is remarkable in 0.3 - 1.0 wt%, and that in the vicinity of 0.5 wt% is the most desirable.

EXAMPLE 5

In this example, a description will be made on a method with an incorporation of a Group I element or a Group V element as a dopant into the source. According to this method, carrier concentration of the CdTe film can easily be controlled. The Group I element and/or the Group V element to be added is/are incorporated into it in a state of single substance or a compound such as organometallic compounds. These elements may be used singly or plurally.

On a surface of a substrate 1 with a thickness of 1.1 mm made from a borosilicate glass, a transparent conductive film 2 with a thickness of 500 - 5,000 Å composed of tin oxide was formed by a sputtering process. Next, a CdS film 3 with a thickness of 500 - 2,000 Å was formed by a CVD process. For the formation of the CdS film 3, any other process, for instance, a solution deposition method, may be employed.

A source substrate 9 provided with the source added with an impurity was arranged on a susceptor 12a in the lower side of the equipment. On the other hand, on a susceptor 12b in the upper side, a substrate 4 was arranged with a gap of 0.1 mm to several mm to the surface of the source. After substituting the atmosphere inside the chamber 14 with argon gas or nitrogen gas, by heating the substrate 4 in a temperature range of 400 - 800°C and the source substrate 9 at a temperature higher than that of the substrate 5 and keeping them there for a certain time period, a semiconductor film was formed on the surface of the substrate 5.

In this step, although it is preferable to keep the pressure of argon gas or nitrogen gas to about 1 - 20 Torr, it is possible to form the film under 1 atm. In that case, it is preferable that the temperature difference between the substrate 4 and the source substrate 9 is not less than 50°C. In the case of forming the film under 1 atm, there is no need for making the chamber to have a pressure-resistant structure, and thus it is possible to simplify the equipment. Further, since a speeds in inlet and outlet of the substrate to and from the equipment can be made high, the productivity is greatly improved.

For the source, a paste is prepared by using the CdTe incorporated with antimony telluride at 0.01 wt%. By printing the obtained paste on a glass substrate and drying, the source substrate 9 was obtained.

By using the obtained source substrate 9, a CdTe film 5 was formed under the atmosphere of argon with a pressure of 1 Torr. In this step, by maintaining the substrate 4 in a temperature range of 400 - 650°C and the source substrate 9 at a temperature higher by 30°C than that of the substrate 4 for 2 minutes, the CdTe film 5 was formed on the CdS film 3.

Separately, a carbon paste was prepared by mixing and kneading a carbon powder with a solution of diethylene glycol monobutyl ether which dissolved polyvinyl butyral.

The obtained carbon paste was applied on the CdTe film 5 by a screen printing process and sintered after being dried, to form a carbon electrode layer 6.

By mixing a mixed powder of silver and indium, and an epoxide with an alcohol consisting mainly of terpineol, and kneading the mixture, a paste was prepared. The obtained paste was applied on the CdS film 3 and the carbon electrode layer 6 by the screen printing process, which was then dried and sintered to form a + electrode 7 and a - electrode 8.

The CdTe films 5 were also formed in a similar manner by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the CdTe paste. By using the respective CdTe films 5 thus obtained, solar cells were produced.

Further, as a comparative example, a solar cell employing a CdTe film prepared by using a CdTe paste with no additional impurity was produced as shown above and was similarly evaluated.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentration of the CdTe films are shown in Table 2.

Table 2

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
Antimony telluride	9.5×10^{14}	14.1
Phosphor	8.4×10^{14}	14.5
Arsenic	8.2×10^{14}	14.0
Antimony	8.1×10^{14}	14.2
Bismuth	8.2×10^{14}	14.1
Lithium	5.4×10^{14}	13.2
Potassium	8.1×10^{14}	14.0
Sodium	5.0×10^{14}	13.5
Rubidium	6.3×10^{14}	13.8
Copper	8.7×10^{14}	14.2
Silver	8.3×10^{14}	13.9
Gold	8.4×10^{14}	14.0
Triphenylantimony	1.2×10^{15}	14.5
Antimony octylate	1.4×10^{15}	14.6
Triphenylbismuth	1.3×10^{15}	14.4
Triphenylphosphine	1.8×10^{15}	14.7
Triphenylphosphate	1.7×10^{15}	14.7
Triphenylphosphite	1.8×10^{15}	14.6
Triallylphosphine	1.8×10^{15}	14.5
Triallylamine	1.6×10^{15}	14.2

Table 2 (continued)

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
None	3.5×10^{14}	13.0

From Table 2, it is appreciated that in the case of incorporating a Group I element or a Group V element into the source, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 6

A CdTe film was formed by the similar method as that in Example 5 except for the use of nitrogen in place of argon as the atmospheric gas. The conditions employed for forming the CdTe film 5 were that the pressure inside the chamber 14 was 1 atm, the substrate 4 was kept in a temperature range of 400 - 650°C, and the source substrate 9 was kept at a temperature higher by about 100°C than that of the substrate 4 for 10 minutes, thereby to form a CdTe film 5. Further, a solar cell was similarly produced by using the obtained CdTe film 5.

Moreover, the CdTe films 5 were also formed by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the paste, and by using the CdTe films 5 thus obtained, solar cells were produced.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentrations of the CdTe films are shown in Table 3.

As a comparative example, a relationship between the conversion efficiency of a solar cell employing a CdTe film produced by using a CdTe paste with no additional impurity, and the carrier concentration of the CdTe film is also shown in Table 3.

Table 3

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Antimony telluride	8.2×10^{14}	14.5
Phosphor	8.4×10^{14}	14.7
Arsenic	7.1×10^{14}	14.2
Antimony	7.9×10^{14}	14.4
Bismuth	6.1×10^{14}	14.1
Lithium	5.4×10^{14}	14.0
Potassium	5.2×10^{14}	14.0
Sodium	4.9×10^{14}	13.8
Rubidium	5.8×10^{14}	14.1
Copper	8.5×10^{14}	14.7
Silver	7.1×10^{14}	14.1
Gold	8.2×10^{14}	14.4
Triphenylantimony	1.0×10^{15}	14.9
Antimony octylate	1.1×10^{15}	14.9
Triphenylbismuth	9.8×10^{15}	14.8
Triphenylphosphine	1.3×10^{15}	15.1
Triphenylphosphate	1.2×10^{15}	15.0
Triphenylphosphite	1.3×10^{15}	15.1

Table 3 (continued)

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Triallylphosphine	1.3×10^{15}	15.1
Triallylamine	1.2×10^{15}	15.0
None	3.2×10^{14}	13.2

From Table 3, it is appreciated that in either case of incorporating a Group I element or a Group V element into the source material, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 7

A solution was prepared by dissolving cadmium isopropyl xanthogenate, which is an organometallic compound with a sulfur bond, in 1-methyl-2-pyrrolidone.

Separately, on a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm shown in FIG. 7(a), a stannic dioxide film 21 with a thickness of about 600 nm was formed.

The solution obtained in the above-mentioned manner was painted on the surface of the stannic dioxide film 21 and dried at 110°C, thereby to evaporate the solvent. Thereafter, it was subjected to a thermal treatment in the air at 450°C for 3 minutes, thereby to decompose the cadmium isopropyl xanthogenate and to form the CdS film 22. At this step, by adjusting the concentration of the solution thus used and the repeat times of the coating, the thickness of the CdS films 22 were set to 70 nm.

Thereafter, by a laser scribing process employing a YAG laser, a pattern for 42 cell series connection as shown by FIG. 7(b) was formed.

Subsequently, a mixed powder was obtained by mixing 1 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, with 6 g of CdTe powder with a purity of 5N.

The mixed powder thus obtained was placed on a glass substrate (Corning # 1737) with a width and a length of 35 cm so as to cover over it, thereby to form a particle layer and to obtain a source substrate. Then, the source substrate and the substrate 20 were placed so as to make the particle layer to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, CdTe films 23 with a thickness of about 6 μm were formed on the CdS films 22 as shown by FIG. 7(c). Thereafter, as shown by FIG. 7(d), etching resists 30 were applied on the surface of the substrate 20 by a screen printing process, and a thermal treatment was conducted in a dryer at 100°C for 5 minutes.

Subsequently, after subjecting the substrate 20 to an etching process for 5 minutes by immersing it in nitric acid, the substrate 20 was immersed in a 10% solution of sodium hydroxide, thereby to fall the resist layer 30 off as shown by FIG. 7(f). Thereafter, the substrate 20 was immersed in a methanol saturated solution of cadmium chloride and dried, and then subjected to a thermal treatment in the air at 400°C for 20 minutes. Thereafter, residue of the cadmium chloride was removed by ultrasonic-wave washing in pure water.

Subsequently, after forming a carbon film 24 which was added with a trace amount of copper on the surface of the substrate 20 by the screen printing process, it was dried and heated at 390°C for 30 minutes, thereby to diffuse the copper into the CdTe films 23. Thereafter, silver-indium films 25 were formed by a similar screen printing process and thermal treatment, thereby to obtain a solar cell of 42 cells series connection as shown by FIG. 7(g).

EXAMPLE 8

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 21 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 50 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate (Corning # 1737) with a width and a length of the same 35 cm, and drying it in the air at 120°C for 4 hours, a particle layer with a thickness of about 100 μm consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate 20 were placed so as to make the particle layer to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, the source in the particle layer was entirely sublimed, thereby to form a CdTe film 23 with a thickness of about 6 μm on the CdS films 22 as shown by FIG. 7(c). Thereafter, as shown by FIG. 7(d), etching resists 30 were painted on the substrate 20 by a screen printing process, and a thermal treatment was performed in a dryer at 100°C for 5 minutes.

By using the obtained CdTe films 23, a solar cell similar to that of Example 7 was produced.

Further, by using powders of carbon black, silicon carbide, silicon dioxide, silicon nitride, aluminum oxide, boron nitride, zirconia, silicon nitride, and aluminum nitride, each of which has a purity of 3N and a particle diameter of not more than 5 μm, in place of graphite, solar cells were similarly produced.

EXAMPLE 9

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 21 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate 100 (Corning # 1737) with a width and a length of the same 35 cm, and drying it in the air at 120°C for 4 hours, a particle layer consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate 20 were placed so as to make the particle layer 120 to face the CdS film, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, and until the CdTe on the source substrate was entirely evaporated (for 5 minutes), thereby to form a CdTe film 23 with a thickness of about 6 μm on the surface of the substrate 20.

By using the obtained CdTe film 23, a solar cell similar to that of Example 7 was produced.

EXAMPLE 10

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 11 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

After forming an indium oxide film on one surface of a glass substrate 200 (Corning # 1737) with a width and a length of the same 35 cm, the indium oxide film 110 was removed by etching excepting the specified portion as shown by FIG. 8. In this step, a ratio occupied by the indium oxide films 110 in the central part of the surface was made higher than that in the peripheral part. On the surface of the other side of this glass substrate 200, the above-mentioned paste was painted and dried in the air at 120°C for 4 hours, thereby to form a particle layer 220 consisting mainly of CdTe and to obtain a source substrate 230.

Then, the source substrate 230 and the substrate 20 which was similar to that used in Example 7 were placed so as to make the particle layer 220 to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate 230 at 60°C under argon atmosphere with a pressure of 1 Torr, until all of the CdTe on the source substrate 230 was evaporated (for 5 minutes), thereby to form a CdTe film 23 with a thickness of about 6 μm.

By using the obtained CdTe film, a solar cell similar to that of Example 7 was produced.

EXAMPLE 11

After roughening one surface of a glass substrate 200 (Corning # 1737) with a length and a width of the same 35 cm by etching with hydrofluoric acid, a particle layer was formed on the other surface with the paste which was similar to that used in Example 10, thereby to obtain a source substrate.

By using the obtained source substrate, a CdTe film was formed, and a solar cell was produced in a manner similar to that in Example 8.

COMPARATIVE EXAMPLE 3

As a comparative example, a paste was prepared in a method similar to that in Example 8 excepting an addition of graphite. The obtained source was applied in a manner similar to that in Example 8 in an amount just required for forming the CdTe film with a thickness of 6 nm. In that case, since it does not contain graphite, the amount of the paste to coat is required to be less as compared with Example 8 so as to adjust the thickness of the coating film to be formed to about 50 μm, but it is impossible to make the amount of the source and the thickness of the coating film uniform. Therefore, by applying the minimum amount for uniformly painting, a source substrate was produced. By using the source substrate, a CdTe film was formed in a manner similar to that in Example 8. In this step, although the thickness of the coating film was made uniform, the dispersion in the thickness of the obtained CdTe film was larger than that of the CdTe film obtained in Example 8. By using this CdTe film, a solar cell was produced in a manner similar to that of Example 8. This was named as the solar cell of Comparative Example 3.

On the solar cells of Example 7 - 11 and of Comparative Example 3, measurements of the open circuit voltage (V_{OC}) and fill factor (FF) which is a standard for the decision of good/bad of the output characteristic were conducted under condition of AM; 1.5, 100 mW/cm^2. The results thereof are shown in Table 4.

Table 4

	Additive	V_{OC}(V)	FF(%)	η(%)
Example 7	Graphite	31.8	57	9.6
Example 8	Carbon black	33.0	61	10.1
	Graphite	33.6	64	10.6
	Silicon dioxide	32.7	59	9.8
	Aluminum oxide	33.3	62	10.2
	Zirconium oxide	31.0	58	9.7
	Boron nitride	32.4	60	10.0
	Silicon nitride	32.6	60	9.9
	Aluminum nitride	32.0	57	9.7
	Silicon carbide	33.0	60	10.0
Example 9	Graphite	33.4	62	10.3
Example 10	Graphite	33.2	63	10.4
Example 11	Graphite	33.6	64	10.5
Comparative Example 3	None	24.2	52	6.8

From Table 4, it is appreciated that the solar cells of Examples 7 - 11 employing the CdTe films which have been formed by using, as the source, a CdTe material added with a material which remains after the heating are excellent in every respect of the characteristics, as compared with the solar cell of Comparative Example 3. It is believed that this is due to the fact that by adding these materials, thermal damage of the CdS film attributable to the radiation heat can be prevented.

In particular, in the case of using graphite, carbon or silicon carbide in Example 8, or in Examples 9 - 11, by using the coating film of an amount just required for the film forming of one time as the source, it is possible to suppress an occurrence of an excessive heating of the substrate for thin-film forming, directly by the radiation heat, after the completion of the vaporization of the source. Tellurium, cadmium and cadmium telluride have a low absorption rate for infrared ray and a low heat conductivity. Therefore, if the source consisting of these semiconductor material is thick, since the temperature of the source is hardly elevated at the heating, the film forming speed is low, the infrared ray transmitted through the source is incident on the CdS film which has previously been formed on the substrate. Since the CdS which is typical as the n-type semiconductor for the solar cells has a very high absorption rate for infrared ray, it is heated by the incident infrared ray and made to be liable to vaporize. Therefore, when the CdS film is made thinner than the suitable thickness and when the vaporization of the CdS film further proceeds, pinholes are produced, thereby to invite micro-short-circuitings. For that reason, by using the infrared-absorption materials being mixed with the source as in these examples, the excessive temperature rise of the substrate is suppressed. Therefore, the mutual diffusion at a joint between the CdS film and the CdTe film is suppressed, thereby to obtain a solar cell which has a high open-circuit voltage and fill factor.

In addition, according to the method of the examples, since the source can be used exhaustively, the utilization rate of the material can greatly be improved. Although the CdTe film of good quality can also be obtained in Example 7 wherein a mixture of the source and the additive is used by filling it in a container as described above, it is limited to the cases where the times of repeatedly using the same source for forming the CdTe film are small. That is, according to this method, the change in the source cannot be avoided if the source is used repeatedly. Therefore, by using the coating film as the source as described in Examples 1 - 9, it is possible to obtain the CdTe film of good quality more effectively.

Further, measurements were made on the thickness distributions in the CdTe film formed in accordance with Example 8 and the CdTe film formed in accordance with Comparative Example 3. The results thereof are shown in Table 5. In this table, distance indicates a distance from the central part of the substrate in the diagonal direction.

Table 5

Distance (mm)	Example 8 (μm)	Comparative Example 3 (μm)
0	6.0	3.0
25	6.2	4.9
50	6.3	6.0
75	6.3	7.0
100	6.4	8.5
125	6.4	8.8
150	6.3	9.5
175	6.4	10.0
200	6.5	10.2
212	6.5	10.4

Moreover, the solar cells which employ the CdTe film obtained in accordance with Example 8 and the solar cells obtained in accordance with Comparative Example 3 were produced in trial, for each five lots, each of which contains 10 pieces, and the measurements were made on the film thickness of CdTe and the solar cell characteristics. The results thereof are shown in Table 6.

Table 6

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
1	6.5	6.8	6.4	6.7	6.0	6.0	8.5	5.0	9.9	6.2
	10.0	9.8	9.8	10.5	9.4	8.0	7.2	8.2	7.5	8.1
2	6.4	6.6	6.5	6.9	6.2	7.0	9.0	5.9	10.0	6.9
	9.9	9.9	10.0	9.5	9.1	8.5	6.9	8.8	7.3	8.2
3	6.7	6.7	6.3	6.2	6.8	6.5	7.6	6.5	9.1	6.5
	10.2	10.0	10.1	10.1	9.9	7.9	8.0	7.9	7.0	7.5
4	6.3	6.9	6.5	6.1	6.9	7.2	9.5	6.1	9.5	6.9
	10.1	9.8	9.9	9.7	9.6	6.9	7.0	5.9	6.9	8.5
5	6.6	6.7	6.7	6.9	6.2	5.3	8.7	5.1	8.7	6.8
	10.2	9.9	9.7	9.8	10.4	7.6	6.8	7.1	7.2	7.4
6	6.5	6.5	6.4	6.7	6.0	5.9	7.1	4.0	8.8	6.6
	9.9	10.1	9.5	9.7	10.2	9.2	5.9	6.9	6.1	7.8

Table 6 (continued)

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
7	6.7	6.9	6.5	6.5	6.9	7.8	6.6	4.9	7.9	6.0
	10.3	9.9	10.1	10.2	10.0	8.4	9.0	7.3	6.9	7.7
8	6.3	6.8	6.6	6.8	6.4	6.3	8.7	6.1	7.8	6.5
	10.0	10.0	9.8	10.5	9.3	8.6	6.4	7.5	7.0	6.3
9	6.6	6.7	6.7	6.7	6.8	6.9	7.5	5.9	10.0	6.8
	9.9	9.7	9.9	10.4	9.7	9.0	8.8	7.7	6.1	5.2
10	6.4	6.9	6.8	6.1	6.3	8.0	6.2	9.0	9.5	6.9
	10.3	9.8	9.6	10.1	9.5	7.1	6.5	8.1	6.8	8.1
Upper column: Thickness of CdTe film at central part of substrate (µm). Lower column: Conversion efficiency (%).										

The difference between the CdTe film of Example 8 and the CdTe film of Comparative Example 3 is only a presence/absence of the addition of graphite to the pastes. That is, as clearly shown from Table 5, by forming with a mixture of the source and the additive, a CdTe film with a stable thickness can be obtained.

Further, it is also appreciated from Table 6 that the CdTe film of Example 8 has a smaller dispersion in thickness within one lot and between the lots as compared with the CdTe film of Comparative Example 3. For that reason, according to Example 8, it is possible to stably obtain a solar cell of more excellent characteristics as compared with Comparative example 3.

As previously described, by using a source mixed with an additive, it is possible to suppress mutual diffusion at a joint between the CdS and the CdTe resulting from an excessive heating by a radiation, thereby to stably obtain a CdTe film of good quality.

As the additive, any stable substance which does not decompose or cause a chemical reaction on the supporting member at the time of heating can be used.

Further, by using a substrate which has an uneven structure on the surface opposite to the surface on which a particle layer is formed as in Example 11, it is possible to absorb the infrared ray by the uneven surface and a similar effect can be obtained.

On the other hand, according to Example 10, by lowering the proportion occupied by a transparent conductive film at the peripheral part of the substrate as compared with that of the central part, it is possible to make the temperature difference of the surface of the substrate small, by utilizing an action of the transparent conductive film to suppress the radiation of the infrared ray. According to this method, the dispersion in the thickness of the CdTe film formed on the surface of the substrate can be made small. A similar effect can also be obtained by directly piling a separate substrate which has a similar structure on a normal source substrate.

Further, in the above-mentioned examples, although CdS is employed as the n-type semiconductor for a solar cell, a similar effect can also be obtained in a case of using CdZnS. For forming these n-type semiconductors, a known method such as a process of thermally decomposing an organometallic compound, a liquid phase film-forming process, a close-spaced sublimation process, a vapor-deposition process, a sputtering process and the like can be employed.

As the transparent conductive film, indium tin oxide or zinc oxide can also be employed in place of tin oxide. For forming the transparent conductive film, a sputtering process, a chemical vapor-phase growing process, a vapor-deposition process or the like can be employed.

In the preciously-mentioned examples, although the glass substrate which has the transparent conductive film and the CdS film on the surface is used as a substrate for forming the CdTe, it is also possible to use, in place of this, any of semiconductor materials of cadmium zinc sulfide, gallium arsenide, indium gallium arsenide, indium gallium phosphor arsenide, zinc selenide, indium selenide, silicon, germanium, indium copper selenide, indium gallium copper selenide, gallium nitride and the like, and metals of iron, nickel, molybdenum and the like, as the substrate. As the substrate, a ceramic material can also be used in addition to the glass.

Further, although a description has exemplary been made on the method for forming the CdTe film, it can also be applied to a thin film formation of other semiconductors such as CdS, cadmium zinc sulfide, zinc selenide, indium selenide, indium copper selenide, indium gallium copper selenide, and the like.

As the viscosity improver used in preparing the paste, such another material as ethylene glycol, methyl cellulose or the like can also be employed, in addition to propylene glycol which was used in the above-mentioned examples.

POSSIBILITY OF INDUSTRIAL UTILIZATION

According to the present invention, it is possible to form a CdTe film of good quality in an inexpensive efficiently. The present invention can be embodied in the manufacture of semiconductor device such as a solar cell, an infrared ray receiving device, and an integrated circuit.

Claims

1. A method for preparing a CdTe film comprising:

   a step of applying a paste containing a material for CdTe semiconductor on a supporting member, thereby to form a coating film containing said material for CdTe semiconductor on the surface of said supporting member,
   a step of closely arranging said supporting member and a substrate on which a CdTe film is to be formed, to make said coating film to face the surface of said substrate, and
   a step of forming a CdTe film on said substrate, by heating said coating film and said substrate, and causing said material for the semiconductor in said coating film to evaporate.

2. The method for preparing a CdTe film in accordance with claim 1, wherein said semiconductor material is a mixture of a cadmium powder and a tellurium powder.

3. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains cadmium chloride.

4. The method for preparing a CdTe film in accordance with claim 3, wherein the added amount of said cadmium chloride is 0.1 - 1.75 wt% to said semiconductor material.

5. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains a Group I element or a Group V element incorporated therein.

6. The method for preparing the CdTe film in accordance with claim 5, wherein said Group I element is at least one member selected from the group consisting of lithium, potassium, sodium, rubidium, copper, silver and gold.

7. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is at least one member selected from the group consisting of arsenic, antimony, bismuth, phosphor and nitrogen.

8. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is antimony, and is contained in said paste in a state of antimony telluride.

9. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is contained in said paste in a state of at least one member selected from the group consisting of triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine.

10. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains an additive of powder state which is stable in composition at the heating step.

11. The method for preparing a CdTe film in accordance with claim 10, wherein said additive is at least one member selected from the group consisting of carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride, and aluminum nitride.

12. The method for preparing a CdTe film in accordance with claim 1, wherein at the step of applying said paste, the painted amount of the paste in the peripheral part of said substrate is made to be larger than the painted amount of the paste in the central part of said substrate.

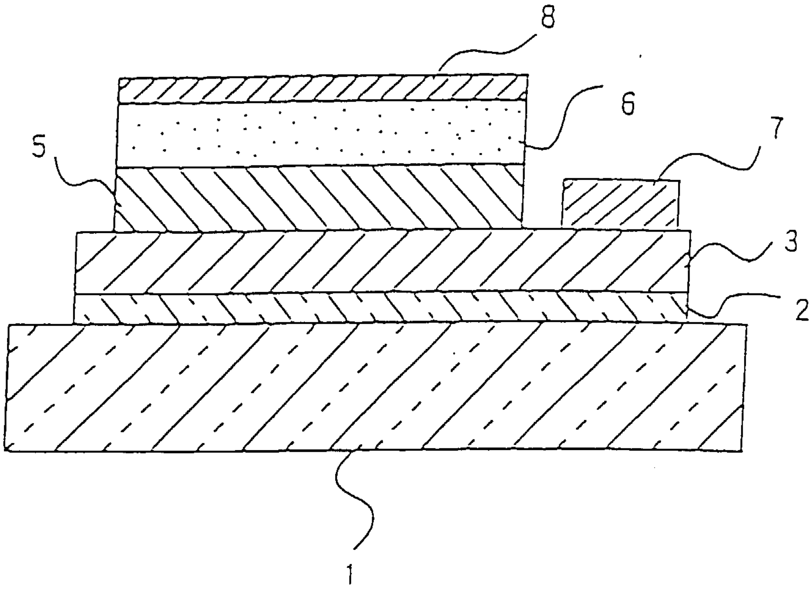
13. The method for preparing a CdTe film in accordance with claim 1, wherein said supporting member is at least one member selected from the group consisting of glass, ceramic material and carbon.

14. The method for preparing a CdTe film in accordance with claim 1, wherein said supporting member is glass having a conductive oxide film on the surface thereof.

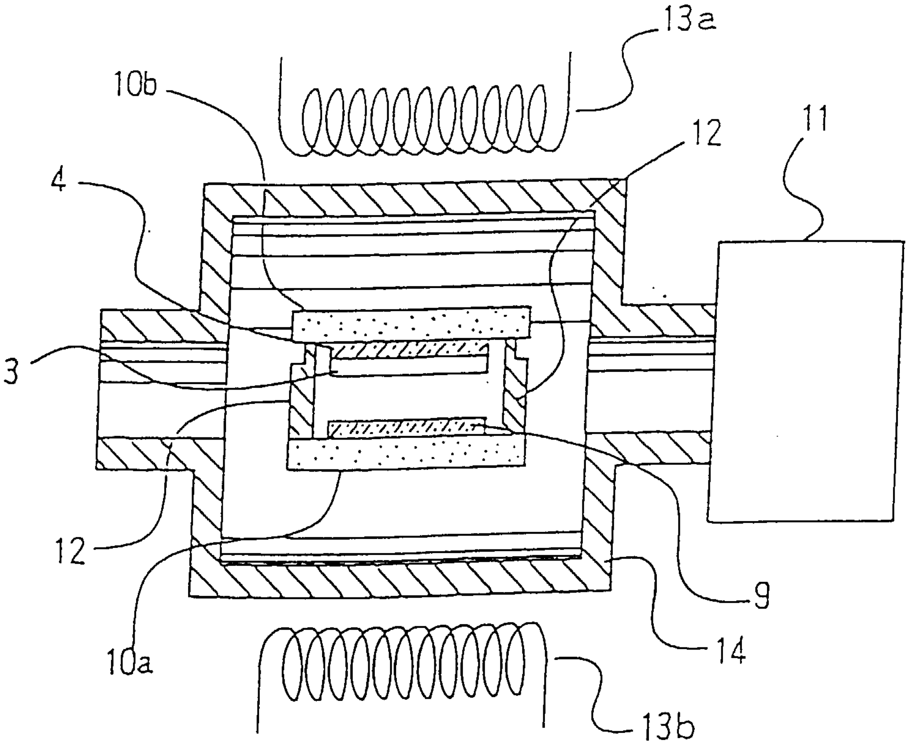
15. The method for preparing a CdTe film in accordance with claim 1, wherein one surface of said supporting member that is opposite to the surface on which said paste is painted is rough.

16. A solar cell comprising: an insulating and transparent substrate, a transparent conductive film formed on said substrate, an n-type semiconductor film formed on said transparent conductive film, a p-type semiconductor layer formed on said n-type semiconductor film as a light absorbing layer, a current collector formed on said p-type semiconductor layer, a + side electrode electrically connected to said current collector, and a - side electrode electrically connected to said n-type semiconductor layer, wherein said p-type semiconductor film is a CdTe film formed by the method in accordance with claim 1.

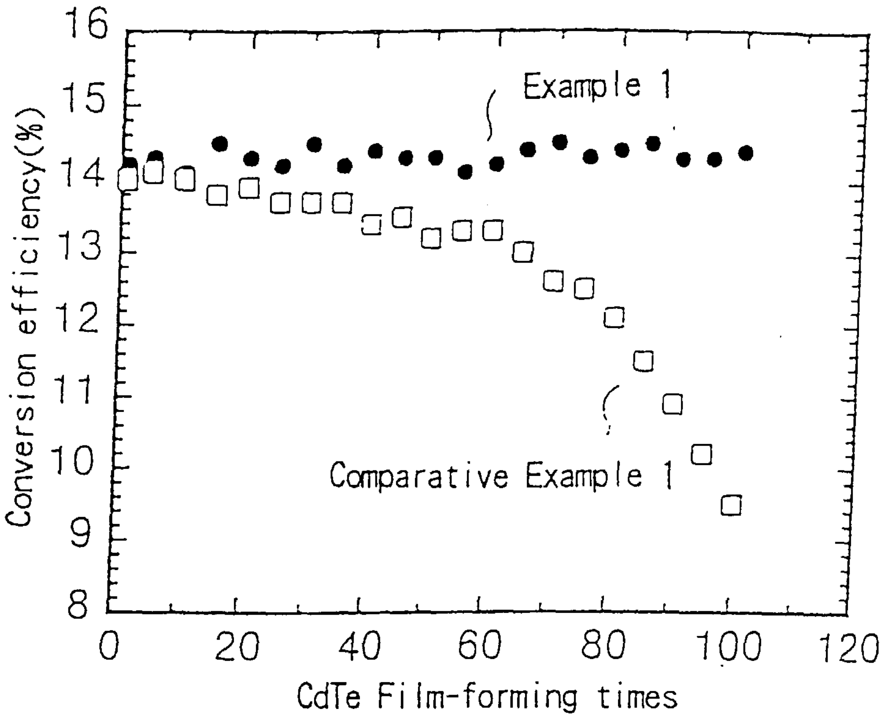
F I G. 1



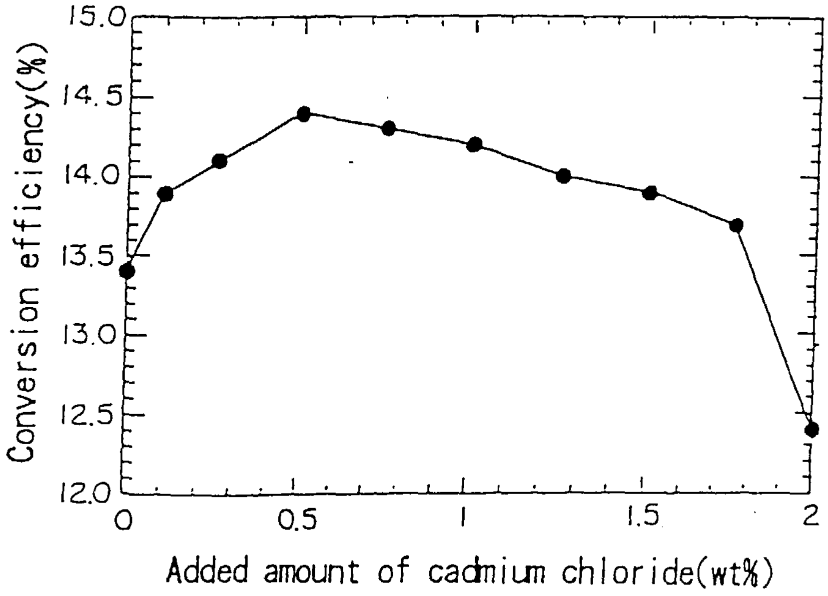
F I G. 2



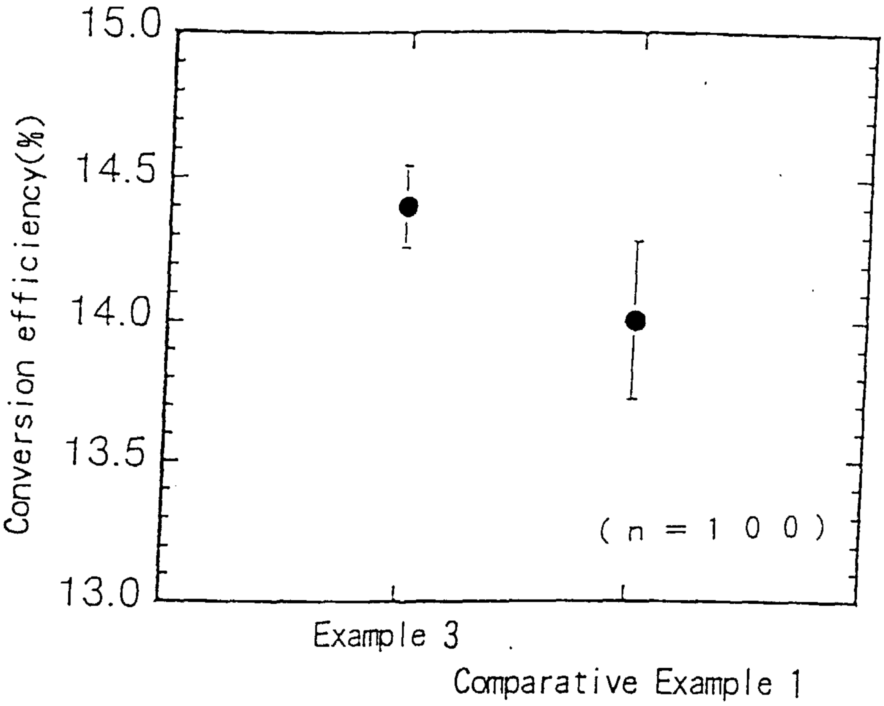
F I G. 3


Conversion efficiency(%)
16
15
14
13
12
11
10
9
8
0
20
40
60
80
100
120
CdTe Film-forming times
Example 1
Comparative Example 1

F I G. 4


Conversion efficiency(%)
15.0
14.5
14.0
13.5
13.0
12.5
12.0
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

F I G. 5


15.0
14.5
14.0
13.5
13.0
Conversion efficiency(%)
(n = 1 0 0)
Example 3
Comparative Example 1

F I G. 6

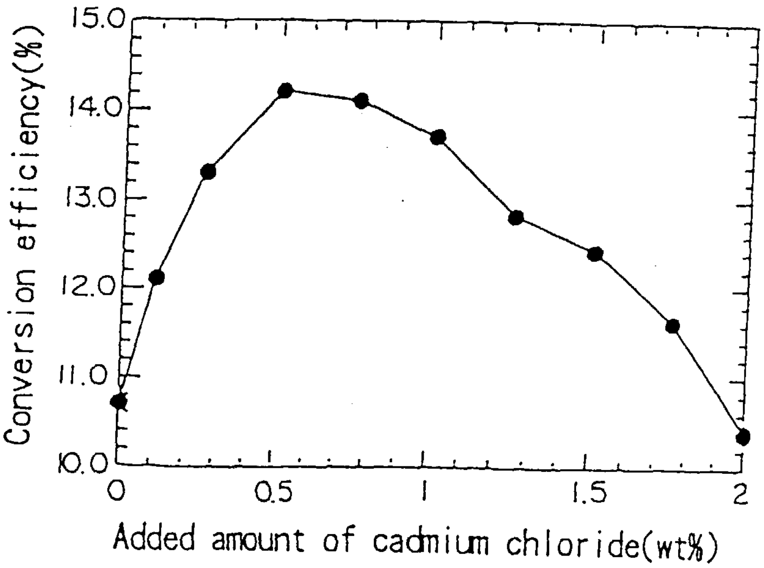

15.0
14.0
13.0
12.0
11.0
10.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 7

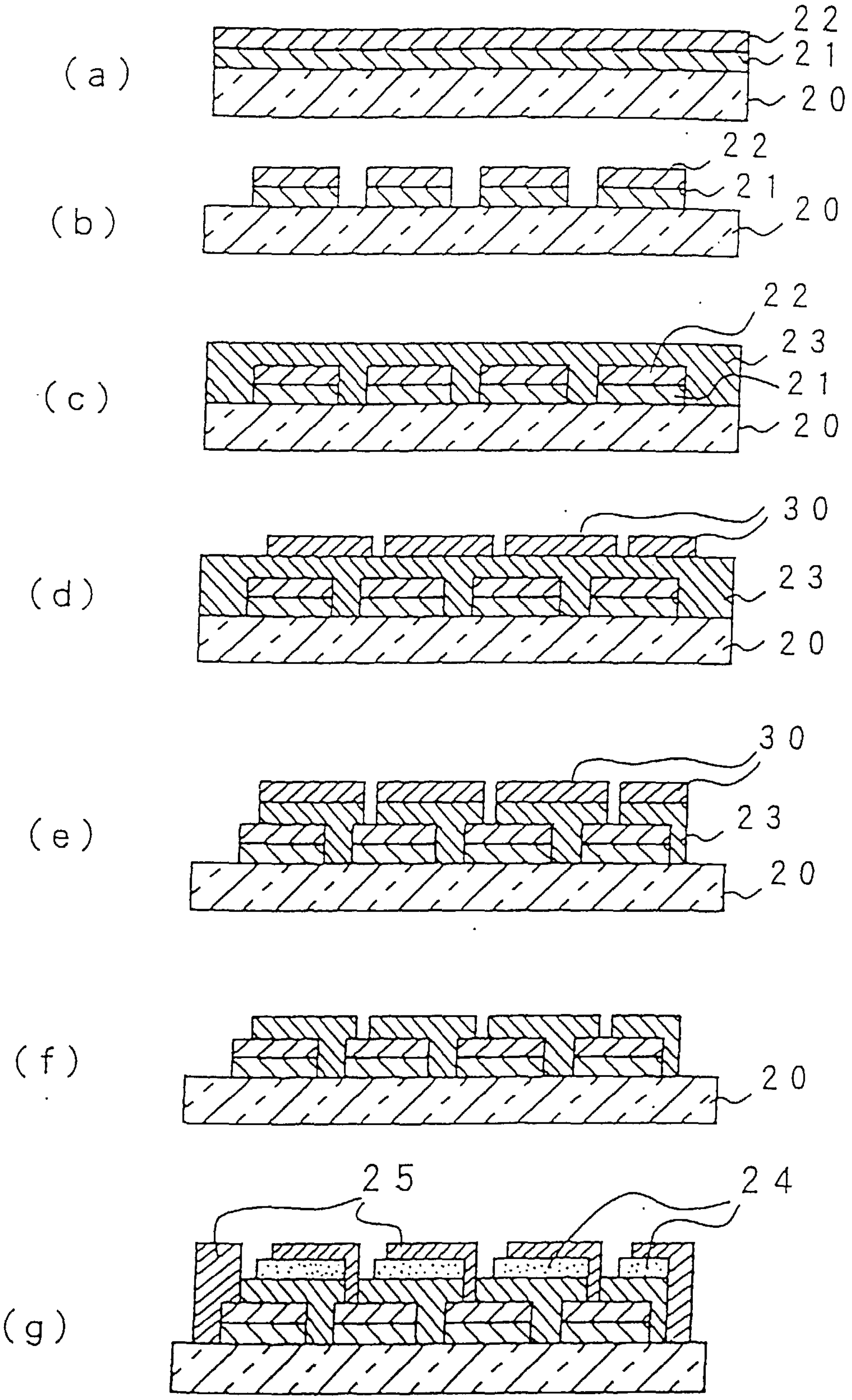
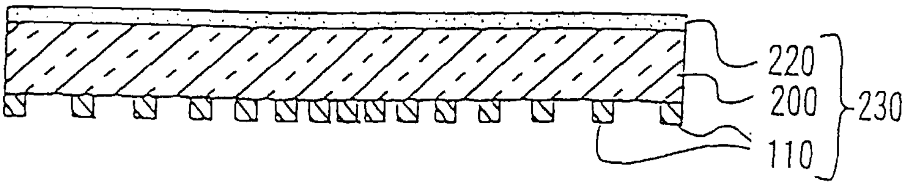


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/01791

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl^6 H01L31/04, H01L21/363

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl^6 H01L31/04, H01L21/363

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP, A1, 6-45626 (Batelle-Institut), February 18, 1994 (18. 02. 94) & EP, A2, 535,522 & DE, A1, 4,132,882 & US, A, 5,304,499	16 1 - 15
Y A	JP, A1, 7-94769 (Matsushita Electric Industrial Co., Ltd.), April 7, 1995 (07. 04. 95)	16 1 - 15
Y A	JP, A1, 7-147421 (Matsushita Electric Industrial Co., Ltd.), June 6, 1995 (06. 06. 95)	16 1 - 15
Y A	JP, A1, 59-115569 (Matsushita Electric Industrial Co., Ltd.), July 4, 1984 (04. 07. 84)	16 1 - 15
A	JP, A1, 52-4167 (Futaba Corp.), January 13, 1977 (13. 01. 77)	1 - 16
Y	T.L. Chu et al., "High Efficiency CdS/CdTe	16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

Date of the actual completion of the international search July 22, 1997 (22. 07. 97)	Date of mailing of the international search report July 29, 1997 (29. 07. 97)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.	PCT/JP97/01791

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Solar Cells from Solution-Grown CdS Films", The Conference Record of the 22nd IEEE Photovoltaic Specialists Conference, Vol. 2 (1991), p. 952-956	1 - 15

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

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(54) A PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

VERFAHREN ZUR GROSSTECHNISCHEN HERSTELLUNG VON CDTE/CDS DÜNNSCHICHT-SOLARZELLEN

PROCEDE PERMETTANT LA PRODUCTION A GRANDE ECHELLE DE PHOTOPILES EN COUCHES MINCES DE CDTE/CDS

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US-A- 5 304 499	**US-A- 5 916 375**

- **ROMEO N ET AL: "A highly efficient and stable CdTe/CdS thin film solar cell" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 2, June 1999 (1999-06), pages 209-218, XP004177956 ISSN: 0927-0248**
- **ROMEO A ET AL: "Recrystallization in CdTe/CdS" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 361-362, no. 1, February 2000 (2000-02), pages 420-425, XP004187511 ISSN: 0040-6090**
- **ROMEO N ET AL: "A highly efficient and stable CdTe/CdS thin film solar cell" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 2, June 1999 (1999-06), pages 209-218, XP004177956 ISSN: 0927-0248 cited in the application**

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EP 1 433 207 B1

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Description

Field of the invention

[0001] The present invention relates to the field of the solar cells technology and more particularly concerns a process for the large-scale production of CdTe/CdS thin film solar cells.

Background art of the invention

[0002] As is known, a typical configuration of a CdTe/CdS solar cell has a film sequence of the multilayer arrangement comprising a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film representing the n-conductor, a CdTe film representing the p-conductor and a metallic back-contact. A solar cell with a layer arrangement and structure of this type is disclosed, for example, in US 5304499.

[0003] The commercial float glass may be used as a transparent substrate, but, in spite of its low cost, special glasses are often preferred to avoid drawbacks of the float glass, in particular Na diffusion into TCO film.

[0004] The most common TCO is In_2O_3 containing 10% of Sn (ITO). This material has a very low resistivity on the order of 3×10^{-4} Ωcm and high transparency (>85%) in the visible spectrum. However, this material is made by sputtering and the ITO target after several runs forms some noodles which contain an In excess and a discharge between noodles can happen during sputtering which can damage the film. Another material which is commonly used is fluorine doped SnO_2 which however exhibits a higher resistivity close to 10^{-3} Ωcm and as a consequence a 1 μm thick layer is needed in order for the sheet resistance to be around 10 $\Omega/_{square}$. A high TCO thickness decreases the transparency and then the photocurrent of the solar cell. Finally a novel material, namely Cd_2SnO_4 has been developed by the NREL group (X. Wu et al., Thin Solid Films, 286 (1996) 274-276)). Also this material has some drawbacks since the target is made up of a mixture of CdO and SnO_2 and, being CdO highly hygroscopic, the stability of the target may result to be unsatisfactory.

[0005] The CdS film is deposited by sputtering or Close-Spaced Sublimation (CSS) from CdS granulate material. This last technique allows the preparation of thin films at a substrate temperature much higher than that used in simple vacuum evaporation or sputtering, because substrate and evaporation source are put very close to each other at a distance of 2-6 mm and the deposition is done in the presence of an inert gas such as Ar, He or N_2 at a pressure of 10^{-1}-100 mbar. A higher substrate temperature allows the growth of a better crystalline quality material. An important characteristic of the close-spaced sublimation is a very high growth rate up to 10 μm/min, which is suitable for large-scale production.

[0006] CdTe film is deposited on top of CdS film by close-spaced sublimation (CSS) at a substrate temperature of 480-520°C. CdTe granulate is generally used as a source of CdTe which is vaporised from an open crucible.

[0007] An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$- Most research groups use to carry out this step by depositing on top of CdTe a layer of $CdCl_2$ by simple evaporation or by dipping CdTe in a methanol solution containing $CdCl_2$ and then anneal the material in air at 400°C for 15-20 min. It is generally believed that the $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of small grains and by removing several defects in the material.

[0008] After $CdCl_2$ treatment, CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ have to be removed in order to make a good back contact onto CdTe. Besides it is believed that, since etching produces a Te-rich surface, the formation of an ohmic contact when a metal is deposited on top of CdTe is facilitated.

[0009] The electric back contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g. in graphite contacts, which, upon annealing, can diffuse in the CdTe film. The use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell has been disclosed by the same applicants (N. Romeo et al., Solar Energy Materials & Solar Cells, 58 (1999), 209-218)

[0010] Industrial interest towards thin films solar cells is increased in recent years also in view of the high conversion efficiency reached so far. A record 16,5% conversion efficiency has been recently reported (see X.Wu et al., 17th European Photovoltaic Solar Energy Conversion Conference, Munich, Germany, 22-26 October 2001, II, 995-1000). Therefore several efforts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells.

[0011] A state-of-the-art report concerning this issue may be found in D. Bonnet, Thin Solid Films 361-362 (2000), 547-552. However, a number of problems still hinder the achievement of this result, in particular concerning some crucial steps which affect either stability and efficiency of CdTe/CdS thin film solar cells or their costs.

[0012] A major problem of the known processes is the etching step to which the CdTe surface must be submitted to remove CdO or $CdTeO_3$ oxides formed thereon. Since etching requires the immersion of substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for a continuous operation presently does not exist. Another significant problem which negatively affects the stability of the TCO films, as well as the cost of the final product are the drawbacks presently encountered with the use of known TCOs, as previously mentioned. In addition to these drawbacks, known TCOs require the use of special glasses, such as borosilicate glass, to avoid the problem of Na diffusion, occurring if a soda-lime glass is used, which would damage the film.

[0013] A further problem concerns the source from which the CdS film and the CdTe film are produced by close-spaced sublimation. When small pieces of these materials containing dust are used as a sublimation source, due to a different thermal contact, some microparticles can be overheated and then split on to the substrate together with the vapour. In order to avoid this inconvenience, complicated metallic masks are used in some cases, which make a continuous operation problematic.

Object and Summary of the invention

[0014] It is the main object of the present invention to provide a process suitable for a large-scale production of stable and efficient CdTe/CdS thin film solar cells on a low cost substrate.

[0015] A particular object of the present invention is to provide a process of the above mentioned type in which the treatment of the CdTe film with $CdCl_2$ is conducted in such a way as not to require an etching treatment to remove the oxides possibly formed on the CdTe film.

[0016] A further object of the present invention is to provide a process of tne above mentioned type, in which the deposition of the TCO film is conducted in such a way that a film of very low resistivity can be deposited without formation of any metal noodles on the target and allowing the use of a inexpensive substrate.

[0017] Still another object of the invention is to provide a process of the above-mentioned type, which allows the formation of CdS and CdTe films completely free of dust.

[0018] A further object of the present invention is to provide a stable, efficient and relatively low-cost CdTe/CdS thin film solar cell.

[0019] The above object are achieved with the process for the large scale production of CdTe/CdS thin film solar cells, the main features of which are set forth in claim 1.

[0020] According to an important aspect of the invention, the treatment of the CdTe film with $CdCl_2$ is carried out by first forming a 100-200 nm thick layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at 380-420°C and 300-1000 mbar under inert gas atmosphere; and finally removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420°C, whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. In this way, there is no need for the etching treatment of the CdTe film and the process can be conducted in a continuous way.

[0021] According to another aspect of the invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing 1-3 vol.% hydrogen and a gaseous fluoroalkyle compound, in particular CHF_3. In this way the TCO is doped whit fluorine

[0022] According to another important aspect of the invention, as a source material for the formation of the CdS and the CdTe films by sputtering or close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

[0023] Further features of the process according to the invention are set forth in the dependent claims.

Brief description of the drawings

[0024] Further features and advantages of the process for large-scale production of CdTe/CdS thin film solar cells according to the present invention will be apparent from the following description of a preferred embodiment made with reference to the attached drawings, wherein:

- Figure 1 is a schematic representation of the film sequence of the CdTe/CdS thin film solar cells according to the invention;
- Figure 2 is a schematic diagram of the process according to the invention.

Description of an embodiment of the invention

[0025] With reference to the figures, the CdTe/CdS solar cells produced with the process according to the invention comprise five layers deposited in a sequence on a transparent base layer or substrate and consisting of a 300-500 nm thick layer of a transparent conducting oxide (TCO), a 80-200 nm thick layer of CdS deposited on top of the TCO layer, a 4-12 μm thick layer of CdTe on top of the CdS layer and a back contact layer formed by at least 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate consists of soda-lime glass and the transparent conducting oxide is fluorine-doped (In_2O_3:F).

[0026] TCO layer consists of In_2O_3, which is doped with fluorine during the growth. The In_2O_3 target, differently from ITO, does not form any noodle. A very low resistivity is obtained by introducing in the sputtering chamber a small amount of fluorine in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a Ar+H_2 mixture, in which H_2 is 20% in respect to Ar. A typical example is a 500 nm film of In_2O_3 deposited with a deposition rate higher than 10 Å/sec at a substrate temperature of 500°C, with an Ar flow-rate of 200 sccm, a CHF_3 flow-rate of 5 sccm and an Ar+H_2 flow-rate of 20 sccm. In this way, the reactive sputtering gas is composed by Ar containing 2.5 viol.% of CHF_3 and 1.8 viol.% of H_2. This film exhibits a sheet resistance of 5 $\Omega/_{square}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than 85% in the wavelength range of 400-800 nm. Another characteristic of this film is its good stability and the ability to stop Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable even if heated up to 180°C when illuminated by "ten suns" for several hours.

[0027] After deposition of the CdS film and CdTe film in the known way by sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ in the following way.

[0028] 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. An annealing of 15-20 min is done at 400°C in a vacuum chamber in which 500 mbar of Ar are introduced. After the annealing the chamber is evacuated keeping the substrate at 400°C for 5 min. and, since $CdCl_2$ has a high vapour pressure at 400°C, any residual $CdCl_2$ re-evaporates from the CdTe surface.

[0029] CdO or $CdTeO_3$ are not formed since the annealing is conducted in an inert atmosphere, which does not contain O_2.

[0030] According to the present invention a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing on top of CdTe film a thin layer of a highly conducting p-type semiconductors such as Sb_2Te_3 or As_2Te_3. A good non-rectifying contact is obtained on a clean CdTe surface if at least 100 nm thick layer of Sb_2Te_3 or As_2Te_3 is deposited by sputtering at a substrate temperature respectively of 250-300°C and 200-250°C. Sb_2Te_3 grows naturally p-type with a resistivity of 10^{-4} Ωcm, while As_2Te_3 grows p-type with a resistivity of 10^{-3} Ωcm. The contact procedure is completed by covering the low resistivity p-type semiconductor with at least 100 nm of Mo, as common practice in the art. A thin layer of Mo is needed in order to have a low sheet-resistance on the back-contact.

[0031] As a source for the CdS and CdTe materials used to form the respective layers by sputtering or CSS a granulate material can be used, as common practice in this field. However, in view of the drawbacks mentioned above when operating in this way, according to a particularly preferred aspect of the invention a new sublimation source can be used which consists of a compact block obtained by melting and solidifying the material in an oven able to sustain a temperature higher than the melting temperature of the material. The procedure to prepare the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3) , which is a low melting point material (450°C) and exhibits a very low vapour pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over CdS and covers CdS completely upon cooling. In this way, CdS covered by B_2O_3, if it is put into an oven containing an inert gas at pressure higher than 50 atm, does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of 1750°C, the oven is heated up to a temperature of 1800°C or more and then cooled down to room temperature. In this way, a unique compact block of CdS is obtained which results to be particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared with this type of source resulted to be very smooth and completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically 100 nm thick. The substrate temperature is kept at 200-300°C when CdS is prepared by sputtering and at 480-520°C when it is prepared by close-spaced-sublimation. The sputtered CdS layer needs an annealing at 500°C in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a high efficiency. In the case CdS is prepared by close-spaced sublimation, O_2 is introduced in the sublimation chamber during the deposition. The role of O_2 is not known, but it is presumed to passivate the CdS grain boundaries.

[0032] In a preferred embodiment of the invention, the CdTe source too is a compact block obtained by melting and solidifying pieces of CdTe in an oven under high pressure as described previously. Since CdTe melts at 1120°C, the oven needs to be heated up to 1200°C in order to have a complete melting of the CdTe pieces. CdTe films are deposited on top of CdS by close-spaced sublimation at a substrate temperature of 480-520°C. Deposition rates during the CdTe growth are typically 4 μm/min. In this way 8 μm of CdTe are deposited in 2 min.

[0033] By following the procedure described above several solar cells have been prepared by using as a substrate a 1 inch square low-cost soda-lime glass.

[0034] A typical area of these cells is 1 cm^2. The finished cells are generally put under 10-20 suns for several hours at a temperature of 180°C in the open-circuit-voltage (V_{oc}) conditions. No degradation has been notified but rather a 20% or more increase in the efficiency has been found.

[0035] The efficiency of these cells are in the range 12%-14% with open-circuit-voltages (V_{oc}) larger than 800 mV, short-circuit-currents (J_{sc}) of 22-25 mA/cm^2 and fill-factors (ff) ranging from 0.6 to 0.66.

Example

[0036] A cell exhibiting a 14% efficiency has been prepared in the following way: a soda-lime glass has been covered by 500nm of In_2O_3:F (fluorine-doped) deposited at 500°C substrate temperature as described above. 100 nm of CdS have been deposited by sputtering at 300°C substrate temperature and annealed for 15 min at 500°C in 500mbar of Ar containing 20% of 0_2. 8 μm of CdTe have been deposited on top of CdS by CSS at a substrate temperature of 500°C. Both CdS and CdTe films are produced from a compact block source as described above. A treatment with 150 nm of $CdCl_2$ has been done in an Ar atmosphere as described above. Finally a back contact has been created, without any etching, by depositing in sequence by sputtering 150 nm of Sb_2Te_3 and 150 nm of Mo.

[0037] After one hour under 10 suns at a temperature of 180°C in open-circuit conditions the solar cell prepared in this way exhibited the following parameters:

V_{oc}	852 mv
J_{sc}	25 mA/cm^2
ff	0.66
efficiency	14 %

[0038] The techniques used in this process such as sputtering and close-spaced sublimation are both fast, reproducible and easily scalable.

[0039] Sputtering systems capable to cover 1x0.5 m^2 area glass are already commercial, while close-spaced sublimation , which at a laboratory scale can cover easily 20x20 cm^2 area glass, does not give any problem in being scaled up to 1x0.5 m^2. An in-line process can work well if a large area glass is made to move slowly over the different sources namely TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3 and Mo. In order to make a series connection between the single cells the in-line system should also contain three laser scribing processes, the first after the TCO deposition, the second one before the back-contact deposition and the third one at the end of the process. An important part of the process according to the present invention is that no use is made of acids or liquids and, as a consequence, the process can operate on a continuous basis without the interruption which is needed to make the etching in acid or in a Br-methanol solution.

Claims

1. Process for the large-scale production of CdTe/CdS thin film solar cells, said films being deposited as a sequence on a transparent substrate, comprising the steps of:

- depositing a film of a transparent conductive oxide (TCO) on said substrate;
- depositing a film of CdS on said TCO film;
- depositing a film of CdTe on said CdS film;
- treating said CdTe film with CdCl2;
- depositing a back-contact film on said treated CdTe film;

the process being **characterised in that** the treatment of the CdTe film with $CdCl_2$ comprises the following steps:

- forming a layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature;
- annealing said $CdCl_2$ layer in a vacuum chamber at 380-420°C and 300-1000 mbar under inert gas atmosphere;
- removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420°C whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process according to claim 1, wherein said $CdCl_2$ layer is 100-200 nm thick

3. The process according to claims 1 or 2, wherein the annealing of the $CdCl_2$ layer is carried out for 15-20 min.

4. The process according to any one of the previous claims, wherein the inert gas is Ar.

5. The process according to any one of the previous claims, wherein wherein the back-contact film is formed by a Sb_2Te_3 layer covered by a layer of Mo.

6. The process according to claim 5, wherein said Sb_2Te_3 layer is formed by sputtering at 250-300°C.

7. The process according to any one of the previous claims, wherein the back-contact film is formed by a As_2Te_3 layer covered by a layer of Mo.

8. The process according to claim 7, wherein said As_2Te_3 layer is formed by sputtering at 200-250°C

9. The process according to any of the previous claims, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process according to claim 9, wherein the TCO layer is formed by sputtering in an inert gas atmosphere containing hydrogen and a gaseous fluoroalkyle compound.

11. The process according to claim 10, wherein a mixture of Ar and hydrogen is used, in which hydrogen is comprised between 1 and 3% vol.% and the flouoroalkyle compound is CHF_3 .

12. The process according to any one of the previous claims, wherein, as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

13. The process according to claim 12, wherein said compact block CdS (or CdTe) material is formed by covering with boron oxide pieces of CdS (or CdTe) material, heating the covered material to a temperature higher than its melting point under inert gas atmosphere and a pressure higher than 50 atm and then cooling down to room temperature, whereby the material is solidified in a compact block form.

14. The process according to any one of the previous claims, wherein said transparent substrate is soda-lime glass.

Patentansprüche

1. Verfahren zur großtechnischen Herstellung von Cd-

Te/CdS-Dünnschicht-Solarzellen, welche Schichten als Abfolge auf einem transparenten Substrat aufgetragen werden, enthaltend die Schritte:

- Auftragen einer Schicht eines transparenten leitenden Oxids (TCO) auf dem Substrat;
- Auftragen einer Schicht von CDs auf der TCO-Schicht;
- Auftragen einer Schicht von CdTe auf der CD-Schicht;
- Behandeln der CdTe-Schicht mit $CdCl_2$;
- Auftragen einer Rückwärtskontaktschicht auf der behandelten CdTe-Schicht in Verbindung;

welches Verfahren **dadurch gekennzeichnet ist, dass** die Behandlung der CdTe-Schicht mit $CdCl_2$ die folgenden Schritte enthält:

- Ausbilden einer Schicht von $CdCl_2$ auf der CdTe-Schicht durch Aufdampfen, während das Substrat auf Raumtemperatur gehalten wird;
- Annealen der $CdCl_2$-Schicht in einer Vakuumkammer bei 380 - 420°C und 300 - 1000 mbar in einer Inertgasatmosphäre;
- Entfernen des Inertgases aus der Kammer, um eine Vakuumbedingung zu erzeugen, während das Substrat auf einer Temperatur von 350 - 420 °C gehalten wird, wodurch jegliches verbleibendes $CdCl_2$ von CdTe-Schichtoberfläche verdampft wird.

2. Verfahren nach Anspruch 1, wobei die $CdCl_2$-Schicht 100 - 200 Nanometer dick ist.

3. Verfahren nach Anspruch 1 oder 2, wobei das Annealen der $CdCl_2$-Schicht für 15 - 20 Minuten ausgeführt wird.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Inertgas Ar ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Rückwärtskontaktschicht durch eine Sb_2Te_3-Schicht gebildet wird, die von einer Schicht aus MO bedeckt ist.

6. Verfahren nach Anspruch 5, wobei die Sb_2Te_3-Schicht durch Sputtern bei 250 - 300°C gebildet wird.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Rückwärtskontaktschicht durch eine As_2Te_3-Schicht gebildet wird, die von einer Schicht aus MO bedeckt ist.

8. Verfahren nach Anspruch 7, wobei die As_2Te_3-Schicht durch Sputtern bei 200 - 250 °C gebildet wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei das transparente leitende Oxid In_2O_3 dotiert mit Fluor ist.

10. Verfahren nach Anspruch 9, wobei die TCO-Schicht durch Sputtern in einer Inertgasatmosphäre gebildet wird, die Wasserstoff und einen gasförmigen Fluoroalkyl-Bestandteil enthält.

11. Verfahren nach Anspruch 10, wobei eine Mischung aus Ar und Wasserstoff benutzt wird, worin Wasserstoff zwischen 1 und 3 Vol.-% enthalten ist, und der das Fluoroalkyl-Bestandteil CHF_3 ist.

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei als Ausgangsstoff für die Bildung der CdS- und der CdTe-Schichten durch closed-space Sublimation ein CdS- oder entsprechend CdTe-Material in der Form eines kompakten Blockes benutzt wird.

13. Verfahren nach Anspruch 12, wobei das Kompaktblock-CdS-(oder CdTe-) Material gebildet wird durch Bedecken von CdS- (oder CdTe-) Material mit Boroxidstücken, Heizen des bedeckten Materials auf eine Temperatur höher als seinen Schmelzpunkt in einer Inertgasatmosphäre und einem Druck von mehr als 50 atm, und dann Abkühlen auf Raumtemperatur, wodurch das Material in einer Kompaktblockform verfestigt wird.

14. Verfahren nach einem der vorhergehenden Ansprüche, wobei das transparente Substrat Kalknatronglas ist.

Revendications

1. Procédé pour la production à grande échelle de piles solaires en films couches minces de CdTe/CdS, lesdits films étant déposés séquentiellement sur un substrat transparent, comprenant les étapes suivantes :

- dépôt d'un film d'un oxyde conducteur transparent (TCO) sur ledit substrat ;
- dépôt d'un film de CdS sur ledit film de TCO ;
- dépôt d'un film de CdTe sur ledit film de CdS ;
- traitement du dit film de CdTe avec du $CdCl_2$;
- dépôt d'un film contact arrière sur ledit film de CdTe traité ;

le procédé étant **caractérisé en ce que** le traitement du film de CdTe avec du $CdCl_2$ comprend les étapes suivantes :

- formation d'une couche de $CdCl_2$ sur le film de CdTe, par évaporation, tout en maintenant le substrat à la température ambiante ;
- recuit de ladite couche de $CdCl_2$ dans une chambre à vide à 380-420°C et sous 300-1000

millibars sous atmosphère de gaz inerte ;
- élimination du gaz inerte de ladite chambre pour obtenir des conditions de vide, tout en maintenant le substrat à une température de 350-420°C, ce en quoi tout $CdCl_2$ résiduel est évaporé de la surface du film de CdTe.

2. Le procédé selon la revendication 1, où ladite couche de $CdCl_2$ a une épaisseur de 100-200 nanomètres.

3. Le procédé selon l'une des revendications 1 et 2, où le recuit de la couche de $CdCl_2$ est effectué perdant 15-20 minutes.

4. Le procédé selon l'une quelconque des revendications précédentes, où le gaz inerte est de l'Argon.

5. Le procédé selon l'une quelconque des revendications précédentes, où le film contact arrière est constitué d'une couche de Sb_2Te_3 recouverte d'une couche de Mo.

6. Le procédé selon la revendication 5, où ladite couche de Sb_2Te_3 est obtenue par pulvérisation à 250-300°C.

7. Le procédé selon l'une quelconque des revendications précédentes, où le film contact arrière est constitué d'une couche de As_2Te_3 recouverte d'une couche de Mo.

8. Le procédé selon la revendication 7, où ladite couche de As_2Te_3 est obtenue par pulvérisation à 200-250°C.

9. Le procédé selon l'une quelconque des revendications précédentes, où l'oxyde conducteur transparent est du In_2O_3 dopé au Fluor.

10. Le procédé selon la revendication 9, où la couche de TCO est obtenue par pulvérisation sous atmosphère de gaz inerte contenant de l'Hydrogène et un composé de fluoroalkyle gazeux.

11. Le procédé selon la revendication 10, où un mélange d'Argon et d'Hydrogène est utilisé, dans lequel l'Hydrogène est compris entre 1 et 3% en vol. en % et le composé de flouoroalkyle est du CHF_3.

12. Le procédé selon l'une quelconque des revendications précédentes, où, comme matériau source pour la formation des films de CdS et de CdTe par sublimation en espace fermé, est utilisé un matériau de CdS ou, respectivement, de CdTe sous forme d'un bloc compact.

13. Le procédé selon la revendication 12, où ledit matériau de CdS (ou CdTe) en bloc compact est obtenu par recouvrement de morceaux de CdS (ou CdTe) avec de l'oxyde de Bore, en chauffant le matériau recouvert à une température supérieure à son point de fusion sous une atmosphère de gaz inerte et une pression supérieure à 50 atmosphères et ensuite en refroidissant jusqu'à la température ambiante, ce en quoi le matériau est solidifié sous une forme de bloc compact.

14. Le procédé selon l'une quelconque des revendications précédentes, où ledit substrat transparent est du verre à base de chaux sodée.

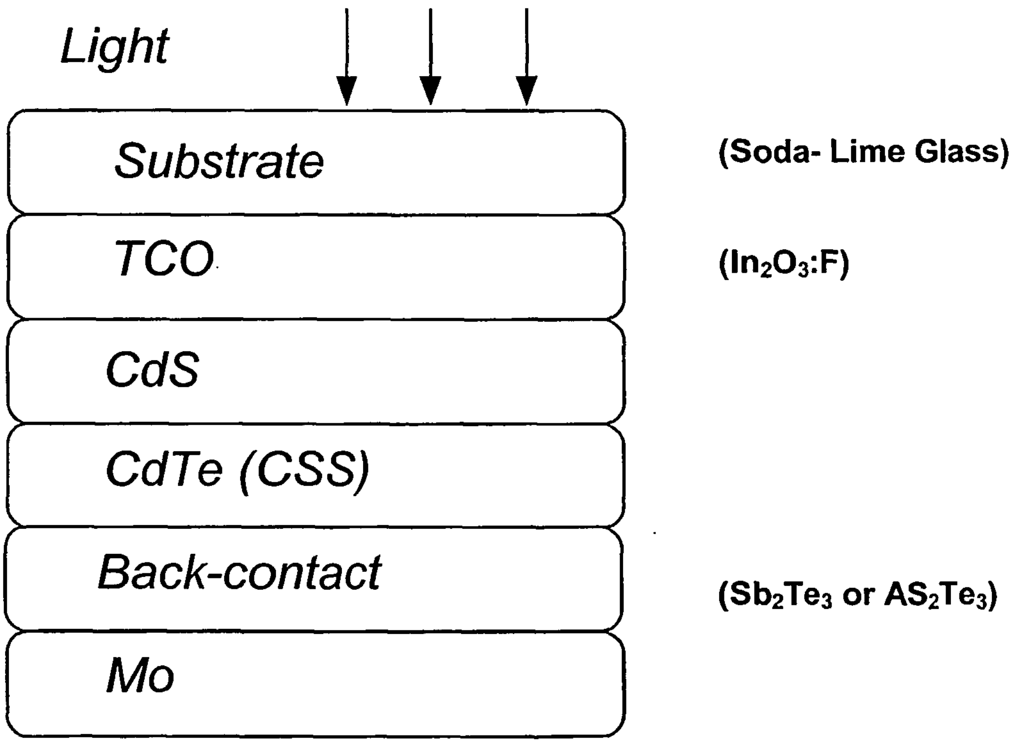
Light
Substrate
(Soda- Lime Glass)
TCO
(In_2O_3:F)
CdS
CdTe (CSS)
Back-contact
(Sb_2Te_3 or AS_2Te_3)
Mo

Fig. 1

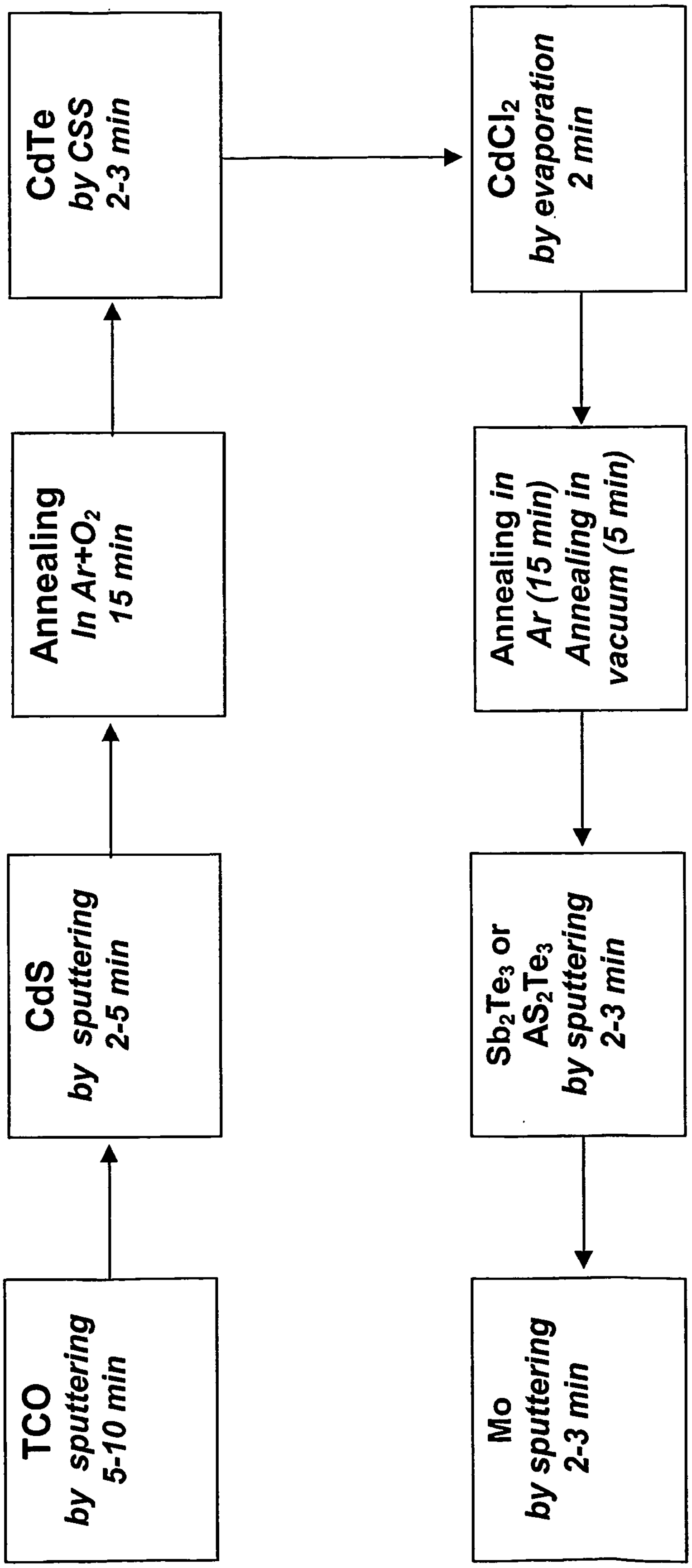
TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In Ar+O$_2$
15 min
CdTe
by CSS
2-3 min
CdCl$_2$
by evaporation
2 min
Annealing *in Ar (15 min)*
Annealing in vacuum (5 min)
Sb$_2$Te$_3$ or AS$_2$Te$_3$
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

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United States Patent [19]

Tyan

[11] **4,207,119**

[45] **Jun. 10, 1980**

[54] POLYCRYSTALLINE THIN FILM CDS/CDTE PHOTOVOLTAIC CELL

[75] Inventor: **Yuan-Sheng Tyan**, Webster, N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[21] Appl. No.: **911,843**

[22] Filed: **Jun. 2, 1978**

[51] **Int. Cl.**^{2} **H01L 31/06**

[52] **U.S. Cl.** .... **136/89 TF**; 136/89 CD; 357/16; 357/30; 357/59; 427/76; 427/85; 427/255.3

[58] **Field of Search** .... 136/89 TF, 89 CD, 89 ST; 357/16, 30, 59; 204/192 P; 427/74, 76, 85, 248 C

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J. Lebrun, "Thin Film Cadmium Telluride Solar Cell", *Proc. Int'l Conf. Phys. & Chem. of Semicond. Heterojunctions,* Hungary (1970), pp. IV-163-170.

Primary Examiner—Aaron Weisstuch

Attorney, Agent, or Firm—Dana M. Schmidt

[57] ABSTRACT

A photovoltaic cell and a process of making and using it are disclosed wherein extremely thin semiconductor layers are provided through the use of polycrystalline CdS and CdTe. The cell has conversion efficiencies as high as 6% or more when exposed to AM2 light.

31 Claims, 2 Drawing Figures

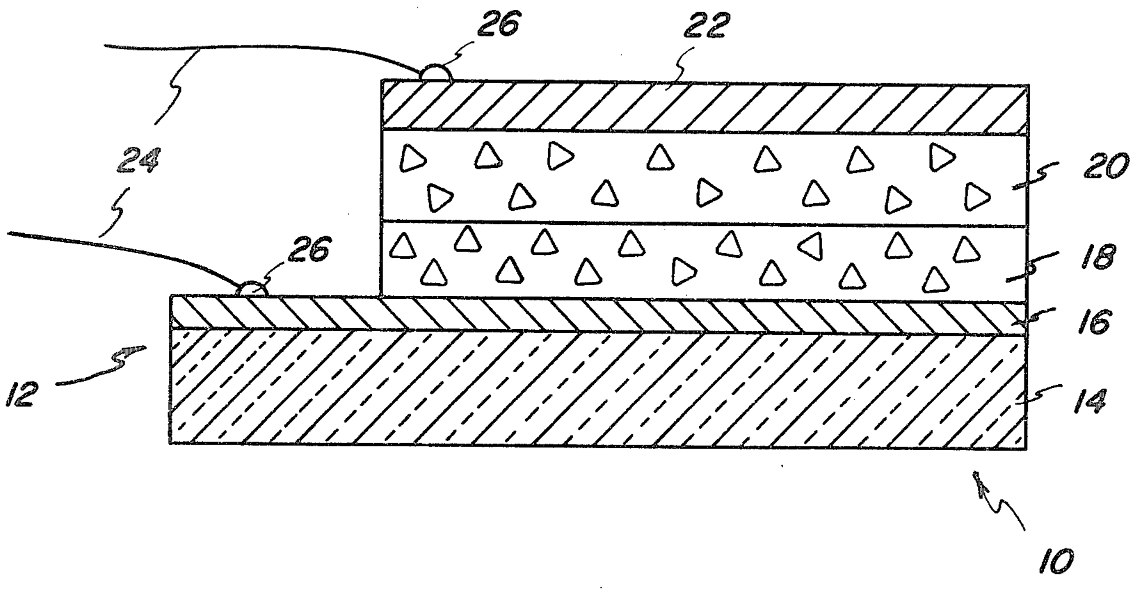
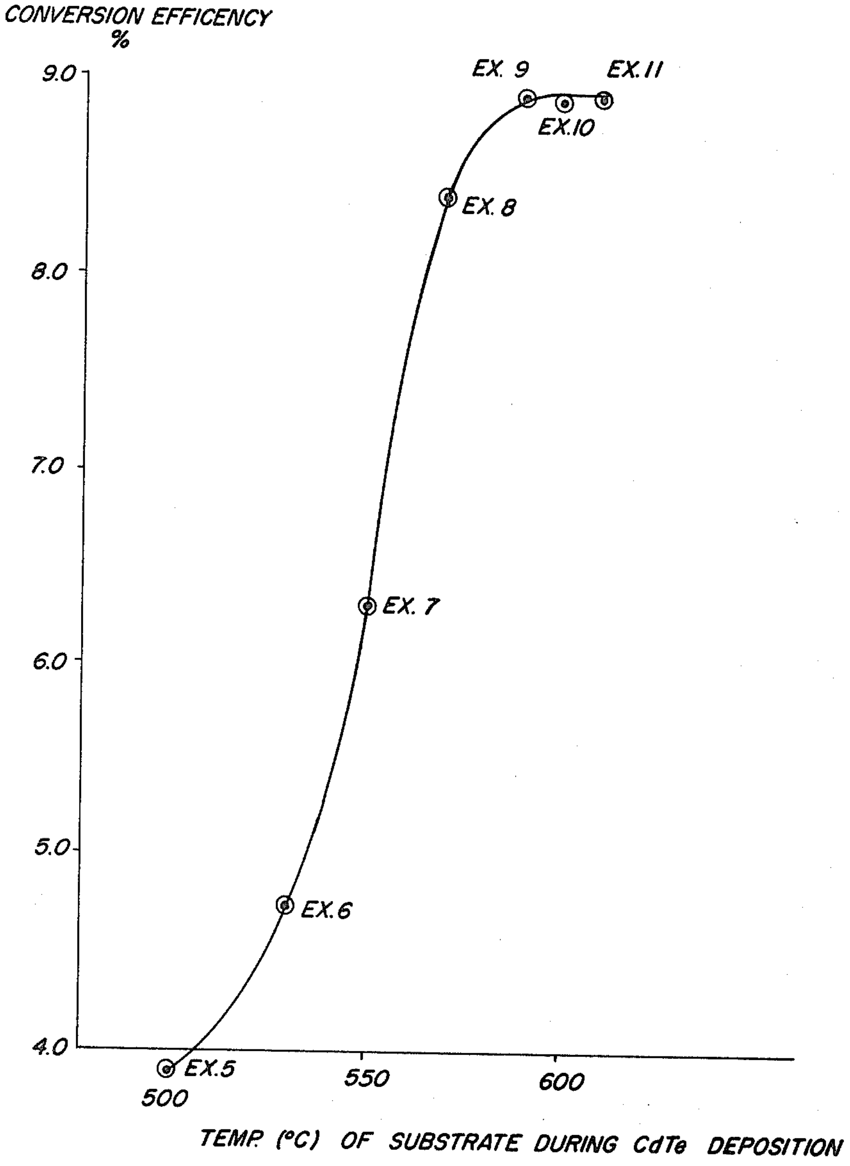


FIG. 1


CONVERSION EFFICENCY
%
9.0
8.0
7.0
6.0
5.0
4.0
EX. 9
EX. 11
EX. 10
EX. 8
EX. 7
EX. 6
EX. 5
500
550
600
TEMP. (°C) OF SUBSTRATE DURING CdTe DEPOSITION

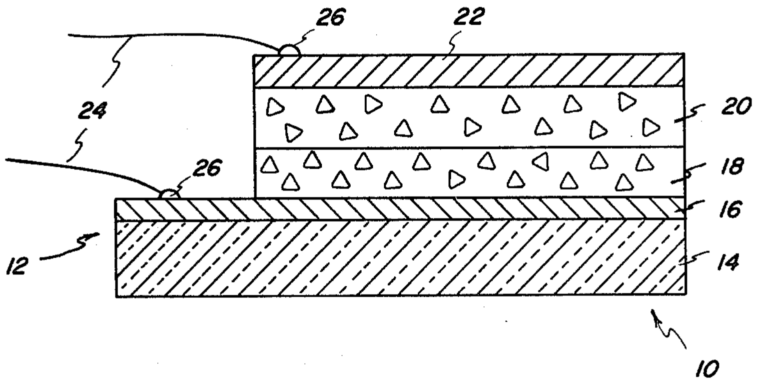


FIG. 2

POLYCRYSTALLINE THIN FILM CDS/CDTE PHOTOVOLTAIC CELL

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to p-n cadmium telluride-cadmium sulfide photovoltaic cells, particularly of the thin-film type.

(2) State of the Prior Art

Effective conversion from expensive petroleum-based energy sources to solar energy sources, such as photovoltaic cells, has been delayed prior to this invention by two factors—the cost of mass-producing such cells and the low conversion efficiency achieved by such cells. Any improvement in either factor can move industry towards the use of more solar cells, and an improvement in both has been a long-sought goal.

A study by R. Moore reported in *Solar Energy,* 18, p. 225 (1976) indicates that thin-film inorganic semiconductor photovoltaic cells should be able to meet the two-fold goal noted above if the individual semiconductive layers do not exceed 5 microns in thickness, assuming conversion efficiencies of at least 5%. Implied is the conclusion that such cells would be even more useful if the conversion efficiencies were higher. The study concludes with the statement that such thin-film cells as described are predicated on "a currently non-existent technological base."

Conversion efficiencies of 5% or more have been difficult to achieve in thin-film solar cells, particularly in solar cells fabricated from CdS and CdTe, hereinafter identified as CdS/CdTe solar cells. Such CdS/CdTe cells have a distinct cost advantage, compared for example to single-crystal silicon cells. Conversion efficiencies, however, must be increased to render them useful. Therefore, considerable effort has been expended to establish techniques for manufacturing such cells with improved conversion efficiencies, as well as reduced thicknesses. Vapor deposition or similar vapor-phase formation of either CdTe upon a crystal of CdS, or of CdS upon a crystal of CdTe, has been used as a means of partially reducing the film thickness, enhancing conversion efficiency, or both, as is reported in articles by A. Fahrenbruch et al, *Appl. Phys. Letters,* 25, p. 605 (1974); R. Bube et al, Report NSF/RANN-/Se/AER-75-1679/76/1; and K. Yamaguchi et al, *Japan J. Appl. Phys.,* 15, p. 1575 (1976). Such prior techniques have relied largely upon the use of single crystal substrates for the vapor deposition. Utilization of single crystal substrates, however, precludes the achievement of the economic advantages associated with thin-film cells, since a single crystal must be grown and sliced. The slicing operation necessarily involves waste of material and produces cells which at best are 50 to 100 microns thick. Thus, it is not possible to manufacture a bilayer solar cell, one layer of which is a single crystal, that is as thin as 10 microns as suggested in the Moore study. In each of the foregoing, the vapor deposition or similar process was done in the absence of oxygen.

In Bonnet, "New Results on the Development of a Thin-Film p-CdTe-n-CdS Heterojunction Solar Cell", 9th IEEE Photovoltaic Specialist Conference, p. 129 (1972), there is reported a thin-film cell of polycrystalline material alleged to have produced a conversion efficiency of 5%. However, the reported I_{sc} value, measured with 50 mW/cm^2 illumination, was 1.5 mA per 10 mm^2, or 15 mA/cm^2. This corresponds to an I_{sc} value of 30 mA/cm^2 for a 100 mW/cm^2 illumination, the standard "AM1" sunlight condition. Since the theoretical limit of I_{sc} under AM1 conditions is only about 24 mA/cm^2, clearly there was a positive error in the observations and the conversion efficiency was less than the reported value of 5%.

SUMMARY OF THE INVENTION

In accord with the present invention, there is advantageously featured a photovoltaic cell having the dual properties of greatly reduced cost and a markedly improved conversion efficiency compared to similar cells previously produced.

In accord with a related aspect of the invention, there is advantageously featured such a cell wherein the overall thickness is greatly reduced.

These features of the invention are based upon the discovery that CdS/CdTe solar cells can be manufactured to have both thin-film characteristics, and conversion efficiencies in excess of 5 and even 6% in AM2 light, characteristics not available in the prior art. More specifically, in accordance with one aspect of the invention, there is provided a cell for converting incident radiation into electricity, comprising first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of the layers, at least one of the electrodes being transparent or semi-transparent to the incident radiation, said cell being further characterized by a conversion efficiency of at least about 6.0% when exposed to AM2 light.

In accordance with another aspect of the invention, there is provided an n-type CdS and p-type CdTe photovoltaic cell containing operative electrodes, wherein both the cadmium telluride and the cadmium sulfide are polycrystalline, and together the layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms present.

In accordance with yet another aspect of the invention, there is provided an n-type CdS and p-type CdTe photovoltaic cell containing operative electrodes, the improvement being that the total thickness of the cell does not exceed about 10 microns and at least one of the layers contains oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms in the layer.

Such cells can be manufactured by a process of depositing, in the vapor phase, contiguous layers of the semiconductor material, in a manner such that at least one of the layers is deposited in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without the oxgen atmosphere.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a plot of conversion efficiencies achievable by cells of the invention, versus the substrate temperature useful for the formation of the CdTe layer; and

FIG. 2 is a partially schematic section view of a cell prepared in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

"Photovoltaic cell" as used herein means a solid state device which produces an electric current in response to light of appropriate wavelengths, from any source.

It has been found that the dual results of reduced cost and enhanced conversion efficiency can be produced by a photovoltaic cell having polycrystalline cadmium sulfide and polycrystalline cadmium telluride in contiguous layers. Such polycrystalline semiconductive materials allow the inexpensive layered formation of a truly thin cell, inasmuch as the combined thickness of two layers of polycrystalline semiconductor materials need not exceed about 100 microns, and preferably does not exceed about 10 microns.

The enhancement of the conversion efficiency of such cells is achieved by forming one or both of the semiconductive layers in an oxygen-containing atmosphere. Maximum enhancement occurs when the layers are formed at a particular range of temperatures.

As used herein, "enhanced conversion efficiency" means a conversion efficiency that is about 10% greater than the conversion efficiency of a control cell produced without the enhancing step. In practice, much larger enhancements than 10% are common when using the invention.

Because of their simplicity, preferred methods of forming the layers using an oxygen-containing atmosphere are those in which the semiconductive layers are deposited in the vapor phase. As used herein, "depositing in the vapor phase" is used to mean any process wherein material is transferred in the vapor phase from a source, usually heated, to a substrate where the material forms a new layer. Therefore, as used here "depositing in the vapor phase" includes, but is not limited to, close-space sublimation, vapor transporting, vacuum evaporation, vapor growth, and sputtering or ion plating wherein ionized or plasma gas, respectively, is the activating medium. "Close-space sublimation" means sublimation from a source to a substrate positioned from the source a distance no greater than the square root of the smaller of the surface areas of the source and of the substrate. All of these are known processes, and except as noted hereinafter, follow conventional procedures.

The atmosphere for the vapor-phase depositing can be either pure oxygen, oxygen artificially admixed with other gases, or air. As will be readily apparent, the actual amount of the oxygen present during deposition will depend upon the specific form of vapor-phase depositing that is selected. For example, close-space sublimation, a highly preferred form of the process of the invention, can tolerate much higher levels of gas than can vacuum evaporation, which preferably utilizes about 10^{-4} torr of gas. The other forms of vapor-phase depositing mentioned above have known or standard tolerance levels of gas, and the amount of oxygen pressure or partial pressure is selected to comply with such tolerance levels.

The process preferably proceeds by depositing, in the vapor phase, cadmium sulfide onto a suitable electrode, described below, with or without oxygen present in the atmosphere. Thereafter, the cadmium telluride and, optionally, a p-type dopant such as gold are similarly deposited in the vapor phase onto the previously formed cadmium sulfide, with or without oxygen present in the atmosphere, except that at least one of the two layers is deposited with oxygen gas present.

