

Transparent conducting thin films by co-sputtering of ZnO-ITO targets

Paz Carreras, Aldrin Antony*, Rubén Roldán, Oriol Nos, Paolo.A Frigeri, José M. Asensi and Joan Bertomeu

Grup d'Energia Solar, Universitat de Barcelona, Martí i Franquès 1-11, E-08028, Barcelona, Spain

Received ZZZ, revised ZZZ, accepted ZZZ

Published online ZZZ (Dates will be provided by the publisher.)

PACS 81.15.Cd, 81.05.Gc, 78.66.Li, 73.61.Le, 79.60.-i

* Corresponding author: aldrinantony@ub.edu, Phone: +34934039223, Fax: +349340339219

Transparent and conductive ZnO-ITO (ZITO) amorphous thin films have been deposited by the rf magnetron co-sputtering of ITO (In_2O_3 with 10wt % SnO_2) and ZnO targets at room temperature. A constant rf power of 50W was used for the ITO target, whereas the rf power to ZnO target was varied from 25W to 150W. The zinc content ratio in the films was varied from 17 to 67% when the rf power to the ZnO was changed from 25W to 150W. A lowest resistivity of $6.6 \times 10^{-4} \Omega\text{cm}$, was achieved for the films with Zn content ratio 17%. A highest mobility of $4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed at lower zinc concentrations in the film. The carrier concentration decreased with in-

creasing Zn content from $5.0 \times 10^{20} \text{ cm}^{-3}$ for pure ITO to $6.7 \times 10^{19} \text{ cm}^{-3}$ for the films deposited at 150W for ZnO. The films showed an average transmittance over 80% in the visible wavelength range and due to the decreased free carrier density, the transparency in the near infra red region increased with increase in Zn content of the film. The band gap of the samples varied from 3.64 for the ITO to 3.28eV for the ZITO films with zinc content ratio 67%. The ZITO films deposited at room temperature with lower Zn content ratio showed better optical transmission and electrical properties compared to ITO film.

Copyright line will be provided by the publisher

1 Introduction Transparent conductive oxides (TCO's), which are highly degenerate wide band gap semiconductors, have attracted much interest due to their electrical and optical properties. Therefore, are widely used in optoelectronics such as solar cells [1] and liquid crystal displays [2]. Indium tin oxide (ITO) is one of the most used TCO because of its low resistivity and high transparency [3] but it deals with the drawback of toxicity, scarcity of the raw material [4] and high temperature deposition to get good properties [5]. ZnO seems to be the best substitute for ITO [4] because it has good electrical and optical properties although its resistivity is not as low as ITO's one. Multicomponent oxides, like $\text{In}_2\text{O}_3:\text{SnO}_2$ co-doped ZnO (ZITO), are an alternative option which would reduce the In content and would give the opportunity to control the properties varying the chemical content. Films of ZITO have the remarkable property of still being good conductors and present a higher transmittance in the visible and near infra-red part of the spectra.

In order to use TCO's on plastic materials or as back reflectors in p-i-n silicon thin film solar cells a low tem-

perature process is needed [6]. The radiofrequency (rf) co-sputtering of ITO and ZnO at room temperature will lead to an amorphous material. They are sometimes preferred over polycrystalline ones due to its low processing temperature and high uniformity of device characteristics [7].

Degenerate band conduction in amorphous oxide semiconductors containing post-transition metal cations (like Zn, Sn or In) will let relatively high mobilities to be achieved [7]. The bottom of the conduction band in these oxide semiconductors, characterized by its electronic configuration $(n-1)d^{10}ns^0$ with $n \geq 4$, is composed of spherically symmetric ns orbital with isotropic shapes and direct overlap with next ns orbital is possible [8]. This characteristic lets them to behave similarly to its polycrystalline phase [9].

In this study we investigated the structural electrical and optical properties of the ZITO deposited by radiofrequency magnetron co-sputtering by varying the power from 0 to 150 W, and consequently the content of ZnO from 0 to 67% as a method to overcome the problems found with ITO films.

