Contents lists available at ScienceDirect

# Thin Solid Films



journal homepage: www.elsevier.com/locate/tsf

# Application of high mobility transparent conductors to enhance long wavelength transparency of the intermediate solar cell in multi-junction solar cells

S. Calnan<sup>a,\*</sup>, H.M. Uphadhyaya<sup>a</sup>, S. Buecheler<sup>b</sup>, G. Khrypunov<sup>c</sup>, A. Chirila<sup>b</sup>, A. Romeo<sup>d</sup>, R. Hashimoto<sup>e</sup>, T. Nakada<sup>e</sup>. A.N. Tiwari<sup>f</sup>

<sup>a</sup> Centre for Renewable Energy Systems Technology, Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire LE11 3TU, UK

<sup>b</sup> Thin Film Physics Group, Laboratory for Solid State Physics, ETH (Swiss Federal Institute of Technology) Zurich, ETH Building, Technoparkstr. 1, CH-8005 Zürich, Switzerland <sup>c</sup> Kharkov State Polytechnic University, UA-310002 Kharkov, Ukraine

<sup>d</sup> Faculty of Science, University of Verona, Ca', Vignal 2, Strada Delle Grazie, 37134 Verona, Italy

e Department of Electrical Engineering and Electronics, L-317, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa, Pref. 229-8558, Japan

<sup>f</sup> Laboratory for Thin Films Photovoltaics, Empa, Swiss Federal Laboratory Material Testing and Research, Ueberlandstr. 129 CH-8600, Duebendorf, Switzerland

#### ARTICLE INFO

Available online 8 November 2008

Keywords: High mobility TCO CdTe Multi-junction solar cells Bifacial solar cells Optical losses

### ABSTRACT

High mobility transparent conducting oxide (HMTCO) materials (mobility>60 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) have a high transmission over the visible to near infra red wavelength region with resistivity  ${<}2{ imes}10^{-4}\,\Omega$  cm. We investigate the application of HMTCO materials as transparent contacts for multi-junction and bifacial solar cells to increase the device NIR transmission. Using the HMTCO materials as front contacts significantly reduces absorption and reflection losses of the solar cells, from 850–1500 nm. The need to develop a low temperature process to prepare HMTCO materials as back contacts in semi-transparent solar cells is also emphasized.

© 2008 Elsevier B.V. All rights reserved.

#### 1. Introduction

The maximum achievable efficiency of single junction solar cells is limited by the inability for any known semiconductor material to utilise the entire light spectrum available under solar irradiation for photo-conversion. Multi-junction solar cell structures consisting of stacks of different semiconductors with appropriately matched band gaps are used to increase the spectral response of the photovoltaic device over a wide wavelength range. The close matching of the current from each solar cell of the stack is imperative in series connected multi-junction cells since the overall photo-current is determined by the solar cell that generates the lower photo-current.

Cadmium telluride (energy band gap  $E_{g}$ ~ 1.45 eV) is a promising material for the intermediate cell in a triple junction cell as it can transmit photons with energy E < 1.45 eV which could be used by a bottom cell e.g.  $CuIn_{1-x}Ga_xSe$  (CIGS). Current matching can then be achieved by using CdTe solar cells with thinner absorbers or smaller area than the bottom cell to transmit some of the photons with energy >1.45 eV to the bottom cell. Alternatively, the transmission of unused NIR photons through the CdTe absorber may be employed. In this contribution, we focus on increasing the NIR transmission of the intermediate cell which is simpler to realise in terms of current collection and solar cell fabrication, than reducing either the CdTe layer thickness or the intermediate cell area.

However, optical losses from the front and back contacts, various inactive window layers of the cell as well as at interfaces between the layers in the stack may reduce the amount of light reaching the bottom cell, causing a current mismatch [1]. Fig. 1(a) shows the J-V characteristics of a CIGS solar cell illuminated by AM1.5 light with or without a semi transparent solar cell (a 1µm thick CdTe absorber layer with In<sub>2</sub>O<sub>3</sub>: Sn (ITO) front and back contacts) acting as a filter in front of it. Fig. 1(b) shows the transmission T, reflection R and absorption A spectra of the CdTe solar cell from which it can be seen that the NIR transmission is limited by considerable absorption losses exceeding 40%. However, despite the relatively low NIR transmission (<50%) through the CdTe cell, the bottom CIGS solar cell achieves an appreciable current density  $J_{sc}$  of 7.13 mA cm<sup>-2</sup> leading to an efficiency  $\eta$  of 3.16%.

