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A Marikkannan, J Dinesh, J. Mayandi, V Vishnukanthan, J. Pearce

Preprint: M. Marikkannan, A. Dinesh, J. Mayandi, V. Vishnukanthan, J.M. Pearce. Properties of Al-Doped Zinc Oxide and In-Doped Zinc Oxide Bilayer Transparent Conducting Oxides for Solar Cell Applications *Materials Express*. 222, (2018) pp. 50-53. doi:10.1016/j.matlet.2018.03.097

Properties of Al-Doped Zinc Oxide and In-Doped Zinc Oxide Bilayer Transparent Conducting Oxides towards Solar Cell Applications

M. Marikkannan[1], A. Dinesh[1], J. Mayandi[1*], V. Vishnukanthan[2, 3] and J. M. Pearce[4*]

[1]*Department of Materials Science, School of Chemistry, Madurai Kamaraj University, Tamil Nadu, Madurai-625021, India.*
[2] Department of Physics, Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126 Blindern, N-0318 Oslo, Norway.
[3]Department of Materials Science, National Research Nuclear University "MEPhI", 31 Kashirskoe sh, Moscow, Russian Federation
[4] *Department of Materials Science & Engineering, Michigan Technological University, USA*
* Contact author: *jeyanthinath.chem@mkuniversity.org*, *pearce@mtu.edu*

Abstract

Novel aluminum and indium doped zinc oxide bilayer transparent conducting oxide thin films have been developed by simple sol gel spin coating and annealed at 500 °C for an hour under nitrogen ambient towards solar cell applications. The structural, electrical and optical properties of both the as deposited and annealed bilayer thin films are characterized. X-ray diffraction studies showed a hexagonal wurtzite-type structure of ZnO with (002) orientation, which was enhanced with annealing. In atomic force microscopy studies minimum surface roughness is attained for the Al-doped ZnO/In-doped ZnO bilayer TCO films. The best Al-doped ZnO/In-doped ZnO films had sheet resistance of 0.057 M ohm/square and the films had an average transmittance in the visible region over 90%. Further results are discussed with single and bilayer structure.

Key words: AZO, IZO, Sol-gel spin coating, electrical and optical properties, solar cell applications.

I. INTRODUCTION

Transparent conducting oxides (TCOs) have been widely used for various kinds of optical and electrical devices due to their excellent combined electrical conductivity and optical transparency in the visible range of the electromagnetic spectrum [1]. Currently, the different types of TCO structures such as TCO/Metal/TCO and TCO/TCO have been proposed to enhance the TCO properties towards solar photovoltaic (PV) applications [2, 3]. The dominant TCO is indium tin oxide (ITO) as it shows moderate electrical resistivity and good transmittance in the visible range [4]. However, indium availability is a challenge, which has led to a rise in costs of this material every year [5]. There is thus a need to find a low-cost material for replacement of ITO. Among these materials, zinc oxide (ZnO), which has excellent electrical, optical, mechanical, and chemical sensing properties, as well as thermal stability and more widespread availability in earth (and concomitant lower costs of the material), has been widely used for a wide array of practical applications such as gas sensors, catalysis, liquid crystal display, light emitting diodes, electronics, solar PV cells, and transparent electrodes [5, 6]. Aluminium doped ZnO (AZO) and indium doped ZnO (IZO) films are attractive candidates in the opto-electronic industry due to their excellent electrical and optical properties [7, 8] and have attracted attention to replace the ITO films with low cost [7, 9]. AZO has attained high thermal stability, lowest sheet resistance, highest optical transmission, while the chemical sensitivity and mechanical properties are similar to the ITO [9, 10]. Zhao *et al*. prepared the AZO films by spin coating method and annealed using forming gas (H_2:N_2) ambient, they achieved necessary electrical and optical properties for solar cell applications [11]. Likewise, IZO thin films exhibit superior electrical conductivity and optical transmission in the visible region and is widely used for device applications [12]. Hence

AZO and IZO thin films have become the most attractive materials in the past decades [13, 14]. To build on this past work, the main motivation of the present work is to investigate the alternative TCO bilayer composed films to substitute the ITO films.

