A New TCO/window-buffer Front Stack for CdTe Solar Cells and its Implementation

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Abstract — A new TCO/window-buffer combination is presented for use in thin film CdTe solar cells. The TCO layer is cadmium tin oxide (CTO) and the window-buffer layer is tin magnesium oxide (TMO). Zinc magnesium oxide (ZMO), previously utilized by other groups and our group, was also prepared. The layers were produced by hollow cathode sputtering and were characterized by optical and Hall effect measurements. It was found that the carrier concentration of the window (buffer) layer at a fixed Mg concentration could be controlled over a wide range. CdTe solar cells were fabricated on glass/TCO/TMO and other bilayers without use of CdS. Quantum efficiency data confirmed the greatly improved blue response of the cells.

I. INTRODUCTION

The efficiency of solar cells based on thin film CdTe depends strongly on the nature and properties of the transparent conducting oxide (TCO) and buffer front stack layers as well as the doping and lifetime of the CdTe [1-4]. Proper engineering of the front stack offers several opportunities for improvement of $J_{sc}$, $V_{oc}$, and $FF$, namely: i) increased $J_{sc}$ via reduction of TCO optical absorption and reduction of the blue loss stemming from buffer layer absorption; ii) increased $FF$ via reduced TCO sheet resistance; and iii) increased $V_{oc}$ via reduction of dark current and recombination at the absorber-buffer interface. The interface recombination is controlled by the size and sign of the absorber-buffer conduction band offset (CBO).

This work targets a high mobility, low absorption TCO and a wide gap buffer layer offering minimal blue loss and an optimized $\Delta E_{c \text{abs-buff}}$ band offset. Modeling using SCAPS, both at NJIT and elsewhere (e.g. CSU), has shown that a type I heterojunction (straddling, with $\Delta E_{c} > 0$) is preferable to a type II heterojunction (staggered, with $\Delta E_{c} < 0$), with $\Delta E_{c}$ preferably lying in the range 0.1 – 0.3 eV. (In this paragraph, $\Delta E_{c} > 0$ means that the CBM rises in going from the absorber to the buffer.) If $\Delta E_{c} > 0.4$ eV the collection of the photocurrent would be hindered and temperature dependent.

We have explored various combinations of TCO and buffer, including cadmium oxide Cd$_{x}$Sn$_{1-x}$O (CTO) as the TCO, and Zn$_{1-x}$Mg$_{x}$O and Sn$_{1-x}$Mg$_{x}$O as the buffer layer. The use of Sn$_{1-x}$Mg$_{x}$O in this capacity has not previously been reported. The workhorse front end structure has, for several decades, been SnO$_{2}$/F/CdS. Record cells have been reported using the TCO/HRT/buffer combinations Cd$_{3}$SnO$_{4}$/Zn$_{1-x}$Sn$_{x}$O/CdS [1] and more recently SnO$_{2}$/F/Zn$_{1-x}$Mg$_{x}$O which contains neither a separate HRT layer nor a CdS layer [5].

II. EXPERIMENTAL

In the work reported here, the metal oxides CTO, ZMO and TMO are deposited by hollow cathode sputtering (HCS) using a proprietary dual-cathode linear source operated in a reactive mode [6]. HCS is a versatile, scalable process for metal oxide deposition featuring low lattice damage in the deposited layers. Low cost metal targets are used and mixed metal oxides can be produced. A photo of the deposition system is shown in Fig. 1.

Fig. 1. Advanced hollow cathode sputtering system at NJIT.

Film thicknesses are determined using a Dektak IIA stylus profilometer. Optical properties are determined using a
Filmetrics F10-RT-UVX measurement system. Resistivity and mobility are determined using an Ecopia 21 HMS-3000 Hall system in a square van der Pauw configuration formed by etching. The magnetic field (0.57 T) was measured using an AlphaLab Hall magnetometer. Solar cell fabrication involves the steps of CdTe deposition on glass/TCO/ZMO by close-spaced sublimation ($T_e \leq 610 \ ^{\circ}C$), CdCl$_2$ treatment, NP etch, back contact application (including Cu$_2$O deposition and annealing), and scribing for cell definition. The use of O$_2$ during CSS [7] was discontinued for these experiments. Solar cells were characterized by J-V curves at AM1.5 100 mW/cm$^2$ obtained using a Newport xenon solar simulator and a Keithley 2401 sourcemeter, and by quantum efficiency measurements using a tungsten-halogen source with light dispersed by a grating monochromator and referenced to a calibrated silicon sensor from Gamma Scientific.

