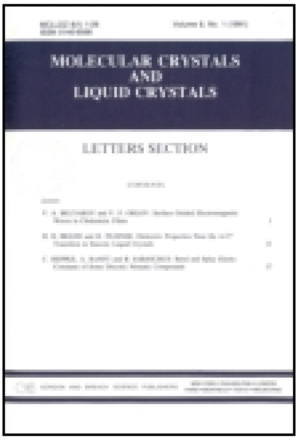

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Comparison of Aluminum Zinc Oxide and Indium Tin Oxide for Transparent Conductive Oxide layer in $Cu(In,Ga)Se_2$ Solar Cell

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The photovoltaic performances of i-ZnO/CdS/Cu(In,Ga)Se_2 (CIGS) solar cell with different window architectures of SnO_2:In_2O_3 (ITO), Al_2O_3:ZnO (AZO) and ITO/AZO, were experimentally compared. The solar cell with ITO deposited directly on i-ZnO layer showed an abnormal current-voltage characteristic as having a shunt path. Both of AZO and ITO/AZO resulted in normal current-voltage behavior as far as AZO is contacting ZnO.

Keywords CIGS solar cell; indium tin oxide; aluminum zinc oxide; transparent conducting oxide

Introduction

For CIGS solar cells, as front contact, transparent electrode layer essentially should have both high optical transmittance and high electrical conductivity. The typical transparent electrode layer of CIGS solar cell has the bi-layer structure of a conductive layer on insulating layer [1]. The undoped ZnO is a common choice for the insulating layer and it is believed to eliminate the shunt paths possibly left by the not-conformal coverage of CIGS surface by a buffer layer deposited by a chemical bath deposition [2]. Either of AZO or ITO deposited by sputtering and B:ZnO (BZO) by MOCVD are currently used for the transparent conductive oxide (TCO) layer. ITO has superior to AZO in terms of transmittance and conductivity [3]. Although it is rather expensive to be acceptable for the photovoltaic industry, ITO has been widely used in many groups. Of course, ITO definitely has better optical transmittance and electrical conductivity compared to ZnO-based TCO, and therefore is expected to yield higher conversion efficiency in turn. Especially in the long wavelength spectral range of 1-sun irradiation, the poor transmittance of AZO is one of the main reasons for the current loss of CIGS solar cell. In this study, sputter deposited AZO and ITO were used for the window material of CIGS solar cells and the effect of material selection on the device performance were evaluated.

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Table 1. Electrical properties of TCO thin films used in this study

Sample	thickness (nm)	R_{sq} (Ω/square)	μ (cm^2/Vs)	n ($1e20/cm^{-3}$)
AZO	500	43.0	11.7	2.5
ITO	320	50.0	6.9	5.6
ITO/AZO	300/150	41.8	6.8	4.4

Experimental

The CIGS absorbers (∼2 μm) were deposited by three stage co-evaporation process using molecular beam epitaxy (MBE) system on Mo-coated (∼0.6 μm) soda-lime glass (SLG) substrate. The detailed deposition method of CIGS has been reported previously [4]. Subsequently the CdS (∼50 nm) thin films were deposited by the chemical bath deposition (CBD) on CIGS absorber. The i-ZnO layer (∼80 nm) was deposited by RF magnetron sputter. Subsequently AZO (∼500 nm), AZO(∼150 nm)/ITO(∼300 nm), or ITO(∼300 nm) were deposited by RF (or DC) magnetron sputter.

Measurements

The optical transmittance of each TCO film was examined by using UV-Vis-NIR spectroscopy over 300–1500 nm range. The thickness was measured by a surface profilometry (α-step). The electrical characteristics were evaluated using Hall Effect Measurement System. The hole concentration of absorber layer was confirmed by capacitance-voltage analysis. The evaluation of photovoltaic performance of CIGS solar cell has been performed using solar simulator under AM1.5, 100 mW/cm^2 illumination at 25°C or from 10°C to 50°C.

Results and Discussion

The electrical properties of each TCO layer are listed in Table 1. The thickness was adjusted to give similar sheet resistance to minimize the contribution of TCO resistance to the solar cell performance. In fact, it was confirmed by profiling the capacitances as shown in Figure 1. The $1/C^2$ vs V curves were taken from the completed devices show good linearity

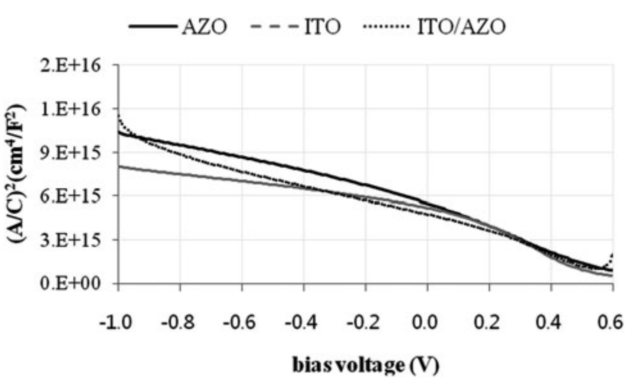


Figure 1. $1/C^2$-V characteristics of the three CIGS solar cells with different TCO configuration.