II. EXPERIMENTAL

The AZO and IZO layers were prepared by sol-gel process [5]. The dopant level of aluminum in zinc is 1.5 at %. The solution is aged for 24 hours at room temperature. Then the single layer AZO precursor solution was spun on the cleaned glass substrate at a rotation speed of 3,000 rpm for 30s in air. The wet precursor films were placed on a hot plate for 10 minutes at 400 ºC in air to evaporate the solvent and annealed at 500 °C for an hour under nitrogen ambient.

III. RESULTS AND DISCUSSIONS

Fig. 1(A). depicts the ZnO, AZO, IZO, AZO/IZO and IZO/AZO films annealed in nitrogen ambient at 500 ºC for an hour. The results show that all the films had the expected hexagonal wurtzite structure of ZnO. They were highly oriented along the (002) plane and it indicates the preferred orientation along the crystallographic c-axis and perpendicular to the glass substrate.
The minor higher angle shift was exhibited for the AZO, AZO/IZO and IZO/AZO films (shown in the Fig.1 B). A similar trend has been reported for AZO films deposited by magnetron sputtering [15]. However, the IZO showed a lower angle shift and it was ascribed to the change in the ionic radius of Zn^{2+} (0.074 nm) and In^{3+} (0.080 nm) [16, 17], which induced stress in the IZO films. The crystallinity of the films were changed with respect to the single layer and bilayer AZO and IZO films as the crystalline nature of the AZO/IZO films increased over the single layer. In this present results, the observed diffraction lines were in good agreement with previously reported results [18]. The full width at half maximum values obtained such as 0.38, 0.37, 0.45, 0.40 and 0.42º for ZnO, AZO, IZO, AZO/IZO and IZO/AZO nanostructures, respectively and its reflected grain size values are shown in Table 1.

Fig. 2 (a-d) depicts the surface topography from atomic force microscopy (AFM) of AZO, IZO, AZO/IZO and IZO/AZO thin films, which were annealed at 500 ˚C in nitrogen ambient for an hour. From the result, it is observed that the surface roughness (rms) value of the AZO, IZO and AZO/IZO and IZO/AZO films were 4.78, 4.92, 15.58 and 26.19 nm, respectively. The roughness of the films were increased with respect to the thickness of the TCO film. Similar trends has been observed for the bilayer AZO films deposited by pulsed laser technique and the roughness was increased upto 30.74 nm [19]. The highest roughness value was attained for IZO/AZO films. Fig. 2 (c) indicates that the IZO layer was entirely covered by the AZO layer as most of the IZO surface spikes were covered with AZO layer. So it decreases the surface roughness of AZO/IZO bilayer TCO film and enhance the transmission properties. The heat treated AZO layer microstructure was increased with more porosity and it showed a highest average optical transmission in the visible range [20].

The sheet resistance values of ZnO, AZO, IZO, AZO/IZO and IZO/AZO films was measured using four probe technique. From the observed values, the minimum sheet resistance was 0.057 M Ω/□ achieved for the AZO/IZO bilayer TCO annealed in nitrogen ambient and the highest value (104.20 M Ω/□) was attained for the as deposited ZnO film. Similar results have been reported for CdO/ITO coated on glass substrates [21]. The optical transmittance spectra for the as deposited and nitrogen ambient annealed TCO films are shown in Fig.3. (A) and (B), respectively. Fig.3 (A) and (B). shows all the as deposited and annealed TCOs films which attained more than 95% in the visible region (400-800 nm) of the electromagnetic spectrum. The typical transmittance spectrum clearly indicates that the observed values were in the range from 96 to 97%. In these results, the highest optical average transmittance 97.92 % was observed for as deposited ZnO films. Duan *et al.* reported the oxygen and nitrogen ambient annealed Mg, Al, and Co doped ZnO thin films exhibited the highest optical transmittance, which is compared to the vacuum annealed films [22]. The sol gel method based AZO films exhibited the lowest resistivity1.8 × 10^{-3} Ω cm and higher optical transparency 90% wavelength over 400 nm [11]. Compare to the AZO film result, this present AZO/IZO bilayer structure observed the higher optical transmittance and sufficient sheet resistance for solar cell applications. The extrapolation of **$(\alpha h\upsilon)^2$ vs $h\upsilon$** plots (not shown here) and the linear region of the graph to the axis gives the band gap energy of the respective material [23]. The estimated band gap values varied from 3.22 to 3.30 eV and the values depend on the different layers and annealing nature of the bilayer films. In this present work, we have observed the optical band gap of as deposited ZnO films at 3.28 eV, which is in good agreement with previously reported band gap values of the ZnO thin films [23]. Here, the highest optical band gap observed (3.30 eV) was for AZO nitrogen ambient annealed films. Lin *et al.* reported a blue shift increases with the increment of the Al/Zn ratios [10]. The AZO has been found to be the highest value compared to the intrinsic value. Also, the projected IZO band gap was ~3.26 eV for as prepared and annealed films.

