The Roles of Cu Impurity States in CdTe Thin Film Solar Cells

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Despite potential detrimental effects of Cu impurity inclusion in CdTe thin film solar cells, such as degradation caused by Cu diffusion into CdS, or reduced shunt resistance, most devices include Cu as p-dopant in CdTe and/or part of the back contact material [1 - 3]. I-V characterization and time resolved photoluminescence (TRPL) data reveal that depending on the ZnTe:Cu/Ti back contact deposition condition, Cu may cause dramatic changes in the electrical properties of the CdTe thin film. Very low levels of Cu can reduce the already low conductivity of the CdTe thin film, while increasing the Cu concentration can increase both conductivity and minority carrier lifetime. Specifically, a contacting temperature to 250°C - 300°C can produce high efficiency devices that demonstrate long minority carrier lifetimes. Increase the contacting temperature beyond ~300°C can yield a CdTe thin film that becomes insulating, or even to n-type. Such a complicated and puzzling effect on the property and quality of the CdTe thin film — turning from a poor p-type, to a poorer p-type, to a better p-type, to insulating, and then to n-type — is all due to different levels of Cu involvement in the CdTe thin film. In this paper, we try to review such dramatic changes of the CdTe behavior through exploring the roles of Cd vacancy (a double and non-shallow acceptor) and Cu impurity (a substitutional non-shallow acceptor), as well as Cu interstitial (a shallow donor). We study the interaction between the Cd vacancy states and the Cu impurity states, as well as the self compensation of the Cu impurity states. Based on the study, we offer a qualitative explanation of the various CdTe behaviors due to different levels of Cu treatment temperature.
I. Introduction

CdTe based solar panels have emerged in recent years as commercially successful, second generation thin film photovoltaic (PV) products, at a production cost of $0.84/W (First Solar) [1]. Despite intensive research, the ratio of CdS/CdTe lab cell conversion efficiency (16.5%) [2] vs. its theoretical limit ~29% [3, 4] has been low, in comparison with other thin film PV technologies, such as Cu(In,Ga)Se₂ (CIGS), which has a lower theoretical limit ~26% but a higher lab demonstrated efficiency of 19.9% [5]. One of the reasons for this seemingly discrepancy is the low doping level or hole concentration of p-CdTe. It is in the range of $10^{14}$ cm⁻³ [6], instead of the desired level of $10^{16} \sim 10^{17}$ cm⁻³ [7], resulting in lower junction band bending and difficulty in making ohmic contact. Both effects contribute to a lower open circuit voltage $V_{OC}$, and therefore lower efficiency.

Generally speaking, there are three main factors that can limit the desired doping level: (i) low solubility of the dopant, (ii) non-shallow transition energy level of the dopant (also called ionization or activation energy), (iii) self compensation of the dopants [8]. Although it is debated which localized impurity/defect state (or states) is responsible for the p-doping of the CdTe polycrystalline thin film used in n-CdS/p-CdTe solar cells, it is noticed that all the CdTe solar cells of good performance involves Cu impurities. The CdTe thin film uses low cost 5N tellurium, which, either as a byproduct of copper refinery or a raw material from independent tellurium mine, may have up to $2 \times 10^{-6}$ (2 ppm) Cu impurity content [9]. In addition, as part of the back contact material, Cu diffuses into the CdTe thin film [10, 11]. In this paper we assume that the dominant p-type dopant of CdTe is Cd vacancy $V_{Cd}$ and Cu substitution on Cd site $Cu_{Cd}$. Unlike in CIGS, where $V_{Cu}$ can form easily and has a shallow acceptor level, both $V_{Cd}$ and $Cu_{Cd}$ have relatively deep acceptor levels, especially for CuCd. Therefore, it seems reasonable to attribute the undesired low p-doping level of CdTe to be due to these differences.