Copyright line will be provided by the publisher

2 Experimental ZITO layers were deposited by rf magnetron co-sputtering of ZnO and ITO in pure argon gas atmosphere. The targets were 3 inch in diameter and with purities of 99.995% for ZnO and 99.99% in the case of ITO (In₂O₃ with 10 wt % SnO₂). A constant rf power of 50W was used for the ITO target, whereas the rf power to ZnO target was varied from 25W to 150W in steps of 25W (see Table 1, for sample identification). The target to substrate distance was kept at 12cm and a substrate rotation of 10 rpm was used to achieve uniform composition in the films during co-sputtering. These films were deposited onto 5×5 cm² Corning glasses (1737F) at a pressure of 2.6 mTorr without any intentional heating of the substrate. The deposition time was controlled to achieve a thickness around 215 nm for all the films.

Table 1 The deposition powers of the ZITO samples with the cation content estimated from XPS

Sample	ITO (W)	ZnO (W)	In (%)	Zn(%)	Sn(%)
ITO	50	0	89.3	0	10.7
ZITO25	50	25	75.5	17.1	7.5
ZITO50	50	50	57.6	36.6	5.8
ZITO75	50	75	46.7	48.5	4.8
ZITO100	50	100	41.8	53.8	4.4
ZITO125	50	125	34.5	62.8	2.7
ZITO150	50	150	30.2	67.3	2.6

The thickness of the film was measured by using a Dektak 3030 profilometer. The structure of the films was analysed using powder X-ray diffractometer (PANalytical X'Pert PRO MPD Alpha powder system) using copper K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) as the source. The film composition was analysed using X-ray Photoelectron Spectroscopy (XPS) with a PHI 5500 Multitechnique System from Physical Electronics. The optical transmission (T) and reflection (R) spectra were recorded by using a UV-vis-NIR spectrophotometer (Perkin Elmer Lambda 19). The sheet resistance was measured by using a four point probe system (Jandel RM3). Mobility (μ) and carrier concentration (n) were determined from the Hall effect

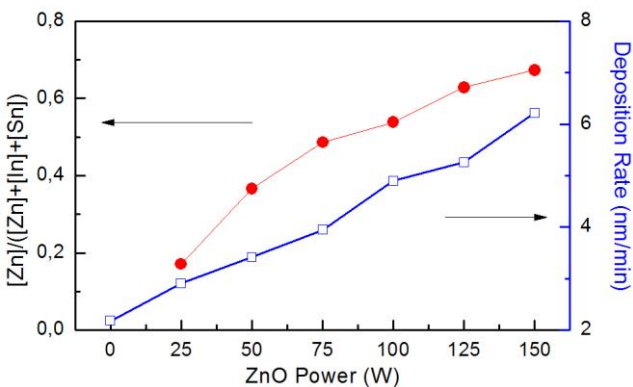


Figure 1: The growth rate and the Zn content ratio of the ZITO films deposited with different ZnO powers.

measurements by using standard Van der Pauw method in a magnetic field of 0.3T.

3 Results and discussion All the films showed good adhesion to the substrate and were physically stable. As the power of ZnO increased, the deposition rate increased linearly till it reached 6.2 nm/min at 150 W of ZnO and 50 W of ITO. It has to be considered that ITO has a deposition rate of 2.2 nm/min while ZnO shows a deposition rate of 1.2 nm/min at the same power (50W). This means that as we sputtered both the ITO content was almost twice for the same power. As we increased the ZnO RF power, the Zn content increased till it overcame the In content due to the increased sputtering rate of ZnO target. In our case this happened at 75W as can be seen in Table 1.

The composition of the films were analysed using XPS and the percentage of cations in the films with the sample identity are shown in Table 1. The Sn/In composition ratios were nearly constant (~ 0.10) in all the films, because both Sn and In came from the same ITO target. The plot of Zn content ratio in the film $[Zn]/([In]+[Sn]+[Zn])$ with the ZnO power is shown in Figure 1. The Zn content ratio varies from 17% for ZITO25 to 67.3% for ZITO150. The Zn content in the film is found to be proportional to the rf power applied to the ZnO target, therefore we will consider the rf power of ZnO to discuss the film properties.