Thereafter, an electrode capable of making a low impedance contact is formed on at least a portion of the cadmium telluride. A preferred process of such electrode formation is vacuum deposition.

The vapor-phase depositing of the semiconductor material can be done either as a batch process, e.g., in a vacuum chamber containing a single source and a single substrate, or as a continuous process in which a substrate is moved through appropriate zones of treatment.

As indicated, a highly useful form of the vapor-phase depositing is close-space sublimation. The oxygen atmosphere of the sublimation can be at a pressure between about 0.01 and about 100 torr, and preferably is at a pressure between about 0.1 and about 10 torr. The spacing between source and substrate preferably is between about 0.5 and about 5 mm. The temperature of the substrate upon which each of the semiconductor layers is to be crystallized can be varied, depending on which material is being sublimated. Preferably, each of the CdS and CdTe materials is deposited for a time of between about 0.1 sec to about 10 minutes onto a substrate held at a temperature of between about 300° C. and about 650° C. As is customary in sublimation, the source temperature is maintained in each instance between about 10° and about 500° C. higher than the substrate temperature, preferably about 100°-300° C. higher for the CdS deposition and 20°-50° C. higher for the CdTe deposition. Conventional heating techniques for the source and/or the substrate include, e.g., resistance heating, induction heating, and the like.

Within this process of close-space sublimation, higher conversion efficiencies are achieved when the CdTe layer is sublimated in an oxygen-containing atmosphere on a CdS substrate at a temperature of at least about 575° C., the CdS layer also having been sublimated in O_2. It has been found, when keeping constant other variables such as deposition time and thickness of the two layers as well as the amount of oxygen present in the atmosphere, that such a substrate temperature provides a substantial further increase in the conversion efficiency compared to a cell wherein the CdTe is sublimated in oxygen at a lower substrate temperature. Although still further increases in efficiency are achieved at still higher temperatures, the rate of increase decreases significantly beyond the 575° C. temperature.

The mechanism by which this occurs is not as yet fully understood. The effect is illustrated in FIG. 1. The CdS substrate in this case was also sublimated in a 0.4 torr oxygen-containing atmosphere, and each data point represents a separate cell wherein the only difference in the preparation of the cell is the temperature of the CdS substrate for the CdTe sublimation. Whereas a substrate temperature of 500° C. produced a conversion efficiency of about 3.9%, a substrate temperature increased to about 550° C. raised the conversion efficiency to about 6.3%, and an increase to 570° C. raised it still further to about 8.4%. A further increase in substrate temperature to about 600° C. produced a slight increase in efficiency to 8.9%.

It is possible that the critical substrate temperature, i.e., the temperature above which further substantial increases in conversion efficiency are not achievable, can be lowered below about 575° C. if other variables of the sublimation process are further optimized.

In at least certain instances, and particularly for CdTe layers deposited at temperatures below the above-noted substrate temperature of about 575° C., further enhancement of the conversion efficiency can be achieved by an optional process step of heating the already formed CdTe layer in an oxygen-containing atmosphere for a suitable length of time. In this case, normal or even pressurized atmospheres of oxygen can be used, a highly preferred example being air at ambient pressure. Partial pressures of oxygen can also be used, as can an alternating non-oxidizing and oxidizing atmosphere of the type described in U.S. Pat. No. 4,035,197, issued on July 12, 1977, the details of which are hereby expressly incorporated herein by reference. The temperature of such post-treatment can be between about 100° C. and about 600° C., for a time of between about 1 second to about 20 minutes. As will be apparent, the higher the temperature that is used, the lower the length of time of exposure that is needed to further enhance the conversion efficiency.

Such post-heating of the CdTe layer can increase the conversion efficiency by 1 or 2% over that achieved by the same cell lacking the post-heating step.

It is believed that the vapor depositing of one or both of the semiconductor materials in an oxygen-containing atmosphere produces enhanced cconversion efficiencies by the incorporation of oxygen atoms into the semiconductor layer formed in the presence of the oxygen. However, the exact amounts of such oxygen incorporation are so minute that they are difficult to detect or assay.

To complete the cell, electrodes are selected to provide low-impedance contact with at least portions of the exterior surfaces of the two contiguous semiconductor layers formed as described. As used herein, "low impedance" means an impedance that is no greater than that which gives a contact resistance of 50 ohm-cm^2. Although such low-impedance contacts at least approach a true ohmic contact, some rectification in the contact can also be tolerated, as is well known.

Each of the electrodes is also in operative contact with its respective layer; that is, in the cell is contacts only its layer, and at least one of the electrodes transmits sufficient activating radiation as to photogenerate an electric potential in the cell. Conveniently, such transmission of radiation is accomplished by rendering one of the electrodes, sometimes called the "window" electrode, transparent or semitransparent to radiation having wavelengths bebetween about 350 and about 900 nm. A useful material having this property is "Nesatron" ® brand glass, a semitransparent electrode material comprising a conductive $In_2O_3(Sn)$ layer coated onto a transparent glass, available from PPG Industries, Inc. Such an electrode typically has a sheet resistance of about 10 to about 50 ohm/square and an optical transmittance of about 80% for visible light. The "Nesatron" ® electrode provides a low-impedance contact with the n-type cadmium sulfide, and as such comprises a highly useful substrate for the first semiconductive layer formation. Other conventional electrode materials also can be selected, providing they have sufficient conductivity, light transmittance, and the appropriate work function that insures the low-impedance contact with n-type CdS. Examples include transparent layers of CdO, SnO_2, Cd_2SnO_4, and the like on glass, with or without dopants.

Conventionally, the "Nesatron" ® electrodes are cleaned prior to layer formation of the semiconductor material. This can be accomplished by hand-rubbing the surface of the conductive coating with cleansers such as a sulfonate detergent available under the trademark "Alconox" from Alconox, Inc., followed by rinsing with water.

Electrode materials for low-impedance contact with the p-type CdTe are also conventional, and include, for example, gold, silver, copper, nickel, tin, platinum, palladium, chromium, iridium, rhodium, and non-metallic materials such as Cu_2S and Cu_2Te having high electrical conductance and a work function approximately matching that of p-CdTe. These materials may be used singly or in any combination, either in one layer or in successive layers.

FIG. 2 illustrates a typical photovoltaic cell **10** produced in accordance with the invention. Transparent electrode **12** comprises a support layer **14** of glass bearing a conductive layer **16** of $In_2O_3(Sn)$ such as a "Nesatron" ® electrode, on which is formed layer **18** of n-type CdS. A contiguous layer **20** of p-type CdTe is formed on layer **18**, and an electrode layer **22** contacts at least a portion of layer **20**. Leads **24** attached as by solder **26** carry away power from the cell. Because layers **18** and **20** are polycrystalline, they can be prepared by a thin-film preparation process to be extremely thin, for example, no greater than about 50 microns thick and preferably from about 0.05 to about 5 microns thick. The total thickness then of the combined semiconductor materials is generally less than about 100 microns, and preferably no greater than about 10 microns. The triangles are indicative of the fact that the layer is polycrystalline.

Electrode layers **16** and **22** are extremely thin conventionally, from about 1000 to about 10,000 Å, and from about 30 to about 1000 Å respectively. Glass support layer **14** is of course comparatively thick, typically about 1000 microns.

Photovoltaic cells of this invention can be used to photogenerate electric power when exposed to activating radiation, preferably through the window electrode. The potential created across the junction can be used as a voltage source, or the current generated by the cell can be drawn off. Thus, among other things, the cell can be used as a voltage generator or as an exposure meter operating from the cell's short circuit current. Such uses are in accordance with conventional practices following well-known procedures.

The following examples further illustrate the invention. Except where noted, pure oxygen atmospheres at stated partial pressures were used. In each example simulated sunlight illumination of 75 mW/cm^2 (AM2) was achieved by using a Kodak Carousel projector, Model 600, containing a 500 W tungsten-lamp, with the heat-absorbing glass removed, and a spectrum-correcting-filter set. Conversion efficiencies were calculated from the measured I_{sc}, V_{oc}, fill factor and the known input illumination. As used herein, "fill factor" means the fraction of the product of I_{sc} and V_{oc} that is available as power output for the cell.

EXAMPLE 1

A cell was prepared of the type shown in FIG. 2, as follows:

On a Nesatron ® glass substrate a CdS layer was deposited at a temperature of about 550° C., in an oxygen-containing atmosphere of about 0.4 torr O_2 to a thickness of about 0.2 micron. A CdTe layer about 2 microns thick was then deposited on the CdS layer heated at a temperature of about 590° C., in an atmosphere containing 1.5 torr O_2 and 1.5 torr Ar. A 500 Å thick gold electrode layer 6 was vacuum-deposited on the CdTe layer. Under simulated sunlight illumination of 75 mW/Cm^2, the cell had a V_{oc} of about 0.7 volts, an I_{sc} of about 16 mA/cm^2, and a fill factor of about 0.6. The conversion efficiency was about 8.9%.

Example 2: Enhancement Due to CdS Deposition in O_2

To demonstrate the effect of the use of an oxygen-containing atmosphere only during the CdS deposition, a control cell and 5 test cells were prepared as follows: Nesatron ® substrates having a nominal resistivity of 25 ohm/square were cleaned by hand-rubbing with Alconox ® detergent and rinsing with hot tap water prior to deposition of the semiconductor layers. The CdS layer was then prepared by close-space sublimation, wherein the source was a hot-pressed disc of phosphor-grade CdS powder obtained from General Electric. The process was carried out with a source temperature of about 750° C. and a substrate temperature of about 535° C. In the case of the control cell, a vacuum was used containing a partial pressure of O_2 of less than 0.01 torr, which was achieved with a mechanical vacuum pump. The five test cells, on the other hand, incorporated 2.5 torr oxygen in the atmosphere during the CdS sublimation. The deposition time was about 2 to 4 minutes, leading to a layer thickness of between about 1 micron and 2 microns. After cooling the substrate to near room temperature, it was placed on another holder for the CdTe deposition. The source was a polycrystalline disc sliced from an ingot which had been prepared by reacting 99.9999% pure Cd and Te in a melt doped with 10 ppm of Au. A source temperature of about 550° C., a substrate temperature of about 450° C. and a deposition time of about 2 minutes were used to achieve a film thickness of about 0.5 microns. The deposition of all CdTe layers was carried out under a partial pressure of O_2 of less than about 0.01 torr, provided by a mechanical vacuum pump. The CdTe/CdS structure was post-heated in air at 325° C. for 3 minutes, after which the cell was completed by vapor-depositing a 500 Å thick layer of Au on the CdTe layer.

The photovoltaic response of the control cell lacking the oxygen atmosphere for the CdS deposition was, $V_{oc}=0.37$, $I_{sc}=7.1$ mA/cm^2, fill factor approximately equal to about 0.4 and conversion efficiency = 1.38%. In contrast, the average photovoltaic response of the 5 test cells was $V_{oc}=0.48\pm0.03$ mV, $I_{sc}=9.1\pm1.6$ mA/cm^2, fill factor of approximately 0.4, and conversion efficiency = 2.5±0.3%, an improvement in conversion efficiency of more than 1%.

Examples 3 and 3A:

To further illustrate the effect of the presence of oxygen during CdS deposition, two different cells were made with the CdS layer prepared under two different pressures of air. Preparation of a "Nesatron" electrode was generally as described in Example 2. One of the cells, Example 3, was prepared by close-space sublimating the CdS layer in a vacuum prepared by evacuating the air using a rotary mechanical pump, to a pressure of less than 0.01 torr, flushing with argon several times, and reducing the argon atmosphere to less than 0.01 torr. The CdTe layer was formed by close-space sublimation for 2 min. on the CdS substrate maintained at 610° C., in an atmosphere of 1.5 torr O_2 and 1.5 torr Ar, from a source held at 630° C. Example 3A was prepared identically as Example 3, except that air was used as the atmosphere for the close-space sublimation of the CdS, at a pressure of 0.15 torr. Table 1 illustrates the results.

Table 1

Example	Ambient Air Pressure, Torr	η, %	V_{oc}, mV	I_{sc}, mA/cm^2	FF
3	essentially zero	4.0	390	15.1	0.51
3A	0.15	8.3	650	17.0	0.56

Very little improvement in conversion efficiency was noted upon increasing the air pressure above 0.15 torr. This example demonstrated that although the presence of oxygen in the atmosphere for the deposition of the CdTe produced a significant conversion efficiency, an even higher value is achieved if oxygen is present for the deposition of the CdS also.

Example 4: Enhancement Due to CdTe Deposition in O_2

To demonstrate the enhancement achievable by depositing the CdTe layer in an oxygen-containing atmosphere, eight cells were prepared by the procedure of Example 2 on CdS prepared in an atmosphere containing 2.5 torr of oxygen, except that the CdTe layer was deposited using an atmosphere containing 5.0 torr of oxygen. These eight cells showed an average V_{oc} of 0.618 ± 0.012 volts, an average I_{sc} of 11.5 ± 1.5 mA/cm^2, a fill factor of approximately 0.5±0.01, and an average conversion efficiency of 4.89±0.54%. Thus, an improvement of more than 2% in conversion efficiency was achieved by depositing the CdTe in an oxygen-containing atmosphere.

Examples 5-11

To demonstrate the effect of the substrate temperature for CdTe deposition, seven cells were made under the following conditions: a CdS layer was deposited by close-space sublimation on a Nesatron ® glass substrate with a nominal electrical resistance of 10 ohm/square. The source temperature was 720° C., the substrate temperature was 550° C., the deposition time was 5 seconds, and the process was carried out in an 0.4 torr oxygen atmosphere. Then a CdTe layer was deposited, again by the close-space sublimation process. The source temperature was 630° C. or 640° C., the substrate temperature varied as shown in Table II, the deposition time was 2 minutes, and the process was carried out in an atmosphere consisting essentially of 1.5 torr O_2 and 1.5 L torr Ar. Cell preparation was completed by evaporation of a 500 Å Au layer, using the technique of conventional vacuum evaporation under a pressure of 10^{-6} torr. (For the cells with 600° C. or higher substrate temperature, a slightly higher source temperature was used to provide a CdTe layer thickness similar to that of the other cells.) The results are summarized in Table II, and represent the data points in FIG. 1.

Table II

	CdTe Deposition					
Ex.	Source Temp., °C.	Substrate Temp., °C.	η, %	V_{oc},mV	I_{sc}, mA/cm^2	FF
5	630	500	3.9	560	12.5	0.42
6	630	530	4.7	610	13.7	0.43
7	630	550	6.3	630	14.7	0.50
8	630	570	8.4	680	16.7	0.55
9*	630	590	8.9	705	16.3	0.58
10	640	600	8.9	695	16.7	0.58

Table II-continued

	CdTe Deposition					
Ex.	Source Temp., °C.	Substrate Temp., °C.	η, %	V_{oc},mV	I_{sc}, mA/cm^2	FF
11	644	610	8.9	710	16.5	0.58

*This is the cell described in Example 1.

Example 12:

To further illustrate the effect of oxygen during CdTe deposition, a series of cells was prepared by varying the oxygen pressure during CdTe deposition while maintaining the other conditions of preparation essentially constant. That is, the deposition of the CdS was either in a 0.4, 0.5 or 1.0 torr oxygen atmosphere, using a T_{source} (source temperature) of 710°, 720° or 725° C. and a $T_{substrate}$ (substrate temperature) of 500° C. or 550° C. The CdTe deposition used a T_{source} of 630° or 640° C. and a $T_{substrate}$ of 600° or 610° C. None of these minor variations are believed to be significant or capable of producing significantly different conversion efficiencies.

It was found that an oxygen pressure of 0.5 torr produced a cell with a conversion efficiency of about 4.6%, whereas at an oxygen pressure of about 1.0 torr or higher, the conversion efficiency was generally constant at about 8.75%±1.25.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadmium sulfide are polycrystalline, and together said layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without said oxygen atoms present.

2. A cell as defined in claim 1, wherein said oxygen-containing layer is the cadmium telluride layer.

3. A cell as defined in claim 1, wherein said oxygen-containing layer is the cadmium sulfide layer.

4. A cell as defined in claim 1, wherein both of said layers contain oxygen atoms in said amount.

5. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein said layers are polycrystalline and the total combined thickness of said layers does not exceed about 10 microns, at least one of said layers containing oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms in said layer.

6. A cell as defined in claim 5, wherein said oxygen-containing layer is the cadmium telluride layer.

7. A cell as defined in claim 5, wherein said oxygen-containing layer is the cadmium sulfide layer.

8. A cell as defined in claim 5, wherein both of said layers contain oxygen atoms in said amount.

9. A cell as defined in claim 5, wherein one of said electrodes is a layer of conductive oxide in low-impedance contact with at least part of said CdS layer, said oxide layer being transparent or semitransparent to incident radiation.

10. A cell as defined in claim 9, wherein said oxide is indium tin oxide.

11. A cell as defined in claim 9, wherein the other of said electrodes is a layer of metal in low-impedance contact with at least part of said CdTe layer.

12. A cell as defined in claim 11, wherein said metal is gold.

13. A cell for converting incident radiation into electricity, comprising

first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semi-transparent to said incident radiation,

said cell being further characterized by a conversion efficiency of at least about 6.0% when exposed to AM2 light.

14. A cell for converting incident radiation into electricity, comprising

first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semitransparent to said incident radiation,

said cell being further characterized by a combined thickness of said layers that is no greater than about 10 microns and a conversion efficiency of at least about 6% when exposed to AM2 light.

15. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadmium sulfide are polycrystalline, at least one of said layers having been formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without said at least one layer having been formed in said oxygen-containing atmosphere.

16. In a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein the combined thickness of said layers does not exceed about 10 microns, at least one of said layers having been formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without said at least one layer having been formed in said oxygen-containing atmosphere.

17. A cell as defined in claim **16**, wherein said layer formed in an oxygen-containing atmosphere is the cadmium telluride layer.

18. A cell as defined in claim **17**, wherein said oxygen-containing atmosphere was at a pressure of at least about 1 torr of oxygen.

19. A cell as defined in claim **16**, wherein said layer formed in an oxygen-containing atmosphere is the cadmium sulfide layer.

20. A cell as defined in claim **16**, wherein both of said layers were formed in an oxygen-containing atmosphere.

21. In a process for manufacturing a photovoltaic cell by depositing, in the vapor phase, contiguous polycrystalline layers of n-type cadmium sulfide and p-type cadmium telluride and securing an electrode to at least a portion of each of said layers,

the improvement comprising depositing at least one of said layers in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without said oxygen atmosphere.

22. A process as defined in claim **21**, wherein both of said layers are deposited by close-space sublimation in an oxygen-containing atmosphere and the temperature of the substrate during the depositing of CdTe is at least about 575° C., the amount of time of said depositing of said layers being sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but at a CdTe substrate temperature less than about 575° C.

23. A process as defined in claim **21** and further including the step of heating in an oxygen-containing atmosphere either or both of said layers after their deposition, for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without said post-deposition heating.

24. A process as defined in claim **21**, wherein the deposition of said CdTe is in an atmosphere containing at least about 1 torr oxygen.

25. A process of converting incident radiation into electrical power, comprising the steps of

(a) exposing to said radiation, a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, said layers together containing oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without said oxygen atoms, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semitransparent to said incident radiation; and

(b) drawing off power from said cell in proportion to said enhanced conversion efficiency.

26. A process of converting incident radiation into electrical power, comprising the steps of

(a) exposing to said radiation, a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, at least one of said layers being formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without being formed in said oxygen-containing atmosphere; and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent of semitransparent to said incident radiation; the total combined thickness of said layers not exceeding about 10 microns; and

(b) drawing off power from said cell in proportion to said enhanced conversion efficiency.

27. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadium sulfide are polycrystalline, and together said layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell generally identical in structure but containing only the amount of oxygen atoms in said layers that is present when the layers are formed in an atmosphere that has an oxygen partial pressure of less than 0.01 Torr.

28. A cell as defined in claim **27**, wherein one of said electrodes is a layer of conductive oxide in low-impedance contact with at least part of said CdS layer, said oxide layer being transparent or semi-transparent to incident radiation.

29. A cell as defined in claim **28**, wherein said oxide is indium tin oxide.

30. A cell as defined in claim **28**, wherein the other of said electrodes is a layer of metal in low-impedance contact with at least part of said CdTe layer.

31. A cell as defined in claim **30**, wherein said metal is gold.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,207,119
DATED : June 10, 1980
INVENTOR(S) : Y. S. Tyan

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 59, "oxgen", should read --oxygen--.

Col. 5, line 22, "cconversion", should read --conversion--; line 38, "cell is", should read --cell it--; line 45, "bebetween", should read --between--.

Col. 8, line 50, delete "L".

Col. 12, line 25, "transparent of", should read --transparent or--.

Signed and Sealed this

Sixth Day of *January 1981*

[SEAL]

Attest:

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Attesting Officer

Commissioner of Patents and Trademarks

United States Patent [19]
McCandless et al.

[11] **Patent Number: 4,709,466**
[45] **Date of Patent: Dec. 1, 1987**

[54] PROCESS FOR FABRICATING THIN FILM PHOTOVOLTAIC SOLAR CELLS

[75] Inventors: **Brian E. McCandless; Robert W. Birkmire,** both of Newark, Del.

[73] Assignee: **The University of Delaware,** Newark, Del.

[21] Appl. No.: **723,054**

[22] Filed: **Apr. 15, 1985**

[51] **Int. Cl.**⁴ **H01L 31/18**
[52] **U.S. Cl.** **437/5**; 136/260; 136/264; 427/76; 437/248
[58] **Field of Search** 29/572; 136/260, 264, 136/265; 357/30; 427/76

[56] **References Cited**

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58-18969 2/1983 Japan 136/260

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B. M. Basol et al., *Proceedings, 5th E.C. Photovoltaic Solar Energy Conf.*, (1983), pp. 888–891, Reidel Pub. Co., (1984).

Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Connolly & Hutz

[57] ABSTRACT

Thin film photovoltaic solar cells are made by forming the cell structure from a number of layers including the contact layers and semiconductor layers. At least one of the semiconductor layers is a tellurium containing II-VI compound. After the structure is formed, it is heated to temperatures above 300° C. and then rapidly cooled at rates greater than 10° C./s. Cells comprising CdS and CdTe have increased fill factor when the fabrication process includes heating and rapid cooling.

10 Claims, 2 Drawing Figures

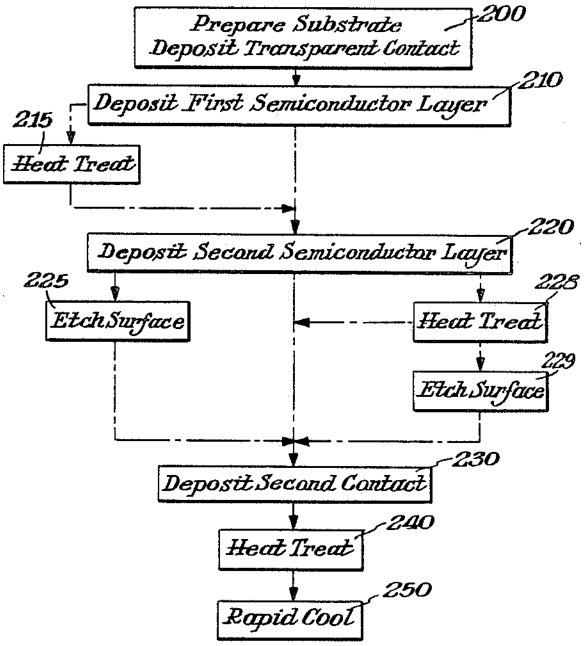


Fig. 1.

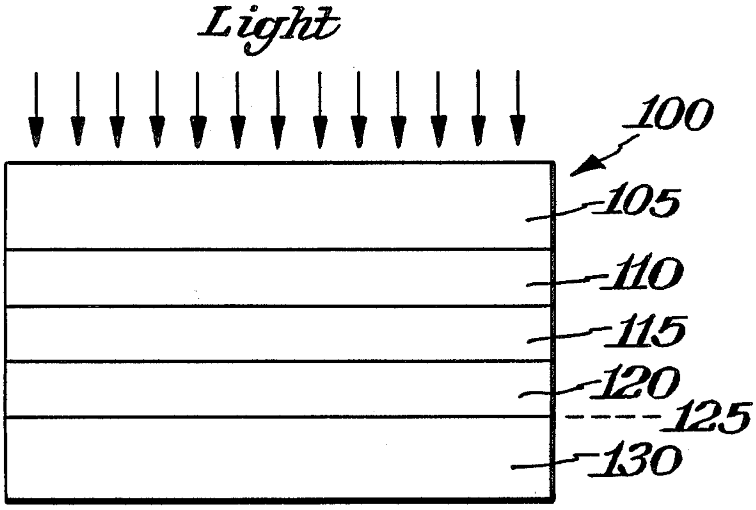
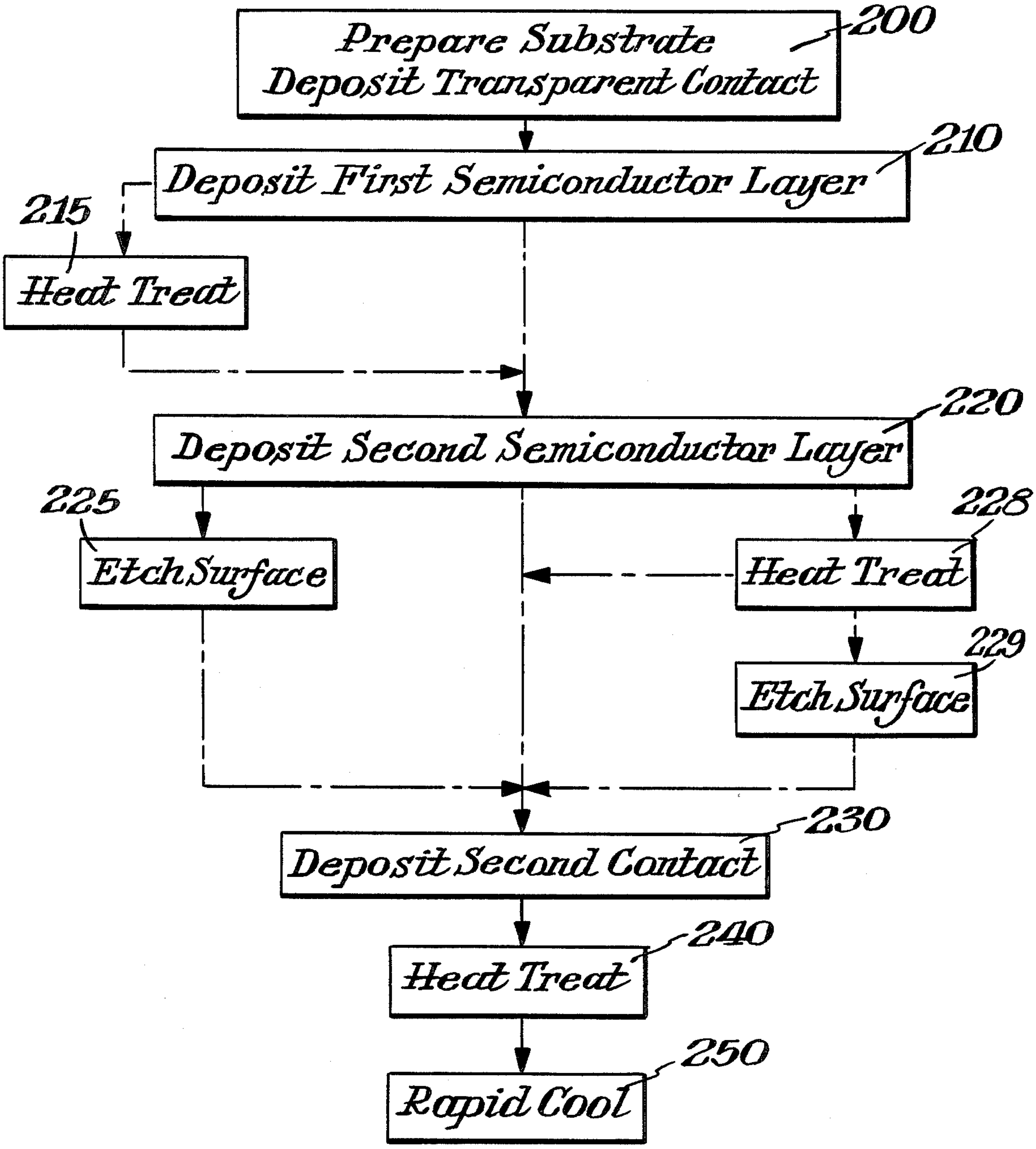


Fig. 2.


Prepare Substrate
Deposit Transparent Contact
200
Deposit First Semiconductor Layer
210
215
Heat Treat
Deposit Second Semiconductor Layer
220
225
Etch Surface
228
Heat Treat
229
Etch Surface
Deposit Second Contact
230
Heat Treat
240
Rapid Cool
250

PROCESS FOR FABRICATING THIN FILM PHOTOVOLTAIC SOLAR CELLS

BACKGROUND OF THE INVENTION

While thin film solar cells, such as CdS/CdTe solar cells, made according to methods known in the art have achieved efficiencies near 10%, further improvements in efficiency require increased fill factor. In order to increase the fill factor of a cell the electrical resistance at the contact between the CdTe semiconductor layer and the contact layer needs to be reduced. A measure of this resistance is the slope of the current-voltage curve at the open circuit voltage point. Moreover, high efficiencies have been mostly obtained using gold for the contact metal. However, gold is not only an expensive material, but there is evidence that cells utilizing gold contacts are not stable for long periods of time. Therefore, there is a need for a fabrication process that provides for increased fill factor and permits substitution for gold with other metals. The art also teaches various etches for preparing the surface of CdTe before forming the contact. However, wet etching may not always be desirable or feasible for fabricating thin film cells.

SUMMARY OF THE INVENTION

An object of this invention is to provide a process for fabricating thin film photovoltaic solar cells, such as of the CdS/CdTe type, wherein there is an increase in fill factor.

In accordance with this invention, the object of the invention is achieved by heat treating the cell after the contact layer has been deposited on the CdTe layer and then rapidly cooling the cell.

THE DRAWINGS

FIG. **1** is a side elevation view of a thin film photovoltaic solar cell formed in accordance with this invention; and

FIG. **2** is a flow diagram showing the steps used in fabricating the cell of FIG. **1**.

DETAILED DESCRIPTION

FIG. **1** shows a thin film photovoltaic solar cell **100** fabricated in accordance with this invention. As shown therein, cell **100** includes a transparent substrate **105** on which is formed a transparent contact layer **110**. Transparent substrate **105** may be glass or a polymeric material. Transparent contact layer **110** is tin oxide, indium-tin-oxide, cadmium stannate or other transparent conductive oxide materials known in the art.

Next is formed first semiconductor layer **115** and then second semiconductor layer **120**. Semiconductor layers **115** and **120** should be of opposite conductivity tyep. For example, first semiconductor layer **115** may be n-type CdS or (ZnCd)S and second semiconductor layer **120** may be p-type CdTe or HgCdTe. Finally contact layer **130** is formed. The specific materials and dimensions for the cell structure may be those conventionally used in the art.

FIG. **2** shows the steps for forming cell **100**. Steps **200** through **230** are carried out in the conventional manner. As indicated in FIG. **2**, certain of the heating and etching steps (i.e., Steps **215**, **225**, **228** and **229**) are optional steps.

Reference is made to the publication of Y.S. Tyan et al in *Proceedings of the 16th IEEE Photovoltaic Specialists Conference* (1983), p. 794, for Steps **210** and **220** of depositing CdS layer **115** and CdTe layer **120** in an oxygen-containing atmosphere at high temperatures using a method called "close space sublimation". Step 225 is chemically etching CdTe surface **125** as taught in U.S. Pat. No. 4,319,019. The cell is completed by depositing, in Step **230**, a metal layer **130**, such as gold or nickel.

Reference is made to U.S. Pat. No. 4,456,630 and the publication of B. M. Basol, in the Journal Applied Physics, Vol. 55, No. 2, (1984), p. 601 for the steps involving electrodepositing CdS and CdTe semiconductor layers **115** and **120** (Steps **210** and **220**); heat treating at 400° C.in air for about 10 minutes (Step **228**), followed by etching CdTe surface **125** (Step **229**); and finally depositing a conductive metal layer **130**, such as gold, by evaporative techniques (Step **230**).

The improved process of the present invention includes, as Step **240**, heating at a temperature of about 300° C. to 500° C. for about 10 to 100 minutes and Step **250** rapidly cooling to room temperature at a rate of at least 10° C./s and preferably at 100° C./s. Heating Step **240** can be carried out in an oven or furnace or on a heated surface, such as a hot plate. It is preferred to carry out Step **240** in air at a temperature of 400° C. for 15 minutes. Rapid cooling, Step **250**, is carried out by removing the device from the furnace and placing it in thermal contact with a heat sink adapted to provide the required cooling rate.

Experiments have been conducted to show the utility of heating and rapid cooling. These experiments were performed by first sputter depositing an indium-tin-oxide TCO layer **110** on Corning 7059 glass substrate **105** (Step **200**). Next, the CdS layer **115** was deposited to a thickness of 5 microns by physical vapor deposition (Step **210**). The specimen was heat treated (Step **215**) for 3 hours in air at 350° C. CdTe layer **120** was deposited in Step **220** to a thickness of 10 microns by close space sublimation in the presence of 2 torr oxygen and at a substrate temperature of 600° C. CdTe surface **125** was etched (Step **225**) according to U.S. Pat. No. 4,456,630. A gold metal contact **130** was deposited in Step **230** by electron beam evaporation. Heating Step **240** was conducted by placing the cell in the 400° C. zone of a quartz lined tube furnace for 15 minutes. Finally, rapid cooling Step **250** was carried out at an estimated rate of 100° C./s by removing the cell from the furnace and pressing it against a precooled aluminum plate.

Comparative experiments were also carried out. In order to test the effect of cooling rate, specimens were cooled slowly. The effect of heating and quick cooling prior to depositing metal layer **130** was also examined.

It was found that rapid cooling gave higher fill factor and that the effect was essentially reversible with respect to slow cooling. That is, when a cell made in accordance with the invention and having a fill factor of 0.53 was heated for 15 minutes in air at 400° C.and allowed to cool slowly at a rate of less than 1° C./s, the fill factor diminished by 14% to 0.46. However, when the same cell was reheated and cooled rapidly at a rate of about 100° C./s , the fill factor was found to increase some 15% to a new value of 0.54. Examination of the current-voltage characteristics of this cell after each heating and cooling cycle confirmed that the observed changes in fill factor were due to changes in series resistance. Furthermore, changes in open circuit voltage and short circuit current were negligible.

Regarding the significance of carrying out Steps **240** and **250** after metal deposition Step **230**, it was found that air heating Step **228** merely functioned as taught by the above noted Basol publication. The degree of effectiveness depended on the conditions of CdTe deposition Step **220**. For example, heating in air prior to depositing metal contact layer **130** was more beneficial for cells having CdTe deposited in an argon atmosphere than for CdTe deposited in an oxygen atmosphere. In either case, however, the rate of cooling had no effect. In contrast, heat treating and rapid cooling after contact deposition Step **230**, in accordance with the invention, always improved fill factor.

It was also found that etching Steps **225** or **229** can be omitted when the cell is heated and rapidly cooled according to the invention.

These observations are consistent with the hypothesis that heating and rapid cooling act to improve the electrical properties of the CdTe/metal contact.

It is believed that the scientific principle governing the invention is related to the phase equilibria of CdTe. Examination of the phase diagram in W. Abers, "Physical Chemistry of Defects", *Physics and Chemistry of II-VI Compounds,* M. Aven and J. S. Prenner, eds. American Elsevier, N.Y. (1967) shows that the single phase region for CdTe is quite broad at temperatures above 400° C., but narrows rapidly at lower temperatures. The implication of this is that slightly non-stoichiometric CdTe will contain precipitates of Cd or Te if equilibrated at low temperatures. Rapid cooling, however, will "freeze in" the high temperature equilibrium.

The process of the invention has also been applied to cells having a structure which is the inverse of that shown in FIG. **1**. Such a cell would be fabricated by first depositing the CdTe on a suitable substrate, optionally heat treating the CdTe, next depositing CdS, and finally depositing a transparent conductive layer onto the CdS. Positive results were indicated when a cell having the configuration glass/metal/CdTe/CdS/ITO, with the semiconductor layers deposited by physical vapor deposition, was heat treated and rapidly cooled in accordance with the teachings of the invention.

Substitution by (ZnCd)S for CdS and/or by (HgCd)Te or (ZnCd)Te for CdTe are within the scope of the invention. Moreover, the practice of the invention need not be limited by the method selected for depositing the semiconductor and contact layers. Among deposition methods that may be selected by one skilled in the art are: physical vapor deposition; close space transport; close space sublimation; sputtering; chemical vapor deposition; electrodeposition; screen printing; electrophoresis; spray pyrolysis; electron beam evaporation; ion plating; and liquid phase epitaxy.

Furthermore, it is contemplated that heating and rapid cooling in accordance with the teachings of this invention may be adapted by those skilled in the art for improving the electrical contact behavior of devices utilizing Te containing II–VI compound semiconductors such as tandem photovoltaic solar cells, optical and infrared detectors, photoemissive displays, light emitting diodes, thin film transistors and the like.

What is claimed is:

1. In a method of fabricating thin film photovoltaic solar cells made by sequentially forming a first contact layer on a substrate, a first semiconductor layer, and a second semiconductor layer, and a second contact layer, wherein at least one of the contact layers is transparent and at least one of the semiconductor layers comprises a tellurium containing II–VI compound the improvement being the steps of heat treating the cell after the second contact layer has been formed, and then rapidly cooling the cell at a temperature reduction rate of at least 10° C. per second.

2. In the method of claim **1** wherein the heat treating step is at a temperature of from 300° C. to 500° C. for a period of time from 10 minutes to 100 minutes.

3. In the method of claim **2** wherein the heat treating step is at 400° C. for about 15 minutes.

4. In the method of claim **2** wherein the rapid cooling step results in a temperature reduction of 100° C. per second.

5. In the method of claim **2** wherein the heat treating step is performed in air.

6. The method of claim **2** wherein the rapid cooling step is performed by placing the cell in thermal contact with a heat sink.

7. The method of claim **1** wherein one of the semiconductor layers is selected from the group consisting of CdTe, (HgCd)Te and (ZnCd)Te.

8. In the method of claim **8** wherein said one of the semiconductor layers is CdTe.

9. The method of claim **8** wherein the other semiconductor layer selected from the group consisting of CdS and (ZnCdS).

10. The method of claim **10** wherein said other semiconductor is CdS.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,709,466

DATED : December 1, 1987

INVENTOR(S) : Brian E. McCandless and Robert W. Birkmire

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 4, lines 42 and 44 "8" should be --7--;

Col. 4, line 47 "10" should be --9--.

Signed and Sealed this

Sixth Day of September, 1988

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

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PCT/JP97/01791

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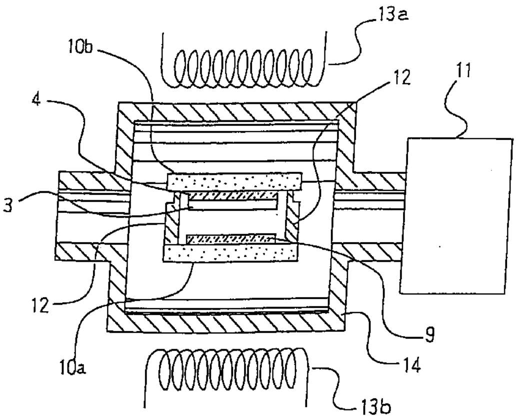
(54) METHOD FOR FORMING CdTe FILM AND SOLAR BATTERY USING THE FILM

(57) A method for forming a CdTe film of good quality by an improved close-spaced sublimation process is disclosed. This method comprises: a step of applying a paste which contains material for CdTe semiconductor on a supporting member, thereby to form a coating film which contains the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, and causing the material for the semiconductor in the coating film to evaporate.

F I G. 2



Description

TECHNICAL FIELD

The present invention relates to a method for preparing a CdTe semiconductor film which is used mainly for solar cells, in particular, to a method for preparing the CdTe film by a close-spaced sublimation process.

BACKGROUND ART

In recent years, global environmental problems such as global warming due to carbon dioxide, depletion of the ozone layer, and the like have been highlighted. For that reason, expectation for development of new energy, in particular, that for solar cells have become glowingly great. However, for popularization of the solar cells, there are a number of problems which must be solved. In particular, an improvement in conversion efficiency of the solar cells and a reduction in price are desired.

A CdS/CdTe solar cell uses CdTe which has an forbidden band gap (=1.44 eV) being suitable for a light absorption layer, and thus it is one of the solar cells which are expected to yield a high conversion efficiency.

In the manufacturing process of the CdS/CdTe solar cell, a cadmium telluride (CdTe) film is formed on a surface of a cadmium sulfide (CdS) film in general. As a method for forming the CdTe film, the close-spaced sublimation process which can produce the CdTe film of high quality is attracting attention. The close-spaced sublimation process is a kind of the vapor deposition process. A CdTe solar cell which has a conversion efficiency of the world highest level (15.8%) at present is obtained by this process. The close-spaced sublimation process is disclosed in, for instance, "HIGH EFFICIENCY CdS/CdTe SOLAR CELLS FROM SOLUTION-GROWN CdS FILMS" (The Conference Record of the 22nd IEEE Photovoltaic Specialists Conference (1991) Vol. 2, p.952) by T. L. Chu et. al., or the like. According to this process, a material for forming the CdTe film (hereinafter referred to as a source) and a substrate are so placed as to face each other, with a gap of about 0.5 - 5 mm, and heated under a reduced pressure. In this manner, the source is caused to sublime and then deposit on the substrate. According to this process, since the sublimed source is rearranged and crystallized on the substrate placed at a short distance as long as the mean free path level, a CdTe film which has a high crystallinity is obtained. Further, since the treatment is performed under the reduced pressure, the film-forming speed is high.

However, the above-mentioned conventional close-spaced sublimation process has the following problems.

In general, in the close-spaced sublimation process, as a source, a CdTe powder placed on a dish-shaped container so as to cover over it is used. In the above-mentioned literature for instance, a commercially-available polycrystal of CdTe with a purity of 5N, or a powder produced by pulverizing a polycrystal ingot of CdTe obtained by directly implanting a dopant as one of the constituting element, is used as the source.

In addition to the fact that this process uses an expensive CdTe powder, it has a low utilization efficiency. In this process, it is difficult to evenly place as much amount of the source for forming the film just once for covering over the container. For that reason, the same source is repeatedly used for forming the CdTe films. It is difficult to control the CdTe powder or the source since it changes in particle size, powder density, stoichiometric ratio and the like by the sublimation, and hence, with the repetition of the film-forming, dispersions in thickness and in quality of the CdTe film increases gradually. Therefore, the obtained solar cell has a large dispersion in performance. For that reason, in order to make the dispersion in performance of the solar cell small, of the source placed for covering, only about 10% is actually consumed for the film-forming, and the rest is discarded without being used.

Further, according to this process, since the film is formed under the reduced pressure, an equipment must once be stopped when the source is exchanged. Therefore, the production efficiency is also low.

When a CdTe film is formed by this process, on a substrate which has a large area, a central part of the obtained CdTe film is made thicker than that of a peripheral part because the central part of the source is liable to trap a heat flowed from circumference, as opposed to the peripheral part where the heat is liable to escape. Therefore, the variation in thickness within the same film is large.

Moreover, according to this process, when the source is used repeatedly, the particle diameter of the material decreases gradually and the surface area of the material increases, and in addition, the surface temperature of the source rises because the particles combine together by sintering. Therefore, the thermal conductivity increases and the film-forming speed increases gradually. When the same source is used repeatedly still more and the remaining amount of the source decreases accordingly, pores are produced between and among the particles and the thermal conductivity of the source is gradually lowered, thereby to decrease the film-forming speed conversely. For that reason, even when the manufacturing is performed under the same conditions, the thickness of the obtained CdTe film varies for every film-forming processes.

As previously described, according to the conventional close-spaced sublimation process, it is difficult to obtain CdTe film having uniform quality and thickness within the same film and between a plurality of the films. For that reason, although the CdTe film theoretically has the forbidden band gap which is the most ideal for converting the solar light as a compound semiconductor, a CdTe film as an ideal p-type semiconductor has not actually been obtained by the conventional close-spaced sublimation process.

In order to improve the conversion efficiency of the CdTe solar cells, means of making the CdTe film a weak p-type one by diffusing copper or the like into the CdTe film from the electrode side has widely been used, as reported, for instance, by B. E. Mccandless et. al., in "A treatment to allow contacting CdTe with different conductors" (Conference record of the 24th IEEE photovoltaic specialists conference 1994 volume II, p. 107-110). However, according to this method, a solar cell having a satisfactory conversion efficiency has not been obtained.

DISCLOSURE OF THE INVENTION

The present invention intends to solve the above-mentioned conventional problems, and has, as its object, a provision of a method for preparing a CdTe film of good quality simply.

The method for preparing the CdTe film in accordance with the present invention comprises: a step of coating a paste containing a material for CdTe semiconductor on a supporting member thereby to form a coating film containing the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, thereby to cause the semiconductor material in the coating film to evaporate.

According to this method, it is possible to greatly improve the utilization rate of the material as compared with the case of using the above-mentioned conventional source. That is, since a thin coating film can be formed by coating, the utilization rate of the source which has conventionally been about 10% can be improved to about 50%. For that reason, it is not necessary to use the source for the formation of the film repeatedly. That is, since the source can be made disposable and a new source can constantly be used for the film-forming, it is possible to suppress the dispersion in characteristics of the CdTe film due to the repeated use of the source. Further, since the thin source can be obtained, it is possible to form the CdTe film without giving an excessive thermal damage to the previously formed CdS film.

Moreover, it is preferable to use a mixture of a cadmium powder and a tellurium powder as the semiconductor material. By using the mixture of the cadmium powder and the tellurium powder or, preferably, the pulverized powder, which is very inexpensive as compared with the CdTe powder thereof, the material cost can be reduced in great deal. In particular, by pulverizing Cd and Te in a mixed state, a mixed power can be obtained in a short time period. Further, with an energy for the pulverization, a part of the mixture can be synthesized into CdTe.

Moreover, by adding cadmium chloride into the paste, the crystallinity of the formed CdTe film is improved and the grain size of CdTe increases. In this manner, it is possible to obtain a solar cell of a high conversion efficiency. It is believed that the improvement in the crystallinity of the CdTe film is due to the fact that position of lattice defect of tellurium is substituted by chlorine, thereby to improve the crystallinity of the CdTe film. Moreover, since cadmium chloride is mixed into a paste and then coated, it is possible to constantly use the new source wherein cadmium chloride is uniformly dispersed. Therefore, it is possible to repeatedly and stably manufacture a CdTe film of high quality. If the added amount of cadmium chloride is smaller than 0.1 wt%, great effect cannot be obtained for the improvement in the performance of the solar cell. In contrast, if it is larger than 1.75 wt%, the performance is deteriorated conversely. For that reason, the added amount of cadmium chloride is preferably 0.1 - 1.75 wt%, and particularly 0.3 - 1.0 wt%.

In addition, it is preferable that the paste is one with a Group I element or a Group V element incorporated therein. By incorporating an impurity which acts as a carrier into the paste, it is possible to control the carrier concentration of the CdTe film in simple means. Incidentally, use of the Group I element or the Group V element in the conventional process employing a source prepared by placing the semiconductor material of powder state in a container so as to cover over it causes a variation in composition of the source, if such films are formed for plural times by using the same source, due to the differences in the sublimation speeds of the semiconductor material and the impurities. Therefore, a semiconductor film of stable composition cannot be obtained. On the other hand, according to the present invention, since the coating film of the semiconductor material formed on the surface of a heat-resistant supporting member is used as the source, it is possible to use a very small amount of the semiconductor material as the source. Therefore, a semiconductor film which has a constant concentration of the impurity can be formed. It is preferable that the Group I element to be mixed is lithium, potassium, sodium, rubidium, copper, silver or gold. Further, it is preferable that the Group V element to be mixed is arsenic, antimony, bismuth, phosphor or nitrogen. These can be used singly or plurally.

Moreover, by adding to the paste a substance which is stable in composition against the heat applied at the time of forming the semiconductor film and remains on the supporting member after the heating, it is possible to place the semiconductor material of an amount which is exactly necessary for one time film-forming on the supporting member in a stable state with a small dispersion. By causing all semiconductor materials to sublime, it is possible to manufacture a CdTe film of large area which is stable in thickness and quality. For instance, according to a screen-printing, it is difficult to form a coating film of a uniform thickness unless the thickness of the coating film to be formed is not less than 50 μm.

However, in a case of adding no additive to the paste, when a coating film with the thickness of 50 μm is entirely sublimed, a CdTe film with a thickness of about 20 μm is obtained. If such a thick CdTe film is used in the solar cell, resistance of the CdTe film in the thickness direction is large and thus the characteristics of the obtained solar cell are poor. That is, a thinner CdTe film is desired for employing it in the solar cell. The most suitable thickness is about 6 μm. That is, if no additive is added to the paste, it is necessary to stop the film formation halfway while the source remains. On the other hand, by adding an additive to the paste as in this example, the amount of the semiconductor material in the coating film can easily be adjusted and thus it becomes possible to form a semiconductor film which has a preferable thickness. Since to control the thickness of the coating film becomes so easy, it is possible to use only a necessary amount of the semiconductor material for one film formation as the source. As the substance to be added, carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride or aluminum nitride is preferable. Further, these substances can be used by mixing them. Since the carbon and silicon carbide can absorb radiated infrared ray, the source can be heated efficiently by using them. Moreover, since they can protect the CdS film which has previously been formed from a thermal damage, it is possible to suppress an occurrence of micro-short-circuiting resulting from a thinning of the CdS film by the sublimation, and an excessive mutual diffusion at an interface between the CdS film and the CdTe film.

Further, at the time of painting the paste, by making more amount of the paste adhere to the peripheral part of the supporting member where its temperature at heating is relatively lower than the central part of the supporting member, some more amount of semiconductor material may be placed there.

The supporting member for holding the paste is preferably a plate-shaped carbon material which has a heat soaking property and a small heat capacity. A glass substrate is preferable in viewpoints of price and easiness in handling. As the glass, borosilicate glass, a low alkali glass, soda-lime glass and the like may be used. In a case of using the glass substrate, it is preferable to place at least one carbon plate beneath the glass substrate. Further, if an expansion of the supporting member due to the thermal treatment is taken into consideration, a ceramics which has a small linear expansion coefficient is preferable. These supporting member can be used repeatedly.

It is preferable that the supporting member is composed of a glass having a conductive oxide film on the surface thereof. By using a glass having the conductive oxide film of, for instance, indium oxide, indium tin oxide, stannic oxide, zinc oxide and the like, as the supporting member, it is possible to suppress a radiation heat which reaches the formed semiconductor film, after the evaporation of the source is completed, thereby to prevent the excessive mutual diffusion at the interface of the CdS film and the CdTe film. Further, by roughening a surface of the supporting member which is opposite to the side where the paste is painted, the radiation heat can similarly be suppressed. In this case, by scatter due to an unevenness of the surface of the supporting member and an improvement in the heat absorbing property due to the increase in the surface area, it is possible to reduce the amount of infrared ray which transmits through the supporting member and reaches the formed semiconductor film.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic longitudinal cross-sectional view of a solar cell which uses CdTe film in accordance with one embodiment of the present invention.

FIG. 2 is a schematic longitudinal cross-sectional view showing a structure of an equipment employed for forming the CdTe film in the same embodiment.

FIG. 3 is a characteristic diagram showing the relationship between the times of forming the CdTe film in the same embodiment and the conversion efficiency of a solar cell produced by using the CdTe film.

FIG. 4 is a characteristic diagram showing the relationship between added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in another embodiment of the present invention.

FIG. 5 is a characteristic diagram showing the dispersion in the conversion efficiency of a solar cell produced by using CdTe film obtained in a still other embodiment of the present invention.

FIG. 6 is a characteristic diagram showing the added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in a still other embodiment of the present invention.

FIG. 7(a) - FIG. 7(g), each is a longitudinal cross-sectional view showing the state of the respective step in manufacture of the solar cell in another embodiment of the present invention.

FIG. 8 is a schematic longitudinal cross-sectional view of source substrate plate used in another embodiment of the present invention.

THE BEST MODE FOR CARRYING OUT THE INVENTION

The method for preparing the CdTe film in accordance with the present invention will be described in detail with reference to the drawings.

In the following examples, a solar cell shown by FIG. 1 is produced by using the obtained CdTe film.

A transparent and insulating substrate 1 is made from borosilicate glass, low-alkaline glass, low-iron soda-lime glass, soda-lime glass and the like. On the surface of this substrate 1, a transparent conductive film 2 with a thickness of 1,000 - 10,000 Å composed of tin oxide, indium tin oxide (ITO) and the like is formed by chemical vapor-phase growing process or sputtering. In this occasion, a silica film (SiO_2 film) may sometime be formed between the substrate 1 and the transparent conductive film 2, in order to prevent an alkali component in the substrate 1 from diffusing into the transparent conductive film 2. Then, by forming a CdS film 3 with a thickness of 500 - 2,000 Å on the transparent conductive film 2 as an n-type semiconductor, a substrate 4 for forming CdTe film is obtained. This CdS film 3 is formed by thermally decomposing such an organometallic complex compound as cadmium isopropyl xanthogenate on the transparent conductive film 2.

In the followings, as examples of the method for preparing CdTe semiconductor film in accordance with the present invention, methods for forming a CdTe film 5 on the surface of the thus obtained CdS film 3 of the substrate 4 will be described.

EXAMPLE 1

By mixing a CdTe powder as a semiconductor material with propylene glycol as a viscosity improver, a paste was prepared. By printing the obtained paste on the glass substrate as the supporting member and drying, a film of the semiconductor material was formed on a glass substrate, thereby to obtain a source substrate 9.

The obtained source substrate 9 and the substrate 4 were installed on a manufacturing equipment shown in FIG. 2, and the CdTe film 5 was formed on the surface of the substrate 4 in the following manner.

A chamber 14 is made of quartz tube, inside of which susceptors 10a and 10b made of carbon with a thickness of 1 mm are arranged as heat-soaking members. On the mutually confronting surfaces of the susceptors 10a and 10b, the source substrate 9 and the substrate 4 are arranged so as to make the semiconductor material film to face the CdS film 3, respectively. In that arrangement, a spacer 12 is disposed between the source substrate 9 and the substrate 4 so that the distance between the both is constant. The source substrate 9 and the substrate 4 may be disposed on the susceptors inversely, bottom to top.

By substituting the atmosphere inside the chamber 14 with an argon gas, and heating the source substrate 9 and the substrate 4 by lamp heaters 13a and 13b for 30 second to several minutes, while maintaining the pressure inside the chamber 14 to 1 Torr by aspirating with a rotary pump 11, a CdTe film 5 was formed on the CdS film 3 of the substrate. In this step, the temperature of the substrate 4 was kept to 400 - 650°C by heating, and the temperature of the source substrate 9 was kept to a temperature which was higher than the temperature of the substrate 4 by 5 - 100°C.

In the above-mentioned manner, 100 pieces of samples wherein the CdTe films 5 were formed on the CdS films 3 of the substrates 4 were prepared. In this preparation, the sources were replaced for every samples. Further, about half of the source was consumed for forming the film.

On the surfaces of the CdTe films 5 of the respective samples thus formed, a methanol or an aqueous saturated solution of cadmium chloride was applied and then the applied methanol or water was evaporated. Further, the substrate 4 for thin film forming was thermally treated at 400°C for 30 minutes. By this thermal treatment, grains in the CdTe film were grown.

A carbon paste was prepared by mixing a carbon powder and a solution obtained by dissolving polyvinylbutyral as a viscosity improver in diethylene glycol monobutyl ether with kneading. After applying this carbon paste on the surface of the CdTe film 5 by screen printing, it was dried and sintered, thereby to form a carbon electrode layer 6 as a current collector. On the other hand, a paste was prepared by mixing and kneading a mixed powder of silver and indium, an epoxide and an alcohol solution consisting mainly of terpineol. By applying the obtained paste on the surface of the CdS film 3 and carbon electrode layer 6 by screen printing, drying and then sintering, a + side electrode 7 and a - side electrode 8 were formed, respectively.

COMPARATIVE EXAMPLE 1

As a comparative example, a CdTe film was formed by using one obtained by filling the CdTe powder similar to that used in Example 1 in a dish-shape container as the source. In that case, the CdTe films were formed with the same source for a plurality of times. By this process, about 90% of the source was left after the formation of the CdTe films for 100 times. By using the obtained CdTe films, solar cells similar to those in Example 1 were produced.

Each 100 pieces of the solar cells of Example 1 and of Comparative Example 1 obtained in the above-mentioned manner were investigated about their conversion efficiencies with a solar simulator at AM 1.5, 100 mW/cm^2. The results are shown in FIG. 3. In this diagram, the abscissa represents the respective solar cells arranged in the orders of forming the CdTe films.

As clearly seen from FIG. 3, according to the manufacturing method of Comparative Example 1, the composition of the source varies with the repetition of the manufacture of the film, thereby to change the quality and the thickness of the obtained CdTe film. Therefore, the characteristics of the cells prepared with these CdTe films deteriorated. In contrast, according to the manufacturing method of Example 1, it is possible to make a small amount of the source to be uniformly held on the glass substrate. By this method, the utilization rate of the material can greatly be improved as compared with the manufacturing method of Comparative Example 1, even if the source is replaced for every film formations. That is, by employing a source of the coating film obtained by making a semiconductor material a paste-state and painting this paste on a substrate, a constantly stable supply of the source is enabled. Therefore, a semiconductor film with a high quality can be manufactured stably at a low cost.

EXAMPLE 2

In this example, a description will be made in a case of adding cadmium chloride into the paste for forming the CdTe film beforehand.

A CdTe powder similar to that in Example 1 was used as a semiconductor material. Pastes were respectively prepared by adding cadmium chloride at a rate of from 0 to 2.0 wt% to 100 parts by weight of this CdTe powder.

By using the obtained pastes, CdTe films were formed and then, solar cells were prepared in a manner similar to that in Example 1.

The relationship between the incorporation ratios of cadmium chloride to the CdTe powder and the conversion efficiency of the obtained solar cells are shown in FIG. 4.

As shown in FIG. 4, it is appreciated that by adding not less than 0.1 wt% of cadmium chloride to the CdTe powder, the conversion efficiency of the obtained cell is improved. However, if it is added in excess over 1.75 wt%, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1 - 1.75 wt% to the CdTe powder. In particular, the improvement in the conversion efficiency is remarkable at 0.3 - 1.0 wt%, and vicinity of 0.5 wt% is the most desirable.

100 parts by weight of the CdTe powder was mixed with 0.5 parts by weight of cadmium chloride. By using the obtained mixture, a paste was prepared as mentioned above. By using a semiconductor film formed by painting this paste as the source, a CdTe film was formed. In this step, the source was replaced for every times of film forming in a similar manner to that in Example 1.

As a comparative example, a CdTe film was also formed by using the same mixture so placed in a dish-shape container as to cover over it at a high density. In this time, the source was used continuously for a plurality of times for the film formation without replacing.

Solar cells were produced by using the CdTe films obtained in the above-mentioned manner. The characteristics of the obtained solar cells were investigated in a similar manner. The results are shown in Table 1.

Table 1

Film forming times (time)	Conversion efficiency (%)	
	Example 2	Comparative Example
1	14.6	13.6
20	14.5	13.5
40	14.7	13.2
60	14.5	12.5
80	14.5	11.3
100	14.6	8.5

As shown in Table 1, in the case of using the semiconductor material of powder state covering over the container, the characteristics of the semiconductor film decrease with the repeated times of the film forming. This is due to the above-mentioned varying in the cadmium chloride concentration and its non-uniformity. According to this method, it is difficult to form a CdTe film of good quality by using a small amount of the semiconductor material. That is, in any other means than discarding the source while consuming only a part of the source and leaving the remaining semiconductor material in a considerable amount, it is impossible to stably manufacture the CdTe film.

In contrast, according to the manufacturing method in accordance with this example, whereby the semiconductor material is made to have a paste-state, and the coating film obtained by applying the paste on the substrate is used as the source, the unevenness in the characteristics of the solar cells produced by using the obtained semiconductor film is small because there is no need for using the source repeatedly. Therefore, it is possible to stably manufacture the semiconductor film of a high quality at a low cost.

As the atmospheric gas, a similar effect is obtained in a case of using an inert gas such as nitrogen, hydrogen or helium gas in place of argon used in the above-mentioned example. In addition, in a film formation under a pressure of not more than 2 atm, a similar effect is also obtained.

EXAMPLE 3

By using a source of the coating film of the CdTe obtained by printing it as in Example 1, a CdTe film with a good quality can be formed. However, due to the fact that the CdTe powder as the raw material is very expensive, the price of the product becomes high. The reason for this is that the single crystal of CdTe is manufactured by Bridgman process in general. According to this process, in addition to the fact that heating at a high temperature of not less than 1,000 °C is required, a long period of time is required for elevating the temperature and cooling for the safety in operation and the improvement in the crystallinity.

Therefore, a description will be made, in this example, on a method for forming the CdTe film of a good quality, by using a starting material of a Cd powder and a Te powder which are inexpensive as compared with the CdTe powder. The price of the commercially available CdTe powder is about 250 yen/g but, in contrast, the prices of the commercially available Cd powder and Te powder are about 20 yen/g, respectively. Therefore, according to the manufacturing method of this example, the material cost can be reduced in great deal.

The Cd powder, the Te powder and a liquid (for instance, water) were mixed together and stirred by using a medium of ring-shape or spherical shape. Subsequently, a paste was prepared by adding propylene glycol to the obtained mixture after being dried. By using the paste thus obtained, a CdTe film was formed and a solar cell was produced in a manner similar to that in Example 1.

The conversion efficiency of the obtained solar cell was measured in a manner similar to that in Example 1. The results thereof are shown in FIG. 5. In this diagram, the ordinate represents mean value ± standard variance in the conversion efficiencies of the solar cells of Example 3 and of the solar cells of Comparative Example 1.

As clearly shown by FIG. 5, according to the manufacturing method of this example, it is possible to obtain a solar cell of an excellent characteristic by using low-priced materials. As the reason for this, there are given the fact that the temperature distribution in the source can be made uniform since the particle diameters of Cd and Te can be made uniform by pulverizing, and the amount of the source can be made small by using the film obtained by applying the pulverized mixture as the source.

The Cd powder and the Te powder were mixed in an equimolar amount, and pulverized in water to give a particle diameter of not more than about 1 μm by using a medium stirring mill. After drying the pulverized powder thus obtained, propylene glycol as a viscosity improver was added to the pulverized powder and kneaded, thereby to prepare a paste. By printing this paste on a carbon plate with a thickness of 1 mm as the supporting member, and drying at 120°C for 1 hour, a coating film was formed and a source substrate was obtained.

On investigating the composition of the formed coating film by X-ray diffraction, diffraction peaks of Cd single substance, Te single substance and CdTe were observed. It is believed that this CdTe is synthesized at the pulverization by the pulverizing energy.

This source substrate 9 and the substrate 4 were arranged so as to make the coating film to face the CdS film, with a gap of 2 mm. Thereafter, the atmosphere inside the chamber 14 was substituted by argon, the source substrate 9 and the substrate 4 were heated to temperatures of 600 - 630°C and of 580 - 600°C, respectively, while maintaining the pressure to 1 - 5 Torr, and kept there for 1 minute. By this procedure, a CdTe film with a thickness of 6 μm was formed on the CdS film of the substrate 4.

An aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the surface of the obtained CdTe film, and then the water was evaporated. Thereafter, by thermally treating the CdTe film at 400°C for 30 minutes, the crystallinity of the CdTe film was improved. Subsequently, a carbon film and an AgIn film were formed as an electrode of the CdTe film side and an electrode of the CdS film side, respectively, thereby to produce a solar cell.

The measurement on the characteristics of the obtained solar cell conducted with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.5 mA/cm^2 and the open-circuit voltage was 0.813 V. Further, the fill factor was 0.696 and the conversion efficiency was 13.3%. These characteristics are about the same degree as the characteristics of the solar cell of Comparative Example 1 produced by using the CdTe film formed by using the CdTe powder placed in the dish-shape container so as to cover over it (short-circuit current of 23.4 mA/cm^2, open-circuit voltage of 0.815 V, fill factor of 0.701 and conversion efficiency of 13.4%).

Next, a paste was prepared by adding an appropriate amount of $CdCl_2$ as a melting point depression agent in addition to propylene glycol as the viscosity improver to the pulverized powder similar to the above-mentioned. After printing the obtained paste on a carbon plate with a thickness of 1 mm, the paste was dried by drying at 120°C for 1 hour, thereby to form a coating film comprising a semiconductor material, and to obtain a source substrate 9. In an X-ray diffraction pattern of the obtained coating film, a peak attributable to the $CdCl_2$ was observed in addition to the diffraction peaks of Cd single substance, Te single substance and CdTe, of course.

By heating the obtained source substrate 9 under a nitrogen atmosphere at a temperature of 600 - 700°C for 1 hour, the coating film was sintered. In an X-ray diffraction pattern of the sintered film thus obtained, only the diffraction peak attributable to CdTe was observed.

Next, the source substrate 9 and the substrate 4 were so placed as to face each other, with a gap of 2 mm, and a CdTe film 5 was formed on the CdS film 3 in a procedure as shown above. After the formation of the CdTe film 5, an aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the CdTe film 5 and water was evaporated, and then, it was thermally treated at 400 °C for 30 minutes. Thereafter, a solar cell was produced in a procedure as shown above and the characteristics of the solar cell were evaluated in a similar manner. Measurements on the characteristics of the solar cell with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.6 mA/cm^2, and the open-circuit voltage was 0.816 V. Further, the fill factor and the conversion efficiency were found to be 0.699 and 13.5%, respectively. These values are the same degree as those of the solar cell of Comparative Example 1.

A film formed by painting a fine powder obtained by pulverizing Cd and Te singly or a CdTe compound and drying it, or a sintered film thereof obtained in the above-mentioned manner was used as the source to obtain a good quality CdTe film.

Incidentally, a similar effect is obtained by using a commercially-available CdTe as the starting material.

EXAMPLE 4

In this example, a description will be made on a method which employs the Cd and Te similar to those in Example 3 as the starting material, wherein cadmium chloride is further added to this mixture.

A muddy mixture was prepared by pulverizing the Cd and Te similar to those used in Example 3 in a wet process. Next, by drying the mixture and adding cadmium chloride and propylene glycol as the viscosity improver to this mixture, a paste was prepared. A CdTe film was formed by using the obtained paste and a solar cell was produced in a manner similar to that in Example 1.

The characteristics of the obtained solar cell were evaluated in a manner similar to those in the above-mentioned examples.

The added amounts of cadmium chloride to the sources and the conversion efficiencies of the solar cells produced by using the respective sources are shown in FIG. 6.

From FIG. 6, it is appreciated that by adding cadmium chloride in an amount of not less than 0.1 wt% for a sum of the weights of Cd and Te to it, the conversion efficiency is improved as compared with a case of not adding cadmium chloride. However, if cadmium chloride is added in an amount of more than 1.75 wt% for a sum of the weights of Cd and Te, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1 - 1.75 wt%. In particular, the improvement in the conversion efficiency is remarkable in 0.3 - 1.0 wt%, and that in the vicinity of 0.5 wt% is the most desirable.

EXAMPLE 5

In this example, a description will be made on a method with an incorporation of a Group I element or a Group V element as a dopant into the source. According to this method, carrier concentration of the CdTe film can easily be controlled. The Group I element and/or the Group V element to be added is/are incorporated into it in a state of single substance or a compound such as organometallic compounds. These elements may be used singly or plurally.

On a surface of a substrate 1 with a thickness of 1.1 mm made from a borosilicate glass, a transparent conductive film 2 with a thickness of 500 - 5,000 Å composed of tin oxide was formed by a sputtering process. Next, a CdS film 3 with a thickness of 500 - 2,000 Å was formed by a CVD process. For the formation of the CdS film 3, any other process, for instance, a solution deposition method, may be employed.

A source substrate 9 provided with the source added with an impurity was arranged on a susceptor 12a in the lower side of the equipment. On the other hand, on a susceptor 12b in the upper side, a substrate 4 was arranged with a gap of 0.1 mm to several mm to the surface of the source. After substituting the atmosphere inside the chamber 14 with argon gas or nitrogen gas, by heating the substrate 4 in a temperature range of 400 - 800°C and the source substrate 9 at a temperature higher than that of the substrate 5 and keeping them there for a certain time period, a semiconductor film was formed on the surface of the substrate 5.

In this step, although it is preferable to keep the pressure of argon gas or nitrogen gas to about 1 - 20 Torr, it is possible to form the film under 1 atm. In that case, it is preferable that the temperature difference between the substrate 4 and the source substrate 9 is not less than 50°C. In the case of forming the film under 1 atm, there is no need for making the chamber to have a pressure-resistant structure, and thus it is possible to simplify the equipment. Further, since a speeds in inlet and outlet of the substrate to and from the equipment can be made high, the productivity is greatly improved.

For the source, a paste is prepared by using the CdTe incorporated with antimony telluride at 0.01 wt%. By printing the obtained paste on a glass substrate and drying, the source substrate 9 was obtained.

By using the obtained source substrate 9, a CdTe film 5 was formed under the atmosphere of argon with a pressure of 1 Torr. In this step, by maintaining the substrate 4 in a temperature range of 400 - 650°C and the source substrate 9 at a temperature higher by 30°C than that of the substrate 4 for 2 minutes, the CdTe film 5 was formed on the CdS film 3.

Separately, a carbon paste was prepared by mixing and kneading a carbon powder with a solution of diethylene glycol monobutyl ether which dissolved polyvinyl butyral.

The obtained carbon paste was applied on the CdTe film 5 by a screen printing process and sintered after being dried, to form a carbon electrode layer 6.

By mixing a mixed powder of silver and indium, and an epoxide with an alcohol consisting mainly of terpineol, and kneading the mixture, a paste was prepared. The obtained paste was applied on the CdS film 3 and the carbon electrode layer 6 by the screen printing process, which was then dried and sintered to form a + electrode 7 and a - electrode 8.

The CdTe films 5 were also formed in a similar manner by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the CdTe paste. By using the respective CdTe films 5 thus obtained, solar cells were produced.

Further, as a comparative example, a solar cell employing a CdTe film prepared by using a CdTe paste with no additional impurity was produced as shown above and was similarly evaluated.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentration of the CdTe films are shown in Table 2.

Table 2

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
Antimony telluride	9.5×10^{14}	14.1
Phosphor	8.4×10^{14}	14.5
Arsenic	8.2×10^{14}	14.0
Antimony	8.1×10^{14}	14.2
Bismuth	8.2×10^{14}	14.1
Lithium	5.4×10^{14}	13.2
Potassium	8.1×10^{14}	14.0
Sodium	5.0×10^{14}	13.5
Rubidium	6.3×10^{14}	13.8
Copper	8.7×10^{14}	14.2
Silver	8.3×10^{14}	13.9
Gold	8.4×10^{14}	14.0
Triphenylantimony	1.2×10^{15}	14.5
Antimony octylate	1.4×10^{15}	14.6
Triphenylbismuth	1.3×10^{15}	14.4
Triphenylphosphine	1.8×10^{15}	14.7
Triphenylphosphate	1.7×10^{15}	14.7
Triphenylphosphite	1.8×10^{15}	14.6
Triallylphosphine	1.8×10^{15}	14.5
Triallylamine	1.6×10^{15}	14.2

Table 2 (continued)

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
None	3.5×10^{14}	13.0

From Table 2, it is appreciated that in the case of incorporating a Group I element or a Group V element into the source, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 6

A CdTe film was formed by the similar method as that in Example 5 except for the use of nitrogen in place of argon as the atmospheric gas. The conditions employed for forming the CdTe film 5 were that the pressure inside the chamber 14 was 1 atm, the substrate 4 was kept in a temperature range of 400 - 650°C, and the source substrate 9 was kept at a temperature higher by about 100°C than that of the substrate 4 for 10 minutes, thereby to form a CdTe film 5. Further, a solar cell was similarly produced by using the obtained CdTe film 5.

Moreover, the CdTe films 5 were also formed by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the paste, and by using the CdTe films 5 thus obtained, solar cells were produced.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentrations of the CdTe films are shown in Table 3.

As a comparative example, a relationship between the conversion efficiency of a solar cell employing a CdTe film produced by using a CdTe paste with no additional impurity, and the carrier concentration of the CdTe film is also shown in Table 3.

Table 3

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Antimony telluride	8.2×10^{14}	14.5
Phosphor	8.4×10^{14}	14.7
Arsenic	7.1×10^{14}	14.2
Antimony	7.9×10^{14}	14.4
Bismuth	6.1×10^{14}	14.1
Lithium	5.4×10^{14}	14.0
Potassium	5.2×10^{14}	14.0
Sodium	4.9×10^{14}	13.8
Rubidium	5.8×10^{14}	14.1
Copper	8.5×10^{14}	14.7
Silver	7.1×10^{14}	14.1
Gold	8.2×10^{14}	14.4
Triphenylantimony	1.0×10^{15}	14.9
Antimony octylate	1.1×10^{15}	14.9
Triphenylbismuth	9.8×10^{15}	14.8
Triphenylphosphine	1.3×10^{15}	15.1
Triphenylphosphate	1.2×10^{15}	15.0
Triphenylphosphite	1.3×10^{15}	15.1

Table 3 (continued)

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Triallylphosphine	1.3×10^{15}	15.1
Triallylamine	1.2×10^{15}	15.0
None	3.2×10^{14}	13.2

From Table 3, it is appreciated that in either case of incorporating a Group I element or a Group V element into the source material, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 7

A solution was prepared by dissolving cadmium isopropyl xanthogenate, which is an organometallic compound with a sulfur bond, in 1-methyl-2-pyrrolidone.

Separately, on a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm shown in FIG. 7(a), a stannic dioxide film 21 with a thickness of about 600 nm was formed.

The solution obtained in the above-mentioned manner was painted on the surface of the stannic dioxide film 21 and dried at 110°C, thereby to evaporate the solvent. Thereafter, it was subjected to a thermal treatment in the air at 450°C for 3 minutes, thereby to decompose the cadmium isopropyl xanthogenate and to form the CdS film 22. At this step, by adjusting the concentration of the solution thus used and the repeat times of the coating, the thickness of the CdS films 22 were set to 70 nm.

Thereafter, by a laser scribing process employing a YAG laser, a pattern for 42 cell series connection as shown by FIG. 7(b) was formed.

Subsequently, a mixed powder was obtained by mixing 1 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, with 6 g of CdTe powder with a purity of 5N.

The mixed powder thus obtained was placed on a glass substrate (Corning # 1737) with a width and a length of 35 cm so as to cover over it, thereby to form a particle layer and to obtain a source substrate. Then, the source substrate and the substrate 20 were placed so as to make the particle layer to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, CdTe films 23 with a thickness of about 6 μm were formed on the CdS films 22 as shown by FIG. 7(c). Thereafter, as shown by FIG. 7(d), etching resists 30 were applied on the surface of the substrate 20 by a screen printing process, and a thermal treatment was conducted in a dryer at 100°C for 5 minutes.

Subsequently, after subjecting the substrate 20 to an etching process for 5 minutes by immersing it in nitric acid, the substrate 20 was immersed in a 10% solution of sodium hydroxide, thereby to fall the resist layer 30 off as shown by FIG. 7(f). Thereafter, the substrate 20 was immersed in a methanol saturated solution of cadmium chloride and dried, and then subjected to a thermal treatment in the air at 400°C for 20 minutes. Thereafter, residue of the cadmium chloride was removed by ultrasonic-wave washing in pure water.

Subsequently, after forming a carbon film 24 which was added with a trace amount of copper on the surface of the substrate 20 by the screen printing process, it was dried and heated at 390°C for 30 minutes, thereby to diffuse the copper into the CdTe films 23. Thereafter, silver-indium films 25 were formed by a similar screen printing process and thermal treatment, thereby to obtain a solar cell of 42 cells series connection as shown by FIG. 7(g).

EXAMPLE 8

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 21 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 50 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate (Corning # 1737) with a width and a length of the same 35 cm, and drying it in the air at 120°C for 4 hours, a particle layer with a thickness of about 100 μm consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate 20 were placed so as to make the particle layer to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, the source in the particle layer was entirely sublimed, thereby to form a CdTe film 23 with a thickness of about 6 μm on the CdS films 22 as shown by FIG. 7(c). Thereafter, as shown by FIG. 7(d), etching resists 30 were painted on the substrate 20 by a screen printing process, and a thermal treatment was performed in a dryer at 100°C for 5 minutes.

By using the obtained CdTe films 23, a solar cell similar to that of Example 7 was produced.

Further, by using powders of carbon black, silicon carbide, silicon dioxide, silicon nitride, aluminum oxide, boron nitride, zirconia, silicon nitride, and aluminum nitride, each of which has a purity of 3N and a particle diameter of not more than 5 μm, in place of graphite, solar cells were similarly produced.

EXAMPLE 9

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 21 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate 100 (Corning # 1737) with a width and a length of the same 35 cm, and drying it in the air at 120°C for 4 hours, a particle layer consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate 20 were placed so as to make the particle layer 120 to face the CdS film, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate at 630°C under argon atmosphere with a pressure of 1 Torr for 2 minutes, and until the CdTe on the source substrate was entirely evaporated (for 5 minutes), thereby to form a CdTe film 23 with a thickness of about 6 μm on the surface of the substrate 20.

By using the obtained CdTe film 23, a solar cell similar to that of Example 7 was produced.

EXAMPLE 10

On a glass substrate 20 (Corning # 1737) with a length and a width of the same 35 cm, a stannic dioxide film 11 with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film 22 with a thickness of 70 nm was formed on the surface of the stannic dioxide film 21. Thereafter, by a laser scribing process employing a YAG laser, the CdS film 22 was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

After forming an indium oxide film on one surface of a glass substrate 200 (Corning # 1737) with a width and a length of the same 35 cm, the indium oxide film 110 was removed by etching excepting the specified portion as shown by FIG. 8. In this step, a ratio occupied by the indium oxide films 110 in the central part of the surface was made higher than that in the peripheral part. On the surface of the other side of this glass substrate 200, the above-mentioned paste was painted and dried in the air at 120°C for 4 hours, thereby to form a particle layer 220 consisting mainly of CdTe and to obtain a source substrate 230.

Then, the source substrate 230 and the substrate 20 which was similar to that used in Example 7 were placed so as to make the particle layer 220 to face the CdS film 22, with a gap of 2 mm. By heating the substrate 20 at 600°C and the source substrate 230 at 60°C under argon atmosphere with a pressure of 1 Torr, until all of the CdTe on the source substrate 230 was evaporated (for 5 minutes), thereby to form a CdTe film 23 with a thickness of about 6 μm.

By using the obtained CdTe film, a solar cell similar to that of Example 7 was produced.

EXAMPLE 11

After roughening one surface of a glass substrate 200 (Corning # 1737) with a length and a width of the same 35 cm by etching with hydrofluoric acid, a particle layer was formed on the other surface with the paste which was similar to that used in Example 10, thereby to obtain a source substrate.

By using the obtained source substrate, a CdTe film was formed, and a solar cell was produced in a manner similar to that in Example 8.

COMPARATIVE EXAMPLE 3

As a comparative example, a paste was prepared in a method similar to that in Example 8 excepting an addition of graphite. The obtained source was applied in a manner similar to that in Example 8 in an amount just required for forming the CdTe film with a thickness of 6 nm. In that case, since it does not contain graphite, the amount of the paste to coat is required to be less as compared with Example 8 so as to adjust the thickness of the coating film to be formed to about 50 μm, but it is impossible to make the amount of the source and the thickness of the coating film uniform. Therefore, by applying the minimum amount for uniformly painting, a source substrate was produced. By using the source substrate, a CdTe film was formed in a manner similar to that in Example 8. In this step, although the thickness of the coating film was made uniform, the dispersion in the thickness of the obtained CdTe film was larger than that of the CdTe film obtained in Example 8. By using this CdTe film, a solar cell was produced in a manner similar to that of Example 8. This was named as the solar cell of Comparative Example 3.

On the solar cells of Example 7 - 11 and of Comparative Example 3, measurements of the open circuit voltage (V_{OC}) and fill factor (FF) which is a standard for the decision of good/bad of the output characteristic were conducted under condition of AM; 1.5, 100 mW/cm^2. The results thereof are shown in Table 4.

Table 4

	Additive	V_{OC}(V)	FF(%)	η(%)
Example 7	Graphite	31.8	57	9.6
Example 8	Carbon black	33.0	61	10.1
	Graphite	33.6	64	10.6
	Silicon dioxide	32.7	59	9.8
	Aluminum oxide	33.3	62	10.2
	Zirconium oxide	31.0	58	9.7
	Boron nitride	32.4	60	10.0
	Silicon nitride	32.6	60	9.9
	Aluminum nitride	32.0	57	9.7
	Silicon carbide	33.0	60	10.0
Example 9	Graphite	33.4	62	10.3
Example 10	Graphite	33.2	63	10.4
Example 11	Graphite	33.6	64	10.5
Comparative Example 3	None	24.2	52	6.8

From Table 4, it is appreciated that the solar cells of Examples 7 - 11 employing the CdTe films which have been formed by using, as the source, a CdTe material added with a material which remains after the heating are excellent in every respect of the characteristics, as compared with the solar cell of Comparative Example 3. It is believed that this is due to the fact that by adding these materials, thermal damage of the CdS film attributable to the radiation heat can be prevented.

In particular, in the case of using graphite, carbon or silicon carbide in Example 8, or in Examples 9 - 11, by using the coating film of an amount just required for the film forming of one time as the source, it is possible to suppress an occurrence of an excessive heating of the substrate for thin-film forming, directly by the radiation heat, after the completion of the vaporization of the source. Tellurium, cadmium and cadmium telluride have a low absorption rate for infrared ray and a low heat conductivity. Therefore, if the source consisting of these semiconductor material is thick, since the temperature of the source is hardly elevated at the heating, the film forming speed is low, the infrared ray transmitted through the source is incident on the CdS film which has previously been formed on the substrate. Since the CdS which is typical as the n-type semiconductor for the solar cells has a very high absorption rate for infrared ray, it is heated by the incident infrared ray and made to be liable to vaporize. Therefore, when the CdS film is made thinner than the suitable thickness and when the vaporization of the CdS film further proceeds, pinholes are produced, thereby to invite micro-short-circuitings. For that reason, by using the infrared-absorption materials being mixed with the source as in these examples, the excessive temperature rise of the substrate is suppressed. Therefore, the mutual diffusion at a joint between the CdS film and the CdTe film is suppressed, thereby to obtain a solar cell which has a high open-circuit voltage and fill factor.

In addition, according to the method of the examples, since the source can be used exhaustively, the utilization rate of the material can greatly be improved. Although the CdTe film of good quality can also be obtained in Example 7 wherein a mixture of the source and the additive is used by filling it in a container as described above, it is limited to the cases where the times of repeatedly using the same source for forming the CdTe film are small. That is, according to this method, the change in the source cannot be avoided if the source is used repeatedly. Therefore, by using the coating film as the source as described in Examples 1 - 9, it is possible to obtain the CdTe film of good quality more effectively.

Further, measurements were made on the thickness distributions in the CdTe film formed in accordance with Example 8 and the CdTe film formed in accordance with Comparative Example 3. The results thereof are shown in Table 5. In this table, distance indicates a distance from the central part of the substrate in the diagonal direction.

Table 5

Distance (mm)	Example 8 (μm)	Comparative Example 3 (μm)
0	6.0	3.0
25	6.2	4.9
50	6.3	6.0
75	6.3	7.0
100	6.4	8.5
125	6.4	8.8
150	6.3	9.5
175	6.4	10.0
200	6.5	10.2
212	6.5	10.4

Moreover, the solar cells which employ the CdTe film obtained in accordance with Example 8 and the solar cells obtained in accordance with Comparative Example 3 were produced in trial, for each five lots, each of which contains 10 pieces, and the measurements were made on the film thickness of CdTe and the solar cell characteristics. The results thereof are shown in Table 6.

Table 6

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
1	6.5	6.8	6.4	6.7	6.0	6.0	8.5	5.0	9.9	6.2
	10.0	9.8	9.8	10.5	9.4	8.0	7.2	8.2	7.5	8.1
2	6.4	6.6	6.5	6.9	6.2	7.0	9.0	5.9	10.0	6.9
	9.9	9.9	10.0	9.5	9.1	8.5	6.9	8.8	7.3	8.2
3	6.7	6.7	6.3	6.2	6.8	6.5	7.6	6.5	9.1	6.5
	10.2	10.0	10.1	10.1	9.9	7.9	8.0	7.9	7.0	7.5
4	6.3	6.9	6.5	6.1	6.9	7.2	9.5	6.1	9.5	6.9
	10.1	9.8	9.9	9.7	9.6	6.9	7.0	5.9	6.9	8.5
5	6.6	6.7	6.7	6.9	6.2	5.3	8.7	5.1	8.7	6.8
	10.2	9.9	9.7	9.8	10.4	7.6	6.8	7.1	7.2	7.4
6	6.5	6.5	6.4	6.7	6.0	5.9	7.1	4.0	8.8	6.6
	9.9	10.1	9.5	9.7	10.2	9.2	5.9	6.9	6.1	7.8

Table 6 (continued)

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
7	6.7	6.9	6.5	6.5	6.9	7.8	6.6	4.9	7.9	6.0
	10.3	9.9	10.1	10.2	10.0	8.4	9.0	7.3	6.9	7.7
8	6.3	6.8	6.6	6.8	6.4	6.3	8.7	6.1	7.8	6.5
	10.0	10.0	9.8	10.5	9.3	8.6	6.4	7.5	7.0	6.3
9	6.6	6.7	6.7	6.7	6.8	6.9	7.5	5.9	10.0	6.8
	9.9	9.7	9.9	10.4	9.7	9.0	8.8	7.7	6.1	5.2
10	6.4	6.9	6.8	6.1	6.3	8.0	6.2	9.0	9.5	6.9
	10.3	9.8	9.6	10.1	9.5	7.1	6.5	8.1	6.8	8.1
Upper column: Thickness of CdTe film at central part of substrate (μm). Lower column: Conversion efficiency (%).										

The difference between the CdTe film of Example 8 and the CdTe film of Comparative Example 3 is only a presence/absence of the addition of graphite to the pastes. That is, as clearly shown from Table 5, by forming with a mixture of the source and the additive, a CdTe film with a stable thickness can be obtained.

Further, it is also appreciated from Table 6 that the CdTe film of Example 8 has a smaller dispersion in thickness within one lot and between the lots as compared with the CdTe film of Comparative Example 3. For that reason, according to Example 8, it is possible to stably obtain a solar cell of more excellent characteristics as compared with Comparative example 3.

As previously described, by using a source mixed with an additive, it is possible to suppress mutual diffusion at a joint between the CdS and the CdTe resulting from an excessive heating by a radiation, thereby to stably obtain a CdTe film of good quality.