Cadmium stannate thin films (charge carrier mobility  $\mu$ ~53.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, resistivity  $\rho \sim 1.8 \times 10^{-4} \Omega$  cm) used as a front contact can enhance the NIR transparency of CdTe solar cells to above 50% [2]. However, even higher values of  $\mu$  ( above 60 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) can be achieved, with similar opto-electronic properties, by doping indium oxide with molybdenum [3-6], titanium [5,7-9] and zirconium [6], to name a few. The solar cell research and development community has long been aware of the benefits of a wide transmission window extending into the NIR range region with a simultaneously high conductivity [10]. Already, In<sub>2</sub>O<sub>3</sub>:Ti (ITiO) thin films have been used as a transparent front contact for CIGS solar cells [5], to improve the rear side efficiency of bifacial CIGS solar cells [11] and to improve the NIR transmission of dye sensitized titanium dioxide solar cells [12]. Also, In<sub>2</sub>O<sub>3</sub>:Mo (IMO) thin films have been used as a front contact for

<sup>\*</sup> Corresponding author. Tel.: +44 1509 63 5323; fax: +44 1509 63 5301. E-mail address: s.calnan@lboro.ac.uk (S. Calnan).

<sup>0040-6090/\$ -</sup> see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.tsf.2008.11.007



**Fig. 1.** (a) J-V characteristics of a CIGS solar cell under AM1.5 global illumination  $(\eta = 14.2\%, J_{sc} = 31.4 \text{ mA cm}^{-2})$  and with the illumination filtered  $(\eta = 3.16\%, J_{sc} = 7.13 \text{ mA cm}^{-2})$  through a semi-transparent CdTe solar cell. (b) Transmission *T*, reflection *R* and absorption *A* spectra of the semi-transparent CdTe solar cell used as a filter in (a). The solar cell "filter" consists of a 1 µm thick CdTe absorber layer and uses ITO as the front and back contact material.

nano-crystalline silicon solar cells to enhance the current generation from long wavelength photons [13].

Therefore, this work was aimed at investigating the effect of using high mobility transparent conducting oxide (HMTCO) materials as front contacts of CdTe solar cells designed as the middle cell in a triple junction solar cell. We also briefly investigate the use of an HMTCO thin film as a contact in another interesting type of CdTe solar cells in the bifacial configuration that require a highly transparent electrode at both the front and back of the cell [14].

## 2. Experimental methods

The IMO thin films were prepared in a sputter chamber (ATC Orion 8 UHV system, Aja International Inc., USA) equipped with a load lock allowing a base pressure of about  $5 \times 10^{-6}$  Pa. Low iron 1.1 mm soda lime glass substrates were coated with IMO thin films sputtered by pulsed DC magnetron sputtering (2.75 W cm<sup>-2</sup> at 150 kHz and a 55% duty cycle) from a 2 wt.% Mo doped In<sub>2</sub>O<sub>3</sub>. The sputter gas consisted of argon with 0.53 vol.% oxygen added and the gas flow was adjusted and throttled to achieve a sputter pressure of 0.13 Pa. The heater temperature was 450 °C and it is estimated that the substrate temperature would be about 10% less. The IMO thin films were used to prepare solar cells without intentional post deposition annealing. The ITiO thin films were fabricated at Aoyama Gakuin University, Japan by RF magnetron sputtering from a 1 wt.% TiO<sub>2</sub> doped In<sub>2</sub>O<sub>3</sub> target. Post deposition annealing at 530 °C in vacuum was used to achieve a high carrier mobility of 105 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>. A detailed description of the process

#### Table 1

Electrical properties of IMO, IMO and FTO thin films on 1.1 mm thick low iron soda lime glass

ГСО	Thickness (nm)	Mobility (cm2 V <sup>-1</sup> s <sup>-1</sup> )	Carrier density (10 <sup>20</sup> cm <sup>-3</sup> )	Resistivity $(10^{-4} \Omega \text{ cm})$	Sheet resistance $(\Omega/sq)$
ITiO	250	105	3.1	1.9	6.3
IMO	200	77	5.0	1.6	7.5
ITO	120	27	18	1.3	11
FTO	415	25	6.5	3.9	9

used to prepare the ITiO thin films is presented elsewhere [9]. ITO and SnO<sub>2</sub>:F (FTO) coated 1.1 mm low iron soda lime glass substrates, obtained commercially, were used for comparison in this study.

