

RAPID COMMUNICATION

The effect of the transparent conductive oxide on the performance of thin film CdS/CdTe solar cells

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Abstract. Thin film CdS/CdTe solar cells fabricated on SnO_x-coated glass have been found to give higher efficiencies than similar cells produced on indium–tin oxide (ITO) coated glass substrates. Further investigation implicated the CdS/ITO interface as the cause of the problem; current–voltage measurements revealed that on heating in air the CdS/ITO junction became rectifying. This is consistent with recently reported findings which show that the work function of ITO is raised above that of CdS by oxidative treatments (such as heating in air) which would make the ITO/CdS junction rectifying rather than ohmic.

Polycrystalline thin film n-CdS/p-CdTe heterojunction solar cells have become one of the more promising contenders for use in large scale photovoltaic terrestrial power generation [1]. The near optimal bandgap energy and high optical absorption of CdTe, and the ease of thin film fabrication by a wide variety of scaleable techniques, combine to make this system a cost effective option [2]. Currently, best reported efficiencies for this cell are around 16% [3], and calculations of theoretical maximum efficiency yield values of ~28% [4].

Normally the cell is constructed in the superstrate configuration comprising successive layers of transparent conducting oxide (TCO), CdS, CdTe and a back contact on a glass substrate. Much of the recent development has been concerned with the performance of the back contact (typically Cu-loaded graphite) in order to reduce series resistance effects and improve stability [5]. Comparatively little research has been focused on the TCO (front) contact, although as a series element of the cell it is clearly important. Generally the TCO is either tin oxide (SnO_x) or indium–tin oxide (ITO), sometimes doped or in combination. Ideally for solar cell use, the TCO should have a low sheet resistance ($< 10\Omega/\square$) and a high optical transmission ($> 90\%$) [6]. Importantly, but seldom acknowledged explicitly, the TCO/CdS interface should be thermally stable during the subsequent processing steps of cell preparation.

We have observed substantial differences in the measured performance of CdS/CdTe solar cells fabricated on ITO and SnO_x. Although essentially identical in terms of processing, the cells produced on SnO_x coated glass substrates are up to twice as efficient as those formed on ITO coated glass substrates. Accordingly, we have carried

out a more detailed investigation of this effect focusing, in particular, on the TCO/CdS interface.

The problem is illustrated in figure 1, which shows the photovoltaic output characteristics of three cells measured under AM1.5 illumination at room temperature. The characteristics labelled ITO30 and ITO15 were recorded from cells formed on indium–tin oxide coated glass; that labelled SnO₂ was from a cell on tin oxide coated glass. The basic structure of all three cells was the same: ~200 nm CdS deposited by physical vapour deposition (PVD) onto the TCO, followed by ~5.5 μm CdTe deposited by close space sublimation at source and substrate temperatures of 600 °C and 500 °C respectively. The cells were then treated with CdCl₂ (known to improve the performance significantly [7]) by depositing ~150 nm CdCl₂ by PVD and then heated in air at 400 °C for 30 min (SnO₂ and ITO30) and 15 min in the case of ITO15. After thorough rinsing in water to remove any remaining CdCl₂, they were etched in 0.03% Br–methanol for 10–15 s before gold contacts were deposited. The photovoltaic parameters (short circuit current density, J_{sc} , open circuit voltage, V_{oc} , fill factor, FF , and conversion efficiency, η , series resistance, R_s , and shunt resistance, R_{sh}) of the three cells are listed in table 1.

The superiority of the cell produced on the SnO₂ coated glass is clearly apparent in figure 1. The characteristics for the two cells fabricated on ITO show characteristic saturation in forward bias at bias voltages $V > V_{oc}$ generally associated with the presence of an additional series diode component such as a rectifying barrier at one of the contacts [8,9]. This is reflected in the higher series resistances observed for the ITO cells. Often it has been assumed that the barrier is located at the back contact, due to the difficulty of forming an injecting contact to p-type CdTe [10]. However, figure 1 suggests that