As the additive, any stable substance which does not decompose or cause a chemical reaction on the supporting member at the time of heating can be used.

Further, by using a substrate which has an uneven structure on the surface opposite to the surface on which a particle layer is formed as in Example 11, it is possible to absorb the infrared ray by the uneven surface and a similar effect can be obtained.

On the other hand, according to Example 10, by lowering the proportion occupied by a transparent conductive film at the peripheral part of the substrate as compared with that of the central part, it is possible to make the temperature difference of the surface of the substrate small, by utilizing an action of the transparent conductive film to suppress the radiation of the infrared ray. According to this method, the dispersion in the thickness of the CdTe film formed on the surface of the substrate can be made small. A similar effect can also be obtained by directly piling a separate substrate which has a similar structure on a normal source substrate.

Further, in the above-mentioned examples, although CdS is employed as the n-type semiconductor for a solar cell, a similar effect can also be obtained in a case of using CdZnS. For forming these n-type semiconductors, a known method such as a process of thermally decomposing an organometallic compound, a liquid phase film-forming process, a close-spaced sublimation process, a vapor-deposition process, a sputtering process and the like can be employed.

As the transparent conductive film, indium tin oxide or zinc oxide can also be employed in place of tin oxide. For forming the transparent conductive film, a sputtering process, a chemical vapor-phase growing process, a vapor-deposition process or the like can be employed.

In the preciously-mentioned examples, although the glass substrate which has the transparent conductive film and the CdS film on the surface is used as a substrate for forming the CdTe, it is also possible to use, in place of this, any of semiconductor materials of cadmium zinc sulfide, gallium arsenide, indium gallium arsenide, indium gallium phosphor arsenide, zinc selenide, indium selenide, silicon, germanium, indium copper selenide, indium gallium copper selenide, gallium nitride and the like, and metals of iron, nickel, molybdenum and the like, as the substrate. As the substrate, a ceramic material can also be used in addition to the glass.

Further, although a description has exemplary been made on the method for forming the CdTe film, it can also be applied to a thin film formation of other semiconductors such as CdS, cadmium zinc sulfide, zinc selenide, indium selenide, indium copper selenide, indium gallium copper selenide, and the like.

As the viscosity improver used in preparing the paste, such another material as ethylene glycol, methyl cellulose or the like can also be employed, in addition to propylene glycol which was used in the above-mentioned examples.

POSSIBILITY OF INDUSTRIAL UTILIZATION

According to the present invention, it is possible to form a CdTe film of good quality in an inexpensive efficiently. The present invention can be embodied in the manufacture of semiconductor device such as a solar cell, an infrared ray receiving device, and an integrated circuit.

Claims

1. A method for preparing a CdTe film comprising:

   a step of applying a paste containing a material for CdTe semiconductor on a supporting member, thereby to form a coating film containing said material for CdTe semiconductor on the surface of said supporting member,
   a step of closely arranging said supporting member and a substrate on which a CdTe film is to be formed, to make said coating film to face the surface of said substrate, and
   a step of forming a CdTe film on said substrate, by heating said coating film and said substrate, and causing said material for the semiconductor in said coating film to evaporate.

2. The method for preparing a CdTe film in accordance with claim 1, wherein said semiconductor material is a mixture of a cadmium powder and a tellurium powder.

3. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains cadmium chloride.

4. The method for preparing a CdTe film in accordance with claim 3, wherein the added amount of said cadmium chloride is 0.1 - 1.75 wt% to said semiconductor material.

5. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains a Group I element or a Group V element incorporated therein.

6. The method for preparing the CdTe film in accordance with claim 5, wherein said Group I element is at least one member selected from the group consisting of lithium, potassium, sodium, rubidium, copper, silver and gold.

7. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is at least one member selected from the group consisting of arsenic, antimony, bismuth, phosphor and nitrogen.

8. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is antimony, and is contained in said paste in a state of antimony telluride.

9. The method for preparing a CdTe film in accordance with claim 5, wherein said Group V element is contained in said paste in a state of at least one member selected from the group consisting of triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine.

10. The method for preparing a CdTe film in accordance with claim 1, wherein said paste contains an additive of powder state which is stable in composition at the heating step.

11. The method for preparing a CdTe film in accordance with claim 10, wherein said additive is at least one member selected from the group consisting of carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride, and aluminum nitride.

12. The method for preparing a CdTe film in accordance with claim 1, wherein at the step of applying said paste, the painted amount of the paste in the peripheral part of said substrate is made to be larger than the painted amount of the paste in the central part of said substrate.

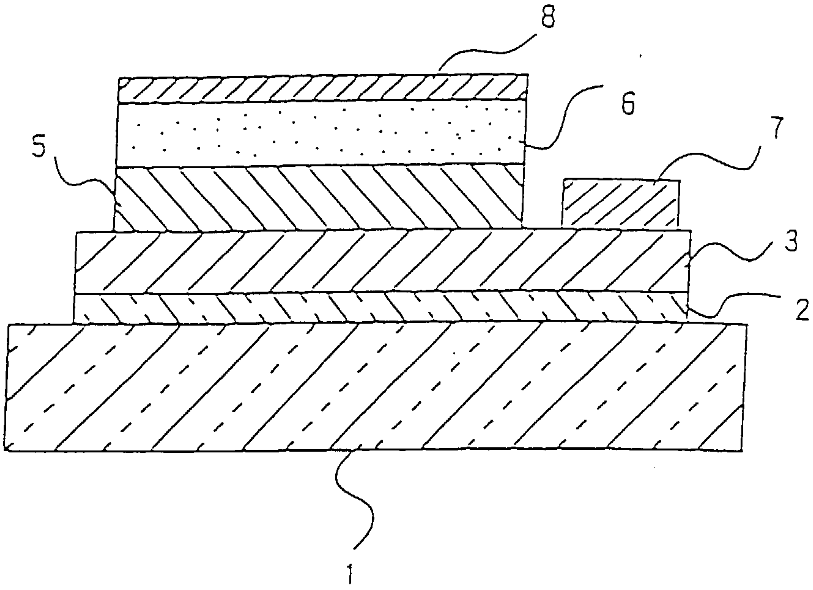
13. The method for preparing a CdTe film in accordance with claim 1, wherein said supporting member is at least one member selected from the group consisting of glass, ceramic material and carbon.

14. The method for preparing a CdTe film in accordance with claim 1, wherein said supporting member is glass having a conductive oxide film on the surface thereof.

15. The method for preparing a CdTe film in accordance with claim 1, wherein one surface of said supporting member that is opposite to the surface on which said paste is painted is rough.

16. A solar cell comprising: an insulating and transparent substrate, a transparent conductive film formed on said substrate, an n-type semiconductor film formed on said transparent conductive film, a p-type semiconductor layer formed on said n-type semiconductor film as a light absorbing layer, a current collector formed on said p-type semiconductor layer, a + side electrode electrically connected to said current collector, and a - side electrode electrically connected to said n-type semiconductor layer, wherein said p-type semiconductor film is a CdTe film formed by the method in accordance with claim 1.

F I G. 1



F I G. 2

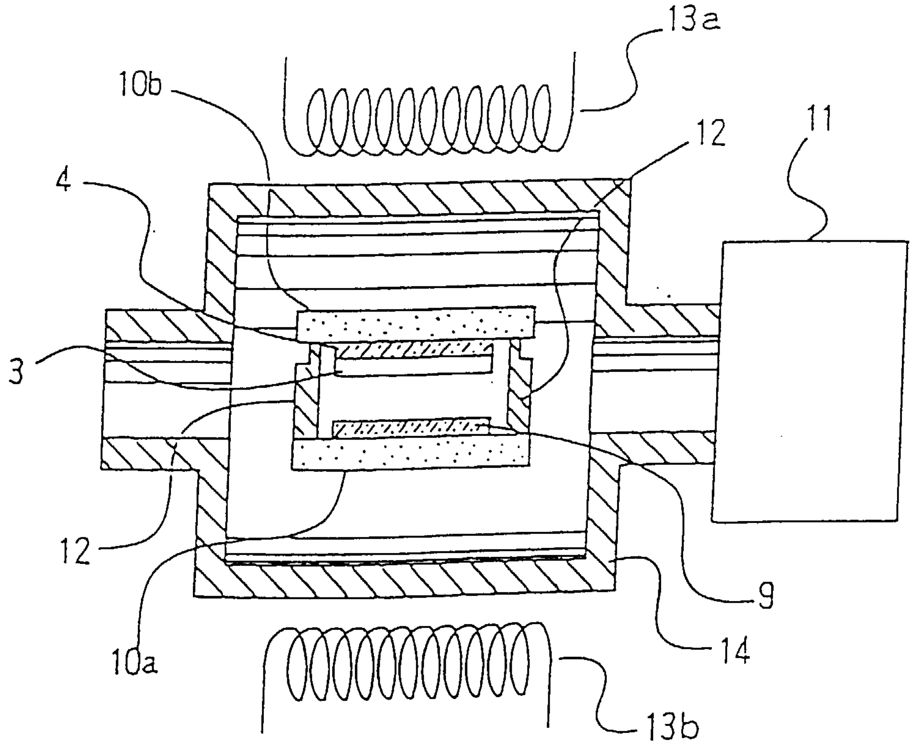


FIG. 3

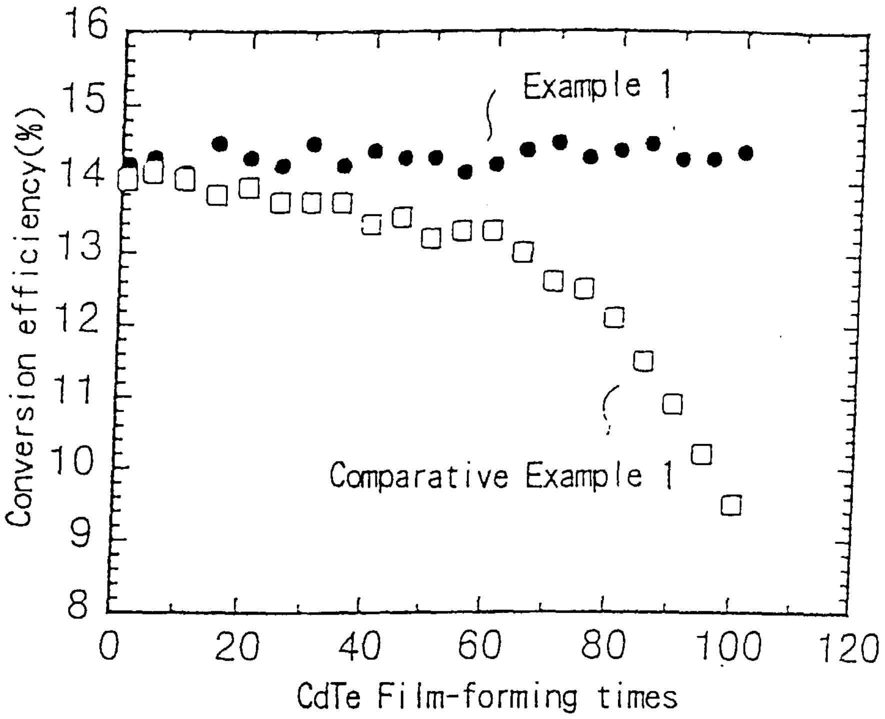

16
15
14
13
12
11
10
9
8
Conversion efficiency(%)
0
20
40
60
80
100
120
CdTe Film-forming times
Example 1
Comparative Example 1

FIG. 4

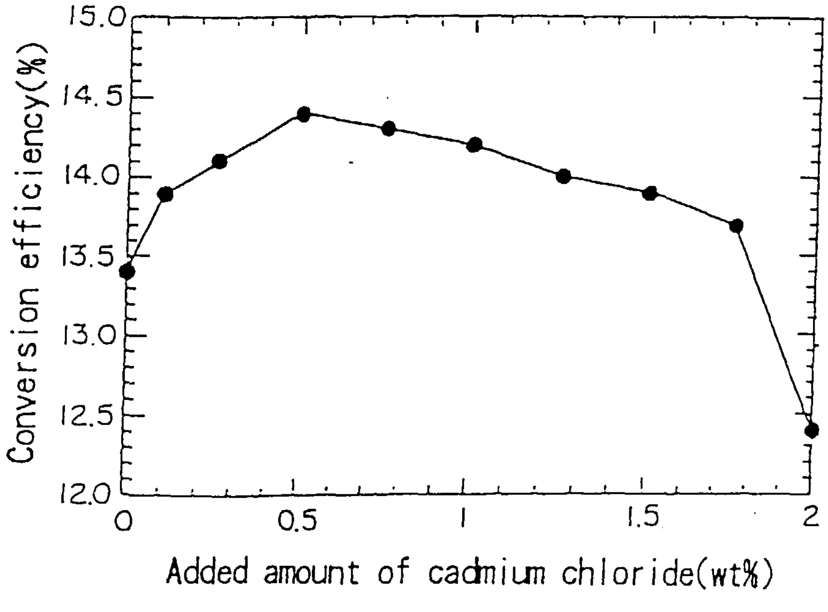

15.0
14.5
14.0
13.5
13.0
12.5
12.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 5

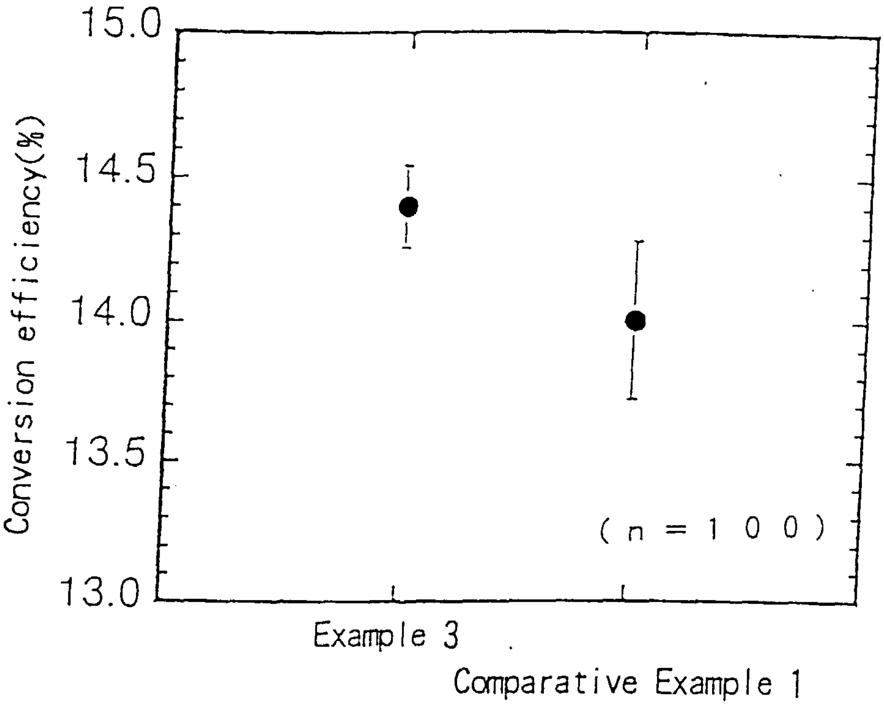

15.0
14.5
14.0
13.5
13.0
Conversion efficiency(%)
(n = 100)
Example 3
Comparative Example 1

FIG. 6

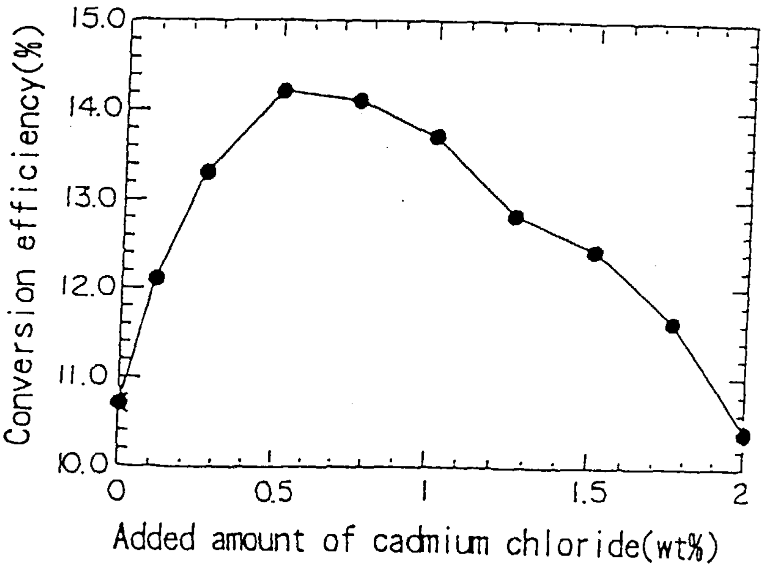

15.0
14.0
13.0
12.0
11.0
10.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 7

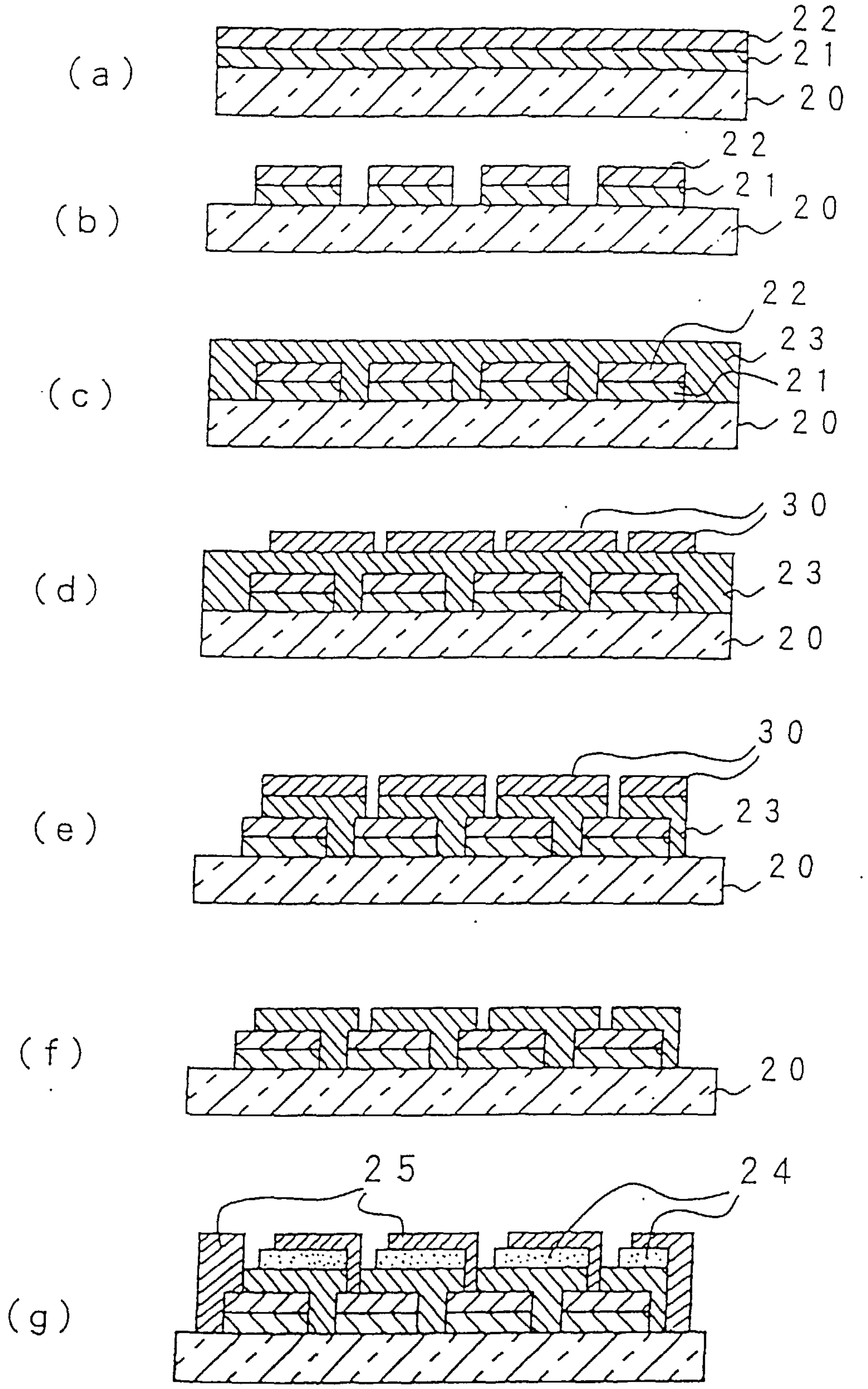
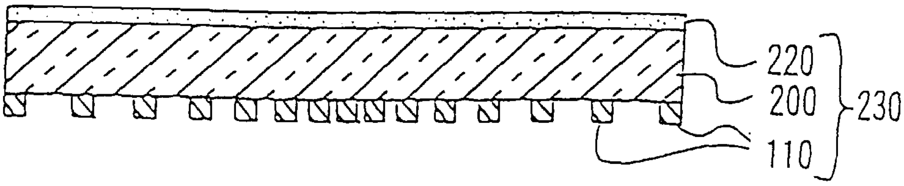


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/01791

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl^6 H01L31/04, H01L21/363

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl^6 H01L31/04, H01L21/363

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP, A1, 6-45626 (Batelle-Institut), February 18, 1994 (18. 02. 94) & EP, A2, 535,522 & DE, A1, 4,132,882 & US, A, 5,304,499	16 1 - 15
Y A	JP, A1, 7-94769 (Matsushita Electric Industrial Co., Ltd.), April 7, 1995 (07. 04. 95)	16 1 - 15
Y A	JP, A1, 7-147421 (Matsushita Electric Industrial Co., Ltd.), June 6, 1995 (06. 06. 95)	16 1 - 15
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- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search July 22, 1997 (22. 07. 97)	Date of mailing of the international search report July 29, 1997 (29. 07. 97)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/01791

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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(54) A PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

VERFAHREN ZUR GROSSTECHNISCHEN HERSTELLUNG VON CDTE/CDS DÜNNSCHICHT-SOLARZELLEN

PROCEDE PERMETTANT LA PRODUCTION A GRANDE ECHELLE DE PHOTOPILES EN COUCHES MINCES DE CDTE/CDS

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- **ROMEO A ET AL: "Recrystallization in CdTe/CdS" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 361-362, no. 1, February 2000 (2000-02), pages 420-425, XP004187511 ISSN: 0040-6090**
- **ROMEO N ET AL: "A highly efficient and stable CdTe/CdS thin film solar cell" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 58, no. 2, June 1999 (1999-06), pages 209-218, XP004177956 ISSN: 0927-0248 cited in the application**

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Description

Field of the invention

[0001] The present invention relates to the field of the solar cells technology and more particularly concerns a process for the large-scale production of CdTe/CdS thin film solar cells.

Background art of the invention

[0002] As is known, a typical configuration of a CdTe/CdS solar cell has a film sequence of the multilayer arrangement comprising a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film representing the n-conductor, a CdTe film representing the p-conductor and a metallic back-contact. A solar cell with a layer arrangement and structure of this type is disclosed, for example, in US 5304499.

[0003] The commercial float glass may be used as a transparent substrate, but, in spite of its low cost, special glasses are often preferred to avoid drawbacks of the float glass, in particular Na diffusion into TCO film.

[0004] The most common TCO is In_2O_3 containing 10% of Sn (ITO). This material has a very low resistivity on the order of $3x10^{-4}$ Ωcm and high transparency (>85%) in the visible spectrum. However, this material is made by sputtering and the ITO target after several runs forms some noodles which contain an In excess and a discharge between noodles can happen during sputtering which can damage the film. Another material which is commonly used is fluorine doped SnO_2 which however exhibits a higher resistivity close to 10^{-3} Ωcm and as a consequence a 1 μm thick layer is needed in order for the sheet resistance to be around 10 $\Omega/_{square}$. A high TCO thickness decreases the transparency and then the photocurrent of the solar cell. Finally a novel material, namely Cd_2SnO_4 has been developed by the NREL group (X. Wu et al., Thin Solid Films, 286 (1996) 274-276)). Also this material has some drawbacks since the target is made up of a mixture of CdO and SnO_2 and, being CdO highly hygroscopic, the stability of the target may result to be unsatisfactory.

[0005] The CdS film is deposited by sputtering or Close-Spaced Sublimation (CSS) from CdS granulate material. This last technique allows the preparation of thin films at a substrate temperature much higher than that used in simple vacuum evaporation or sputtering, because substrate and evaporation source are put very close to each other at a distance of 2-6 mm and the deposition is done in the presence of an inert gas such as Ar, He or N_2 at a pressure of 10^{-1}-100 mbar. A higher substrate temperature allows the growth of a better crystalline quality material. An important characteristic of the close-spaced sublimation is a very high growth rate up to 10 μm/min, which is suitable for large-scale production.

[0006] CdTe film is deposited on top of CdS film by close-spaced sublimation (CSS) at a substrate temperature of 480-520°C. CdTe granulate is generally used as a source of CdTe which is vaporised from an open crucible.

[0007] An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$- Most research groups use to carry out this step by depositing on top of CdTe a layer of $CdCl_2$ by simple evaporation or by dipping CdTe in a methanol solution containing $CdCl_2$ and then anneal the material in air at 400°C for 15-20 min. It is generally believed that the $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of small grains and by removing several defects in the material.

[0008] After $CdCl_2$ treatment, CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ have to be removed in order to make a good back contact onto CdTe. Besides it is believed that, since etching produces a Te-rich surface, the formation of an ohmic contact when a metal is deposited on top of CdTe is facilitated.

[0009] The electric back contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g. in graphite contacts, which, upon annealing, can diffuse in the CdTe film. The use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell has been disclosed by the same applicants (N. Romeo et al., Solar Energy Materials & Solar Cells, 58 (1999), 209-218)

[0010] Industrial interest towards thin films solar cells is increased in recent years also in view of the high conversion efficiency reached so far. A record 16,5% conversion efficiency has been recently reported (see X.Wu et al., 17th European Photovoltaic Solar Energy Conversion Conference, Munich, Germany, 22-26 October 2001, II, 995-1000). Therefore several efforts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells.

[0011] A state-of-the-art report concerning this issue may be found in D. Bonnet, Thin Solid Films 361-362 (2000), 547-552. However, a number of problems still hinder the achievement of this result, in particular concerning some crucial steps which affect either stability and efficiency of CdTe/CdS thin film solar cells or their costs.

[0012] A major problem of the known processes is the etching step to which the CdTe surface must be submitted to remove CdO or $CdTeO_3$ oxides formed thereon. Since etching requires the immersion of substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for a continuous operation presently does not exist. Another significant problem which negatively affects the stability of the TCO films, as well as the cost of the final product are the drawbacks presently encountered with the use of known TCOs, as previously mentioned. In addition to these drawbacks, known TCOs require the use of special glasses, such as borosilicate glass, to avoid the problem of Na diffusion, occurring if a soda-lime glass is used, which would damage the film.

[0013] A further problem concerns the source from which the CdS film and the CdTe film are produced by close-spaced sublimation. When small pieces of these materials containing dust are used as a sublimation source, due to a different thermal contact, some microparticles can be overheated and then split on to the substrate together with the vapour. In order to avoid this inconvenience, complicated metallic masks are used in some cases, which make a continuous operation problematic.

Object and Summary of the invention

[0014] It is the main object of the present invention to provide a process suitable for a large-scale production of stable and efficient CdTe/CdS thin film solar cells on a low cost substrate.

[0015] A particular object of the present invention is to provide a process of the above mentioned type in which the treatment of the CdTe film with $CdCl_2$ is conducted in such a way as not to require an etching treatment to remove the oxides possibly formed on the CdTe film.

[0016] A further object of the present invention is to provide a process of tne above mentioned type, in which the deposition of the TCO film is conducted in such a way that a film of very low resistivity can be deposited without formation of any metal noodles on the target and allowing the use of a inexpensive substrate.

[0017] Still another object of the invention is to provide a process of the above-mentioned type, which allows the formation of CdS and CdTe films completely free of dust.

[0018] A further object of the present invention is to provide a stable, efficient and relatively low-cost CdTe/CdS thin film solar cell.

[0019] The above object are achieved with the process for the large scale production of CdTe/CdS thin film solar cells, the main features of which are set forth in claim 1.

[0020] According to an important aspect of the invention, the treatment of the CdTe film with $CdCl_2$ is carried out by first forming a 100-200 nm thick layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at 380-420°C and 300-1000 mbar under inert gas atmosphere; and finally removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420°C, whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. In this way, there is no need for the etching treatment of the CdTe film and the process can be conducted in a continuous way.

[0021] According to another aspect of the invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing 1-3 vol.% hydrogen and a gaseous fluoroalkyle compound, in particular CHF_3. In this way the TCO is doped whit fluorine

[0022] According to another important aspect of the invention, as a source material for the formation of the CdS and the CdTe films by sputtering or close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

[0023] Further features of the process according to the invention are set forth in the dependent claims.

Brief description of the drawings

[0024] Further features and advantages of the process for large-scale production of CdTe/CdS thin film solar cells according to the present invention will be apparent from the following description of a preferred embodiment made with reference to the attached drawings, wherein:

- Figure 1 is a schematic representation of the film sequence of the CdTe/CdS thin film solar cells according to the invention;
- Figure 2 is a schematic diagram of the process according to the invention.

Description of an embodiment of the invention

[0025] With reference to the figures, the CdTe/CdS solar cells produced with the process according to the invention comprise five layers deposited in a sequence on a transparent base layer or substrate and consisting of a 300-500 nm thick layer of a transparent conducting oxide (TCO), a 80-200 nm thick layer of CdS deposited on top of the TCO layer, a 4-12 μm thick layer of CdTe on top of the CdS layer and a back contact layer formed by at least 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate consists of soda-lime glass and the transparent conducting oxide is fluorine-doped (In_2O_3:F).

[0026] TCO layer consists of In_2O_3, which is doped with fluorine during the growth. The In_2O_3 target, differently from ITO, does not form any noodle. A very low resistivity is obtained by introducing in the sputtering chamber a small amount of fluorine in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a Ar+H_2 mixture, in which H_2 is 20% in respect to Ar. A typical example is a 500 nm film of In_2O_3 deposited with a deposition rate higher than 10 Å/sec at a substrate temperature of 500°C, with an Ar flow-rate of 200 sccm, a CHF_3 flow-rate of 5 sccm and an Ar+H_2 flow-rate of 20 sccm. In this way, the reactive sputtering gas is composed by Ar containing 2.5 viol.% of CHF_3 and 1.8 viol.% of H_2. This film exhibits a sheet resistance of 5 $\Omega/_{\text{square}}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than 85% in the wavelength range of 400-800 nm. Another characteristic of this film is its good stability and the ability to stop Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable even if heated up to 180°C when illuminated by "ten suns" for several hours.

[0027] After deposition of the CdS film and CdTe film in the known way by sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ in the following way.

[0028] 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. An annealing of 15-20 min is done at 400°C in a vacuum chamber in which 500 mbar of Ar are introduced. After the annealing the chamber is evacuated keeping the substrate at 400°C for 5 min. and, since $CdCl_2$ has a high vapour pressure at 400°C, any residual $CdCl_2$ re-evaporates from the CdTe surface.

[0029] CdO or $CdTeO_3$ are not formed since the annealing is conducted in an inert atmosphere, which does not contain O_2.

[0030] According to the present invention a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing on top of CdTe film a thin layer of a highly conducting p-type semiconductors such as Sb_2Te_3 or As_2Te_3. A good non-rectifying contact is obtained on a clean CdTe surface if at least 100 nm thick layer of Sb_2Te_3 or As_2Te_3 is deposited by sputtering at a substrate temperature respectively of 250-300°C and 200-250°C. Sb_2Te_3 grows naturally p-type with a resistivity of 10^{-4} Ωcm, while As_2Te_3 grows p-type with a resistivity of 10^{-3} Ωcm. The contact procedure is completed by covering the low resistivity p-type semiconductor with at least 100 nm of Mo, as common practice in the art. A thin layer of Mo is needed in order to have a low sheet-resistance on the back-contact.

[0031] As a source for the CdS and CdTe materials used to form the respective layers by sputtering or CSS a granulate material can be used, as common practice in this field. However, in view of the drawbacks mentioned above when operating in this way, according to a particularly preferred aspect of the invention a new sublimation source can be used which consists of a compact block obtained by melting and solidifying the material in an oven able to sustain a temperature higher than the melting temperature of the material. The procedure to prepare the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3) , which is a low melting point material (450°C) and exhibits a very low vapour pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over CdS and covers CdS completely upon cooling. In this way, CdS covered by B_2O_3, if it is put into an oven containing an inert gas at pressure higher than 50 atm, does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of 1750°C, the oven is heated up to a temperature of 1800°C or more and then cooled down to room temperature. In this way, a unique compact block of CdS is obtained which results to be particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared with this type of source resulted to be very smooth and completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically 100 nm thick. The substrate temperature is kept at 200-300°C when CdS is prepared by sputtering and at 480-520°C when it is prepared by close-spaced-sublimation. The sputtered CdS layer needs an annealing at 500°C in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a high efficiency. In the case CdS is prepared by close-spaced sublimation, O_2 is introduced in the sublimation chamber during the deposition. The role of O_2 is not known, but it is presumed to passivate the CdS grain boundaries.

[0032] In a preferred embodiment of the invention, the CdTe source too is a compact block obtained by melting and solidifying pieces of CdTe in an oven under high pressure as described previously. Since CdTe melts at 1120°C, the oven needs to be heated up to 1200°C in order to have a complete melting of the CdTe pieces. CdTe films are deposited on top of CdS by close-spaced sublimation at a substrate temperature of 480-520°C. Deposition rates during the CdTe growth are typically 4 μm/min. In this way 8 μm of CdTe are deposited in 2 min.

[0033] By following the procedure described above several solar cells have been prepared by using as a substrate a 1 inch square low-cost soda-lime glass.

[0034] A typical area of these cells is 1 cm^2. The finished cells are generally put under 10-20 suns for several hours at a temperature of 180°C in the open-circuit-voltage (V_{oc}) conditions. No degradation has been notified but rather a 20% or more increase in the efficiency has been found.

[0035] The efficiency of these cells are in the range 12%-14% with open-circuit-voltages (V_{oc}) larger than 800 mV, short-circuit-currents (J_{sc}) of 22-25 mA/cm^2 and fill-factors (ff) ranging from 0.6 to 0.66.

Example

[0036] A cell exhibiting a 14% efficiency has been prepared in the following way: a soda-lime glass has been covered by 500nm of In_2O_3:F (fluorine-doped) deposited at 500°C substrate temperature as described above. 100 nm of CdS have been deposited by sputtering at 300°C substrate temperature and annealed for 15 min at 500°C in 500mbar of Ar containing 20% of 0_2. 8 μm of CdTe have been deposited on top of CdS by CSS at a substrate temperature of 500°C. Both CdS and CdTe films are produced from a compact block source as described above. A treatment with 150 nm of $CdCl_2$ has been done in an Ar atmosphere as described above. Finally a back contact has been created, without any etching, by depositing in sequence by sputtering 150 nm of Sb_2Te_3 and 150 nm of Mo.

[0037] After one hour under 10 suns at a temperature of 180°C in open-circuit conditions the solar cell prepared in this way exhibited the following parameters:

V_{oc}	852 mv
J_{sc}	25 mA/cm^2
ff	0.66
efficiency	14 %

[0038] The techniques used in this process such as sputtering and close-spaced sublimation are both fast, reproducible and easily scalable.

[0039] Sputtering systems capable to cover 1x0.5 m^2 area glass are already commercial, while close-spaced sublimation , which at a laboratory scale can cover easily 20x20 cm^2 area glass, does not give any problem in being scaled up to 1x0.5 m^2. An in-line process can work well if a large area glass is made to move slowly over the different sources namely TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3 and Mo. In order to make a series connection between the single cells the in-line system should also contain three laser scribing processes, the first after the TCO deposition, the second one before the back-contact deposition and the third one at the end of the process. An important part of the process according to the present invention is that no use is made of acids or liquids and, as a consequence, the process can operate on a continuous basis without the interruption which is needed to make the etching in acid or in a Br-methanol solution.

Claims

1. Process for the large-scale production of CdTe/CdS thin film solar cells, said films being deposited as a sequence on a transparent substrate, comprising the steps of:

   - depositing a film of a transparent conductive oxide (TCO) on said substrate;
   - depositing a film of CdS on said TCO film;
   - depositing a film of CdTe on said CdS film;
   - treating said CdTe film with CdCl2;
   - depositing a back-contact film on said treated CdTe film;

   the process being **characterised in that** the treatment of the CdTe film with $CdCl_2$ comprises the following steps:

   - forming a layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature;
   - annealing said $CdCl_2$ layer in a vacuum chamber at 380-420°C and 300-1000 mbar under inert gas atmosphere;
   - removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420°C whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process according to claim 1, wherein said $CdCl_2$ layer is 100-200 nm thick

3. The process according to claims 1 or 2, wherein the annealing of the $CdCl_2$ layer is carried out for 15-20 min.

4. The process according to any one of the previous claims, wherein the inert gas is Ar.

5. The process according to any one of the previous claims, wherein wherein the back-contact film is formed by a Sb_2Te_3 layer covered by a layer of Mo.

6. The process according to claim 5, wherein said Sb_2Te_3 layer is formed by sputtering at 250-300°C.

7. The process according to any one of the previous claims, wherein the back-contact film is formed by a As_2Te_3 layer covered by a layer of Mo.

8. The process according to claim 7, wherein said As_2Te_3 layer is formed by sputtering at 200-250°C

9. The process according to any of the previous claims, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process according to claim 9, wherein the TCO layer is formed by sputtering in an inert gas atmosphere containing hydrogen and a gaseous fluoroalkyle compound.

11. The process according to claim 10, wherein a mixture of Ar and hydrogen is used, in which hydrogen is comprised between 1 and 3% vol.% and the flouoroalkyle compound is CHF_3 .

12. The process according to any one of the previous claims, wherein, as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

13. The process according to claim 12, wherein said compact block CdS (or CdTe) material is formed by covering with boron oxide pieces of CdS (or CdTe) material, heating the covered material to a temperature higher than its melting point under inert gas atmosphere and a pressure higher than 50 atm and then cooling down to room temperature, whereby the material is solidified in a compact block form.

14. The process according to any one of the previous claims, wherein said transparent substrate is soda-lime glass.

Patentansprüche

1. Verfahren zur großtechnischen Herstellung von Cd-

Te/CdS-Dünnschicht-Solarzellen, welche Schichten als Abfolge auf einem transparenten Substrat aufgetragen werden, enthaltend die Schritte:

- Auftragen einer Schicht eines transparenten leitenden Oxids (TCO) auf dem Substrat;
- Auftragen einer Schicht von CDs auf der TCO-Schicht;
- Auftragen einer Schicht von CdTe auf der CD-Schicht;
- Behandeln der CdTe-Schicht mit $CdCl_2$;
- Auftragen einer Rückwärtskontaktschicht auf der behandelten CdTe-Schicht in Verbindung;

welches Verfahren **dadurch gekennzeichnet ist, dass** die Behandlung der CdTe-Schicht mit $CdCl_2$ die folgenden Schritte enthält:

- Ausbilden einer Schicht von $CdCl_2$ auf der CdTe-Schicht durch Aufdampfen, während das Substrat auf Raumtemperatur gehalten wird;
- Annealen der $CdCl_2$-Schicht in einer Vakuumkammer bei 380 - 420°C und 300 - 1000 mbar in einer Inertgasatmosphäre;
- Entfernen des Inertgases aus der Kammer, um eine Vakuumbedingung zu erzeugen, während das Substrat auf einer Temperatur von 350 - 420 °C gehalten wird, wodurch jegliches verbleibendes $CdCl_2$ von CdTe-Schichtoberfläche verdampft wird.

2. Verfahren nach Anspruch 1, wobei die $CdCl_2$-Schicht 100 - 200 Nanometer dick ist.

3. Verfahren nach Anspruch 1 oder 2, wobei das Annealen der $CdCl_2$-Schicht für 15 - 20 Minuten ausgeführt wird.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Inertgas Ar ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Rückwärtskontaktschicht durch eine Sb_2Te_3-Schicht gebildet wird, die von einer Schicht aus MO bedeckt ist.

6. Verfahren nach Anspruch 5, wobei die Sb_2Te_3-Schicht durch Sputtern bei 250 - 300°C gebildet wird.

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Rückwärtskontaktschicht durch eine As_2Te_3-Schicht gebildet wird, die von einer Schicht aus MO bedeckt ist.

8. Verfahren nach Anspruch 7, wobei die As_2Te_3-Schicht durch Sputtern bei 200 - 250 °C gebildet wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, wobei das transparente leitende Oxid In_2O_3 dotiert mit Fluor ist.

10. Verfahren nach Anspruch 9, wobei die TCO-Schicht durch Sputtern in einer Inertgasatmosphäre gebildet wird, die Wasserstoff und einen gasförmigen Fluoroalkyl-Bestandteil enthält.

11. Verfahren nach Anspruch 10, wobei eine Mischung aus Ar und Wasserstoff benutzt wird, worin Wasserstoff zwischen 1 und 3 Vol.-% enthalten ist, und der das Fluoroalkyl-Bestandteil CHF_3 ist.

12. Verfahren nach einem der vorhergehenden Ansprüche, wobei als Ausgangsstoff für die Bildung der CdS- und der CdTe-Schichten durch closed-space Sublimation ein CdS- oder entsprechend CdTe-Material in der Form eines kompakten Blockes benutzt wird.

13. Verfahren nach Anspruch 12, wobei das Kompaktblock-CdS-(oder CdTe-) Material gebildet wird durch Bedecken von CdS- (oder CdTe-) Material mit Boroxidstücken, Heizen des bedeckten Materials auf eine Temperatur höher als seinen Schmelzpunkt in einer Inertgasatmosphäre und einem Druck von mehr als 50 atm, und dann Abkühlen auf Raumtemperatur, wodurch das Material in einer Kompaktblockform verfestigt wird.

14. Verfahren nach einem der vorhergehenden Ansprüche, wobei das transparente Substrat Kalknatronglas ist.

Revendications

1. Procédé pour la production à grande échelle de piles solaires en films couches minces de CdTe/CdS, lesdits films étant déposés séquentiellement sur un substrat transparent, comprenant les étapes suivantes :

- dépôt d’un film d’un oxyde conducteur transparent (TCO) sur ledit substrat ;
- dépôt d’un film de CdS sur ledit film de TCO ;
- dépôt d’un film de CdTe sur ledit film de CdS ;
- traitement du dit film de CdTe avec du $CdCl_2$;
- dépôt d’un film contact arrière sur ledit film de CdTe traité ;

le procédé étant **caractérisé en ce que** le traitement du film de CdTe avec du $CdCl_2$ comprend les étapes suivantes :

- formation d’une couche de $CdCl_2$ sur le film de CdTe, par évaporation, tout en maintenant le substrat à la température ambiante ;
- recuit de ladite couche de $CdCl_2$ dans une chambre à vide à 380-420°C et sous 300-1000

millibars sous atmosphère de gaz inerte ;
- élimination du gaz inerte de ladite chambre pour obtenir des conditions de vide, tout en maintenant le substrat à une température de 350-420°C, ce en quoi tout $CdCl_2$ résiduel est évaporé de la surface du film de CdTe.

2. Le procédé selon la revendication 1, où ladite couche de $CdCl_2$ a une épaisseur de 100-200 nanomètres.

3. Le procédé selon l'une des revendications 1 et 2, où le recuit de la couche de $CdCl_2$ est effectué perdant 15-20 minutes.

4. Le procédé selon l'une quelconque des revendications précédentes, où le gaz inerte est de l'Argon.

5. Le procédé selon l'une quelconque des revendications précédentes, où le film contact arrière est constitué d'une couche de Sb_2Te_3 recouverte d'une couche de Mo.

6. Le procédé selon la revendication 5, où ladite couche de Sb_2Te_3 est obtenue par pulvérisation à 250-300°C.

7. Le procédé selon l'une quelconque des revendications précédentes, où le film contact arrière est constitué d'une couche de As_2Te_3 recouverte d'une couche de Mo.

8. Le procédé selon la revendication 7, où ladite couche de As_2Te_3 est obtenue par pulvérisation à 200-250°C.

9. Le procédé selon l'une quelconque des revendications précédentes, où l'oxyde conducteur transparent est du In_2O_3 dopé au Fluor.

10. Le procédé selon la revendication 9, où la couche de TCO est obtenue par pulvérisation sous atmosphère de gaz inerte contenant de l'Hydrogène et un composé de fluoroalkyle gazeux.

11. Le procédé selon la revendication 10, où un mélange d'Argon et d'Hydrogène est utilisé, dans lequel l'Hydrogène est compris entre 1 et 3% en vol. en % et le composé de flouoroalkyle est du CHF_3.

12. Le procédé selon l'une quelconque des revendications précédentes, où, comme matériau source pour la formation des films de CdS et de CdTe par sublimation en espace fermé, est utilisé un matériau de CdS ou, respectivement, de CdTe sous forme d'un bloc compact.

13. Le procédé selon la revendication 12, où ledit matériau de CdS (ou CdTe) en bloc compact est obtenu par recouvrement de morceaux de CdS (ou CdTe) avec de l'oxyde de Bore, en chauffant le matériau recouvert à une température supérieure à son point de fusion sous une atmosphère de gaz inerte et une pression supérieure à 50 atmosphères et ensuite en refroidissant jusqu'à la température ambiante, ce en quoi le matériau est solidifié sous une forme de bloc compact.

14. Le procédé selon l'une quelconque des revendications précédentes, où ledit substrat transparent est du verre à base de chaux sodée.

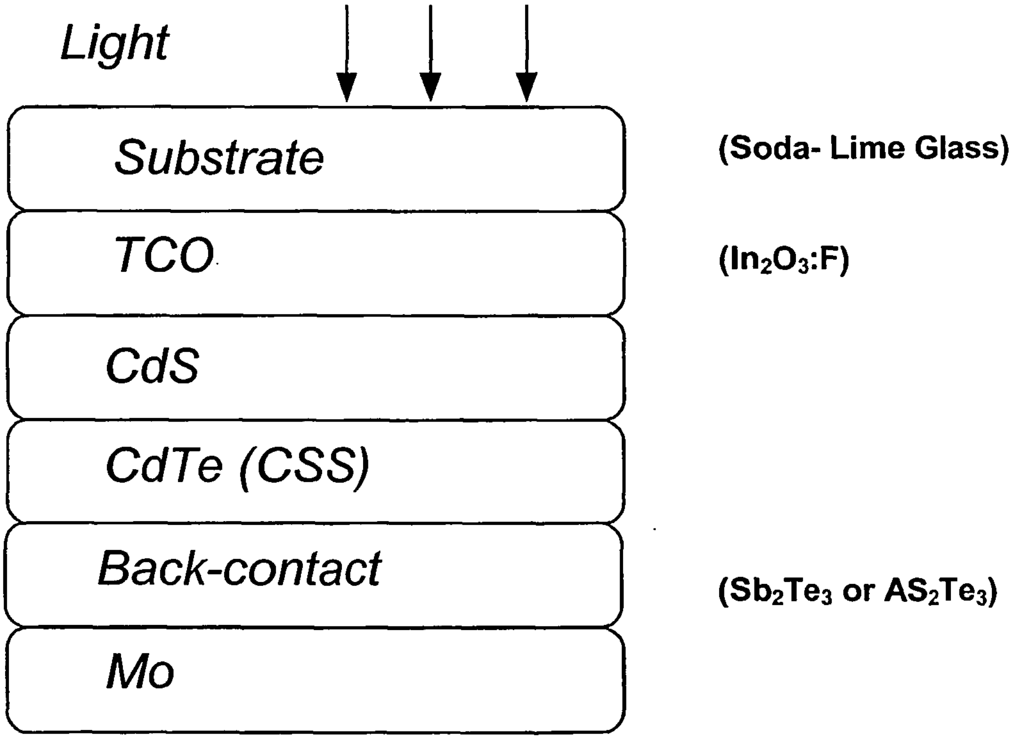
Light
Substrate
(Soda- Lime Glass)
TCO
(In_2O_3:F)
CdS
CdTe (CSS)
Back-contact
(Sb_2Te_3 or AS_2Te_3)
Mo

Fig. 1

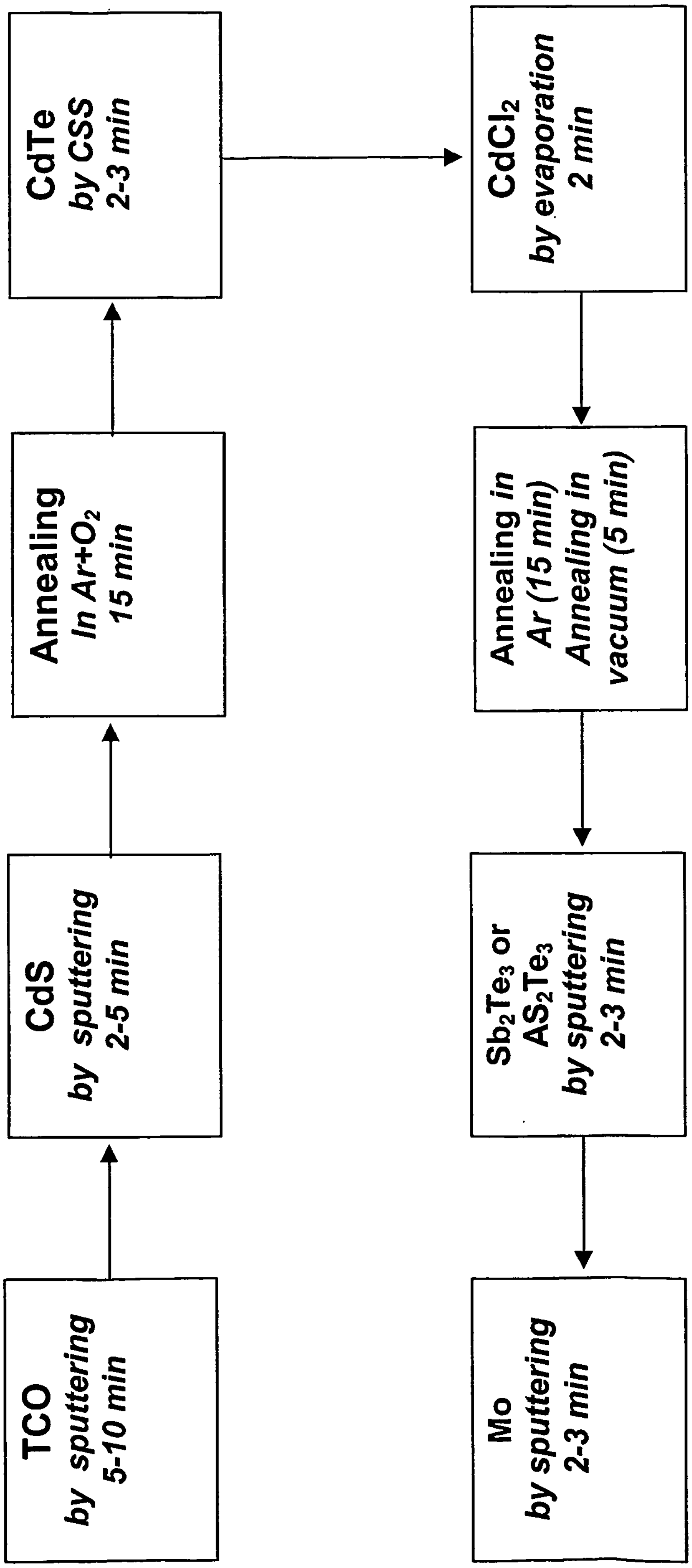
TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In $Ar+O_2$
15 min
CdTe
by CSS
2-3 min
$CdCl_2$
by evaporation
2 min
Annealing in Ar (15 min)
Annealing in vacuum (5 min)
Sb_2Te_3 or
AS_2Te_3
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

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United States Patent [19]
Tyan

[11] **4,207,119**
[45] **Jun. 10, 1980**

[54] POLYCRYSTALLINE THIN FILM CDS/CDTE PHOTOVOLTAIC CELL

[75] Inventor: **Yuan-Sheng Tyan**, Webster, N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[21] Appl. No.: **911,843**

[22] Filed: **Jun. 2, 1978**

[51] **Int. Cl.**^{2} **H01L 31/06**
[52] **U.S. Cl.** .... **136/89 TF**; 136/89 CD; 357/16; 357/30; 357/59; 427/76; 427/85; 427/255.3
[58] **Field of Search** .... 136/89 TF, 89 CD, 89 ST; 357/16, 30, 59; 204/192 P; 427/74, 76, 85, 248 C

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Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Dana M. Schmidt

[57] ABSTRACT

A photovoltaic cell and a process of making and using it are disclosed wherein extremely thin semiconductor layers are provided through the use of polycrystalline CdS and CdTe. The cell has conversion efficiencies as high as 6% or more when exposed to AM2 light.

31 Claims, 2 Drawing Figures

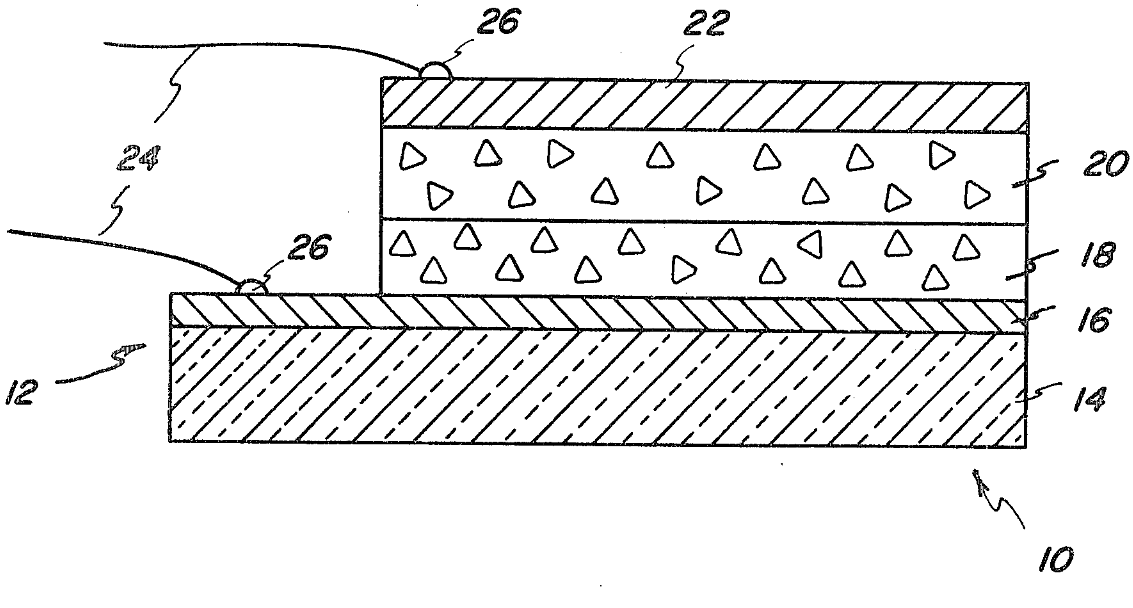
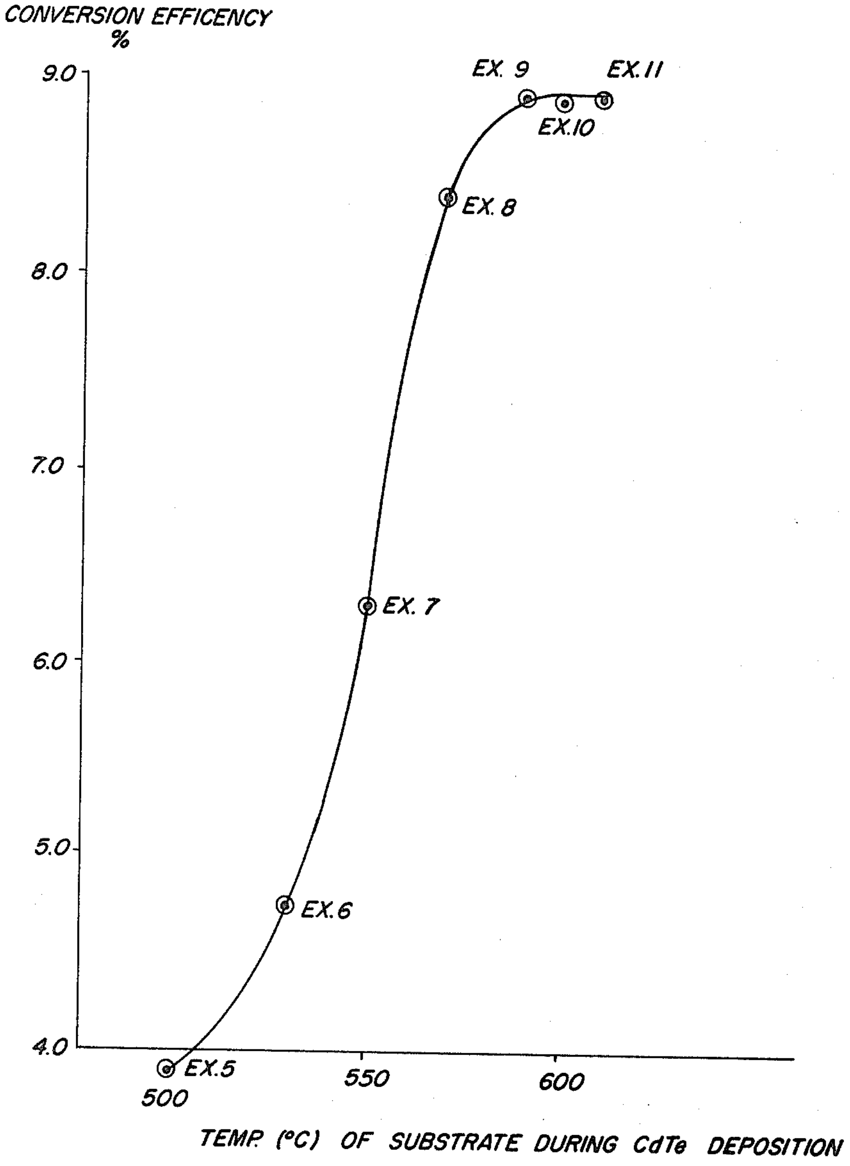


FIG. 1


CONVERSION EFFICENCY
%
9.0
8.0
7.0
6.0
5.0
4.0
EX. 9
EX. 11
EX. 10
EX. 8
EX. 7
EX. 6
EX. 5
500
550
600
TEMP. (°C) OF SUBSTRATE DURING CdTe DEPOSITION

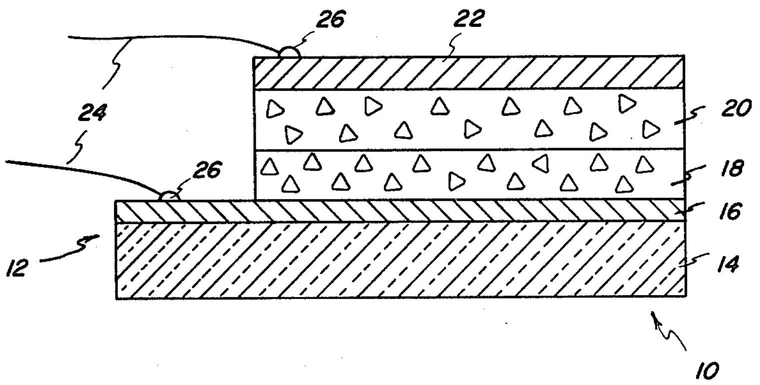


FIG. 2

POLYCRYSTALLINE THIN FILM CDS/CDTE PHOTOVOLTAIC CELL

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to p-n cadmium telluride-cadmium sulfide photovoltaic cells, particularly of the thin-film type.

(2) State of the Prior Art

Effective conversion from expensive petroleum-based energy sources to solar energy sources, such as photovoltaic cells, has been delayed prior to this invention by two factors—the cost of mass-producing such cells and the low conversion efficiency achieved by such cells. Any improvement in either factor can move industry towards the use of more solar cells, and an improvement in both has been a long-sought goal.

A study by R. Moore reported in *Solar Energy,* 18, p. 225 (1976) indicates that thin-film inorganic semiconductor photovoltaic cells should be able to meet the two-fold goal noted above if the individual semiconductive layers do not exceed 5 microns in thickness, assuming conversion efficiencies of at least 5%. Implied is the conclusion that such cells would be even more useful if the conversion efficiencies were higher. The study concludes with the statement that such thin-film cells as described are predicated on "a currently non-existent technological base."

Conversion efficiencies of 5% or more have been difficult to achieve in thin-film solar cells, particularly in solar cells fabricated from CdS and CdTe, hereinafter identified as CdS/CdTe solar cells. Such CdS/CdTe cells have a distinct cost advantage, compared for example to single-crystal silicon cells. Conversion efficiencies, however, must be increased to render them useful. Therefore, considerable effort has been expended to establish techniques for manufacturing such cells with improved conversion efficiencies, as well as reduced thicknesses. Vapor deposition or similar vapor-phase formation of either CdTe upon a crystal of CdS, or of CdS upon a crystal of CdTe, has been used as a means of partially reducing the film thickness, enhancing conversion efficiency, or both, as is reported in articles by A. Fahrenbruch et al, *Appl. Phys. Letters,* 25, p. 605 (1974); R. Bube et al, Report NSF/RANN-/Se/AER-75-1679/76/1; and K. Yamaguchi et al, *Japan J. Appl. Phys.,* 15, p. 1575 (1976). Such prior techniques have relied largely upon the use of single crystal substrates for the vapor deposition. Utilization of single crystal substrates, however, precludes the achievement of the economic advantages associated with thin-film cells, since a single crystal must be grown and sliced. The slicing operation necessarily involves waste of material and produces cells which at best are 50 to 100 microns thick. Thus, it is not possible to manufacture a bilayer solar cell, one layer of which is a single crystal, that is as thin as 10 microns as suggested in the Moore study. In each of the foregoing, the vapor deposition or similar process was done in the absence of oxygen.

In Bonnet, "New Results on the Development of a Thin-Film p-CdTe-n-CdS Heterojunction Solar Cell", 9th IEEE Photovoltaic Specialist Conference, p. 129 (1972), there is reported a thin-film cell of polycrystalline material alleged to have produced a conversion efficiency of 5%. However, the reported I_{sc} value, measured with 50 mW/cm^2 illumination, was 1.5 mA per 10 mm^2, or 15 mA/cm^2. This corresponds to an I_{sc} value of

30 mA/cm^2 for a 100 mW/cm^2 illumination, the standard "AM1" sunlight condition. Since the theoretical limit of I_{sc} under AM1 conditions is only about 24 mA/cm^2, clearly there was a positive error in the observations and the conversion efficiency was less than the reported value of 5%.

SUMMARY OF THE INVENTION

In accord with the present invention, there is advantageously featured a photovoltaic cell having the dual properties of greatly reduced cost and a markedly improved conversion efficiency compared to similar cells previously produced.

In accord with a related aspect of the invention, there is advantageously featured such a cell wherein the overall thickness is greatly reduced.

These features of the invention are based upon the discovery that CdS/CdTe solar cells can be manufactured to have both thin-film characteristics, and conversion efficiencies in excess of 5 and even 6% in AM2 light, characteristics not available in the prior art. More specifically, in accordance with one aspect of the invention, there is provided a cell for converting incident radiation into electricity, comprising first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of the layers, at least one of the electrodes being transparent or semi-transparent to the incident radiation, said cell being further characterized by a conversion efficiency of at least about 6.0% when exposed to AM2 light.

In accordance with another aspect of the invention, there is provided an n-type CdS and p-type CdTe photovoltaic cell containing operative electrodes, wherein both the cadmium telluride and the cadmium sulfide are polycrystalline, and together the layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms present.

In accordance with yet another aspect of the invention, there is provided an n-type CdS and p-type CdTe photovoltaic cell containing operative electrodes, the improvement being that the total thickness of the cell does not exceed about 10 microns and at least one of the layers contains oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms in the layer.

Such cells can be manufactured by a process of depositing, in the vapor phase, contiguous layers of the semiconductor material, in a manner such that at least one of the layers is deposited in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without the oxgen atmosphere.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a plot of conversion efficiencies achievable by cells of the invention, versus the substrate temperature useful for the formation of the CdTe layer; and

FIG. 2 is a partially schematic section view of a cell prepared in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

"Photovoltaic cell" as used herein means a solid state device which produces an electric current in response to light of appropriate wavelengths, from any source.

It has been found that the dual results of reduced cost and enhanced conversion efficiency can be produced by a photovoltaic cell having polycrystalline cadmium sulfide and polycrystalline cadmium telluride in contiguous layers. Such polycrystalline semiconductive materials allow the inexpensive layered formation of a truly thin cell, inasmuch as the combined thickness of two layers of polycrystalline semiconductor materials need not exceed about 100 microns, and preferably does not exceed about 10 microns.

The enhancement of the conversion efficiency of such cells is achieved by forming one or both of the semiconductive layers in an oxygen-containing atmosphere. Maximum enhancement occurs when the layers are formed at a particular range of temperatures.

As used herein, "enhanced conversion efficiency" means a conversion efficiency that is about 10% greater than the conversion efficiency of a control cell produced without the enhancing step. In practice, much larger enhancements than 10% are common when using the invention.

Because of their simplicity, preferred methods of forming the layers using an oxygen-containing atmosphere are those in which the semiconductive layers are deposited in the vapor phase. As used herein, "depositing in the vapor phase" is used to mean any process wherein material is transferred in the vapor phase from a source, usually heated, to a substrate where the material forms a new layer. Therefore, as used here "depositing in the vapor phase" includes, but is not limited to, close-space sublimation, vapor transporting, vacuum evaporation, vapor growth, and sputtering or ion plating wherein ionized or plasma gas, respectively, is the activating medium. "Close-space sublimation" means sublimation from a source to a substrate positioned from the source a distance no greater than the square root of the smaller of the surface areas of the source and of the substrate. All of these are known processes, and except as noted hereinafter, follow conventional procedures.

The atmosphere for the vapor-phase depositing can be either pure oxygen, oxygen artificially admixed with other gases, or air. As will be readily apparent, the actual amount of the oxygen present during deposition will depend upon the specific form of vapor-phase depositing that is selected. For example, close-space sublimation, a highly preferred form of the process of the invention, can tolerate much higher levels of gas than can vacuum evaporation, which preferably utilizes about 10^{-4} torr of gas. The other forms of vapor-phase depositing mentioned above have known or standard tolerance levels of gas, and the amount of oxygen pressure or partial pressure is selected to comply with such tolerance levels.

The process preferably proceeds by depositing, in the vapor phase, cadmium sulfide onto a suitable electrode, described below, with or without oxygen present in the atmosphere. Thereafter, the cadmium telluride and, optionally, a p-type dopant such as gold are similarly deposited in the vapor phase onto the previously formed cadmium sulfide, with or without oxygen present in the atmosphere, except that at least one of the two layers is deposited with oxygen gas present.

Thereafter, an electrode capable of making a low impedance contact is formed on at least a portion of the cadmium telluride. A preferred process of such electrode formation is vacuum deposition.

The vapor-phase depositing of the semiconductor material can be done either as a batch process, e.g., in a vacuum chamber containing a single source and a single substrate, or as a continuous process in which a substrate is moved through appropriate zones of treatment.

As indicated, a highly useful form of the vapor-phase depositing is close-space sublimation. The oxygen atmosphere of the sublimation can be at a pressure between about 0.01 and about 100 torr, and preferably is at a pressure between about 0.1 and about 10 torr. The spacing between source and substrate preferably is between about 0.5 and about 5 mm. The temperature of the substrate upon which each of the semiconductor layers is to be crystallized can be varied, depending on which material is being sublimated. Preferably, each of the CdS and CdTe materials is deposited for a time of between about 0.1 sec to about 10 minutes onto a substrate held at a temperature of between about 300° C. and about 650° C. As is customary in sublimation, the source temperature is maintained in each instance between about 10° and about 500° C. higher than the substrate temperature, preferably about 100°-300° C. higher for the CdS deposition and 20°-50° C. higher for the CdTe deposition. Conventional heating techniques for the source and/or the substrate include, e.g., resistance heating, induction heating, and the like.

Within this process of close-space sublimation, higher conversion efficiencies are achieved when the CdTe layer is sublimated in an oxygen-containing atmosphere on a CdS substrate at a temperature of at least about 575° C., the CdS layer also having been sublimated in O_2. It has been found, when keeping constant other variables such as deposition time and thickness of the two layers as well as the amount of oxygen present in the atmosphere, that such a substrate temperature provides a substantial further increase in the conversion efficiency compared to a cell wherein the CdTe is sublimated in oxygen at a lower substrate temperature. Although still further increases in efficiency are achieved at still higher temperatures, the rate of increase decreases significantly beyond the 575° C. temperature.

The mechanism by which this occurs is not as yet fully understood. The effect is illustrated in FIG. 1. The CdS substrate in this case was also sublimated in a 0.4 torr oxygen-containing atmosphere, and each data point represents a separate cell wherein the only difference in the preparation of the cell is the temperature of the CdS substrate for the CdTe sublimation. Whereas a substrate temperature of 500° C. produced a conversion efficiency of about 3.9%, a substrate temperature increased to about 550° C. raised the conversion efficiency to about 6.3%, and an increase to 570° C. raised it still further to about 8.4%. A further increase in substrate temperature to about 600° C. produced a slight increase in efficiency to 8.9%.

It is possible that the critical substrate temperature, i.e., the temperature above which further substantial increases in conversion efficiency are not achievable, can be lowered below about 575° C. if other variables of the sublimation process are further optimized.

In at least certain instances, and particularly for CdTe layers deposited at temperatures below the above-noted substrate temperature of about 575° C., further enhancement of the conversion efficiency can be achieved by an optional process step of heating the already formed CdTe layer in an oxygen-containing atmosphere for a suitable length of time. In this case, normal or even pressurized atmospheres of oxygen can be used, a highly preferred example being air at ambient pressure. Partial pressures of oxygen can also be used, as can an alternating non-oxidizing and oxidizing atmosphere of the type described in U.S. Pat. No. 4,035,197, issued on July 12, 1977, the details of which are hereby expressly incorporated herein by reference. The temperature of such post-treatment can be between about 100° C. and about 600° C., for a time of between about 1 second to about 20 minutes. As will be apparent, the higher the temperature that is used, the lower the length of time of exposure that is needed to further enhance the conversion efficiency.

Such post-heating of the CdTe layer can increase the conversion efficiency by 1 or 2% over that achieved by the same cell lacking the post-heating step.

It is believed that the vapor depositing of one or both of the semiconductor materials in an oxygen-containing atmosphere produces enhanced cconversion efficiencies by the incorporation of oxygen atoms into the semiconductor layer formed in the presence of the oxygen. However, the exact amounts of such oxygen incorporation are so minute that they are difficult to detect or assay.

To complete the cell, electrodes are selected to provide low-impedance contact with at least portions of the exterior surfaces of the two contiguous semiconductor layers formed as described. As used herein, "low impedance" means an impedance that is no greater than that which gives a contact resistance of 50 ohm-cm^2. Although such low-impedance contacts at least approach a true ohmic contact, some rectification in the contact can also be tolerated, as is well known.

Each of the electrodes is also in operative contact with its respective layer; that is, in the cell is contacts only its layer, and at least one of the electrodes transmits sufficient activating radiation as to photogenerate an electric potential in the cell. Conveniently, such transmission of radiation is accomplished by rendering one of the electrodes, sometimes called the "window" electrode, transparent or semitransparent to radiation having wavelengths bebetween about 350 and about 900 nm. A useful material having this property is "Nesatron" ® brand glass, a semitransparent electrode material comprising a conductive In_2O_3(Sn) layer coated onto a transparent glass, available from PPG Industries, Inc. Such an electrode typically has a sheet resistance of about 10 to about 50 ohm/square and an optical transmittance of about 80% for visible light. The "Nesatron" ® electrode provides a low-impedance contact with the n-type cadmium sulfide, and as such comprises a highly useful substrate for the first semiconductive layer formation. Other conventional electrode materials also can be selected, providing they have sufficient conductivity, light transmittance, and the appropriate work function that insures the low-impedance contact with n-type CdS. Examples include transparent layers of CdO, SnO_2, Cd_2SnO_4, and the like on glass, with or without dopants.

Conventionally, the "Nesatron" ® electrodes are cleaned prior to layer formation of the semiconductor material. This can be accomplished by hand-rubbing the surface of the conductive coating with cleansers such as a sulfonate detergent available under the trademark "Alconox" from Alconox, Inc., followed by rinsing with water.

Electrode materials for low-impedance contact with the p-type CdTe are also conventional, and include, for example, gold, silver, copper, nickel, tin, platinum, palladium, chromium, iridium, rhodium, and non-metallic materials such as Cu_2S and Cu_2Te having high electrical conductance and a work function approximately matching that of p-CdTe. These materials may be used singly or in any combination, either in one layer or in successive layers.

FIG. 2 illustrates a typical photovoltaic cell **10** produced in accordance with the invention. Transparent electrode **12** comprises a support layer **14** of glass bearing a conductive layer **16** of In_2O_3(Sn) such as a "Nesatron" ® electrode, on which is formed layer **18** of n-type CdS. A contiguous layer **20** of p-type CdTe is formed on layer **18**, and an electrode layer **22** contacts at least a portion of layer **20**. Leads **24** attached as by solder **26** carry away power from the cell. Because layers **18** and **20** are polycrystalline, they can be prepared by a thin-film preparation process to be extremely thin, for example, no greater than about 50 microns thick and preferably from about 0.05 to about 5 microns thick. The total thickness then of the combined semiconductor materials is generally less than about 100 microns, and preferably no greater than about 10 microns. The triangles are indicative of the fact that the layer is polycrystalline.

Electrode layers **16** and **22** are extremely thin conventionally, from about 1000 to about 10,000 Å, and from about 30 to about 1000 Å respectively. Glass support layer **14** is of course comparatively thick, typically about 1000 microns.

Photovoltaic cells of this invention can be used to photogenerate electric power when exposed to activating radiation, preferably through the window electrode. The potential created across the junction can be used as a voltage source, or the current generated by the cell can be drawn off. Thus, among other things, the cell can be used as a voltage generator or as an exposure meter operating from the cell's short circuit current. Such uses are in accordance with conventional practices following well-known procedures.

The following examples further illustrate the invention. Except where noted, pure oxygen atmospheres at stated partial pressures were used. In each example simulated sunlight illumination of 75 mW/cm^2 (AM2) was achieved by using a Kodak Carousel projector, Model 600, containing a 500 W tungsten-lamp, with the heat-absorbing glass removed, and a spectrum-correcting-filter set. Conversion efficiencies were calculated from the measured I_{sc}, V_{oc}, fill factor and the known input illumination. As used herein, "fill factor" means the fraction of the product of I_{sc} and V_{oc} that is available as power output for the cell.

EXAMPLE 1

A cell was prepared of the type shown in FIG. 2, as follows:

On a Nesatron ® glass substrate a CdS layer was deposited at a temperature of about 550° C., in an oxygen-containing atmosphere of about 0.4 torr O_2 to a thickness of about 0.2 micron. A CdTe layer about 2 microns thick was then deposited on the CdS layer heated at a temperature of about 590° C., in an atmosphere containing 1.5 torr O_2 and 1.5 torr Ar. A 500 Å thick gold electrode layer 6 was vacuum-deposited on the CdTe layer. Under simulated sunlight illumination of 75 mW/Cm^2, the cell had a V_{oc} of about 0.7 volts, an I_{sc} of about 16 mA/cm^2, and a fill factor of about 0.6. The conversion efficiency was about 8.9%.

Example 2: Enhancement Due to CdS Deposition in O_2

To demonstrate the effect of the use of an oxygen-containing atmosphere only during the CdS deposition, a control cell and 5 test cells were prepared as follows: Nesatron ® substrates having a nominal resistivity of 25 ohm/square were cleaned by hand-rubbing with Alconox ® detergent and rinsing with hot tap water prior to deposition of the semiconductor layers. The CdS layer was then prepared by close-space sublimation, wherein the source was a hot-pressed disc of phosphor-grade CdS powder obtained from General Electric. The process was carried out with a source temperature of about 750° C. and a substrate temperature of about 535° C. In the case of the control cell, a vacuum was used containing a partial pressure of O_2 of less than 0.01 torr, which was achieved with a mechanical vacuum pump. The five test cells, on the other hand, incorporated 2.5 torr oxygen in the atmosphere during the CdS sublimation. The deposition time was about 2 to 4 minutes, leading to a layer thickness of between about 1 micron and 2 microns. After cooling the substrate to near room temperature, it was placed on another holder for the CdTe deposition. The source was a polycrystalline disc sliced from an ingot which had been prepared by reacting 99.9999% pure Cd and Te in a melt doped with 10 ppm of Au. A source temperature of about 550° C., a substrate temperature of about 450° C. and a deposition time of about 2 minutes were used to achieve a film thickness of about 0.5 microns. The deposition of all CdTe layers was carried out under a partial pressure of O_2 of less than about 0.01 torr, provided by a mechanical vacuum pump. The CdTe/CdS structure was post-heated in air at 325° C. for 3 minutes, after which the cell was completed by vapor-depositing a 500 Å thick layer of Au on the CdTe layer.

The photovoltaic response of the control cell lacking the oxygen atmosphere for the CdS deposition was, $V_{oc}=0.37$, $I_{sc}=7.1$ mA/cm^2, fill factor approximately equal to about 0.4 and conversion efficiency = 1.38%. In contrast, the average photovoltaic response of the 5 test cells was $V_{oc}=0.48\pm0.03$ mV, $I_{sc}=9.1\pm1.6$ mA/cm^2, fill factor of approximately 0.4, and conversion efficiency = 2.5±0.3%, an improvement in conversion efficiency of more than 1%.

Examples 3 and 3A:

To further illustrate the effect of the presence of oxygen during CdS deposition, two different cells were made with the CdS layer prepared under two different pressures of air. Preparation of a "Nesatron" electrode was generally as described in Example 2. One of the cells, Example 3, was prepared by close-space sublimating the CdS layer in a vacuum prepared by evacuating the air using a rotary mechanical pump, to a pressure of less than 0.01 torr, flushing with argon several times, and reducing the argon atmosphere to less than 0.01 torr. The CdTe layer was formed by close-space sublimation for 2 min. on the CdS substrate maintained at 610° C., in an atmosphere of 1.5 torr O_2 and 1.5 torr Ar, from a source held at 630° C. Example 3A was prepared identically as Example 3, except that air was used as the atmosphere for the close-space sublimation of the CdS, at a pressure of 0.15 torr. Table 1 illustrates the results.

Table 1

Example	Ambient Air Pressure, Torr	η, %	V_{oc}, mV	I_{sc}, mA/cm^2	FF
3	essentially zero	4.0	390	15.1	0.51
3A	0.15	8.3	650	17.0	0.56

Very little improvement in conversion efficiency was noted upon increasing the air pressure above 0.15 torr. This example demonstrated that although the presence of oxygen in the atmosphere for the deposition of the CdTe produced a significant conversion efficiency, an even higher value is achieved if oxygen is present for the deposition of the CdS also.

Example 4: Enhancement Due to CdTe Deposition in O_2

To demonstrate the enhancement achievable by depositing the CdTe layer in an oxygen-containing atmosphere, eight cells were prepared by the procedure of Example 2 on CdS prepared in an atmosphere containing 2.5 torr of oxygen, except that the CdTe layer was deposited using an atmosphere containing 5.0 torr of oxygen. These eight cells showed an average V_{oc} of 0.618±0.012 volts, an average I_{sc} of 11.5±1.5 mA/cm^2, a fill factor of approximately 0.5±0.01, and an average conversion efficiency of 4.89±0.54%. Thus, an improvement of more than 2% in conversion efficiency was achieved by depositing the CdTe in an oxygen-containing atmosphere.

Examples 5-11

To demonstrate the effect of the substrate temperature for CdTe deposition, seven cells were made under the following conditions: a CdS layer was deposited by close-space sublimation on a Nesatron ® glass substrate with a nominal electrical resistance of 10 ohm/square. The source temperature was 720° C., the substrate temperature was 550° C., the deposition time was 5 seconds, and the process was carried out in an 0.4 torr oxygen atmosphere. Then a CdTe layer was deposited, again by the close-space sublimation process. The source temperature was 630° C. or 640° C., the substrate temperature varied as shown in Table II, the deposition time was 2 minutes, and the process was carried out in an atmosphere consisting essentially of 1.5 torr O_2 and 1.5 L torr Ar. Cell preparation was completed by evaporation of a 500 Å Au layer, using the technique of conventional vacuum evaporation under a pressure of 10^{-6} torr. (For the cells with 600° C. or higher substrate temperature, a slightly higher source temperature was used to provide a CdTe layer thickness similar to that of the other cells.) The results are summarized in Table II, and represent the data points in FIG. 1.

Table II

	CdTe Deposition					
Ex.	Source Temp., °C.	Substrate Temp., °C.	η, %	V_{oc},mV	I_{sc}, mA/cm^2	FF
5	630	500	3.9	560	12.5	0.42
6	630	530	4.7	610	13.7	0.43
7	630	550	6.3	630	14.7	0.50
8	630	570	8.4	680	16.7	0.55
9*	630	590	8.9	705	16.3	0.58
10	640	600	8.9	695	16.7	0.58

Table II-continued

	CdTe Deposition					
Ex.	Source Temp., °C.	Substrate Temp., °C.	η, %	V_{oc},mV	I_{sc}, mA/cm^2	FF
11	644	610	8.9	710	16.5	0.58

*This is the cell described in Example 1.

Example 12:

To further illustrate the effect of oxygen during CdTe deposition, a series of cells was prepared by varying the oxygen pressure during CdTe deposition while maintaining the other conditions of preparation essentially constant. That is, the deposition of the CdS was either in a 0.4, 0.5 or 1.0 torr oxygen atmosphere, using a T_{source} (source temperature) of 710°, 720° or 725° C. and a $T_{substrate}$ (substrate temperature) of 500° C. or 550° C. The CdTe deposition used a T_{source} of 630° or 640° C. and a $T_{substrate}$ of 600° or 610° C. None of these minor variations are believed to be significant or capable of producing significantly different conversion efficiencies.

It was found that an oxygen pressure of 0.5 torr produced a cell with a conversion efficiency of about 4.6%, whereas at an oxygen pressure of about 1.0 torr or higher, the conversion efficiency was generally constant at about 8.75%±1.25.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadmium sulfide are polycrystalline, and together said layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without said oxygen atoms present.

2. A cell as defined in claim **1**, wherein said oxygen-containing layer is the cadmium telluride layer.

3. A cell as defined in claim **1**, wherein said oxygen-containing layer is the cadmium sulfide layer.

4. A cell as defined in claim **1**, wherein both of said layers contain oxygen atoms in said amount.

5. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein said layers are polycrystalline and the total combined thickness of said layers does not exceed about 10 microns, at least one of said layers containing oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without the oxygen atoms in said layer.

6. A cell as defined in claim **5**, wherein said oxygen-containing layer is the cadmium telluride layer.

7. A cell as defined in claim **5**, wherein said oxygen-containing layer is the cadmium sulfide layer.

8. A cell as defined in claim **5**, wherein both of said layers contain oxygen atoms in said amount.

9. A cell as defined in claim **5**, wherein one of said electrodes is a layer of conductive oxide in low-impedance contact with at least part of said CdS layer, said oxide layer being transparent or semitransparent to incident radiation.

10. A cell as defined in claim **9**, wherein said oxide is indium tin oxide.

11. A cell as defined in claim **9**, wherein the other of said electrodes is a layer of metal in low-impedance contact with at least part of said CdTe layer.

12. A cell as defined in claim **11**, wherein said metal is gold.

13. A cell for converting incident radiation into electricity, comprising

first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semi-transparent to said incident radiation,

said cell being further characterized by a conversion efficiency of at least about 6.0% when exposed to AM2 light.

14. A cell for converting incident radiation into electricity, comprising

first and second contiguous polycrystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semitransparent to said incident radiation,

said cell being further characterized by a combined thickness of said layers that is no greater than about 10 microns and a conversion efficiency of at least about 6% when exposed to AM2 light.

15. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadmium sulfide are polycrystalline, at least one of said layers having been formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without said at least one layer having been formed in said oxygen-containing atmosphere.

16. In a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein the combined thickness of said layers does not exceed about 10 microns, at least one of said layers having been formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without said at least one layer having been formed in said oxygen-containing atmosphere.

17. A cell as defined in claim **16**, wherein said layer formed in an oxygen-containing atmosphere is the cadmium telluride layer.

18. A cell as defined in claim **17**, wherein said oxygen-containing atmosphere was at a pressure of at least about 1 torr of oxygen.

19. A cell as defined in claim **16**, wherein said layer formed in an oxygen-containing atmosphere is the cadmium sulfide layer.

20. A cell as defined in claim **16**, wherein both of said layers were formed in an oxygen-containing atmosphere.

21. In a process for manufacturing a photovoltaic cell by depositing, in the vapor phase, contiguous polycrystalline layers of n-type cadmium sulfide and p-type cadmium telluride and securing an electrode to at least a portion of each of said layers,

the improvement comprising depositing at least one of said layers in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without said oxygen atmosphere.

22. A process as defined in claim **21**, wherein both of said layers are deposited by close-space sublimation in an oxygen-containing atmosphere and the temperature of the substrate during the depositing of CdTe is at least about 575° C., the amount of time of said depositing of said layers being sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but at a CdTe substrate temperature less than about 575° C.

23. A process as defined in claim **21** and further including the step of heating in an oxygen-containing atmosphere either or both of said layers after their deposition, for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the efficiency of a cell produced without said post-deposition heating.

24. A process as defined in claim **21**, wherein the deposition of said CdTe is in an atmosphere containing at least about 1 torr oxygen.

25. A process of converting incident radiation into electrical power, comprising the steps of

(a) exposing to said radiation, a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, said layers together containing oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell that is produced without said oxygen atoms, and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent or semitransparent to said incident radiation; and

(b) drawing off power from said cell in proportion to said enhanced conversion efficiency.

26. A process of converting incident radiation into electrical power, comprising the steps of

(a) exposing to said radiation, a photovoltaic cell comprising

first and second contiguous polycrystalline layers containing, respectively, n-type cadmium sulfide and p-type cadmium telluride, at least one of said layers being formed in an oxygen-containing atmosphere for a time and at a temperature, and in an amount of oxygen, which are sufficient to provide a conversion efficiency that is enhanced over the conversion efficiency of a cell produced identically but without being formed in said oxygen-containing atmosphere; and electrodes in operative, low-impedance contact with at least part of said layers, at least one of said electrodes being transparent of semitransparent to said incident radiation; the total combined thickness of said layers not exceeding about 10 microns; and

(b) drawing off power from said cell in proportion to said enhanced conversion efficiency.

27. In a photovoltaic cell comprising

first and second contiguous crystalline layers containing, respectively, p-type cadmium telluride and n-type cadmium sulfide, and electrodes in operative, low-impedance contact with at least part of said layers,

the improvement wherein both said cadmium telluride and said cadium sulfide are polycrystalline, and together said layers contain oxygen atoms in an amount that is effective to produce a cell having a conversion efficiency that is enhanced over the conversion efficiency of a cell generally identical in structure but containing only the amount of oxygen atoms in said layers that is present when the layers are formed in an atmosphere that has an oxygen partial pressure of less than 0.01 Torr.