IV. CONCLUSION

In summary, novel AZO/IZO and IZO/AZO bilayers TCOs using simple cost-effective sol gel synthesis annealed under nitrogen ambient have been developed towards solar cell applications. From the structural results, it is clear the films were oriented along the (002) reflection with the hexagonal wurtzite structure. The AFM result shows the minimum surface roughness was obtained for the AZO/IZO bilayers. In the electrical and optical results, the minimum sheet resistance (0.057 M Ω/⇔) and highest average transmission 96.80% was detected for the AZO/IZO bilayer TCO film. All the prepared TCO films, the AZO/IZO films were observed to have good electrical and optical properties and it could be used as TCO electrodes for solar cell applications after the hydrogen annealing treatment. However, more optimization and hydrogen ambient annealing treatment is required to improve electrical properties of the bilayer structures to utilize for specific applications.

REFERENCES

1. M. Marikkannan, M. Subramanian, J. Mayandi, M. Tanemura, V. Vishnukanthan, J.M. Pearce, AIP Advances. 5 (2015) 017128-017138.
2. S. Calnan, A. N. Tiwari, Thin Solid Films. 518 (2010) 1839–1849.
3. N. Chantarat, S.-H. Hsu, C.-C. Lin, M.-C. Chiang, S.-Yuan Chen, J. Mater. Chem. 22 (2012) 8005-8012.
4. H. Izumi, F. O. Adurodija, T. Kaneyoshi, T. Ishihara, H. Yoshioka, M. Motoyama , J. Appl. Phys. 91 (2002)1213-1218.
5. B. Nasar, S. Dasgupta, D. Wang, N. Mechau, R. Kruk, H. Hahn, J. Appl. Phys. 108 (2010) 103721-103726.
6. N. Park, K. Sun, Z. Sun, Y. Jing, D. Wang, J. Mater. Chem. C. 1 (2013) 7333-7338.
7. J.P. Lin, J.M. Wu, Appl. Phys. Lett. 92 (2008) 134103-134105.
8. E.L. Kim, S. K. Jung, S. H. Sohn, D. K. Park, J. Phys. D: Appl. Phys. 40 (2007) 1784-1788.
9. C. Huang, M. Wang, Q. Liu, Y. Cao, Z. Deng, Z. Huang, Y. Liu, Q. Huang, W. Guo, Semicond. Sci. Technol. 24 (2009) 095019-095024.
10. J.P. Lin, J.M. Wu, Appl. Phys. Lett.92 (2008) 134103.
11. X. Zhao, H. Shen, C. Zhou, S. Lin, X. Li, X. Zhao, X. Dengc, J. Li, H. Lin, Thin Solid Films, 605 (2016) 204-214.
12. S. S. Shinde, P. S Shinde, C. H. Bhosale, K. Y. Rajpure, J. Phys. D: Appl. Phys. 41 (2008) 105109-105114.
13. F.H. Wang, H-P. Chang, C-C Tseng, C-C. Huang, H-W. Liu, Physics. 11, (2011) S12.