III. TCO Layer Properties

To prepare cadmium tin oxide (CTO) the cathode was fitted with one pure Cd target and one pure Sn target. The principal variables studied were substrate temperature, target powers, and oxygen flow. The optical properties (spectral $T, R, A$ and $T(1-R)$) of a representative as-grown CTO layer are shown in Fig. 2. The properties are comparable to films produced in earlier work [8-10]. In contrast to some other TCOs, the free carrier absorption in CTO only becomes significant for $\lambda > 1000$ nm and so does not reduce the $J_{sc}$ of a CdTe-based solar cell ($E_{g}^{CdTe} = 1.5$ eV).

![Fig. 2. Specular spectral transmittance and reflectance of Cd$_x$Sn$_y$O produced by HCS.](image)

We may extract the optical absorption coefficient $a(\lambda)$ using the equation

$$a(\lambda) = \frac{1}{t} \ln \left( \frac{T(\lambda)}{1 - R(\lambda)} \right)$$

where $t$ is the film thickness. Since the fundamental absorption is both direct and allowed the band gap can be found from the usual $(aE)^2$ versus $E$ (Tauc) plot. The bandgap for CTO film B155 is $E_g = 3.41$ eV, with values typically lying between $3.25 - 3.41$ eV.

Table I shows the electrical parameters of three of the more interesting CTO films. Film B265, with resistivity $\rho = 3.78 \times 10^4 \ \Omega \cdot$cm, had an excellent mobility $\mu = 46.5 \ \text{cm}^2/\text{Vs}$, and a sheet resistance of 6.5 $\Omega$/sq. We note that films with high carrier concentrations (e.g. B166, with $n_c = 1.05 \times 10^{21} \ \text{cm}^{-3}$) tend to have lower mobilities because of increased ionized impurity scattering [6, 11].

**TABLE I**

<table>
<thead>
<tr>
<th>Run #</th>
<th>Matl.</th>
<th>$R_{sh}$ $\Omega$/sq</th>
<th>Carrier conc. $n_c$ $(\text{cm}^{-3})$</th>
<th>Mobility $\mu$ $(\text{cm}^2/\text{Vs})$</th>
<th>Resistivity $\rho$ $(\Omega \cdot \text{cm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B265</td>
<td>CTO</td>
<td>6.5</td>
<td>$3.55 \times 10^{20}$</td>
<td>46.5</td>
<td>$3.78 \times 10^4$</td>
</tr>
<tr>
<td>B160</td>
<td>CTO</td>
<td>7.9</td>
<td>$4.08 \times 10^{20}$</td>
<td>41.9</td>
<td>$3.65 \times 10^4$</td>
</tr>
<tr>
<td>B166</td>
<td>CTO</td>
<td>4.3</td>
<td>$1.05 \times 10^{21}$</td>
<td>30.5</td>
<td>$1.95 \times 10^4$</td>
</tr>
<tr>
<td>B184</td>
<td>ZMO</td>
<td>4.5k</td>
<td>$1.05 \times 10^{19}$</td>
<td>8.64</td>
<td>$6.89 \times 10^2$</td>
</tr>
<tr>
<td>B189</td>
<td>ZMO</td>
<td>17M</td>
<td>$5.52 \times 10^{15}$</td>
<td>1.94</td>
<td>$5.83 \times 10^2$</td>
</tr>
<tr>
<td>B274</td>
<td>TMO</td>
<td>157M</td>
<td>$1.84 \times 10^{14}$</td>
<td>6.0</td>
<td>$5.63 \times 10^3$</td>
</tr>
<tr>
<td>B322</td>
<td>ZTMO</td>
<td>1.59M</td>
<td>$1.16 \times 10^{17}$</td>
<td>5.2</td>
<td>$1.04 \times 10^1$</td>
</tr>
</tbody>
</table>

Scrutiny of the deposition conditions for these and other CTO films suggests that the Cd/Sn ratio in the film plays a strong role in determining carrier concentration $n_c$, resistivity $\rho$, and also optical properties. A temperature-dependent Cd desorption process at the film surface appears to exist, and film mass measurements support this hypothesis. The Cd loss could be mitigated by increasing the oxygen partial pressure. We concluded that $n_c$ declined with decreasing Cd/Sn ratio. Mamazza et al. co-sputtered CdO and SnO$_2$ at RT to produce amorphous CTO films that became polycrystalline after annealing above 580 $^\circ$C [9]. In contrast, we have produced CTO films with $\mu > 40 \ \text{cm}^2/\text{Vs}$ in the as-deposited state. Meng et al. also produced CTO by RF magnetron sputtering but the films required annealing to attain a low resistivity [10].

