EFFECT OF POST ANNEALING ON SURFACE MORPHOLOGY, ELECTRICAL AND OPTICAL PROPERTIES OF DC REACTIVE MAGNETRON SPUTTERED ZINC ALUMINUM OXIDE THIN FILMS FOR OPTOELECTRONIC DEVICES

B.RAJESH KUMAR[a,b*], T. SUBBA RAO[b]
[a]*Department of Physics, Sri Venkateswara University, Tirupati-517502, A.P, India*
[b]*Materials Research Lab, Department of Physics, S.K.University, Anantapur-515003, A.P, India*

In the present work Zinc Aluminum Oxide (ZAO) thin films were deposited on glass substrate using DC reactive magnetron sputtering method. The thin films were post annealed at 200 ^{o}C after deposition for 15 min, 30 min, 45 min, 60 min and 90 min. The grain size obtained from SEM images of ZAO thin films are found to be in the range of 20 – 26 nm. The resistivities of annealed ZAO films are found to be in the range of 8.8 X 10^{-4} Ω.cm to 3.2 X 10^{-4} Ω.cm. All films exhibit an average transmittance of >85% in visible region. The optical band gap of nanostructured ZAO thin films increased from 3.49 to 3.60 eV with increase of annealing time due to Burstein-Moss effect.

(Received August 28, 2012; Accepted October 10, 2012)

Keywords: ZAO thin films, DC magnetron sputtering, Scanning electron microscope, Optical transmittance

1. Introduction

Transparent conducting oxide (TCO) films have been widely used in optoelectronic applications such as flat panel displays and transparent electrode in solar cells. Recently Al doped zinc oxide films have attracted much attention as transparent and conductive film materials because they exhibit a wide band gap, high transparency and low resistivity. ZAO has a lot of advantages such as non-toxicity, low cost and high stability against hydrogen plasma [1-6]. ZAO thin films have been prepared by several techniques such as RF sputtering process [7], sol-gel method [8], pulsed laser deposition (CVD) [10]. Among these processes, the sputtering process is one of the best methods for preparation of Zinc Aluminum Oxide (ZAO) films because it has a lot of advantages such as low substrate temperature, good surface roughness, and low cost [11-14]. In the present study the effect of post annealing time on surface morphology, electrical and optical properties of ZAO films were investigated. This paper reports the first observation of ZAO thin films sputtered by taking two individual metal targets of Zn and Al.

2. Experimental details

Zinc oxide thin films were prepared by DC reactive magnetron sputtering technique. High purity metal targets of Zn (99.999%) and Al (99.99%) with 2 inch diameter and 4 mm thickness are used for deposition on glass substrates. The base pressure in chamber was 3.5 - 4.5 X 10^{-6} Torr and the distance between target and substrate was set at 60 mm. The glass substrates were ultrasonically cleaned in acetone and ethanol, rinsed in an ultrasonic bath in deionized water for 15 min, with subsequent drying in an oven before deposition. High purity (99.99%) Ar and O_2 gas

* Corresponding author: rajphyind@gmail.com

was introduced into the chamber and was metered by mass flow controllers (Model GFC 17, Aalborg, Germany) for a total flow rate fixed at 30 sccm. Deposition was carried out at a working pressure of 2 mTorr after pre-sputtering with argon for 10 min. The O_2 flow rate is fixed at 2 sccm and the deposition time is 25 min. The sputtering power of Zn was ~ 105 W and sputtering power of Al was maintained at 40 W during deposition. The films were post annealed at 200°C after deposition for 15 min, 30 min, 45 min, 60 min and 90 min. Film thickness was measured by Talysurf thickness profilometer. The resulting thickness of all the films is about ~300 nm. Optical transmittance of the films was recorded as a function of wavelength in the range of 300 – 1200 nm using JASCO Model V-670 UV-Vis-NIR spectrophotometer (Japan). Surface morphology of the samples has been studied using HITACHI S-3400 Scanning Electron Microscope (SEM). The elementary composition of the films was determined from results obtained from Energy Dispersive X-ray Spectroscopy (EDS, Horiba EMAX, 137 eV).

3. Results and discussion

Fig. 1 shows the SEM images of ZAO films post annealed at 200 °C for 15 min, 30 min, 60 min and 90 min. The grains in the SEM probably are the domains formed by aggregation of nanoscale crystallites. The nanocrystalline surface of ZAO thin films exhibits coalescence of the grains. The grain size obtained from SEM images of ZAO thin films are found to be in the range of 20 – 26 nm. This surface morphology can enhance light trapping for solar cells. The compositional elementary data determined from EDS is shown in Fig. 2 for the ZAO film annealed at 200 °C for 30 min.