14. P. M. Ratheesh Kumar, C. Sudha Kartha, K. P. Vijayakumar, T. Abe, Y. Kashiwaba, F. Singh, D. K. Avasthi, Semicond. Sci. Technol. 20 (2005) 120-126.
15. M-C. Jun, S-U. Park, J-H Koh, Nano. Res. Lett. 7 (2012)1-6.
16. J-H. Lee, B-O. Park, Thin Solid Films. 426 (2003) 94-99.
17. B. Murali, J. Parui, M. Madhuri , S.B. Krupanidhi, J. Phys. D: Appl. Phys. 48 (2015) 015301.
18. J.H. Lee, C.-Y. Chou, Z. Bi, C.-F. Tsai, H. Wang, Nanotechnology. 20 (2009) 0395704-7.
19. H.A.-H. Mohamed, H.-M., Sci.Technol.Adv. Mater. 9 (2008) 025016-9.
20. J. Liu, A.-W. Hains, J.D. Servaites, M.A. Ratner, T.J. Marks, Chem. Mater.21 (2009)5258-5263.
21. L.B. Duan, X. R. Zhao, J. M. Liu, W. C. Geng, H. Y. Xie, H. N. Sun, Phys. Scr. 85 (2012) 035709-7.
22. A. Leenheer, J.D. Perkins, M. F.A.M. Van Hest, J.J. Berry, R.P.O'Hayre, D. S. Ginley, Physical Review. B 77 (2008) 115215-5.

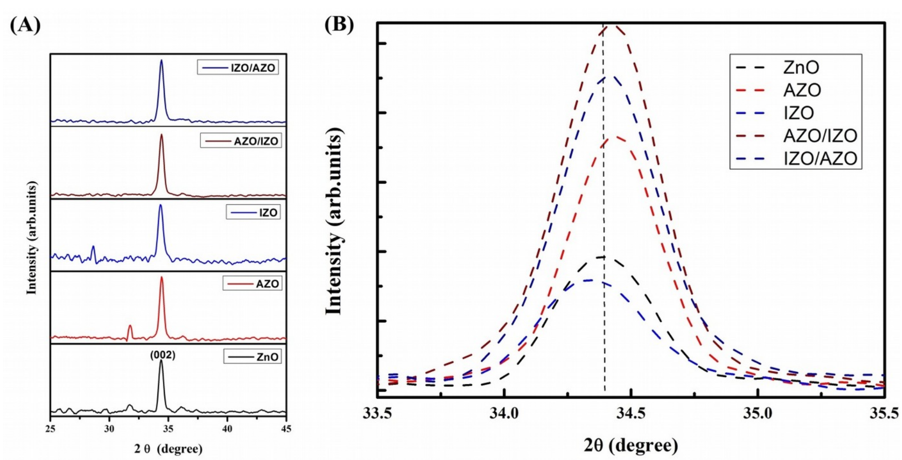
23. N. Park, K. Sun, Z. Sun, Y. Jing, D. Wang, J. Mater.Chem.C.1 (2013) 7333-7338.