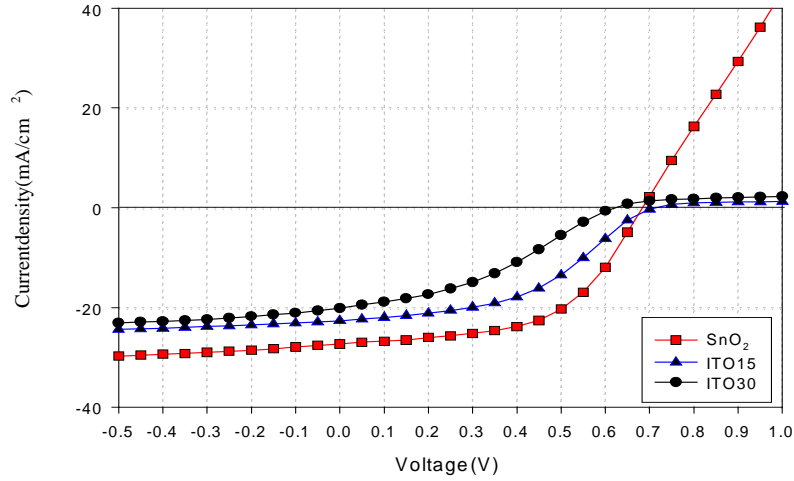
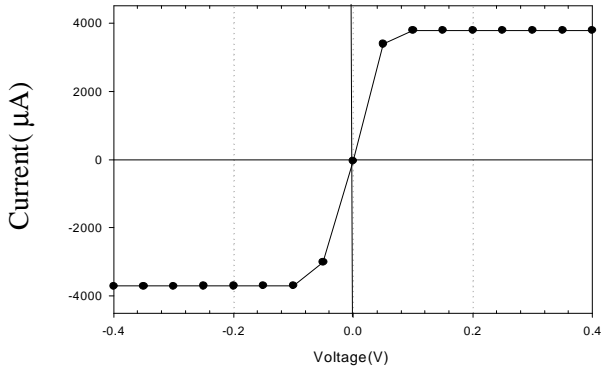
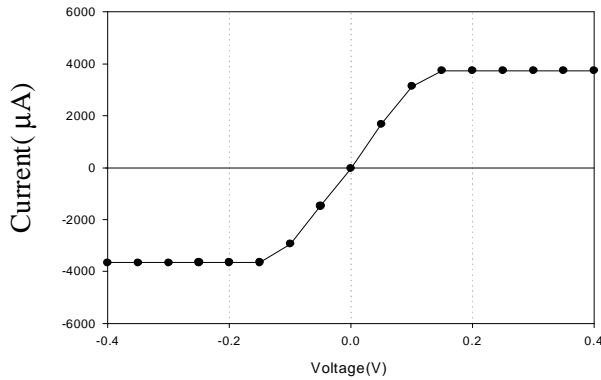


Figure 1. Photovoltaic characteristics of SnO₂, ITO15 and ITO30 samples.



(a)

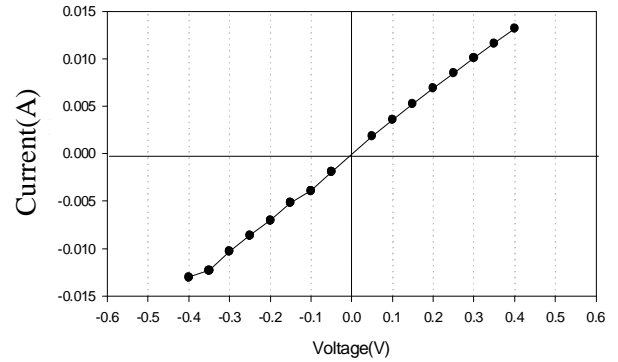


(b)

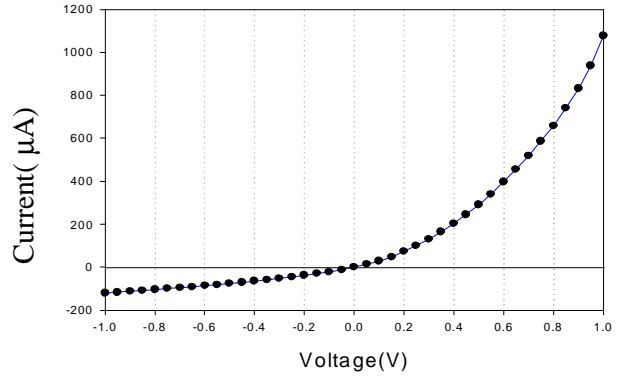
Figure 2. Dark $I-V$ characteristics of SnO₂/CdS/In (a) before and (b) after heating.

any such barrier is probably located at the CdS/TCO interface, since all three devices have the same back contact system.