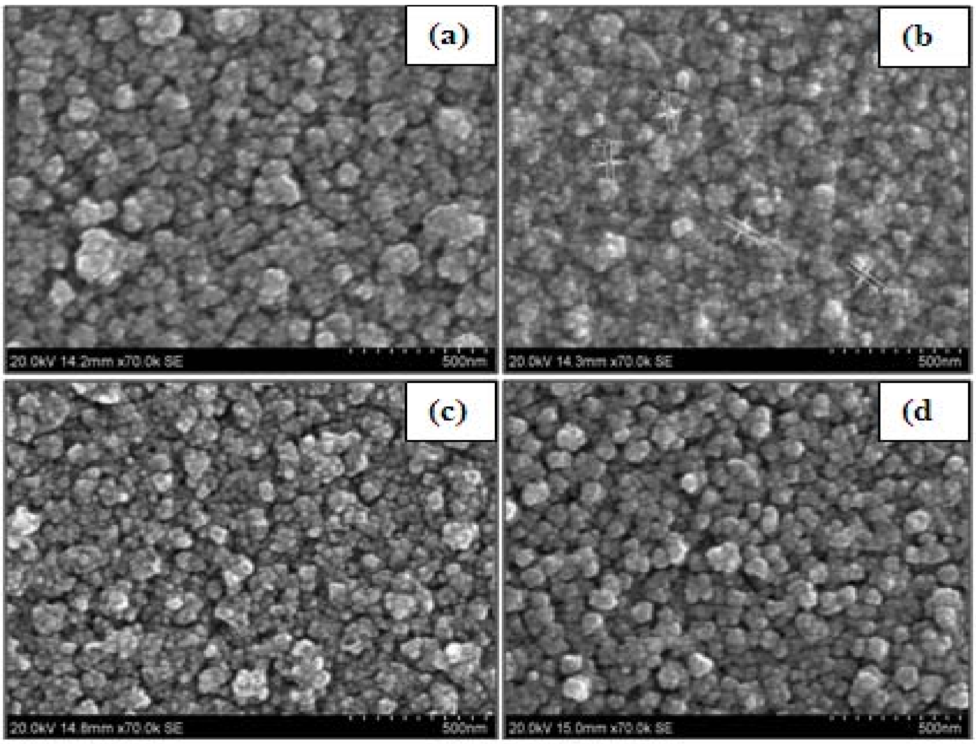

Fig. 1 SEM images of ZAO thin films post annealed at 200 °C for (a) 15 min (b) 30 min (c) 60 min and (d) 90 min.

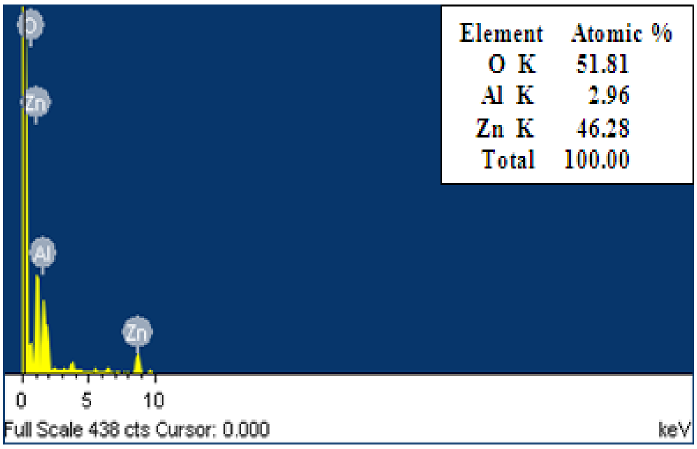

Fig. 2 EDS plot for ZAO thin film post annealed at 200 °C for 30 min.

The electrical properties of ZAO films were analyzed because of the strong influence they exert on the final performance of the optoelectronic devices such as solar cells. The electrical resistivity of the ZAO films was investigated by four-point probe method at room temperature. Fig. 3 shows the variation of the resistivity of ZAO films deposited on glass substrates at different annealing times. The electrical resistivity is in the range of 8.87 X 10^{-4} Ω.cm – 3.2 X10^{-4} Ω.cm. The lowest resistivity of 1.74X 10^{-4} Ω.cm is obtained for the thin film post annealed at 200°C for 30 min.

The sheet resistance of the film (R_s) was calculated using the equation

$$R_s = \frac{\rho}{t} \ \Omega/sq \quad (1)$$

where t is the film thickness. The sheet resistance values for the films annealed for 15 min, 30 min, 60 min and 90 min are 25.3, 5, 6.6 and 9.1 Ω/sq respectively.