II. Quality Factor of CdTe Thin Film
The desired CdTe layer in a thin film solar cell needs to have a hole density higher than \(10^{16}\) cm\(^{-3}\) for more available band bending and better ohmic contact, as well as a minority carrier (electron) life time longer than 1 ns for less dark current. For conceptual guidance, in the R&D of CdTe thin film, we may introduce a quality factor of the CdTe thin film

\[
Q = \sigma \tau \tag{1}
\]

where \(\sigma\) is the conductivity of the thin film, which is proportional to the hole density and easy to monitor by electrical measurement, and \(\tau\) is the minority carrier life time measurable with time resolved photoluminescence (TRPL).

### III. Experimental: CdTe Thin Film Quality Varies with Cu Treatment Temperature

After the CdTe polycrystalline thin film is deposited using a method such as close space sublimation (CSS), and a CdCl\(_2\) process is performed, the film is coated with ZnTe:Cu (~9 atomic percentage of Cu), sputtered, thermally evaporated, or pasted, followed by annealing to a certain temperature for back contact. It is interesting to note that Cu may cause dramatic changes of the character of the CdTe thin film. Very low level of Cu inclusion may further reduce the undesired low conductivity (due to low p-doping level) of the CdTe thin film. Increasing the level of Cu involvement to a certain level, a reversal from deterioration to improvement of conductivity occurs. Raising the treatment temperature to about 280–300 °C will lead to an optimized CdTe thin film, indicated by its long minority carrier lifetime (>1 ns) and confirmed by the high efficiency of the solar cell. Increase the temperature further, and the CdTe thin film will turn from p-type to insulating, or even n-type. Such a complicated and puzzling effect on the property and quality of the CdTe thin film — turning from a poor p-type \((A)\) to a poorer p-type \((B)\), to a better and optimized p-type \((C)\), to insulating \((D)\), and to n-type \((E)\), all due to different Cu treatment temperature — can be qualitatively explained by a
sketch of the thin film quality factor $Q$ as a function of Cu treatment temperature $T$ (Fig. 1).

![Graph showing sketch of the thin film quality factor as a function of Cu treatment temperature]

**Fig. 1** Quality of CdTe thin film varies with Cu treatment temperature

**Table 1.** Transition energy levels (assigned, using experimental and calculated data [6]) above the valence band maximum (VBM, for acceptors) or below the conduction band minimum (CBM, for donors) and defect formation energies of neutral $V_{Cd}$, $Cu_{Cd}$, and $Cu_i$ (calculated in Ref. [8] under Cd-rich and Cu-rich conditions).

<table>
<thead>
<tr>
<th></th>
<th>Transition Level (eV)</th>
<th>Formation Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>$V_{Cd}$</td>
<td>Acceptor</td>
<td>(-/0) 0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2/-) 0.40</td>
</tr>
<tr>
<td>$Cu_{Cd}$</td>
<td>Acceptor</td>
<td>(-/0) 0.35</td>
</tr>
<tr>
<td>$Cu_i$</td>
<td>Donor</td>
<td>(0/+0) 0.01</td>
</tr>
</tbody>
</table>
IV. Qualitative Explanation: CdTe Thin Film Quality Varies with Cu Treatment Temperature

The transition energy level and energy of formation of the dopant and compensator involved are listed in Table 1. The experimental demonstration of the variation of the “quality” of the CdTe thin film with the back contact annealing or Cu treatment temperature as shown in the sketch (Fig. 1) can be qualitatively explained as follows:

(1) \( A \rightarrow B \) From poor p-type CdTe to poorer p-type CdTe

As grown CdTe thin film usually show low level p-type doping due to the presence of \( V_{Cd} \) (and/or its variation the single acceptor defect complex \( V_{Cd}-Cl_{Te} \)). It is observed that the low conductivity of the CdTe thin film can become even lower at the beginning of the Cu contacting treatment. This can be understood as follows: Inclusion of Cu impurity in the form of interstitial \( Cu_i \), a shallow donor, may compensate the p-dopants, and lower the hole density, and therefore the conductivity, further. Two \( Cu_i \) are required to compensate a single \( V_{Cd} \), whereas \( V_{Cd}-Cl_{Te} \) can be compensated by a single \( Cu_i \).