The progressive decrease in performance with increased CdCl₂ annealing time suggested that the effect was associated with heating. To investigate the effects of heating on the TCO/CdS interface, a number of SnO₂/CdS/In and ITO/CdS/In samples were prepared. Indium was used as the back contact as it is known to make a good ohmic contact to CdS. Room temperature current-voltage ($I-V$) characteristics were measured in the dark for both as-



(a)



(b)

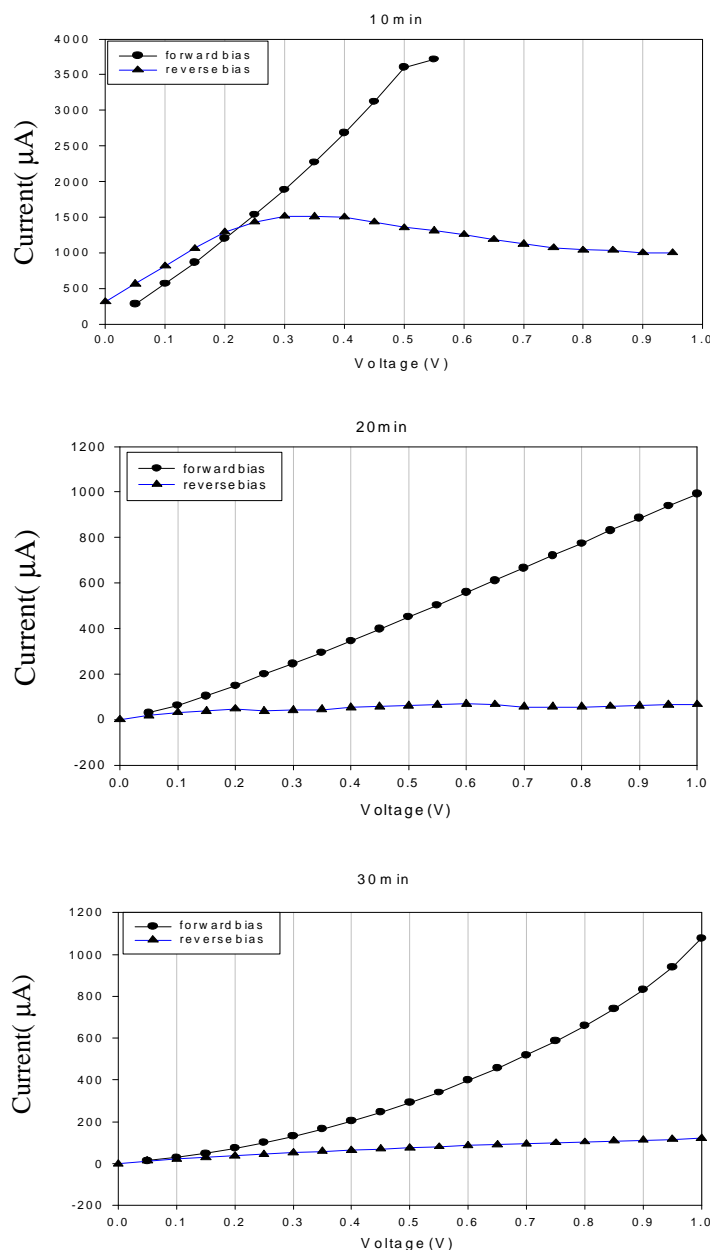
Figure 3. Dark $I-V$ characteristics of ITO/CdS/In (a) before and (b) after heating.

deposited devices and after heating in air for 30 min at 400 °C, i.e. mimicking the CdCl₂ treatment. The results are shown in figures 2 and 3. (The saturation at $\sim \pm 3.8$ mA was a consequence of the current limit on the instrumentation.)

Figure 2(a) shows that the dark $I-V$ measurements in forward (TCO positive) and reverse bias for the SnO₂/CdS/In sample were similar and indicated that the contact between the CdS and SnO₂ was ohmic [11]. This behaviour remained after annealing, as shown in figure 2(b), although the resistance appeared to have increased slightly (from 0.62 to

Table 1. Parameters determined for the cells in figure 1.