The XRD profiles of the films are shown in Figure 2. All the films appeared to be amorphous in nature. The broad peak that appeared at around 25° corresponds to the Corning glass. Another halo peak is superposed with this and its maximum varies between 31.7° for ITO to 33.7° for ZITO150. This peak shift suggests the presence of a few grains changing its orientation from the ITO byxby cubic (111) to the wurtzite ZnO (001). However, we can-

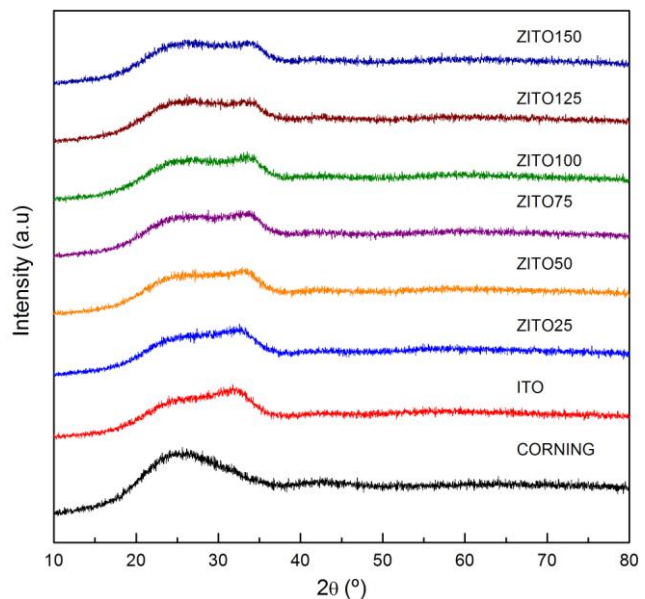


Figure 2: The XRD profiles of the ZITO films deposited with different ZnO powers.

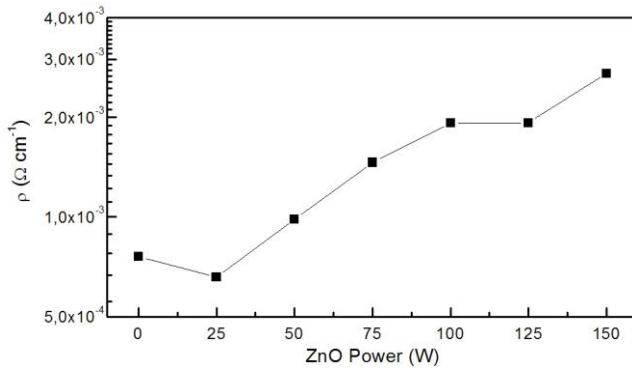


Figure 3: The resistivity of the ZITO films deposited with different ZnO powers.

not confirm any kind of crystallinity because the peak intensity is too low. Further studies should be done to confirm a possible hypothesis of nano grains.

The ITO film showed a resistivity of $7.58 \times 10^{-4} \Omega \text{cm}$. Resistivity of the as deposited ZITO samples slightly decreased as we started introducing ZnO (ZITO25) reaching the minimum value of $6.6 \times 10^{-4} \Omega \text{cm}$ for ZnO power of 25W corresponding to a Zn content ratio of 17%. Such low resistive ZnO-ITO films have been reported earlier for Zn content fraction of about 0.2 to 0.4. The low resistivity of the films deposited at room temperature with a lower Zn concentration is attributed to the formation of an amorphous-like ternary compound of $\text{Zn}_2\text{In}_2\text{O}_5$ [10]. The conductivity of ITO is due to the free carriers generated by the oxygen vacancies and from the substitutional doping of In^{3+} by the Sn^{4+} ions. When ZnO is added to ITO in relatively low concentrations, the Zn^{2+} ions may substitute Sn^{4+} , possibly due to the fact that the ionic radius of Sn^{4+} (0.71Å) is very close to that of Zn^{2+} (0.74Å), whereas the ionic radius of In^{3+} is 0.8Å. This may favour the formation of this ternary amorphous phase ($\text{Zn}_2\text{In}_2\text{O}_5$). At higher ZnO concentrations, may either fill the oxygen vacancies or the