The CdTe cell window and absorber layers were prepared using evaporation under high vacuum with the substrate temperatures kept below 450 °C [15]. First, the CdS layers (300-500 nm) were deposited onto the TCO substrates, heated to 150 °C, by evaporation and then heated again at 450 °C for re-crystallisation. Next, the CdTe layers (3-4.8 µm) were deposited with a substrate temperature of 300 °C. CdTe can be deposited at temperatures lower than 300 °C but this was not investigated because of an anticipated reduction in efficiency as a result of poor structural quality [16,17]. Some of the samples on ITiO were further coated by evaporation of CdCl<sub>2</sub> without intentional substrate heating followed by heat treatment at 430 °C in air for 25 min. A post deposition CdCl<sub>2</sub> treatment is essential for the recrystallisation of the CdTe regardless of the deposition method [17,18]. This heat treatment can increase efficiency from about 2-3% to 10-12% for low temperature (330 °C) grown CdTe. A tellurium rich layer required for a low resistance back contact was created by etching the exposed CdTe in a bromine-methanol solution, then coating with an



**Fig. 2.** (a) Transmission *T* and reflection *R* as well as (b) absorption *A* spectra for ITiO, IMO, ITO and FTO thin films on glass with illumination from the glass side.



**Fig. 3.** Transmission *T* and absorption *A* spectra for front side illumination of CdS|CdTe stacks on different TCO coated substrates. The CdS thickness is 500 nm for all samples while the CdTe thickness is 2.8  $\mu$ m, 4.3  $\mu$ m, and 4.5  $\mu$ m for FTO, ITO and IMO coated substrates, respectively.

ultra thin copper film and the resultant  $Cu_x$ Te was annealed at 200 °C for a short time. To complete the cell, an ITO back contact was deposited by RF magnetron sputtering at 200 °C substrate temperature with the remaining deposition parameters set as reported elsewhere [14].

The thickness of the different thin films was determined using surface profilometry. The total transmission *T* as well as the reflection *R* under both front side (glass first) and rear side (films first) illumination were measured by a double beam spectrophotometer (Cary 5000 Varian Inc.) fitted with an integrating sphere. All optical spectra were measured using air as the reference to simulate the actual amount of light incident on the solar cell layers. Total transmission through any media is independent regardless of the direction of illumination and thus only measurements under front side illumination were made. The total absorption was calculated using the relation *A*=100-T-R. The majority carrier density *N* and mobility  $\mu$  of the TCO thin films were obtained by Hall effect measurements (HMS 3000, Ecopia).

## 3. Results

Table 1 summarises the electrical properties of the TCO thin films used in this study. The high mobility of the ITiO and IMO thin films results in low resistivity similar to ITO but with low values of *N* comparable to the more resistive FTO thin film. Fig. 2(a), and (b) show the transmission *T*, reflection *R* and absorption *A* spectra of the TCO thin films on 1.1 mm soda lime glass. The ITiO and IMO coated



**Fig. 4.** Transmission *T* spectra of a complete and various incomplete CdTe solar cells on ITiO and one additional stack, consisting of ITO|CdS|CdTe, for comparison. The CdS thickness is 300 nm while the CdTe thickness is 3 µm.

substrates have a high transmission over a much wider spectral range than the other TCO materials, which adequately covers photons from 400 nm to 1300 nm required for a multi-junction solar based on a stack of CdTe and CIGS. The IMO thin film has a slightly lower transmission of visible light than the ITiO thin film as a result of absorption close to 5%. The plasma wavelength  $\lambda_p$  occurs at higher values in the order ITO, FTO, IMO and ITiO. The NIR light transmission of ITO is limited by high reflection for wavelengths above 1100 nm whilst that of the FTO is limited by the enhanced absorption, in both cases due to high carrier density and low mobility. The gain in transmission from 800–1200 nm, by replacing FTO and ITO with HMTCO thin films, is only about 5-10%. However, this gain becomes significant when a transparent contact is required both at the front and the back of the cell as will be shown later.