28. A cell as defined in claim **27**, wherein one of said electrodes is a layer of conductive oxide in low-impedance contact with at least part of said CdS layer, said oxide layer being transparent or semi-transparent to incident radiation.

29. A cell as defined in claim **28**, wherein said oxide is indium tin oxide.

30. A cell as defined in claim **28**, wherein the other of said electrodes is a layer of metal in low-impedance contact with at least part of said CdTe layer.

31. A cell as defined in claim **30**, wherein said metal is gold.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,207,119
DATED : June 10, 1980
INVENTOR(S) : Y. S. Tyan

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 59, "oxgen", should read --oxygen--.

Col. 5, line 22, "cconversion", should read --conversion--; line 38, "cell is", should read --cell it--; line 45, "bebetween", should read --between--.

Col. 8, line 50, delete "L".

Col. 12, line 25, "transparent of", should read --transparent or--.

Signed and Sealed this

Sixth **Day of** *January 1981*

[SEAL]

Attest:

SIDNEY A. DIAMOND

Attesting Officer

Commissioner of Patents and Trademarks

United States Patent [19]
McCandless et al.

[11] **Patent Number:** **4,709,466**
[45] **Date of Patent:** **Dec. 1, 1987**

[54] PROCESS FOR FABRICATING THIN FILM PHOTOVOLTAIC SOLAR CELLS

[75] Inventors: **Brian E. McCandless; Robert W. Birkmire,** both of Newark, Del.

[73] Assignee: **The University of Delaware,** Newark, Del.

[21] Appl. No.: **723,054**

[22] Filed: **Apr. 15, 1985**

[51] **Int. Cl.**^{4} **H01L 31/18**
[52] **U.S. Cl.** **437/5;** 136/260; 136/264; 427/76; 437/248
[58] **Field of Search** 29/572; 136/260, 264, 136/265; 357/30; 427/76

[56] **References Cited**

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58-18969 2/1983 Japan 136/260

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B. M. Basol et al., *Proceedings, 5th E.C. Photovoltaic Solar Energy Conf.*, (1983), pp. 888–891, Reidel Pub. Co., (1984).

Primary Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Connolly & Hutz

[57] **ABSTRACT**

Thin film photovoltaic solar cells are made by forming the cell structure from a number of layers including the contact layers and semiconductor layers. At least one of the semiconductor layers is a tellurium containing II-VI compound. After the structure is formed, it is heated to temperatures above 300° C. and then rapidly cooled at rates greater than 10° C./s. Cells comprising CdS and CdTe have increased fill factor when the fabrication process includes heating and rapid cooling.

10 Claims, 2 Drawing Figures

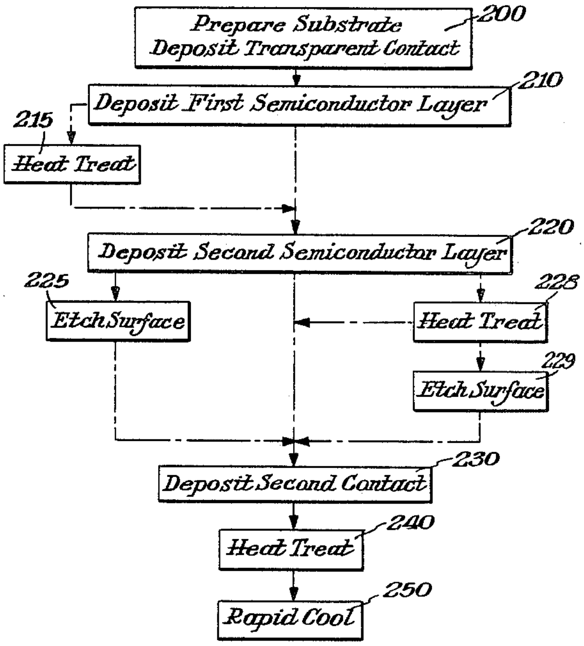


Fig. 1.

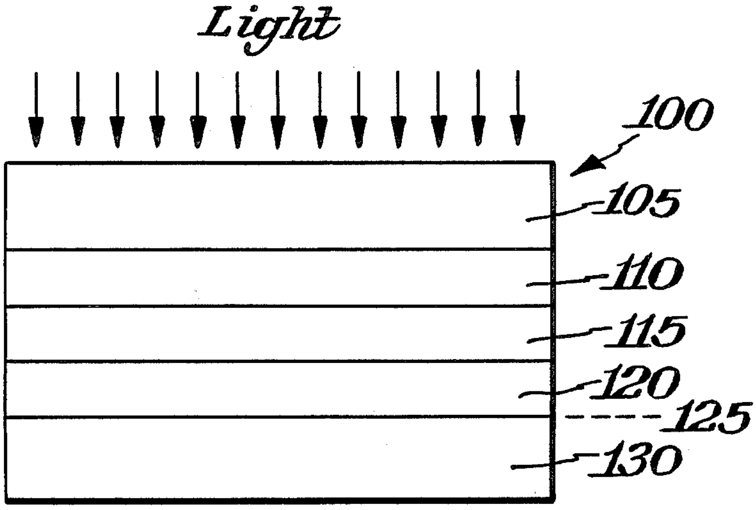
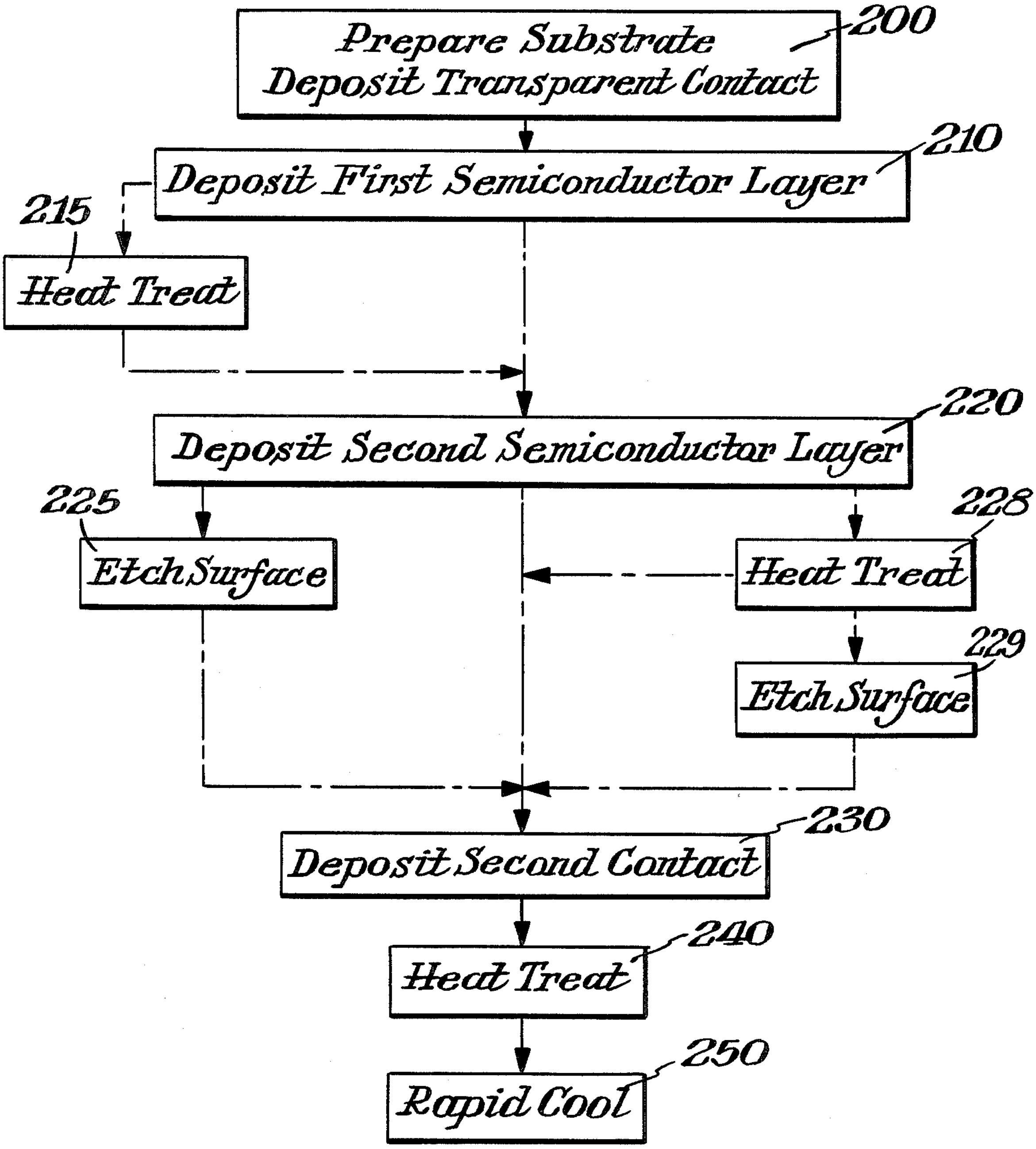


Fig. 2.


Prepare Substrate
Deposit Transparent Contact
200
Deposit First Semiconductor Layer
210
215
Heat Treat
Deposit Second Semiconductor Layer
220
225
Etch Surface
228
Heat Treat
229
Etch Surface
Deposit Second Contact
230
Heat Treat
240
Rapid Cool
250

PROCESS FOR FABRICATING THIN FILM PHOTOVOLTAIC SOLAR CELLS

BACKGROUND OF THE INVENTION

While thin film solar cells, such as CdS/CdTe solar cells, made according to methods known in the art have achieved efficiencies near 10%, further improvements in efficiency require increased fill factor. In order to increase the fill factor of a cell the electrical resistance at the contact between the CdTe semiconductor layer and the contact layer needs to be reduced. A measure of this resistance is the slope of the current-voltage curve at the open circuit voltage point. Moreover, high efficiencies have been mostly obtained using gold for the contact metal. However, gold is not only an expensive material, but there is evidence that cells utilizing gold contacts are not stable for long periods of time. Therefore, there is a need for a fabrication process that provides for increased fill factor and permits substitution for gold with other metals. The art also teaches various etches for preparing the surface of CdTe before forming the contact. However, wet etching may not always be desirable or feasible for fabricating thin film cells.

SUMMARY OF THE INVENTION

An object of this invention is to provide a process for fabricating thin film photovoltaic solar cells, such as of the CdS/CdTe type, wherein there is an increase in fill factor.

In accordance with this invention, the object of the invention is achieved by heat treating the cell after the contact layer has been deposited on the CdTe layer and then rapidly cooling the cell.

THE DRAWINGS

FIG. **1** is a side elevation view of a thin film photovoltaic solar cell formed in accordance with this invention; and

FIG. **2** is a flow diagram showing the steps used in fabricating the cell of FIG. **1**.

DETAILED DESCRIPTION

FIG. **1** shows a thin film photovoltaic solar cell **100** fabricated in accordance with this invention. As shown therein, cell **100** includes a transparent substrate **105** on which is formed a transparent contact layer **110**. Transparent substrate **105** may be glass or a polymeric material. Transparent contact layer **110** is tin oxide, indium-tin-oxide, cadmium stannate or other transparent conductive oxide materials known in the art.

Next is formed first semiconductor layer **115** and then second semiconductor layer **120**. Semiconductor layers **115** and **120** should be of opposite conductivity tyep. For example, first semiconductor layer **115** may be n-type CdS or (ZnCd)S and second semiconductor layer **120** may be p-type CdTe or HgCdTe. Finally contact layer **130** is formed. The specific materials and dimensions for the cell structure may be those conventionally used in the art.

FIG. **2** shows the steps for forming cell **100**. Steps **200** through **230** are carried out in the conventional manner. As indicated in FIG. **2**, certain of the heating and etching steps (i.e., Steps **215**, **225**, **228** and **229**) are optional steps.

Reference is made to the publication of Y.S. Tyan et al in *Proceedings of the 16th IEEE Photovoltaic Specialists Conference* (1983), p. 794, for Steps **210** and **220** of depositing CdS layer **115** and CdTe layer **120** in an oxygen-containing atmosphere at high temperatures using a method called "close space sublimation". Step 225 is chemically etching CdTe surface **125** as taught in U.S. Pat. No. 4,319,019. The cell is completed by depositing, in Step **230**, a metal layer **130**, such as gold or nickel.

Reference is made to U.S. Pat. No. 4,456,630 and the publication of B. M. Basol, in the Journal Applied Physics, Vol. 55, No. 2, (1984), p. 601 for the steps involving electrodepositing CdS and CdTe semiconductor layers **115** and **120** (Steps **210** and **220**); heat treating at 400° C.in air for about 10 minutes (Step **228**), followed by etching CdTe surface **125** (Step **229**); and finally depositing a conductive metal layer **130**, such as gold, by evaporative techniques (Step **230**).

The improved process of the present invention includes, as Step **240**, heating at a temperature of about 300° C. to 500° C. for about 10 to 100 minutes and Step **250** rapidly cooling to room temperature at a rate of at least 10° C./s and preferably at 100° C./s. Heating Step **240** can be carried out in an oven or furnace or on a heated surface, such as a hot plate. It is preferred to carry out Step **240** in air at a temperature of 400° C. for 15 minutes. Rapid cooling, Step **250**, is carried out by removing the device from the furnace and placing it in thermal contact with a heat sink adapted to provide the required cooling rate.

Experiments have been conducted to show the utility of heating and rapid cooling. These experiments were performed by first sputter depositing an indium-tin-oxide TCO layer **110** on Corning 7059 glass substrate **105** (Step **200**). Next, the CdS layer **115** was deposited to a thickness of 5 microns by physical vapor deposition (Step **210**). The specimen was heat treated (Step **215**) for 3 hours in air at 350° C. CdTe layer **120** was deposited in Step **220** to a thickness of 10 microns by close space sublimation in the presence of 2 torr oxygen and at a substrate temperature of 600° C. CdTe surface **125** was etched (Step **225**) according to U.S. Pat. No. 4,456,630. A gold metal contact **130** was deposited in Step **230** by electron beam evaporation. Heating Step **240** was conducted by placing the cell in the 400° C. zone of a quartz lined tube furnace for 15 minutes. Finally, rapid cooling Step **250** was carried out at an estimated rate of 100° C./s by removing the cell from the furnace and pressing it against a precooled aluminum plate.

Comparative experiments were also carried out. In order to test the effect of cooling rate, specimens were cooled slowly. The effect of heating and quick cooling prior to depositing metal layer **130** was also examined.

It was found that rapid cooling gave higher fill factor and that the effect was essentially reversible with respect to slow cooling. That is, when a cell made in accordance with the invention and having a fill factor of 0.53 was heated for 15 minutes in air at 400° C.and allowed to cool slowly at a rate of less than 1° C./s, the fill factor diminished by 14% to 0.46. However, when the same cell was reheated and cooled rapidly at a rate of about 100° C./s , the fill factor was found to increase some 15% to a new value of 0.54. Examination of the current-voltage characteristics of this cell after each heating and cooling cycle confirmed that the observed changes in fill factor were due to changes in series resistance. Furthermore, changes in open circuit voltage and short circuit current were negligible.

Regarding the significance of carrying out Steps **240** and **250** after metal deposition Step **230**, it was found that air heating Step **228** merely functioned as taught by the above noted Basol publication. The degree of effectiveness depended on the conditions of CdTe deposition Step **220**. For example, heating in air prior to depositing metal contact layer **130** was more beneficial for cells having CdTe deposited in an argon atmosphere than for CdTe deposited in an oxygen atmosphere. In either case, however, the rate of cooling had no effect. In contrast, heat treating and rapid cooling after contact deposition Step **230**, in accordance with the invention, always improved fill factor.

It was also found that etching Steps **225** or **229** can be omitted when the cell is heated and rapidly cooled according to the invention.

These observations are consistent with the hypothesis that heating and rapid cooling act to improve the electrical properties of the CdTe/metal contact.

It is believed that the scientific principle governing the invention is related to the phase equilibria of CdTe. Examination of the phase diagram in W. Abers, "Physical Chemistry of Defects", *Physics and Chemistry of II-VI Compounds,* M. Aven and J. S. Prenner, eds. American Elsevier, N.Y. (1967) shows that the single phase region for CdTe is quite broad at temperatures above 400° C., but narrows rapidly at lower temperatures. The implication of this is that slightly non-stoichiometric CdTe will contain precipitates of Cd or Te if equilibrated at low temperatures. Rapid cooling, however, will "freeze in" the high temperature equilibrium.

The process of the invention has also been applied to cells having a structure which is the inverse of that shown in FIG. **1**. Such a cell would be fabricated by first depositing the CdTe on a suitable substrate, optionally heat treating the CdTe, next depositing CdS, and finally depositing a transparent conductive layer onto the CdS. Positive results were indicated when a cell having the configuration glass/metal/CdTe/CdS/ITO, with the semiconductor layers deposited by physical vapor deposition, was heat treated and rapidly cooled in accordance with the teachings of the invention.

Substitution by (ZnCd)S for CdS and/or by (HgCd)Te or (ZnCd)Te for CdTe are within the scope of the invention. Moreover, the practice of the invention need not be limited by the method selected for depositing the semiconductor and contact layers. Among deposition methods that may be selected by one skilled in the art are: physical vapor deposition; close space transport; close space sublimation; sputtering; chemical vapor deposition; electrodeposition; screen printing; electrophoresis; spray pyrolysis; electron beam evaporation; ion plating; and liquid phase epitaxy.

Furthermore, it is contemplated that heating and rapid cooling in accordance with the teachings of this invention may be adapted by those skilled in the art for improving the electrical contact behavior of devices utilizing Te containing II-VI compound semiconductors such as tandem photovoltaic solar cells, optical and infrared detectors, photoemissive displays, light emitting diodes, thin film transistors and the like.

What is claimed is:

1. In a method of fabricating thin film photovoltaic solar cells made by sequentially forming a first contact layer on a substrate, a first semiconductor layer, and a second semiconductor layer, and a second contact layer, wherein at least one of the contact layers is transparent and at least one of the semiconductor layers comprises a tellurium containing II-VI compound the improvement being the steps of heat treating the cell after the second contact layer has been formed, and then rapidly cooling the cell at a temperature reduction rate of at least 10° C. per second.

2. In the method of claim **1** wherein the heat treating step is at a temperature of from 300° C. to 500° C. for a period of time from 10 minutes to 100 minutes.

3. In the method of claim **2** wherein the heat treating step is at 400° C. for about 15 minutes.

4. In the method of claim **2** wherein the rapid cooling step results in a temperature reduction of 100° C. per second.

5. In the method of claim **2** wherein the heat treating step is performed in air.

6. The method of claim **2** wherein the rapid cooling step is performed by placing the cell in thermal contact with a heat sink.

7. The method of claim **1** wherein one of the semiconductor layers is selected from the group consisting of CdTe, (HgCd)Te and (ZnCd)Te.

8. In the method of claim **8** wherein said one of the semiconductor layers is CdTe.

9. The method of claim **8** wherein the other semiconductor layer selected from the group consisting of CdS and (ZnCdS).

10. The method of claim **10** wherein said other semiconductor is CdS.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,709,466

DATED : December 1, 1987

INVENTOR(S) : Brian E. McCandless and Robert W. Birkmire

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 4, lines 42 and 44 "8" should be --7--;

Col. 4, line 47 "10" should be --9--.

Signed and Sealed this

Sixth Day of September, 1988

Attest:

DONALD J. QUIGG

Attesting Officer

Commissioner of Patents and Trademarks

US005304499A

United States Patent [19]

Bonnet et al.

[11] **Patent Number: 5,304,499**

[45] **Date of Patent: Apr. 19, 1994**

[54] **METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS**

[75] Inventors: **Dieter Bonnet**, Friedrichsdorf; **Beate Henrichs**, Eschborn; **Karlheinz Jager**, Kronberg; **Hilmar Richter**, Frankfurt am Main, all of Fed. Rep. of Germany

[73] Assignee: **Battelle-Institut e.V.**, Frankfurt am Main, Fed. Rep. of Germany

[21] Appl. No.: **929,514**

[22] Filed: **Sep. 28, 1992**

[30] **Foreign Application Priority Data**

Oct. 3, 1991 [DE] Fed. Rep. of Germany 4132882

[51] **Int. Cl.**^{5} **H01L 31/18**; H01L 31/072

[52] **U.S. Cl.** **437/5**; 136/260; 136/264; 437/102; 437/234; 427/76

[58] **Field of Search** 437/4-5, 437/81, 87, 103, 139, 234; 427/74, 76; 136/260, 264

[56] **References Cited**

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4,650,921	3/1987	Mitchell	136/258

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"Thin Film Solar cells", Katsuri Lal Chopr, Suhit Ranjan Das, Plenum Press, New York (1983), pp. 288-290; 295-304; 408-409.

Primary Examiner—Aaron Weisstuch

Attorney, Agent, or Firm—Lane, Aitken & McCann

[57] **ABSTRACT**

A method of making pn CdTe/CdS thin film solar cells, in which a transparent TCO layer is deposited as a front contact on a transparent substrate in the form of inexpensive soda-lime glass, and is preferably provided with an ultra-thin indium layer, which is in turn coated with the CdS layer, wherein the thus coated substrate is brought to the CdTe coating at a temperature between 480° C. and 520° C., which is maintained during the ensuing rapid CdTe deposition using the close-spaced sublimation method with a preferred rate of deposition of 5 to 15 μm/min in an inert atmosphere. The indium layer dissolves during this deposition and effects the necessary n-doping of the CdS layer, without an additional method step. Solar cells can be made in this way with high efficiency in an inexpensive method, suitable for mass production.

10 Claims, 2 Drawing Sheets

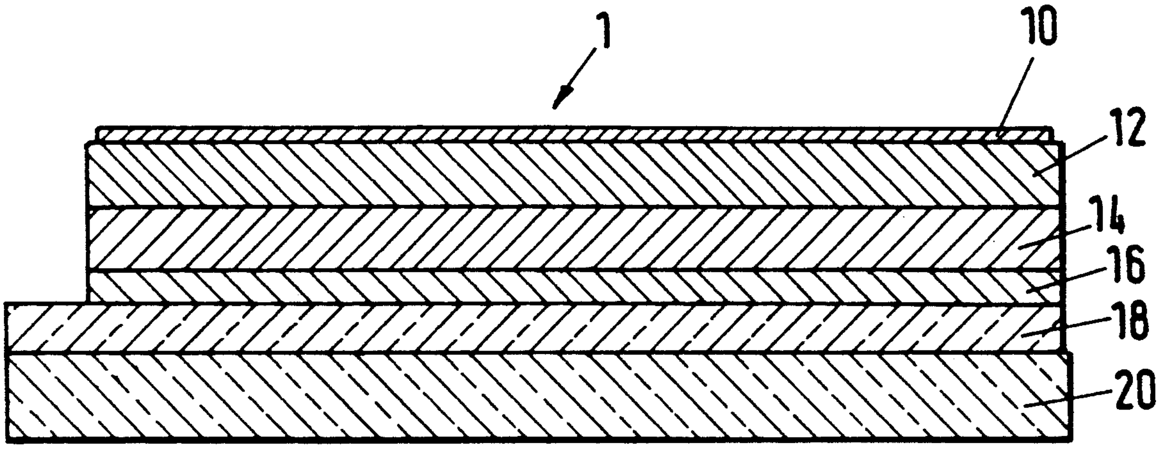


Fig.1

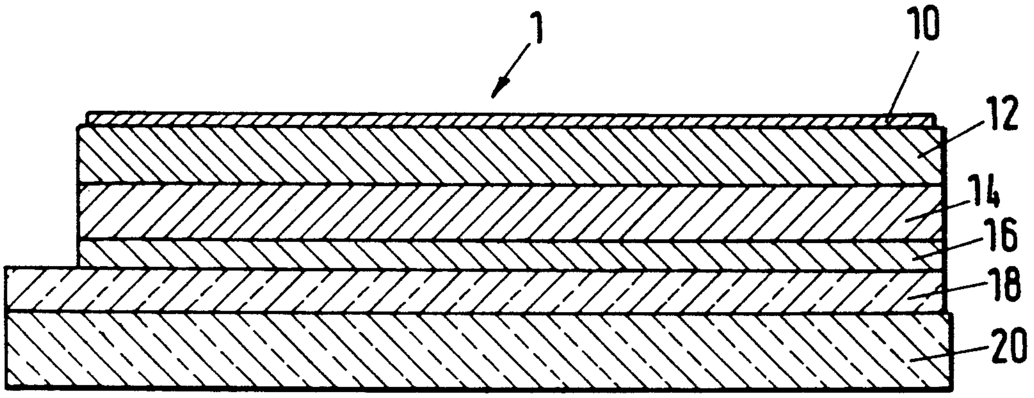


Fig.2

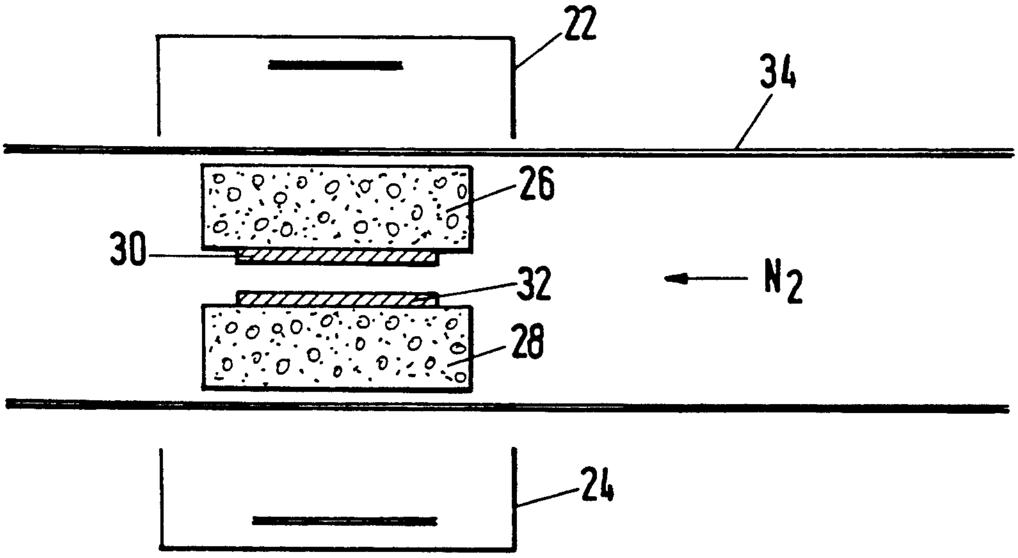


Fig.3

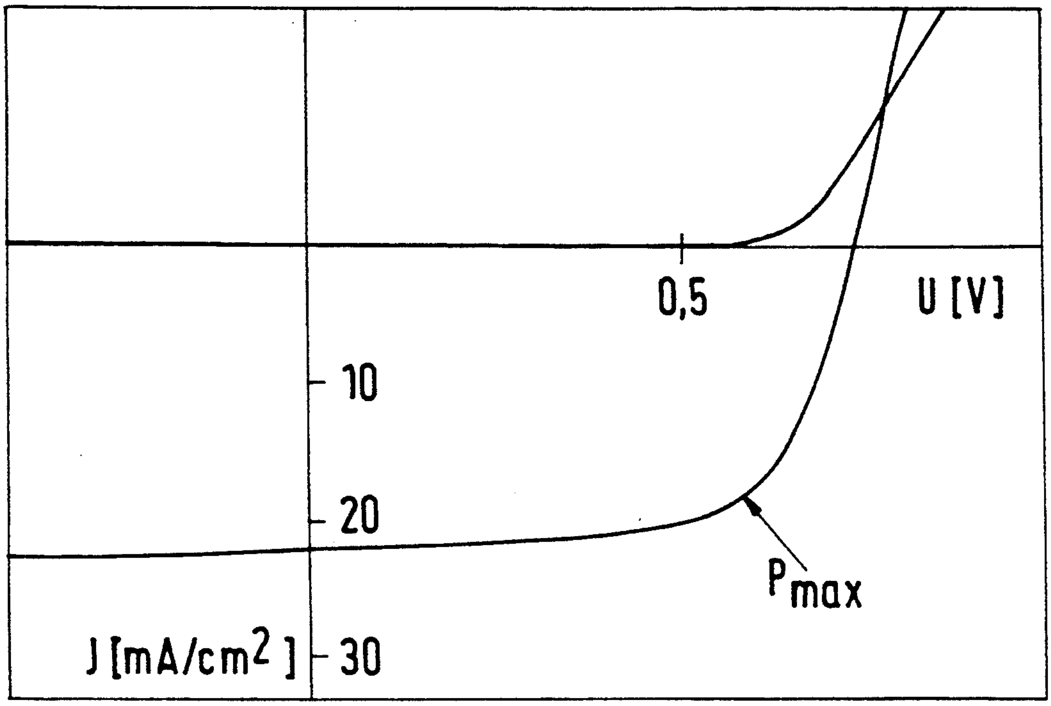
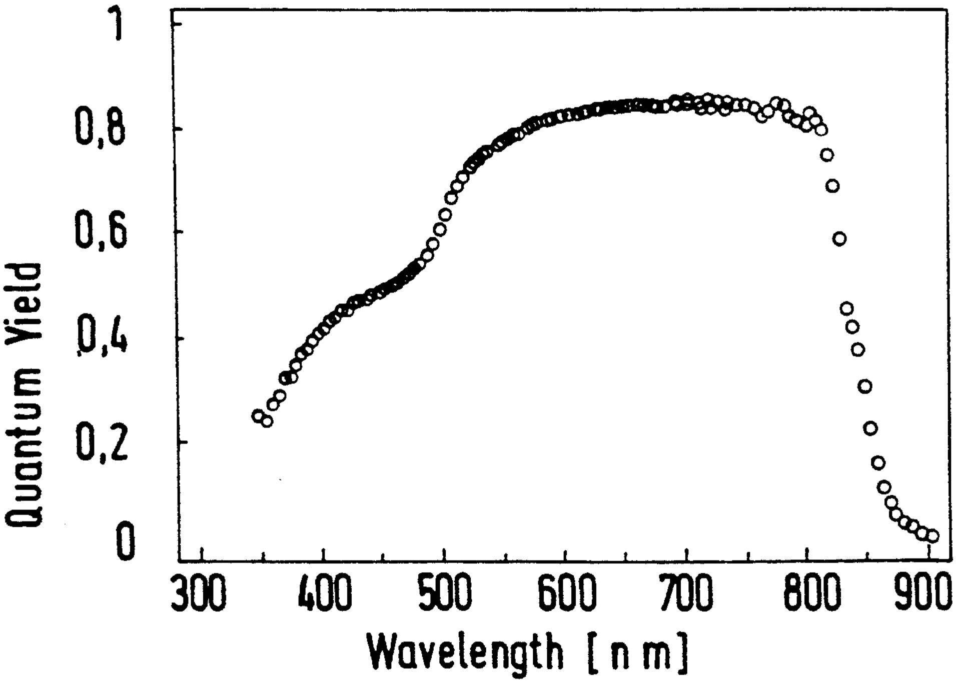

0,5
U [V]
10
20
30
J [mA/cm2]
Pmax

Fig.4


Quantum Yield
1
0,8
0,6
0,4
0,2
0
300
400
500
600
700
800
900
Wavelength [nm]

METHODS OF MAKING PN CDTE/CDS THIN FILM SOLAR CELLS

The present invention relates to methods of making polycrystalline pn CdTe/CdS thin film solar cells and especially such methods which make inexpensive mass production possible.

Because of its favorable energy gap of 1.45 eV, CdTe is ideally suited as photo-active material for solar cells. Moreover, polycrystalline layers of a few μm thickness can be made by various methods (physical or chemical evaporation/sublimation in a vacuum, electrolytic deposition, screen printing, spray methods), which in general are subjected to a chemical-thermal post-treatment to improve their electronic properties (R. W. Birkmire et al, Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77–84). These two characteristics make CdTe one of the most interesting candidates for inexpensive thin film solar cells.

CdTe came into use in thin film solar cells for the first time around 1960. At the end of the 70's efficiencies for such solar cells of around 9% were reported. For example, U.S. Pat. No. 4,207,119 (Yuan-Sheng Tyan, 1980) describes a CdS/CdTe solar cell with oxygen as the dopant in both semiconductor layers CdS and CdTe of the cells. There is a disadvantage in the use of oxygen during the manufacture of the layers, since oxidation of the CdTe source can occur easily at too high an oxygen concentration in the deposition chamber, whereby the process of deposition is adversely affected or even interrupted. Moreover, the temperature of the substrate on which the polycrystalline CdTe layer was deposited is at least 575° C. and expensive temperature resistant glass substrates are used (with softening temperatures of 650° to 700° C.). Below a substrate temperature of 575° C. a significant fall-off in the attainable efficiency is observed. Thus, the CdTe layer was deposited experimentally at low temperatures in an atmosphere containing oxygen down to 500° C., when, however, an efficiency of less than 4% resulted. The possibility of increasing the efficiency by 1 to 2% by additional subsequent oxygen post-treatment was also proposed, whereby only values of 6% maximum resulted at 500° C. Attempts were also made to deposit the CdS layer free from oxygen, in contrast to the CdTe layer. The attempts showed, however, that the CdS layer also had to be deposited in an atmosphere containing oxygen, in order to be able to attain an efficiency of up to 8.9% at substrate temperatures above 575° C. In the experiments performed, CdTe layers 0.5 μm thick were deposited in 2 min. With a minimum thickness of around 2 to 3 μm needed for physical reasons, approximately 10 min. is already needed for the deposition.

In U.S. Pat. No. 4,650,921 (Kim W. Mitchell, 1987) there is described a pn CdTe/SnO_2 thin film solar cell, in which the polycrystalline CdTe layer is also deposited at high substrate temperatures (600°–650° C.), whereby the usual expensive temperature resistant glass substrates are also used. The CdTe source is first heated to 600° C. and, on attaining this temperature, the substrate previously heated to 450° C. is rapidly heated up to 650° C. The CdTe deposition rates to obtain a CdTe layer about 10 μm thick in the CSVT (closed space vapor transport) methods are very small, and deposition must take place for approximately 20 minutes.

As well as these vacuum-assisted deposition methods, electrolytic methods were described in the 80's (e.g. B. M. Basol, *Solar Cells*, 23, (1988) pp. 69–88; V. Ramanathan et al. *Proc. 20th IEEE Photovoltaic Specialists Conf.*, Las Vegas, (1988) pp. 1417–1421), as well as screen printing (e.g., S. Ikegami, *Solar Cells*, 23, (1988) pp. 89–105) or spray methods (e.g. J. F. Jordan, *Solar Cells*, 23, (1988) pp. 107–113), for making polycrystalline CdTe layers.

The electrolytic deposition takes place in an aqueous solution of $CdSO_4$ and Te_2O_3 at temperatures of about 90° C. In order to avoid fluctuations in the stoichiometric composition of the growing CdTe layer, it is necessary to adhere to very small and hence uneconomic rates of deposition of only about 1 μm/hour.

In the screen printing method, suspensions of Cd and Te powders are applied to a substrate and sintered with high usage of material into relatively thick layers of around 30 μm, whereby Cd and Te react to form CdTe. High temperatures of more than 700° C. are also required here, which necessitates the use of expensive substrates.

In the spray method, an aqueous solution of compounds containing Cd and Te in the form of a fine droplet aerosol is sprayed onto a substrate heated to about 400° C. The growing CdTe layer is markedly inclined to porosity, so that relatively thick layers have to be made in order to ensure the necessary impermeability of the layers. An uneconomic high usage of materials is again involved. Furthermore, a significant loss of the sprayed solution is inherent in the method, in that this fills the whole reaction chamber as a fine aerosol and is lost on the walls and through the exhaust air, whereby only a moderate material yield of the compounds of the Cd and Te compounds can be achieved. The chemical-thermal post treatment proves to be particularly critical in the spray method.

The invention is thus based on the problem of providing an improved method for making pn CdTe thin film solar cells which is especially suitable for inexpensive mass production and makes the production of satisfactory solar cells possible.

The solution to this problem according to the invention involves a complete departure from the high substrate temperatures hitherto regarded as necessary in order to be able to make solar cells with efficiencies around and above all in excess of 10%. Thus, the inventor has surprisingly ascertained that it is possible to make satisfactory solar cells with high efficiency if care is taken that the temperature of the transparent substrate provided with the TCO layer and the CdS layer is brought to a temperature below about 520° C. and above about 480° C. before the CdTe coating and this temperature is maintained also during the following coating. During this time the CdTe layer is deposited steadily in an inert gas atmosphere. In the oxygen-free processes in the state of the art, substrate temperatures of 600° C. and more were universally employed.

It has furthermore been found that inexpensive soda-lime glass (window glass) can be used as the substrate material and resulted in solar cells with a high efficiency of more than 10% in all embodiments tested. This represents a significant technical advance, since the substantial reduction in cost widens the scope for use of the mass-produced product. Hitherto, it has not been considered or even thought possible for solar cells of this kind to be made with window glass and be not merely functional but seriously capable of use.

Furthermore, it has been found that, with such temperature control of the substrate, it is possible to work

with a high CdTe deposition rate of between 5 and 15 μm/min, so that the growth of the CdTe layer takes place from the very start at a temperature favoring the attainment of the required (photo)electronic characteristics, so that a good efficiency of the cells is likewise obtainable. Such high rates of deposition have not been possible hitherto, either in oxygen or in inert gases.

Preferably, one proceeds in accordance with the invention as follows. Inexpensive, ordinary soda-lime glass ("window glass") is used as the transparent substrate and is coated with a transparent, electrically conductive TCO (transparent conducting oxide) layer. This consists, for example, of a suitably doped tin oxide layer, for example of ITO or a modified ITO layer. The TCO layer also forms the electrical front contact of the solar cell. A thin CdS layer (thickness approximately 80 to 120 nm, preferably 100 nm) is then evaporated on in a high vacuum, with doping preferably achieved in the manner indicated below.

The deposition of the photo-active CdTe layer then takes place directly on the CdS layer, according to the close-space (CSS) method (close-spaced sublimation). The substrate carrying the CdS layer is brought for this to a temperature, of 480° to 520° C., preferably 500° C., in a steady heating process, preferably in approximately 3 min. The TCO layer suffers no adverse effects in the course of this short heating phase, since it is protected by the CdS layer. During this time the CdTe source attains a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the substrate temperature has reached (after e.g. the 3 minutes) 480° to 520° C., preferably 500° C., is the CdTe source brought in approximately 1 minute to such a temperature (e.g., in the range from 700° to about 770° C., preferably about 740° C.), that a CdTe deposition rate of 5 to 15 μm/min., preferably about 10 μm/min., is attained, so that the required CdTe layer 5 to 10 μm thick can be created in the short time of approximately 1 minute.

During the CdTe deposition a pressure of about 0.1 mbar nitrogen (or similar inert gases such as helium, argon or hydrogen) is preferably so maintained in the reaction chamber (quartz tube) that the same amount of gas is fed in as is pumped out, in the nature of a dynamic balance through the various connections of the reaction chamber.

The CdTe source from which the material to be deposited on the CdS layer sublimes is preferably located at a small distance of only about 2 to 3 mm from the substrate surface. On account of the small distance between the substrate and the CdTe source, as well as their direct opposition, there is nearly 100% usage of the CdTe starting material. Furthermore, the small thickness of the CdTe layer possible according to the invention contributes to inexpensive handling of the valuable semiconductor material. The short deposition time also acts inexpensively in the course of this method.

During the described operation of the CdTe deposition, the substrate and CdTe source are preferably held in opposed graphite blocks, which are heated by heating elements (e.g. halogen lamps), in order to create the required temperatures. The latter are adjusted by suitable manual or computer-controlled regulation of the heating load of the heating element. The $CdCl_2$ tempering which is carried out at the end of the CdTe deposition is known per se.

The further development of the method in accordance with the present invention contributes significantly to mass-production, in that the method of doping of the CdS layer is substantially facilitated. It is also possible to increase the efficiency of the finished solar cell by this measure.

Finally, in contrast to the known critical oxygen doping, it is possible to operate without endangering the CdTe source by oxidation during the CdTe coating at high pressure.

It is beneficial for obtaining a good efficiency of the pn CdTe/CdS thin film solar cell to use an n-type CdS with high conductivity, of the order of magnitude of 0.1 S/cm. While a CdS layer made at about 150° C. fulfills this condition well, a CdS layer subjected to a thermal process, as in the CdTe deposition, only exhibits a very small conductivity of $<10^{-5}$ S/cm. In order to obtain a desirable order of magnitude of 0.1 S/cm for the conductivity of the CdS even after the thermal stress of the CdTe deposition, an ultra-thin indium layer with a thickness of approximately 0.1 to 0.5 nm, preferably 0.2 nm, is applied in a high vacuum to the TCO layer at approximately 25° C., before the CdS layer is applied preferably in the manner given above. The thickness of the indium layer is so selected that the diffusion of the indium into the CdS layer during the CdTe deposition at the predetermined substrate temperature, which preferably lies between 480° and 520° C., creates such n-type doping in the CdS that the conductivity value stays in the required order of magnitude of 0.1 S/cm. The required and desirable n-type doping of the CdS layer is thus effected inexpensively without additional expense during the CdTe deposition. It should further be noted that, even without the indium doping of the CdS layer, efficiencies of around and in excess of 10% are obtained.

After the customary $CdCl_2$ tempering (R. W. Birkmire et al., Proc. Polycrystalline Thin Film Program Meeting, Lakewood, Colo., USA, (1989) pp. 77-84), a gold layer approximately 5 to 10 μm thick is evaporated onto the CdTe layer as the back contact. In order to avoid series resistance, the gold layer preferably has an evaporated inexpensive metal layer (e.g. aluminum) (about 100-200 nm) or is painted with a conductive paste and so brought up to the conductivity necessary for the flow of the photocurrent.

The illumination of the solar cell takes place through the transparent glass substrate.

The features of the special doping of the CdS layer according to the invention are preferably combined with the other features according to the invention. Thus, with the substrate temperatures controlled in accordance with the invention, the mixing of the CdS layer and the indium layer can be well achieved. In combination with the likewise possible high rate of deposition, the efficiency of the method and its suitability for mass production are further improved.

The features according to the invention, taken alone and in their combination, thus promote inexpensive mass production of pn CdTe/CdS thin film solar cells with a type of construction previously known. Inexpensive substrate materials can be used and high yields of the expensive substrate materials with high rates of deposition for the semiconductor layers are possible. The doping step which was previously frequently critical is markedly improved and rationalized. In addition, the features referred to contribute to high efficiency. The inventive features thus contribute an important step towards an alternative energy source through solar

cells, which arises both from the mass production and from a high efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be further explained below with reference to the drawings, in which:

FIG. 1 shows a section, in a schematic view, through a pn CdTe/CdS thin film solar cell made according to a preferred embodiment of the method according to the invention,

FIG. 2 shows a section, in a schematic view, through an apparatus suitable for carrying out the method according to the invention,

FIG. 3 shows the current/voltage characteristic of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1, and

FIG. 4 shows the graph of the (external) absolute quantum yield as a function of wavelength of a pn CdTe/CdS thin film solar cell made according to the method explained with reference to FIG. 1.

FIG. 1 shows a schematic section through a pn CdTe/CdS thin film solar cell **1**, which has been made by a preferred embodiment of the method according to the invention. The transparent substrate **20** consists of soda-lime glass ("window glass") and is coated with a transparent, electrically conductive TCO layer **18**. There follow an ultra-thin indium layer **16** and a CdS layer **14** (e.g. 0.10 μm thick). The photo-active CdTe layer **12** (preferably around 5 μm thick but not critical in thickness for the cell as a whole so long as it stays above 2 to 3 μm) is deposited on the CdS layer according to the foregoing techniques. As has further been indicated, the layers **16** and **14** mix so tht the indium layer **16** dissolves in the layer **14** because of the diffusion of the indium atoms and is no longer identifiable as such in the finished solar cell **1**. The CdS layer thus contains the indium atoms of the indium layer **16** in dispersed form after manufacture, as the desired and necessary n-type doping.

This n-type doping of the CdS layer taking place at the same time as the deposition of the CdTe layer **12** represents a further advance both in relation to improving the suitability of the method to inexpensive mass production, as well as to the creation of a solar cell with high efficiency. The indium layer **16**, preferably 0.1 to 0.5 nm thick and preferably evaporated in a high vacuum at about 25° C., is therefore only identifiable as such up to the method step preceding the CdTe deposition.

After completion of the CdTe deposition, there follows after the $CdCl_2$ tempering the application of an electrically conductive metal contact **10** on the CdTe layer **12**, serving as the back contact of the solar cell **1**. The TCO layer **18** functions as the front contact of the solar cell **1**. The illumination of the solar cell **1** takes place through the glass substrate **20** and the TCO layer **18**.

The CdTe deposition method is also especially important. In FIG. 2 there is shown a reaction chamber which is preferably used, likewise in schematic cross-section. This consists of a quartz reactor **34** and graphite blocks **26** and **28**, as well as heating elements **22** and **24** (e.g. halogen lamps), with which the graphite blocks **26** and **28** are heated. The glass substrate **20** with the TCO layer **18** as well as the indium layer **16** and the CdS layer **14**, shown as element **30** in FIG. 2, is so attached to the upper graphite block **26** that the glass substrate lies against the graphite block **26** and the CdS layer **24** is directed towards the CdTe source. The CdTe source **32**, e.g. in the form of a polycrystalline disc, is located on the lower graphite block **28**. Instead of a polycrystalline disc, a pressed blank of CdTe powder or a device with CdTe powder can obviously be used as the CdTe source **32**.

The CdTe deposition is effected in the reaction chamber **33** according to a procedure in which, as already particularly explained above, it is crucial that the variation with time of the temperature of the element **30** and of the CdTe source **32** is such that the element **30** including the CdS layer is brought up to a temperature of 480°-520° C., preferably 500° C., in a steady heating process (without interruption) in e.g., 3 min., whereby the TCO layer **18** does not suffer any adverse effects in the course of this short heating phase, since it is protected by the CdS layer **24**. During this time the CdTe source **32** reaches a temperature at which as yet no appreciable sublimation of the CdTe takes place. Only when the temperature of the element **30** has reached 480°-520° C., preferably 500° C., is the CdTe source **32** brought up in about 1 min. to such a temperature that a CdTe deposition rate onto the CdS layer **14** of 5 to 15 μm/min, preferably about 10 μm/min, is obtained and the required CdTe layer **12** of 5 to 10 μm thickness can be created in the short time of about 1 minute. This procedure results in the growth of the CdTe layer **12** taking place from the start at a temperature favoring the required (photo) electronic characteristics. The temperature of the element **30** is so selected that cheap soda-lime glass can be used as the material for the substrate **20**. The pressure in the reaction chamber **34** amounts during the CdTe deposition to about 0.1 mbar and is maintained by inflow or pumping out nitrogen (or helium, argon or hydrogen).

The heating load of the heating elements **22** and **24** can be optionally varied manually or by computer control.

In FIGS. **3** and **4** there are shown the current/voltage characteristic and the (external) absolute quantum yield as a function of the wavelength respectively of a pn CdTe/CdS thin film solar cell made in accordance with the above method. As can be seen from FIG. **3**, the short-circuit current density of the manufactured solar cell amounts to 22.8 mA/cm^2 with a no-load voltage of 0.750 V and a space factor of 65%. The active surface of the solar cell of the embodiment set forth amounts to 0.388 cm^2. This gives an efficiency of 11.0% (relative to illumination with 100 mW/cm^2, 1.5 AM overall).

The (external) absolute quantum yield according to FIG. **4** exhibits a constant value over the substantial part of the spectrum (about 820–520 nm) with a value around 85%. The fall off at 520 μm is caused by the absorption of the CdS layer **14**.

We claim:

1. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO layer and an n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere free of oxygen according to the close-spaced sublimation method from a CdTe source and is provided with an electrically conducting back contact,

characterized in that,

a substrate of soda-lime glass is used, the substrate is provided with the TCO layer, and the CdS layer is brought to a temperature between approximately 480° C. and 520° C. before coating with the CdTe

layer, said temperature being maintained during the CdTe coating.

2. A method according to claim 1, characterized in that a $CdCl_2$ tempering step is employed after the CdTe coating.

3. A method according to claim 1, characterized in that the substrate with the TCO layer and the CdS layer is brought to a temperature of about 500° C. before the CdTe coating, which temperature is maintained during the CdTe coating.

4. A method according to claim 1, characterized in that the heating of the substrate provided with the TCO layer and the CdS layer is effected in a steady heating process over between approximately 1 and 5 min.

5. A method according to claim 4, characterized in that the heating is effected in approximately 3 min.

6. A method according to claim 1, characterized in that the deposition rate of the CdTe on the CdS layer is approximately 5 to 15 μm/min.

7. A method according to claim 6, characterized in that the CdTe layer is deposited in approximately 1 min.

8. A method according to claim 6, characterized in that the CdTe deposition rate is adjusted to 10 μm/min.

9. A method according to claim 1, characterized in that the variation with time of the temperature of the substrate provided with the TCO layer and the CdS layer and of the CdTe source is so controlled that the substrate is brought in a steady heating process to a temperature of 480° to 520° C. in approximately 1 to 5 min. and, during this time, the CdTe source is brought to a temperature at which there is no appreciable sublimation of the CdTe, and in that, only when the temperature of the substrate with the TCO and CdS layers has attained the desired temperature between 480° and 520° C., the CdTe source is brought in approximately 1 min. to a temperature at which a deposition rate on to the CdS layer is obtained such that the required CdTe layer can be applied in approximately 1 min.

10. A method of making a pn CdTe/CdS thin film solar cell, in which a transparent substrate is provided with a transparent, electrically conducting TCO front contact layer and an overlying n-doped CdS layer, on which a CdTe layer is deposited in an inert atmosphere according to the close-spaced sublimation method and is provided with an electrically conducting back contact, characterized in that indium is used for the n-doping of the CdS layer and in that, before the deposition of the CdS layer, an ultra-thin indium layer less than 0.5 nm thick is applied to the TCO layer and in that the In and CdS layers so mix during the deposition of the CdTe layer that the indium layer is dissolved by diffusion of the indium atoms into the CdS layer and is no longer identifiable as such in the finished solar cell and the CdS layer includes the indium atoms of the indium layer in dispersed form as n-doping.

* * * * *

US005994642A

United States Patent [19]

Higuchi et al.

[11] **Patent Number: 5,994,642**

[45] **Date of Patent: Nov. 30, 1999**

[54] **METHOD FOR PREPARING CDTE FILM AND SOLAR CELL USING THE SAME**

[75] Inventors: **Hiroshi Higuchi**, Katano; **Seiji Kumazawa**, Kadoma; **Takashi Arita**, Hirakata; **Akira Hanafusa**, Hirakata; **Mikio Murozono**, Hirakata; **Tetsuya Aramoto**, Osaka, all of Japan

[73] Assignee: **Matsushita Battery Industrial Co., Ltd.**, Osaka, Japan

[21] Appl. No.: **09/000,089**

[22] PCT Filed: **May 27, 1997**

[86] PCT No.: **PCT/JP97/01791**

§ 371 Date: **Mar. 13, 1998**

§ 102(e) Date: **Mar. 13, 1998**

[87] PCT Pub. No.: **WO97/45880**

PCT Pub. Date: **Dec. 4, 1997**

[30] **Foreign Application Priority Data**

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Apr. 28, 1997	[JP]	Japan	9-110727
Apr. 28, 1997	[JP]	Japan	9-110728

[51] **Int. Cl.**^{6} **H01L 31/00**

[52] **U.S. Cl.** **136/260**; 136/264; 427/74; 427/76; 427/255.2; 438/761; 438/763

[58] **Field of Search** 136/260, 264; 427/74, 76, 255.2; 438/761, 763

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Primary Examiner—Mark Chapman
Attorney, Agent, or Firm—Akin, Gump, Strauss, Hauer & Feld, L.L.P.

[57] **ABSTRACT**

A method for forming a CdTe film of good quality by an improved close-spaced sublimation process is disclosed. This method comprises: a step of applying a paste which contains material for CdTe semiconductor on a supporting member, thereby to form a coating film which contains the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, and causing the material for the semiconductor in the coating film to evaporate.

16 Claims, 5 Drawing Sheets

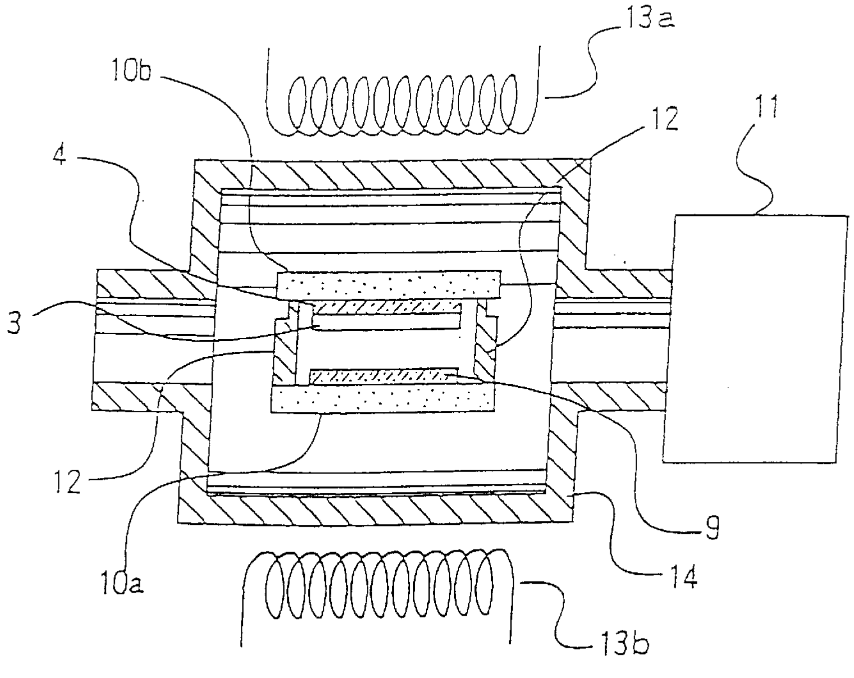


FIG. 1

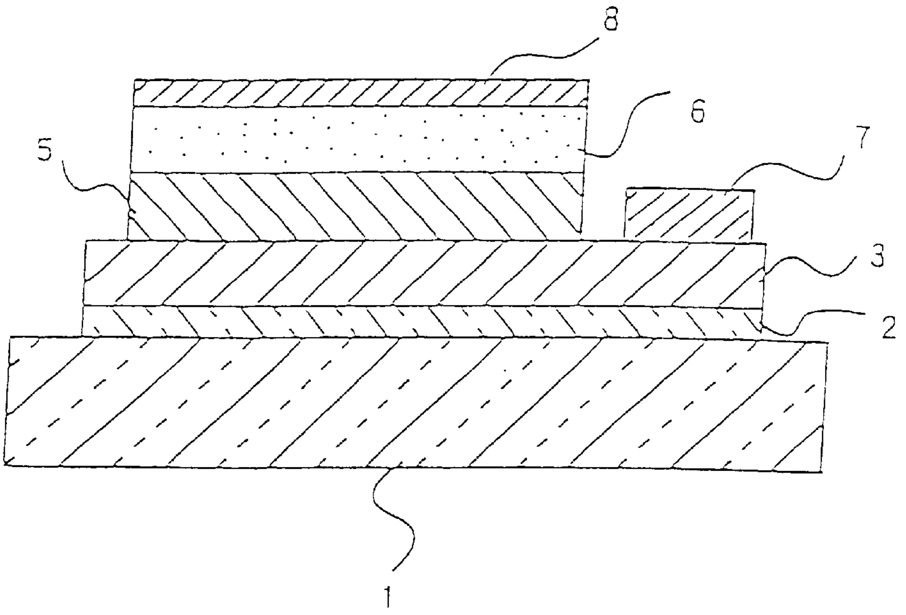
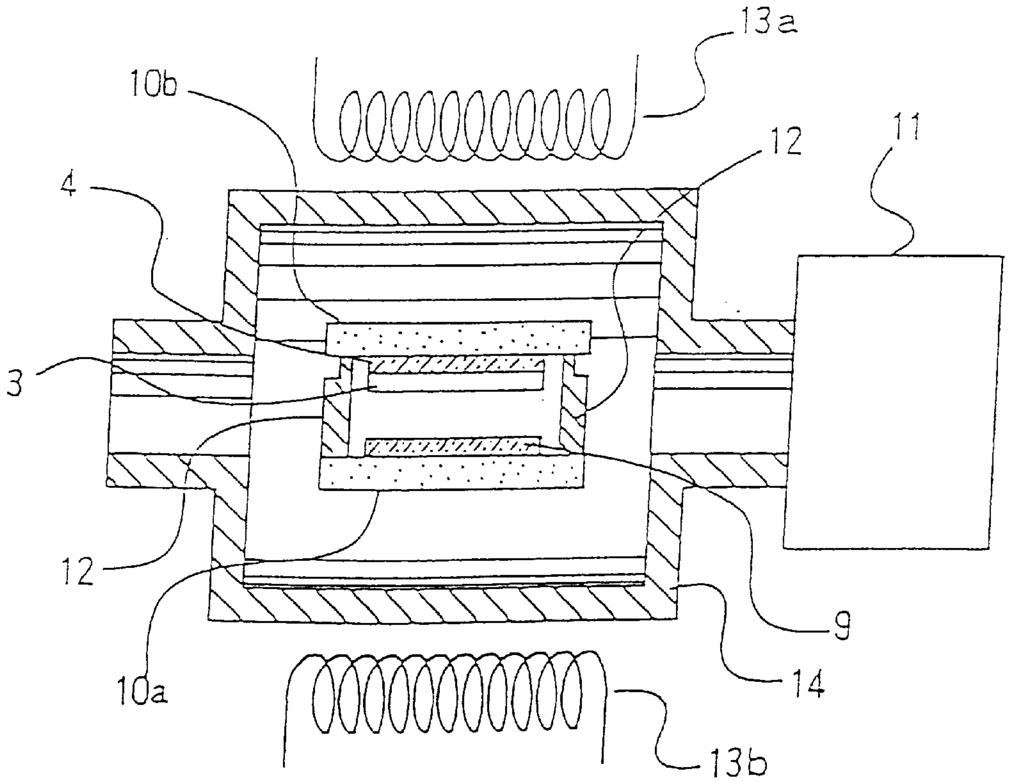
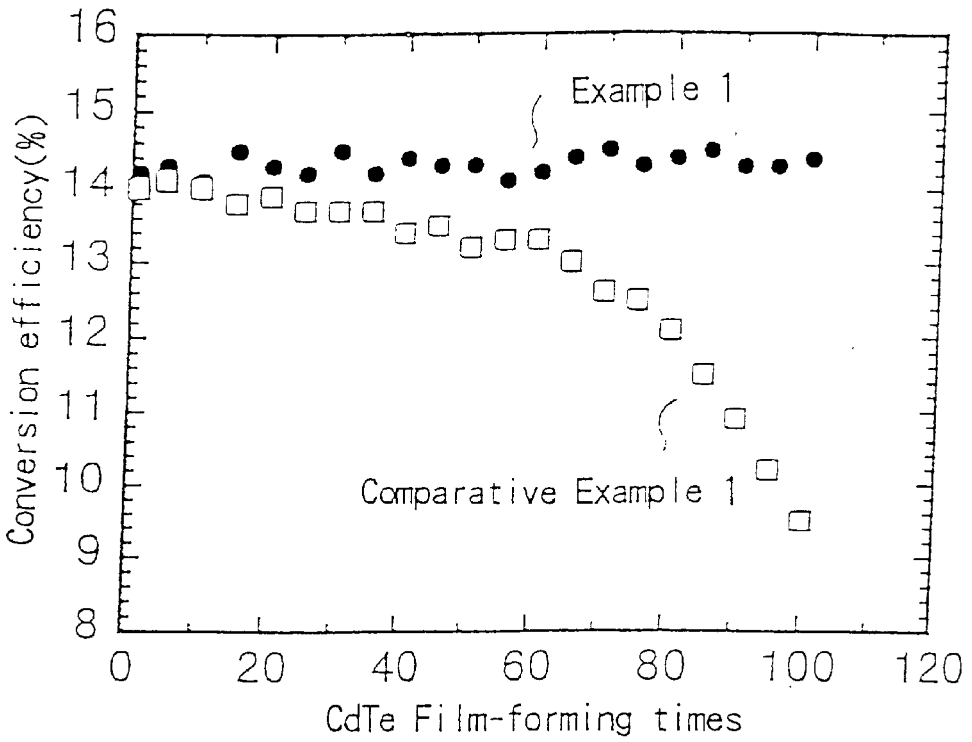


FIG. 2



F I G. 3


16
15
14
13
12
11
10
9
8
Conversion efficiency(%)
0
20
40
60
80
100
120
CdTe Film-forming times
Example 1
Comparative Example 1

F I G. 4

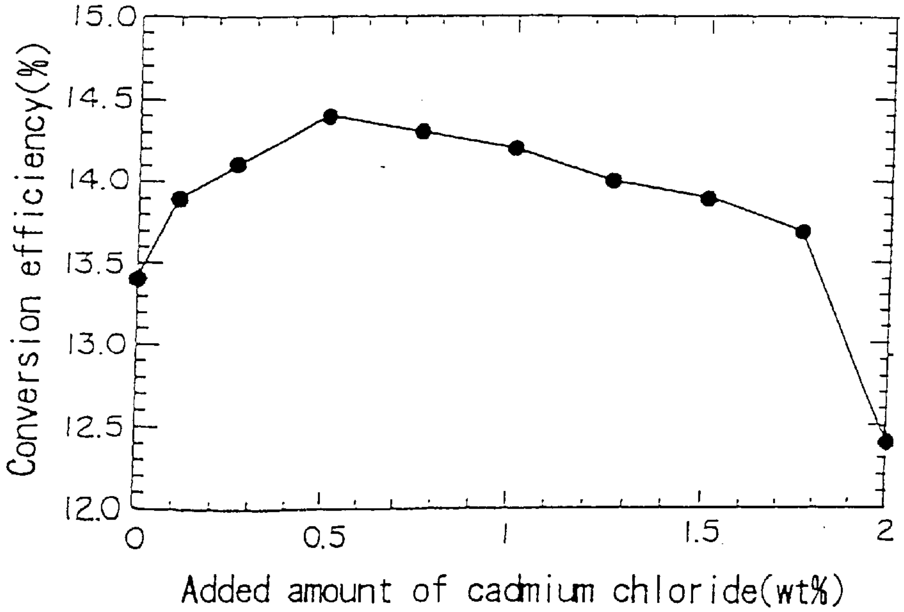

15.0
14.5
14.0
13.5
13.0
12.5
12.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 5

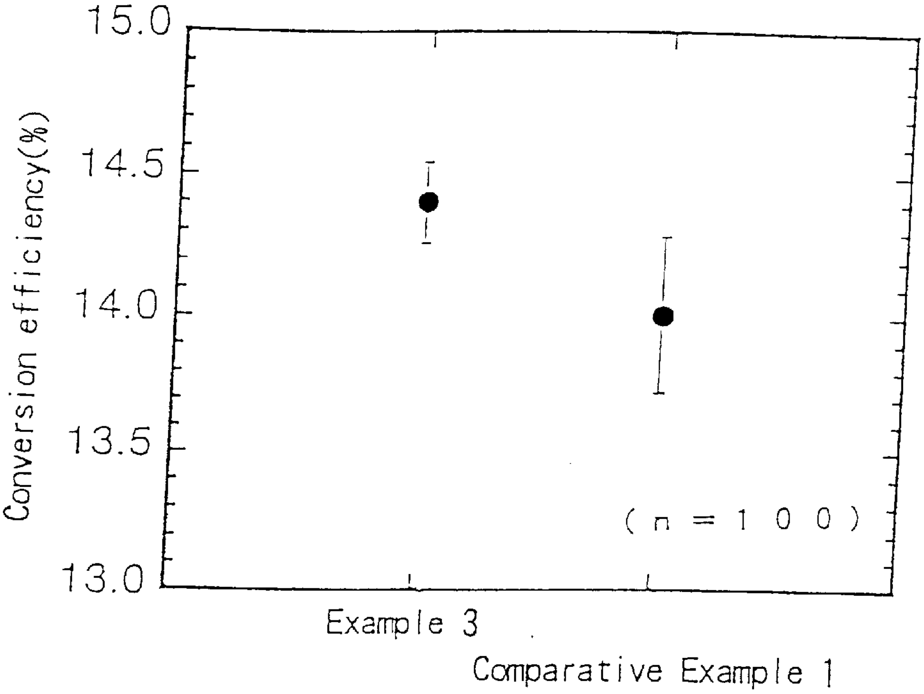

15.0
14.5
14.0
13.5
13.0
Conversion efficiency(%)
(n = 100)
Example 3
Comparative Example 1

FIG. 6

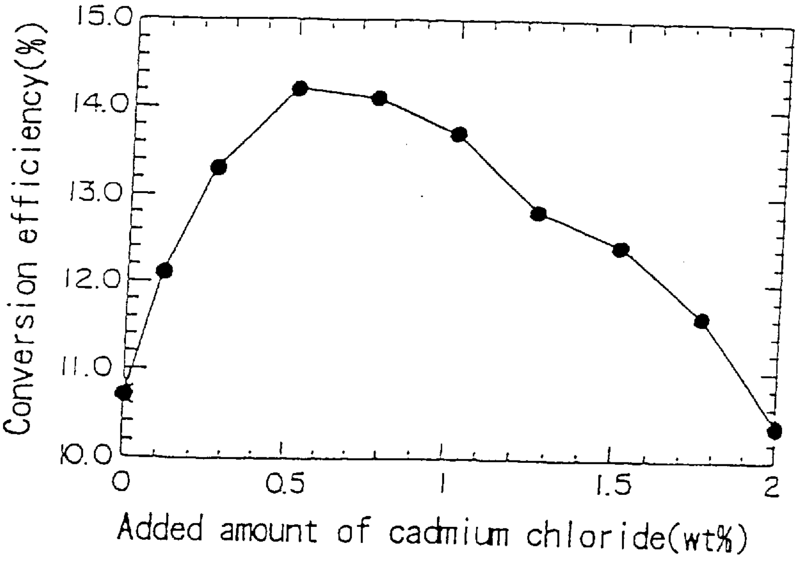

15.0
14.0
13.0
12.0
11.0
10.0
Conversion efficiency(%)
0
0.5
1
1.5
2
Added amount of cadmium chloride(wt%)

FIG. 7

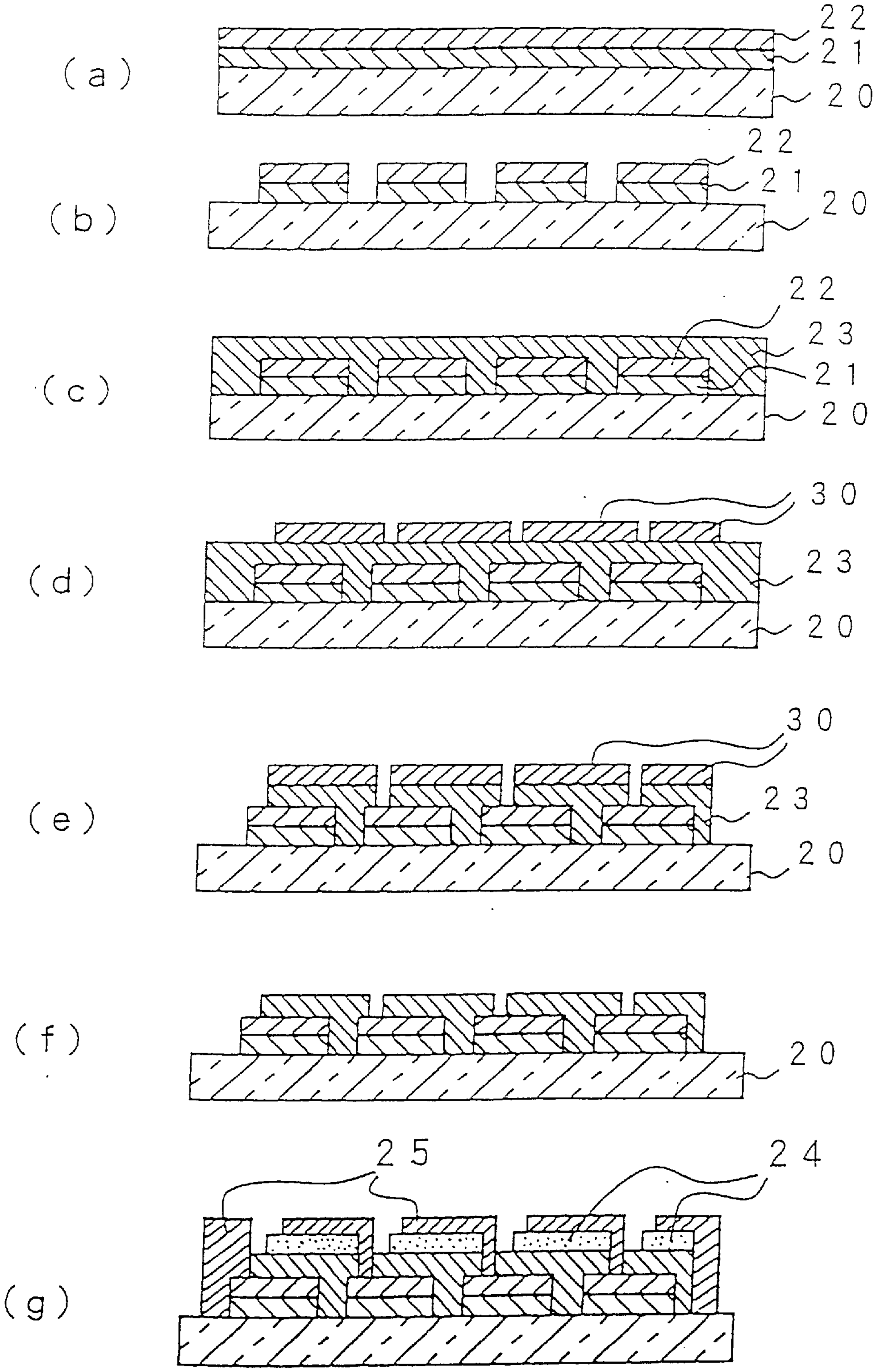
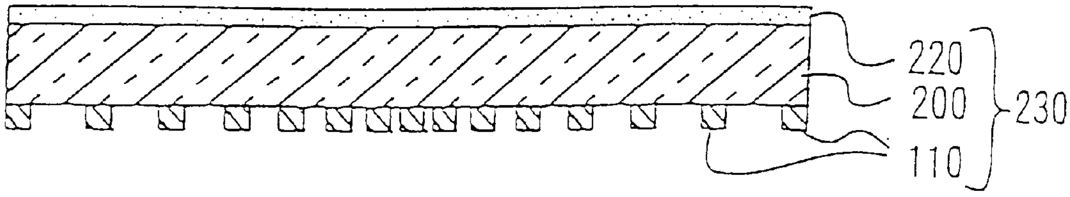


FIG. 8



METHOD FOR PREPARING CDTE FILM AND SOLAR CELL USING THE SAME

TECHNICAL FIELD

The present invention relates to a method for preparing a CdTe semiconductor film which is used mainly for solar cells, in particular, to a method for preparing the CdTe film by a close-spaced sublimation process.

BACKGROUND ART

In recent years, global environmental problems such as global warming due to carbon dioxide, depletion of the ozone layer, and the like have been highlighted. For that reason, expectation for development of new energy, in particular, that for solar cells have become glowingly great. However, for popularization of the solar cells, there are a number of problems which must be solved. In particular, an improvement in conversion efficiency of the solar cells and a reduction in price are desired.

A CdS/CdTe solar cell uses CdTe which has an forbidden band gap (=1.44 eV) being suitable for a light absorption layer, and thus it is one of the solar cells which are expected to yield a high conversion efficiency.

In the manufacturing process of the CdS/CdTe solar cell, a cadmium telluride (CdTe) film is formed on a surface of a cadmium sulfide (CdS) film in general. As a method for forming the CdTe film, the close-spaced sublimation process which can produce the CdTe film of high quality is attracting attention. The close-spaced sublimation process is a kind of the vapor deposition process. A CdTe solar cell which has a conversion efficiency of the world highest level (15.8%) at present is obtained by this process. The close-spaced sublimation process is disclosed in, for instance, “HIGH EFFICIENCY CdS/CdTe SOLAR CELLS FROM SOLUTION-GROWN CdS FILMS” (The Conference Record of the 22nd IEEE Photovoltaic Specialists Conference (1991) Vol. 2, p.952) by T. L. Chu et. al., or the like. According to this process, a material for forming the CdTe film (hereinafter referred to as a source) and a substrate are so placed as to face each other, with a gap of about 0.5–5 mm, and heated under a reduced pressure. In this manner, the source is caused to sublime and then deposit on the substrate.

According to this process, since the sublimed source is rearranged and crystallized on the substrate placed at a short distance as long as the mean free path level, a CdTe film which has a high crystallinity is obtained. Further, since the treatment is performed under the reduced pressure, the film-forming speed is high.

However, the above-mentioned conventional close-spaced sublimation process has the following problems.

In general, in the close-spaced sublimation process, as a source, a CdTe powder placed on a dish-shaped container so as to cover over it is used. In the above-mentioned literature for instance, a commercially-available polycrystal of CdTe with a purity of 5N, or a powder produced by pulverizing a polycrystal ingot of CdTe obtained by directly implanting a dopant as one of the constituting element, is used as the source.

In addition to the fact that this process uses an expensive CdTe powder, it has a low utilization efficiency. In this process, it is difficult to evenly place as much amount of the source for forming the film just once for covering over the container. For that reason, the same source is repeatedly used for forming the CdTe films. It is difficult to control the CdTe powder or the source since it changes in particle size, powder density, stoichiometric ratio and the like by the sublimation, and hence, with the repetition of the film-forming, dispersions in thickness and in quality of the CdTe film increases gradually. Therefore, the obtained solar cell has a large dispersion in performance. For that reason, in order to make the dispersion in performance of the solar cell small, of the source placed for covering, only about 10% is actually consumed for the film-forming, and the rest is discarded without being used.

Further, according to this process, since the film is formed under the reduced pressure, an equipment must once be stopped when the source is exchanged. Therefore, the production efficiency is also low.

When a CdTe film is formed by this process, on a substrate which has a large area, a central part of the obtained CdTe film is made thicker than that of a peripheral part because the central part of the source is liable to trap a heat flowed from circumference, as opposed to the peripheral part where the heat is liable to escape. Therefore, the variation in thickness within the same film is large.

Moreover, according to this process, when the source is used repeatedly, the particle diameter of the material decreases gradually and the surface area of the material increases, and in addition, the surface temperature of the source rises because the particles combine together by sintering. Therefore, the thermal conductivity increases and the film-forming speed increases gradually. When the same source is used repeatedly still more and the remaining amount of the source decreases accordingly, pores are produced between and among the particles and the thermal conductivity of the source is gradually lowered, thereby to decrease the film-forming speed conversely. For that reason, even when the manufacturing is performed under the same conditions, the thickness of the obtained CdTe film varies for every film-forming processes.

As previously described, according to the conventional close-spaced sublimation process, it is difficult to obtain CdTe film having uniform quality and thickness within the same film and between a plurality of the films. For that reason, although the CdTe film theoretically has the forbidden band gap which is the most ideal for converting the solar light as a compound semiconductor, a CdTe film as an ideal p-type semiconductor has not actually been obtained by the conventional close-spaced sublimation process.

In order to improve the conversion efficiency of the CdTe solar cells, means of making the CdTe film a weak p-type one by diffusing copper or the like into the CdTe film from the electrode side has widely been used, as reported, for instance, by B. E. Mccandless et. al., in “A treatment to allow contacting CdTe with different conductors” (Conference record of the 24th IEEE photovoltaic specialists conference 1994 volume II, p. 107–110). However, according to this method, a solar cell having a satisfactory conversion efficiency has not been obtained.

DISCLOSURE OF THE INVENTION

The present invention intends to solve the above-mentioned conventional problems, and has, as its object, a provision of a method for preparing a CdTe film of good quality simply.

The method for preparing the CdTe film in accordance with the present invention comprises: a step of coating a paste containing a material for CdTe semiconductor on a supporting member thereby to form a coating film containing the material for the semiconductor on the surface of the supporting member; a step of closely arranging the supporting member and a substrate on which a CdTe film is to be formed, to make the coating film to face the surface of the substrate; and a step of forming a CdTe film on the substrate, by heating the coating film and the substrate, thereby to cause the semiconductor material in the coating film to evaporate.

According to this method, it is possible to greatly improve the utilization rate of the material as compared with the case of using the above-mentioned conventional source. That is, since a thin coating film can be formed by coating, the utilization rate of the source which has conventionally been about 10% can be improved to about 50%. For that reason, it is not necessary to use the source for the formation of the film repeatedly. That is, since the source can be made disposable and a new source can constantly be used for the film-forming, it is possible to suppress the dispersion in characteristics of the CdTe film due to the repeated use of the source. Further, since the thin source can be obtained, it is possible to form the CdTe film without giving an excessive thermal damage to the previously formed CdS film.

Moreover, it is preferable to use a mixture of a cadmium powder and a tellurium powder as the semiconductor material. By using the mixture of the cadmium powder and the tellurium powder or, preferably, the pulverized powder, which is very inexpensive as compared with the CdTe powder thereof, the material cost can be reduced in great deal. In particular, by pulverizing Cd and Te in a mixed state, a mixed power can be obtained in a short time period. Further, with an energy for the pulverization, a part of the mixture can be synthesized into CdTe.

Moreover, by adding cadmium chloride into the paste, the crystallinity of the formed CdTe film is improved and the grain size of CdTe increases. In this manner, it is possible to obtain a solar cell of a high conversion efficiency. It is believed that the improvement in the crystallinity of the CdTe film is due to the fact that position of lattice defect of tellurium is substituted by chlorine, thereby to improve the crystallinity of the CdTe film. Moreover, since cadmium chloride is mixed into a paste and then coated, it is possible to constantly use the new source wherein cadmium chloride is uniformly dispersed. Therefore, it is possible to repeatedly and stably manufacture a CdTe film of high quality. If the added amount of cadmium chloride is smaller than 0.1 wt %, great effect cannot be obtained for the improvement in the performance of the solar cell. In contrast, if it is larger than 1.75 wt %, the performance is deteriorated conversely. For that reason, the added amount of cadmium chloride is preferably 0.1–1.75 wt %, and particularly 0.3–1.0 wt %.

In addition, it is preferable that the paste is one with a Group I element or a Group V element incorporated therein. By incorporating an impurity which acts as a carrier into the paste, it is possible to control the carrier concentration of the CdTe film in simple means. Incidentally, use of the Group I element or the Group V element in the conventional process employing a source prepared by placing the semiconductor material of powder state in a container so as to cover over it causes a variation in composition of the source, if such films are formed for plural times by using the same source, due to the differences in the sublimation speeds of the semiconductor material and the impurities. Therefore, a semiconductor film of stable composition cannot be obtained. On the other hand, according to the present invention, since the coating film of the semiconductor material formed on the surface of a heat-resistant supporting member is used as the source, it is possible to use a very small amount of the semiconductor material as the source. Therefore, a semiconductor film which has a constant concentration of the impurity can be formed. It is preferable that the Group I element to be mixed is lithium, potassium, sodium, rubidium, copper, silver or gold. Further, it is preferable that the Group V element to be mixed is arsenic, antimony, bismuth, phosphor or nitrogen. These can be used singly or plurally.

Moreover, by adding to the paste a substance which is stable in composition against the heat applied at the time of forming the semiconductor film and remains on the supporting member after the heating, it is possible to place the semiconductor material of an amount which is exactly necessary for one time film-forming on the supporting member in a stable state with a small dispersion. By causing all semiconductor materials to sublime, it is possible to manufacture a CdTe film of large area which is stable in thickness and quality. For instance, according to a screen-printing, it is difficult to form a coating film of a uniform thickness unless the thickness of the coating film to be formed is not less than 50 μm. However, in a case of adding no additive to the paste, when a coating film with the thickness of 50 μm is entirely sublimed, a CdTe film with a thickness of about 20 μm is obtained. If such a thick CdTe film is used in the solar cell, resistance of the CdTe film in the thickness direction is large and thus the characteristics of the obtained solar cell are poor. That is, a thinner CdTe film is desired for employing it in the solar cell. The most suitable thickness is about 6 μm. That is, if no additive is added to the paste, it is necessary to stop the film formation halfway while the source remains. On the other hand, by adding an additive to the paste as in this example, the amount of the semiconductor material in the coating film can easily be adjusted and thus it becomes possible to form a semiconductor film which has a preferable thickness. Since to control the thickness of the coating film becomes so easy, it is possible to use only a necessary amount of the semiconductor material for one film formation as the source. As the substance to be added, carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride or aluminum nitride is preferable. Further, these substances can be used by mixing them. Since the carbon and silicon carbide can absorb radiated infrared ray, the source can be heated efficiently by using them. Moreover, since they can protect the CdS film which has previously been formed from a thermal damage, it is possible to suppress an occurrence of micro-short-circuiting resulting from a thinning of the CdS film by the sublimation, and an excessive mutual diffusion at an interface between the CdS film and the CdTe film.

Further, at the time of painting the paste, by making more amount of the paste adhere to the peripheral part of the supporting member where its temperature at heating is relatively lower than the central part of the supporting member, some more amount of semiconductor material may be placed there.

The supporting member for holding the paste is preferably a plate-shaped carbon material which has a heat soaking property and a small heat capacity. A glass substrate is preferable in viewpoints of price and easiness in handling. As the glass, borosilicate glass, a low alkali glass, soda-lime glass and the like may be used. In a case of using the glass substrate, it is preferable to place at least one carbon plate beneath the glass substrate. Further, if an expansion of the supporting member due to the thermal treatment is taken into consideration, a ceramics which has a small linear expansion coefficient is preferable. These supporting member can be used repeatedly.

It is preferable that the supporting member is composed of a glass having a conductive oxide film on the surface thereof. By using a glass having the conductive oxide film of, for instance, indium oxide, indium tin oxide, stannic oxide, zinc oxide and the like, as the supporting member, it is possible to suppress a radiation heat which reaches the formed semiconductor film, after the evaporation of the source is completed, thereby to prevent the excessive mutual diffusion at the interface of the CdS film and the CdTe film. Further, by roughening a surface of the supporting member which is opposite to the side where the paste is painted, the radiation heat can similarly be suppressed. In this case, by scatter due to an unevenness of the surface of the supporting member and an improvement in the heat absorbing property due to the increase in the surface area, it is possible to reduce the amount of infrared ray which transmits through the supporting member and reaches the formed semiconductor film.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is a schematic longitudinal cross-sectional view of a solar cell which uses CdTe film in accordance with one embodiment of the present invention.

FIG. **2** is a schematic longitudinal cross-sectional view showing a structure of an equipment employed for forming the CdTe film in the same embodiment.

FIG. **3** is a characteristic diagram showing the relationship between the times of forming the CdTe film in the same embodiment and the conversion efficiency of a solar cell produced by using the CdTe film.

FIG. **4** is a characteristic diagram showing the relationship between added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in another embodiment of the present invention.

FIG. **5** is a characteristic diagram showing the dispersion in the conversion efficiency of a solar cell produced by using CdTe film obtained in a still other embodiment of the present invention.

FIG. **6** is a characteristic diagram showing the added amount of cadmium chloride to the source and the conversion efficiency of a solar cell produced by using the obtained CdTe film in a still other embodiment of the present invention.

FIG. **7**(*a*)–FIG. **7**(*g*), each is a longitudinal cross-sectional view showing the state of the respective step in manufacture of the solar cell in another embodiment of the present invention.

FIG. **8** is a schematic longitudinal cross-sectional view of source substrate plate used in another embodiment of the present invention.

THE BEST MODE FOR CARRYING OUT THE INVENTION

The method for preparing the CdTe film in accordance with the present invention will be described in detail with reference to the drawings.

In the following examples, a solar cell shown by FIG. **1** is produced by using the obtained CdTe film.

A transparent and insulating substrate **1** is made from borosilicate glass, low-alkaline glass, low-iron soda-lime glass, soda-lime glass and the like. On the surface of this substrate **1**, a transparent conductive film **2** with a thickness of 1,000–10,000 Å composed of tin oxide, indium tin oxide (ITO) and the like is formed by chemical vapor-phase growing process or sputtering. In this occasion, a silica film (SiO_2 film) may sometime be formed between the substrate **1** and the transparent conductive film **2**, in order to prevent an alkali component in the substrate **1** from diffusing into the transparent conductive film **2**. Then, by forming a CdS film **3** with a thickness of 500–2,000 Å on the transparent conductive film **2** as an n-type semiconductor, a substrate **4** for forming CdTe film is obtained. This CdS film **3** is formed by thermally decomposing such an organometallic complex compound as cadmium isopropyl xanthogenate on the transparent conductive film **2**.

In the followings, as examples of the method for preparing CdTe semiconductor film in accordance with the present invention, methods for forming a CdTe film **5** on the surface of the thus obtained CdS film **3** of the substrate **4** will be described.

EXAMPLE 1

By mixing a CdTe powder as a semiconductor material with propylene glycol as a viscosity improver, a paste was prepared. By printing the obtained paste on the glass substrate as the supporting member and drying, a film of the semiconductor material was formed on a glass substrate, thereby to obtain a source substrate **9**.

The obtained source substrate **9** and the substrate **4** were installed on a manufacturing equipment shown in FIG. **2**, and the CdTe film **5** was formed on the surface of the substrate **4** in the following manner.

A chamber **14** is made of quartz tube, inside of which susceptors **10***a* and **10***b* made of carbon with a thickness of 1 mm are arranged as heat-soaking members. On the mutually confronting surfaces of the susceptors **10***a* and **10***b*, the source substrate **9** and the substrate **4** are arranged so as to make the semiconductor material film to face the CdS film **3**, respectively. In that arrangement, a spacer **12** is disposed between the source substrate **9** and the substrate **4** so that the distance between the both is constant. The source substrate **9** and the substrate **4** may be disposed on the susceptors inversely, bottom to top.

By substituting the atmosphere inside the chamber **14** with an argon gas, and heating the source substrate **9** and the substrate **4** by lamp heaters **13***a* and **13***b* for 30 second to several minutes, while maintaining the pressure inside the chamber **14** to 1 Torr by aspirating with a rotary pump **11**, a CdTe film **5** was formed on the CdS film **3** of the substrate. In this step, the temperature of the substrate **4** was kept to 400–650° C. by heating, and the temperature of the source substrate **9** was kept to a temperature which was higher than the temperature of the substrate **4** by 5–100° C.

In the above-mentioned manner, 100 pieces of samples wherein the CdTe films **5** were formed on the CdS films **3** of the substrates **4** were prepared. In this preparation, the sources were replaced for every samples. Further, about half of the source was consumed for forming the film.

On the surfaces of the CdTe films **5** of the respective samples thus formed, a methanol or an aqueous saturated solution of cadmium chloride was applied and then the applied methanol or water was evaporated. Further, the substrate **4** for thin film forming was thermally treated at 400° C. for 30 minutes. By this thermal treatment, grains in the CdTe film were grown.