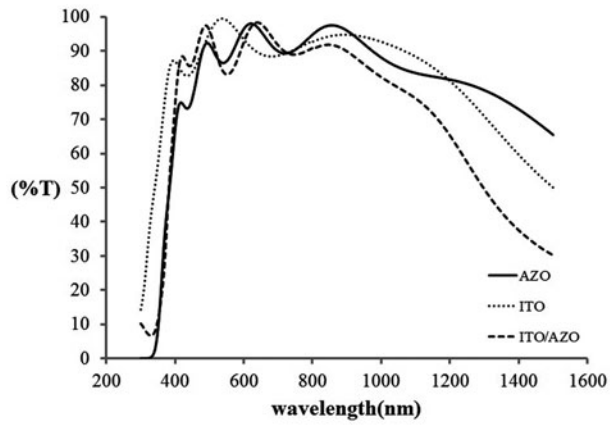


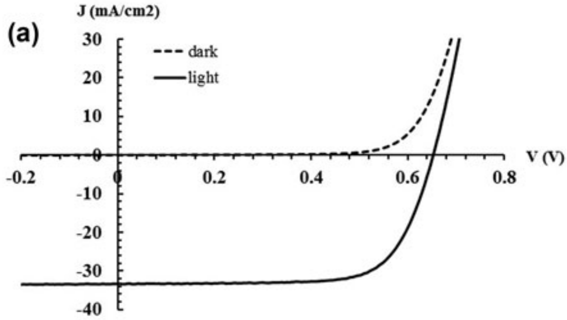
Figure 2. Optical transmittance curves of TCO thin films.

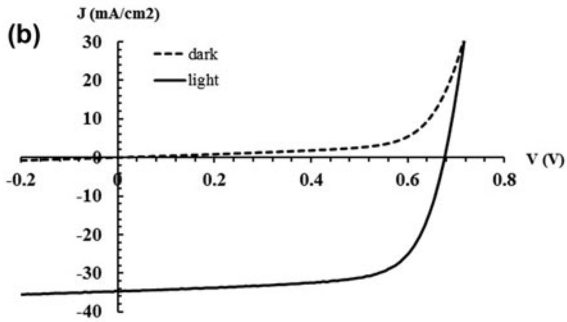
over reverse bias range and similar capacitance values. Also, the hole concentration of CIGS absorber calculated from the linear portion of the curves are very alike; 4.3e15, 3.6e15, and 4.5e15/cm^3 for AZO, ITO, and ITO/AZO devices respectively. Therefore, it is suggested that the TCO deposition process didn't change both the absorber and CdS/CIGS junction properties. The optical transmittances are compared in Figure 2. ITO has wider transmittance spectrum due to its higher bandgap energy of 3.8 eV compared to AZO (3.4 eV) containing layers [4]. The ITO/AZO bilayer was found to have same band-edge absorption as AZO and similar transmittance to ITO but much higher than AZO at short wavelength range. Overall, ITO-containing TCO's (either ITO itself or ITO/AZO) are optically more transparent at shorter wavelength less than roughly 800 nm, over which most of the absorption will take place in top half of the absorber. Therefore, ITO-containing TCO's is expected to yield a better photo-current generation.

The solar cells consisted of TCO/i-ZnO/CdS/CIGS/Mo/sodalime glass were fabricated and their current-voltage characteristics are shown in Figure 3. The major performance parameters are summarized in Table 2. Among three TCO's, the solar cell with ITO showed the best conversion efficiency. The short circuit current densities (J_{sc}) of the three solar cells are well consistent with the above mentioned transmittance, where the ITO-containing TCO's show greater J_{sc}'s. Also, the ITO-only device was found to give a substantially higher open circuit voltage (V_{oc}) value than AZO-containing devices. Considering the ideality factors of all three devices are less than 2.0, which means that CdS/CIGS interface recombination limits the open circuit voltage, the temperature dependence of V_{oc} can be described by following equation; [5]

$$V_{oc} = \frac{\Phi_b^p}{q} - \frac{kT}{q} \ln\left(\frac{qS_pN_V}{J_{sc}}\right) \tag{1}$$

Where, Φ_b^p, S_p, and N_V are the built-in barrier height, the interface recombination velocity, and effective density of state in valence band. The experimentally measured temperature dependences of V_{oc} are also shown in Figure 4. As indicated in the Figure 4, the barrier heights are well consistent with the order of V_{oc} values and ITO-only device showed the greatest among the three. So far, the reason why ITO increased the barrier height is not well understood yet. Since all the three TCO's has well over 1e20/cm^3 of electron density,





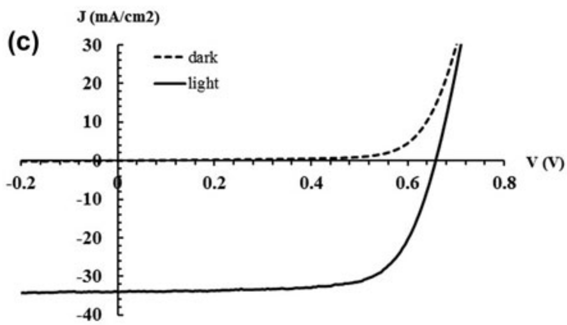


Figure 3. I-V characteristics of various solar cells with TCO of (a) AZO, (b) ITO, and (c) ITO/AZO grown on ZnO/CdS/CIGS/Mo/glass.