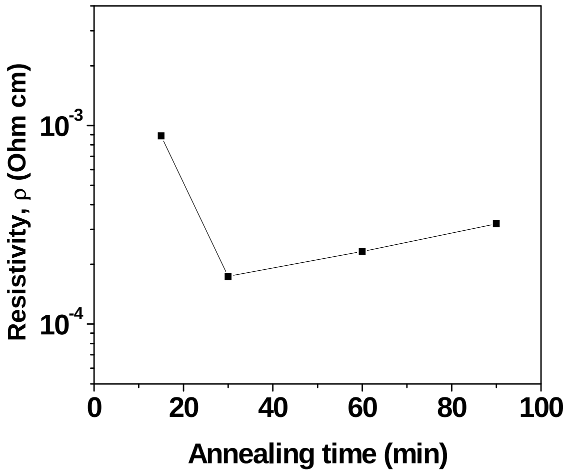

Fig. 3 Electrical resistivity of ZAO thin films as function of post annealing time

Fig. 4(a) shows the optical transmission spectra of ZAO thin films post annealed at 200 °C from 15 min to 90 min. All films exhibit an average optical transmittance of > 85% in the visible range and a sharp fundamental absorption edge. The maximum average optical transmittance of 92% and a minimum resistivity is obtained for the ZAO film deposited post annealed for 30 min which can be used in photovoltaic devices either as front electrode or back side reflector.

The absorption coefficient α is calculated using Lambert's law

$$\alpha = \ln (1/T) / t \qquad (2)$$

where T is the transmittance and t is the film thickness.

Absorption coefficient (α) decreases with increase of wavelength (λ). The absorption coefficient (α) is found to be in order of 10^6 cm^{-1} at shorter wavelength regions. For higher values of photon energy, the energy dependence of absorption coefficient ($\alpha > 10^4$ cm^{-1}) suggests the occurrence of direct electron transitions.

Optical band gap, E_g is determined from the dependence of absorption coefficient values (α) on the photon energy, using Tauc's relation [15]

$$(\alpha h\nu) = B (h\nu - E_g)^{n} \qquad (3)$$

where B is a parameter that depends on the transition probability, E_g is the optical band gap energy of the material, hν is the photon energy and n is an index that characterizes the optical absorption process and is theoretically equal to 2 and ½ for indirect and direct allowed transitions respectively. The optical band gap is determined from the Tauc's plot $(\alpha h\nu)^2$ versus (hν) shown in Fig. 4(b).

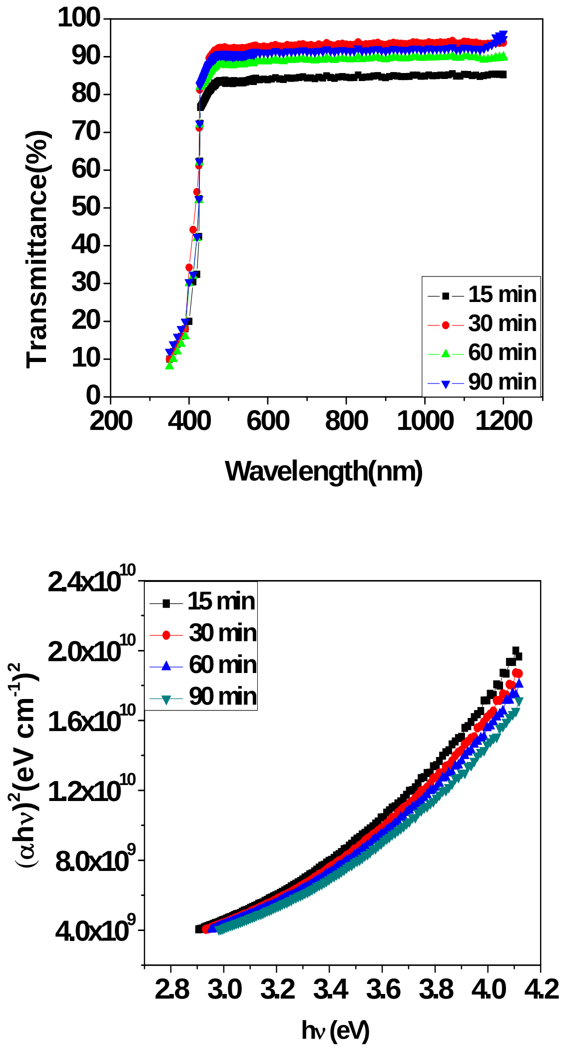

Fig. 4 (a) Optical transmission spectra and (b) Tauc's plot for post annealed ZAO thin films