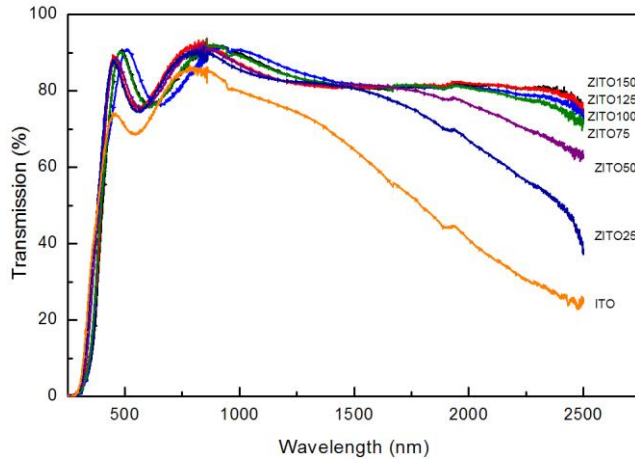


Figure 5: The transmission spectra of the ZITO films deposited with different ZnO powers.

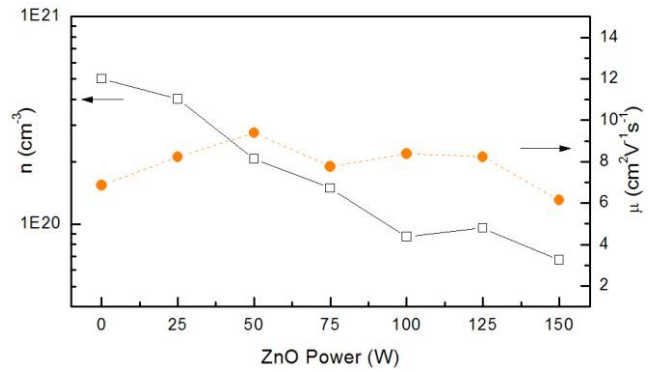


Figure 4: The variation of mobility and carrier concentration of the ZITO films deposited with different ZnO powers.

Zn^{2+} ions will occupy the In^{3+} sites resulting in an increase in resistivity. In our results, the films deposited with ZnO power around 50W and above showed an increase in resistance. The ZITO150 film which was deposited with a ZnO power of 150W showed a resistivity of $2.7 \times 10^{-3} \Omega \text{cm}$. The variation of resistivity of the asdeposited ITO and ZITO samples are shown in Figure 3.

The ZITO films showed electron concentration above $6.7 \times 10^{19} \text{cm}^{-3}$, whereas the as deposited ITO film showed $5.0 \times 10^{20} \text{cm}^{-3}$. The electron concentration was found to decrease with the ZnO power (Figure 4). The decrease in carrier concentration could be understood in terms of the carrier compensation due to Zn^{2+} occupying In^{3+} sites or due to the filling up of oxygen vacancies.

The variation of mobility of the ZITO films is shown in Figure 4. Mobility was found to be high for the films deposited with a rf power 25 to 50W. The highest value was $9.4 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for ZITO50 and the lowest was just $6.1 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for ZITO150. The films with the higher mobility at lower concentrations of Zn might be due to the formation of the amorphous like ternary compound as explained in the case of resistivity. The optical properties of the films were analysed using the transmission and reflectance spectra. The ITO film showed an average transmittance of 75% in the visible wavelength range (400-800nm) while the ZITO samples showed an average transmittance above 80% in all cases. The transmission spectra of the ITO and ZITO films are shown in Figure 5. The films showed an increase in transmittance in the near infrared region with the increase in Zn content in the film. This increase in transmittance is caused by the reduction in free carriers. The absorption coefficient (α) was determined from the transmittance and reflectance value by means of Eq. (3) [12].

$$T = (1-R)^2 e^{-\alpha d} \quad (1)$$

where d is the layer thickness, R is the reflectance and T is the transmittance.

For direct transitions, the absorption coefficient is given by Eq. 2 [11].