A carbon paste was prepared by mixing a carbon powder and a solution obtained by dissolving polyvinylbutyral as a viscosity improver in diethylene glycol monobutyl ether with kneading. After applying this carbon paste on the surface of the CdTe film **5** by screen printing, it was dried and sintered, thereby to form a carbon electrode layer **6** as a current collector. On the other hand, a paste was prepared by mixing and kneading a mixed powder of silver and indium, an epoxide and an alcohol solution consisting mainly of terpineol. By applying the obtained paste on the surface of the CdS film **3** and carbon electrode layer **6** by screen printing, drying and then sintering, a + side electrode **7** and a − side electrode **8** were formed, respectively.

COMPARATIVE EXAMPLE 1

As a comparative example, a CdTe film was formed by using one obtained by filling the CdTe powder similar to that used in Example 1 in a dish-shape container as the source. In that case, the CdTe films were formed with the same source for a plurality of times. By this process, about 90% of the source was left after the formation of the CdTe films for 100 times. By using the obtained CdTe films, solar cells similar to those in Example 1 were produced.

Each 100 pieces of the solar cells of Example 1 and of Comparative Example 1 obtained in the above-mentioned manner were investigated about their conversion efficiencies with a solar simulator at AM 1.5, 100 mW/cm^2. The results are shown in FIG. **3**. In this diagram, the abscissa represents the respective solar cells arranged in the orders of forming the CdTe films.

As clearly seen from FIG. **3**, according to the manufacturing method of Comparative Example 1, the composition of the source varies with the repetition of the manufacture of the film, thereby to change the quality and the thickness of the obtained CdTe film. Therefore, the characteristics of the cells prepared with these CdTe films deteriorated. In contrast, according to the manufacturing method of Example 1, it is possible to make a small amount of the source to be uniformly held on the glass substrate. By this method, the utilization rate of the material can greatly be improved as compared with the manufacturing method of Comparative Example 1, even if the source is replaced for every film formations. That is, by employing a source of the coating film obtained by making a semiconductor material a paste-state and painting this paste on a substrate, a constantly stable supply of the source is enabled. Therefore, a semiconductor film with a high quality can be manufactured stably at a low cost.

EXAMPLE 2

In this example, a description will be made in a case of adding cadmium chloride into the paste for forming the CdTe film beforehand.

A CdTe powder similar to that in Example 1 was used as a semiconductor material. Pastes were respectively prepared by adding cadmium chloride at a rate of from 0 to 2.0 parts by weight to 100 parts by weight of this CdTe powder.

By using the obtained pastes, CdTe films were formed and then, solar cells were prepared in a manner similar to that in Example 1.

The relationship between the incorporation ratios of cadmium chloride to the CdTe powder and the conversion efficiency of the obtained solar cells are shown in FIG. **4**.

As shown in FIG. **4**, it is appreciated that by adding not less than 0.1 wt % of cadmium chloride to the CdTe powder, the conversion efficiency of the obtained cell is improved. However, if it is added in excess over 1.75 wt %, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1–1.75 wt % to the CdTe powder. In particular, the improvement in the conversion efficiency is remarkable at 0.3–1.0 wt %, and vicinity of 0.5 wt % is the most desirable.

100 parts by weight of the CdTe powder was mixed with 0.5 parts by weight of cadmium chloride. By using the obtained mixture, a paste was prepared as mentioned above. By using a semiconductor film formed by painting this paste as the source, a CdTe film was formed. In this step, the source was replaced for every times of film forming in a similar manner to that in Example 1.

As a comparative example, a CdTe film was also formed by using the same mixture so placed in a dish-shape container as to cover over it at a high density. In this time, the source was used continuously for a plurality of times for the film formation without replacing.

Solar cells were produced by using the CdTe films obtained in the above-mentioned manner. The characteristics of the obtained solar cells were investigated in a similar manner. The results are shown in Table 1.

TABLE 1

Film forming	Conversion efficiency (%)	
times (time)	Example 2	Comparative Example
1	14.6	13.6
20	14.5	13.5
40	14.7	13.2
60	14.5	12.5
80	14.5	11.3
100	14.6	8.5

As shown in Table 1, in the case of using the semiconductor material of powder state covering over the container, the characteristics of the semiconductor film decrease with the repeated times of the film forming. This is due to the above-mentioned varying in the cadmium chloride concentration and its non-uniformity. According to this method, it is difficult to form a CdTe film of good quality by using a small amount of the semiconductor material. That is, in any other means than discarding the source while consuming only a part of the source and leaving the remaining semiconductor material in a considerable amount, it is impossible to stably manufacture the CdTe film.

In contrast, according to the manufacturing method in accordance with this example, whereby the semiconductor material is made to have a paste-state, and the coating film obtained by applying the paste on the substrate is used as the source, the unevenness in the characteristics of the solar cells produced by using the obtained semiconductor film is small because there is no need for using the source repeatedly. Therefore, it is possible to stably manufacture the semiconductor film of a high quality at a low cost.

As the atmospheric gas, a similar effect is obtained in a case of using an inert gas such as nitrogen, hydrogen or helium gas in place of argon used in the above-mentioned example. In addition, in a film formation under a pressure of not more than 2 atm, a similar effect is also obtained.

EXAMPLE 3

By using a source of the coating film of the CdTe obtained by printing it as in Example 1, a CdTe film with a good quality can be formed. However, due to the fact that the CdTe powder as the raw material is very expensive, the price of the product becomes high. The reason for this is that the single crystal of CdTe is manufactured by Bridgman process in general. According to this process, in addition to the fact that heating at a high temperature of not less than 1,000° C. is required, a long period of time is required for elevating the temperature and cooling for the safety in operation and the improvement in the crystallinity.

Therefore, a description will be made, in this example, on a method for forming the CdTe film of a good quality, by using a starting material of a Cd powder and a Te powder which are inexpensive as compared with the CdTe powder. The price of the commercially available CdTe powder is about 250 yen/g but, in contrast, the prices of the commercially available Cd powder and Te powder are about 20 yen/g, respectively. Therefore, according to the manufacturing method of this example, the material cost can be reduced in great deal.

The Cd powder, the Te powder and a liquid (for instance, water) were mixed together and stirred by using a medium of ring-shape or spherical shape. Subsequently, a paste was prepared by adding propylene glycol to the obtained mixture after being dried. By using the paste thus obtained, a CdTe film was formed and a solar cell was produced in a manner similar to that in Example 1.

The conversion efficiency of the obtained solar cell was measured in a manner similar to that in Example 1. The results thereof are shown in FIG. **5**. In this diagram, the ordinate represents mean value ± standard variance in the conversion efficiencies of the solar cells of Example 3 and of the solar cells of Comparative Example 1.

As clearly shown by FIG. **5**, according to the manufacturing method of this example, it is possible to obtain a solar cell of an excellent characteristic by using low-priced materials. As the reason for this, there are given the fact that the temperature distribution in the source can be made uniform since the particle diameters of Cd and Te can be made uniform by pulverizing, and the amount of the source can be made small by using the film obtained by applying the pulverized mixture as the source.

The Cd powder and the Te powder were mixed in an equimolar amount, and pulverized in water to give a particle diameter of not more than about 1 μm by using a medium stirring mill. After drying the pulverized powder thus obtained, propylene glycol as a viscosity improver was added to the pulverized powder and kneaded, thereby to prepare a paste. By printing this paste on a carbon plate with a thickness of 1 mm as the supporting member, and drying at 120° C. for 1 hour, a coating film was formed and a source substrate was obtained.

On investigating the composition of the formed coating film by X-ray diffraction, diffraction peaks of Cd single substance, Te single substance and CdTe were observed. It is believed that this CdTe is synthesized at the pulverization by the pulverizing energy.

This source substrate **9** and the substrate **4** were arranged so as to make the coating film to face the CdS film, with a gap of 2 mm. Thereafter, the atmosphere inside the chamber **14** was substituted by argon, the source substrate **9** and the substrate **4** were heated to temperatures of 600–630° C. and of 580–600° C., respectively, while maintaining the pressure to 1–5 Torr, and kept there for 1 minute. By this procedure, a CdTe film with a thickness of 6 μm was formed on the CdS film of the substrate **4**.

An aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the surface of the obtained CdTe film, and then the water was evaporated. Thereafter, by thermally treating the CdTe film at 400° C. for 30 minutes, the crystallinity of the CdTe film was improved. Subsequently, a carbon film and an AgIn film were formed as an electrode of the CdTe film side and an electrode of the CdS film side, respectively, thereby to produce a solar cell.

The measurement on the characteristics of the obtained solar cell conducted with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.5 mA/cm^2 and the open-circuit voltage was 0.813 V. Further, the fill factor was 0.696 and the conversion efficiency was 13.3%. These characteristics are about the same degree as the characteristics of the solar cell of Comparative Example 1 produced by using the CdTe film formed by using the CdTe powder placed in the dish-shape container so as to cover over it (short-circuit current of 23.4 mA/cm^2, open-circuit voltage of 0.815 V, fill factor of 0.701 and conversion efficiency of 13.4%).

Next, a paste was prepared by adding an appropriate amount of $CdCl_2$ as a melting point depression agent in addition to propylene glycol as the viscosity improver to the pulverized powder similar to the above-mentioned. After printing the obtained paste on a carbon plate with a thickness of 1 mm, the paste was dried by drying at 120° C. for 1 hour, thereby to form a coating film comprising a semiconductor material, and to obtain a source substrate **9**. In an X-ray diffraction pattern of the obtained coating film, a peak attributable to the $CdCl_2$ was observed in addition to the diffraction peaks of Cd single substance, Te single substance and CdTe, of course.

By heating the obtained source substrate **9** under a nitrogen atmosphere at a temperature of 600–700° C. for 1 hour, the coating film was sintered. In an X-ray diffraction pattern of the sintered film thus obtained, only the diffraction peak attributable to CdTe was observed.

Next, the source substrate **9** and the substrate **4** were so placed as to face each other, with a gap of 2 mm, and a CdTe film **5** was formed on the CdS film **3** in a procedure as shown above. After the formation of the CdTe film **5**, an aqueous solution of $CdCl_2$ at a concentration of 0.3 mol/l was allowed to adhere to the CdTe film **5** and water was evaporated, and then, it was thermally treated at 400° C. for 30 minutes. Thereafter, a solar cell was produced in a procedure as shown above and the characteristics of the solar cell were evaluated in a similar manner. Measurements on the characteristics of the solar cell with a solar simulator at AM 1.5, 100 mW/cm^2 revealed that the short-circuit current was 23.6 mA/cm^2, and the open-circuit voltage was 0.816 V. Further, the fill factor and the conversion efficiency were found to be 0.699 and 13.5%, respectively. These values are the same degree as those of the solar cell of Comparative Example 1.

A film formed by painting a fine powder obtained by pulverizing Cd and Te singly or a CdTe compound and drying it, or a sintered film thereof obtained in the above-mentioned manner was used as the source to obtain a good quality CdTe film.

Incidentally, a similar effect is obtained by using a commercially-available CdTe as the starting material.

EXAMPLE 4

In this example, a description will be made on a method which employs the Cd and Te similar to those in Example 3 as the starting material, wherein cadmium chloride is further added to this mixture.

A muddy mixture was prepared by pulverizing the Cd and Te similar to those used in Example 3 in a wet process. Next, by drying the mixture and adding cadmium chloride and propylene glycol as the viscosity improver to this mixture, a paste was prepared. A CdTe film was formed by using the obtained paste and a solar cell was produced in a manner similar to that in Example 1.

The characteristics of the obtained solar cell were evaluated in a manner similar to those in the above-mentioned examples.

The added amounts of cadmium chloride to the sources and the conversion efficiencies of the solar cells produced by using the respective sources are shown in FIG. **6**.

From FIG. **6**, it is appreciated that by adding cadmium chloride in an amount of not less than 0.1 wt % for a sum of the weights of Cd and Te to it, the conversion efficiency is improved as compared with a case of not adding cadmium chloride. However, if cadmium chloride is added in an amount of more than 1.75 wt % for a sum of the weights of Cd and Te, the conversion efficiency decreases. Therefore, the added amount of cadmium chloride is desirably 0.1–1.75 wt %. In particular, the improvement in the conversion efficiency is remarkable in 0.3–1.0 wt %, and that in the vicinity of 0.5 wt % is the most desirable.

EXAMPLE 5

In this example, a description will be made on a method with an incorporation of a Group I element or a Group V element as a dopant into the source. According to this method, carrier concentration of the CdTe film can easily be controlled. The Group I element and/or the Group V element to be added is/are incorporated into it in a state of single substance or a compound such as organometallic compounds. These elements may be used singly or plurally.

On a surface of a substrate **1** with a thickness of 1.1 mm made from a borosilicate glass, a transparent conductive film **2** with a thickness of 500–5,000 Å composed of tin oxide was formed by a sputtering process. Next, a CdS film **3** with a thickness of 500–2,000 Å was formed by a CVD process. For the formation of the CdS film **3**, any other process, for instance, a solution deposition method, may be employed.

A source substrate **9** provided with the source added with an impurity was arranged on a susceptor **12***a* in the lower side of the equipment. On the other hand, on a susceptor **12***b* in the upper side, a substrate **4** was arranged with a gap of 0.1 mm to several mm to the surface of the source. After substituting the atmosphere inside the chamber **14** with argon gas or nitrogen gas, by heating the substrate **4** in a temperature range of 400–800° C. and the source substrate **9** at a temperature higher than that of the substrate **4** and keeping them there for a certain time period, a semiconductor film was formed on the surface of the substrate **4**.

In this step, although it is preferable to keep the pressure of argon gas or nitrogen gas to about 1–20 Torr, it is possible to form the film under 1 atm. In that case, it is preferable that the temperature difference between the substrate **4** and the source substrate **9** is not less than 50° C. In the case of forming the film under 1 atm, there is no need for making the chamber to have a pressure-resistant structure, and thus it is possible to simplify the equipment. Further, since a speeds in inlet and outlet of the substrate to and from the equipment can be made high, the productivity is greatly improved.

For the source, a paste is prepared by using the CdTe incorporated with antimony telluride at 0.01 wt %. By printing the obtained paste on a glass substrate and drying, the source substrate **9** was obtained.

By using the obtained source substrate **9**, a CdTe film **5** was formed under the atmosphere of argon with a pressure of 1 Torr. In this step, by maintaining the substrate **4** in a temperature range of 400–650° C. and the source substrate **9** at a temperature higher by 30° C. than that of the substrate **4** for 2 minutes, the CdTe film **5** was formed on the CdS film **3**.

Separately, a carbon paste was prepared by mixing and kneading a carbon powder with a solution of diethylene glycol monobutyl ether which dissolved polyvinyl butyral. The obtained carbon paste was applied on the CdTe film **5** by a screen printing process and sintered after being dried, to form a carbon electrode layer **6**.

By mixing a mixed powder of silver and indium, and an epoxide with an alcohol consisting mainly of terpineol, and kneading the mixture, a paste was prepared. The obtained paste was applied on the CdS film **3** and the carbon electrode layer **6** by the screen printing process, which was then dried and sintered to form a + electrode **7** and a − electrode **8**.

The CdTe films **5** were also formed in a similar manner by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the CdTe paste. By using the respective CdTe films **5** thus obtained, solar cells were produced.

Further, as a comparative example, a solar cell employing a CdTe film prepared by using a CdTe paste with no additional impurity was produced as shown above and was similarly evaluated.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentration of the CdTe films are shown in Table 2.

TABLE 2

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency (%)
Antimony telluride	9.5×10^{14}	14.1
Phosphor	8.4×10^{14}	14.5
Arsenic	8.2×10^{14}	14.0
Antimony	8.1×10^{14}	14.2
Bismuth	8.2×10^{14}	14.1
Lithium	5.4×10^{14}	13.2
Potassium	8.1×10^{14}	14.0
Sodium	5.0×10^{14}	13.5
Rubidium	6.3×10^{14}	13.8
Copper	8.7×10^{14}	14.2
Silver	8.3×10^{14}	13.9
Gold	8.4×10^{14}	14.0
Triphenylantimony	1.2×10^{15}	14.5
Antimony octylate	1.4×10^{15}	14.6
Triphenylbismuth	1.3×10^{15}	14.4
Triphenylphosphine	1.8×10^{15}	14.7
Triphenylphosphate	1.7×10^{15}	14.7
Triphenylphosphite	1.8×10^{15}	14.6
Triallylphosphine	1.8×10^{15}	14.5
Triallylamine	1.6×10^{15}	14.2
None	3.5×10^{14}	13.0

From Table 2, it is appreciated that in the case of incorporating a Group I element or a Group V element into the source, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 6

A CdTe film was formed by the similar method as that in Example 5 except for the use of nitrogen in place of argon as the atmospheric gas. The conditions employed for forming the CdTe film **5** were that the pressure inside the chamber **14** was 1 atm, the substrate **4** was kept in a temperature range of 400–650° C., and the source substrate **9** was kept at a temperature higher by about 100° C. than that of the substrate **4** for 10 minutes, thereby to form a CdTe film **5**. Further, a solar cell was similarly produced by using the obtained CdTe film **5**.

Moreover, the CdTe films **5** were also formed by using each of arsenic, antimony, bismuth, phosphor, lithium, potassium, sodium, rubidium, copper, silver, gold, triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine, in place of antimony telluride as the impurity to be incorporated into the paste, and by using the CdTe films **5** thus obtained, solar cells were produced.

The relationships between the conversion efficiencies of the obtained solar cells and the carrier concentrations of the CdTe films are shown in Table 3.

As a comparative example, a relationship between the conversion efficiency of a solar cell employing a CdTe film produced by using a CdTe paste with no additional impurity, and the carrier concentration of the CdTe film is also shown in Table 3.

TABLE 3

Impurity	Carrier concentration (cm^{-3})	Conversion efficiency of solar cell element (%)
Antimony telluride	8.2×10^{14}	14.1
Phosphor	8.4×10^{14}	14.7
Arsenic	7.1×10^{14}	14.2
Antimony	7.9×10^{14}	14.4
Bismuth	6.1×10^{14}	14.1
Lithium	5.4×10^{14}	14.0
Potassium	5.2×10^{14}	14.0
Sodium	4.9×10^{14}	13.8
Rubidium	5.8×10^{14}	14.1
Copper	8.5×10^{14}	14.7
Silver	7.1×10^{14}	14.1
Gold	8.2×10^{14}	14.4
Triphenylantimony	1.0×10^{15}	14.9
Antimony octylate	1.1×10^{15}	14.9
Triphenylbismuth	9.8×10^{15}	14.8
Triphenylphosphine	1.3×10^{15}	15.1
Triphenylphosphate	1.2×10^{15}	15.0
Triphenylphosphite	1.3×10^{15}	15.1
Triallylphosphine	1.3×10^{15}	15.1
Triallylamine	1.2×10^{15}	15.0
None	3.2×10^{14}	13.2

From Table 3, it is appreciated that in either case of incorporating a Group I element or a Group V element into the source material, the carrier concentration of the obtained CdTe film becomes higher and the conversion efficiency of the solar cell becomes higher as compared with the case of no incorporation.

EXAMPLE 7

A solution was prepared by dissolving cadmium isopropyl xanthogenate, which is an organometallic compound with a sulfur bond, in 1-methyl-2-pyrrolidone.

Separately, on a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm shown in FIG. **7**(*a*), a stannic dioxide film **21** with a thickness of about 600 nm was formed.

The solution obtained in the above-mentioned manner was painted on the surface of the stannic dioxide film **21** and dried at 110° C., thereby to evaporate the solvent. Thereafter, it was subjected to a thermal treatment in the air at 450° C. for 3 minutes, thereby to decompose the cadmium isopropyl xanthogenate and to form the CdS film **22**. At this step, by adjusting the concentration of the solution thus used and the repeat times of the coating, the thickness of the CdS films **22** were set to 70 nm.

Thereafter, by a laser scribing process employing a YAG laser, a pattern for 42 cell series connection as shown by FIG. **7**(*b*) was formed.

Subsequently, a mixed powder was obtained by mixing 1 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, with 6 g of CdTe powder with a purity of 5N.

The mixed powder thus obtained was placed on a glass substrate (Corning #1737) with a width and a length of 35 cm so as to cover over it, thereby to form a particle layer and to obtain a source substrate. Then, the source substrate and the substrate **20** were placed so as to make the particle layer to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source at 630° C. under argon atmosphere with a pressure of 1 Torr for 2 minutes, CdTe films **23** with a thickness of about 6 μm were formed on the CdS films **22** as shown by FIG. **7**(*c*). Thereafter, as shown by FIG. **7**(*d*), etching resists **30** were applied on the surface of the substrate **20** by a screen printing process, and a thermal treatment was conducted in a dryer at 100° C. for 5 minutes.

Subsequently, after subjecting the substrate **20** to an etching process for 5 minutes by immersing it in nitric acid, the substrate **20** was immersed in a 10% solution of sodium hydroxide, thereby to fall the resist layer **30** off as shown by FIG. **7**(*f*). Thereafter, the substrate **20** was immersed in a methanol saturated solution of cadmium chloride and dried, and then subjected to a thermal treatment in the air at 400° C. for 20 minutes. Thereafter, residue of the cadmium chloride was removed by ultrasonic-wave washing in pure water.

Subsequently, after forming a carbon film **24** which was added with a trace amount of copper on the surface of the substrate **20** by the screen printing process, it was dried and heated at 390° C. for 30 minutes, thereby to diffuse the copper into the CdTe films **23**. Thereafter, silver-indium films **25** were formed by a similar screen printing process and thermal treatment, thereby to obtain a solar cell of 42 cells series connection as shown by FIG. **7**(*g*).

EXAMPLE 8

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **21** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **21**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 50 g of graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate (Corning #1737) with a width and a length of the same 35 cm, and drying it in the air at 120° C. for 4 hours, a particle layer with a thickness of about 100 μm consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate **20** were placed so as to make the particle layer to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate at 630° C. under argon atmosphere with a pressure of 1 Torr for 2 minutes, the source in the particle layer was entirely sublimed, thereby to form a CdTe film **23** with a thickness of about 6 μm on the CdS films **22** as shown by FIG. **7**(*c*). Thereafter, as shown by FIG. **7**(*d*), etching resists **30** were painted on the substrate **20** by a screen printing process, and a thermal treatment was performed in a dryer at 100° C. for 5 minutes.

By using the obtained CdTe films **23**, a solar cell similar to that of Example 7 was produced.

Further, by using powders of carbon black, silicon carbide, silicon dioxide, silicon nitride, aluminum oxide, boron nitride, zirconia, silicon nitride, and aluminum nitride, each of which has a purity of 3N and a particle diameter of not more than 5 μm, in place of graphite, solar cells were similarly produced.

EXAMPLE 9

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **21** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **21**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

By applying the obtained paste on a glass substrate **100** (Corning #1737) with a width and a length of the same 35 cm, and drying it in the air at 120° C. for 4 hours, a particle layer consisting mainly of CdTe was formed, thereby to obtain a source substrate.

The source substrate and the substrate **20** were placed so as to make the particle layer **120** to face the CdS film, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate at 630° C. under argon atmosphere with a pressure of 1 Torr, and until the CdTe on the source substrate was entirely evaporated (for 5 minutes), thereby to form a CdTe film **23** with a thickness of about 6 μm on the surface of the substrate **20**.

By using the obtained CdTe film **23**, a solar cell similar to that of Example 7 was produced.

EXAMPLE 10

On a glass substrate **20** (Corning #1737) with a length and a width of the same 35 cm, a stannic dioxide film **11** with a thickness of about 600 nm was formed. Next, in a manner similar to that in Example 7, a CdS film **22** with a thickness of 70 nm was formed on the surface of the stannic dioxide film **11**. Thereafter, by a laser scribing process employing a YAG laser, the CdS film **22** was worked into a pattern for 42 cell series connection.

Separately, a paste was prepared by mixing 100 g of a graphite powder with a purity of 3N and a particle diameter of not more than 5 μm, and 500 g of a CdTe powder with a purity of 5N, with propylene glycol.

After forming an indium oxide film on one surface of a glass substrate **200** (Corning #1737) with a width and a length of the same 35 cm, the indium oxide film **110** was removed by etching excepting the specified portion as shown by FIG. **8**. In this step, a ratio occupied by the indium oxide films **110** in the central part of the surface was made higher than that in the peripheral part. On the surface of the other side of this glass substrate **200**, the above-mentioned paste was painted and dried in the air at 120° C. for 4 hours, thereby to form a particle layer **220** consisting mainly of CdTe and to obtain a source substrate **230**.

Then, the source substrate **230** and the substrate **20** which was similar to that used in Example 7 were placed so as to make the particle layer **220** to face the CdS film **22**, with a gap of 2 mm. By heating the substrate **20** at 600° C. and the source substrate **230** at 630° C. under argon atmosphere with a pressure of 1 Torr, until all of the CdTe on the source substrate **230** was evaporated (for 5 minutes), thereby to form a CdTe film **23** with a thickness of about 6 μm.

By using the obtained CdTe film, a solar cell similar to that of Example 7 was produced. EXAMPLE 11

After roughening one surface of a glass substrate **200** (Corning #1737) with a length and a width of the same 35 cm by etching with hydrofluoric acid, a particle layer was formed on the other surface with the paste which was similar to that used in Example 10, thereby to obtain a source substrate.

By using the obtained source substrate, a CdTe film was formed, and a solar cell was produced in a manner similar to that in Example 8.

COMPARATIVE EXAMPLE 3

As a comparative example, a paste was prepared in a method similar to that in Example 8 excepting an addition of graphite. The obtained paste was applied in a manner similar to that in Example 8 in an amount just required for forming the CdTe film with a thickness of 6 nm. In that case, since it does not contain graphite, the amount of the paste to coat is required to be less as compared with Example 8 so as to adjust the thickness of the coating film to be formed to about 50 μm, but it is impossible to make the amount of the source and the thickness of the coating film uniform. Therefore, by applying the minimum amount for uniformly painting, a source substrate was produced. By using the source substrate, a CdTe film was formed in a manner similar to that in Example 8. In this step, although the thickness of the coating film was made uniform, the dispersion in the thickness of the obtained CdTe film was larger than that of the CdTe film obtained in Example 8. By using this CdTe film, a solar cell was produced in a manner similar to that of Example 8. This was named as the solar cell of Comparative Example 3.

On the solar cells of Example 7–11 and of Comparative Example 3, measurements of the open circuit voltage (V_{oc}) and fill factor (FF) which is a standard for the decision of good/bad of the output characteristic were conducted under condition of AM; 1.5, 100 mW/cm^2. The results thereof are shown in Table 4.

TABLE 4

	Additive	V_{cc} (V)	FF (%)	η (%)
Example 7	Graphite	31.8	57	9.6
Example 8	Carbon black	33.0	61	10.1
	Graphite	33.6	64	10.6
	Silicon dioxide	32.7	59	9.8
	Aluminum oxide	33.3	62	10.2
	Zirconium oxide	31.0	58	9.7
	Boron nitride	32.4	60	10.0
	Silicon nitride	32.6	60	9.9
	Aluminum nitride	32.0	57	9.7
	Silicon carbide	33.0	60	10.0
Example 9	Graphite	33.4	62	10.3
Example 10	Graphite	33.2	63	10.4
Example 11	Graphite	33.6	64	10.5
Comparative Example 3	None	24.2	52	6.8

From Table 4, it is appreciated that the solar cells of Examples 7–11 employing the CdTe films which have been formed by using, as the source, a CdTe material added with a material which remains after the heating are excellent in every respect of the characteristics, as compared with the solar cell of Comparative Example 3. It is believed that this is due to the fact that by adding these materials, thermal damage of the CdS film attributable to the radiation heat can be prevented.

In particular, in the case of using graphite, carbon or silicon carbide in Example 8, or in Examples 9–11, by using the coating film of an amount just required for the film forming of one time as the source, it is possible to suppress an occurrence of an excessive heating of the substrate for thin-film forming, directly by the radiation heat, after the completion of the vaporization of the source. Tellurium, cadmium and cadmium telluride have a low absorption rate for infrared ray and a low heat conductivity. Therefore, if the source consisting of these semiconductor material is thick, since the temperature of the source is hardly elevated at the heating, the film forming speed is low, the infrared ray transmitted through the source is incident on the CdS film which has previously been formed on the substrate. Since the CdS which is typical as the n-type semiconductor for the solar cells has a very high absorption rate for infrared ray, it is heated by the incident infrared ray and made to be liable to vaporize. Therefore, when the CdS film is made thinner than the suitable thickness and when the vaporization of the CdS film further proceeds, pinholes are produced, thereby to invite micro-short-circuitings. For that reason, by using the infrared-absorption materials being mixed with the source as in these examples, the excessive temperature rise of the substrate is suppressed. Therefore, the mutual diffusion at a joint between the CdS film and the CdTe film is suppressed, thereby to obtain a solar cell which has a high open-circuit voltage and fill factor.

In addition, according to the method of the examples, since the source can be used exhaustively, the utilization rate of the material can greatly be improved. Although the CdTe film of good quality can also be obtained in Example 7 wherein a mixture of the source and the additive is used by filling it in a container as described above, it is limited to the cases where the times of repeatedly using the same source for forming the CdTe film are small. That is, according to this method, the change in the source cannot be avoided if the source is used repeatedly. Therefore, by using the coating film as the source as described in Examples 1–9, it is possible to obtain the CdTe film of good quality more effectively.

Further, measurements were made on the thickness distributions in the CdTe film formed in accordance with Example 8 and the CdTe film formed in accordance with Comparative Example 3. The results thereof are shown in Table 5. In this table, distance indicates a distance from the central part of the substrate in the diagonal direction.

TABLE 5

Distance (mm)	Example 8 (μm)	Comparative Example 3 (μm)
0	6.5	10.4
25	6.5	10.2
50	6.4	10.0
75	6.3	9.5
100	6.4	8.8
125	6.4	8.5
150	6.3	7.0
175	6.3	6.0
200	6.2	4.9
212	6.0	3.0

Moreover, the solar cells which employ the CdTe film obtained in accordance with Example 8 and the solar cells obtained in accordance with Comparative Example 3 were produced in trial, for each five lots, each of which contains 10 pieces, and the measurements were made on the film thickness of CdTe and the solar cell characteristics The results thereof are shown in Table 6.

TABLE 6

	Example 8 (Graphite)					Comparative Example 3				
lot	1	2	3	4	5	6	7	8	9	10
1	6.5	6.8	6.4	6.7	6.0	6.0	8.5	5.0	9.9	6.2
	10.0	9.8	9.8	10.5	9.4	8.0	7.2	8.2	7.5	8.1
2	6.4	6.6	6.5	6.9	6.2	7.0	9.0	5.9	10.0	6.9
	9.9	9.9	10.0	9.5	9.1	8.5	6.9	8.8	7.3	8.2
3	6.7	6.7	6.3	6.2	6.8	6.5	7.6	6.5	9.1	6.5
	10.2	10.0	10.1	10.1	9.9	7.9	8.0	7.9	7.0	7.5
4	6.3	6.9	6.5	6.1	6.9	7.2	9.5	6.1	9.5	6.9
	10.1	9.8	9.9	9.7	9.6	6.9	7.0	5.9	6.9	8.5
5	6.6	6.7	6.7	6.9	6.2	5.3	8.7	5.1	8.7	6.8
	10.2	9.9	9.7	9.8	10.4	7.6	6.8	7.1	7.2	7.4
6	6.5	6.5	6.4	6.7	6.0	5.9	7.1	4.0	8.8	6.6
	9.9	10.1	9.5	9.7	10.2	9.2	5.9	6.9	6.1	7.8
7	6.7	6.9	6.5	6.5	6.9	7.8	6.6	4.9	7.9	6.0
	10.3	9.9	10.1	10.2	10.0	8.4	9.0	7.3	6.9	7.7
8	6.3	6.8	6.6	6.8	6.4	6.3	8.7	6.1	7.8	6.5
	10.0	10.0	9.8	10.5	9.3	8.6	6.4	7.5	7.0	6.3
9	6.6	6.7	6.7	6.7	6.8	6.9	7.5	5.9	10.0	6.8
	9.9	9.7	9.9	10.4	9.7	9.0	8.8	7.7	6.1	5.2
10	6.4	6.9	6.8	6.1	6.3	8.0	6.2	9.0	9.5	6.9
	10.3	9.8	9.6	10.1	9.5	7.1	6.5	8.1	6.8	8.1

Upper column: Thickness of CdTe film at central part of substrate (μm).
Lower column: Conversion efficiency (%).

The difference between the CdTe film of Example 8 and the CdTe film of Comparative Example 3 is only a presence/absence of the addition of graphite to the pastes. That is, as clearly shown from Table 5, by forming with a mixture of the source and the additive, a CdTe film with a stable thickness can be obtained.

Further, it is also appreciated from Table 6 that the CdTe film of Example 8 has a smaller dispersion in thickness within one lot and between the lots as compared with the CdTe film of Comparative Example 3. For that reason, according to Example 8, it is possible to stably obtain a solar cell of more excellent characteristics as compared with Comparative example 3.

As previously described, by using a source mixed with an additive, it is possible to suppress mutual diffusion at a joint between the CdS and the CdTe resulting from an excessive heating by a radiation, thereby to stably obtain a CdTe film of good quality.

As the additive, any stable substance which does not decompose or cause a chemical reaction on the supporting member at the time of heating can be used.

Further, by using a substrate which has an uneven structure on the surface opposite to the surface on which a particle layer is formed as in Example 11, it is possible to absorb the infrared ray by the uneven surface and a similar effect can be obtained.

On the other hand, according to Example 10, by lowering the proportion occupied by a transparent conductive film at the peripheral part of the substrate as compared with that of the central part, it is possible to make the temperature difference of the surface of the substrate small, by utilizing an action of the transparent conductive film to suppress the radiation of the infrared ray. According to this method, the dispersion in the thickness of the CdTe film formed on the surface of the substrate can be made small. A similar effect can also be obtained by directly piling a separate substrate which has a similar structure on a normal source substrate.

Further, in the above-mentioned examples, although CdS is employed as the n-type semiconductor for a solar cell, a similar effect can also be obtained in a case of using CdZnS. For forming these n-type semiconductors, a known method such as a process of thermally decomposing an organometallic compound, a liquid phase film-forming process, a close-spaced sublimation process, a vapor-deposition process, a sputtering process and the like can be employed.

As the transparent conductive film, indium tin oxide or zinc oxide can also be employed in place of tin oxide. For forming the transparent conductive film, a sputtering process, a chemical vapor-phase growing process, a vapor-deposition process or the like can be employed.

In the preciously-mentioned examples, although the glass substrate which has the transparent conductive film and the CdS film on the surface is used as a substrate for forming the CdTe, it is also possible to use, in place of this, any of semiconductor materials of cadmium zinc sulfide, gallium arsenide, indium gallium arsenide, indium gallium phosphor arsenide, zinc selenide, indium selenide, silicon, germanium, indium copper selenide, indium gallium copper selenide, gallium nitride and the like, and metals of iron, nickel, molybdenum and the like, as the substrate. As the substrate, a ceramic material can also be used in addition to the glass.

Further, although a description has exemplary been made on the method for forming the CdTe film, it can also be applied to a thin film formation of other semiconductors such as CdS, cadmium zinc sulfide, zinc selenide, indium selenide, indium copper selenide, indium gallium copper selenide, and the like.

As the viscosity improver used in preparing the paste, such another material as ethylene glycol, methyl cellulose or the like can also be employed, in addition to propylene glycol which was used in the above-mentioned examples.

POSSIBILITY OF INDUSTRIAL UTILIZATION

According to the present invention, it is possible to form a CdTe film of good quality in an inexpensive efficiently. The present invention can be embodied in the manufacture of semiconductor device such as a solar cell, an infrared ray receiving device, and an integrated circuit.

We claim:

1. A method for preparing a CdTe film comprising:
   - a step of applying a paste containing a material for CdTe semiconductor on a supporting member, thereby to form a coating film containing said material for CdTe semiconductor on the surface of said supporting member,
   - a step of closely arranging said supporting member and a substrate on which a CdTe film is to be formed, to make said coating film to face the surface of said substrate, and
   - a step of forming a CdTe film on said substrate, by heating said coating film and said substrate, and causing said material for the semiconductor in said coating film to evaporate.

2. The method for preparing a CdTe film in accordance with claim **1**, wherein said semiconductor material is a mixture of a cadmium powder and a tellurium powder.

3. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains cadmium chloride.

4. The method for preparing a CdTe film in accordance with claim **3**, wherein the added amount of said cadmium chloride is 0.1–1.75 wt % to said semiconductor material.

5. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains a Group I element or a Group V element incorporated therein.

6. The method for preparing the CdTe film in accordance with claim **5**, wherein said Group I element is at least one member selected from the group consisting of lithium, potassium, sodium, rubidium, copper, silver and gold.

7. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is at least one member selected from the group consisting of arsenic, antimony, bismuth, phosphor and nitrogen.

8. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is antimony, and is contained in said paste in a state of antimony telluride.

9. The method for preparing a CdTe film in accordance with claim **5**, wherein said Group V element is contained in said paste in a state of at least one member selected from the group consisting of triphenylantimony, antimony octylate, triphenylbismuth, triphenylphosphine, triphenylphosphate, triphenylphosphite, triallylphosphine and triallylamine.

10. The method for preparing a CdTe film in accordance with claim **1**, wherein said paste contains an additive of powder state which is stable in composition at the heating step.

11. The method for preparing a CdTe film in accordance with claim **10**, wherein said additive is at least one member selected from the group consisting of carbon, silicon carbide, silicon dioxide, aluminum oxide, zirconium oxide, boron nitride, silicon nitride, and aluminum nitride.

12. The method for preparing a CdTe film in accordance with claim **1**, wherein at the step of applying said paste, the painted amount of the paste in the peripheral part of said substrate is made to be larger than the painted amount of the paste in the central part of said substrate.

13. The method for preparing a CdTe film in accordance with claim **1**, wherein said supporting member is at least one member selected from the group consisting of glass, ceramic material and carbon.

14. The method for preparing a CdTe film in accordance with claim **1**, wherein said supporting member is glass having a conductive oxide film on the surface thereof.

15. The method for preparing a CdTe film in accordance with claim **1**, wherein one surface of said supporting member that is opposite to the surface on which said paste is painted is rough.

16. A solar cell comprising: an insulating and transparent substrate, a transparent conductive film formed on said substrate, an n-type semiconductor film formed on said transparent conductive film, a p-type semiconductor layer formed on said n-type semiconductor film as a light absorbing layer, a current collector formed on said p-type semiconductor layer, a + side electrode electrically connected to said current collector, and a − side electrode electrically connected to said n-type semiconductor layer, wherein said p-type semiconductor film is a CdTe film formed by the method in accordance with claim **1**.

* * * * *

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(12) **United States Patent**
Gegenwart et al.

(10) **Patent No.: US 6,444,043 B1**
(45) **Date of Patent: Sep. 3, 2002**

(54) **APPARATUS FOR DEPOSITING CDS AND CDTE LAYERS ON SUBSTRATES BY MEANS OF A CSS PROCESS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(58) **Field of Search** 118/726; 392/389

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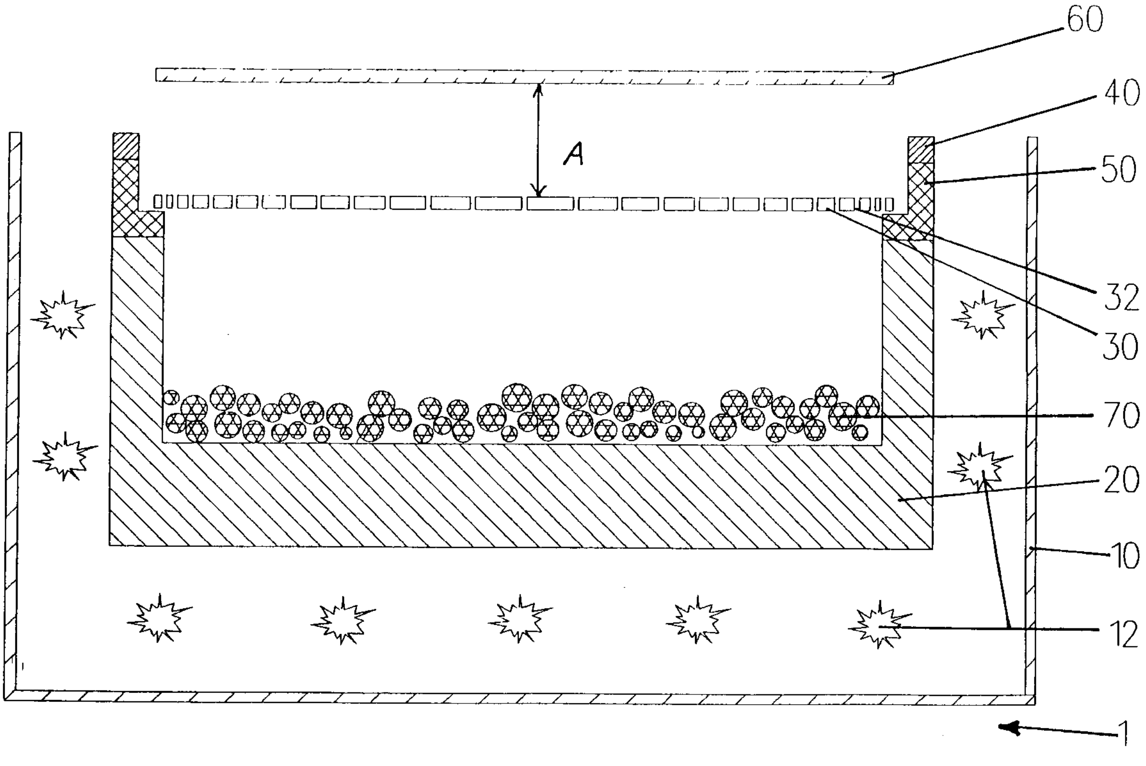
(57) **ABSTRACT**

Apparatus for depositing substrates by means of a CSS process comprising a heated receptacle (**20**) for a supply (**70**) of material to be deposited and carrier means for holding the substrate (**60**) with its side to be deposited towards an opening (**22**) of said receptacle, said receptacle opening (**22**) being provided with a cover (**30**) including a plurality of through-holes (**32**) for the sublimated material, said cover separating said material supply (**70**) from said substrate (**60**) and, due to being heated to a temperature higher than that of said receptacle (**20**), acting as sublimation source for said substrate.

16 Claims, 3 Drawing Sheets



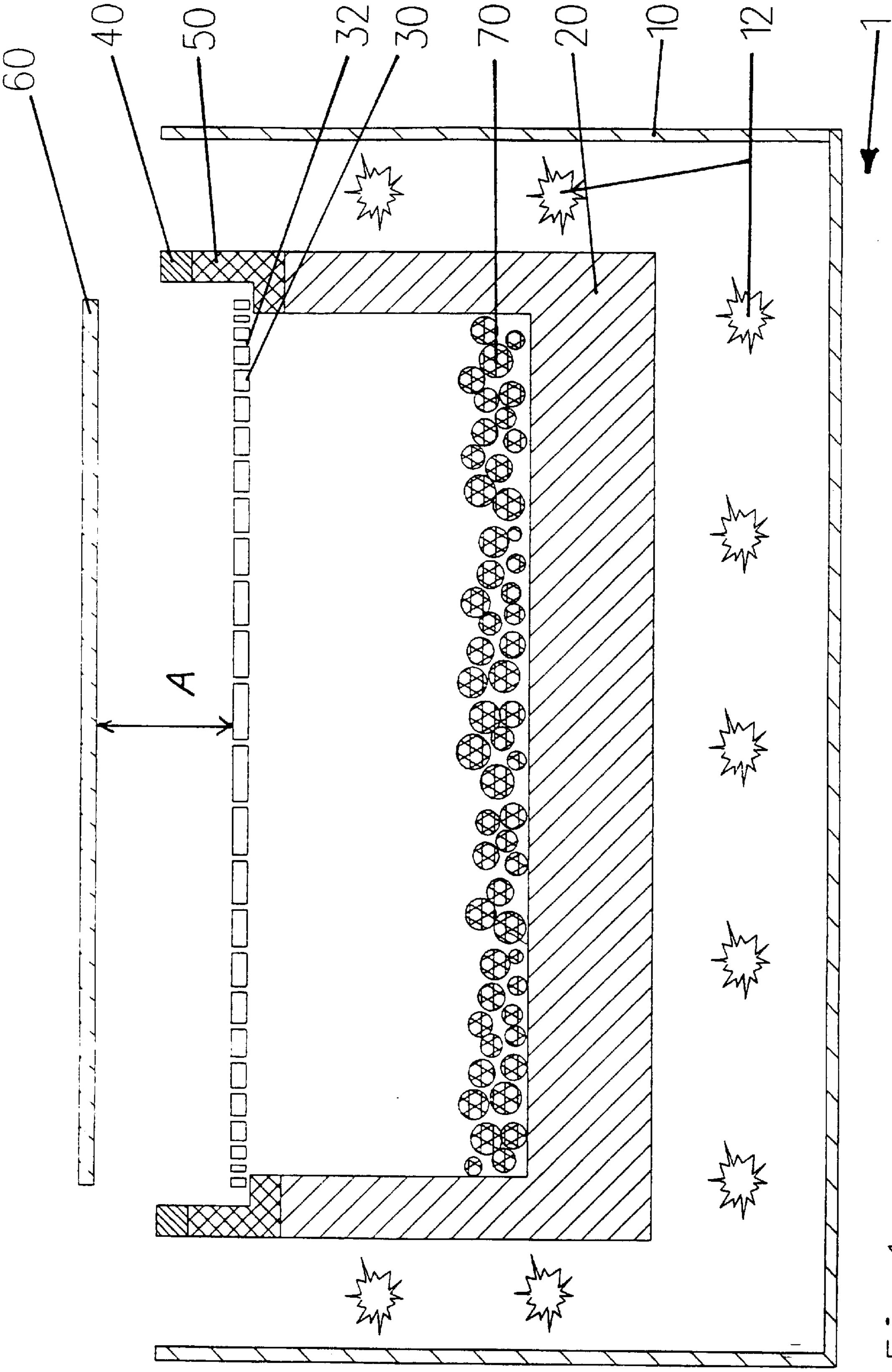


Fig. 1

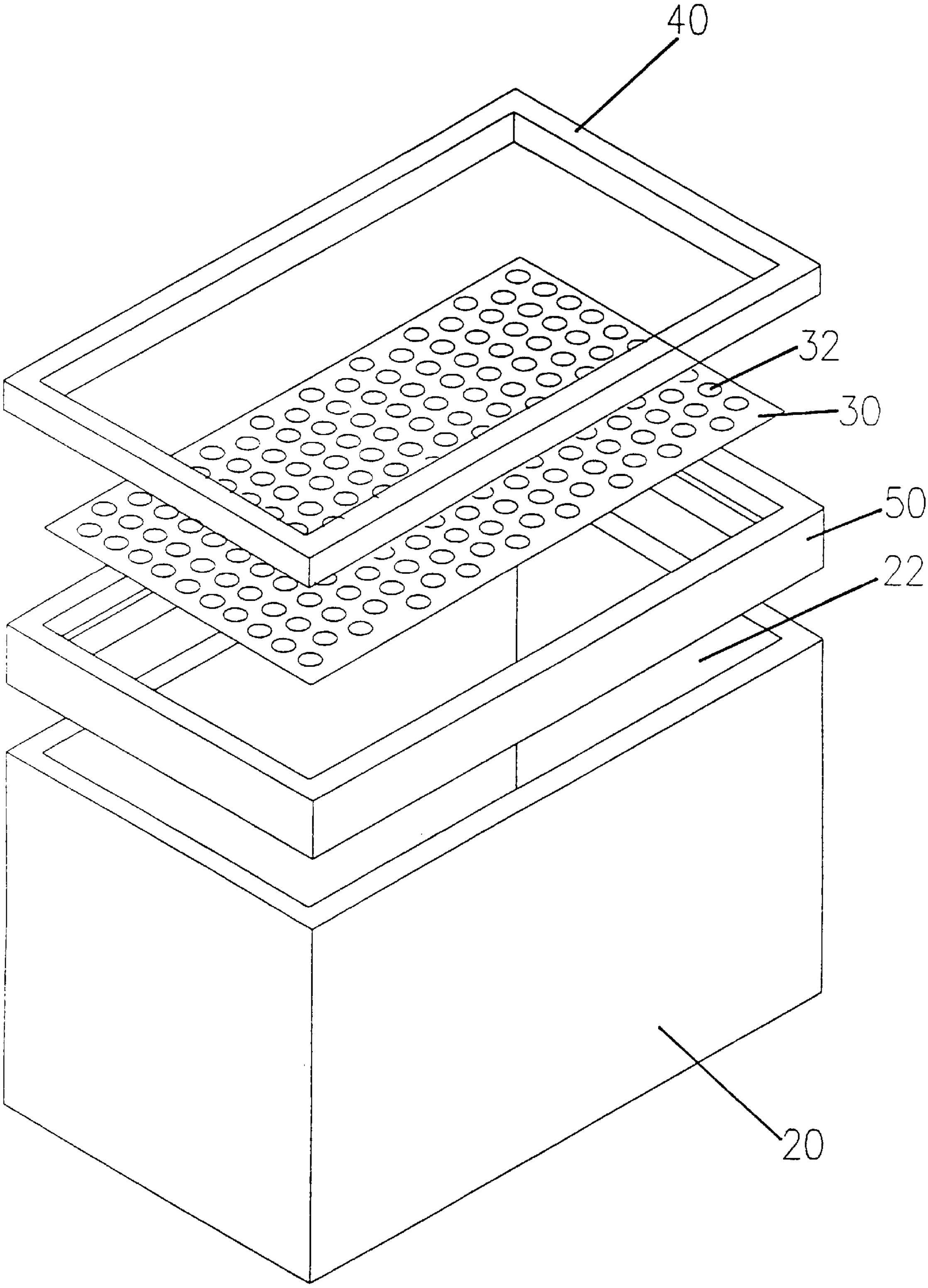


Fig.2

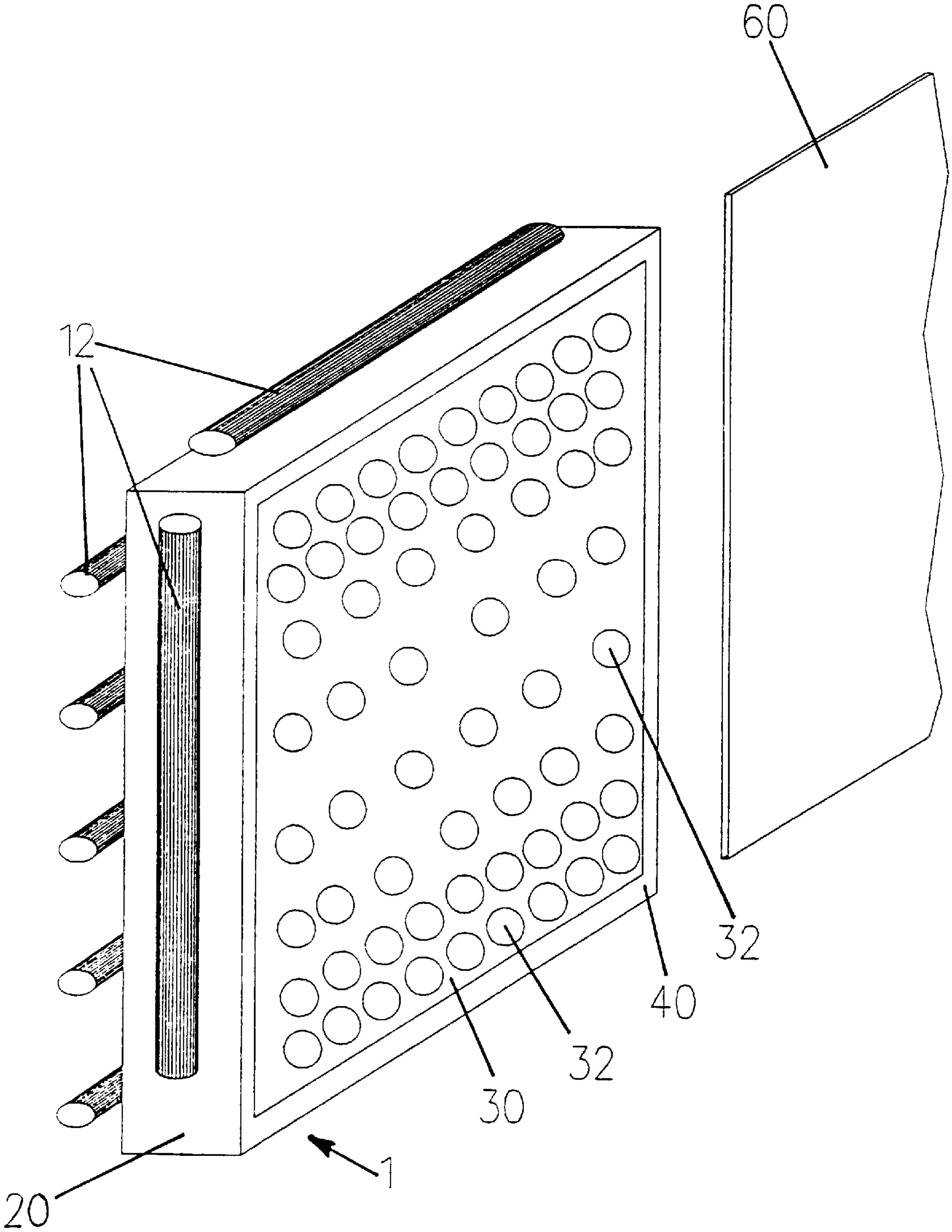


Fig.3

APPARATUS FOR DEPOSITING CDS AND CDTE LAYERS ON SUBSTRATES BY MEANS OF A CSS PROCESS

CROSS REFERENCES TO RELATED APPLICATIONS

Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

Not Applicable

BACKGROUND OF THE INVENTION

The present invention relates to an apparatus for depositing CdS and CdTe layers on substrates by means of a PVD process (Physical Vapor Deposition Process) in the form of a CSS (Close Spaced Sublimation) process. In particular, the invention is directed to a process for deposition of sublimated materials onto substrates for the production of CdS/CdTe solar cells.

In industrial semiconductor deposition processes and in those processes for manufacturing large-area electronic components CVD processes (Chemical Vapor deposition Processes) are employed for depositing, particularly silicon or dielectrics, such as SiO_2, Si_3N_4. Corresponding devices for mass production have been known. For the production of electronic and optical components, furthermore, selenium layers have been applied by CVD processes since a long time, as will be described in more detail in the following.

For the production of e.g. electroluminescence displays or certain solar or photovoltaic cells, such as CdS/CdTe solar cells, on the other hand, PVD processes are suited which provide thin layers or films by vapor deposition of material from a heated source. In addition to thermal evaporizers utilized, for instance, in the field of large area electronics (e.g. for the production of displays), particularly the CSS technology has been used during the last decades for CdS/CdTe solar cells. The devices hitherto known have not been suited for a continuous production of larger modules, neither with a view to their dimensions nor to their material sources.

The CSS technology as compared to CVE technology (Combination of Vapors of Elements) offers the advantage that, for instance, CdTe can be deposited with very high deposition rate. The microstructure, on the other hand, and the resulting electric properties of the CdTe layer-generated are suited for solar cell technology only if and when the close space or CSS distance between the sublimation material and the substrate is accurately adjusted and maintained and all the components of the source material, in the present case of the dissociated CdTe, are directly transported to the substrate surface for recombination thereon, independently from the remaining system parameters and the conditions elsewhere in the system. The close space distance is generally smaller than a few percent of the substrate dimensions. In order to ensure, moreover, that the condensation process remains limited to the small distance area between substrate and source material and that the desired temperature-depending dissociation pressure is obtained, pressure and temperature of source material and substrate should sensitively be adapted to each other.

When adapting a CSS apparatus to production scales including large deposition surfaces and high throughput, it should be ensured that the apparatus can be integrated in a continuous production line. The possibility of using a large number of adjacent evaporator sources was turned down because of the immense constructional efforts and the necessity of adjusting similar conditions of deposition at all sources. It was furthermore turned down to employ large-volume receptacles and to vary the temperatures thereof during the course of the deposition in order to adapt for deposition rate changes depending on the filling level of the material source or supply. Such temperature changes are hardly manageable the more so as layer formation on the substrate is considerably affected thereby.

BRIEF SUMMARY OF THE INVENTION

In view of long years of experience in connection with the critical deposition parameters for CdS/CdTe solar cells in CSS processes, the present inventors were indeed surprised that notwithstanding the problematic nature as outlined above it was possible to substantially uncouple the source material from the substrate in a spatial and physical manner and to locally displace the CSS distance between source material and substrate out of a source material receptacle in the area between the substrate and the cover provided at the opening of the receptacle of the inventional apparatus. Accordingly, the source material and substrate are actually separated by a multiple of the CSS distance from each other. Thereby, it became possible to operate with practically any receptacle and material supply.

An object of the present invention is to provide an apparatus for depositing CdS and CdTe layers on substrates by means of a PVD process in form of a CSS process, which is suited for a large-size deposition and a continuous deposition process. The object is solved by the subject matter of claim 1. Advantageous further developments are defined in the subclaims.

Based on the solution revealed in claim 1, it is possible to employ a large-surface sublimation source which allows sufficient material supply for a long uninterrupted production period without having to resort to corrective measures which depend on the actual filling level or having to refill the material supply. The cover provided according to the invention uncouples the deposition process from the material supply. Because of the higher temperature of the cover, the substrate does no longer "see" the material supply, as was the case in CSS apparatuses hitherto used, but, instead, the substrate rather "sees" the cover as sublimation source which thereby acts as physical deposition source and determines the thermal and kinetic behavior of the evaporated or sublimated materials, respectively. Consequently, the cover provides for spatial and physical separation of the material supply from the substrate. Contrary to disturbances and problems otherwise observed even in case of smallest interferences into the parameters of the deposition process, the deposition behavior, nevertheless, does not change. The inventors using the now completely differently dimensioned CSS deposition apparatus were able to successfully produce CdS/CdTe solar cells of high efficiency and output by applying temperature and pressure parameters which had proved of advantage in a typical conventional CSS device. According to the invention, changes of distribution and rate of deposition, otherwise occurring with decreasing filling level in the material receptacle, can successfully be avoided.

As described further above, substrates have been provided with selenium layers for a number of years using selenium which was evaporated in a material receptacle and impinged from the evaporation receptacle upon the material to be provided with the layer. Since as a rule evaporation and vapor exhaust from the receptacles are non-uniform, it has become, and still is, the practice to close the receptacles by a sieve or a perforated plate with through-holes (See, U.S. Pat. No. 5,532,102; DE 24 36 431 A; and WO 91 04 348 A). These holes plates provided a uniform deposition and vapor transport. Clogging of the holes is avoided in that the hole plate is heated in order to evaporize any condensing material. DE 24 36 431 A utilizes a hole plate the temperature of which is about 5 to 30° C. higher than the temperature of the material receptacle. A further advantage of the hole plate is that it blocks material spatters. According to U.S. Pat. No. 5,532,102, the hole plate is brought at the beginning of the deposition to a temperature significantly higher than the material receptacle and subsequently is lowered to that of the receptacle or somewhat higher. The holes in the cover are larger at the marginal zones of the plate in order to obtain a more uniform deposition of the vapor passing through the holes. WO 91 04 348 A employs heating means which are distributed over the complete height of an evaporation crucible in order to ensure highly uniform heat distribution. Uniform heat distribution is further promoted by a perforated cover arranged on the crucible, which is heated to a higher temperature relative to the crucible and should also block material spatters and the like. DE 26 53 909 A describes a thermal evaporization for large-surface substrates, which includes a perpendicularly disposed perforated cover. The surface area of the outlet openings of this vertical evaporization source should be less than 30%, preferably 15%, of the total cover surface. Condensations on the cover are avoided in that the cover material automatically heats up during the course of the deposition operation. In this way, reproducible vapor streams e.g. of evaporated silver, may be obtained.

The present invention, however, was not concerned with the problem to direct and distribute the evaporation cloud of a thermal evaporation source into a uniform and reproducible vapor stream onto a substrate using a perforated plate. The present invention, instead, had to solve the problem to precipitate elements having been dissociated by sublimation on a substrate such that the dissociated elements directly recombine on the substrate with a given micro structure of the resulting layer.

Preferred further developments of the present invention are defined in the subclaims. In this connection it is for instance possible to improve the deposition at the substrate edge zone by means of a particular hole pattern. A considerable improvement is, furthermore, accomplished by using a frame heated to a higher temperature than the temperature of the receptacle. Condensations of the sublimated material at the colder, outer upper edge of the material receptacle are thereby avoided, which otherwise would lead, in addition to material loss, also to transport problems. The material loss at the small gap between frame and substrate is, moreover, substantially reduced because this gap can be considerably smaller adjusted than the CSS distance between substrate and perforated cover. Hence, by means of that frame, considerably longer production periods can be obtained since precipitates at the upper edges of the receptacle which cannot be completely avoided anyway, grow more slowly because of the frame and need be removed less frequently. The frame may be a separate part arranged on the receptacle. It may also be integrated in a receptacle rim extending beyond the cover.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following, a preferred embodiment of the present invention is explained in more detail referring to the drawings wherein

FIG. **1** is a diagrammatic sectional view of a preferred embodiment of the apparatus of the invention for horizontal deposition;

FIG. **2** is a perspective exploded view of a material receptacle, a cover and a heated frame of FIG. **1**; and

FIG. **3** is a view on a material receptacle having a cover and a heated frame for vertical deposition according to a further embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The apparatus of the invention is used as a CSS apparatus particularly for the production of CdS/CdTe solar cells. The apparatus can, in principle, also be provided with different sublimation sources for alternative applications. It is also suited for the production of other photovoltaic elements such as CIS modules (Cu In Se_2 modules) for instance with a CdS deposition to be applied.

Apparatus **1** shown in FIG. **1** differs from prior art CSS deposition devices basically in that the close space distance for the deposition process is no longer defined between the material (CdS or CdTe, respectively) to be sublimated in the form of a granulate, of a polycrystalline disc or the like and the substrate (as shown for example EP 92 116 254.1 corresponding to EP 0,535,522 A2 and U.S. Pat. No. 5,304, 499). In a vacuum chamber, not shown, a plurality of apparatuses **1** are arranged in series. The vacuum chamber is held by means of mechanical pumps at a residual gas pressure of 10^{-4} to 10 mbar, preferably 10^{-2} mbar, and the substrate deposition of the present embodiment is made in this residual gas atmosphere. Optionally, flushing can be performed by means of inert gases such as nitrogen, helium, argon and the like. Substrates **60** are moved in a continuous passage via entrance and exit locks into the vacuum chamber and moved over apparatuses **1**. Rollers are provided between apparatuses **1** as carrier devices on which substrates **60** move on their passage over the apparatuses. The planar substrates **60** are directed with the deposition side downward. In FIG. **1**, substrates **60** are guided perpendicular to paper plane.

Apparatus **1** comprises a heated shield **10** rectangular in cross section made of graphite (for instance fiber-reinforced graphite) or other high-melting materials, such as tantalum or molybdenum, which are inert against the material to be evaporized. Within the heat shield, a rectangular receptacle **20** is provided. In the present embodiment, it is made of graphite.

Receptacle **20** having a large volume as compared to graphite crucibles formerly used includes a large-area top opening **22** and has a height which is sufficient to hold a material supply **70** (in the present case CdTe granulate) for a highest possible production period. In the present embodiment, rectangular opening **22** has dimensions of 250 mm by 700 mm and the receptacle can hold, at a depth of 200 mm, about 80 kg CdTe. With one receptacle filling, production periods of several days can be obtained. If a plurality of receptacles are successively arranged in the moving direction of the substrate, the production period can be extended without any difficulties up to one week.

According to FIG. **2**, a perforated hole plate **30** made of graphite (SIGRA-BOND (registered trade mark) by SGL Carbon Group) is embedded into the upper receptacle edge. Plate **30** may however also include other materials as mentioned above which are inert against the deposition material. Plate **30** is not placed directly on the receptacle edge but rather in an insulating ceramic holder **50**. In the present embodiment, the latter is L-shaped in cross section and is fastened in the receptacle edge by means of pins, not shown. In the shown example, plate **30** rests in the ceramic holder **50** consisting for instance of alumina. In the present embodiment, through-holes **32** of plate **30** have a medium diameter of about two mm. On one hand, through-holes **32** are so large that they do not significantly prevent the passage of the sublimation-evaporated material through plate **30**, and on the other hand, are small enough not to impair the desired uncoupling from the material supply. This is made possible in that, as shown, a plurality of holes having a diameter of about one to four mm are uniformly arranged at a small distance relative to each other, as can particularly be taken from FIG. **3**. In the present embodiment, holes **32** are arranged in a cubic face centered hole pattern having dimensions of 8 by 8 mm. Therefrom results an open surface area portion of 10% of the total surface of plate **30** passing the sublimated material. At the marginal zones of the substrate, the holes are provided larger and/or tighter in order to obtain a uniform deposition over the total plate width. (A substrate point is not only impacted by material passing through the hole disposed directly under it but also by the surrounding holes, and that is why in case of an unchanged hole structure deposition in marginal zones would be smaller.)

A plate as compared to wire-mesh shaped embodiments of electrically and thermally conductive material which in principle are possible is well, has the advantage that the percentage of the open passage area may be adjusted by one single plate to suitable values of between 5 and 25%. The passage through the hole pattern may, moreover, be locally changed. In the case of a wire mesh, the passage percentage, as a rule, is too large for the desired uncoupling so that two or more meshes arranged one above the other would have to be employed.

Graphite as the material for the plate offers the advantage of good electric conductivity and also thermal conductivity, and as corrosion proof material has the advantage of not reacting with the vapor particles. Graphite plate **30** can also be heated directly. To this end, the plate is directly connected to a separate ohmic heater.

Distance A (exaggeratedly represented in the Figure) between substrate **60** and hole plate **30** is adjusted by guiding and distance means, not shown, to 2 to 50 mm. In the present embodiment, the distance amounts to about 10 mm. It corresponds to the CSS distance normally to be adjusted between the substrate and the source material.

A heatable frame **40** also made of graphite is disposed at an elevated position relative to plate **30**. In this case the material alternatives described above in connection with plate **30** and shield **10** as well as with receptacle **20** are in principle possible too. Frame **40** is secured as shown to the upper side of ceramic holder **50** and can be heated, again by direct ohmic heating, independently from plate **30** and receptacle **20**. Rigid electric feed wires may be used for stabilizing the light frame **40**. In the present embodiment, ceramic holder **50** is so designed that it provides, as a one-piece part, both for electric insulation of receptacle **20** relative to plate **30** and of plate **30** relative to frame **40**, so that separate heating circuits are possible for frame **40** and plate **30**. Numerous further insulation measures can, however, be selected by those versed in the art. In the actual apparatus, the substrate is guided at smallest possible distance over frame **40** (e.g. 1 or 2 mm).

Receptacle **20** is also independently heated, in the present embodiment by means of heating lamps **12** in the form of halogen lamps or special infrared lamps with carbon filaments, so called “Carbonstrahler” (carbon radiators). For the deposition process, heating is generally effected so that hole plate **30** is hotter for a few degrees Celsius, preferably about 2 to 5° C., than receptacle **20** which in the present embodiment is heated to about 750° C. as compared to substrate **60** which is preheated to a temperature of about 500° C. When moved over apparatus **1**, the substrate retains its preheating temperature of about 500° C. because it is heated up by hot apparatus elements **12**, **20** and **30**. Frame **40** on the other hand, is again heated to a higher temperature than hole plate **30**, in the present case about preferably 2 to 5° C. higher. With the particular deposition parameters, the temperature ranges here specified have proved to be suitable. The temperature ranges for substrate (480° C. to 520° C.) and the receptacle or the CdTe source (700° C. to 770° C.), respectively, correspond to the data specified in EP 92,116,254.1 corresponding to EP 0,535,522 A2 and U.S. Pat. No. 5,304,499. The present inventors found out that the deposition parameters specified in that patent specification for the conventional small CSS apparatus (including pressures, deposition thickness, etc) can also be successfully applied in the large scale apparatus of the present invention. As to these parameters which are also considered preferred in the present invention, reference is explicitly made to that prior art patent.

It is not impossible that the above mentioned temperature differences may be smaller or higher. In general, however, a temperature difference of less than 2° C. between hole plate **30** and receptacle **20** as well as plate **30** and frame **40** will not be sufficient for the effects described in the following. Larger temperature differences above 10° C. are possible in principle, the respective deposition parameters should, however, not be changed by the temperature gradients which means that the temperature difference between hole plate **30** acting as physical deposition source and substrate **60** should fulfil the respective deposition parameters and that in the material supply, moreover, an optimum sublimation temperature can be adjusted.

As already described, the temperature difference between hole plate **30** and receptacle **20** ensures that the deposition parameters do not depend on the filling level of receptacle **20**. Furthermore, changes of the deposition rate distribution due to shadowing effects caused by the decreasing filling level need not be compensated. Uninterrupted production period of one week is possible by utilizing the apparatus described and adjusting a deposition rate of about 10 μm/minute and performing continuous deposition of about 0.7 m^2 large substrates. The local distribution of the deposition rate can be adjusted by the design of the hole pattern in hole plate **30** so that the deposition rate distribution can be selected by changing the plate. In other words, the deposition rate distribution is uncoupled from the source consisting of heated receptacle and material supply or material source.

The heating frame **40** offers the advantage that due to its increased temperature the material loss at the edge of receptacle **20** which is open on top may be reduced up to 80%. Undesired condensation effects in those otherwise colder edge zone are furthermore avoided that might also impede the quality of the deposition at the marginal zones of the substrate.

A further advantage offered by the apparatus of the present invention can be taken from FIG. **3** wherein hole plate **30** is perpendicularly disposed in front of opening **22** of receptacle **20** which has an open side. Thereby, a deposition process in continuously working vertical plants becomes possible. Within receptacle **20** moreover, fan-like divisions have been made and additional hole plates have been provided in order to obtain a uniform distribution of the deposition material. In view of the uncoupling effect according to the invention it is very well possible to provide in a perpendicularly disposed apparatus according to FIG. **3** a container for the material supply, the opening of which covered by hole plate **30** joins a container side wall in the area of which a larger material supply is provided on the bottom of the container. It is also possible to stack a plurality of such containers one upon the other to obtain a single large-surface deposition source.

In the present embodiment, a plate was inserted to cover the opening of receptacle **20**. Such plane structure is necessary for common deposition operations. If for instance different deposition parameters are to be adjusted over the substrate, it is, however, also conceivable to employ a curved structure provided with throughholes as cover. Neither need the substrate be always plane. In case of nonplanar substrates, the different distance between hole plate and deposition surface can, moreover, be adjusted by varying the hole pattern of the hole plate or cover.

In the case of evaporation material tending to particle emission, it is possible to use e.g. two slightly spaced hole plates having hole patterns offset relative to each other instead of a single plate. In this way, it is avoided that particles chipping off from the evaporation material find their way as sputters through a hole in the plate and reach the substrate. By means of the two plates and by offsetting the hole pattern, optical shielding is ensured.

What is claimed is:

1. An apparatus for depositing CdS and CdTe layers on a substrate by means of a CSS process, said apparatus comprising:

a heated receptacle having an opening, said receptacle being heated to a first temperature;

an initially fixed volume of material supply disposed in said receptacle, and selected from a group consisting of CdS and CdTe, wherein said heated receptacle sublimates said material supply to form a sublimated material which exits said receptacle through said opening to decrease said initially fixed volume of material supply;

a heated plate covering said opening, and including a plurality of through-holes through which said sublimated material passes, said plate being heated to a second temperature which is higher than said first temperature to form a sublimation source;

a substrate disposed outside of said receptacle and having a face facing said plate for receiving said sublimated material, said face being spaced a distance between about 2 and about 50 mm from said plate.

2. Apparatus according to claim **1**, characterized in that said through-holes are perforations.

3. Apparatus according to claim **2**, characterized in that said through-holes define a pattern in said plate **(30)**, wherein said plate is more porous proximal edges of said plate than in a central portion of said plate.

4. Apparatus according to claim **1**, characterized in that said plate **(30)** consists of electrically conductive material.

5. Apparatus according to claim **4**, characterized in that said electrically conductive material is graphite.

6. Apparatus according to claim **1**, characterized in that a frame **(40)** extends past said plate toward said substrate and adjacent at least one edge of said plate, and that second means are provided for independently heating said frame **(40)** such that it is kept at a temperature higher than that of said plate.

7. Apparatus according to claim **6**, characterized in that said plate **(30)** and said frame **(40)** each are electrically insulated relative to each other and said plate **(30)** and said frame **(40)** each are connected to an ohmic heating means.

8. Apparatus according to claim **1**, characterized in that for perpendicular substrate deposition, said plate **(30)** is disposed in a side opening of said receptacle **(20)**.

9. Apparatus according to claim **8**, characterized in that in said receptacle **(20)** includes divisions subdividing the interior of the receptacle.

10. Apparatus according to claim **1**, characterized in that said receptacle is a graphite receptacle **(20)**.

11. Apparatus according to claim **1**, characterized in that said receptacle **(20)** consists of a high-melting point material.

12. Apparatus according to claim **1**, characterized in that said material supply is granular.

13. Apparatus according to claim **1**, characterized in that said plate **(30)** is flat.

14. Apparatus according to claim **1**, characterized in that said plate **(30)** is curved.

15. Apparatus according to claim **6**, characterized in that said frame **(40)** is a separate part attached to the upper edge of the receptacle at an elevated position relative to said plate **(30)**.

16. Apparatus according to claim **6**, characterized in that said frame **(40)** is formed as an integral part of said receptacle.

* * * * *

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(45) **Date of Patent:** **May 1, 2007**

(54) **PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS**

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Oct. 17, 2001	(IT)		LU2001A0012
Oct. 17, 2001	(IT)		LU2001A0011

(51) **Int. Cl.**
H01L 21/00 (2006.01)

(52) **U.S. Cl.** **438/95**; 438/93; 438/102; 438/57; 257/184

(58) **Field of Classification Search** 438/57, 438/93, 94, 95, 98, 102; 257/183, 184
See application file for complete search history.

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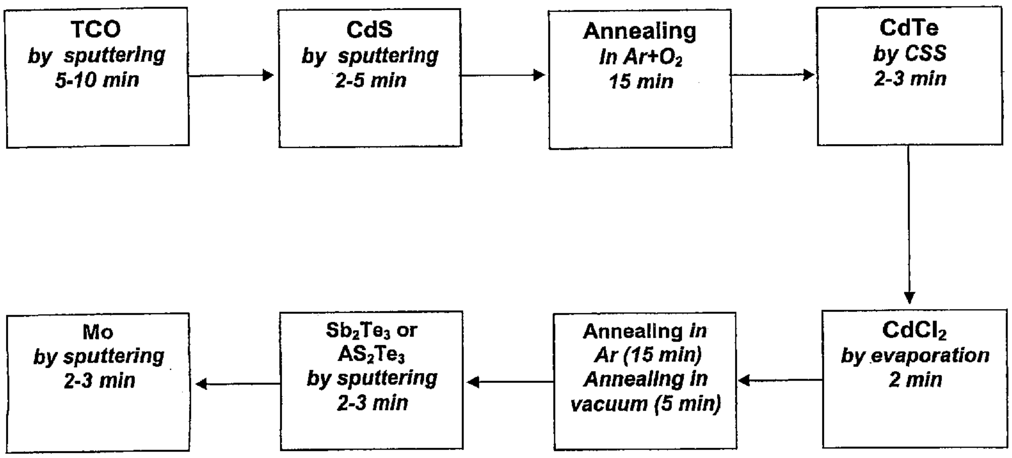
(57) **ABSTRACT**

A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; depositing a back-contact film on the treated CdTe film. Treatment of the CdTe film with $CdCl_2$ comprises the steps of: forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature; annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

19 Claims, 2 Drawing Sheets



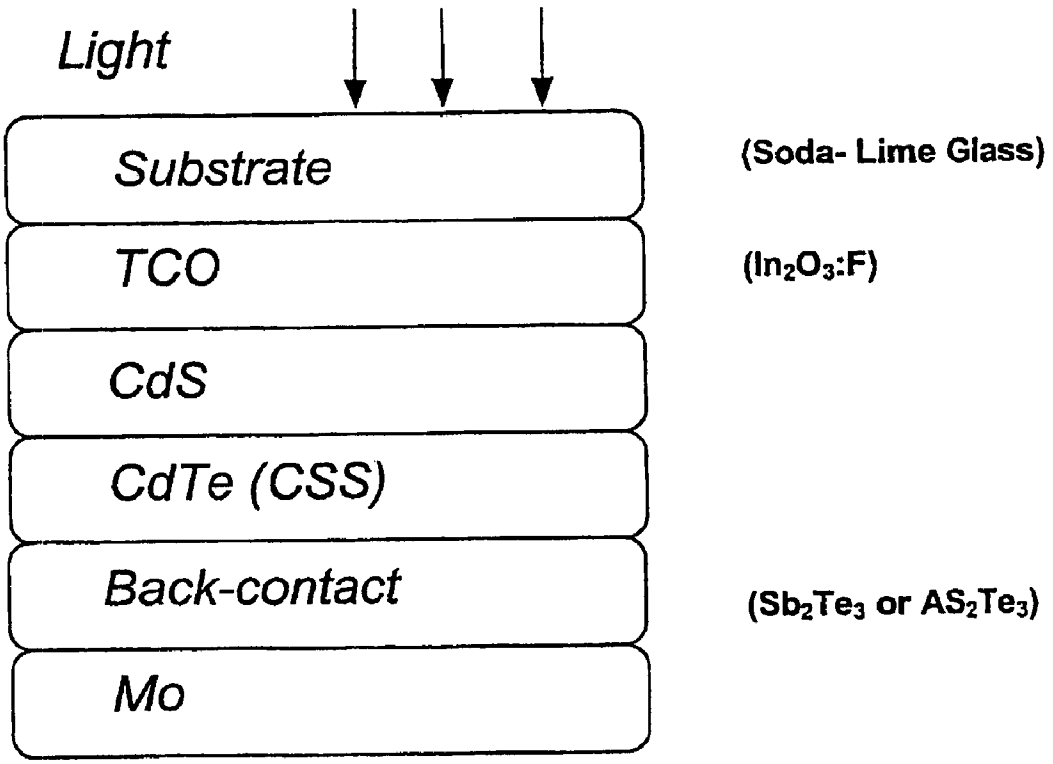

Light
Substrate
TCO
CdS
CdTe (CSS)
Back-contact
Mo
(Soda- Lime Glass)
(In2O3:F)
(Sb2Te3 or AS2Te3)

Fig. 1

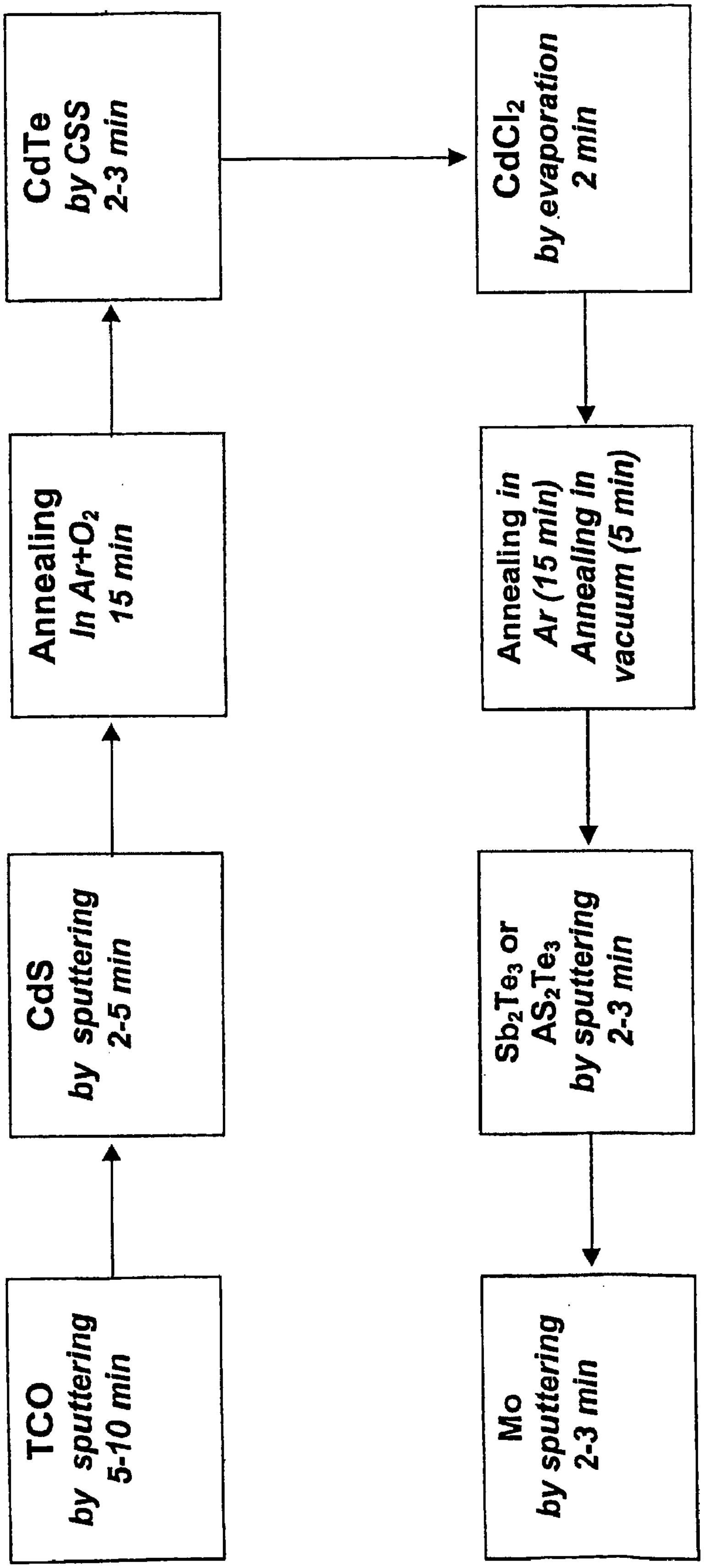

TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In Ar+O2
15 min
CdTe
by CSS
2-3 min
CdCl2
by evaporation
2 min
Annealing in
Ar (15 min)
Annealing in
vacuum (5 min)
Sb2Te3 or
AS2Te3
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

FIELD OF THE INVENTION

The present invention relates generally to alternative energy resources technology and, more particularly, to solar energy storage and the like.

BACKGROUND OF THE INVENTION

Conventional CdTe/CdS solar cells typically comprise a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film serving as the n-conductor, a CdTe film serving as the p-conductor and a metallic back-contact. A solar cell of this general description is disclosed, for example, in U.S. Pat. No. 5,304,499, which issued on Apr. 19, 1994.

While this "float" glass concept may be adapted for commercial use as a transparent substrate, frequent diffusion of Na into the TCO film has often resulted. Consequently, despite its relatively low cost, special glasses are often preferred over such a "float" glass arrangement.

Perhaps the most common TCO material is In_2O_3 which contains about 10% Sn (ITO). This material is usually characterized by a very low resistivity on the order of 3×10^{-4} Ωcm and a relatively high transparency (>85%) in the visible spectrum. While useful this material is made by sputtering and, after several runs, the ITO target forms noodles which contain excess In. In addition, a discharge may occur between noodles during sputtering which can damage the film.

Another material that is commonly used for the transparent conductive oxide film is fluorine doped SnO_2. Although helpful, this material exhibits a higher resistivity close to about 10^{-3} Ωcm. As a result, a 1 μm thick layer is necessary to keep the sheet resistance at about $10\ \Omega/_{square}$. Generally, a high TCO thickness decreases the transparency and, in turn, the photocurrent of the solar cell. In addition, a novel material, namely Cd_2SnO_4, developed by the NREL group (X. Wu et al., *Thin Solid Films,* 286 (1996) 274–276)) has been utilized. However, since the target is made up of a mixture of CdO and SnO_2, CdO being considered highly hygroscopic, the stability of the target has often been found unsatisfactory.

Generally speaking, the CdS film is deposited either by sputtering or Close-Spaced Sublimation (CSS) from a CdS granulate material. The latter technique allows thin films to be prepared at a substrate temperature considerably higher than that used in simple vacuum evaporation or sputtering. This is because the substrate and evaporation source are positioned very close to one another, i.e., at a distance of 2–6 mm, and deposition is performed in the presence of an inert gas such as Ar, He or N_2 at a pressure of about 10^{-1}–100 mbar. A higher substrate temperature usually allows growth of a better quality crystalline material. A significant characteristic of close-spaced sublimation is a very high growth rate up to about 10 μm/min, which is suitable for large-scale production.

Next, a CdTe film is deposited on the CdS film through close-spaced sublimation at a substrate temperature of 480–520° C. CdTe granulate is generally used as a source of CdTe which is vaporized from an open crucible.

An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$. Traditionally, most research groups would perform this step by depositing a layer of $CdCl_2$ on top of CdTe by simple evaporation or by dipping the CdTe in a methanol solution containing $CdCl_2$, and then annealing the material in air at about 400° C. for between about 15 and about 20 min. It is generally believed that $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of the small grains and removing defects in the material.

After $CdCl_2$ treatment, the CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ must be removed in order to provide for good back-contact onto the CdTe film. Also, it is believed that, since etching produces a Te-rich surface, formation of an ohmic contact when a metal is deposited on CdTe is facilitated.

The electric back-contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g., in graphite contacts, which, upon annealing, can diffuse in the CdTe film. Use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell is set forth by applicants in N. Romeo et al., *Solar Energy Materials & Solar Cells,* 58 (1999), 209–218).

Industrial interest in thin films solar cells has increased in recent years, especially in view of the relatively high conversion efficiency achieved. Recently, for instance, a record 16.5% conversion efficiency was reported (see X. Wu et al., 17th *European Photovoltaic Solar Energy Conversion Conference,* Munich, Germany, 22–26 Oct. 2001, II, 995–1000). Accordingly, a number of attempts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells. A state-of-the art report of these efforts may be found in D. Bonnet, *Thin Solid Films* 361–362 (2000), 547–552. While helpful, they include crucial steps that also affect either the stability and efficiency of CdTe/CdS thin film solar cells or their costs, thereby hindering achievement of a commercially viable process.

A significant problem of these processes is the etching step to which the CdTe surface must be submitted for removing CdO or $CdTeO_3$ oxides that form thereon. Although etching requires the steps of immersing substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for such continuous operation does not currently exist. Another difficulty that can negatively affect the stability of TCO films, as well as the cost of the final product, are the aforementioned disadvantages encountered using known TCOs. Moreover, known TCOs typically require the use of special glasses, such as borosilicate glass, to avoid Na diffusion and associated damage to the film that often occurs when soda-lime glass is used.