Hall effect data confirms the n-type conductivity of all CTO films made to date. The nature of the donors was in the past commonly ascribed to point defects such as oxygen vacancies or interstitial Cd [12] but more recent work indicates that the oxygen vacancy is a very deep donor with transition energy at $E_{CBM} = 0.66$ eV while the Sn$_{Cd}$ anti-site defect is a shallow donor at $E_{CBM} = 0.05$ eV with a low formation energy [13].

Figure 3 shows an uncalibrated depth profile of a CTO film on soda-lime glass. There would appear to be a slight gradient in the Cd/Sn ratio. (We plan to investigate this using optical emission spectroscopy conducted on the HC discharge.)
IV. WINDOW LAYER PROPERTIES

To prepare Zn$_{1-x}$Mg$_x$O films two Zn$_{0.85}$Mg$_{0.15}$ metal alloy targets were fitted to the cathode; Sn$_{1-x}$Mg$_x$O films were prepared using two Sn$_{0.85}$Mg$_{0.15}$ targets; Zn$_x$Sn$_{1-x}$Mg$_x$O films were prepared using one of each of the two target types.

The optical data for the ZMO film B189 is shown in Fig. 4. A sharp absorption edge is seen, blue shifted from that of ZnO.

Regarding ZMO, the ionic radius of Mg$^{2+}$ (0.57 Å) is close to that of Zn$^{2+}$ (0.60 Å) [14] and allows it to substitute without change in the wurzite structure, at least for $x < 0.4$. The variation of bandgap of with $x$ is found to be approximately linear and we deduce from a figure given in [15] that $E_g(x)$ is given by

$$E_g(x) = 3.296 + 2.19x \text{ eV}$$

Based on this equation, the Mg contents in the two ZMO films B240 and B189 are $x = 0.04$ and 0.10, respectively. For larger values of $x$ phase separation may occur with some MgO (rocksalt structure) occurring. We found that the ZMO films prepared using two Zn$_{0.85}$Mg$_{0.15}$ targets exhibited exceptionally bright photoluminescence even at room temperature [16].

The as-deposited ZMO films were n-type and, for a given Mg content, it was found that the carrier concentration could be varied over a wide range ($10^{15} - 10^{19} \text{ cm}^{-3}$) through control of the oxygen flow rate during deposition (see Fig. 6).
Detailed electrical properties for ZMO, TMO, and ZTMO films are given in Table I above.

V. Device Properties

The superstrate devices being investigated in this program have the general structure: glass/TCO/window/CdTe/ohmic contact. With ZMO replacing CdS as the window layer, the band diagram of this type 1 (straddling) heterojunction (HJ) device becomes that shown in Fig. 7. The relevant material parameters needed to construct such a diagram are shown in Table II.

\[
\Delta E_c = E_c^{\text{abs}} - E_c^{\text{window}} = \chi_{\text{window}} - \chi_{\text{abs}}
\]

By raising \( E_c \) of the Zn\(_{1-x}\)Mg\(_x\)O window layer by introducing Mg, the magnitude of \( \Delta E_c^{\text{And}} \) can be brought into the favorable range of 0.1 – 0.3 eV (spike rather than cliff offset). The introduction of ZMO into thin-film solar cells was first studied in the context of CIGS [17-21] and later in CdTe [4,5].

Hollow cathode sputtering (HCS) was successfully used to prepare an entire front stack on glass suitable for CdTe solar cells that performed the roles of TCO, high resistance layer, window layer, and emitter. Using such stacks, viable CdTe solar cells were fabricated. The \( J-V \) curve of such a cell prepared on glass coated with CTO and overcoated with a ZMO window layer is shown in Fig. 8. This preliminary experiment yielded a very good \( J_{sc} \) of 25.8 mA/cm\(^2\). The reason for the poor \( V_{oc} \) is not known at present but could be due either to the use of CTO or ZMO, or to sub-optimal cell processing. It was decided after these early experiments that the number of uncertainties should be reduced and subsequent ZMO development was conducted on commercial FTO.

Fig. 8. Light \( J-V \) curve for CdS-free CdTe solar cell on HCS CTO as TCO and HCS ZMO as wide-gap window layer.

For the glass/FTO/ZMO/CdTe cells we observed that the linear dark \( J-V \) curves maintained a conventional diode shape with low series resistance and high shunt resistance in the dark. Interestingly, the curves exhibited an increased turn-on voltage relative to that obtained using CdS, as shown in Fig. 9. The magnitude of the \( J-V \) voltage shift was found to correlate with ZMO thickness, with O\(_2\) flow also playing a role.