Fig. 3 shows *T* and *A* spectra of CdS|CdTe stacks on IMO, ITO and FTO coated glass. The CdS thickness is 500 nm for all samples while the CdTe thickness is 2.8  $\mu$ m, 4.3  $\mu$ m, and 4.5  $\mu$ m for FTO, ITO and IMO coated substrates, respectively. The stack on the IMO substrate has a total transmission exceeding 60% from 800–1300 nm compared to about 50% for the stacks on ITO and FTO, respectively. The absorption in the visible wavelength range is less than 100% because of reflection losses of about 10% for all the TCO coated substrates. Over the NIR wavelength range, the stack absorption increases with that of the corresponding bare TCO thin film (see Fig. 2b). The NIR transmission of the stacks on ITO and FTO are limited by the high reflection and/or absorption, respectively of the related TCO materials over the same wavelength range. The relatively high NIR transmission of the stack on the IMO substrate is a result of a comparatively lower absorption and reflection in this wavelength region.



**Fig. 5.** Absorption A spectra for (a) front and (b) rear side illumination of different consecutive layers of a CdTe solar cell and one additional, ITO|CdS|CdTe stack, for comparison. The CdS thickness is 300 nm while the CdTe thickness is 3 µm.

Semi transparent CdTe solar cells can also be used either as a middle junction in a multi-junction solar cell or as a single bifacial solar cell. Therefore, additionally, the influence of using ITiO as a front contact for a semi transparent CdTe solar cell under both front side and rear side illumination was investigated. Fig. 4 shows the transmission spectra of CdTe solar cells, at various stages of completion, with an ITiO front contact. Fig. 4 also shows the T spectrum of a |CdS|CdTe stack on an ITO front contact, for comparison. The NIR wavelength transmission of the ITiO|CdS|CdTe oscillates between 60% and 70%. In contrast, the NIR transmission of the ITO CdS|CdTe stack is less than 60% at 800 nm and then gradually decreases to about 40% at 1500 nm. When the ITO back contact is added to complete the CdTe solar cell on the ITiO front contact, the NIR transmission drops steadily from 65% at about 820 nm to below 10% at 1500 nm. It is expected that using an ITiO back contact instead may reduce the NIR wavelength optical losses by at least 10%. However, this is dependent on the ability to prepare reasonably conducting ITiO thin films at temperatures below 300 °C to prevent diffusion of the copper into the CdTe layer.

Fig. 5 shows the absorption A spectra of the stacks considered in Fig. 4 under (a) front and (b) rear side illumination. The visible wavelength absorption is less than 100% because of reflection losses at the front of the stack. Over the NIR wavelength range up to 1500 nm, the absorption decreases from about 20% to 10% when the ITO front contact of the CdS|CdTe treated stack is replaced by ITiO. However when an ITO back contact is added to complete the cell on the ITiO front contact, the NIR absorption increases from about 20% at 900 nm to about 50% at 1500 nm. Under rear side illumination, the visible wavelength absorption of the CdS|CdTe treated stack on ITO is around 70% and increases slightly as the ITO is replaced with ITiO. Addition of an ITO back contact to the solar cell stack results in an increase in visible wavelength absorption by up to 10% absolute. For longer wavelengths from 850-1800 nm, the absorption is nearly independent of the wavelength and reduces by about 10% when the ITO front contact is replaced by ITiO. However, when an ITO back contact is added to the complete cell, the NIR absorption increases by about 20% absolute at about 850 nm and rises with increasing wavelength up to 55% about 1200 nm where it peaks before reducing to about 10% at 1800 nm. . Under front side illumination, the high absorption and/or reflection by either the front TCO and/or the ITO back contacts significantly contribute to optical losses over 1100 -1500 nm. For visible light, under rear side illumination, higher reflection losses by CdTe in the complete cell are dominant. Again, here it is clear that using an HMTCO film as the back contact could substantially reduce the NIR optical losses.

## 4. Discussion

Several factors contribute to the reduced transmission of the CdS CdTe stacks under both front side and back side illumination namely, absorption due to free carriers and various scattering processes as well as reflection at interfaces. However, the results presented show that at least in the NIR wavelength range over 850–1300 nm, the TCO material used either as a front or rear side contact can contribute significantly to these losses. Therefore the development of transparent conducting oxides where both the reflection and absorption in the NIR wavelength region are minimal is desirable to improve the performance of multi-junction- and bifacial solar cells. It is also imperative to use an HMTCO both as the front and back contact in order to preserve high NIR transmission of a CdTe solar cell. In order to maximise the benefits of using HMTCO materials in both multi-junction and bifacial solar cells, several issues still remain to be investigated and where necessary addressed, namely:

- 1. the temperature compatibility of HMTCO during deposition of subsequent layers in the superstrate (absorber layers deposited on the TCO) configuration,
- 2. the influence of IMO and ITiO on the CdS and CdTe crystallisation process in the superstrate configuration,
- 3. the development of an HMTCO back contact with good electrical contact with CdTe,
- the need to develop a process where by HMTCO can be prepared at low deposition temperatures,
- 5. and in the long term, a high mobility TCO based on more abundant and thus cheaper materials than indium.