A further drawback of conventional processes relates to the source from which the CdS film and the CdTe film are produced through close-spaced sublimation. When relatively small pieces of these materials which contain dust, are used as a sublimation source, because of a different thermal contact, some micro-particles can overheat and, together with the vapor, split onto the substrate. In an attempt to avoid this inconvenience, complicated metallic masks are often used which make continuous operation problematic.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a process suitable for large-scale production of stable and efficient CdTe/CdS thin film solar cells using a low cost substrate.

Another object of the present invention is to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells in which the CdTe film is treated with $CdCl_2$ so as to eliminate the need for an etching step for removal of oxides that may form on the CdTe film.

It is a further object of the present invention to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells in which deposition of the TCO film is conducted such that a film of very low resistivity can be deposited without formation of metal noodles on the target, thereby enabling a relatively inexpensive substrate to be used.

Still another object of the present invention is to provide a process for large-scale production of stable and efficient CdTe/CdS thin film solar cells which allows formation of CdS and CdTe films that are entirely free of dust.

It is yet another object of the present invention to provide a CdTe/CdS thin film solar cell that is stable, efficient and relatively low-cost.

According to one aspect of the present invention, treatment of CdTe film with $CdCl_2$ is accomplished by first forming a layer of $CdCl_2$ having a thickness between about 100 and about 200 nm on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380 and 420° C. and a pressure between about 300 and about 1000 mbar under an inert gas atmosphere; and, finally, removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is maintained at a temperature generally within a range of 350 and 420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. As a result, etching treatment of the CdTe film is unnecessary and the process can be conducted continuously.

According to another aspect of the present invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing approximately 1–3 vol. % hydrogen and a gaseous fluoroalkyle compound, in particular, CHF_3. In this manner, the TCO is doped with fluorine.

According to a further aspect of the present invention, as a source material for formation of the CdS and CdTe films by sputtering or close-spaced sublimation, a CdS or CdTe material, respectively, is used in the form of a relatively compact block.

Further features of the process according to the invention are set forth in the dependent claims.

In accordance with still another aspect of the present invention, a process is provided for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; and depositing a back-contact film on the treated CdTe film. In treatment of the CdTe film with CdCl, initially a layer of $CdCl_2$ is formed on the CdTe film by evaporation, while maintaining the substrate at room temperature. Second, the $CdCl_2$ layer is annealed in a vacuum chamber at a temperature, generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere. Finally, the inert gas is removed from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

According to yet another aspect of the present invention, a process is provided for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of (i) depositing a film of a transparent conductive oxide (TCO) on the substrate; (ii) depositing a film of CdS on the TCO film; (iii) depositing a film of CdTe on the CdS film; (iv) treating the CdTe film with $CDCl_2$; and (v) depositing a back-contact film on the treated CdTe film, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

In accordance with still a further aspect of the present invention, a process for large-scale production of CdTe/CdS thin film solar cells is provided. Films of the cells are deposited, in sequence, on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; and depositing a back-contact film on the treated CdTe film, wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or CdTe material, respectively, generally in the form of a compact block is used.

Yet a further aspect of the present invention is directed to a CdTe/CdS thin film solar cell comprising a transparent substrate on which a layer of a transparent conductive oxide (TCO) is deposited. A CdS layer is deposited on the TCO layer, a CdTe layer is deposited on the CdS layer and a back-contact layer on the CdTe layer, wherein the transparent conductive oxide is In_2O_3 doped with fluorine and the back-contact layer is formed by a layer of Sb_2Te_3 or As_2Te_3 covered by a layer of Mo.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and advantages of the process for large-scale production of CdTe/CdS thin film solar cells, according to the present invention, will become apparent from the following description of specific, illustrative embodiments thereof made with reference to the following drawings, in which:

FIG. **1** is a schematic diagram showing a film deposition sequence for producing CdTe/CdS thin film solar cells, according to one aspect of the present invention;

FIG. **2** is a flow diagram showing a process for producing CdTe/CdS thin film solar cells, according to another aspect of the present invention.

The same numerals are used throughout the drawing figures to designate similar elements. Still other objects and advantages of the present invention will become apparent from the following description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings and, more particularly, to FIGS. **1**–**2**, there is shown generally a specific, illustrative process for producing CdTe/CdS solar cells, according to the present invention. Such solar cells comprise five layers deposited in a selected sequence on a transparent base layer or substrate, the layers consisting of about a 300 nm to about a 500 nm thick layer of a transparent conducting oxide

(TCO), about an 80 nm to about a 200 nm thick layer of CdS deposited on the TCO layer, about a 4 μm to about a 12 μm thick layer of CdTe on the CdS layer and a back contact layer formed of at least about a 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate preferably comprises soda-lime glass and the transparent conducting oxide is desirably fluorine-doped (In_2O_3.F).

TCO layer consists of In_2O_3, which is doped with fluorine during growth. The In_2O_3 target, unlike ITO, does not form any noodles. A very low resistivity is obtained by introducing a relatively small amount of fluorine to the sputtering chamber in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a $Ar+H_2$ mixture, in which H_2 is around 20% in respect to Ar. A typical example is a generally 500 nm thick film of In_2O_3 deposited with a deposition rate generally higher than about 10 Å/sec at a substrate temperature of approximately 500° C., with an Ar flow-rate of about 200 sccm, a CHF_3 flow-rate of roughly 5 sccm and an $Ar+H_2$ flow-rate of around 20 sccm. Accordingly, the reactive sputtering gas comprises Ar in the amount of about 2.5 vol. % of CHF_3 and about 1.8 vol. % of H_2. This film exhibits a sheet resistance of approximately 5 $\Omega/_{square}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than about 85% in the wavelength generally within a range of 400 and 800 nm. Another characteristic of this film is its high degree of stability as well as its ability to prevent Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable, even if heated to about 180° C. when illuminated by "ten suns" for several hours.

After deposition of the CdS and CdTe films in the known way of sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ as follows.

First, 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. Annealing is then performed for about 15–20 min at approximately 400° C. in a vacuum chamber in which roughly 500 mbar of Ar is introduced. After annealing, the chamber evacuated while keeping the substrate at a temperature of about 400° C. for 5 min. Since $CdCl_2$ has a relatively high vapor pressure at about 400° C., any residual $CdCl_2$ re-evaporates from the CdTe surface. It is noted that CdO or CdTeO, are not formed since annealing is conducted in an inert atmosphere, which does not generally contain O_2.

According to various aspects of the present invention, a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing a thin layer of a relatively highly conducting p-type semiconductor, such as Sb_2Te_3 or As_2Te_3, on top of the CdTe film. Generally speaking, a good, non-rectifying contact is achieved on a clean CdTe surface if a layer of Sb_2Te_3 or As_2Te_3 at least about 100 mm thick is deposited by sputtering at a substrate temperature of between about 250 and about 300° C. and between about 200 and about 250° C., respectively. Sb_2Te_3 grows naturally as p-type with a resistivity of around 10^{-4} Ωcm, whereas As_2Te_3 also grows as p-type but with a resistivity of roughly 10^{-3} Ωcm. The contact procedure is then completed by covering the low resistivity p-type semiconductor with at least about 100 nm of Mo_2 as is considered common practice in the art. A relatively thin layer of Mo is necessary in order to have a relatively low sheet-resistance on the back-contact.

As a source of CdS and CdTe materials used to form the respective layers by sputtering or CSS, a granulate material can be used, as is common practice in the art. However, in view of the disadvantages indicated above, when operating in this way, according to a preferred embodiment of the present invention, a new sublimation source can be used which consists of a relatively compact block obtained by melting and solidifying the material in an oven capable of sustaining a temperature generally higher than the melting temperature of the material.

A procedure for preparing the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3), which is a low melting point material (450° C.) and exhibits a very low vapor pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over the CdS and covers the CdS completely upon cooling. In this way, CdS covered with B_2O_3, if it is placed in an oven containing an inert gas at a pressure higher than approximately 50 atm. does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of about 1750° C., the oven is heated up to a temperature of about 1800° C. or more, and then cooled down to room temperature. In this manner, a unique compact block of CdS is obtained that is particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared using this type of source resulted in a very smooth film that is completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically approximately 100 nm thick. The substrate temperature is preferably kept between about 200 and 300° C. when CdS is prepared by sputtering and generally within a range of 480 and 520° C. when it is prepared by close-spaced-sublimation. The sputtered CdS layer generally requires annealing at about 500° C. in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a relatively high efficiency. In the case where CdS is prepared by close-spaced sublimation, O_2 is introduced to the sublimation chamber during deposition. While the role of O_2 is not known, it is presumed to passivate the CdS grain boundaries.

In accordance with another embodiment of the present invention, the CdTe source too is a generally compact block obtained through melting and solidifying pieces of CdTe in an oven under high pressure, as described previously. Since CdTe melts at around 1120° C., the oven must be heated to about 1200° C. in order to have complete melting of the CdTe pieces. CdTe films are deposited on the CdS by close-spaced sublimation at a substrate temperature generally within a range of 480 and 520° C. Deposition rates during CdTe growth are typically about 4 μm/min. In this manner, about 8 μm of CdTe are deposited in approximately 2 minutes.

By following the procedure described above, several solar cells have been prepared using as a substrate a I inch square low-cost soda-lime glass. A typical area of these cells is 1 cm^2. The finished cells are generally put under 10–20 suns for several hours at a temperature of around 180° C. in the open-circuit-voltage (V_{oc}) conditions. Advantageously, an increase in efficiency of about 20% or more is, thereby, achieved and without any material degradation.

The efficiency of these cells is generally within a range of 12% and 14% with open-circuit-voltages (V_{oc}) larger than approximately 800 mV, short-circuit-currents (J_{ac}) of between about 22 and about 25 MA/cm^2 and fill-factors (ff) ranging from about 0.6 to about 0.66.

EXAMPLE

A cell exhibiting an efficiency of around 14% has been prepared in the following way: soda-lime glass is covered with 500 nm of In_2O_3.F (fluorine-doped) deposited at a substrate temperature of about 500° C. as described above. 100 nm of CdS are then deposited thereon by sputtering at approximately 300° C. substrate temperature and annealed for about 15 min. at approximately 500° C. in 500 mbar of Ar containing about 20% O_2. 8 μm of CdTe are deposited on top of the CdS by CSS at a substrate temperature of approximately 500° C. Both the CdS and CdTe films are produced from a relatively compact block source as described above. A treatment with 150 nm of $CdCl_2$ is then performed in an Ar atmosphere, as described above. Finally, a back-contact is created, without any etching, by depositing, in sequence, through sputtering about 150 nm of Sb_2Te_3 and 150 nm of Mo.

After one hour under 10 suns at a temperature of about 180° C. in open-circuit conditions, the solar cell prepared in this way exhibited the following characteristics:

V_{OC}	852 mv
J_{SC}	25 mA/cm^2
ff	0.66
efficiency	14%

The techniques used in this process, such as sputtering and close-spaced sublimitation, are fast, reproducible and easily scalable.

In general, sputtering systems capable of covering an area of around 1×0.5 m^2 of glass are already commercially available, while close-spaced sublimation, which at a laboratory scale can readily cover 20×20 cm^2 area glass, does not yield any problems in being scaled up to about 1.5×0.5 m^2. An in-line process can work well if a large area glass is moved slowly over the different sources, namely, TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3, and Mo. In order to connect the single cells in series, the in-line system desirably also includes three laser scribing processes, the first one after the TCO deposition, the second one before the back-contact deposition, and the third at the end of the process. An relatively important part of the process, according to the present invention, is that no acids or liquids are used and, as a consequence, the process can be conducted on a continuous basis without interruption as is often needed to for etching in acid or in a Br-methanol solution.

Various modifications and alterations to the invention may be appreciated based on a review of this disclosure. These changes and additions are intended to be within the scope and spirit of the invention as defined by the following claim.

What is claimed is:

1. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the treatment of the CdTe film with $CdCl_2$ comprises the steps of:

forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature;

annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; and

removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process set forth in claim **1**, wherein the $CdCl_2$ layer is between about 100 nm and about 200 nm thick.

3. The process set forth in claim **1**, wherein annealing of the $CdCl_2$ layer is carried out for about 15–20 minutes.

4. The process set forth in claim **1**, wherein the inert gas is Ar.

5. The process set forth in claim **1**, wherein the back-contact film is formed of a Sb_2Te_3 layer covered by a layer of Mo.

6. The process set forth in claim **5**, wherein the Sb_2Te_3 layer is formed by sputtering at a temperature between about 250° C. and about 300° C.

7. The process set forth in claim **1**, wherein the back-contact film is formed of a As_2Te_3 layer covered with a layer of Mo.

8. The process set forth in claim **7**, wherein the As_2Te_3 layer is formed by sputtering at a temperature between about 200° C. and about 250° C.

9. The process set forth in claim **1**, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process set forth in claim **9**, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

11. The process set forth in claim **10**, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume, and wherein the fluoroalkyle compound is CHF_3.

12. The process set forth in claim **1**, wherein, as a source material for formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

13. The process set forth in claim **12**, wherein the compact block CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

14. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

15. The process set forth in claim **14**, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

16. The process set forth in claim **15**, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume, and wherein the fluoroalkyle compound is CHF_3.

17. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

18. The process set forth in claim **17**, wherein the compact block of CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than about 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

19. The process set forth in claim **1**, wherein the transparent substrate is soda-lime glass.

* * * * *

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(12) **United States Patent**
Barth et al.

(10) **Patent No.: US 7,220,321 B2**
(45) **Date of Patent: May 22, 2007**

(54) APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 465 days.

(21) Appl. No.: **10/808,050**

(22) Filed: **Mar. 24, 2004**

(65) **Prior Publication Data**

US 2005/0158891 A1 Jul. 21, 2005

Related U.S. Application Data

(62) Division of application No. 10/200,265, filed on Jul. 22, 2002, now abandoned, which is a division of application No. 09/583,381, filed on May 30, 2000, now Pat. No. 6,423,565.

(51) **Int. Cl.**
C23G 16/00 (2006.01)

(52) **U.S. Cl.** **118/729**; 117/109

(58) **Field of Classification Search** 438/542; 118/729, 50.1; 117/109
See application file for complete search history.

(56) **References Cited**

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6,291,799 B1 * 9/2001 Heyer et al. 219/388

FOREIGN PATENT DOCUMENTS

JP 357095624 * 6/1982 .... 29/25.02

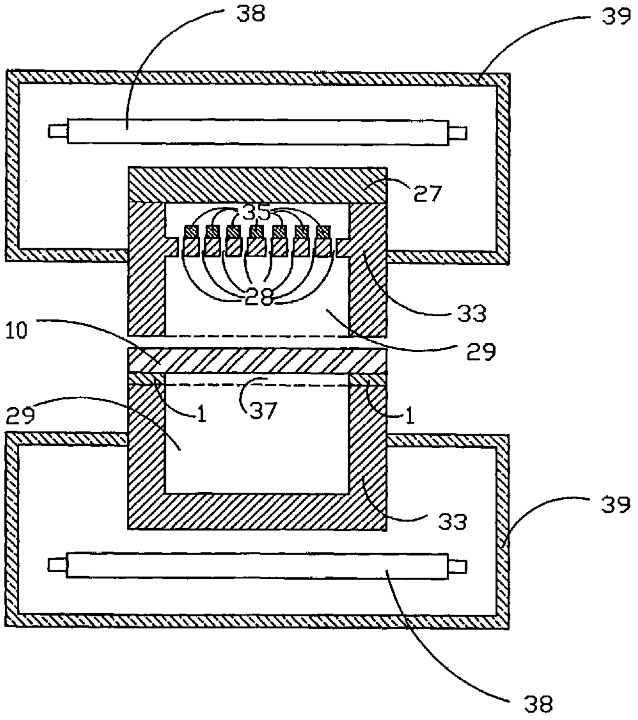
* cited by examiner

Primary Examiner—Caridad Everhart
(74) *Attorney, Agent, or Firm*—William E. Hein

(57) ABSTRACT

An apparatus and processes for large scale inline manufacturing of CdTe photovoltaic modules in which all steps, including rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation, are performed within a single vacuum boundary at modest vacuum pressures. A p+ ohmic contact region is formed by subliming a metal salt onto the CdTe layer. A back electrode is formed by way of a low cost spray process, and module scribing is performed by means of abrasive blasting or mechanical brushing through a mask. The vacuum process apparatus facilitates selective heating of substrates and films, exposure of substrates and films to vapor with minimal vapor leakage, deposition of thin films onto a substrate, and stripping thin films from a substrate. A substrate transport apparatus permits the movement of substrates into and out of vacuum during the thin film deposition processes, while preventing the collection of coatings on the substrate transport apparatus itself.

5 Claims, 14 Drawing Sheets



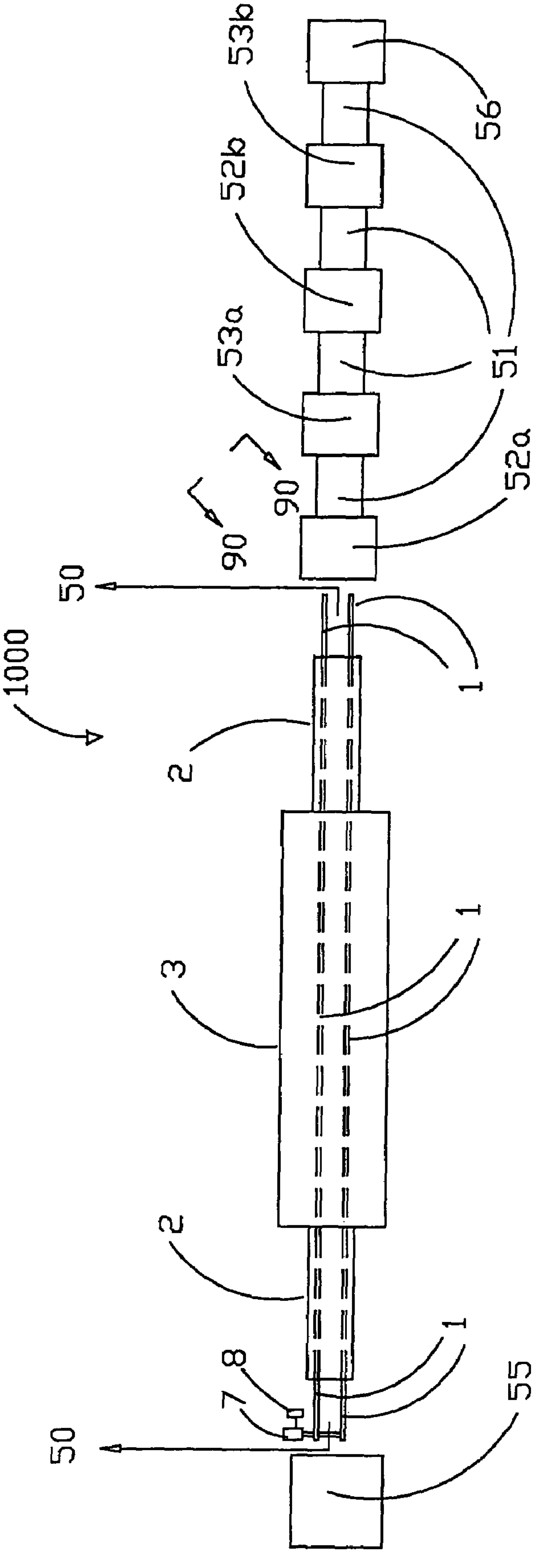


Fig. 1

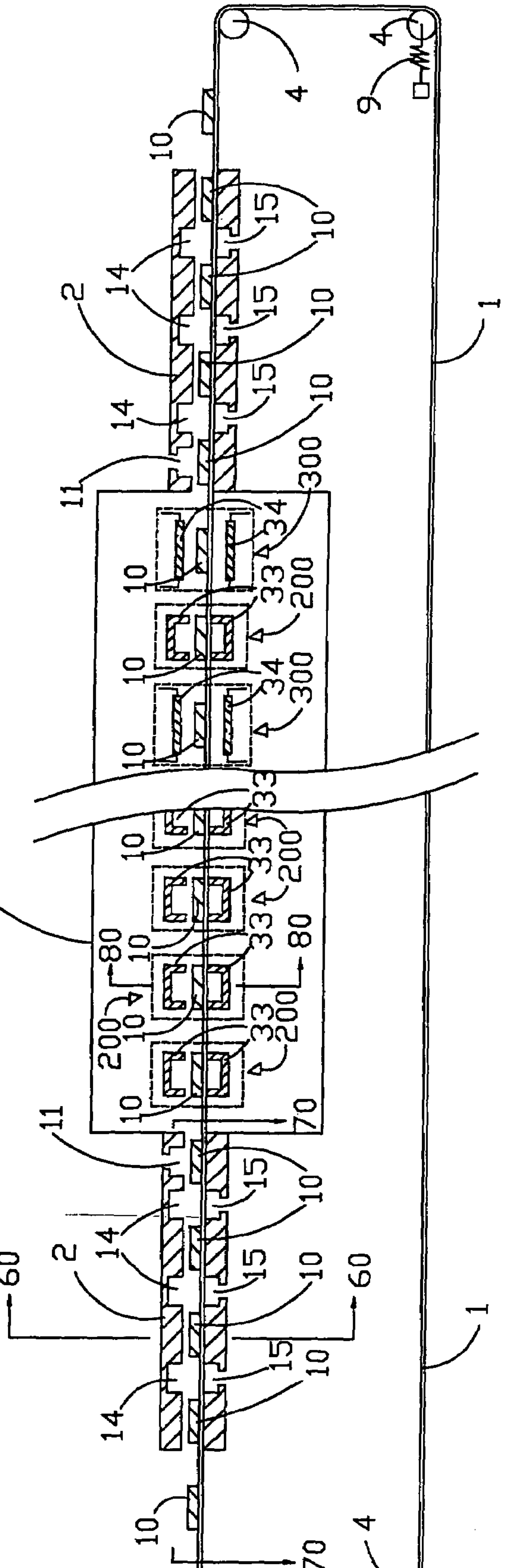


Fig. 2A

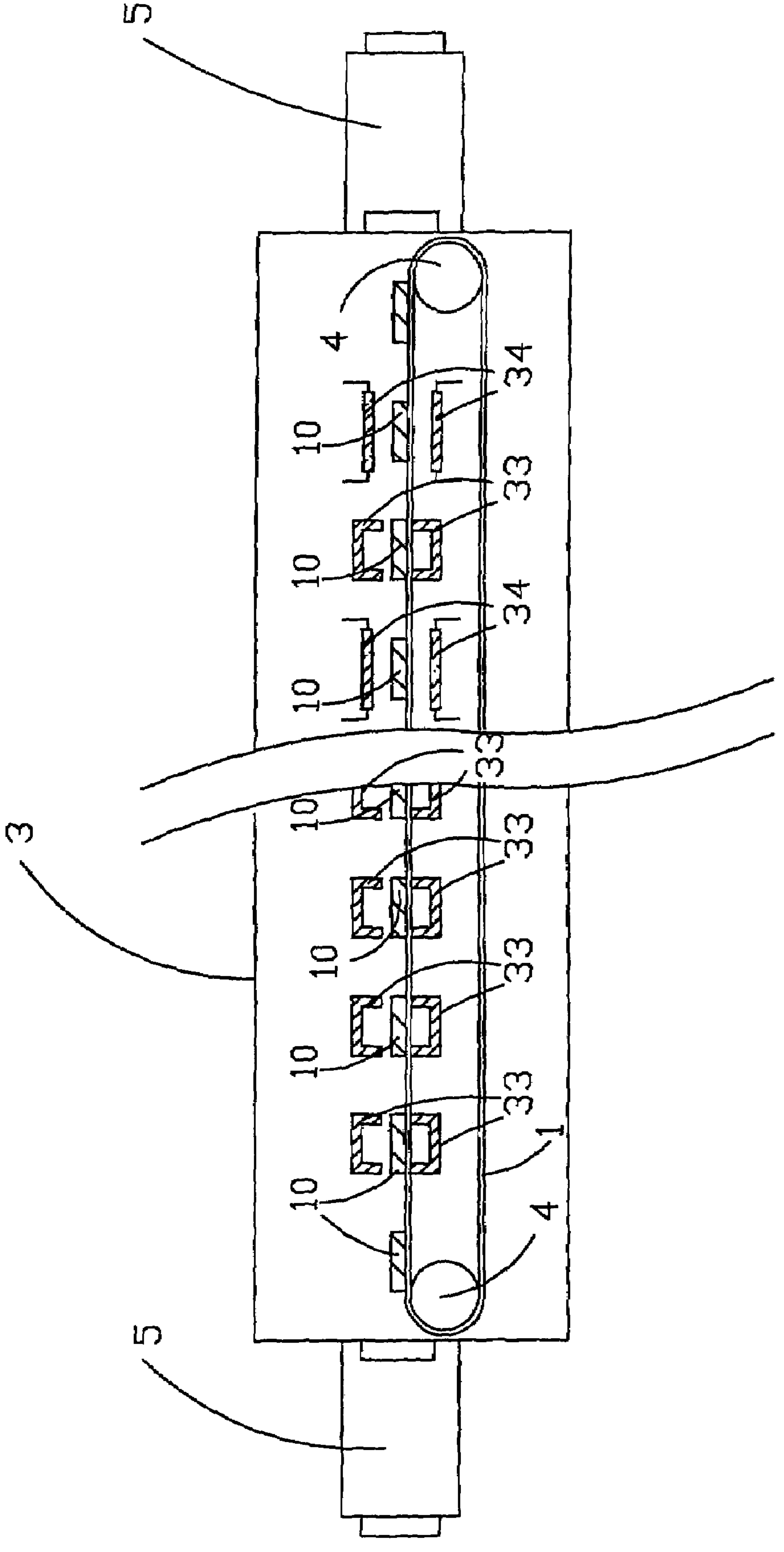


Fig. 2B

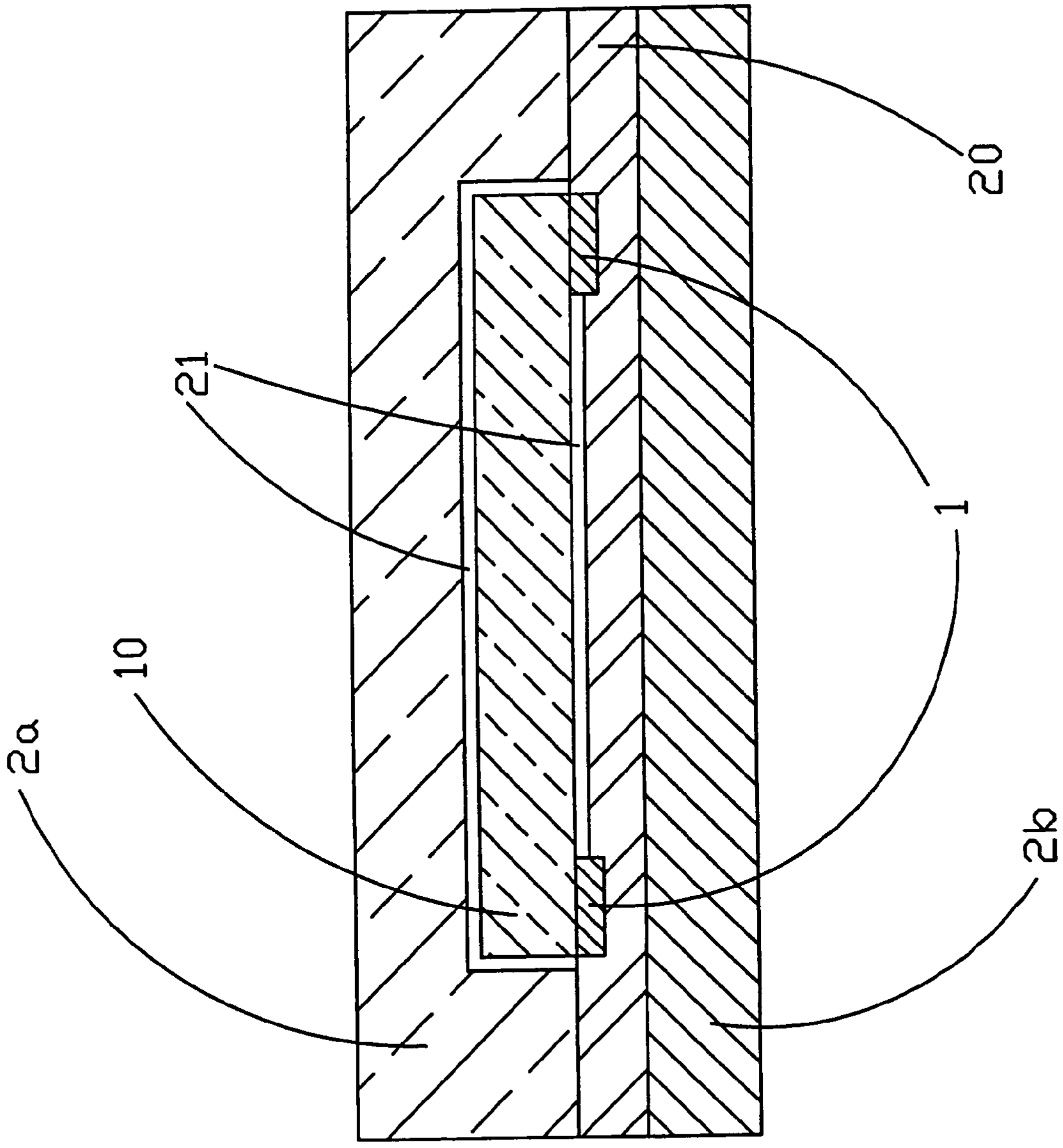


Fig. 3

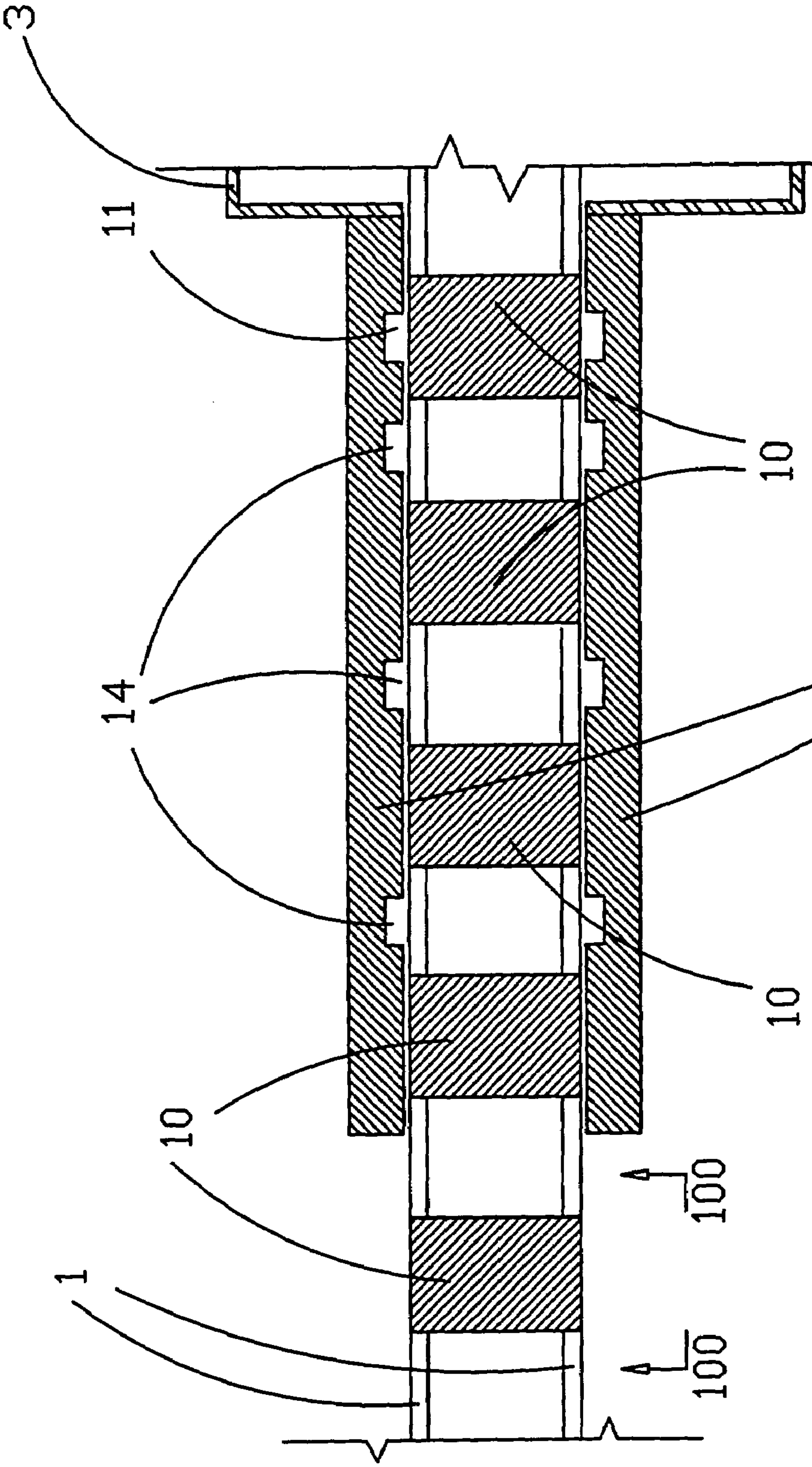


Fig. 4

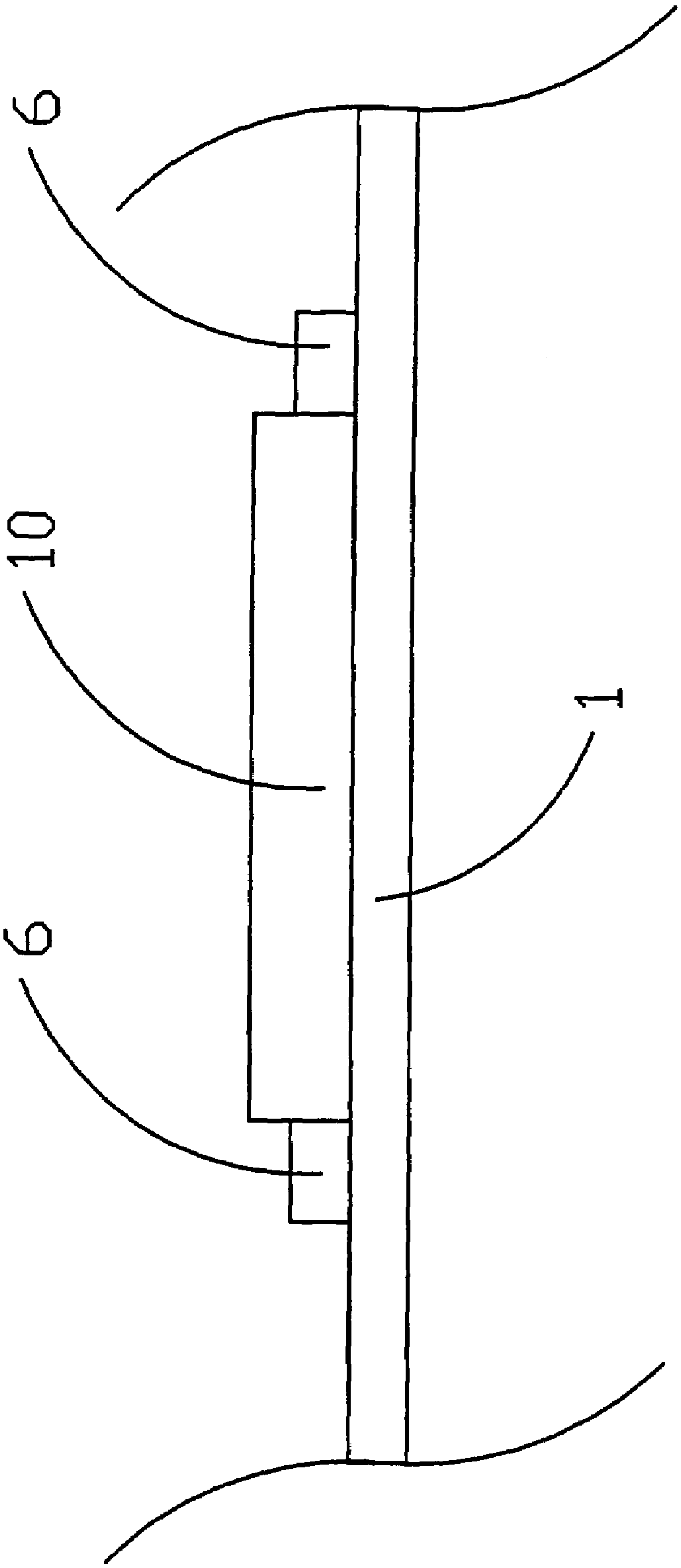


Fig. 5

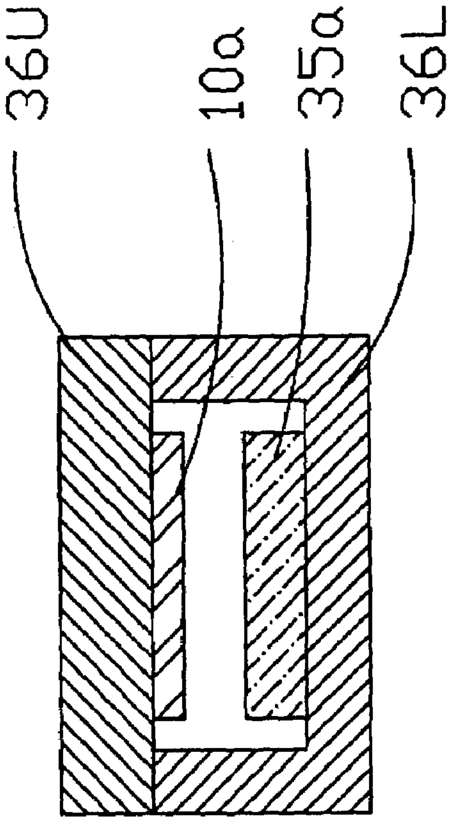


Fig. 6A (PRIOR ART)

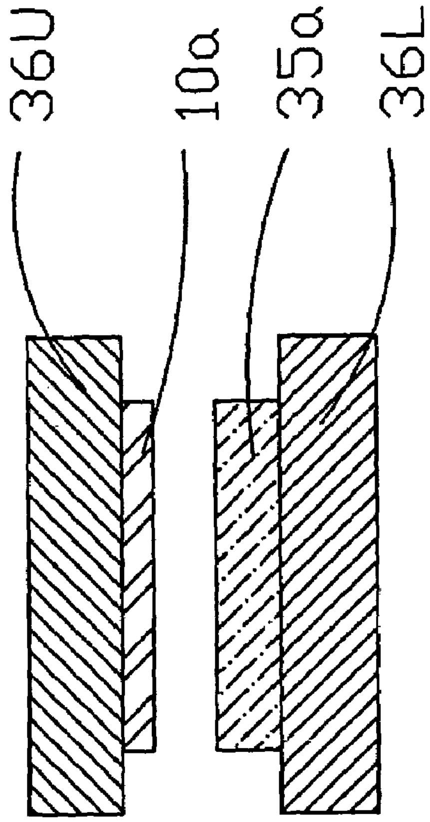


Fig. 6B (PRIOR ART)

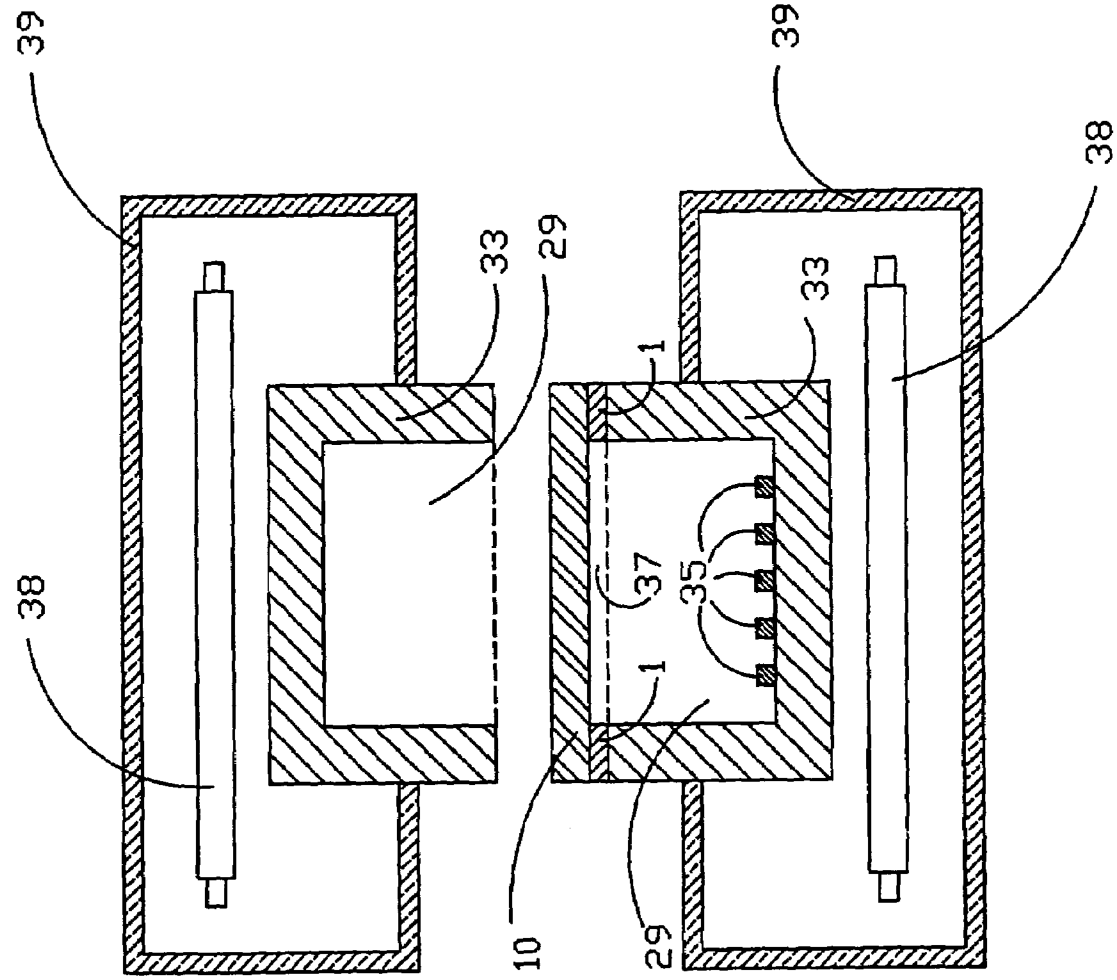


Fig. 7A

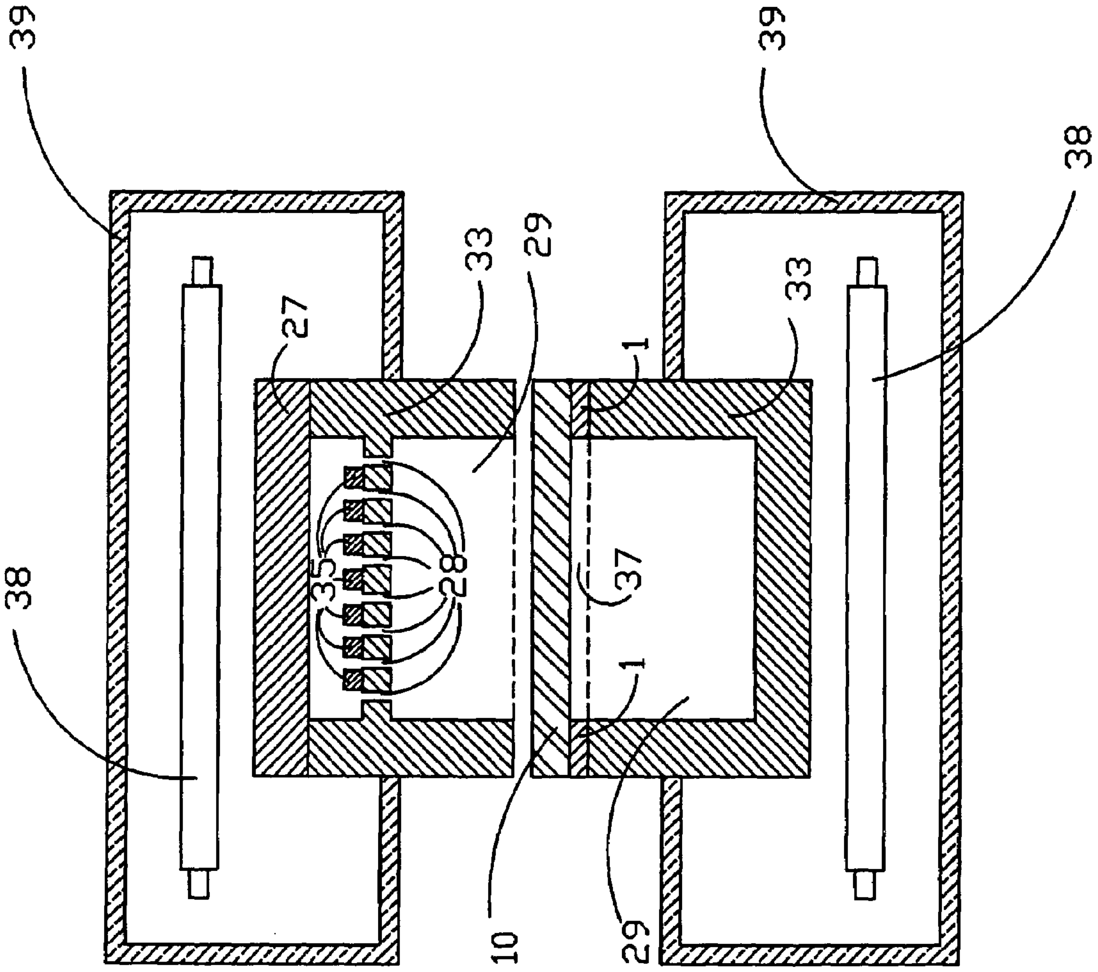


Fig. 7B

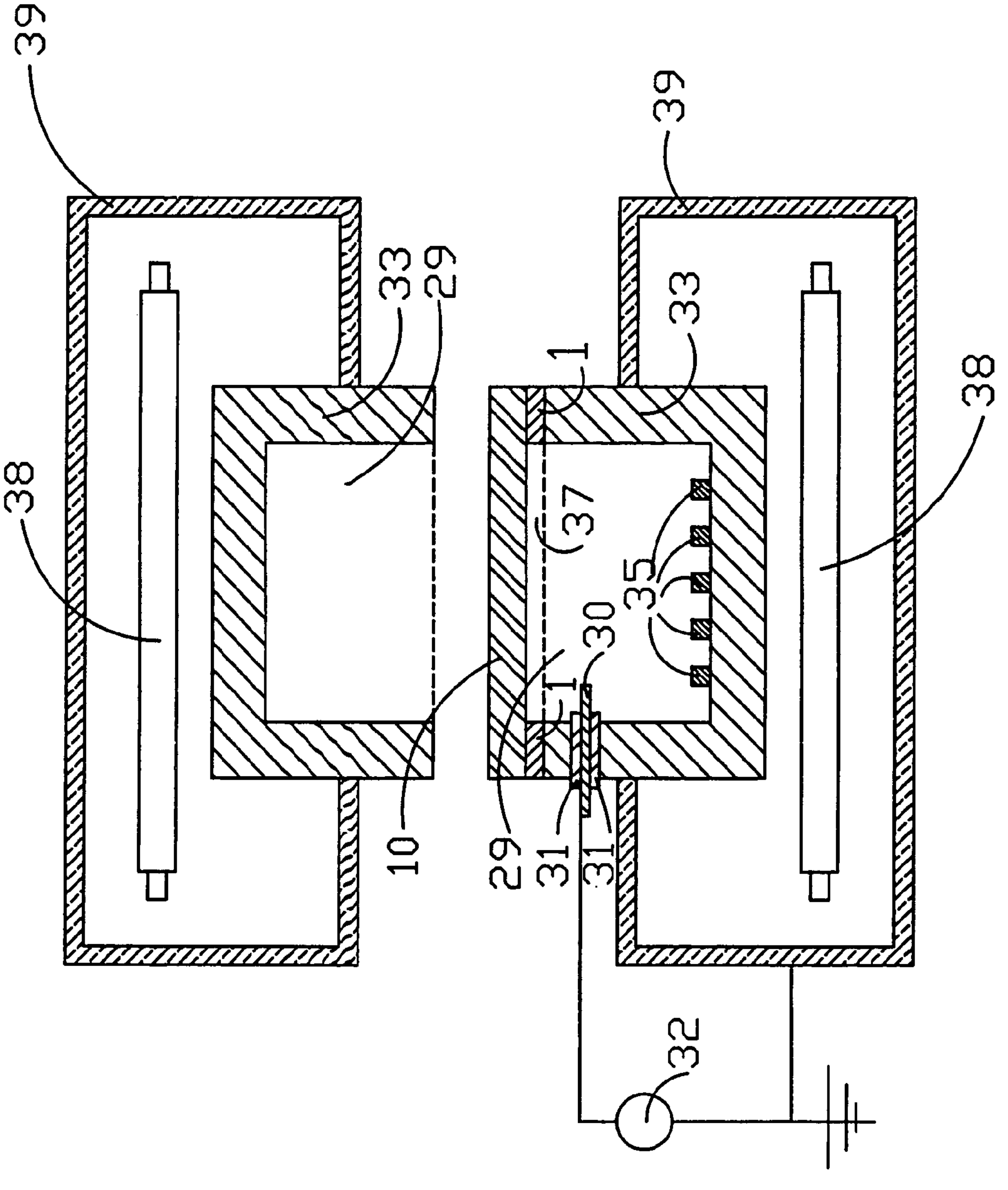


Fig. 8

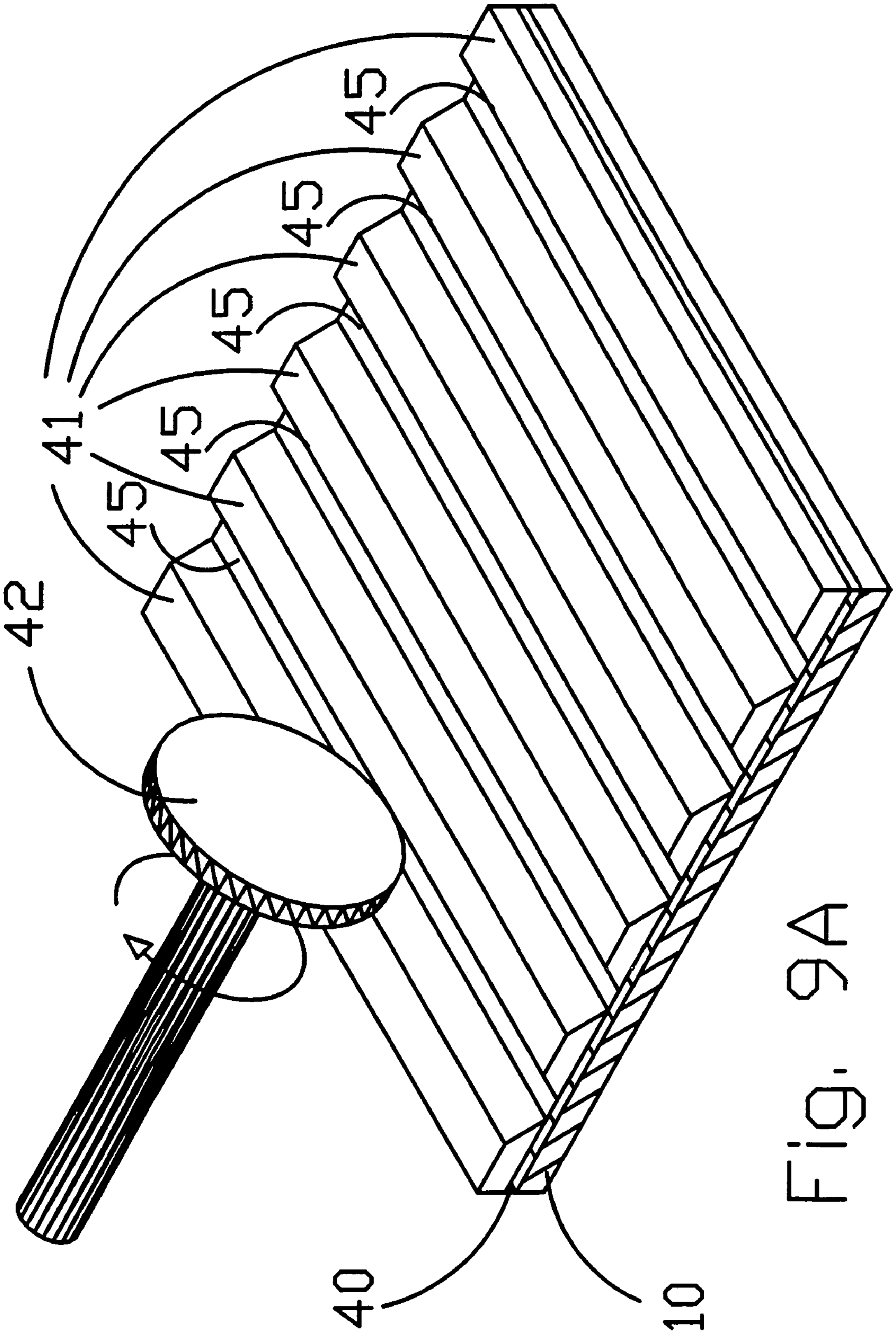


Fig. 9A

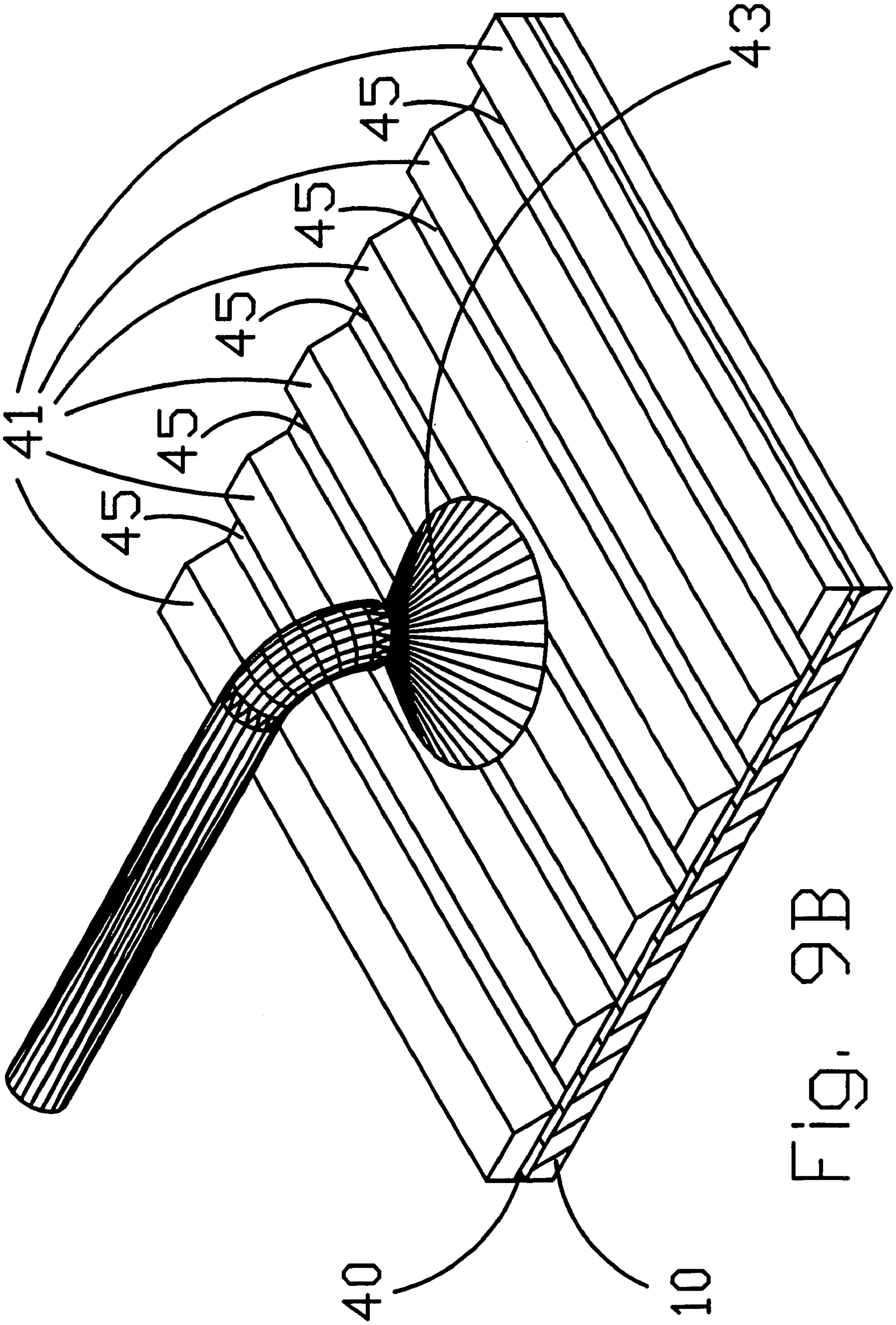


Fig. 9B

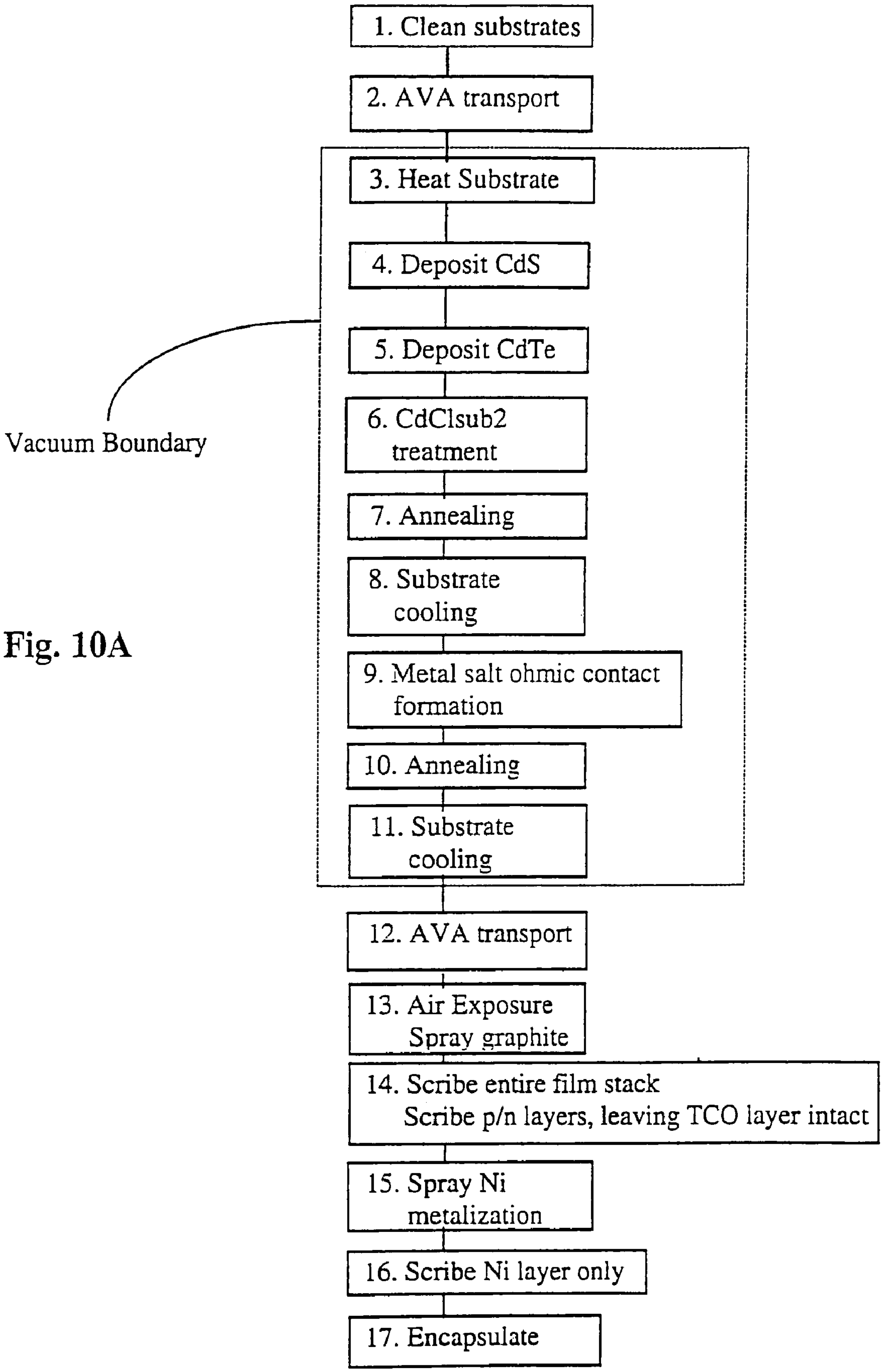

1. Clean substrates
2. AVA transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. CdClsub2 treatment
7. Annealing
8. Substrate cooling
9. Metal salt ohmic contact formation
10. Annealing
11. Substrate cooling
12. AVA transport
13. Air Exposure Spray graphite
14. Scribe entire film stack Scribe p/n layers, leaving TCO layer intact
15. Spray Ni metalization
16. Scribe Ni layer only
17. Encapsulate
Vacuum Boundary

Fig. 10A

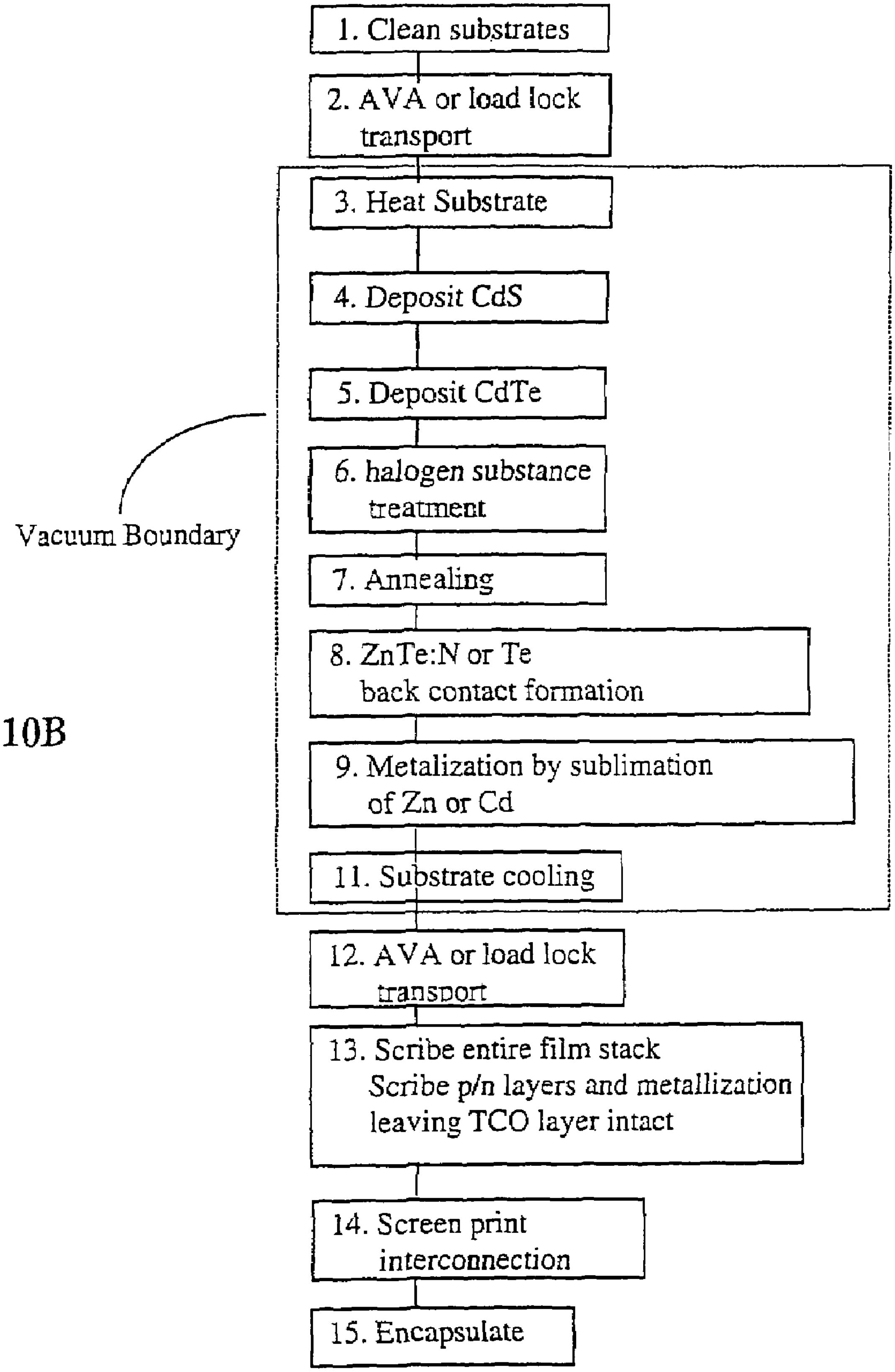

1. Clean substrates
2. AVA or load lock transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. halogen substance treatment
7. Annealing
8. ZnTe:N or Te back contact formation
9. Metalization by sublimation of Zn or Cd
11. Substrate cooling
12. AVA or load lock transport
13. Scribe entire film stack Scribe p/n layers and metallization leaving TCO layer intact
14. Screen print interconnection
15. Encapsulate
Vacuum Boundary

Fig. 10B

APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES

REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of application Ser. No. 10/200,265 filed on Jul. 22, 2002 now abandoned, which is in turn a divisional application of prior application Ser. No. 09/583,381 filed on May 30, 2000, now issued as U.S. Pat. No. 6,423,565.

GOVERNMENT SUPPORT

This invention was made with Government support under grants awarded by the National Science Foundation and the Department of Energy. The Government has certain rights in this invention.

FIELD OF THE INVENTION

The present invention relates to apparatus and processes for the mass production of low cost photovoltaic modules and, more specifically to an inline continuous vacuum apparatus and process for fabricating the critical semiconductor layers, which together with attendant non-vacuum processes, are all accomplished at high throughput.

BACKGROUND OF THE INVENTION

Photovoltaic (PV) modules are used to generate electricity from sunlight by the photovoltaic effect. It has been recognized for decades that if these modules could be mass produced at low cost, they could be used to meet a considerable portion of the world's energy needs. Major companies, such as Royal Dutch/Shell and BP-Amoco, have stated that PV modules have the potential to become a major energy source and that their use has significant benefits to the global environment. However, for these benefits to be realized, PV modules must be produced at many times the current volume and at costs below $\$100/m^2$, as discussed by Bonnet et. al. in "Cadmium-telluride material for thin film solar cells", J. Mater. Res., Vol. 13, No. 10 (1998). Currently, PV modules are manufactured in small quantities at costs of about $\$500/m^2$. About one hundred times the current yearly production is required to sustain a PV module manufacturing capacity that can contribute just 5% of the current electricity generated. Consequently, the manufacturing volume of PV modules needs to be greatly increased and costs significantly reduced.

To realize the required increases in production volume and decreases in manufacturing costs, PV modules must be produced as a commodity. Commodity level manufacturing requires innovation to develop highly automated production processes and equipment, which are designed to specifically fabricate the commodity product. Commodity manufacturing necessitates high production speeds (high throughput), minimal labor costs, and a continuous process flow. Low capital costs and ease of expanding production capacity also facilitate commodity manufacturing. There are a variety of known PV devices, but only the cadmium telluride (CdTe) thin film PV device has the potential to satisfy the requirements for commodity manufacturing.

Since 1974, there have been many industrial efforts to create technologies for CdTe PV module manufacturing. Most of these industrial efforts, as exemplified by the teachings of U.S. Pat. Nos. 4,319,069, 4,734,381, and 5,501,744, have been terminated because of fundamental inadequacies in their manufacturing technologies. To date, no technology suitable for commodity level manufacturing of CdTe PV modules has been developed, thus demonstrating the need for innovation in this area.

The most common CdTe PV cells are thin film polycrystalline devices, in which the CdTe layer is paired with a cadmium sulfide (CdS) layer to form a heterojunction. The thin films of a CdS/CdTe PV device can be produced through a variety of vacuum and non-vacuum processes. Of the many types of thin film deposition methods, sublimation in vacuum is most amenable to commodity manufacturing. This is because vacuum sublimation of CdS/CdTe PV modules exhibits deposition rates 10 to 100 times higher than any other PV module deposition method. Vacuum sublimation of the semiconductor layers for CdS/CdTe PV modules can also be performed in modest vacuum levels and does not require costly high vacuum equipment. Vacuum deposition methods for other thin film PV devices require costly, complex high vacuum equipment and results in low throughput.

Due to the high rate of deposition and low capital cost, the CdS/CdTe thin film cell fabricated by vacuum sublimation is the most suitable for commodity level manufacturing of PV modules. However, cadmium is a Group B carcinogen. According to U.S. government regulations, the quantity of this material which can be lawfully released into the environment or into an occupational setting is extremely small. The known prior art in CdS/CdTe vacuum sublimation requires process and hardware innovations to achieve occupational and environmental safety as required by federal regulations, as well as commodity scale manufacturing.

One known configuration for a CdTe device is the back wall configuration, in which the thin films are deposited onto a glass superstrate, hereinafter referred to as a substrate. The CdTe device is most often fabricated on a glass substrate coated with a transparent conductive oxide (TCO) film onto which other film layers are deposited in the following order: a) a CdS film, b) a CdTe film, c) an ohmic contact layer, and d) a metal film. Along with the deposition of these films, many heat treatments are also needed to enhance the device properties. The TCO and the metal films form the front and back electrodes, respectively. The CdS layer (n-type) and the CdTe layer (p-type) form the p/n junction of the device. The cells are deployed with the substrate facing the sun. Photons travel through the glass and TCO film before reaching the p/n junction of the device. A module is formed by interconnecting individual cells in series to produce a useful voltage.

Thus, a process for manufacturing CdS/CdTe modules includes the following steps: 1) cleaning the TCO coated glass substrates, 2) heating the substrates, 3) depositing an n-type CdS layer, 4) depositing a p-type CdTe layer, 5) performing a $CdCl_2$ treatment to improve CdTe grain structure and electrical properties, 6) forming a p+ ohmic low resistance contact layer to improve current collection from the CdTe, 7) depositing a metal layer (metallization) to form the back electrode, 8) scribing the film layers into individual cells, 9) interconnecting the cells in series and providing a means of electrical connection to the module, and 10) encapsulating the finished module.

All of the prior art methods for the production of CdTe modules have limitations that render them unsuitable for commodity level manufacturing. For example, prior art methods of $CdCl_2$ treatment are disconnected, low throughput batch operations, rather than continuous flow processes. These batch type processes are inefficient and involve extremely high costs in order to increase throughput to the commodity manufacturing level. Most of the known methods of $CdCl_2$ treatment also require rinsing, which generates liquid wastes that contain cadmium. Known methods of ohmic contact formation are also batch type processes that exhibit low throughput rates. Prior art metallization steps also exhibit low throughput and require costly process equipment. It is necessary to improve the current methods of $CdCl_2$ treatment, ohmic contact formation, and metallization in order to achieve high throughput continuous processes.

Prior art methods for scribing the layers to form a module include laser scribing, mechanical scribing, and abrasive blasting. Known laser scribing methods used in the PV industry are associated with low production speed and high capital cost. Laser scribing was abandoned recently in one industrial setting due to laser equipment failure as discussed by Borg in, "Commercial Production of Thin-Film CdTe Photovoltaic Modules", NREL/SR-520-23733, October 1997. Known mechanical and abrasive blast scribing methods have only been shown on a small scale as typified by U.S. Pat. No. 5,501,744 to Albright and require innovation and improvement to be suitable for commodity level manufacturing.

Specific examples of prior art relating to CdS deposition and CdTe deposition performed by vacuum sublimation are described in detail below. The other prior art steps that are necessary to form a complete CdTe PV module are also discussed below.

One known vacuum method of producing CdTe solar cells by vacuum sublimation is taught in U.S. Pat. No. 5,536,333 to Foote et. al. This method is further described by Sasala et. al. in "Technology Support for Initiation of High-Throughput Processing of Thin-Film CdTe PV Modules", NREL/SR-520-23542, pp. 1–2, (1997). These references discuss a technique known as vapor transport deposition (VTD), which involves heating of the semiconductor materials in a contained vessel in order to create vapor. An inert carrier gas, such as nitrogen, transports the vapor of the semiconductor to the substrate through heated conduits. The substrate is held horizontally in a heated environment and supported from beneath by ceramic rollers in the heated environment. The deposition of the semiconductor is made onto the top surface of the substrate. In accordance with this prior art method, the ceramic rollers prevent the glass substrate from sagging under its own weight due to the elevated temperatures involved.

The entire VTD method is very complex and costly. It is possible to deposit a complete CdTe solar cell in a very short time and at sufficiently low substrate temperatures to eliminate glass sagging completely or reduce it to a very small acceptable value. Thus, the expensive ceramic rollers of the VTD method are not needed. Reloading starting material may also be performed in a much simple manner than as shown in this prior art. Since the films are thin, only small amounts of material are required to form them. Consequently, only very small volumes of starting material are needed for many days of operation, thus eliminating the need for this complex reloading arrangement. The heated vessels of this method contain toxic vapors, which pose significant occupational safety problems when they are opened for reloading during processing. In the VTD method, vapors are transported through long distances in a carrier gas, an arrangement which will likely lead to the formation of very small nano-particles through condensation of the vapors. These nano-particles degrade the film qualities and lead to occupational hazards when the system is serviced. Furthermore, in the VTD method, the continuous flow of carrier gas has to be maintained along the substrate. Any CdS or CdTe vapors that are carried past the substrate will be wasted. Any deposits of waste material on the inner surface of the vacuum chamber, pumps, exhaust, etc. must be cleaned, thereby exposing maintenance workers to toxic materials and raising occupational safety issues. In order to prevent unwanted condensation of CdS and CdTe vapors, the VTD method also requires continued heating of large portions of the equipment, including the vaporization vessel itself, the conduits, the deposition chamber, etc. This wastes energy and increases the capital costs. The VTD method is only used for depositing the p/n junction layers. Other processing steps, such as the $CdCl_2$ treatment, ohmic contact formation, and metallization are inherently low throughput batch processes. Scribing is taught to be either laser scribing or photolithography, both of which are slow and costly processes.

In another prior art reference entitled "The CdTe Thin Film Solar Cell," International Journal of Solar Energy, vol. 12, 1992, Bonnet proposes an inline production method for fabricating CdS/CdTe layers using a close-spaced sublimation (CSS) type deposition process. This prior art reference describes inline deposition within one vacuum boundary for only the steps of substrate heating, CdS deposition, and CdTe deposition. The other steps of $CdCl_2$ treatment, ohmic contact formation, and metallization are not shown as part of a continuous inline vacuum process, and are presumably performed by previously known methods. As described above, known methods for performing these steps have limitations. The Bonnet method does allow multiple substrate processing of more than one film. However, it is not clear if long term operation and uniformity of deposition over time and across large substrates are achieved. Furthermore, the Bonnet method relies on CSS, which by definition, requires a space of 2–3 mm between the source and the substrate. This gap will allow a vapor leak at the edge of the substrate. As the source charge sublimes away over time the gap will increase. It is the present inventors' experience that this gap and the associated vapor leak causes non-uniform deposition on the substrates and also results in condensation of toxic materials on unwanted areas on the inner surfaces of the process chamber. This leak will be reduced if the background chamber pressure is held high enough to decrease the mean free path between gas molecules in the process chamber. However, higher pressures lead to lower deposition rates and greater nano-particle formation. An operating pressure of 750 millitorr is specified. At these pressures, nano-particles will be formed, since the vapor will homogeneously condense in the ambient gas near the edge of the deposition space. These very small particles degrade film quality and pose a health hazard to workers during routine maintenance inside the vacuum chamber.

Each of the individual prior art process steps required to produce a CdTe PV module exhibits limitations, as outlined above. In addition, nothing in the prior art describes an overall process to perform the series of steps of substrate heating, depositing an n-type CdS layer, depositing a p-type CdTe layer, performing a $CdCl_2$ treatment, and forming an ohmic contact inline, continuously, and in one vacuum boundary. In particular, the steps of $CdCl_2$ treatment and ohmic contact formation require significant innovation before they can be included in a continuous inline vacuum process. Such a continuous inline vacuum process would have significant advantages for commodity manufacturing of CdTe PV modules.

Any vacuum process for manufacturing CdTe PV modules would also require an apparatus to transport substrates through the process steps within vacuum and to transport the substrates into and out of vacuum rapidly. This apparatus should be robust, simple, and low cost. The apparatuses described in the prior art simply do not meet these requirements.

BRIEF SUMMARY OF THE INVENTION

The present invention is directed to commodity scale manufacturing of CdTe PV modules and involves innovations in both manufacturing processes and hardware.

One aspect of the present invention involves providing all of the processing steps for the critical semiconductor layers of a CdTe PV device inline, with all of those steps being completely performed within one vacuum boundary, at high throughput. They include rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation. These steps are performed at modest vacuum pressures without requiring costly high vacuum equipment. By utilizing inline vacuum processing to form all of the critical layers without breaking vacuum, an improvement in process throughput, film quality, device efficiency, and device stability is realized, while at the same time avoiding pinhole formation. All inline vacuum processing is also advantageous in that it limits the production of toxic waste and environmental and occupational exposure to toxic compounds.

Another aspect of the present invention is a novel $CdCl_2$ treatment step, which may be performed in the same vacuum boundary and inline with the other fabrication steps. Our $CdCl_2$ treatment process has the advantage of a high throughput rate while producing stable, high efficiency devices and, at the same time, limiting environmental and occupational exposure to toxic compounds.

Another aspect of the present invention is a novel vacuum process to produce a p+ ohmic contact region by subliming a metal salt onto a CdTe layer. Our ohmic contact formation process has the advantage of producing, at high throughput rates, a low resistance ohmic contact that is stable over time.

Another aspect of the present invention is a unique high throughput, low cost spray process to form the back electrode. This process has the advantage of producing a durable, high conductivity back electrode using known low cost industrial spray methods.

Another aspect of the present invention is to provide novel high throughput, low cost processes to perform module scribing using abrasive blasting or mechanical brushing through a mask. These novel scribing processes have the advantage of selectively scribing the semiconductor layers without scribing the TCO layer. In addition, the scribe process may be adjusted so that the TCO layer may be removed as well.

Another aspect of the present invention is a novel vacuum process station to selectively heat substrates and films, to expose substrates and films to vapor, to deposit thin films on a substrate, and to strip thin films off of a substrate. This vacuum process station allows substrates to be transported into and out of vacuum. When used as a deposition source, our vacuum process station has the advantage of very minimal vapor leakage, which significantly reduces occupational exposure to toxic materials. This unique deposition source deposits very uniform layers and is suitable for long term continuous operation.

Another aspect of the present invention is a novel substrate transport apparatus, which is employed to move substrates within vacuum or, in combination with a unique opening, to transport substrates rapidly into and out of vacuum. This substrate transport apparatus is robust, simple, and low cost and has the additional advantage of not collecting any coatings as it moves substrates through the thin film deposition processes.

Yet another aspect of the present invention is to provide substrate cleaning in a clean mini-environment at the entrance to the inline continuous vacuum process, which has the advantage of greatly reduced cost resulting from the elimination of a clean room to contain the entire process line.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic top plan view of a system for making photovoltaic modules in accordance with the present invention.

FIG. **2**A is a partially broken away schematic elevation view in longitudinal section along the line **50**—**50** of FIG. **1**, illustrating a substrate transport apparatus and a plurality of vacuum processing stations.

FIG. **2**B is a partially broken away schematic elevation view in longitudinal section, illustrating an alternate embodiment of the substrate transport apparatus of FIG. **2**A.

FIG. **3** is a schematic elevation view in cross section along the line **60**—**60** of FIG. **2**A illustrating the sealing arrangement by which the introduction of outside air into the vacuum chamber is minimized.

FIG. **4** is a partial schematic top plan view in longitudinal section along the line **70**—**70** of FIG. **2**A, further illustrating the sealing arrangement of FIG. **3**.

FIG. **5** is a schematic elevation view along the line **100**—**100** of FIG. **4**, further illustrating the substrate transport apparatus of FIG. **2**A.

FIGS. **6**A–B are schematic sectional elevation views illustrating enclosed and unenclosed substrates as they are positioned in prior art apparatuses.

FIG. **7**A is a schematic elevation view in cross section along the line **80**—**80** in FIG. **2**A, illustrating details of a vacuum process station of the substrate transport apparatus of FIG. **2**A.

FIG. **7**B is a schematic elevation view in cross section to illustrate an alternative embodiment of the vacuum process station of FIG. **7**A.

FIG. **8** is a schematic elevation view in cross section to illustrate a second alternate embodiment of the vacuum process station of FIG. **7**A.

FIG. **9**A is a schematic perspective view along the line **90**—**90** of FIG. **1**, illustrating the way in which photovoltaic modules are scribed.

FIG. **9**B is a schematic perspective view along the line **90**—**90** of FIG. **1**, illustrating an alternative way to scribe photovoltaic modules.

FIG. **10**A is a flow chart illustrating the process steps of the present invention.

FIG. **10**B is a flow chart of some of the alternate embodiments of the process steps of FIG. **10**A.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to FIG. **1**, there is shown an overview of the preferred embodiment of an apparatus **1000** for producing photovoltaic modules in accordance with the present invention. A substrate cleaning station **55** cleans the commercially available substrates that typically comprise low cost soda lime glass coated with transparent conducting oxide (TCO). After cleaning, a pair of metal strip belts **1** transport the substrates through the next portion of the apparatus **1000**. The belts may be moved bidirectionally by means of a known stepper motor **7**. Precise indexing of the position of the pair of belts **1** is accomplished by the use of a commercially available stepper motor controller **8**. The pair of metal strip belts **1** pass through a pair of openings **2** and a vacuum chamber **3**. A plurality of process stations for the processing of the critical semiconductor layers are contained within the vacuum chamber **3**, and are described in detail below. Another series of process stations are linked by a plurality of conveyor belts **51**. These process stations do not require vacuum. A first spray process station **52***a* is followed by a first film scribing process station **53***a*. These process stations are followed by a second spray process station **52***b* and a second film scribing process station **53***b*. The final process station in the apparatus **1000** is an encapsulation station **56**. The description of the apparatus and processes of the instant invention is presented in the following order: the substrate transport apparatus and openings, the vacuum process stations, the metallization method, the film scribing method, and the process steps to produce a photovoltaic module. Following the description of the preferred embodiment is a description of alternate embodiments.

FIGS. **2**A, **3**, **4**, and **5** in combination illustrate the complete assembly of the preferred embodiment of a pair of air-to-vacuum-to-air (AVA) openings and the substrate transport system of the present invention. The pair of AVA openings **2** facilitate the rapid transport of substrates from air into vacuum and then back into air. FIG. **2**A illustrates vacuum chamber **3**, which is pumped to a suitable vacuum by known techniques. A pair of AVA openings **2** is shown on either side of the vacuum chamber **3**. A pair of continuous metal strip belts **1** pass through both of the AVA openings **2** and also through the entire length of the vacuum chamber **3**. A plurality of substrates **10**, which are carried on the twin metal belts **1**, are also shown. The AVA openings **2** are shown with a plurality of pockets **14** and a plurality of vacuum pump ports **15** for vacuum pumping. A pair of injection ports **11** are shown for the injection of process gas. A plurality of pulleys **4** are provided for moving the belts **1**. A belt tensioner **9** maintains the belts **1** at a predetermined tension.

FIG. **3** shows the details of the AVA openings **2** in cross section. A top channel **2***a* and a bottom plate **2***b* are split by a belt bearing plate **20**. In total, parts **2***a*, **2***b*, and **20** form the cross section of the opening **2** of FIGS. **2**A, **3**, and **4**. A clearance distance **21** on the order of 0.005 in. ±0.002 in. is formed around the substrate **10**. This clearance distance **21** is formed between the substrate **10** and the top channel **2***a* and between the substrate **10** and the belt bearing plate **20**. The clearance distance **21** is large enough so that the substrate **10** may move freely, but is small enough to provide resistance to fluid flow through the clearance distance **21**. This resistance to fluid flow allows the vacuum chamber **3** to be maintained at a desired vacuum level. The pair of continuous metal strip belts **1** provide a substrate carrier to convey the plurality of substrates **10**.

FIG. **5** is a detailed view of a pair of tabs **6** which are attached to the metal strip belt **1**. The tabs **6**, a plurality of which are placed periodically along the belt **1**, provide a means of locating the substrate **10**.

The pair of continuous metal strip belts **1** provide a substrate carrier that will not be coated by the vacuum deposition processes. The elimination of coating on the belt **1** is a significant improvement over the prior art. As exemplified by Charschan in U.S. Pat. No. 3,294,670 (1966), the prior art utilized substrate carriers which enclosed the perimeter of the substrate in a "picture frame" type arrangement. The picture frame type substrate carriers are necessarily coated during deposition. These coatings lead to jamming in the close tolerance seals during motion, present occupational safety issues due to particle generation, and result in cross contamination between the processes. In the present invention, these problems have been addressed by exposing only the substrates **10** to coating during a vacuum deposition. In addition, unlike all of the prior art, the clearance distance **21** is not formed between the substrate carrier and the openings. Rather, the clearance distance **21** is formed between the precisely cut substrate **10** and the AVA openings **2**. The clearance **21** is formed specifically between the substrate **10** and the top channel **2***a* and between the substrate **10** and the linear bearing plate **20**.

The use of the pair of metal strip belts **1** as the substrate carrier in accordance with the present invention has many other advantages. The fact that the belts **1** have a low mass will create less wear on any bearing surface used. The low mass will also greatly decrease the inertia of the substrate carrier, thus allowing the substrate to be moved quickly between processing stations.

Continuous metal strip belts **1** also have advantages in situations calling for a series of vacuum processes to be carried out in one vacuum chamber **3**. Continuous metal strip belts **1** of 200 feet in length can be fabricated by known methods. This allows a large number of process steps to be carried out in one vacuum chamber **3**.

Another advantage is the cost of fabrication of this type of substrate carrier, which is considerably less than the cost of machining close tolerance picture frame type substrate carriers of the prior art. The present substrate carriers also facilitate scaling up the process. For larger substrates **10**, the openings **2** must be increased in size. However, the strip belts **1** may be simply spaced further apart.

The continuous metal strip belts **1** are preferably formed of metal alloys that have high resistance to corrosion and that retain high strength at elevated temperatures. These belts may be coated with other materials to alter the surface properties further, if needed. Many different attachments or tabs **6** for retaining the substrate **10** may be welded or fixed to the metal strip belts **1** at relatively low cost.

A cut tolerance of ±0.003 inch is required for the glass substrates **10** which are carried on the continuous metal strip belts **1**. High throughput, low cost equipment is commercially available for cutting the substrates **10** to the required tolerances. The precision glass cutting required for this invention is not an additional processing step, since the substrates **10** must be cut to size in any method.

The continuous metal strip belts **1** are also relatively small in cross section. The small cross section decreases the thermal expansion as the belts pass through high temperature vacuum processes, which will decrease any tendency to jam in the AVA openings **2** due to thermal expansion.