Table 2. The photovoltaic parameters of the CIGS solar cells with different TCO's

	AZO	ITO	ITO/AZO
J_{sc} (mA/cm^2)	33.34	34.66	34.08
V_{oc} (V)	0.653	0.681	0.658
FF (%)	72.22	66.87	70.63
Efficiency (%)	15.72	16.28	15.84
R_{sh} (ohm cm^2)	3833	259	1089
R_s (ohm cm^2)	0.84	0.52	0.91
J_o (mA/cm^2)	2.2e–6	6.1e–7	8.0e–7
Ideality factor	1.56	1.52	1.49

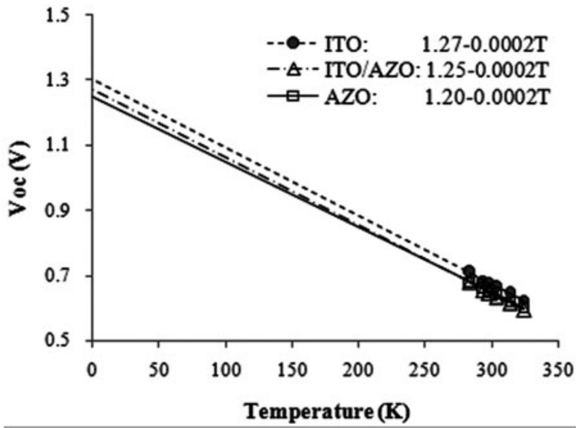


Figure 4. I-V-T characteristics of the solar cell with ITO as TCO.

the Fermi levels of TCO's are regarded same as their conduction band edge and hence the barrier heights (energy distance from the Fermi level of the absorber) are supposed to be identical.

It is noteworthy that the solar cell with ITO, which has superior optical and comparable electrical conductivity to the other two TCO's, showed the lowest fill factor (FF) due to the poor shunt resistance (R_{sh}). It is clear that the plateau around V=0 for ITO case is non-zero slope from the Figure 3(b), which yielded a low shunt resistance and hence a low fill factor. Therefore, we will focus on the shunt resistance behavior of ITO device. In general, the shunt path is formed through either open structure like voids or electrically conductive metallic phase embedded along the grain boundaries in CIGS. Considering that the CIGS layers were deposited at a same time, the common shunt paths are not likely to exist. The abnormal I-V behavior found in ITO-only device may be attributed to lateral non-uniformity of sheet resistance of ITO film, which was deposited at 150°C. The crystalline perfection of ITO is known to abruptly change above 170°C during deposition. Therefore, the ITO film of this study is believed to be partially crystallized, so that the resistance of the film is varying laterally. For instance, S. Bowden et al [6] reported a simulation result on the exactly same phenomenon that I-V curve seems to have a very low shunt resistance when a very high resistance, for example 150 ohm, affects a small portion as much as 10% of the cell. This means that the effect is due solely to the lateral non-uniformity of sheet resistance of ITO.

It is worthwhile to exploit the effect of the different stacking architecture of conductive oxide/ZnO on the low shunt resistance behavior of the I-V's. Again, it is striking to find that only the device having ITO directly deposited on ZnO shows significantly low R_{sh} value. Either AZO/ZnO (AZO is contacting ZnO) or ITO/AZO/ZnO (AZO is inserted between ITO and ZnO) yields much better R_{sh} performance. Also, the AZO-buffered case (ITO/AZO/ZnO) shows intermediate R_{sh} value among the three devices (refer to Table 2). ITO is known to form a Schottky barrier of about 0.35 eV when junctioned with ZnO [7]. Of course, AZO forms an ohmic contact with ZnO. In case of ITO/AZO contact, the Schottky barrier doesn't affect the electron transport because both materials are degenerated semiconductors with same conductivity type and thus a tunneling current is allowed.

It is rather difficult to tell which of the above described reasons would be applicable for the abnormal I-V behavior of the ITO/ZnO device. Nevertheless, based on the above mentioned analyses, it is suggested that the direct contact of ITO with ZnO will give rise to a poor fill factor due to either lateral non-uniformity of TCO resistance or Schottky barrier, which can be alleviated by inserting AZO-buffer layer between ITO and ZnO.

Conclusions

The solar cell with ITO as TCO in TCO/ZnO/CdS/CIGS device showed the highest conversion efficiency due to increased Voc but very poor fill factor compared to the devices with AZO and ITO/AZO for TCO. The recombination barrier height increased by adopting ITO as part of TCO and it may contribute to the V_{oc} increase. The shunt-like behavior may be originated from either Schottky barrier formed at ITO/i-ZnO hetero-interface or lateral non-uniform resistance distribution in ITO layer and seems to be inherent to the ITO/ZnO configuration. By inserting AZO as a buffer material between ITO and ZnO, the abnormal shunt behavior was almost overcome.

Acknowledgments

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