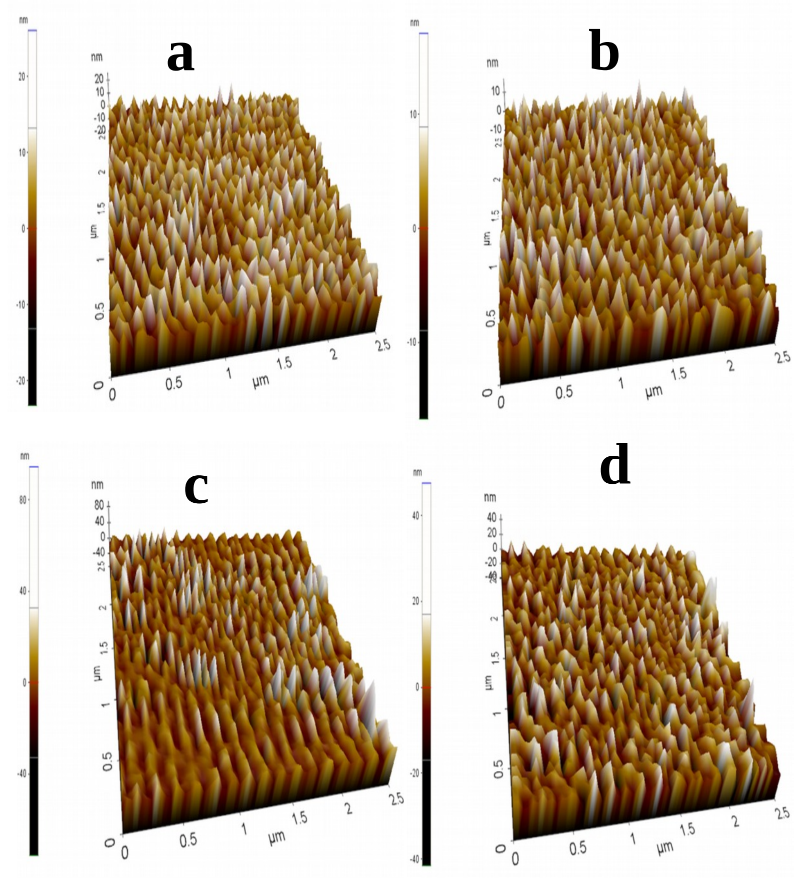
Figure Captions

Fig. 1 (A). XRD patterns of ZnO, AZO, IZO, AZO/IZO and IZO/AZO thin films annealed at nitrogen ambient (B). enlarged XRD spectra for single layer and bilayer TCO films

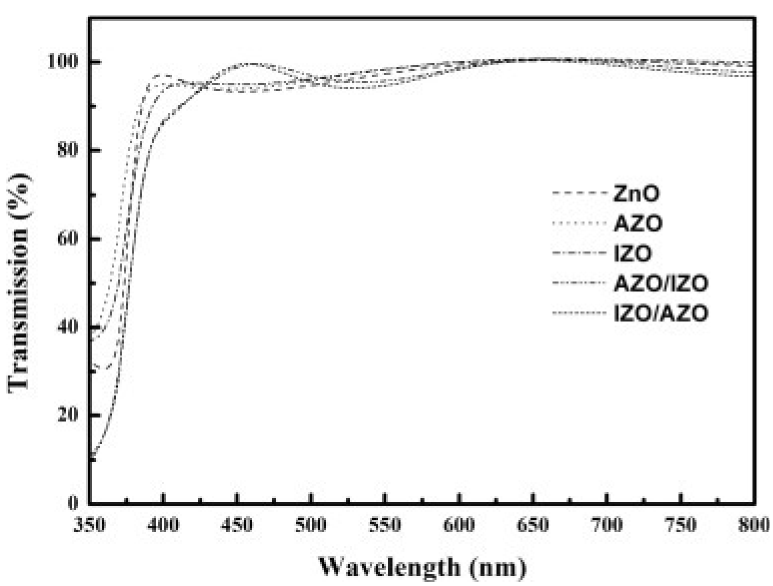
Fig.2. AFM 3D images for (a) AZO (b) IZO (c) AZO/IZO and (d) IZO/AZO thin films annealed in nitrogen ambient

Fig.3. Optical transmission spectra measured for (a) as deposited and (b) annealed TCO single and bilayer films





a
b
c
d



Transmission (%)
Wavelength (nm)
ZnO
AZO
IZO
AZO/IZO
IZO/AZO

Table Captions

Table.1. Structural parameters of ZnO,AZO,IZO and AZO/IZO and IZO/AZO TCO films

Sample	d Spacing (Å)	Lattice Constant (Å)	Grain size (nm)	Micro Strain (ε)	Net Lattice Distortion	Bond Length (Å)
ZnO	2.605	5.210	22	0.090	0.0010	1.98
AZO	2.603	5.205	23	0.087	-0.0006	1.97
IZO	2.609	5.217	19	0.107	0.0023	1.98
AZO/IZO	2.604	5.208	21	0.096	0.0005	1.97
IZO/AZO	2.604	5.208	20	0.099	0.0005	1.97