The relatively low mass of the metal strip belts **1** also allows the substrate carrier to cool and heat more rapidly than the prior art picture frame type substrate carrier. The low mass of the metal strip belts **1** allows the belt temperature to match the glass temperature during processing, thereby reducing thermal gradients in the glass substrates **10** which could otherwise lead to stresses that may crack the glass.

Referring now to FIG. **2**A, the vacuum chamber **3** and a plurality of vacuum processing stations, generally indicated by **200** and **300**, are illustrated in a partial schematic elevation view in section. The metal strip belts **1** carry the plurality of substrates **10** through the plurality of vacuum processing stations **200** and **300**. The process stations **300** provide for cooling of substrates **10** by radiation to a pair of water cooled plates **34**.

Each of the process stations **200** of FIG. **2**A contain a pair of heated pockets **33**. These heated pockets **33** provide a flux of heat or vapor and are suitably shaped blocks of a material with a high thermal conductivity. In FIG. **7**A the pair of heated pockets **33** are shown with details of the pair of continuous metal strip belts **1** in cross section. Both upper and lower heated pockets **33** have a machined pocket **29**. A deposition material **35** is shown in the pocket **29** of the lower heated pocket **33**. Only the substrate **10** spans the pocket **29**. No part of the belts **1** crosses the pocket **29**, thus avoiding deposition anywhere but on the substrate **10**. The upper heated pocket **33** serves as a heater for the substrate **10**.

Heated pocket **33** may be fabricated using any material which has an acceptable level of thermal conductivity. Further, that material should have a low level of porosity to prevent adsorption of air and water vapor and a low level of impurities. One material which has proven useful is purified pyrolitic grade graphite. However, metals and metals coated with ceramics, as well as other suitable materials, may be chosen.

In the preferred embodiment of the invention, the heated pockets **33** are heated by a plurality of quartz halogen lamps **38**, which are not damaged when used in vacuum at high temperatures. The temperature control of the heated pocket **33** may be accomplished by placing a thermocouple in the wall of the heated pocket **33** and using well known proportional with integral and derivative (PID) temperature control of the power to the lamps **38**. Lamps **38** are contained in boxes **39** for protection. Boxes **39** also serve as support structure for the lamps **38** and the heated pocket **33**. The boxes **39** also provide electrical isolation for safety, prevent arcing from the lamps **38**, and also serve as radiation shields to reduce the loss of energy. Other means of heating the heated pocket **33**, including resistive heating and inductive heating, for example, may be used as well.

Each of the process stations **200** may perform a variety of processes on a substrate **10**. These processes include: i) rapidly heating a substrate, ii) annealing a substrate and films, iii) thermally stripping a film from a substrate, iv) exposing a substrate and films to a vapor treatment, or v) depositing a thin film on a substrate. The chosen processes performed by station **200** depend on three parameters: a) the temperature of the lower heated pocket **33**, b) the temperature of the upper heated pocket **33**, and c) the presence or absence of the deposition material **35**. For processes i) through iii) described above, no deposition material **35** is loaded into the pocket **29**. For process i) the upper and lower heated pockets **33** are maintained at temperatures such that the rapid heating of glass substrates **10** may be done in a short cycle time, on the order of one minute. The uniformity of heating prevents cracking of the substrates **10**. For process ii), the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature which will not resublime thin films off of the substrate **10**. For process iii) the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature that is high enough to cause films on the substrate **10** to sublime away.

For processes iv) and v) described above, deposition material **35** is loaded into the pocket **29**. For process iv), the upper heated pocket **33** and substrate **10** are maintained at a higher temperature than the lower heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33** and expose the lower surface of the substrate **10** to vapor, but the vapor will not be deposited as a film on the substrate **10**. For process v), the lower heated pocket **33** is maintained at a relatively higher temperature than the substrate **10** and the upper heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33**, and the vapor will condense and be deposited as a film on the lower surface of the substrate **10**. All of these processes are robust, may be performed at high throughput, are occupationally and environmentally safe, and involve low capital cost.

In accordance with the present invention, the pair of metal belts **1** transports the substrates **10** through the plurality of process stations **200** or **300**. The metal belts **1** and the substrates **10** may be moved continuously. However, the preferred embodiment of the present invention provides for intermittent motion of the metal belt **1** and the substrates **10**. This motion is accomplished using a conventional stepper motor **7** and a stepper motor motion controller **8**. The substrates **10** are placed at equal pitch distances on the belts **1**, and the process stations **200** or **300** are placed one pitch distance apart. The intermittent motion consists of pauses in the motion of the belts **1** for processing and brief periods of motion of the belts **1** to advance the plurality of substrates **10** through the series of process steps. In this manner, an individual substrate **10** will pause at each process station **200** or **300** for an equal amount of time. A useful period of time, hereinafter defined as the cycle time, consists of the total period of time for one pause and one movement of the belts **1**. One substrate **10** will complete the series of inline vacuum process steps for each period of cycle time.

Since the process stations **200** or **300** are modular, a plurality of one type of process may be placed in series. If a given process step requires a processing time which exceeds the cycle time, then the given process step may be carried out over a series of similar processing stations **200** or **300**. For example, an annealing step, which requires a longer period of time to complete than the cycle time, may be carried out over a series of annealing process stations **200**.

The deposition of thin films onto substrates **10** is a critical processing step of the present invention. A detailed description of the deposition apparatus is given below.

The intermittent motion of the belts **1** allows a pause for deposition. During the pause, as shown in FIG. **2**A, the individual substrates **10**, which are spaced at regular pitch intervals on the metal strip belts **1**, will be in a sealing relationship with individual heated pockets **33**. During this pause, the individual heated pockets **33** will deposit a film onto the substrates **10**. For a given pause time, the thickness of the films can be varied by varying the temperature of each individual heated pocket **33**. Closed loop control of film thickness may be achieved by measuring film thickness with known thickness monitors and adjusting the heated pocket **33** temperature as needed. Very precise control may be achieved since the deposition rate is a function of the temperature of the heated pocket **33**.

The present invention is specifically designed to produce very uniform film deposition across the surface of the substrate **10** at high throughput so that in a mass manufacturing environment the reproducibility of the film uniformity from one substrate **10** to another substrate **10** is tightly controlled over long periods of time. In order to accomplish this desired aspect of the present invention, the substrate **10** is held in a novel sealing relationship with the pocket **29**.

The novel sealing relationship is unique and is not shown or suggested in the prior art. FIG. **6**A and FIG. **6**B show an elevation view of two prior art devices used for film deposition by vacuum sublimation. In FIG. **6**A, the known method of Bozler in U.S. Pat. No. 3,636,919 (1972) shows the source deposition material **35***a* and substrate **10***a* in an enclosed space. The enclosed space is formed by an upper heater **36** U and a lower heater **36** L. Because the substrate **10***a* is sealed in the enclosed space, the substrate **10***a* could not be moved and only one film could be deposited for each pump down of the vacuum chamber. FIG. **6**B details another known method according to Bonnet in U.S. Pat. No. 5,304,499 (1994) which is commonly known as close spaced sublimation (CSS). In this known method, the deposition material **35***a* is placed on a flat heated plate **36** L and the substrate is held at a typical distance of 2 to 3 mm from the deposition material **35***a*. The disadvantage of this known method is that the clearance between the deposition material **35***a* and the substrate **10***a* forms a leak path for the vapor. This leak will lead to non-uniform deposition and the formation of toxic nano particles in the process space.

The heated pocket deposition apparatus of the present invention overcomes the limitations of the prior art. With reference to FIG. **7**A, there is a clearance distance **37** on the order of 0.001 in. to 0.018 in. between the substrate **10** and the top surface of the heated pocket **33** block. Clearance distance **37** is formed on the two sides of the substrate **10** where the substrate **10** spans the belts **1**. The clearance distance **37** is necessary to prevent the substrates **10** from touching the heated pocket **33** and damaging the deposited films. The clearance distance **37** is formed in such a manner as to provide a close tolerance slip fit seal between the top of the heated pocket **33** and the bottom of each of the substrates **10**. Any vapor leak through the clearance distance **37** will be in the molecular flow regime and will be very small. This effectively eliminates vapor leaks through the clearance distance **37** and allows the substrates **10** to act as a shutter across the source pocket **29**.

Furthermore, the walls of the pocket **29** will collimate the vapor flux from the subliming material **35**. Since the clearance distance **37** is at the top of the pocket **29** and at a right angle to the collimated vapor flux, nearly all of the vapor flux will pass the entry of the clearance distance **37** without directly entering it. Any vapor which does enter the clearance distance **37** due to gas scattering will be readily deposited on the surface of the substrate **10**. The design of the clearance distance **37** allows for movement of multiple substrates **10** while maintaining a vapor seal. This design has advantages over the prior art since it will maintain the deposition uniformity across the substrate **10**. In the present invention, the use of the substrates **10** to act as a shutter virtually eliminates cross contamination between heated pockets **33**. The elimination of cross contamination allows the use of one vacuum boundary for the multiple processing steps and reduces the capital cost of the system. In most vacuum processes for processing PV devices, load locks or load locks in combination with intermediate chambers are used to prevent cross contamination between processing steps.

As shown in FIG. **7**A, the deposition material **35** must be distributed in an evenly spaced pattern across the floor of the pocket **29**. The deposition material **35** may be in the form of powder, pellets pressed from powder, or random chunks. All of these forms of material for the fabrication of CdTe PV are commercially available. Also, the distance between the deposition material **35** and the lower surface of the substrate **10**, which is provided by the depth of the pocket **29** in the lower heated pocket **33**, must be sufficient to allow for gas scattering of the sublimed species.

Gas scattering is the result of collisions among the sublimed species or between the sublimed species and the molecules of the ambient background gas. These collisions deflect and scatter the sublimed species from following a straight line path from the deposition material **35** to the substrate **10**. This scattering of the sublimed species results in a uniform deposition on the substrate **10** The Knudsen number is a known dimensionless parameter which is used to quantify the amount of gas scattering present. The Knudsen number is the ratio of the mean free path in the pocket **29**, at a given temperature and pressure, divided by the distance between the deposition material **35** and the substrate **10**. If the Knudsen number is less than 0.01, then the species within the pocket **29** are in viscous flow and gas scattering will be significant In this viscous flow regime, the gas scattering may lead to such a loss of energy from the sublimed species that they condense to form nano-particles. For Knudsen numbers greater than 1, the species will be in a molecular flow regime with very little gas scattering. In this molecular flow regime, the sublimed species will travel in straight lines to the substrate. This line of sight deposition causes non-uniform film thickness across the substrate **10**. For Knudsen numbers between 0.01 and 1, the species will be in transition flow with some gas scattering. In the transition regime, the vapor flux is randomized by gas scattering. However, the number of collisions are few enough that the sublimed species retain most of their energy and therefore do not condense into nano-particles before striking the substrate **10**. In the present invention, deposition has been done with Knudsen numbers in the transition regime from 0.07 to 0.44, which has led to uniform film thickness across the substrate **10**.

An additional advantage of the present invention is the heating of the process gas in the pocket **29**. Since the substrates **10** act as a shutter for the heated pocket **33**, the process gas in the source pocket **29** comes to a uniform high temperature. The high temperature of the process gas in the heated pocket **33** is another factor which prevents the formation of nano-particles due to the gas scattering collisions described above.

The preferred embodiment of the present invention provides a means of forming a back electrode layer at high throughput and using equipment that is low capital cost. This layer is adherent to the other layers in the film stack and has a very low electrical resistivity. As shown in FIG. **1**, the back electrode is fabricated by a novel spray process at atmospheric pressure in process stations **52***a* and **52***b*. A layer of conductive graphite coating followed by a layer of conductive Ni coating are applied by known industrial spray methods to form the back electrode for carrying current. Sprays containing other metals besides Ni are known and may also be used. A metal conductive coating layer may also be applied by spray directly to the ohmic contact layer without an intervening carbon layer. In this description, carbon is not considered a metal. To limit the inclusion of oxygen and water vapor into the metallization layer, the gas used as a propellant in the spray process may be a dry inert gas such as N_2 or Ar, and the process may be performed in a controlled environment.

The thick film of the back electrode contains a polymer binder, which provides a level of encapsulation and protection for the completed device. The spray is performed at room temperatures and does not harm or introduce defects into the previously fabricated semiconductor layers. The spray method has the advantage of low capital cost. Other known methods of metallization for PV devices, such as sputtering, require expensive high vacuum equipment.

The preferred embodiment of the present invention also provides a means of scribing that exhibits high throughput and low cost. As shown in FIG. **1**, a scribing step may be performed at the film scribing station **53***a* after the graphite layer is formed by the spray process at the process station **52***a*. The scribing is performed after the application of the graphite layer to prevent any damage to the semiconductor layers by handling.

FIG. **9**A illustrates the details of the preferred embodiment of the film scribing method. A rotating wire brush **42** is brought into contact through openings **45** in a mask **41** to remove portions of the film **40** from the substrate **10**. The openings **45** in the mask **41** are tapered in cross section and are narrower near the contact of the mask **41** and the film layers **40**. This facilitates the entry of the rotating brush **42** into the openings **45**. The mask **41** may be coated with a hard coating, such as titanium nitride, to reduce wear.

The preferred embodiment of the film scribing method shown in FIG. **9**A does not require a precisely defined rotating brush **42** since the openings **45** in the mask **41** define the area of the film **40** which will be removed. The rotating wire brush **42** is passed axially along the openings **45** in the mask **41** over the substrate **10** to perform a scribe. A plurality of rotating metal brushes **42** may also be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes on an entire substrate **10**. This film scribing method has the ability to scribe layers selectively. By using an abrasive powder with the rotating brush **42**, the TCO layer may be scribed. By using the rotating brush **42** alone, all of the layers except the TCO layer may be removed.

The process steps of the preferred embodiment of the present invention are shown in the flow chart of FIG. **10**A. The overall system **1000** required to perform the process is shown in FIG. **1**. The apparatus required to perform the vacuum portion of the process, from step **2**) of FIG. **10**A through step **12**) of FIG. **10**A, is illustrated in FIG. **2**A. With reference to FIG. **2**A, the substrates **10** are transported through the vacuum process stations **200** and **300** on the metal strip belts **1**. As shown in FIG. **10**A, these process steps may be performed by a single one or a series of the vacuum process stations **200** or **300** illustrated in FIG. **2**A. The total time required for processing at each process station **200** or **300** and the transport of the substrate **10** to the next process station **200** or **300** is a unit of cycle time as defined above. The cycle time in the process description below is in the range of 30 seconds to 2 minutes.

With reference to FIG. **10**A, a description of the process steps performed on each individual substrate **10** as the plurality of substrates **10** pass through the process is given below.

In step (**1**) the substrate **10**, which may have a TCO layer on one surface, is ultrasonically cleaned, rinsed, dipped in isopropyl alcohol to remove water from the surface, and dried in a clean room type mini-environment.

In step (**2**) the substrate **10** is transported into the vacuum chamber **3** through the AVA opening **2** using the metal strip belts **1**.

In step (**3**) the substrate **10** is heated to a temperature in the range of 500° C. to 560° C. and transported to the next process.

In step (**4**) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdS film is deposited onto the TCO layer on the substrate **10** and the substrate **10** is transported to the next process.

In step (**5**) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdTe film is deposited onto the CdS layer on the substrate **10** and the substrate **10** is transported to the next process.

In step (**6**) and step (**7**) a $CdCl_2$ treatment is performed on the CdS/CdTe layers. In step (**6**) with the temperature of the substrate **10** in the range of 300° C. to 500° C., the CdS/CdTe layers on the substrate **10** are exposed to $CdCl_2$ and the substrate **10** is transported to the next process. The $CdCl_2$ exposure of the CdS/CdTe layers on the substrate **10** may be to a $CdCl_2$ vapor or a $CdCl_2$ film may be deposited on the CdTe layer. Either method of $CdCl_2$ exposure will produce high efficiency CdTe PV devices. For this process step, a series of $CdCl_2$ treatment stations may be required.

In step (**7**) with the temperature of the substrate **10** in the range of 400° C. to 450° C., the $CdCl_2$ treated layers on the substrate **10** are annealed, any $CdCl_2$ film is removed, and the substrate **10** is transported to the next process. For this process step, a series of annealing stations may be required. In combination, step (**6**) and step (**7**) provide the $CdCl_2$ treatment of the CdS/CdTe layers. The $CdCl_2$ treatment of CdTe PV devices in vacuum is known. However, no prior art shows the $CdCl_2$ treatment step performed inline between the deposition of the CdTe layer and the formation of the ohmic contact layer and without the substrate leaving vacuum. Also, no prior art shows directly transporting substrates from CdTe deposition to $CdCl_2$ treatment.

In step (**8**) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

In step (**9**) and step (**10**) an ohmic low resistance contact is formed on the CdTe layer. In step (**9**) with the substrate **10** temperature in a range of 150° C. to 300° C., a metal salt is deposited onto the CdTe layer on the substrate **10**, and the substrate **10** is transported to the next process. One metal salt which has been used for this process step is CuCl. In step (**10**) with the temperature of the substrate **10** in a range of 150° C. to 250° C., the CdS/CdTe/metal salt layers on the substrate **10** are annealed, and the substrate **10** is transported to the next process. For this process step a series of annealing stations may be required. In combination, step (**9**) and step (**10**) produce a reaction between the metal salt and the surface of the CdTe layer and this reaction produces a thin p+ semiconductor layer on the CdTe surface to form the ohmic contact. In the case of a Cu salt, a copper telluride such as $CuTe_X$ or Cu doped CdTe:Cu or both may be formed. The thin p+ layer provides a low resistance ohmic contact on the surface of the CdTe layer and is stable. The prior art does not show the formation of an ohmic contact layer on CdTe by deposition of a metal salt onto the CdTe layer in vacuum.

In step (**11**) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

In step (**12**) the substrate **10** is transported out of the vacuum chamber **3** through the AVA opening **2** on the metal strip belts **1**.

In step (**13**) the ohmic contact layer is exposed to air for an optimum time in the range of 4 to 16 hours before a layer of conductive coating containing carbon is applied onto the ohmic contact layer by a spray process. The air exposure has led to PV devices with increased long term stability.

As described in the prior art, a series of scribes in selected film layers on the substrate **10** are required to isolate individual PV cells on the substrate and to interconnect the individual cells on the substrate **10** to form a completed module.

In step (**14**) a plurality of first scribes through the all of the film layers on the substrate **10** including the transparent conductive oxide are performed. A second plurality of scribes through the carbon and the p/n layers without removing the TCO are performed parallel to the first set of scribes. Both of these sets of scribes are performed by the novel film scribing method described above with reference to FIG. **9**A.

In step (**15**) a layer of conductive coating containing Ni is applied by spray onto the layer of conductive coating containing carbon. Since the Ni metalization layer is formed after the second set of scribes, the Ni layer will fill the cuts in the semiconductor layers from the second scribe. This will cause an electrical connection of the back electrode of one cell to the front electrode of another cell. This step in combination with the following step of the final scribe of the metalization layer will complete the interconnection of the PV cells in series to form the PV module.

In step (**16**) a plurality of third scribes through only the metallization layers are performed. This third set of scribes is performed by the novel film scribing method described above with reference to FIG. **9**A.

In step (**17**) electrical connections are made and the finished module is encapsulated.

In any of the film deposition steps, including the steps **4**), **5**), **6**), or **9**) of FIG. **10**A, more than one layer of a particular material may be deposited. These multiple layers may be deposited by a series of heated pocket deposition apparatuses. If one layer of material is deposited in a given cycle time, to a given thickness, then this single layer may be replaced by many thinner layers built up to the thickness of the single layer of material by using many depositions at shorter cycle times. Multiple depositions are advantageous since for every decrease in cycle time there is a corresponding increase in production rate. Multiple processing stations can also be used to decrease the cycle time for the other steps including annealing, vapor treatment, cooling, etc.

It would also be possible to create a multijunction solar cell in accordance with the teachings of the present invention. In this case, a monolithic multijunction structure could be fabricated on the substrate. In this structure, two or more solar cells would be stacked on one substrate in such a way that solar radiation passes through the larger band gap material first, and residual radiation passes through the stack to a smaller band gap material. The band gap of the materials needed could be tailored by using semiconductors formed by the combination of any of the elements Zn, Cd, Hg, S, Se, or Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may be in the form of alloys containing three or more elements. The multiple layers may be deposited by a series of heated pocket deposition apparatuses. Also, by varying the composition of the deposition material in the multiple heated pockets, a graded band gap photovoltaic device may be fabricated.

Many devices were fabricated by following the process steps (**1**) through (**13**) and step (**15**) of FIG. **10**A described above. CuCl was used as the metal salt in step (**9**). Individual PV devices with an area of 0.3 sq. cm. were formed on many substrates **10**. These devices were defined by masking certain areas and removing the rest of the films on the substrates **10** with an abrasive blast. The best device had a conversion efficiency of 11.8% and was produced on a commercially available low cost SnO_X:F coated soda lime glass substrate **10**. Such high efficiency devices have also proven to be stable. Accelerated stress testing by light soaking at 1000 W/m^2 and 65° C. at open circuit condition was performed on many devices. Over a time period of hundreds of hours, measured device efficiencies were at least 98% of the original efficiencies.

A description of the preferred embodiment of the present invention was given above. Other alternate embodiments of the present invention are described below. These specific alternate embodiments are best described with reference to FIG. **10**A, which is a flow chart of the process steps of the preferred embodiment of the invention.

In alternate embodiments of step **9**) in FIG. **10**A, the deposition of the metal compound may include compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb. These compounds may be metal salts as described in the preferred embodiment or organometallic compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb may also be used. These compounds may be deposited onto CdTe in vacuum to form an ohmic low resistance contact layer by reaction with the CdTe layer. This ohmic low resistance contact may be formed by tellurides of Cu, Ag, Au, Hg, Sn, Sb, and Pb, or the ohmic contact may be highly doped CdTe. An alternative embodiment to step **10**) of FIG. **10**A is to anneal the ohmic contact layer in air, inert gas or other atmospheres outside the vacuum chamber.

In other embodiments of the process steps **4**) and **5**) of FIG. **10**A other semiconductors may be used instead of CdS and CdTe. These semiconductors are formed by the combination of any of the elements Zn, Cd, Hg, S, Se or, Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may also be in the form of alloys containing three or more elements. These compound semiconductors are known to be useful in the formation of PV devices, are readily sublimable, and may be deposited in vacuum by the present invention. A series of stations may be used to deposit the n-type and p-type semiconductors. Thus, more than one layer may be used to form the n-type and p-type regions of the device This allows a faster cycle time while still maintaining adequate semiconductor film thickness. Also, the different stations may deposit different IIB-VIB compound semiconductors made up of the elements Zn, Cd, Hg, S, Se or, Te.

In alternate embodiments of step **6**) of FIG. **10**A, halogen containing substances such as HCl or Cl_2 gas may be used in place of or in addition to $CdCl_2$. In this case, a controlled amount of the gas can be introduced into the heated pocket **33**. Other halogen containing substances which are known to have effects similar to $CdCl_2$ may also be used. Some known examples of these compounds are $CdBr_2$ and CdI_2.

In another alternate embodiment of the process steps of FIGS. **10**A, a CdTe PV device may be fabricated without the deposition of CdS shown in step **4**) of FIG. **10**A. In this embodiment, the p/n junction is formed between the n-type TCO and the p-type CdTe or other IIB-VIB compounds.

In another embodiment of the process steps of FIG. **10**A, a CdTe device may be fabricated by depositing the CdS layer on the substrate **10** outside of the vacuum chamber **3** by known methods, including chemical bath deposition. In this embodiment, the substrate **10** with the CdS layer would be brought into the vacuum chamber **3** and steps **3**) through step **11**) of FIG. **10**A would be performed in vacuum.

In another embodiment of the process steps of FIG. **10**A, a $CdCl_2$ treatment may be performed after step **4**) CdS deposition and before step **5**) CdTe deposition. This $CdCl_2$ treatment is in addition to the step **6**) $CdCl_2$ treatment as shown in FIG. **10**A. The additional $CdCl_2$ treatment is known to further increase the device performance.

In other alternative embodiments of FIG. **10**A, the HPD deposition heated pocket **33** may be used to apply other film layers which would improve the performance of a CdS/CdTe PV device. One such layer is an anti-reflection (AR) coating which would be deposited on the glass substrate **10** on the opposite side of the substrate **10** from the TCO. The AR coating would face the sun and reduce the amount of incoming sunlight which is reflected off of the glass surface. This would increase the current that the device could produce. One such AR coating is a thin film of MgF_2. Since MgF_2 is sublimable, this film may be applied with the heated pocket **33** deposition. The AR coating can be done at a suitable location in the vacuum chamber **3**. Another layer which is known to increase the efficiency of a CdS/CdTe device is a layer of high resistivity intrinsic tin oxide (i-SnO_X). This layer would be applied between the TCO layer and the CdS layer or a layer of SnO_X of the desired resistivity could be deposited directly on the glass substrate **10**. This intrinsic layer has a much higher electrical resistivity than the TCO layer and has been shown to increase device efficiency. This resistive layer would allow the CdS layer to be thinner. The thinner CdS layer would allow more light to pass into the CdTe layer and increase the current the device would produce. The heated pocket **33** could be used to sublime i-SnO_X. The i-SnO_X deposition would be performed before the CdS deposition of step **4**) of FIG. **10**A.

An alternate embodiment to step **15**) of FIG. **10**A is that the graphite and Ni may be sprayed through a mask to form a patterned deposition. This patterned back electrode would eliminate the need for the second and third set of scribes shown in steps **14**) and **16**) of FIG. **10**A. In another embodiment, a spray through a mask may also be used to fill the cut of the first scribe with an insulating compound before the spraying of the Ni conductive coating. The insulating compound eliminates electrical shunts between the Ni layer and the TCO.

Other alternate embodiments of the present invention are described below. The figures which show these alternative embodiments are FIGS. **2**B, **7**B, **8**, **9**B, and **10**B. These alternative embodiments are described with reference to these figures.

FIG. **2**B shows an alternate embodiment of the present invention in which the pair of continuous metal strip belts **1** are entirely contained within the vacuum chamber **3**. A pair of known load locks **5** on either side of the chamber **3** provide a means of transporting the substrates **10** into and out of vacuum.

FIG. **7**B illustrates an alternate embodiment of the vacuum process station of FIG. **7**A involving a different arrangement for the upper heated pocket **33**. This alternate embodiment involves the addition of a baffle having a plurality of holes **28**. The deposition material **35** is placed above the baffle in a confined space. The confined space has a lid **27**, which may be removed to reload the deposition material **35**. As the upper heated pocket **33** is heated, the deposition material **35** will sublime, and vapor will pass through the holes **28** into the source pocket **29** of the upper heated pocket **33**. This alternative embodiment of the vacuum process station **200** may be used as the heated pocket **33** to deposit films on the upper surface of the substrate **10**. When the deposition is on the upper surface of the substrates **10**, the substrates **10** can be transported by arrangements such as rollers, robotic arms, etc., which are well known. This would be especially useful for the deposition of the AR coating.

FIG. **8** illustrates an alternative to the heated pocket **33**. This embodiment can be used to generate plasma in the pocket **29**. This arrangement is called plasma enhanced heated pocket deposition (PEHPD). The alternate embodiment of the heated pocket **33** provides a high voltage pin **30** for the generation of plasma, the pin **30** may be made from graphite. The pin **30** is electrically isolated by insulation **31** which may be a quartz tube. The high voltage from the DC power supply **32** generates the plasma. The heated pocket-to-substrate distance in the PEHPD heated pocket must be large enough to produce ions within the pocket **29**. If the pocket **29** is too shallow it will not produce a glow discharge at desirable pressures, when the substrate **10** is sealing the pocket **29** during deposition. In alternate embodiments of the present invention, both the CdS and CdTe heated pocket may optionally be of the PEHPD type so that the advantages of plasma enhanced deposition may be incorporated. These advantages of plasma enhanced deposition, which serve to improve the device efficiency, include: (i) doping of CdTe with nitrogen, (ii) passivation of the defects in CdTe, (iii) alteration of the morphology of CdS, (iv) doping of CdS, and (v) mixing of the CdS/CdTe interface. In addition, ZnTe may be doped with nitrogen by PEHPD to form ZnTe:N, a p+ semiconductor layer which may be used as an ohmic contact to CdTe.

FIG. **10**B is a flow chart of the process steps of some of the alternate embodiments of the invention. The processing steps as shown schematically in that figure include (**1**) cleaning the substrate by known means in a clean room type mini-environment, (**2**) transporting the substrate into the vacuum chamber using AVA or load lock transport, (**3**) heating the substrate, (**4**) depositing a CdS film on the substrate using heated pockets with or without plasma, (**5**) depositing a CdTe film onto the CdS film using heated pockets with or without plasma, (**6**) performing a treatment, with a halogen containing substance, on the CdS/CdTe films using a heated pocket, (**7**) annealing the substrate and films, (**8**) forming an ohmic contact on the CdTe layer by heated pocket deposition of a Te layer on the CdTe layer or by heated pocket deposition with plasma of a ZnTe:N layer on the CdTe layer, (**9**) depositing a metallization layer onto the ohmic contact layer by heated pocket deposition of a sublimable metal layer such as Zn or Cd, (**10**) annealing the substrate and films, (**11**) cooling the substrate and films, (**12**) transporting the substrate and films from the vacuum chamber using AVA or load lock transport, (**13**) performing a first scribe through the entire film stack including the metallization and the transparent conductive oxide, (**14**) screen printing the electrical connection of the back electrode of one cell to the front electrode of the next cell by known screen printing methods, and (**15**) encapsulating the furnished module. Step (**13**) involves a first scribe that may be performed in accordance with the teachings of the present invention or by one of several known means including mechanical or laser scribing and a second scribe through the carbon and the p/n layers without removing the TCO.

Step **8**) in FIG. **10**B illustrates another alternative embodiment of the present invention in which Te is used as an ohmic contact layer Te is easily sublimed and is known to form an ohmic contact material for CdTe devices. After the $CdCl_2$ treatment and annealing steps, Te could be deposited inline by heated pocket deposition with or without a cooling step. A metal back electrode can be applied to the Te ohmic contact by either a vacuum deposition step or by the spray process of the present invention.

Step **9**) of FIG. **10**B illustrates an alternate embodiment of the present invention in which the back electrode metallization may be accomplished inline in vacuum. In this embodiment, the back electrode metallization may be applied by a heated pocket deposition of metals including, but not limited to, Zn or Cd, which are readily sublimable and electrically conductive.

FIG. **9**B illustrates an alternative embodiment of the scribing method of the present invention involving the use of an abrasive blast **43** which is provided by known methods.

The abrasive blast **43** is performed through openings **45** in the mask **41** to remove portions of the film **40** from the substrate **10**. This embodiment of the scribing method does not require a precisely defined abrasive blast **43** since the mask **41** defines the area of the film **40** which will be removed. The abrasive blast **43** is passed over the substrate **10** to perform a scribe. Each abrasive blast **43** may enter more than one opening **45** in the mask **41** so that one abrasive blast **43** may perform more than one scribe for each pass over the substrate **10**. A plurality of abrasive blasts **43** may be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes of an entire substrate **10**. Different abrasive media with different hardness and size may be provided so that various layers in the film stack **40** may be scribed selectively. This allows the scribing method of the present invention to: **1**) scribe all the way through the film stack including the relatively hard TCO layer, and **2**) selectively scribe through all of the layers above the TCO layer without removing the TCO.

We claim:

1. Apparatus for transporting substrates within a vacuum chamber, the apparatus comprising:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert; and

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts.

2. Apparatus for transporting substrates within a vacuum chamber as in claim **1**, wherein the vacuum chamber includes front and rear openings through which the pair of metal belts and the substrates pass, extending outside said front and rear openings, the apparatus further comprising:

a clearance distance between each of the substrates and the front and rear openings so as to permit motion of the substrates while at the same time restricting air leaks, to thereby maintain a desired level of vacuum in the chamber.

3. Apparatus for transporting and processing a plurality of substrates by exposing them to heating, film deposition or vapor treatment within a vacuum chamber, the apparatus comprising:

a plurality of heated pockets positioned in proximity to and in correspondence with each of the plurality of substrates such that a clearance distance between a surface of each of the substrates and the corresponding one of the heated pockets is minimized so as to permit motion of the substrates while restricting vapor leaks from the heated pockets; and

a transporter for moving the substrates from one heated pocket to the next.

4. Apparatus as in claim **3**, wherein the transporter comprises:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert;

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts; and

a controller, coupled to said translator, for indexing the belts incrementally to move each of the substrates from one heated pocket to another.

5. Apparatus as in claim **3**, wherein a selected one or more of the heated pockets includes a high voltage pin coupled to a source of D.C. voltage for creating a plasma within a selected one or more of the heated pockets.

* * * * *

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Barth et al. (43) **Pub. Date: Jul. 10, 2003**

(54) **APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES**

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Publication Classification

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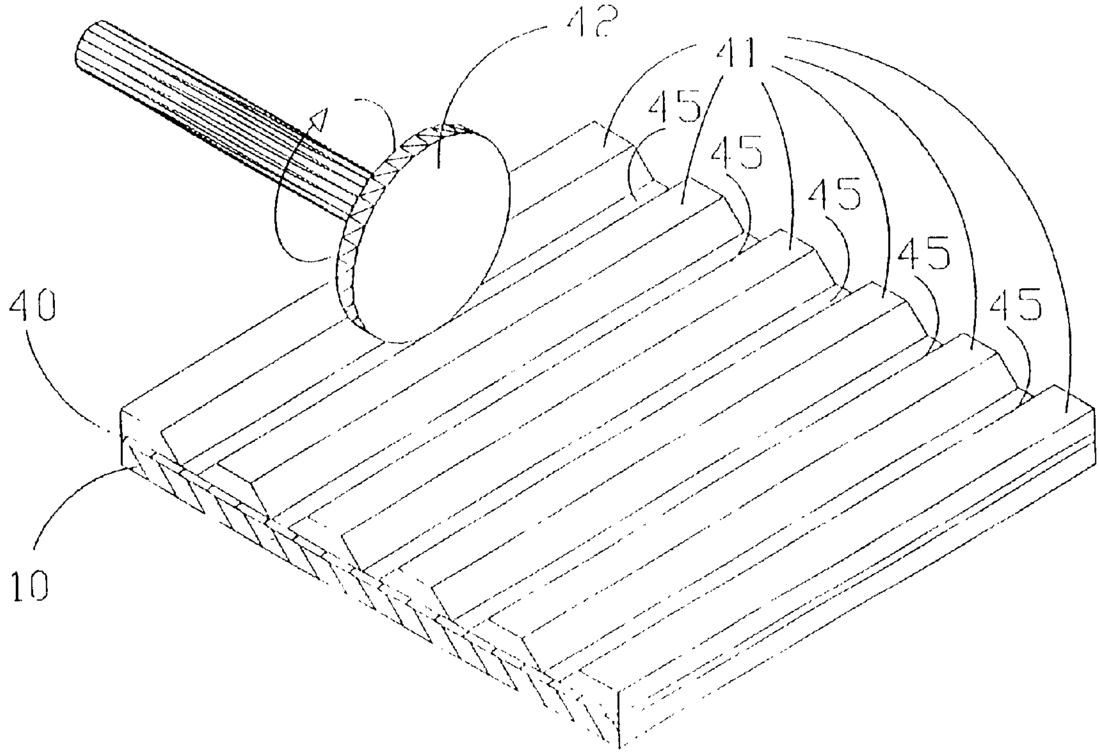
(52) **U.S. Cl.** **438/462**

(57) **ABSTRACT**

An apparatus and processes for large scale inline manufacturing of CdTe photovoltaic modules in which all steps, including rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation, are performed within a single vacuum boundary at modest vacuum pressures. A p+ ohmic contact region is formed by subliming a metal salt onto the CdTe layer. A back electrode is formed by way of a low cost spray process, and module scribing is performed by means of abrasive blasting or mechanical brushing through a mask. The vacuum process apparatus facilitates selective heating of substrates and films, exposure of substrates and films to vapor with minimal vapor leakage, deposition of thin films onto a substrate, and stripping thin films from a substrate. A substrate transport apparatus permits the movement of substrates into and out of vacuum during the thin film deposition processes, while preventing the collection of coatings on the substrate transport apparatus itself.



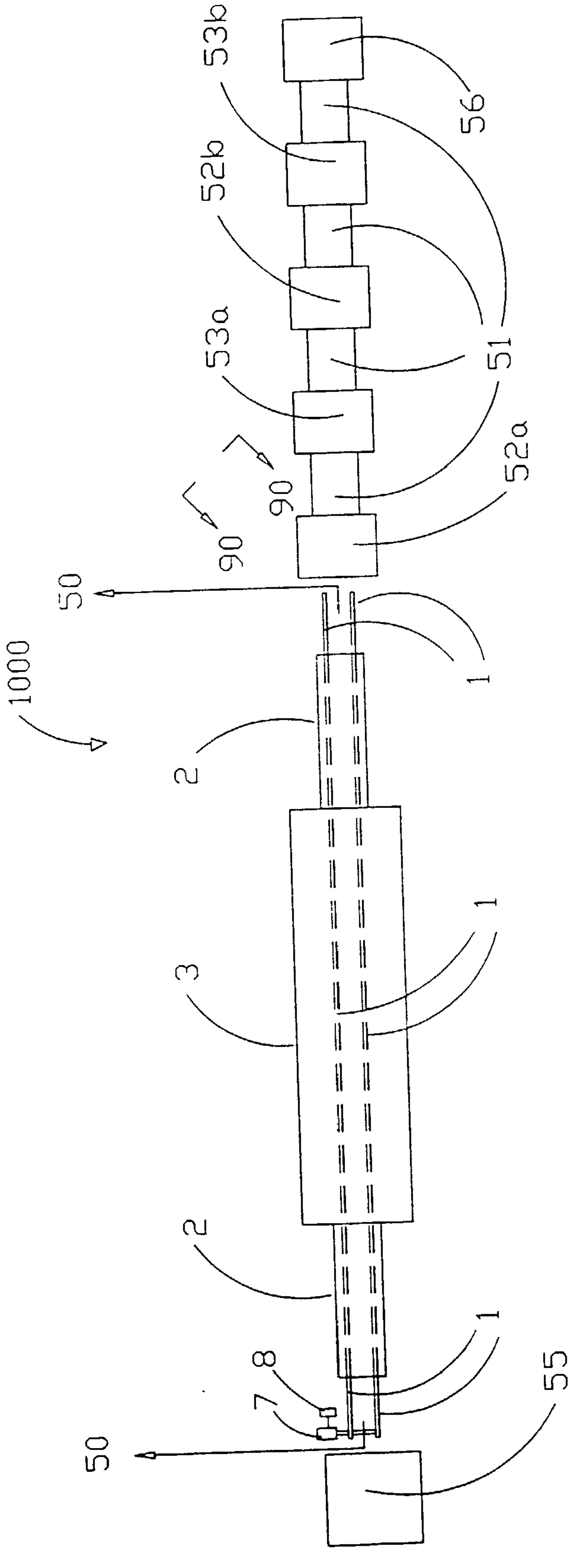


Fig. 1

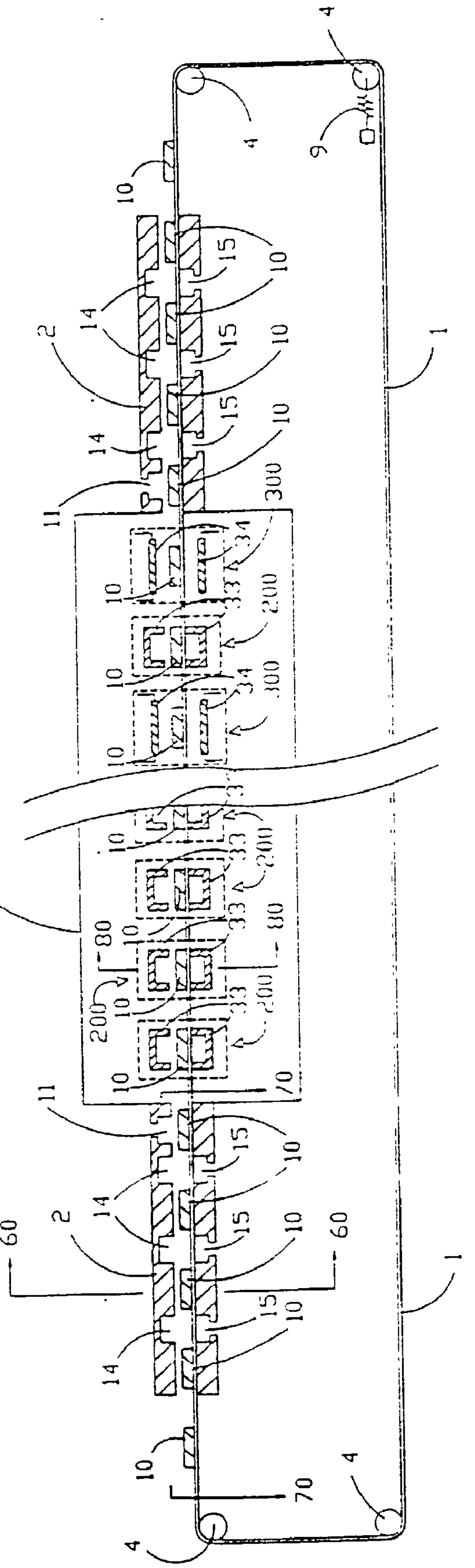

4
4
9
10
2
14
15
10
1
11
300
34
33
200
3
80
200
70
60
60
14
2
15
10
1
4
10
70
4

Fig. 2A

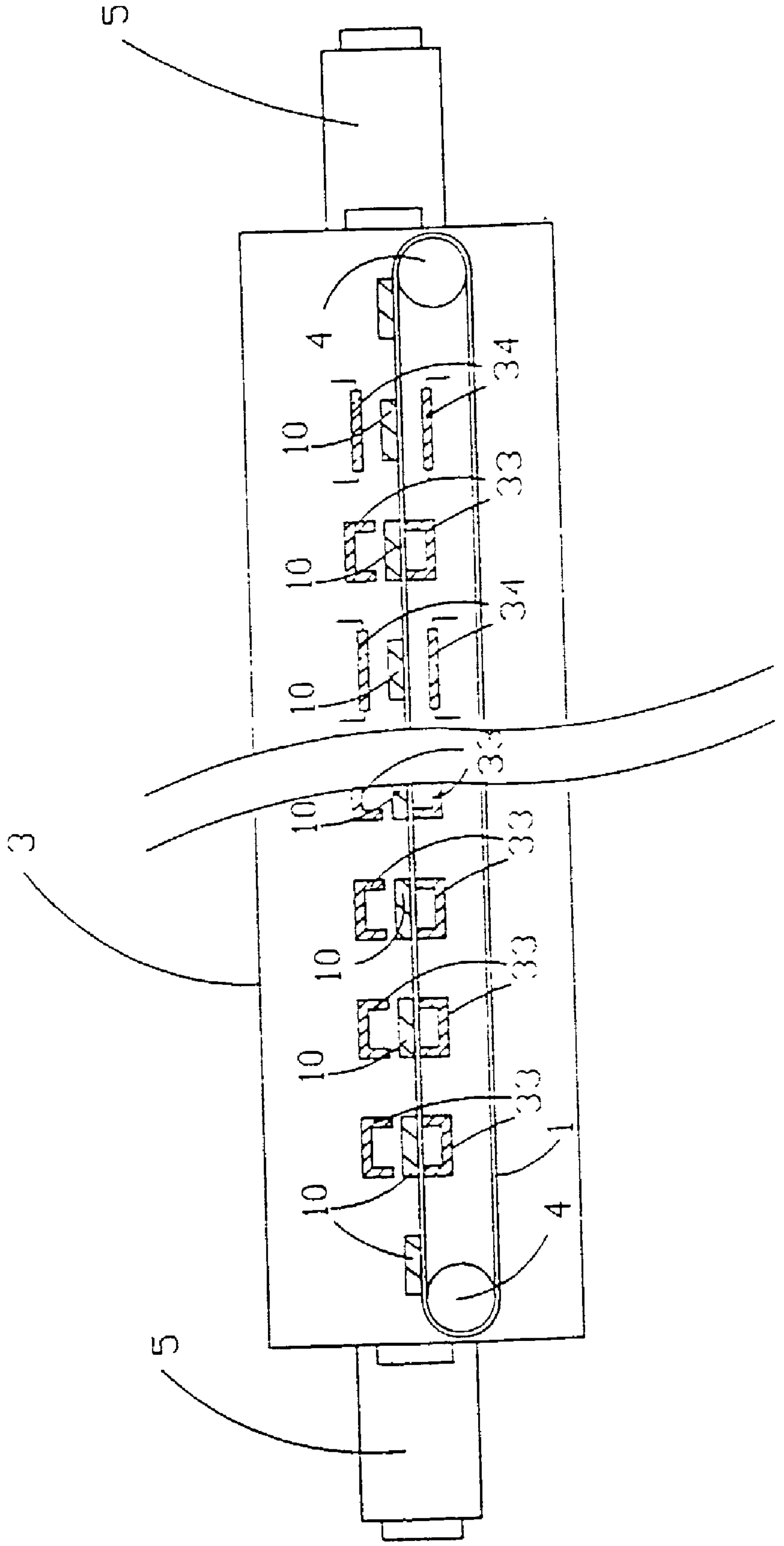


Fig. 2B

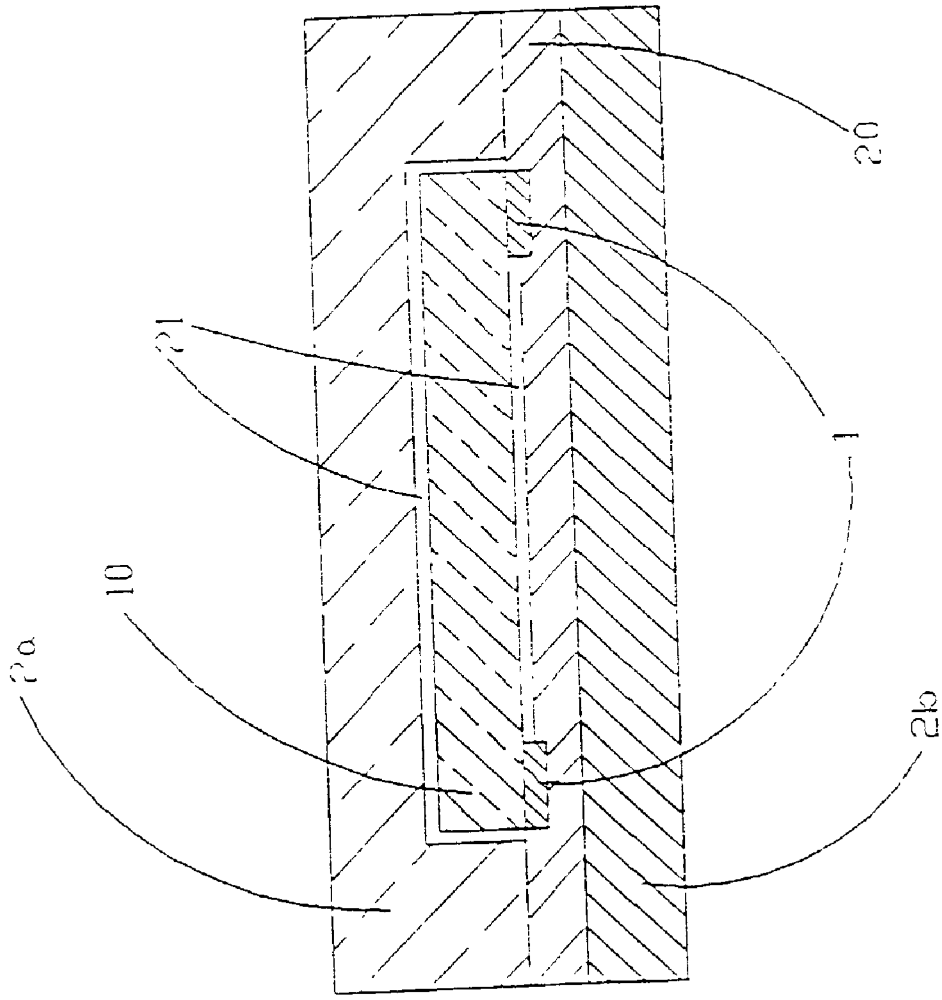


Fig. 3

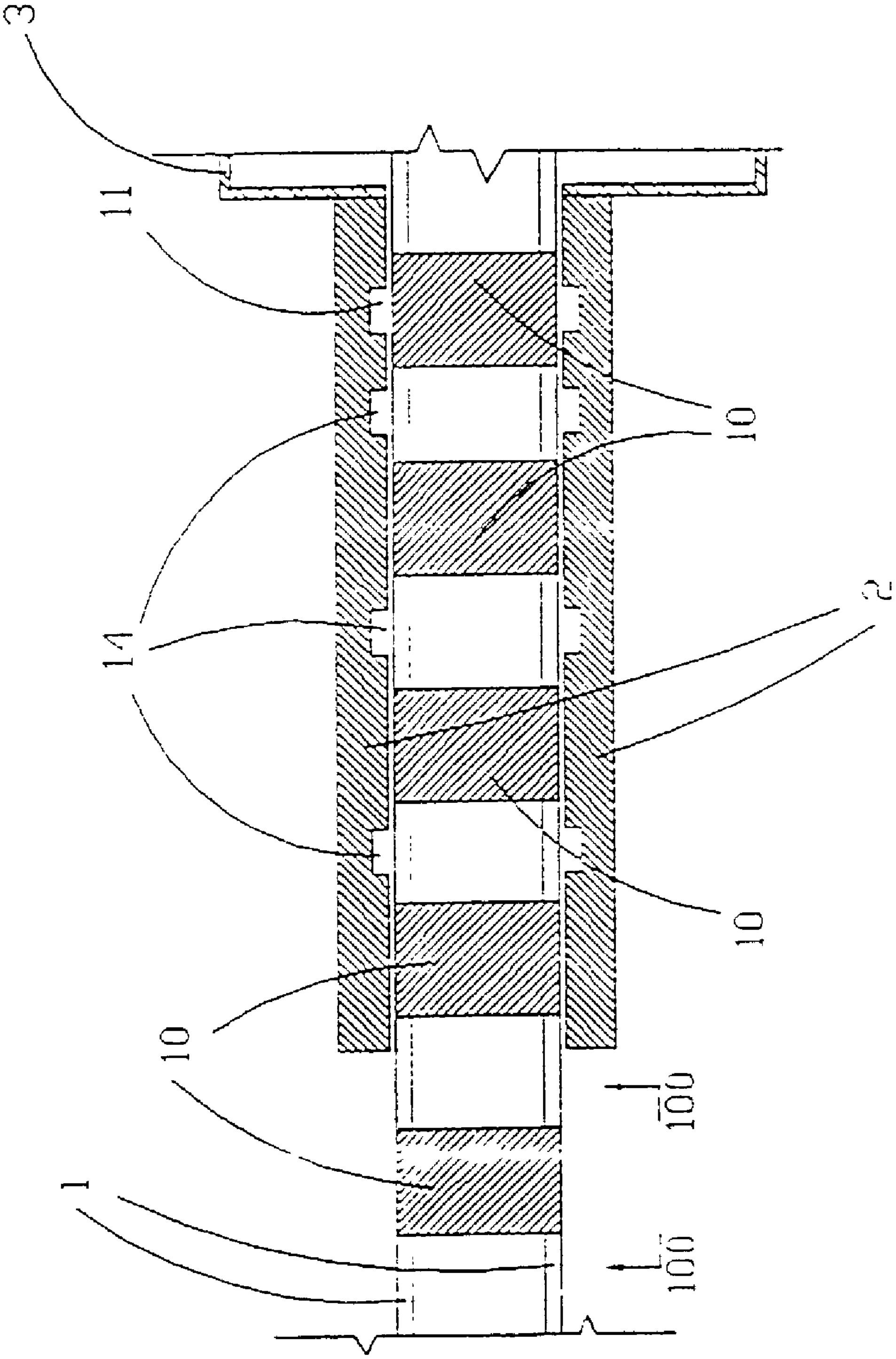


Fig. 4

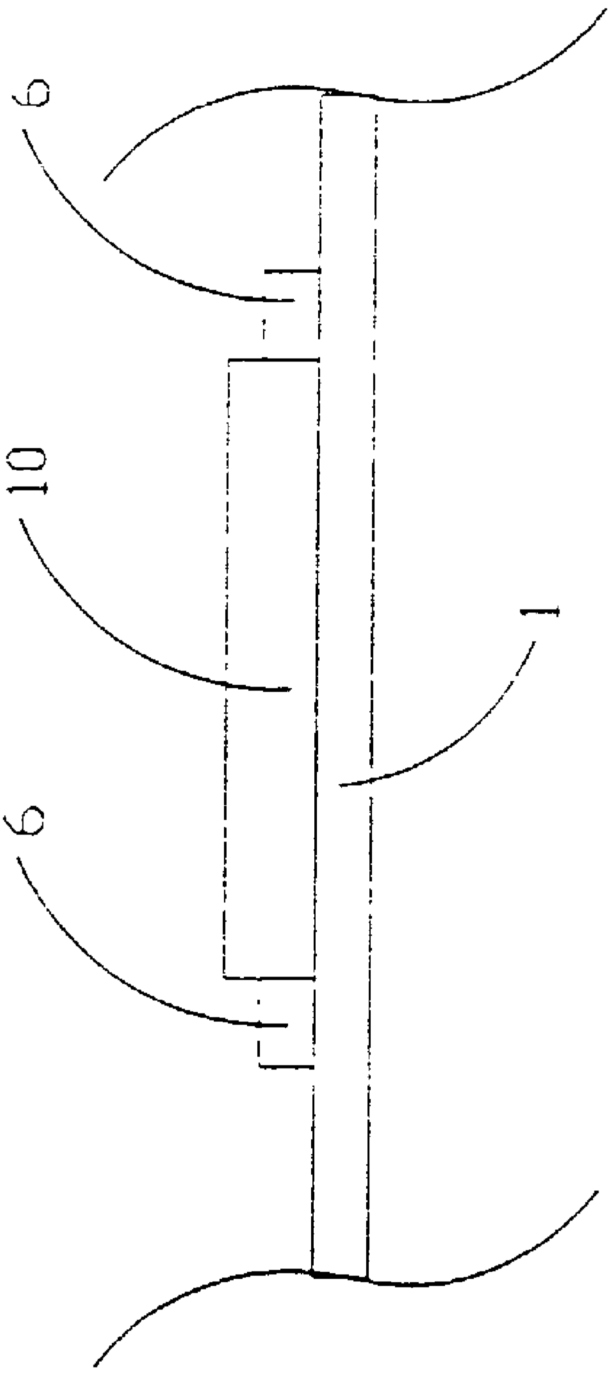


Fig. 5

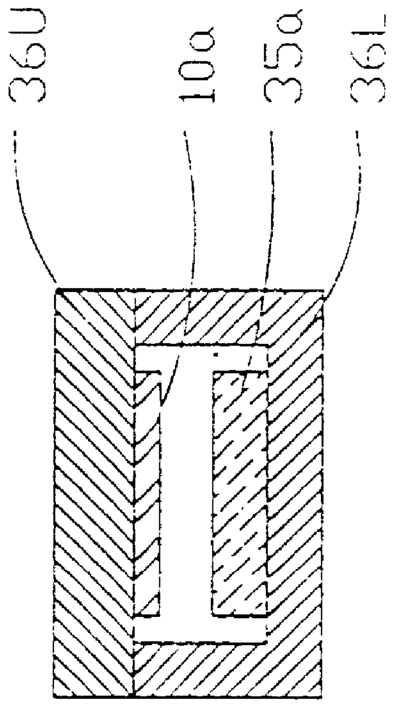


Fig. 6A (PRIOR ART)

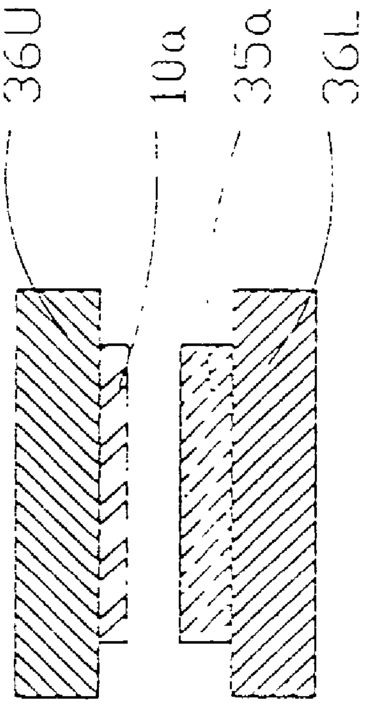


Fig. 6B (PRIOR ART)

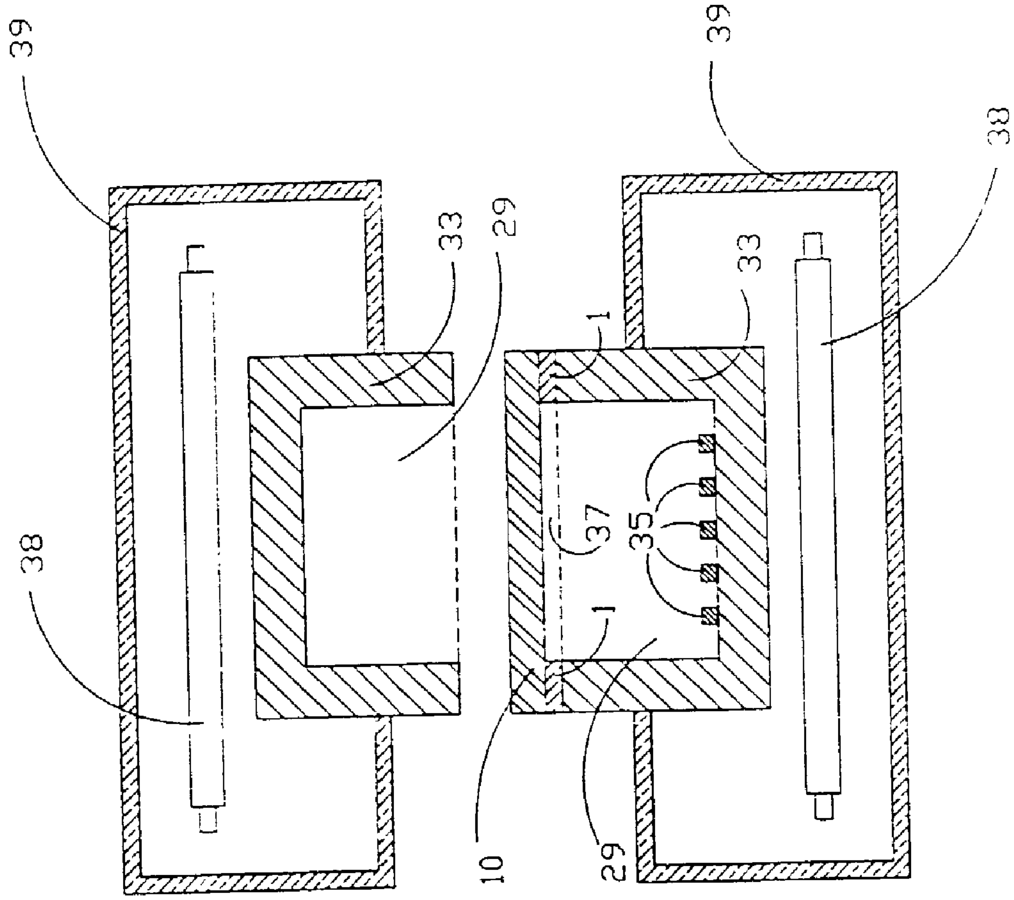


Fig. 7A

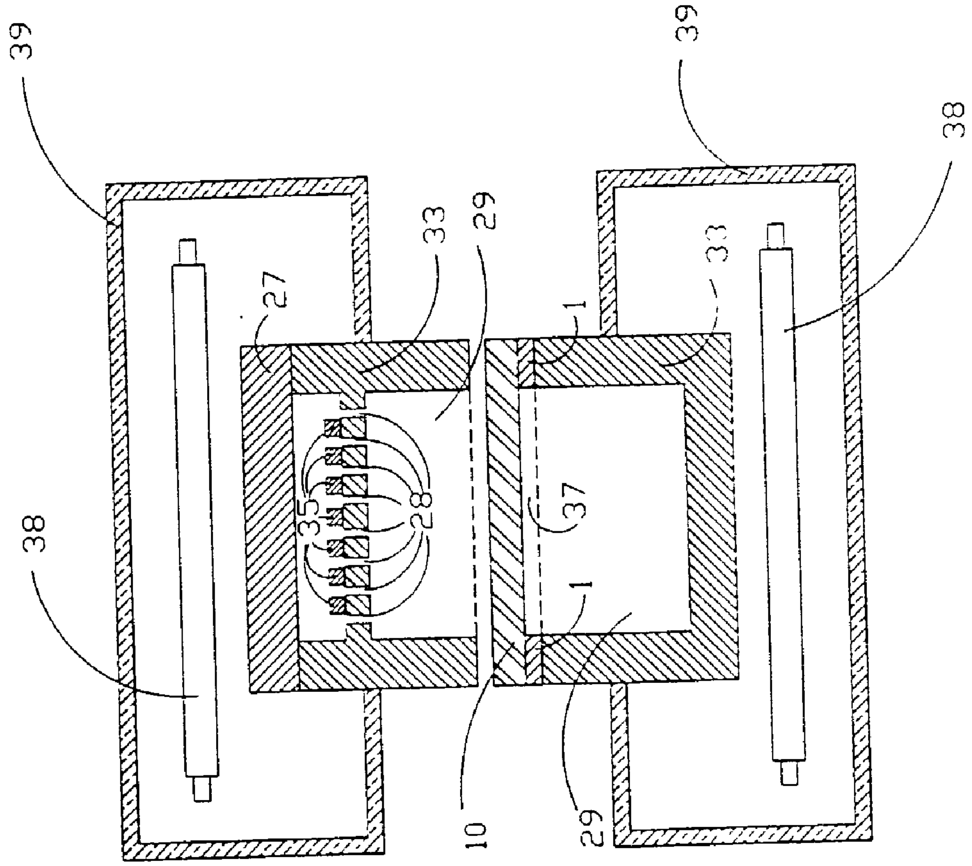


Fig. 7B

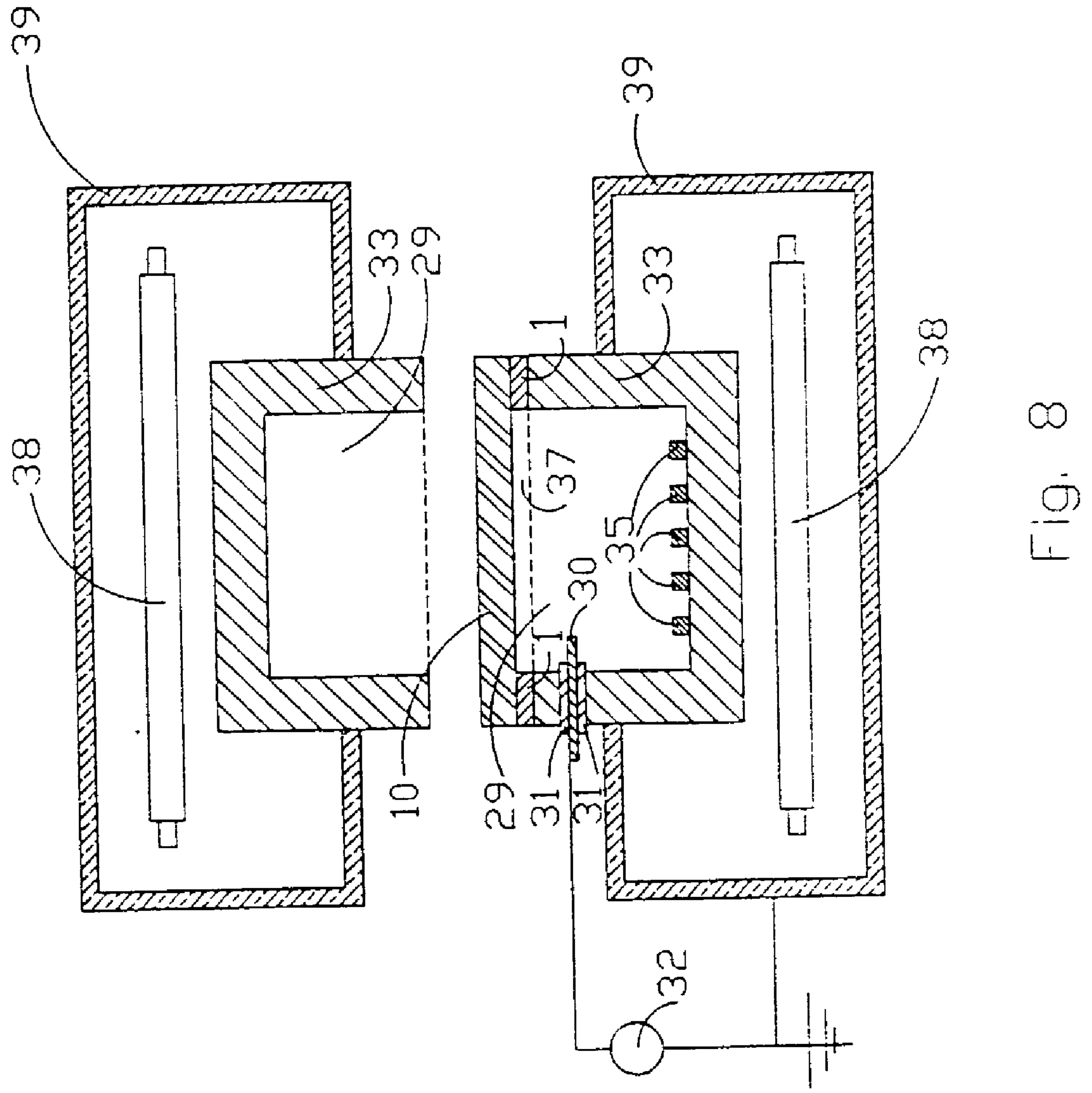


Fig. 8

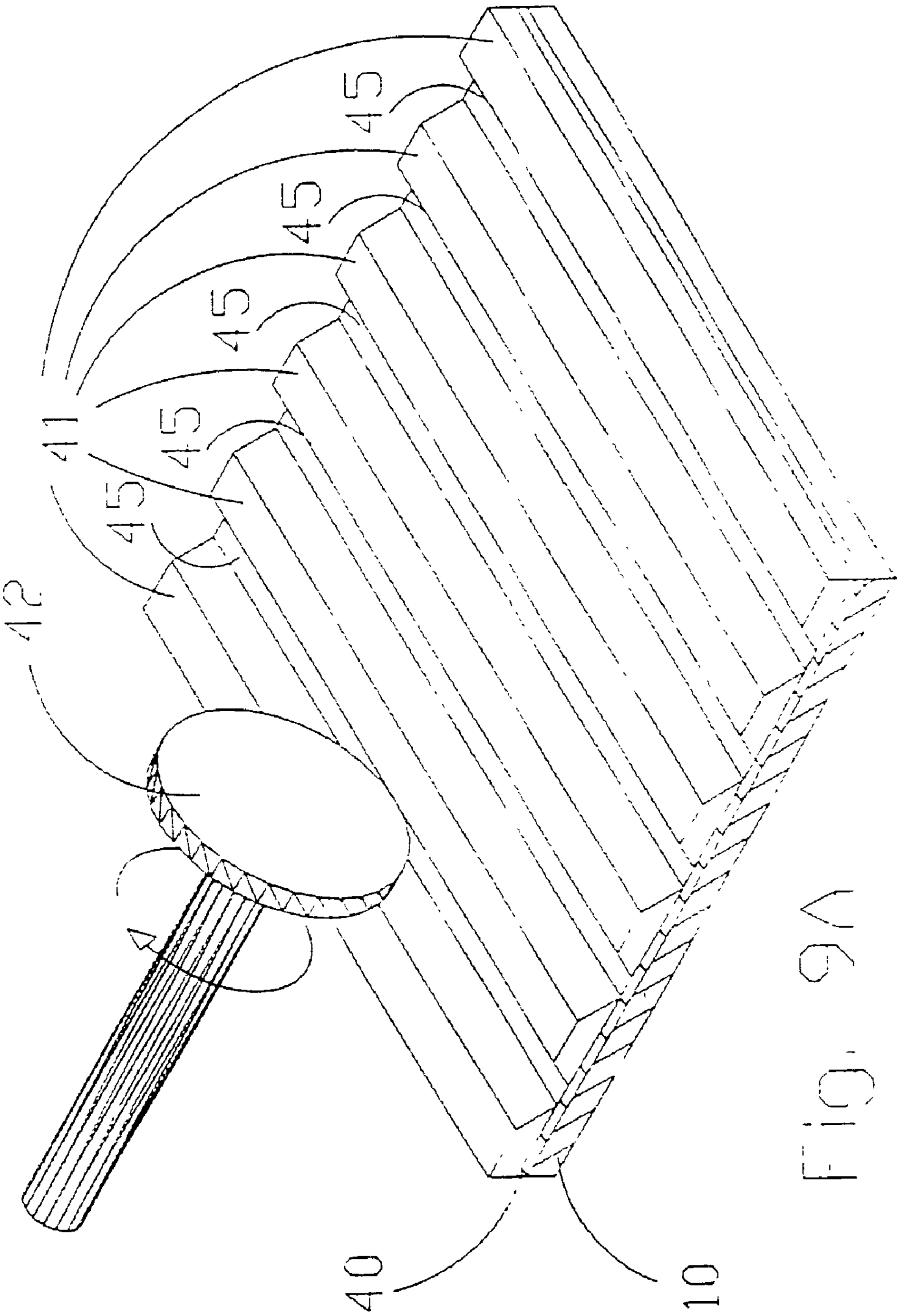


Fig. 9A

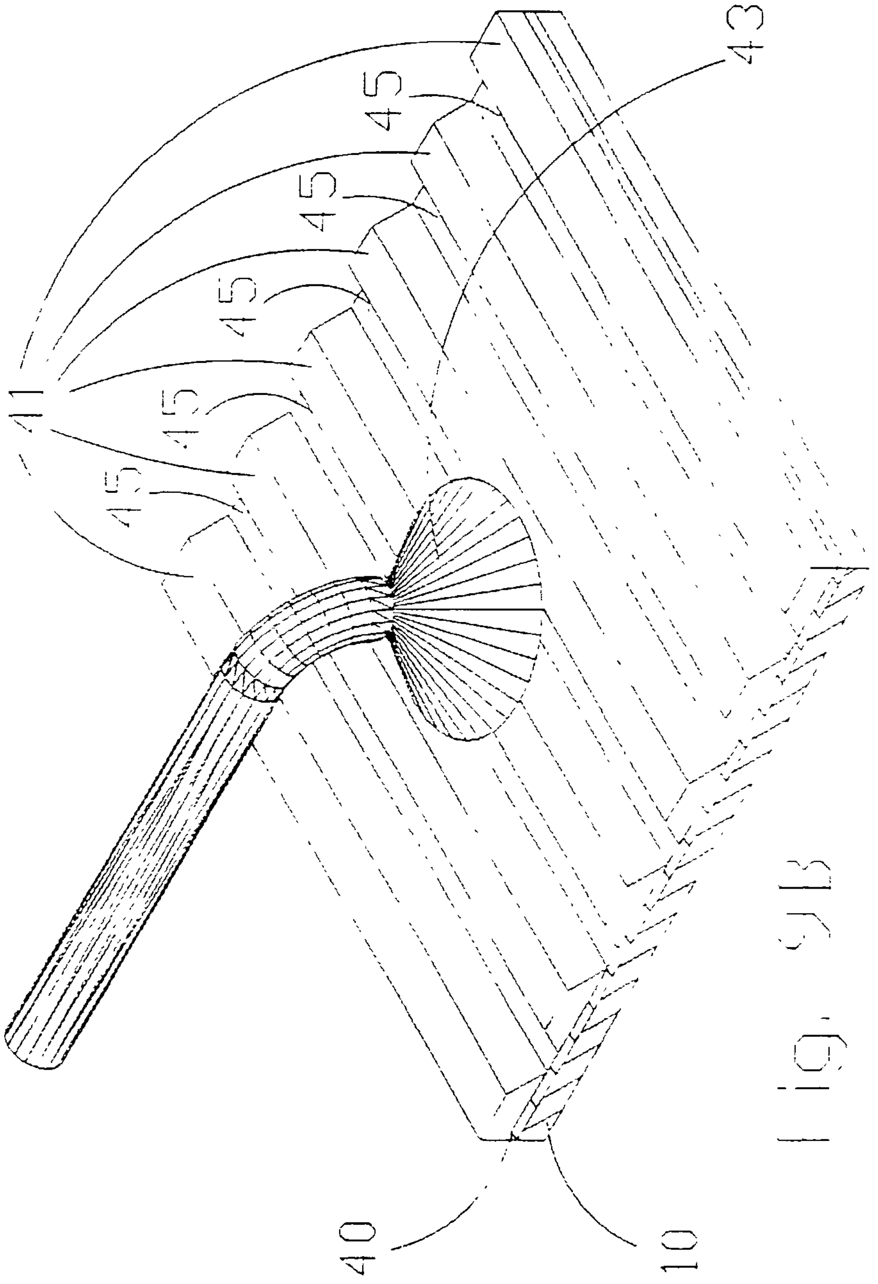


Fig. 9B

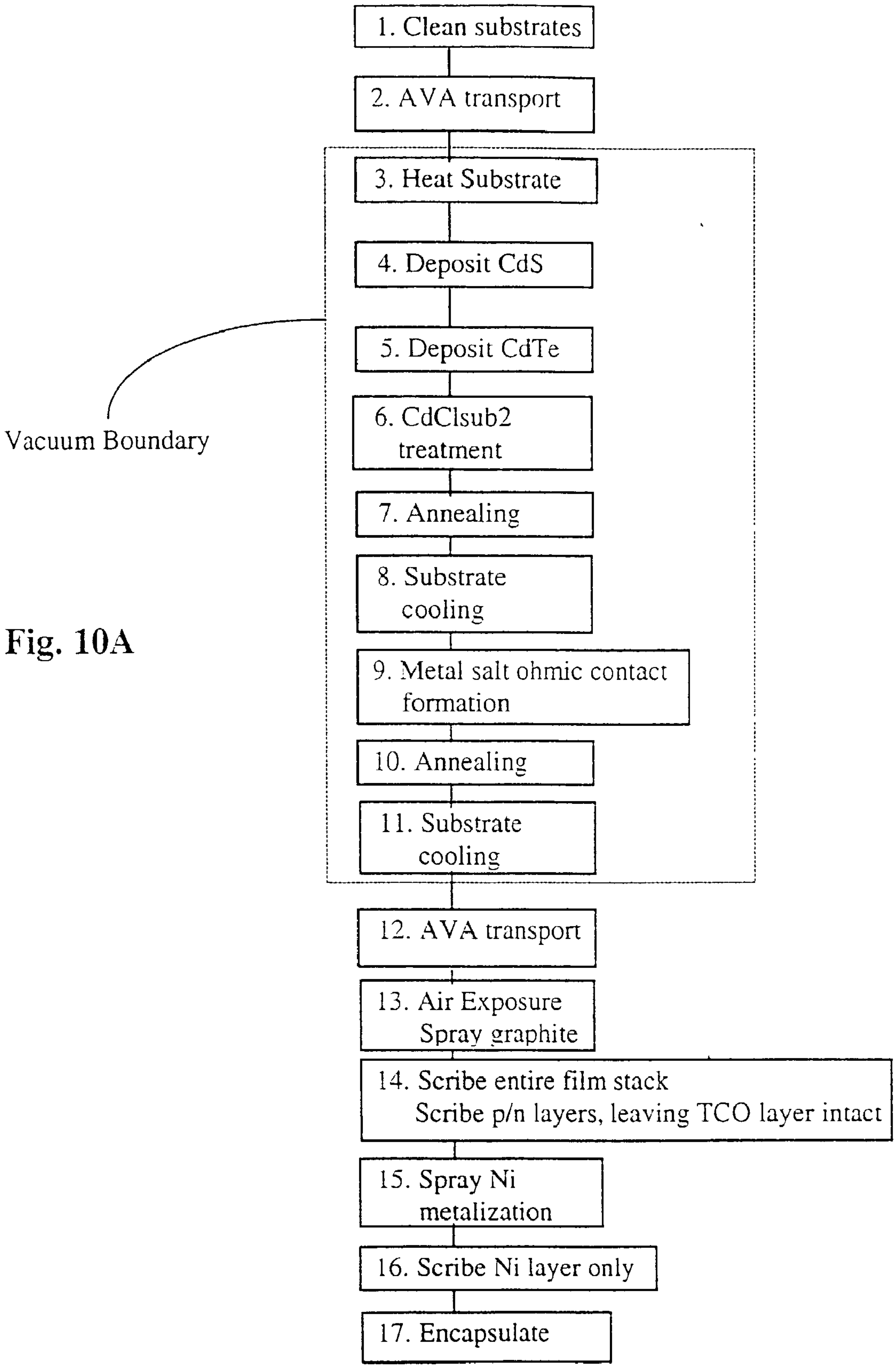

1. Clean substrates
2. AVA transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. CdClsub2 treatment
7. Annealing
8. Substrate cooling
9. Metal salt ohmic contact formation
10. Annealing
11. Substrate cooling
12. AVA transport
13. Air Exposure Spray graphite
14. Scribe entire film stack Scribe p/n layers, leaving TCO layer intact
15. Spray Ni metalization
16. Scribe Ni layer only
17. Encapsulate
Vacuum Boundary

Fig. 10A

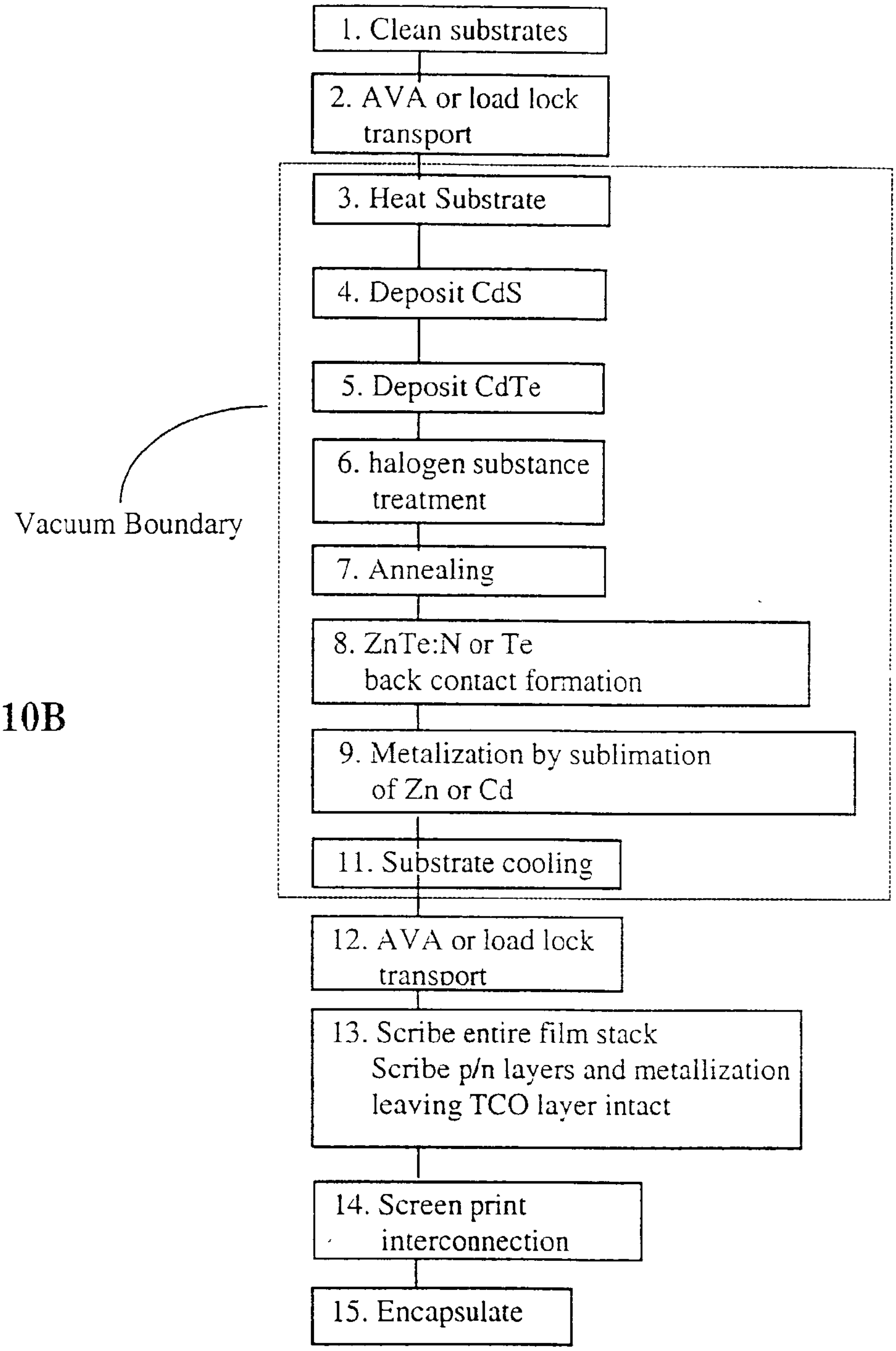

1. Clean substrates
2. AVA or load lock transport
3. Heat Substrate
4. Deposit CdS
5. Deposit CdTe
6. halogen substance treatment
7. Annealing
8. ZnTe:N or Te back contact formation
9. Metalization by sublimation of Zn or Cd
11. Substrate cooling
12. AVA or load lock transport
13. Scribe entire film stack Scribe p/n layers and metallization leaving TCO layer intact
14. Screen print interconnection
15. Encapsulate
Vacuum Boundary

Fig. 10B

APPARATUS AND PROCESSES FOR THE MASS PRODUCTION OF PHOTOVOLTAIC MODULES

[0001] Government Support

[0002] This invention was made with Government support under grants awarded by the National Science Foundation and the Department of Energy. The Government has certain rights in this invention.

FIELD OF THE INVENTION

[0003] The present invention relates to apparatus and processes for the mass production of low cost photovoltaic modules and, more specifically to an inline continuous vacuum apparatus and process for fabricating the critical semiconductor layers, which together with attendant non-vacuum processes, are all accomplished at high throughput.

BACKGROUND OF THE INVENTION

[0004] Photovoltaic (PV) modules are used to generate electricity from sunlight by the photovoltaic effect. It has been recognized for decades that if these modules could be mass produced at low cost, they could be used to meet a considerable portion of the world's energy needs. Major companies, such as Royal Dutch/Shell and BP-Amoco, have stated that PV modules have the potential to become a major energy source and that their use has significant benefits to the global environment. However, for these benefits to be realized, PV modules must be produced at many times the current volume and at costs below \$100/m^2, as discussed by Bonnet et. al. in "Cadmium-telluride material for thin film solar cells", J. Mater. Res., Vol. 13, No. 10 (1998). Currently, PV modules are manufactured in small quantities at costs of about \$500/m^2. About one hundred times the current yearly production is required to sustain a PV module manufacturing capacity that can contribute just 5% of the current electricity generated. Consequently, the manufacturing volume of PV modules needs to be greatly increased and costs significantly reduced.

[0005] To realize the required increases in production volume and decreases in manufacturing costs, PV modules must be produced as a commodity. Commodity level manufacturing requires innovation to develop highly automated production processes and equipment, which are designed to specifically fabricate the commodity product. Commodity manufacturing necessitates high production speeds (high throughput), minimal labor costs, and a continuous process flow. Low capital costs and ease of expanding production capacity also facilitate commodity manufacturing. There are a variety of known PV devices, but only the cadmium telluride (CdTe) thin film PV device has the potential to satisfy the requirements for commodity manufacturing.

[0006] Since 1974, there have been many industrial efforts to create technologies for CdTe PV module manufacturing. Most of these industrial efforts, as exemplified by the teachings of U.S. Pat. Nos. 4,319,069, 4,734,381, and 5,501,744, have been terminated because of fundamental inadequacies in their manufacturing technologies. To date, no technology suitable for commodity level manufacturing of CdTe PV modules has been developed, thus demonstrating the need for innovation in this area.

[0007] The most common CdTe PV cells are thin film polycrystalline devices, in which the CdTe layer is paired with a cadmium sulfide (CdS) layer to form a heterojunction. The thin films of a CdS/CdTe PV device can be produced through a variety of vacuum and non-vacuum processes. Of the many types of thin film deposition methods, sublimation in vacuum is most amenable to commodity manufacturing. This is because vacuum sublimation of CdS/CdTe PV modules exhibits deposition rates 10 to 100 times higher than any other PV module deposition method. Vacuum sublimation of the semiconductor layers for CdS/CdTe PV modules can also be performed in modest vacuum levels and does not require costly high vacuum equipment. Vacuum deposition methods for other thin film PV devices require costly, complex high vacuum equipment and results in low throughput.

[0008] Due to the high rate of deposition and low capital cost, the CdS/CdTe thin film cell fabricated by vacuum sublimation is the most suitable for commodity level manufacturing of PV modules. However, cadmium is a Group B carcinogen. According to U.S. government regulations, the quantity of this material which can be lawfully released into the environment or into an occupational setting is extremely small. The known prior art in CdS/CdTe vacuum sublimation requires process and hardware innovations to achieve occupational and environmental safety as required by federal regulations, as well as commodity scale manufacturing.

[0009] One known configuration for a CdTe device is the back wall configuration, in which the thin films are deposited onto a glass superstrate, hereinafter referred to as a substrate. The CdTe device is most often fabricated on a glass substrate coated with a transparent conductive oxide (TCO) film onto which other film layers are deposited in the following order: a) a CdS film, b) a CdTe film, c) an ohmic contact layer, and d) a metal film. Along with the deposition of these films, many heat treatments are also needed to enhance the device properties. The TCO and the metal films form the front and back electrodes, respectively. The CdS layer (n-type) and the CdTe layer (p-type) form the p/n junction of the device. The cells are deployed with the substrate facing the sun. Photons travel through the glass and TCO film before reaching the p/n junction of the device. A module is formed by interconnecting individual cells in series to produce a useful voltage.

[0010] Thus, a process for manufacturing CdS/CdTe modules includes the following steps: 1) cleaning the TCO coated glass substrates, 2) heating the substrates, 3) depositing an n-type CdS layer, 4) depositing a p-type CdTe layer, 5) performing a $CdCl_2$ treatment to improve CdTe grain structure and electrical properties, 6) forming a p+ohmic low resistance contact layer to improve current collection from the CdTe, 7) depositing a metal layer (metallization) to form the back electrode, 8) scribing the film layers into individual cells, 9) interconnecting the cells in series and providing a means of electrical connection to the module, and 10) encapsulating the finished module.