	Sheet resistance Ω/\square	J_{sc} mA cm^{-2}	V_{oc} V	FF %	η %	R_s $\Omega \text{ cm}^2$	R_{sh} $\Omega \text{ cm}^2$
SnO ₂	17	27.3	0.684	54.4	10.1	6	196
ITO15	7	22.6	0.714	44.9	7.3	54.1	171
ITO30	7	20.2	0.623	36.7	4.6	34	82

**Figure 4.** Dark I - V characteristics of ITO/CdS/In after heating for different times.

$1.3 \Omega \text{ cm}^2$). This suggests, that any interaction between the CdS and SnO₂ was probably of minimal significance for the performance of the cell.

Figure 3(a) shows that the dark I - V measurements in forward and reverse bias for as-deposited ITO/CdS/In devices were also similar and thus that the contact between the CdS and ITO was also ohmic though more resistive ($1.2 \Omega \text{ cm}^2$). However, after heating, figure 3(b) shows that the dark

I - V characteristics became rectifying. Assuming that the contact between the In and CdS layer was ohmic, since that was common to both the SnO₂/CdS/In and the ITO/CdS/In devices, then the rectifying effect which appeared after heating of the samples would seem to be due to the contact between the ITO and CdS. Hence, annealing the CdS/ITO interface for 30 min at 400°C in air, as used in the CdCl₂ treatment, clearly resulted in some interaction, which

impeded the flow of charge. The behaviour of the ITO/CdS interface was studied in more detail by investigating the effect of annealing time on the dark $I-V$ characteristics. Figure 4 shows the effect of time (10, 20 and 30 min) of heating at 400 °C in air on the dark $I-V$ characteristics of the ITO/CdS/In device.

It is clear from figure 4 that the ITO/CdS interface started to become rectifying within 10 min heating time at 400 °C, and had become fully rectifying after ~20 min.

The use of ITO in electroluminescent devices is known to be problematic, and unless appropriate surface treatments are carried out prior to the deposition of the active layers, the device performance is poor [12]. Although relatively little is known about the effects of ITO on the performance of CdS/CdTe thin film solar cells, it is perhaps indicative that many of the most efficient cells reported to date have been fabricated on SnO_x coated glass (often F doped) [13]. Depuydt *et al* [14] have observed that an ITO/CdS interface contributes to an increase in series resistance after CdTe deposition (i.e. after heating), while behaving as a good injecting contact beforehand, although no explanation was given.

Since In is a donor impurity in CdS, cross diffusion of In from the ITO into the CdS would act to increase its conductivity. Generally, this might be expected to improve the injection of carriers across the ITO/CdS interface, reducing the contact resistance and rendering the contact even more ohmic, i.e. the reverse of what was observed.

A recent study [12] of the oxidative-reductive behaviour of ITO surfaces using x-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy has indicated that the work function is dependent on the surface oxygen concentration. In particular, the UPS measured work function of as-received ITO was found to be low (~4 eV) as a consequence of adventitious contamination, but increased substantially (5 eV) following various surface treatments. Importantly, oxidative treatments raised the work function of the surface. The annealing treatments carried out in the present study were all undertaken in air and, assuming that oxygen was able to diffuse through the thin CdS layer, may be presumed to be oxidative. In that case, the UPS studies would imply an increase in the work function. However, since CdS is a n-type semiconductor, contact materials should have a low work function, ideally less than the electron affinity if they are to be injecting. The electron affinity of CdS is 4.5 eV [15], greater than as-received ITO, but less than fully

oxidized (i.e. heat treated) ITO. The implication is that the heat treatment changes the ITO from an injecting (ohmic) to a rectifying (Schottky barrier) contact by raising the ITO work function through surface oxidation. While this would certainly explain the observed behaviour rather well, it should be remembered that the surface state of the as-received ITO used in the present study was unknown and, although it is reasonable to assume the surface was contaminated, the nature of that contamination and its effects may not have been the same as in the material used in the UPS study [12].

The observations presented here strongly suggest that ITO is not well suited to use in CdS/CdTe thin film solar cells. Although the sheet resistance of ITO coated glass is generally less than corresponding SnO_x coated glass, ITO is not as stable to subsequent processing steps as SnO_x. Moreover, it would appear that in its 'clean' state, i.e. the more controlled surface, the high work function of ITO makes it unsuitable in principle as an ohmic contact to n-CdS.

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