Because Cu can diffuse easily in CdTe, and because the formation energy (Table I)

\[
\Delta H = \Delta E_{Cu_{Cd}} - \left( \Delta E_{Cu_i} + \Delta E_{V_{Cd}} \right) = 1.31 - (2.19 + 2.67) = -3.55 \text{ eV}
\]

is strongly negative, which indicates that the reaction

\[
Cu_i + V_{Cd} \rightarrow Cu_{Cd}
\]

is exothermal, or energy favorable. That is, Cu atoms will diffuse into the Cd vacancy site, forming the substitutional acceptor \( Cu_{Cd} \). Because \( Cu_{Cd} \) has higher (-/0) transition energy level than \( V_{Cd} \), this also explains why carrier density, thus conductivity reduces initially when Cu is introduced in CdTe thin films.
From poorer p-type CdTe to better and optimized p-type CdTe

When more and more Cu is introduced into CdTe, more $Cu_{Cd}$ will be formed, because it causes the least perturbation to the lattice, thus it has smaller formation energy than the other defects listed in Table 1. Despite the higher (-/0) transition energy level, the enhanced $Cu_{Cd}$ concentration will eventually increase the hole concentration in the system, thus making the system from a poorer p-type CdTe to a better CdTe.

Note that the transition energy level of the second ionization state of $V_{Cd}$ is deep. Adding Cu will eliminate this deep level, thus reducing the SRH recombination — the main cause of short minority carrier lifetime and large dark current — and improve the performance of the CdS/CdTe solar cell. Experimentally, it is observed that the minority carrier (electron) lifetime depends on the temperature at which the back contact layer containing Cu is deposited (the so-called Cu treatment temperature) (Fig. 3). The optimal temperature is often found to be 280 ~ 300 °C (point C in Fig. 1), at which the minority carrier lifetime reaches maximum.

Fig. 2. Time resolved photoluminescence (TRPL) analysis for CdS/CdTe/ZnTe:Cu/Ti solar cell, in which the ZnTe:Cu contact interface was deposited at the indicated temperatures.
(3) $C \rightarrow D \rightarrow E$ From p-type CdTe to insulating CdTe to n-type CdTe

We argue that at the optimized Cu treatment temperature of 280 ~ 300 °C, most Cu is converted to acceptors $Cu_{Cd}$ because it has lower formation energy than other type of defects. However, further increasing the treatment temperature will lead to more formation of $Cu_i$ because (1) the increased entropy effect. There are more interstitial sites than substitutional sites. And (2) $Cu_{Cd}$ is an acceptor. When more and more $Cu_{Cd}$ is ionized, the Fermi energy moves towards the VBM. In this case, the formation energy of the charged donor defect $Cu_i^+$ decreases linearly as a function of Fermi energy, so it can form more easily in a p-type sample. The increased formation of the donor defect $Cu_i$ can turn a p-type CdTe to insulating and even to an n-type CdTe when the donor density $N_{Cu_i}$ is greater than the acceptor density $N_{Cu_{Cd}}$ in some cases.

In conclusion, in this work by analyzing the competition between the dominant defects $V_{Cd}$, $Cu_{Cd}$, and $Cu_i$ using the concept of compensation among the multi-level Cd vacancy defect states, and the multi-configurational Cu impurity states, we have proposed a qualitative explanation why the properties of the CdTe thin film show such dramatic changes when the deposition temperature of the back contact layer ZnTe:Cu is gradually raised. The quality of the CdTe thin film first deteriorates, and then improves to become a better and optimized thin film for PV applications at 280 ~ 300 °C. When the temperature is further raised, the p-type CdTe turns into insulating, and even to n-type.
REFERENCES