### 5. Conclusion

Two types of high mobility TCO materials namely ITiO and IMO have been developed and compared to FTO and ITO thin films which are commercially available. When the high mobility TCO thin films are used as front contacts in CdTe solar cells, the NIR transmission can be enhanced as the parasitic absorption and reflection losses are minimised. Also, the need to develop a high mobility TCO as the back contact of the CdTe solar cells, in order to preserve the high NIR transmission, has been demonstrated. Therefore, further investigation and understanding of the doping mechanisms of HMTCO materials and their interfaces with solar cell absorber layers is expected to increase the efficiency of both multi-junction and bifacial solar cells.

#### Acknowledgement

One of the authors, SC, is grateful for the funding under a doctoral training grant by EPSRC, UK.

#### References

- T.J. Coutts, J.S. Ward, D.L. Young, K.A. Emery, T.A. Gessert, R. Noufi, Prog. Photovoltaics Res. Appl. 11 (2003) 359.
- [2] X. Wu, J. Zhou, A. Duda, J.C. Keane, T.A. Gessert, Y. Yan, R. Nouli, Prog. Photovolt: Res. Appl. 14 (2006) 471.
- [3] Y. Meng, X.L. Yang, H. Chen, J. Shen, Y.M. Jiang, Z.J. Zhang, Z.Y. Hua, Thin Solid Films 394 (2001) 219.
- [4] Y. Yoshida, D.M. Wood, T.A. Gessert, T.J. Coutts, Appl. Phys. Lett. Vol.84 (No.12) (2004) 2097.
- [5] A.E. Delahoy, L. Chen, M. Akhtar, B. Sang, S. Guo, Solar Energy 77 (2004) 785.
- [6] A.E. Delahoy, S.Y. Guo, J. Vac. Sci. Technol. A 23 (4) (2005) 1215.
- [7] M.F.A.M. van Hest, M.S. Dabney, J.D. Perkins, D.S. Ginley, M.P. Taylor, Appl. Phys. Lett. 87 (2005) 032111.
- [8] Y. Abe, N. Ishiyama, J. Mater. Sci. 41 (2006) 7580.
- [9] R. Hashimoto, Y. Abe, T. Nakada, Appl. Phys. Expr. 88 (2008) 015002-1.
- [10] S.S. Hegedus, S. Albright, F. Jeffrey, T.J. McMahon, S. Wiedeman, Prog. Photovoltaics Res. Appl. 5 (1997) 365.
- [11] T. Nakada, Y. Kanda, R. Hashimoto, T. Miyano, In Proceedings of the 22nd European Photovoltaic Solar Energy Conference, 2007, p. 1870.
- [12] J.W. Bowers, H.M.Upadhyaya, S. Calnan, R. Hashimoto, T. Nakada, A.N. Tiwari, Development of nano-TiO<sub>2</sub> dye sensitised solar cells on high mobility transparent conducting oxide thin films, Prog. Photovoltaics Res. Appl. (2008), doi:10.1002/pip.872.
- [13] J.A. Anna Selvan, A.E. Delahoy, S. Guo, Y.-M. Li, Sol. Energy Mater. Sol. Cells 90 (2006) 3371.
- [14] A.N. Tiwari, G. Khrypunov, F. Kurdzesau, D.L. Bätzner, A. Romeo, H. Zogg, Prog. Photovoltaics Res. Appl. 12 (2004) 33.
- [15] A. Romeo, H. Zogg, A.N. Tiwari, Proceedings of Second World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria, 1998, p. 1105.
- [16] U. Hiroshi, I. Seiji, S. Hajimu, Jpn. J. of Appl. Phys. 29 (1990) 2003.
  [17] A. Romeo, D.L. Baetzner, H. Zogg, C. Vignali, A.N. Tiwari, Solar Energy Mater. Solar Cells 67 (2001) 311.
- [18] T. Potlog, L. Ghimpu, P. Gashin, A. Pudov, T. Nagle, J. Site, Solar Energy Mater. Solar Cells 80 (2003) 327.