[0011] All of the prior art methods for the production of CdTe modules have limitations that render them unsuitable for commodity level manufacturing. For example, prior art methods of $CdCl_2$ treatment are disconnected, low throughput batch operations, rather than continuous flow processes. These batch type processes are inefficient and involve extremely high costs in order to increase throughput to the commodity manufacturing level. Most of the known methods of $CdCl_2$ treatment also require rinsing, which generates liquid wastes that contain cadmium. Known methods of ohmic contact formation are also batch type processes that exhibit low throughput rates. Prior art metallization steps also exhibit low throughput and require costly process equipment. It is necessary to improve the current methods of $CdCl_2$ treatment, ohmic contact formation, and metallization in order to achieve high throughput continuous processes.

[**0012**] Prior art methods for scribing the layers to form a module include laser scribing, mechanical scribing, and abrasive blasting. Known laser scribing methods used in the PV industry are associated with low production speed and high capital cost. Laser scribing was abandoned recently in one industrial setting due to laser equipment failure as discussed by Borg in, "Commercial Production of Thin-Film CdTe Photovoltaic Modules", NREL/SR-520-23733, October 1997. Known mechanical and abrasive blast scribing methods have only been shown on a small scale as typified by U.S. Pat. No. 5,501,744 to Albright and require innovation and improvement to be suitable for commodity level manufacturing.

[**0013**] Specific examples of prior art relating to CdS deposition and CdTe deposition performed by vacuum sublimation are described in detail below. The other prior art steps that are necessary to form a complete CdTe PV module are also discussed below.

[**0014**] One known vacuum method of producing CdTe solar cells by vacuum sublimation is taught in U.S. Pat. No. 5,536,333 to Foote et. al. This method is further described by Sasala et. al. in "Technology Support for Initiation of High-Throughput Processing of Thin-Film CdTe PV Modules", NREL/SR-520-23542, pp. 1-2, (1997). These references discuss a technique known as vapor transport deposition (VTD), which involves heating of the semiconductor materials in a contained vessel in order to create vapor. An inert carrier gas, such as nitrogen, transports the vapor of the semiconductor to the substrate through heated conduits. The substrate is held horizontally in a heated environment and supported from beneath by ceramic rollers in the heated environment. The deposition of the semiconductor is made onto the top surface of the substrate. In accordance with this prior art method, the ceramic rollers prevent the glass substrate from sagging under its own weight due to the elevated temperatures involved.

[**0015**] The entire VTD method is very complex and costly. It is possible to deposit a complete CdTe solar cell in a very short time and at sufficiently low substrate temperatures to eliminate glass sagging completely or reduce it to a very small acceptable value. Thus, the expensive ceramic rollers of the VTD method are not needed. Reloading starting material may also be performed in a much simple manner than as shown in this prior art. Since the films are thin, only small amounts of material are required to form them. Consequently, only very small volumes of starting material are needed for many days of operation, thus eliminating the need for this complex reloading arrangement. The heated vessels of this method contain toxic vapors, which pose significant occupational safety problems when they are opened for reloading during processing. In the VTD method, vapors are transported through long distances in a carrier gas, an arrangement which will likely lead to the formation of very small nano-particles through condensation of the vapors. These nano-particles degrade the film qualities and lead to occupational hazards when the system is serviced. Furthermore, in the VTD method, the continuous flow of carrier gas has to be maintained along the substrate. Any CdS or CdTe vapors that are carried past the substrate will be wasted. Any deposits of waste material on the inner surface of the vacuum chamber, pumps, exhaust, etc. must be cleaned, thereby exposing maintenance workers to toxic materials and raising occupational safety issues. In order to prevent unwanted condensation of CdS and CdTe vapors, the VTD method also requires continued heating of large portions of the equipment, including the vaporization vessel itself, the conduits, the deposition chamber, etc. This wastes energy and increases the capital costs. The VTD method is only used for depositing the p/n junction layers. Other processing steps, such as the $CdCl_2$ treatment, ohmic contact formation, and metallization are inherently low throughput batch processes. Scribing is taught to be either laser scribing or photolithography both of which are slow and costly processes.

[**0016**] In another prior art reference entitled "The CdTe Thin Film Solar Cell" International Journal of Solar Energy, vol. 12, 1992, Bonnet proposes an inline production method for fabricating CdS/CdTe layers using a close-spaced sublimation (CSS) type deposition process. This prior art reference describes inline deposition within one vacuum boundary for only the steps of substrate heating, CdS deposition, and CdTe deposition. The other steps of $CdCl_2$ treatment. ohmic contact formation, and metallization are not shown as part of a continuous inline vacuum process, and are presumably performed by previously known methods. As described above, known methods for performing these steps have limitations. The Bonnet method does allow multiple substrate processing of more than one film. However, it is not clear if long term operation and uniformity of deposition over time and across large substrates are achieved. Furthermore, the Bonnet method relies on CSS, which by definition, requires a space of 2-3 mm between the source and the substrate. This gap will allow a vapor leak at the edge of the substrate. As the source charge sublimes away over time the gap will increase. It is the present inventors' experience that this gap and the associated vapor leak causes non-uniform deposition on the substrates and also results in condensation of toxic materials on unwanted areas on the inner surfaces of the process chamber. This leak will be reduced if the background chamber pressure is held high enough to decrease the mean free path between gas molecules in the process chamber. However, higher pressures lead to lower deposition rates and greater nano-particle formation. An operating pressure of 750 millitorr is specified. At these pressures, nano-particles will be formed, since the vapor will homogeneously condense in the ambient gas near the edge of the deposition space. These very small particles degrade film quality and pose a health hazard to workers during routine maintenance inside the vacuum chamber.

[**0017**] Each of the individual prior art process steps required to produce a CdTe PV module exhibits limitations, as outlined above. In addition, nothing in the prior art describes an overall process to perform the series of steps of substrate heating, depositing an n-type CdS layer, depositing a p-type CdTe layer, performing a $CdCl_2$ treatment, and forming an ohmic contact inline, continuously, and in one vacuum boundary. In particular, the steps of $CdCl_2$ treatment and ohmic contact formation require significant innovation before they can be included in a continuous inline vacuum process. Such a continuous inline vacuum process would have significant advantages for commodity manufacturing of CdTe PV modules.

[**0018**] Any vacuum process for manufacturing CdTe PV modules would also require an apparatus to transport substrates through the process steps within vacuum and to transport the substrates into and out of vacuum rapidly. This apparatus should be robust, simple, and low cost. The apparatuses described in the prior art simply do not meet these requirements.

BRIEF SUMMARY OF THE INVENTION

[**0019**] The present invention is directed to commodity scale manufacturing of CdTe PV modules and involves innovations in both manufacturing processes and hardware.

[**0020**] One aspect of the present invention involves providing all of the processing steps for the critical semiconductor layers of a CdTe PV device inline, with all of those steps being completely performed within one vacuum boundary, at high throughput. They include rapid substrate heating, deposition of CdS, deposition of CdTe, $CdCl_2$ treatment, and ohmic contact formation. These steps are performed at modest vacuum pressures without requiring costly high vacuum equipment. By utilizing inline vacuum processing to form all of the critical layers without breaking vacuum, an improvement in process throughput, film quality, device efficiency, and device stability is realized, while at the same time avoiding pinhole formation. All inline vacuum processing is also advantageous in that it limits the production of toxic waste and environmental and occupational exposure to toxic compounds.

[**0021**] Another aspect of the present invention is a novel $CdCl_2$ treatment step, which may be performed in the same vacuum boundary and inline with the other fabrication steps. Our $CdCl_2$ treatment process has the advantage of a high throughput rate while producing stable, high efficiency devices and, at the same time, limiting environmental and occupational exposure to toxic compounds.

[**0022**] Another aspect of the present invention is a novel vacuum process to produce a p+ ohmic contact region by subliming a metal salt onto a CdTe layer. Our ohmic contact formation process has the advantage of producing, at high throughput rates, a low resistance ohmic contact that is stable over time.

[**0023**] Another aspect of the present invention is a unique high throughput, low cost spray process to form the back electrode. This process has the advantage of producing a durable, high conductivity back electrode using known low cost industrial spray methods.

[**0024**] Another aspect of the present invention is to provide novel high throughput, low cost processes to perform module scribing using abrasive blasting or mechanical brushing through a mask. These novel scribing processes have the advantage of selectively scribing the semiconductor layers without scribing the TCO layer. In addition, the scribe process may be adjusted so that the TCO layer may be removed as well.

[**0025**] Another aspect of the present invention is a novel vacuum process station to selectively heat substrates and films, to expose substrates and films to vapor, to deposit thin films on a substrate, and to strip thin films off of a substrate. This vacuum process station allows substrates to be transported into and out of vacuum. When used as a deposition source, our vacuum process station has the advantage of very minimal vapor leakage, which significantly reduces occupational exposure to toxic materials. This unique deposition source deposits very uniform layers and is suitable for long term continuous operation.

[**0026**] Another aspect of the present invention is a novel substrate transport apparatus, which is employed to move substrates within vacuum or, in combination with a unique opening, to transport substrates rapidly into and out of vacuum. This substrate transport apparatus is robust, simple, and low cost and has the additional advantage of not collecting any coatings as it moves substrates through the thin film deposition processes.

[**0027**] Yet another aspect of the present invention is to provide substrate cleaning in a clean mini-environment at the entrance to the inline continuous vacuum process, which has the advantage of greatly reduced cost resulting from the elimination of a clean room to contain the entire process line.

BRIEF DESCRIPTION OF THE DRAWINGS

[**0028**] **FIG. 1** is a schematic top plan view of a system for making photovoltaic modules in accordance with the present invention.

[**0029**] **FIG. 2A** is a partially broken away schematic elevation view in longitudinal section along the line **50-50** of **FIG. 1**, illustrating a substrate transport apparatus and a plurality of vacuum processing stations.

[**0030**] **FIG. 2B** is a partially broken away schematic elevation view in longitudinal section, illustrating an alternate embodiment of the substrate transport apparatus of **FIG. 2A**.

[**0031**] **FIG. 3** is a schematic elevation view in cross section along the line **60-60** of **FIG. 2A** illustrating the sealing arrangement by which the introduction of outside air into the vacuum chamber is minimized.

[**0032**] **FIG. 4** is a partial schematic top plan view in longitudinal section along the line **70-70** of **FIG.** 2A, further illustrating the sealing arrangement of **FIG. 3**.

[**0033**] **FIG. 5** is a schematic elevation view along the line **100-100** of **FIG. 4**, further illustrating the substrate transport apparatus of **FIG. 2A**.

[**0034**] FIGS. **6**A-B are schematic sectional elevation views illustrating enclosed and unenclosed substrates as they are positioned in prior art apparatuses.

[**0035**] **FIG. 7A** is a schematic elevation view in cross section along the line **80-80** in **FIG.** 2A, illustrating details of a vacuum process station of the substrate transport apparatus of **FIG. 2A**.

[**0036**] **FIG. 7B** is a schematic elevation view in cross section to illustrate an alternative embodiment of the vacuum process station of **FIG. 7A**.

[**0037**] **FIG. 8** is a schematic elevation view in cross section to illustrate a second alternate embodiment of the vacuum process station of **FIG. 7A**.

[0038] **FIG. 9A** is a schematic perspective view along the line **90-90** of **FIG. 1**, illustrating the way in which photovoltaic modules are scribed.

[0039] **FIG. 9B** is a schematic perspective view along the line **90-90** of **FIG. 1**, illustrating an alternative way to scribe photovoltaic modules.

[0040] **FIG. 10A** is a flow chart illustrating the process steps of the present invention.

[0041] **FIG. 10B** is a flow chart of some of the alternate embodiments of the process steps of **FIG. 10A**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0042] Referring now to **FIG. 1**, there is shown an overview of the preferred embodiment of an apparatus **1000** for producing photovoltaic modules in accordance with the present invention. A substrate cleaning station **55** cleans the commercially available substrates that typically comprise low cost soda lime glass coated with transparent conducting oxide (TCO). After cleaning, a pair of metal strip belts **1** transport the substrates through the next portion of the apparatus **1000**. The belts may be moved bidirectionally by means of a known stepper motor **7**. Precise indexing of the position of the pair of belts **1** is accomplished by the use of a commercially available stepper motor controller **8**. The pair of metal strip belts **1** pass through a pair of openings **2** and a vacuum chamber **3**. A plurality of process stations for the processing of the critical semiconductor layers are contained within the vacuum chamber **3**, and are described in detail below. Another series of process stations are linked by a plurality of conveyor belts **51**. These process stations do not require vacuum. A first spray process station **52***a* is followed by a first film scribing process station **53***a*. These process stations are followed by a second spray process station **52***b* and a second film scribing process station **53***b*. The final process station in the apparatus **1000** is an encapsulation station **56**. The description of the apparatus and processes of the instant invention is presented in the following order: the substrate transport apparatus and openings, the vacuum process stations, the metallization method, the film scribing method, and the process steps to produce a photovoltaic module. Following the description of the preferred embodiment is a description of alternate embodiments.

[0043] **FIGS. 2A, 3, 4**, and **5** in combination illustrate the complete assembly of the preferred embodiment of a pair of air-to-vacuum-to-air (AVA) openings and the substrate transport system of the present invention. The pair of AVA openings **2** facilitate the rapid transport of substrates from air into vacuum and then back into air. **FIG. 2A** illustrates vacuum chamber **3**, which is pumped to a suitable vacuum by known techniques. A pair of AVA openings **2** is shown on either side of the vacuum chamber **3**. A pair of continuous metal strip belts **1** pass through both of the AVA openings **2** and also through the entire length of the vacuum chamber **3**. A plurality of substrates **10**, which are carried on the twin metal belts **1**, are also shown. The AVA openings **2** are shown with a plurality of pockets **14** and a plurality of vacuum pump ports **15** for vacuum pumping. A pair of injection ports **11** are shown for the injection of process gas. A plurality of pulleys **4** are provided for moving the belts **1**. A belt tensioner **9** maintains the belts **1** at a predetermined tension.

[0044] **FIG. 3** shows the details of the AVA openings **2** in cross section. A top channel **2***a* and a bottom plate **2***b* are split by a belt bearing plate **20**. In total, parts **2***a*, **2***b*, and **20** form the cross section of the opening **2** of **FIGS. 2A, 3**, and **4**. A clearance distance **21** on the order of 0.005 in.±0.002 in. is formed around the substrate **10**. This clearance distance **21** is formed between the substrate **10** and the top channel **2***a* and between the substrate **10** and the belt bearing plate **20**. The clearance distance **21** is large enough so that the substrate **10** may move freely, but is small enough to provide resistance to fluid flow through the clearance distance **21**. This resistance to fluid flow allows the vacuum chamber **3** to be maintained at a desired vacuum level. The pair of continuous metal strip belts **1** provide a substrate carrier to convey the plurality of substrates **10**.

[0045] **FIG. 5** is a detailed view of a pair of tabs **6** which are attached to the metal strip belt **1**. The tabs **6**, a plurality of which are placed periodically along the belt **1**, provide a means of locating the substrate **10**.

[0046] The pair of continuous metal strip belts **1** provide a substrate carrier that will not be coated by the vacuum deposition processes. The elimination of coating on the belt **1** is a significant improvement over the prior art. As exemplified by Charschan in U.S. Pat. No. 3,294,670 (1966), the prior art utilized substrate carriers which enclosed the perimeter of the substrate in a "picture frame" type arrangement. The picture frame type substrate carriers are necessarily coated during deposition. These coatings lead to jamming in the close tolerance seals during motion, present occupational safety issues due to particle generation, and result in cross contamination between the processes. In the present invention, these problems have been addressed by exposing only the substrates **10** to coating during a vacuum deposition. In addition, unlike all of the prior art, the clearance distance **21** is not formed between the substrate carrier and the openings. Rather, the clearance distance **21** is formed between the precisely cut substrate **10** and the AVA openings **2**. The clearance **21** is formed specifically between the substrate **10** and the top channel **2***a* and between the substrate **10** and the linear bearing plate **20**.

[0047] The use of the pair of metal strip belts **1** as the substrate carrier in accordance with the present invention has many other advantages. The fact that the belts **1** have a low mass will create less wear on any bearing surface used. The low mass will also greatly decrease the inertia of the substrate carrier, thus allowing the substrate to be moved quickly between processing stations.

[0048] Continuous metal strip belts **1** also have advantages in situations calling for a series of vacuum processes to be carried out in one vacuum chamber **3**. Continuous metal strip belts **1** of 200 feet in length can be fabricated by known methods. This allows a large number of process steps to be carried out in one vacuum chamber **3**.

[0049] Another advantage is the cost of fabrication of this type of substrate carrier, which is considerably less than the cost of machining close tolerance picture frame type substrate carriers of the prior art. The present substrate carriers also facilitate scaling up the process. For larger substrates **10**, the openings **2** must be increased in size. However, the strip belts **1** may be simply spaced further apart.

[0050] The continuous metal strip belts **1** are preferably formed of metal alloys that have high resistance to corrosion and that retain high strength at elevated temperatures. These belts may be coated with other materials to alter the surface properties further, if needed. Many different attachments or tabs **6** for retaining the substrate **10** may be welded or fixed to the metal strip belts **1** at relatively low cost.

[**0051**] A cut tolerance of ±0.003 inch is required for the glass substrates **10** which are carried on the continuous metal strip belts **1**. High throughput, low cost equipment is commercially available for cutting the substrates **10** to the required tolerances. The precision glass cutting required for this invention is not an additional processing step, since the substrates **10** must be cut to size in any method.

[**0052**] The continuous metal strip belts **1** are also relatively small in cross section. The small cross section decreases the thermal expansion as the belts pass through high temperature vacuum processes, which will decrease any tendency to jam in the AVA openings **2** due to thermal expansion.

[**0053**] The relatively low mass of the metal strip belts **1** also allows the substrate carrier to cool and heat more rapidly than the prior art picture frame type substrate carrier. The low mass of the metal strip belts **1** allows the belt temperature to match the glass temperature during processing, thereby reducing thermal gradients in the glass substrates **10** which could otherwise lead to stresses that may crack the glass.

[**0054**] Referring now to **FIG. 2**A, the vacuum chamber **3** and a plurality of vacuum processing stations, generally indicated by **200** and **300**, are illustrated in a partial schematic elevation view in section. The metal strip belts **1** carry the plurality of substrates **10** through the plurality of vacuum processing stations **200** and **300**. The process stations **300** provide for cooling of substrates **10** by radiation to a pair of water cooled plates **34**.

[**0055**] Each of the process stations **200** of **FIG. 2A** contain a pair of heated pockets **33**. These heated pockets **33** provide a flux of heat or vapor and are suitably shaped blocks of a material with a high thermal conductivity. In **FIG. 7A** the pair of heated pockets **33** are shown with details of the pair of continuous metal strip belts **1** in cross section. Both upper and lower heated pockets **33** have a machined pocket **29**. A deposition material **35** is shown in the pocket **29** of the lower heated pocket **33**. Only the substrate **10** spans the pocket **29**. No part of the belts **1** crosses the pocket **29**, thus avoiding deposition anywhere but on the substrate **10**. The upper heated pocket **33** serves as a heater for the substrate **10**.

[**0056**] Heated pocket **33** may be fabricated using any material which has an acceptable level of thermal conductivity. Further, that material should have a low level of porosity to prevent adsorption of air and water vapor and a low level of impurities. One material which has proven useful is purified pyrolitic grade graphite. However, metals and metals coated with ceramics, as well as other suitable materials, may be chosen.

[**0057**] In the preferred embodiment of the invention, the heated pockets **33** are heated by a plurality of quartz halogen lamps **38**, which are not damaged when used in vacuum at high temperatures. The temperature control of the heated pocket **33** may be accomplished by placing a thermocouple in the wall of the heated pocket **33** and using well known proportional with integral and derivative (PID) temperature control of the power to the lamps **38**. Lamps **38** are contained in boxes **39** for protection. Boxes **39** also serve as support structure for the lamps **38** and the heated pocket **33**. The boxes **39** also provide electrical isolation for safety, prevent arcing from the lamps **38**, and also serve as radiation shields to reduce the loss of energy. Other means of heating the heated pocket **33**, including resistive heating and inductive heating, for example, may be used as well.

[**0058**] Each of the process stations **200** may perform a variety of processes on a substrate **10**. These processes include: i) rapidly heating a substrate, ii) annealing a substrate and films, iii) thermally stripping a film from a substrate, iv) exposing a substrate and films to a vapor treatment, or v) depositing a thin film on a substrate. The chosen processes performed by station **200** depend on three parameters: a) the temperature of the lower heated pocket **33**, b) the temperature of the upper heated pocket **33**, and c) the presence or absence of the deposition material **35**. For processes i) through iii) described above, no deposition material **35** is loaded into the pocket **29**. For process i) the upper and lower heated pockets **33** are maintained at temperatures such that the rapid heating of glass substrates **10** may be done in a short cycle time, on the order of one minute. The uniformity of heating prevents cracking of the substrates **10**. For process ii), the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature which will not resublime thin films off of the substrate **10**. For process iii) the upper and lower heated pocket **33** and substrate **10** are maintained at a temperature that is high enough to cause films on the substrate **10** to sublime away.

[**0059**] For processes iv) and v) described above, deposition material **35** is loaded into the pocket **29**. For process iv), the upper heated pocket **33** and substrate **10** are maintained at a higher temperature than the lower heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33** and expose the lower surface of the substrate **10** to vapor, but the vapor will not be deposited as a film on the substrate **10**. For process v), the lower heated pocket **33** is maintained at a relatively higher temperature than the substrate **10** and the upper heated pocket **33**. In this manner, the deposition material **35** will sublime in the pocket **29** of the lower heated pocket **33**, and the vapor will condense and be deposited as a film on the lower surface of the substrate **10**. All of these processes are robust, may be performed at high throughput, are occupationally and environmentally safe, and involve low capital cost.

[**0060**] In accordance with the present invention, the pair of metal belts **1** transports the substrates **10** through the plurality of process stations **200** or **300**. The metal belts **1** and the substrates **10** may be moved continuously. However, the preferred embodiment of the present invention provides for intermittent motion of the metal belt **1** and the substrates **10**. This motion is accomplished using a conventional stepper motor **7** and a stepper motor motion controller **8**. The substrates **10** are placed at equal pitch distances on the belts **1**, and the process stations **200** or **300** are placed one pitch distance apart. The intermittent motion consists of pauses in the motion of the belts **1** for processing and brief periods of motion of the belts **1** to advance the plurality of substrates **10** through the series of process steps. In this manner, an individual substrate **10** will pause at each process station **200** or **300** for an equal amount of time. A useful period of time, hereinafter defined as the cycle time, consists of the total period of time for one pause and one movement of the belts **1**. One substrate **10** will complete the series of inline vacuum process steps for each period of cycle time.

[**0061**] Since the process stations **200** or **300** are modular, a plurality of one type of process may be placed in series. If a given process step requires a processing time which exceeds the cycle time, then the given process step may be carried out over a series of similar processing stations **200** or **300**. For example, an annealing step, which requires a longer period of time to complete than the cycle time, may be carried out over a series of annealing process stations **200**.

[**0062**] The deposition of thin films onto substrates **10** is a critical processing step of the present invention. A detailed description of the deposition apparatus is given below.

[**0063**] The intermittent motion of the belts **1** allows a pause for deposition. During the pause, as shown in **FIG.** 2A, the individual substrates **10**, which are spaced at regular pitch intervals on the metal strip belts **1**, will be in a sealing relationship with individual heated pockets **33**. During this pause, the individual heated pockets **33** will deposit a film onto the substrates **10**. For a given pause time, the thickness of the films can be varied by varying the temperature of each individual heated pocket **33**. Closed loop control of film thickness may be achieved by measuring film thickness with known thickness monitors and adjusting the heated pocket **33** temperature as needed. Very precise control may be achieved since the deposition rate is a function of the temperature of the heated pocket **33**.

[**0064**] The present invention is specifically designed to produce very uniform film deposition across the surface of the substrate **10** at high throughput so that in a mass manufacturing environment the reproducibility of the film uniformity from one substrate **10** to another substrate **10** is tightly controlled over long periods of time. In order to accomplish this desired aspect of the present invention, the substrate **10** is held in a novel sealing relationship with the pocket **29**.

[**0065**] The novel sealing relationship is unique and is not shown or suggested in the prior art. **FIG. 6**A and **FIG. 6B** show an elevation view of two prior art devices used for film deposition by vacuum sublimation. In **FIG. 6**A, the known method of Bozler in U.S. Pat. No. 3,636,919 (1972) shows the source deposition material **35***a* and substrate **10***a* in an enclosed space. The enclosed space is formed by an upper heater **36** U and a lower heater **36** L. Because the substrate **10***a* is sealed in the enclosed space, the substrate **10***a* could not be moved and only one film could be deposited for each pump down of the vacuum chamber. **FIG. 6B** details another known method according to Bonnet in U.S. Pat. No. 5,304,499 (1994) which is commonly known as close spaced sublimation (CSS). In this known method, the deposition material **35***a* is placed on a flat heated plate **36** L and the substrate is held at a typical distance of 2 to 3 mm from the deposition material **35***a*. The disadvantage of this known method is that the clearance between the deposition material **35***a* and the substrate **10***a* forms a leak path for the vapor. This leak will lead to non-uniform deposition and the formation of toxic nano particles in the process space.

[**0066**] The heated pocket deposition apparatus of the present invention overcomes the limitations of the prior art. With reference to **FIG. 7**A, there is a clearance distance **37** on the order of 0.001 in. to 0.018 in. between the substrate **10** and the top surface of the heated pocket **33** block. Clearance distance **37** is formed on the two sides of the substrate **10** where the substrate **10** spans the belts **1**. The clearance distance **37** is necessary to prevent the substrates **10** from touching the heated pocket **33** and damaging the deposited films. The clearance distance **37** is formed in such a manner as to provide a close tolerance slip fit seal between the top of the heated pocket **33** and the bottom of each of the substrates **10**. Any vapor leak through the clearance distance **37** will be in the molecular flow regime and will be very small. This effectively eliminates vapor leaks through the clearance distance **37** and allows the substrates **10** to act as a shutter across the source pocket **29**.

[**0067**] Furthermore, the walls of the pocket **29** will collimate the vapor flux from the subliming material **35**. Since the clearance distance **37** is at the top of the pocket **29** and at a right angle to the collimated vapor flux, nearly all of the vapor flux will pass the entry of the clearance distance **37** without directly entering it. Any vapor which does enter the clearance distance **37** due to gas scattering will be readily deposited on the surface of the substrate **10**. The design of the clearance distance **37** allows for movement of multiple substrates **10** while maintaining a vapor seal. This design has advantages over the prior art since it will maintain the deposition uniformity across the substrate **10**. In the present invention, the use of the substrates **10** to act as a shutter virtually eliminates cross contamination between heated pockets **33**. The elimination of cross contamination allows the use of one vacuum boundary for the multiple processing steps and reduces the capital cost of the system. In most vacuum processes for processing PV devices, load locks or load locks in combination with intermediate chambers are used to prevent cross contamination between processing steps.

[**0068**] As shown in **FIG. 7**A, the deposition material **35** must be distributed in an evenly spaced pattern across the floor of the pocket **29**. The deposition material **35** may be in the form of powder, pellets pressed from powder, or random chunks. All of these forms of material for the fabrication of CdTe PV are commercially available. Also, the distance between the deposition material **35** and the lower surface of the substrate **10**, which is provided by the depth of the pocket **29** in the lower heated pocket **33**, must be sufficient to allow for gas scattering of the sublimed species.

[**0069**] Gas scattering is the result of collisions among the sublimed species or between the sublimed species and the molecules of the ambient background gas. These collisions deflect and scatter the sublimed species from following a straight line path from the deposition material **35** to the substrate **10**. This scattering of the sublimed species results in a uniform deposition on the substrate **10** The Knudsen number is a known dimensionless parameter which is used to quantify the amount of gas scattering present. The Knudsen number is the ratio of the mean free path in the pocket **29**, at a given temperature and pressure, divided by the distance between the deposition material **35** and the substrate **10**. If the Knudsen number is less than 0.01, then the species within the pocket **29** are in viscous flow and gas scattering will be significant In this viscous flow regime, the gas scattering may lead to such a loss of energy from the sublimed species that they condense to form nano-particles.

For Knudsen numbers greater than 1, the species will be in a molecular flow regime with very little gas scattering. In this molecular flow regime, the sublimed species will travel in straight lines to the substrate. This line of sight deposition causes non-uniform film thickness across the substrate **10**. For Knudsen numbers between 0.01 and 1, the species will be in transition flow with some gas scattering. In the transition regime, the vapor flux is randomized by gas scattering. However, the number of collisions are few enough that the sublimed species retain most of their energy and therefore do not condense into nano-particles before striking the substrate **10**. In the present invention, deposition has been done with Knudsen numbers in the transition regime from 0.07 to 0.44, which has led to uniform film thickness across the substrate **10**.

[**0070**] An additional advantage of the present invention is the heating of the process gas in the pocket **29**. Since the substrates **10** act as a shutter for the heated pocket **33**, the process gas in the source pocket **29** comes to a uniform high temperature. The high temperature of the process gas in the heated pocket **33** is another factor which prevents the formation of nano-particles due to the gas scattering collisions described above.

[**0071**] The preferred embodiment of the present invention provides a means of forming a back electrode layer at high throughput and using equipment that is low capital cost. This layer is adherent to the other layers in the film stack and has a very low electrical resistivity. As shown in **FIG. 1**, the back electrode is fabricated by a novel spray process at atmospheric pressure in process stations **52***a* and **52***b*. A layer of conductive graphite coating followed by a layer of conductive Ni coating are applied by known industrial spray methods to form the back electrode for carrying current. Sprays containing other metals besides Ni are known and may also be used. A metal conductive coating layer may also be applied by spray directly to the ohmic contact layer without an intervening carbon layer. In this description, carbon is not considered a metal. To limit the inclusion of oxygen and water vapor into the metallization layer, the gas used as a propellant in the spray process may be a dry inert gas such as N_2 or Ar, and the process may be performed in a controlled environment.

[**0072**] The thick film of the back electrode contains a polymer binder, which provides a level of encapsulation and protection for the completed device. The spray is performed at room temperatures and does not harm or introduce defects into the previously fabricated semiconductor layers. The spray method has the advantage of low capital cost. Other known methods of metallization for PV devices, such as sputtering, require expensive high vacuum equipment.

[**0073**] The preferred embodiment of the present invention also provides a means of scribing that exhibits high throughput and low cost. As shown in **FIG. 1, a** scribing step may be performed at the film scribing station **53***a* after the graphite layer is formed by the spray process at the process station **52***a*. The scribing is performed after the application of the graphite layer to prevent any damage to the semiconductor layers by handling.

[**0074**] **FIG. 9A** illustrates the details of the preferred embodiment of the film scribing method. A rotating wire brush **42** is brought into contact through openings **45** in a mask **41** to remove portions of the film **40** from the substrate **10**. The openings **45** in the mask **41** are tapered in cross section and are narrower near the contact of the mask **41** and the film layers **40**. This facilitates the entry of the rotating brush **42** into the openings **45**. The mask **41** may be coated with a hard coating, such as titanium nitride, to reduce wear.

[**0075**] The preferred embodiment of the film scribing method shown in **FIG. 9A** does not require a precisely defined rotating brush **42** since the openings **45** in the mask **41** define the area of the film **40** which will be removed. The rotating wire brush **42** is passed axially along the openings **45** in the mask **41** over the substrate **10** to perform a scribe. A plurality of rotating metal brushes **42** may also be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes on an entire substrate **10**. This film scribing method has the ability to scribe layers selectively. By using an abrasive powder with the rotating brush **42**, the TCO layer may be scribed. By using the rotating brush **42** alone, all of the layers except the TCO layer may be removed.

[**0076**] The process steps of the preferred embodiment of the present invention are shown in the flow chart of **FIG. 10A**. The overall system **1000** required to perform the process is shown in **FIG. 1**. The apparatus required to perform the vacuum portion of the process, from step **2**) of **FIG. 10A** through step **12**) of **FIG. 10A**, is illustrated in **FIG. 2A**. With reference to **FIG. 2A**, the substrates **10** are transported through the vacuum process stations **200** and **300** on the metal strip belts **1**. As shown in **FIG. 10A**, these process steps may be performed by a single one or a series of the vacuum process stations **200** or **300** illustrated in **FIG. 2A**. The total time required for processing at each process station **200** or **300** and the transport of the substrate **10** to the next process station **200** or **300** is a unit of cycle time as defined above. The cycle time in the process description below is in the range of 30 seconds to 2 minutes.

[**0077**] With reference to **FIG. 10A, a** description of the process steps performed on each individual substrate **10** as the plurality of substrates **10** pass through the process is given below.

[**0078**] In step (1) the substrate **10**, which may have a TCO layer on one surface, is ultrasonically cleaned, rinsed, dipped in isopropyl alcohol to remove water from the surface, and dried in a clean room type mini-environment.

[**0079**] In step (2) the substrate **10** is transported into the vacuum chamber **3** through the AVA opening **2** using the metal strip belts **1**.

[**0080**] In step (3) the substrate **10** is heated to a temperature in the range of 500° C. to 560° C. and transported to the next process.

[**0081**] In step (4) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdS film is deposited onto the TCO layer on the substrate **10** and the substrate **10** is transported to the next process.

[**0082**] In step (5) with the temperature of the substrate **10** in the range of 500° C. to 560° C., a CdTe film is deposited onto the CdS layer on the substrate **10** and the substrate **10** is transported to the next process.

[**0083**] In step (6) and step (7) a $CdCl_2$ treatment is performed on the CdS/CdTe layers. In step (6) with the temperature of the substrate **10** in the range of 300° C. to

500° C., the CdS/CdTe layers on the substrate **10** are exposed to $CdCl_2$ and the substrate **10** is transported to the next process. The $CdCl_2$ exposure of the CdS/CdTe layers on the substrate **10** may be to a $CdCl_2$ vapor or a $CdCl_2$ film may be deposited on the CdTe layer. Either method of $CdCl_2$ exposure will produce high efficiency CdTe PV devices. For this process step, a series of $CdCl_2$ treatment stations may be required.

[**0084**] In step (7) with the temperature of the substrate **10** in the range of 400° C. to 450° C., the $CdCl_2$ treated layers on the substrate **10** are annealed, any $CdCl_2$ film is removed, and the substrate **10** is transported to the next process. For this process step, a series of annealing stations may be required. In combination, step (6) and step (7) provide the $CdCl_2$ treatment of the CdS/CdTe layers. The $CdCl_2$ treatment of CdTe PV devices in vacuum is known. However, no prior art shows the $CdCl_2$ treatment step performed inline between the deposition of the CdTe layer and the formation of the ohmic contact layer and without the substrate leaving vacuum. Also, no prior art shows directly transporting substrates from CdTe deposition to $CdCl_2$ treatment.

[**0085**] In step (8) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

[**0086**] In step (9) and step (10) an ohmic low resistance contact is formed on the CdTe layer. In step (9) with the substrate **10** temperature in a range of 150° C. to 300° C., a metal salt is deposited onto the CdTe layer on the substrate **10**, and the substrate **10** is transported to the next process. One metal salt which has been used for this process step is CuCl. In step (10) with the temperature of the substrate **10** in a range of 150° C. to 250° C., the CdS/CdTe/metal salt layers on the substrate **10** are annealed, and the substrate **10** is transported to the next process. For this process step a series of annealing stations may be required. In combination, step (9) and step (10) produce a reaction between the metal salt and the surface of the CdTe layer and this reaction produces a thin p+ semiconductor layer on the CdTe surface to form the ohmic contact. In the case of a Cu salt, a copper telluride such as $CuTe_x$ or Cu doped CdTe:Cu or both may be formed. The thin p+ layer provides a low resistance ohmic contact on the surface of the CdTe layer and is stable. The prior art does not show the formation of an ohmic contact layer on CdTe by deposition of a metal salt onto the CdTe layer in vacuum.

[**0087**] In step (11) the substrate **10** and films are cooled to the required temperature in the range of 25° C. to 100° C. and the substrate **10** is transported to the next process. For this process step, a series of cooling stations may be required.

[**0088**] In step (12) the substrate **10** is transported out of the vacuum chamber **3** through the AVA opening **2** on the metal strip belts **1**.

[**0089**] In step (13) the ohmic contact layer is exposed to air for an optimum time in the range of 4 to 16 hours before a layer of conductive coating containing carbon is applied onto the ohmic contact layer by a spray process. The air exposure has led to PV devices with increased long term stability.

[**0090**] As described in the prior art, a series of scribes in selected film layers on the substrate **10** are required to isolate individual PV cells on the substrate and to interconnect the individual cells on the substrate **10** to form a completed module.

[**0091**] In step (14) a plurality of first scribes through the all of the film layers on the substrate **10** including the transparent conductive oxide are performed. A second plurality of scribes through the carbon and the p/n layers without removing the TCO are performed parallel to the first set of scribes. Both of these sets of scribes are performed by the novel film scribing method described above with reference to **FIG. 9A**.

[**0092**] In step (15) a layer of conductive coating containing Ni is applied by spray onto the layer of conductive coating containing carbon. Since the Ni metalization layer is formed after the second set of scribes, the Ni layer will fill the cuts in the semiconductor layers from the second scribe. This will cause an electrical connection of the back electrode of one cell to the front electrode of another cell. This step in combination with the following step of the final scribe of the metalization layer will complete the interconnection of the PV cells in series to form the PV module.

[**0093**] In step (16) a plurality of third scribes through only the metallization layers are performed. This third set of scribes is performed by the novel film scribing method described above with reference to **FIG. 9A**.

[**0094**] In step (17) electrical connections are made and the finished module is encapsulated.

[**0095**] In any of the film deposition steps, including the steps 4), 5), 6), or 9) of **FIG. 10A**, more than one layer of a particular material may be deposited. These multiple layers may be deposited by a series of heated pocket deposition apparatuses. If one layer of material is deposited in a given cycle time, to a given thickness, then this single layer may be replaced by many thinner layers built up to the thickness of the single layer of material by using many depositions at shorter cycle times. Multiple depositions are advantageous since for every decrease in cycle time there is a corresponding increase in production rate. Multiple processing stations can also be used to decrease the cycle time for the other steps including annealing, vapor treatment, cooling, etc.

[**0096**] It would also be possible to create a multifunction solar cell in accordance with the teachings of the present invention. In this case, a monolithic multifunction structure could be fabricated on the substrate. In this structure, two or more solar cells would be stacked on one substrate in such a way that solar radiation passes through the larger band gap material first, and residual radiation passes through the stack to a smaller band gap material. The band gap of the materials needed could be tailored by using semiconductors formed by the combination of any of the elements Zn, Cd, Hg, S, Se, or Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may be in the form of alloys containing three or more elements. The multiple layers may be deposited by a series of heated pocket deposition apparatuses. Also, by varying the composition of the deposition material in the multiple heated pockets, a graded band gap photovoltaic device may be fabricated.

[**0097**] Many devices were fabricated by following the process steps (1) through (13) and step (15) of **FIG. 10A** described above. CuCl was used as the metal salt in step (9). Individual PV devices with an area of 0.3 sq. cm. were formed on many substrates **10**. These devices were defined by masking certain areas and removing the rest of the films on the substrates **10** with an abrasive blast. The best device had a conversion efficiency of 11.8% and was produced on a commercially available low cost SnO_x:F coated soda lime glass substrate **10**. Such high efficiency devices have also proven to be stable. Accelerated stress testing by light soaking at 1000 W/m^2 and 65° C. at open circuit condition was performed on many devices. Over a time period of hundreds of hours, measured device efficiencies were at least 98% of the original efficiencies.

[**0098**] A description of the preferred embodiment of the present invention was given above. Other alternate embodiments of the present invention are described below. These specific alternate embodiments are best described with reference to **FIG. 10A**, which is a flow chart of the process steps of the preferred embodiment of the invention.

[**0099**] In alternate embodiments of step 9) in **FIG. 10A**, the deposition of the metal compound may include compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb. These compounds may be metal salts as described in the preferred embodiment or organometallic compounds of Cu, Ag, Au, Hg, Sn, Sb, and Pb may also be used. These compounds may be deposited onto CdTe in vacuum to form an ohmic low resistance contact layer by reaction with the CdTe layer. This ohmic low resistance contact may be formed by tellurides of Cu, Ag, Au, Hg, Sn, Sb, and Pb, or the ohmic contact may be highly doped CdTe. An alternative embodiment to step 10) of **FIG. 10A** is to anneal the ohmic contact layer in air, inert gas or other atmospheres outside the vacuum chamber.

[**0100**] In other embodiments of the process steps 4) and 5) of **FIG. 10A** other semiconductors may be used instead of CdS and CdTe. These semiconductors are formed by the combination of any of the elements Zn, Cd, Hg, S, Se or, Te. These elements are from group IIB and group VIB of the periodic table. These semiconductors may also be in the form of alloys containing three or more elements. These compound semiconductors are known to be useful in the formation of PV devices, are readily sublimable, and may be deposited in vacuum by the present invention. A series of stations may be used to deposit the n-type and p-type semiconductors. Thus, more than one layer may be used to form the n-type and p-type regions of the device This allows a faster cycle time while still maintaining adequate semiconductor film thickness. Also, the different stations may deposit different IIB-VIB compound semiconductors made up of the elements Zn, Cd, Hg, S, Se or, Te.

[**0101**] In alternate embodiments of step 6) of **FIG. 10A**, halogen containing substances such as HCl or Cl_2 gas may be used in place of or in addition to $CdCl_2$. In this case, a controlled amount of the gas can be introduced into the heated pocket **33**. Other halogen containing substances which are known to have effects similar to $CdCl_2$ may also be used. Some known examples of these compounds are $CdBr_2$ and CdI_2.

[**0102**] In another alternate embodiment of the process steps of **FIG. 10A, a** CdTe PV device may be fabricated without the deposition of CdS shown in step 4) of **FIG. 10A**. In this embodiment, the p/n junction is formed between the n-type TCO and the p-type CdTe or other IIB-VIB compounds.

[**0103**] In another embodiment of the process steps of **FIG. 10A, a** CdTe device may be fabricated by depositing the CdS layer on the substrate **10** outside of the vacuum chamber **3** by known methods, including chemical bath deposition. In this embodiment, the substrate **10** with the CdS layer would be brought into the vacuum chamber **3** and steps 3) through step 11) of **FIG. 10A** would be performed in vacuum.

[**0104**] In another embodiment of the process steps of **FIG. 10A, a** $CdCl_2$ treatment may be performed after step 4) CdS deposition and before step 5) CdTe deposition. This $CdCl_2$ treatment is in addition to the step 6) $CdCl_2$ treatment as shown in **FIG. 10A**. The additional $CdCl_2$ treatment is known to further increase the device performance.

[**0105**] In other alternative embodiments of **FIG. 10A**, the HPD deposition heated pocket **33** may be used to apply other film layers which would improve the performance of a CdS/CdTe PV device. One such layer is an anti-reflection (AR) coating which would be deposited on the glass substrate **10** on the opposite side of the substrate **10** from the TCO. The AR coating would face the sun and reduce the amount of incoming sunlight which is reflected off of the glass surface. This would increase the current that the device could produce. One such AR coating is a thin film of MgF_2. Since MgF_2 is sublimable, this film may be applied with the heated pocket **33** deposition. The AR coating can be done at a suitable location in the vacuum chamber **3**. Another layer which is known to increase the efficiency of a CdS/CdTe device is a layer of high resistivity intrinsic tin oxide (i-SnO_x). This layer would be applied between the TCO layer and the CdS layer or a layer of SnO_x of the desired resistivity could be deposited directly on the glass substrate **10**. This intrinsic layer has a much higher electrical resistivity than the TCO layer and has been shown to increase device efficiency. This resistive layer would allow the CdS layer to be thinner. The thinner CdS layer would allow more light to pass into the CdTe layer and increase the current the device would produce. The heated pocket **33** could be used to sublime i-SnO_x. The i-SnO_x deposition would be performed before the CdS deposition of step 4) of **FIG. 10A**.

[**0106**] An alternate embodiment to step 15) of **FIG. 10A** is that the graphite and Ni may be sprayed through a mask to form a patterned deposition. This patterned back electrode would eliminate the need for the second and third set of scribes shown in steps 14) and 16) of **FIG. 10A**. In another embodiment, a spray through a mask may also be used to fill the cut of the first scribe with an insulating compound before the spraying of the Ni conductive coating. The insulating compound eliminates electrical shunts between the Ni layer and the TCO.

[**0107**] Other alternate embodiments of the present invention are described below. The figures which show these alternative embodiments are **FIGS. 2B**, **7B**, **8**, **9B**, and **10B**. These alternative embodiments are described with reference to these figures.

[**0108**] **FIG. 2B** shows an alternate embodiment of the present invention in which the pair of continuous metal strip belts **1** are entirely contained within the vacuum chamber **3**. A pair of known load locks **5** on either side of the chamber **3** provide a means of transporting the substrates **10** into and out of vacuum.

[**0109**] **FIG. 7B** illustrates an alternate embodiment of the vacuum process station of **FIG. 7A** involving a different arrangement for the upper heated pocket **33**. This alternate embodiment involves the addition of a baffle having a plurality of holes **28**. The deposition material **35** is placed above the baffle in a confined space. The confined space has a lid **27**, which may be removed to reload the deposition material **35**. As the upper heated pocket **33** is heated, the deposition material **35** will sublime, and vapor will pass through the holes **28** into the source pocket **29** of the upper heated pocket **33**. This alternative embodiment of the vacuum process station **200** may be used as the heated pocket **33** to deposit films on the upper surface of the substrate **10**. When the deposition is on the upper surface of the substrates **10**, the substrates **10** can be transported by arrangements such as rollers, robotic arms, etc., which are well known. This would be especially useful for the deposition of the AR coating.

[0110] **FIG. 8** illustrates an alternative to the heated pocket **33**. This embodiment can be used to generate plasma in the pocket **29**. This arrangement is called plasma enhanced heated pocket deposition (PEHPD). The alternate embodiment of the heated pocket **33** provides a high voltage pin **30** for the generation of plasma, the pin **30** may be made from graphite. The pin **30** is electrically isolated by insulation **31** which may be a quartz tube. The high voltage from the DC power supply **32** generates the plasma. The heated pocket-to-substrate distance in the PEHPD heated pocket must be large enough to produce ions within the pocket **29**. If the pocket **29** is too shallow it will not produce a glow discharge at desirable pressures, when the substrate **10** is sealing the pocket **29** during deposition. In alternate embodiments of the present invention, both the CdS and CdTe heated pocket may optionally be of the PEHPD type so that the advantages of plasma enhanced deposition may be incorporated. These advantages of plasma enhanced deposition, which serve to improve the device efficiency, include: (i) doping of CdTe with nitrogen, (ii) passivation of the defects in CdTe, (iii) alteration of the morphology of CdS, (iv) doping of CdS, and (v) mixing of the CdS/CdTe interface. In addition, ZnTe may be doped with nitrogen by PEHPD to form ZnTe:N, a p+ semiconductor layer which may be used as an ohmic contact to CdTe.

[0111] **FIG. 10B** is a flow chart of the process steps of some of the alternate embodiments of the invention. The processing steps as shown schematically in that figure include (1) cleaning the substrate by known means in a clean room type mini-environment, (2) transporting the substrate into the vacuum chamber using AVA or load lock transport, (3) heating the substrate, (4) depositing a CdS film on the substrate using heated pockets with or without plasma, (5) depositing a CdTe film onto the CdS film using heated pockets with or without plasma, (6) performing a treatment, with a halogen containing substance, on the CdS/CdTe films using a heated pocket, (7) annealing the substrate and films, (8) forming an ohmic contact on the CdTe layer by heated pocket deposition of a Te layer on the CdTe layer or by heated pocket deposition with plasma of a ZnTe:N layer on the CdTe layer, (9) depositing a metallization layer onto the ohmic contact layer by heated pocket deposition of a sublimable metal layer such as Zn or Cd, (10) annealing the substrate and films, (11) cooling the substrate and films, (12) transporting the substrate and films from the vacuum chamber using AVA or load lock transport, (13) performing a first scribe through the entire film stack including the metallization and the transparent conductive oxide, (14) screen printing the electrical connection of the back electrode of one cell to the front electrode of the next cell by known screen printing methods, and (15) encapsulating the finished module. Step (13) involves a first scribe that may be performed in accordance with the teachings of the present invention or by one of several known means including mechanical or laser scribing and a second scribe through the carbon and the p/n layers without removing the TCO.

[0112] Step 8) in **FIG. 10B** illustrates another alternative embodiment of the present invention in which Te is used as an ohmic contact layer Te is easily sublimed and is known to form an ohmic contact material for CdTe devices. After the $CdCl_2$ treatment and annealing steps, Te could be deposited inline by heated pocket deposition with or without a cooling step. A metal back electrode can be applied to the Te ohmic contact by either a vacuum deposition step or by the spray process of the present invention.

[0113] Step 9) of **FIG. 10B** illustrates an alternate embodiment of the present invention in which the back electrode metallization may be accomplished inline in vacuum. In this embodiment, the back electrode metallization may be applied by a heated pocket deposition of metals including, but not limited to, Zn or Cd, which are readily sublimable and electrically conductive.

[0114] **FIG. 9B** illustrates an alternative embodiment of the scribing method of the present invention involving the use of an abrasive blast **43** which is provided by known methods. The abrasive blast **43** is performed through openings **45** in the mask **41** to remove portions of the film **40** from the substrate **10**. This embodiment of the scribing method does not require a precisely defined abrasive blast **43** since the mask **41** defines the area of the film **40** which will be removed. The abrasive blast **43** is passed over the substrate **10** to perform a scribe. Each abrasive blast **43** may enter more than one opening **45** in the mask **41** so that one abrasive blast **43** may perform more than one scribe for each pass over the substrate **10**. A plurality of abrasive blasts **43** may be provided so that one pass along the axis of the openings **45** in the mask **41** will complete the plurality of scribes of an entire substrate **10**. Different abrasive media with different hardness and size may be provided so that various layers in the film stack **40** may be scribed selectively. This allows the scribing method of the present invention to: 1) scribe all the way through the film stack including the relatively hard TCO layer, and 2) selectively scribe through all of the layers above the TCO layer without removing the TCO.

We claim:

1. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level, the method comprising the steps of:

providing, in the vacuum chamber, a substrate upon which the photovoltaic cell is to be fabricated;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of n-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto the one or more layers of n-type IIB/VIB semiconductor material in the vacuum chamber;

treating the one or more layers of n-type IIB/VIB and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber by depositing a metal compound onto the treated one or more layers of p-type IIB/VIB semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

2. A method as in claim 1, wherein the n-type semiconductor material comprises cadmium sulfide.

3. A method as in claim 1, wherein the p-type semiconductor material comprises cadmium telluride.

4. A method as in claim 1, wherein the halogen containing substance comprises cadmium chloride.

5. A method as in claim 1, further comprising the step of depositing in the vacuum chamber a layer of a transparent conductive oxide onto the substrate prior to the step of depositing the one or more layers of n-type IIB/VIB semiconductor onto the substrate.

6. A method as in claim 1, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

7. A method as in claim 1, further comprising the step of treating the one or more layers of n-type IIB/VIB semiconductor material with the halogen containing substance prior to depositing the one or more layers of p-type IIB/VIB semiconductor material.

8. A method as in claim 7, wherein the halogen containing substance comprises cadmium chloride.

9. A method as in claim 7, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material with the halogen containing substance comprises:

exposing the one, or more layers of n-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material previously exposed to the vapor of the halogen containing substance.

10. A method as in claim 9, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material is exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of n-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and removing the previously deposited film of the halogen containing substance.

11. A method as in claim 1, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material that have been exposed to the vapor of the halogen containing substance.

12. A method as in claim 11, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material and removing the previously deposited film of the halogen containing substance.

13. A method as in claim 1, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

14. A method as in claim 1, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

15. A method for forming an ohmic contact on one or more layers of p-type IIB/VIB semiconductor material, the method comprising the steps of:

depositing a metal compound onto the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber; and

annealing the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

16. A method as in claim 15, wherein the step of annealing the one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber comprises heating said one or more layers of p-type IIB/VIB semiconductor material in a suitable gas.

17. A method as in claim 15, wherein the one or more layers of p-type IIB/VIB semiconductor material comprises cadmium telluride.

18. A method as in claim 15, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

19. A method as in claim 15, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

20. A method for forming a conductive electrode on a desired surface of a semiconductor device, the method comprising the steps of:

spraying a conductive graphite coating onto the desired surface; and spraying a conductive metal coating onto the conductive graphite coating.

21. A method as in claim 20, wherein the conductive metal coating comprises nickel.

22. A method for forming a conductive electrode on a desired surface of a semiconductor device, the method comprising the steps of:

spraying a conductive metal coating onto the desired surface; and

drying the sprayed conductive metal coating.

23. A method for scribing one or more selected layers of a photovoltaic device, the method comprising the steps of:

positioning a contact mask over the one or more selected layers, the contact mask having openings defining areas of the one or more layers to be removed; and

impacting the one or more selected layers through the openings in the contact mask to remove the defined areas of one or more selected layers.

24. A method as in claim 23, wherein the step of impacting the one or more selected layers through the openings in the contact mask comprises abrasive blasting with a selected medium.

25. A method as in claim 23, wherein the step of impacting the one or more selected layers through the openings in the contact mask comprises applying a rotating abrasive device to the one or more selected layers through the openings in the contact mask.

26. Apparatus for transporting substrates within a vacuum chamber, the apparatus comprising:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert; and

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts.

27. Apparatus for transporting substrates within a vacuum chamber as in claim 26, wherein the vacuum chamber includes front and rear openings through which the pair of metal belts and the substrates pass, extending outside said front and rear openings, the apparatus further comprising:

a clearance distance between each of the substrates and the front and rear openings so as to permit motion of the substrates while at the same time restricting air leaks, to thereby maintain a desired level of vacuum in the chamber.

28. Apparatus for transporting and processing a plurality of substrates by exposing them to heating, film deposition or vapor treatment within a vacuum chamber, the apparatus comprising:

a plurality of heated pockets positioned in proximity to and in correspondence with each of the plurality of substrates such that a clearance distance between a surface of each of the substrates and the corresponding one of the heated pockets is minimized so as to permit motion of the substrates while restricting vapor leaks from the heated pockets; and

a transporter for moving the substrates from one heated pocket to the next.

29. Apparatus as in claim 28, wherein the transporter comprises:

a pair of spaced apart parallel metal belts positioned within the vacuum chamber;

a translator for bidirectionally moving the pair of metal belts in concert;

a plurality of aligned, periodically-spaced tabs positioned on an outer surface of each of the metal belts for retaining a plurality of the substrates in fixed positions spanning the metal belts; and

a controller, coupled to said translator for indexing the belts incrementally to move each of the substrates from one heated pocket to another.

30. Apparatus as in claim 28, wherein a selected one or more of the heated pockets includes a high voltage pin coupled to a source of D.C. voltage for creating a plasma within the selected one or more of the heated pockets.

31. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level the method comprising the steps of:

providing, in the vacuum chamber, a substrate having one or more layers of an n-type transparent conductive oxide upon which the photovoltaic cell is to be fabricated;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

32. A method as in claim 31, wherein the p-type IIB/VIB semiconductor material comprises cadmium telluride.

33. A method as in claim 31, wherein the halogen containing substance comprises cadmium chloride.

34. A method as in claim 31, wherein the step of treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material that have been previously exposed to the vapor of the halogen containing substance.

35. A method as in claim 34, wherein:

the temperature at which the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type transparent conductive oxide and p-type IIB/VIB semidconductor material and removing the film of the previously deposited halogen containing substance.

36. A method as in claim 31, wherein the step of forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material comprises depositing a metal compound onto the treated one or more layers of p-type semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

37. A method as in **36**, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony and mercury.

38. A method as in claim 36, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

39. A method as in claim 31, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

40. A method for fabricating semiconductor layers of a photovoltaic cell, all of the steps of which are carried out in a single vacuum chamber at a constant vacuum level, the method comprising the steps of:

providing, in the vacuum chamber, a substrate upon which the photovoltaic cell is to be fabricated, the substrate having one or more layers of n-type transparent conductive oxide thereon and one or more layers of n-type IIB/VIB semiconductor material on top of the one or more layers of n-type transparent conductive oxide;

heating the substrate to a desired temperature in the vacuum chamber;

depositing one or more layers of p-type IIB/VIB semiconductor material onto a surface of the substrate in the vacuum chamber;

treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance in the vacuum chamber; and

forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material in the vacuum chamber.

41. A method as in claim 40, wherein the n-type IIB/VIB semiconductor material comprises cadmium sulfide.

42. A method as in claim 40, wherein the p-type IIB/VIB semiconductor material comprises cadmium telluride.

43. A method as in claim 40, wherein the halogen containing substance comprises cadmium chloride.

44. A method as in claim 40, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material that have been previously exposed to the vapor of the halogen containing substance.

45. A method as in claim 44, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material are exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance upon the one or more layers of p-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and p-type IIB/VIB semiconductor material and removing the film of the previously deposited halogen containing substance.

46. A method as in claim 40, wherein the step of forming an ohmic contact on the treated one or more layers of p-type IIB/VIB semiconductor material comprises depositing a metal compound onto the treated one or more layers of p-type IIB/VIB semiconductor material and then annealing the treated one or more layers of p-type IIB/VIB semiconductor material.

47. A method as in claim 46, wherein the metal compound is a metal salt selected from the group comprising the salts of copper, silver, gold, tin, lead, antimony, and mercury.

48. A method as in claim 46, wherein the metal compound is an organometallic compound selected from the group comprising the organometallic compounds of copper, silver, gold, tin, lead, antimony, and mercury.

49. A method as in claim 40, further comprising the step of depositing an antireflective layer on an opposite surface of the substrate in the vacuum chamber.

50. A method as in claim 40, further comprising the step of treating the one or more layers of n-type IIB/VIB semiconductor material with a halogen containing substance prior to depositing the one or more layers of p-type IIB/VIB semiconductor material.

51. A method as in claim 50, wherein the halogen containing substance comprises cadmium chloride.

52. A method as in claim 50, wherein the step of treating the one or more layers of n-type IIB/VIB semiconductor material with a halogen containing substance comprises:

exposing the one or more layers of n-type IIB/VIB semiconductor material to the vapor of the halogen containing substance for a predetermined time at a specific temperature; and

annealing the one or more layers of n-type IIB/VIB semiconductor material that has been previously exposed to the vapor of the halogen containing substance.

53. A method as in claim 50, wherein:

the temperature at which the one or more layers of n-type IIB/VIB semiconductor material is exposed to the vapor of the halogen containing substance is suitable for depositing a film of the halogen containing substance onto the one or more layers of n-type IIB/VIB semiconductor material; and

the step of annealing the one or more layers of n-type IIB/VIB semiconductor material is performed at a temperature suitable for treating the one or more layers of n-type IIB/VIB semiconductor material and removing the film of the previously deposited halogen containing substance.

* * * * *

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(54) **PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS**

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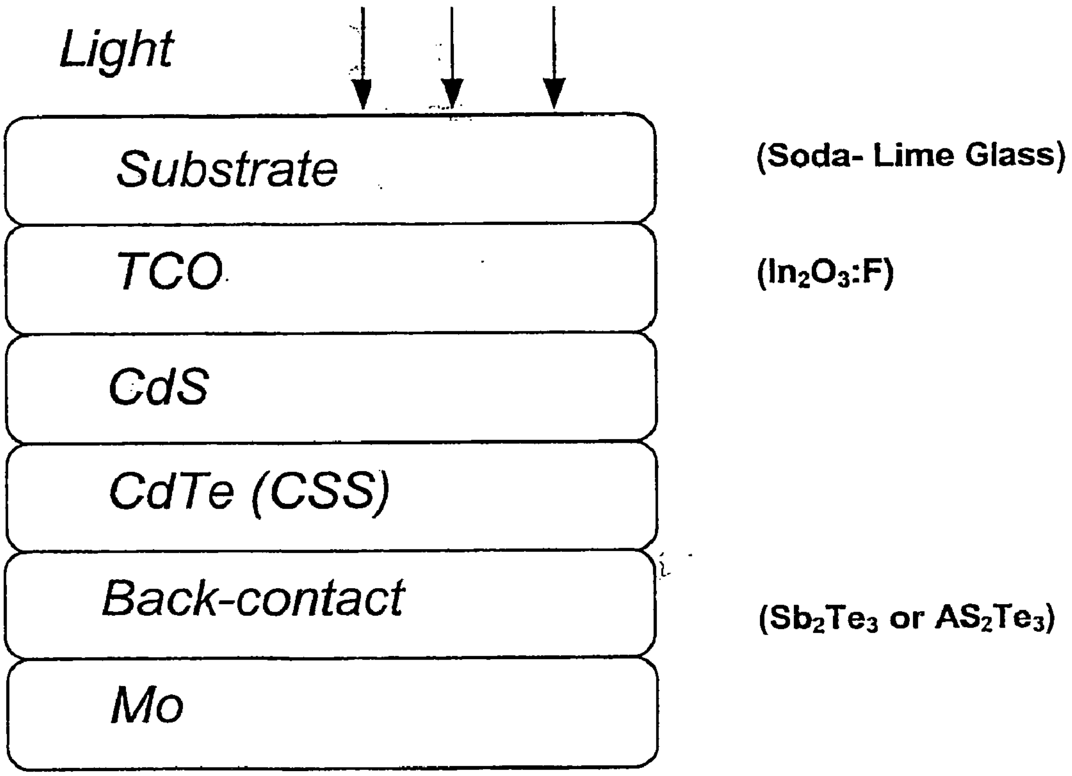
(57) **ABSTRACT**

A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequences on a transparent substrate, the sequence comprising the steps of: depositing a film of a transparent conductive oxide (TCO) on the substrate; depositing a film of CdS on the TCO film; depositing a film of CdTe on the CdS film; treating the CdTe film with $CdCl_2$; depositing a back-contact film on the treated CdTe film. Treatment of the CdTe film with $CdCl_2$ comprises the steps of: forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature; annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.



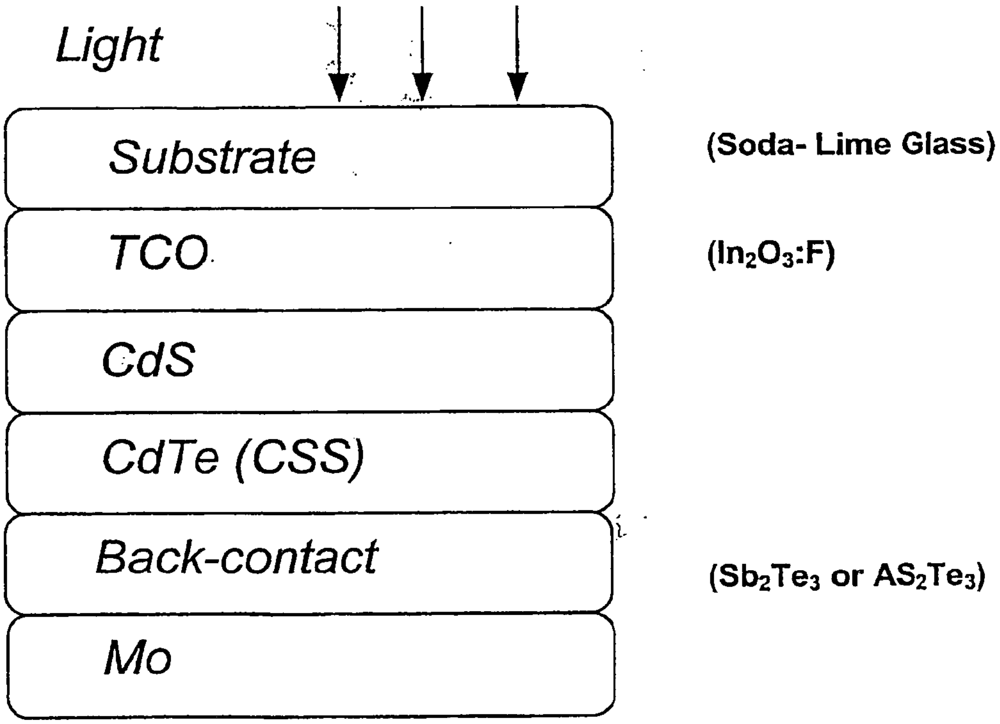

Light
Substrate
(Soda- Lime Glass)
TCO
(In_2O_3:F)
CdS
CdTe (CSS)
Back-contact
(Sb_2Te_3 or AS_2Te_3)
Mo

Fig. 1

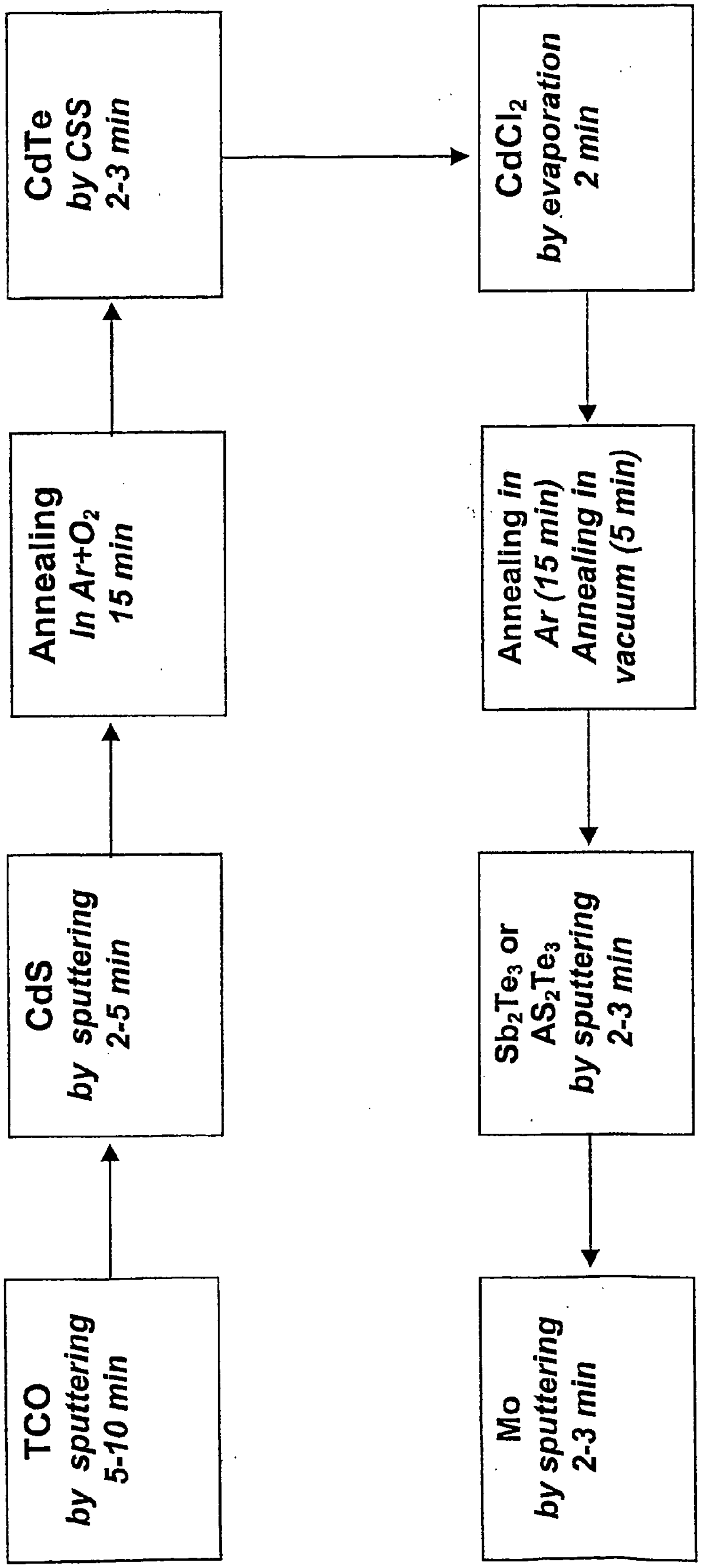

TCO
by sputtering
5-10 min
CdS
by sputtering
2-5 min
Annealing
In Ar+O$_2$
15 min
CdTe
by CSS
2-3 min
CdCl$_2$
by evaporation
2 min
Annealing in Ar (15 min) Annealing in vacuum (5 min)
Sb$_2$Te$_3$ or AS$_2$Te$_3$
by sputtering
2-3 min
Mo
by sputtering
2-3 min

Fig. 2

PROCESS FOR LARGE-SCALE PRODUCTION OF CDTE/CDS THIN FILM SOLAR CELLS

FIELD OF THE INVENTION

[0001] The present invention relates to the field of the solar cells technology and more particularly concerns a process for the large-scale production of CdTe/CdS thin film solar cells.

BACKGROUND ART OF THE INVENTION

[0002] As is known, a typical configuration of a CdTe/CdS solar cell has a film sequence of the multi-layer arrangement comprising a transparent glass substrate carrying a transparent conductive oxide (TCO) film, a CdS film representing the n-conductor, a CdTe film representing the p-conductor and a metallic back-contact. A solar cell with a layer arrangement and structure of this type is disclosed, for example, in U.S. Pat. No. 5,304,499.

[0003] The commercial float glass may be used as a transparent substrate, but, in spite of its low cost, special glasses are often preferred to avoid drawbacks of the float glass, in particular Na diffusion into TCO film.

[0004] The most common TCO is In_2O_3 containing 10% of Sn (ITO). This material has a very low resistivity on the order of 3×10^{-4} Ωcm and high transparency (>85%) in the visible spectrum. However, this material is made by sputtering and the ITO target after several runs forms some noodles which contain an In excess and a discharge between noodles can happen during sputtering which can damage the film. Another material which is commonly used is fluorine doped SnO_2 which however exhibits a higher resistivity close to 10^{-3} Ωcm and as a consequence a 1 μm thick layer is needed in order for the sheet resistance to be around 10 $\Omega/_{\text{square}}$. A high TCO thickness decreases the transparency and then the photocurrent of the solar cell. Finally a novel materia+03−1, namely Cd_2SnO_4 has been developed by the NREL group (X. Wu et al., *Thin Solid Films,* 286 (1996) 274-276)). Also this material has some drawbacks since the target is made up of a mixture of CdO and SnO_2 and, being CdO highly hygroscopic, the stability of the target may result to be unsatisfactory.

[0005] The CdS film is deposited by sputtering or Close-Spaced Sublimation (CSS) from CdS granulate material. This last technique allows the preparation of thin films at a substrate temperature much higher than that used in simple vacuum evaporation or sputtering, because substrate and evaporation source are put very close to each other at a distance of 2-6 mm and the deposition is done in the presence of an inert gas such as Ar, He or N_2 at a pressure of 10^{-1}-100 mbar. A higher substrate temperature allows the growth of a better crystalline quality material. An important characteristic of the close-spaced sublimation is a very high growth rate up to 10 μm/min, which is suitable for large-scale production.

[0006] CdTe film is deposited on top of CdS film by close-spaced sublimation (CSS) at a substrate temperature of 480-520° C. CdTe granulate is generally used as a source of CdTe which is vaporised from an open crucible.

[0007] An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe film with $CdCl_2$. Most research groups use to carry out this step by depositing on top of CdTe a layer of $CdCl_2$ by simple evaporation or by dipping CdTe in a methanol solution containing $CdCl_2$ and then anneal the material in air at 400° C. for 15-20 min. It is generally believed that the $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of small grains and by removing several defects in the material.

[0008] After $CdCl_2$ treatment, CdTe is etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. Etching is necessary as CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ have to be removed in order to make a good back contact onto CdTe. Besides it is believed that, since etching produces a Te-rich surface, the formation of an ohmic contact when a metal is deposited on top of CdTe is facilitated.

[0009] The electric back contact on the CdTe film is generally obtained by deposition of a film of a highly p-dopant metal for CdTe such as copper, e.g. in graphite contacts, which, upon annealing, can diffuse in the CdTe film. The use of a Sb_2Te_3 film as a back-contact in a CdTe/CdS solar cell has been disclosed by the same applicants (N. Romeo et al., *Solar Energy Materials & Solar Cells,* 58 (1999), 209-218)

[0010] Industrial interest towards thin films solar cells is increased in recent years also in view of the high conversion efficiency reached so far. A record 16,5% conversion efficiency has been recently reported (see X.Wu et al., 17th *European Photovoltaic Solar Energy Conversion Conference*, Munich, Germany, 22-26 Oct. 2001, II, 995-1000). Therefore several efforts have been made to provide processes suitable for large-scale, in-line production of CdTe/CdS thin film solar cells.

[0011] A state-of-the-art report concerning this issue may be found in D. Bonnet, *Thin Solid Films* 361-362 (2000), 547-552. However, a number of problems still hinder the achievement of this result, in particular concerning some crucial steps which affect either stability and efficiency of CdTe/CdS thin film solar cells or their costs.

[0012] A major problem of the known processes is the etching step to which the CdTe surface must be submitted to remove CdO or $CdTeO_3$ oxides formed thereon. Since etching requires the immersion of substrates carrying the treated CdTe/CdS films into acid solutions, rinsing and drying, machinery suitable for a continuous operation presently does not exist. Another significant problem which negatively affects the stability of the TCO films, as well as the cost of the final product are the drawbacks presently encountered with the use of known TCOs, as previously mentioned. In addition to these drawbacks, known TCOs require the use of special glasses, such as borosilicate glass, to avoid the problem of Na diffusion, occurring if a soda-lime glass is used, which would damage the film.

[0013] A further problem concerns the source from which the CdS film and the CdTe film are produced by close-spaced sublimation. When small pieces of these materials containing dust are used as a sublimation source, due to a different thermal contact, some micro-particles can be overheated and then split on to the substrate together with the vapour. In order to avoid this inconvenience, complicated metallic masks are used in some cases, which make a continuous operation problematic.

OBJECT AND SUMMARY OF THE INVENTION

[0014] It is the main object of the present invention to provide a process suitable for a large-scale production of stable and efficient CdTe/CdS thin film solar cells on a low cost substrate.

[0015] A particular object of the present invention is to provide a process of the above mentioned type in which the treatment of the CdTe film with $CdCl_2$ is conducted in such a way as not to require an etching treatment to remove the oxides possibly formed on the CdTe film.

[0016] A further object of the present invention is to provide a process of the above mentioned type, in which the deposition of the TCO film is conducted in such a way that a film of very low resistivity can be deposited without formation of any metal noodles on the target and allowing the use of a inexpensive substrate.

[0017] Still another object of the invention is to provide a process of the above-mentioned type, which allows the formation of CdS and CdTe films completely free of dusts.

[0018] A further object of the present invention is to provide a stable, efficient and relatively low-cost CdTe/CdS thin film solar cell.

[0019] The above object are achieved with the process for the large scale production of CdTe/CdS thin film solar cells, the main features of which are set forth in claim **1**.

[0020] According to an important aspect of the invention, the treatment of the CdTe film with $CdCl_2$ is carried out by first forming a 100-200 nm thick layer of $CdCl_2$ on the CdTe film by evaporation, while keeping the substrate at room temperature; then annealing the $CdCl_2$ layer in a vacuum chamber at 380-420° C. and 300-1000 mbar under inert gas atmosphere; and finally removing the inert gas from said chamber to produce vacuum condition, while the substrate is kept to a temperature of 350-420° C., whereby any residual $CdCl_2$ is evaporated from the CdTe film surface. In this way, there is no need for the etching treatment of the CdTe film and the process can be conducted in a continuous way.

[0021] According to another aspect of the invention, the TCO layer is formed by sputtering in an inert gas atmosphere containing 1-3 vol. % hydrogen and a gaseous fluoroalkyle compound, in particular CHF_3. In this way the TCO is doped whit fluorine

[0022] According to another important aspect of the invention, as a source material for the formation of the CdS and the CdTe films by sputtering or close-spaced sublimation, a Cds or, respectively, CdTe material in the form of a compact block is used.

[0023] Further features of the process according to the invention are set forth in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Further features and advantages of the process for large-scale production of CdTe/CdS thin film solar cells according to the present invention will be apparent from the following description of a preferred embodiment made with reference to the attached drawings, wherein:

[0025] **FIG. 1** is a schematic representation of the film sequence of the CdTe/CdS thin film solar cells according to the invention;

[0026] **FIG. 2** is a schematic diagram of the process according to the invention.

DESCRIPTION OF AN EMBODIMENT OF THE INVENTION

[0027] With reference to the figures+, the CdTe/CdS solar cells produced with the process according to the invention comprise five layers deposited in a sequence on a transparent base layer or substrate and consisting of a 300-500 nm thick layer of a transparent conducting oxide (TCO), a 80-200 nm thick layer of CdS deposited on top of the TCO layer, a 4-12 μm thick layer of CdTe on top of the CdS layer and a back contact layer formed by at least 100 nm thick layer of SB_2Te_3 and 100 nm thick layer of Mo. In particular, the transparent base substrate consists of soda-lime glass and the transparent conducting oxide is fluorine-doped (In_2O_3:F).

[0028] TCO layer consists of In_2O_3, which is doped with fluorine during the growth. The In_2O_3 target, differently from ITO, does not form any noodle. A very low resistivity is obtained by introducing in the sputtering chamber a small amount of fluorine in the form of a gaseous fluoroalkyle compound such as CHF_3 and a small amount of H_2 in the form of a mixture with an inert gas such as a Ar+H_2 mixture, in which H_2 is 20% in respect to Ar. A typical example is a 500 nm film of In_2O_3 deposited with a deposition rate higher than 10 Å/sec at a substrate temperature of 500° C., with an Ar flow-rate of 200 sccm, a CHF_3 flow-rate of 5 sccm and an Ar+H_2 flow-rate of 20 sccm. In this way, the reactive sputtering gas is composed by Ar containing 2.5 vol. % of CHF_3 and 1.8 vol. % of H_2. This film exhibits a sheet resistance of 5 $\Omega/_{square}$, a resistivity of 2.5×10^{-4} Ωcm and a transparency higher than 85% in the wavelength range of 400-800 nm. Another characteristic of this film is its good stability and the ability to stop Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable even if heated up to 180° C. when illuminated by "ten suns" for several hours.

[0029] After deposition of the CdS film and CdTe film in the known way by sputtering or close-spaced sublimation, the CdTe film surface is treated with $CdCl_2$ in the following way.

[0030] 200 nm of $CdCl_2$ are deposited by evaporation on top of CdTe film with the substrate kept at room temperature. An annealing of 15-20 min is done at 400° C. in a vacuum chamber in which 500 mbar of Ar are introduced. After the annealing the chamber is evacuated keeping the substrate at 400° C. for 5 min. and, since $CdCl_2$ has a high vapour pressure at 400° C., any residual $CdCl_2$ re-evaporates from the CdTe surface.

[0031] CdO or $CdTeO_3$ are not formed since the annealing is conducted in an inert atmosphere, which does not contain O_2.

[0032] According to the present invention a Te-rich surface is not needed to obtain a non-rectifying contact if the contact is made by depositing on top of CdTe film a thin layer of a highly conducting p-type semiconductors such as Sb_2Te_3 or As_2Te_3. A good not rectifying contact is obtained on a clean CdTe surface if at least 100 nm thick layer of Sb_2Te_3 or As_2Te_3 is deposited by sputtering at a substrate temperature respectively of 250-300° C. and 200-250° C.

Sb_2Te_3 grows naturally p-type with a resistivity of 10^{-4} Ωcm, while As_2Te_3 grows p-type with a resistivity of 10^{-3} Ωcm. The contact procedure is completed by covering the low resistivity p-type semiconductor with at least 100 nm of Mo, as common practice in the art. A thin layer of Mo is needed in order to have a low sheet-resistance on the back-contact.

[**0033**] As a source for the CdS and CdTe materials used to form the respective layers by sputtering or CSS a granulate material can be used, as common practice in this field. However, in view of the drawbacks mentioned above when operating in this way, according to a particularly preferred aspect of the invention a new sublimation source can be used which consists of a compact block obtained by melting and solidifying the material in an oven able to sustain a temperature higher than the melting temperature of the material. The procedure to prepare the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume together with boron oxide (B_2O_3), which is a low melting point material (450° C.) and exhibits a very low vapour pressure when melted. Since boron oxide has a density lower than that of CdS in the molten state, it floats over CdS and covers CdS completely upon cooling. In this way, CdS covered by B_2O_3, if it is put into an oven containing an inert gas at pressure higher than 50 atm, does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of 1750° C., the oven is heated up to a temperature of 1800° C. or more and then cooled down to room temperature. In this way, a unique compact block of CdS is obtained which results to be particularly suitable for use as a sublimation source in a close-spaced sublimation system. CdS films prepared with this type of source resulted to be very smooth and completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically 100 nm thick. The substrate temperature is kept at 200-300° C. when CdS is prepared by sputtering and at 480-520° C. when it is prepared by close-spaced-sublimation. The sputtered CdS layer needs an annealing at 500° C. in an atmosphere containing O_2 in order for the CdS/CdTe solar cell to exhibit a high efficiency. In the case CdS is prepared by close-spaced sublimation, O_2 is introduced in the sublimation chamber during the deposition. The role of O_2 is not known, but it is presumed to passivate the CdS grain boundaries.

[**0034**] In a preferred embodiment of the invention, the CdTe source too is a compact block obtained by melting and solidifying pieces of CdTe in an oven under high pressure as described previously. Since CdTe melts at 1120° C., the oven needs to be heated up to 1200° C. in order to have a complete melting of the CdTe pieces. CdTe films are deposited on top of CdS by close-spaced sublimation at a substrate temperature of 480-520° C. Deposition rates during the CdTe growth are typically 4 μm/min. In this way 8 μm of CdTe are deposited in 2 min.

[**0035**] By following the procedure described above several solar cells have been prepared by using as a substrate a 1 inch square low-cost soda-lime glass.

[**0036**] A typical area of these cells is 1 cm^2. The finished cells are generally put under 10-20 suns for several hours at a temperature of 180° C. in the open-circuit-voltage (V_{oc}) conditions. No degradation has been notified but rather a 20% or more increase in the efficiency has been found.

[**0037**] The efficiency of these cells are in the range 12%-14% with open-circuit-voltages (V_{oc}) larger than 800 mV, short-circuit-currents (J_{sc}) of 22-25 mA/cm^2 and fill-factors (ff) ranging from 0.6 to 0.66.

EXAMPLE

[**0038**] A cell exhibiting a 14% efficiency has been prepared in the following way: a soda-lime glass has been covered by 500 nm of In_2O_3:F (fluorine-doped) deposited at 500° C. substrate temperature as described above. 100 nm of CdS have been deposited by sputtering at 300° C. substrate temperature and annealed for 15 min at 500° C. in 500 mbar of Ar containing 20% of O_2. 8 μm of CdTe have been deposited on top of CdS by CSS at a substrate temperature of 500° C. Both CdS and CdTe films are produced from a compact block source as described above. A treatment with 150 nm of $CdCl_2$ has been done in an Ar atmosphere as described above. Finally a back contact has been created, without any etching, by depositing in sequence by sputtering 150 nm of Sb_2Te_3 and 150 nm of Mo.

[**0039**] After one hour under 10 suns at a temperature of 180° C. in open-circuit conditions the solar cell prepared in this way exhibited the following parameters:

V_{oc}	852 mv
J_{sc}	25 mA/cm^2
ff	0.66
efficiency	14%

[**0040**] The techniques used in this process such as sputtering and close-spaced sublimation are both fast, reproducible and easily scalable.

[**0041**] Sputtering systems capable to cover 1×0.5 m^2 area glass are already commercial, while close-spaced sublimation, which at a laboratory scale can cover easily 20×20 cm^2 area glass, does not give any problem in being scaled up to 1×0.5 m^2. An in-line process can work well if a large area glass is made to move slowly over the different sources namely TCO, CdS, CdTe, Sb_2Te_3 or As_2Te_3 and Mo. In order to make a series connection between the single cells the in-line system should also contain three laser scribing processes, the first after the TCO deposition, the second one before the back-contact deposition and the third one at the end of the process. An important part of the process according to the present invention is that no use is made of acids or liquids and, as a consequence, the process can operate on a continuous basis without the interruption which is needed to make the etching in acid or in a Br-methanol solution.

1. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the treatment of the CdTe film with $CdCl_2$ comprises the steps of

forming a layer of $CdCl_2$ on the CdTe film by evaporation, while maintaining the substrate at room temperature;

annealing the $CdCl_2$ layer in a vacuum chamber at a temperature generally within a range of 380° C. and 420° C. and a pressure generally within a range of 300 mbar and 1000 mbar in an inert gas atmosphere; and

removing the inert gas from the chamber so as to produce a vacuum condition, while the substrate is kept at a temperature generally within a range of 350° C. and 420° C. whereby any residual $CdCl_2$ is evaporated from the CdTe film surface.

2. The process set forth in claim 1, wherein the $CdCl_2$ layer is between about 100 nm and about 200 nm thick.

3. The process set forth in claim 1, wherein annealing of the $CdCl_2$ layer is carried out for about 15-20 minutes.

4. The process set forth in claim 1, wherein the inert gas is Ar.

5. The process set forth in claim 1, wherein the back-contact film is formed of a Sb_2Te_3 layer covered by a layer of Mo.

6. The process set forth in claim 5, wherein the Sb_2Te_3 layer is formed by sputtering at a temperature between about 250° C. and about 300° C.

7. The process set forth in claim 1, wherein the back-contact film is formed of a As_2Te_3 layer covered with a layer of Mo.

8. The process set forth in claim 7, wherein the As_2Te_3 layer is formed by sputtering at a temperature between about 200° C. and about 250° C.

9. The process set forth in claim 1, wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

10. The process set forth in claim 9, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

11. The process set forth in claim 10, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen bv volume, and wherein the fluoroalkyle compound is CHF_3.

12. The process set forth in claim 1, wherein, as a source material for formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

13. The process set forth in claim 12, wherein the compact block CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than 50 atm, and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

14. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein the transparent conductive oxide is In_2O_3 doped with fluorine.

15. The process set forth in claim 14, wherein the TCO layer is formed by sputtering in an inert gas atmosphere comprising a mixture of hydrogen and a gaseous fluoroalkyle compound.

16. The process set forth in claim 15, wherein a mixture of Ar and hydrogen is used which comprises between about 1% and about 3% hydrogen by volume and wherein the fluoroalkyle compound is CHF_3.

17. A process for large-scale production of CdTe/CdS thin film solar cells, films of the cells being deposited, in sequence, on a transparent substrate, the sequence comprising the steps of:

depositing a film of a transparent conductive oxide (TCO) on the substrate;

depositing a film of CdS on the TCO film;

depositing a film of CdTe on the CdS film;

treating the CdTe film with $CdCl_2$; and

depositing a back-contact film on the treated CdTe film;

wherein as a source material for the formation of the CdS and the CdTe films by close-spaced sublimation, a CdS or, respectively, CdTe material generally in the form of a compact block is used.

18. The process set forth in claim 17, wherein the compact block of CdS (or CdTe) material is formed by covering pieces of CdS (or CdTe) material with boron oxide, heating the covered material to a temperature generally greater than its melting point in an inert gas atmosphere and at a pressure generally greater than about 50 atm. and then cooling the material to room temperature, whereby the material is solidified in a generally compact block-like form.

19. The process set forth in claim 1, wherein the transparent substrate is soda-lime glass.

20. A CdTe/CdS thin film solar cell product of the process set forth in claim 14.

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