The optical band gap values for the thin films post annealed at 200 °C for 15 min, 30 min, 60 min and 90 min are obtained as 3.49 eV, 3.51 eV, 3.56 eV and 3.60 eV respectively. The increase of band gap with annealing time is mainly due to the Burstein-Moss effect, which implies an increase in the Fermi level in the conduction band of semiconductors due to increase carriers, leading to widening of optical band-gap. The energy band gap widening ΔE_g is related to carrier concentration through the following equation [16]

$$\Delta E_g = \left(\frac{h^2}{8m^*}\right)\left(\frac{3N}{\pi}\right)^{\frac{3}{2}} \quad (4)$$

where h is the Planck constant, m* is the electron effective mass in conduction band, and n is the carrier concentration. From equation (4) it can be found that the energy band gap widening increases with increases of carrier concentration of ZAO thin films. The carrier concentration of ZAO thin films are determined from equation (4) and its is found to be in the range of 7 X 10^{20} cm^{-3} – 1.38 X 10^{21} cm^{-3}. The carrier concentration increases with increase of annealing time.

Figure of merit (Φ) is the quantity to judge the quality of the transparent conducting oxide films. The figure of merit of the films was evaluated from the optical transmittance and sheet resistance (R_s) using the Haacke's relation [17].

$$\Phi\ (\Omega^{-1}) = \frac{T^{10}}{R_s} \quad (5)$$

where T^{10} is the average optical transmittance and R_s is the sheet resistance. The best figure of merit with 8.7 X 10^{-2} Ω^{-1} and sheet resistance of 5 Ω/sq is obtained for the film post annealed for 30 min.

4. Conclusions

Zinc Aluminum Oxide thin films have been deposited on glass substrates at 200 °C by DC reactive magnetron sputtering technique by varying post annealing time from 15 min to 60 min. The minimum resistivity of 1.74 X 10^{-4} Ω.cm and an average transmittance of 92% is obtained for the thin film post annealed at 200 °C for 30 min, which can be used for photovoltaic devices either as front electrode or back side reflector. The properties of films produced at optimum condition are suitable for optical and electrical applications owing to their low resistivity, high optical transmittance in the visible range.

Acknowledgements

The authors are thankful to UGC, New Delhi, India for financial support under the major research project (F.NO.37-346/2009, SR).

References

[1] X.J.Jiang , F.L.Wong, M.K.Fung, S.T.Lee, Appl.Phys.Lett. **83**, 1875 (2003).
[2] Z.L. Pei, C.Sun, M.H. Tan, J.Q. Xiao, D.H. Guan, R.F.Huang, L.S. Wen, J.Appl.Phys. **90**, 3432 (2001).
[3] R.Cebulla, R.Wendt, K.Ellmer, J.Appl.Phys, **83,** 1087 (1998).
[4] E.G.Fu, D.M. Zhuang,G. Zhang, M. Zhao, W.F.Yang, J.F.Liu, Microelectron. J, **35**, 383 (2004).
[5] D.Song, A.G. Aberle, J. Xia, J. Appl.Surf.Sci. **195**, 291 (2002).
[6] J.M.Ting, B.S. Tsai, Mater.Chem.Phys. **72**, 273 (2001).
[7] F.Quaranta, A.Valentini, F.R.Rizzi, J.Appl.Phys. **74**, 247 (1993).
[8] M.Ohyama, H. Kozuka, T.Yoko, Thin Solid Films **306**, 78 (1997).
[9] V.Cracium,J. Elders, J.G.E. Gardeniers, Appl.Phys.Lett. **65**, 2963 (1994).
[10] S.K.Ghandhi, R.J.Field, J.R.Shealy, Appl.Phys.Lett. **37**, 449 (1980).

[11] S.S.Lin, J.L.Huang, D.F.Lii, Surf.Coat.Technol. **176**, 173 (2004).
[12] F.K.Shan, Y.S.Yu. J.Eur.Ceram.Soc. **24**, 1869 (2004).
[13] D.H.Zhang, Q.P. Wang, Z.Y. Xue, Appl.Surf.Sci. **207**, 20 (2003).
[14] Q.P. Wang, D.H. Zhang, H.L.Ma ,Z.H. Zhang, X.J.Zhang, Appl.Surf.Sci. **220**, 12 (2003).
[15] J.Tauc, R. Grigorovici, A.Vancu, Physica Status Solid, **15**, 627 (1966).
[16] F.Urbach, Phys.Rev. **92**, 1324 (1953).
[17] G. Haacke, J. Appl. Phys. **47**, 4086 (1976).