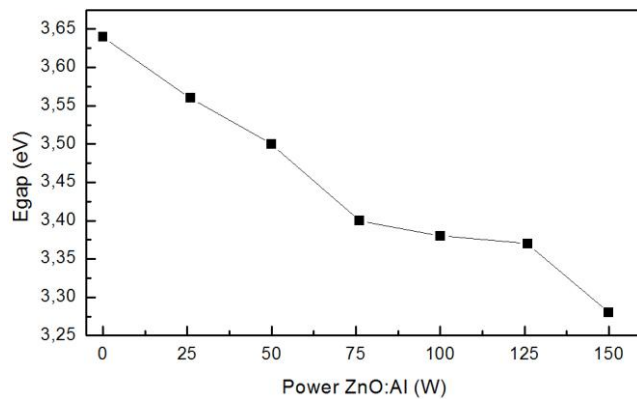


Figura 6: The optical band gap energies of the ZITO films deposited with different ZnO powers.

$$\alpha(h\nu) = A^*(h\nu - E_g)^{1/2} \quad (2)$$

where $h\nu$ is the incident photon energy, E_g is the bandgap energy and A^* is a constant.

The optical band gap energies of the films were deduced from the $(\alpha h\nu)^2$ against $h\nu$ plots. The ITO film showed a band gap of 3.64 eV and the band gap energy of ZITO films were found to decrease with the ZnO power (Figure 6). A lowest valued of 3.28 eV was obtained for ZITO150 film with a Zn content ratio of 67.3%. This band gap shrinkage can be understood in terms of the Moss-Burstein effect, where the decrease of the band gap is correlated with the decrease in carrier concentration.

4 Conclusions Amorphous transparent conducting, zinc indium tin oxide (ZITO) thin films have been developed by the rf magnetron co-sputtering of ITO and ZnO targets at room temperature. The film composition was varied by adjusting the power to the sputtering targets. The ZITO films with less Zn content showed better transmission and electrical conductivity than the ITO film. A lowest resistivity of $6.6 \times 10^{-4} \Omega \text{cm}$ was achieved for the ZITO films with less Zn content ratio of 17%. A highest mobility of $9.4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was observed for the films with 37% zinc content ratio. The carrier concentration and optical band gap was found to decrease with the increase in Zn content in the film. The ZITO films deposited at room temperature with better properties than ITO will find many applications in thin film solar cells, and also in transparent electronics where low temperature deposition is needed.

Acknowledgements This work has been supported by the Ministerio de Ciencia e Innovación through the projects CLASICO (ENE2007-67742-C04-03) and MICROSIL08 (PSE-120000-2008-1).

References

- [1] F. Villar, A. Antony, J. Escarré, D. Ibarz, R. Roldán, M. Stella, D. Muñoz, J. M. Asensi and J. Bertomeu, *Thin Solid Films* **517**, 3575 (2009).

- [2] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature* **432**, 488 (2004).
 [3] J.R. Bellingham, W.A. Phillips and C. J. Adkins, *J. Phys. Condens. Matter* **2** 6207 (1990).
 [4] T. Minami and T. Miyata *Thin Solid Films* **517**, 1474 (2008).
 [5] J. M. Park, J. J. Kim, H. M. Kim, J. H. Kim, S. W. Ryu and S. H. Park, *J. Korean. Phys. Society*, **48**, 1624 (2006).
 [6] J. Müller, B. Rech, J. Springer and M. Vanecek, *Solar Energy* **77**, 917 (2004).
 [7] K. J. Saji, M. K. Jayaraj, K. Nomura, T. Kamiya and H. Hosono, *J. Electrochem. Soc* **155**, H390 (2008).
 [8] H. Hosono, N. Kikuchi, N. Ueda, H. Kawazoe *J. Non-Cryst. Sol.* **198-200** (1996) 165- 169
 [9] S. Narushima, M. Orita, M. Hirano and H. Hosono, *Phys. Rev., B* **66** 035203 (2002).
 [10] D. S. Liu, C. C. Wu and C. T. Lee, *Japn. J. Appl. Phys.*, **44**, No.7A 5119. (2005).
 [11] J. I. Pankove, *Optical Processes in Semiconductors* (Dover Publications, New York, 1971), p. 93.