Fig. 9. Dark \( J-V \) characteristics for CdS/CdTe and two ZMO/CdTe solar cells on FTO revealing the substantial voltage shift obtainable with ZMO.

Regarding the light \( J-V \) characteristics for 1-sun illumination we have found that a large dark \( J-V \) voltage shift correlates with kinky light \( J-V \) curves showing photocurrent suppression and an inflection as \( V_{oc} \) is approached. This type of \( J-V \) curve...
is not uncommon in experimental devices. It has been observed in both CIGS and CdTe solar cells containing Zn$_1-x$Mg$_x$O buffer layers with a Mg content greater than the optimal value [22, 23]. This is shown in Fig. 10 for a ZMO/CdTe cell on FTO that has an impressively high $V_{oc}$ of 878 mV but only a 4.2% efficiency. Use of a higher CdTe deposition temperature and a thinner ZMO layer enabled the kink to be largely eliminated and a respectable efficiency of 10.5% to be achieved [16].

Using ZMO and TMO window layers in devices fully fabricated at NJIT with the structure glass/FTO/ZMO/CdTe, glass/CTO/ZMO/CdTe or glass/FTO/TMO/CdTe has enabled us to almost completely eliminate the blue loss previously caused by optical absorption in the dead CdS layer. The dramatic improvement in external quantum efficiency ($EQE$) for $\lambda < 550$ nm exhibited by devices using ZMO or TMO as a window layer is shown in Fig. 12. At 400 nm, for example, the $EQE$ can be doubled. The short-circuit current density implied by integration of the measured $EQE$ multiplied by the 100 mW cm$^{-2}$ AM1.5 solar photon flux distribution is 25.8 mA cm$^{-2}$ for a device with ZMO, and 25.4 mA cm$^{-2}$ for TMO, compared to 20.4 mA cm$^{-2}$ for a standard device with CdS.

Since carriers have to surmount the $\Delta E_c$ barrier by thermionic emission (TE) it is clear that a sufficiently large $\Delta E_c$ offset will affect the transport properties of these HJ devices. For barriers > 0.4 eV, TE cannot support a $J_{ph}$ of 25 mA cm$^{-2}$ and so reduced collection will occur. If the dark current is modulated by a factor exp(-$\Delta E_c/kT$) this can account for the observed shift in the dark $J-V$ curve. We have conducted simulations of TCO/ZMO/CdTe devices using SCAPS and can qualitatively reproduce the photocurrent suppression if the doping of the ZMO is too low (Fig. 11).

Fig. 10. Light and dark J-V curves for ZMO/CdTe solar cells with different ZMO thickness.

Fig. 11. SCAPS simulation of J-V curves of CdTe solar cells as a function of ZMO doping ($\Delta E_c =$ 0.4eV, TCO doping $10^{18}$ cm$^{-3}$). Green, light blue (overlapped), pink and red indicate ZMO doping of $0, 10^{14}, 10^{16}$ and $10^{18}$ cm$^{-3}$, respectively.

Fig. 12. External quantum efficiency versus wavelength for conventional CdTe cells on FTO/CdS and the new cells on FTO/ZMO or FTO/TMO.

The use of TMO as the window layer in CdTe solar cells eliminated the photocurrent suppression often seen with ZMO.
Thus, the dark and light J-V curves for a TMO/CdTe cell are shown in Fig. 13. A good $J_{sc}$ of 24 mA/cm² was achieved and the cell efficiency was 10.7%. The somewhat disappointing $V_{oc}$ of 760 mV suggests that $\Delta E_c$ remains to be more favorably adjusted. While ZTO has been prepared, results for cells using this type of window layer are not yet available.

VI. CONCLUSIONS

A custom-built hollow cathode sputtering (HCS) system was used to prepare high quality CTO, ZMO, TMO, and ZTMO layers for use in CdTe solar cells. CTO layers with electron mobilities up to 46.5 cm²/Vs were demonstrated. Carrier concentrations in ZMO could be controlled over the range $10^{14} - 10^{19}$ /cm³. High $J_{sc}$'s up to 26 mA/cm² demonstrate that ZMO and TMO provide a means to obtain competitive CdTe solar cells with improved blue response due to elimination of CdS. With ZMO, $V_{oc}$'s up to 878 mV were achieved. The flexibility of HCS to produce almost any type of metal oxide offers a route for comprehensive optimization of the entire front side (TCO/window layer) of thin film CdTe solar cells including control of $\Delta E_c$ at the absorber-buffer interface.

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REFERENCES


