Study of ZnO: Al Thin Films Prepared by RF Magnetron Sputtering under Different Ar Flow

Rajesh Das[1] Sayani Bindai[2] Himadri Sekhar Das[3]
[1,3]Haldia Institute of Technology, Haldia, West Bengal, India [2]Maulana Abul Kalam Azad University of Technology, West Bengal, India

Abstract— Transparent conductive ZnO: Al thin films with different Ar flow (from 30 to 60 sccm with a step of 10 sccm) with sputtering power of 150 W were prepared on the Coring glass substrate by using rf magnetron sputtering. The lowest resistivity of 3.7×10-4 Ω-cm and highest transmittance of 90% was obtained at Ar flow of 40 sccm. Transmittances for all thin films are about 80-90 % in the visible range. The observed property of the ZnO:Al thin films is suitable for transparent conductive electrode applications.

Key words: ZnO:Al, RF Magnetron Sputtering, Transparent Conductive Oxides, Ar Flow

I. INTRODUCTION

Transparent conductive oxides (TCOs) have been extensively studied because they are essential elements in thin film optoelectronic devices applications such as thin film solar cells, flat-panel displays, and light emitting diodes [1-3].Transparent conducting oxide (TCO) thin film is a special type of materials with wide band gap oxide (>3eV), high optical transmittance (≥ 85%) over wide range of solar spectrum, and low sheet resistance. Main important TCOs are Fluorine doped tin oxide (FTO), Indium tin oxide (ITO), Aluminum doped zinc oxide (ZnO:Al), Antimony doped tin oxide (ATO), Galium doped Zinc Oxide (ZnO:Ga), Galium doped Indium Zinc Oxide (IZO:Ga), and Indium doped Cadmium Oxide thin films. Other Ternary Compounds based TCO Materials are Zn_2SnO_4, $MgIn_2O_4$, $CdSb_2O_6$:Y, $ZnSnO_3$, GaInO, $Zn_2In_2O_5$ and $In_4Sn_3O_{12}$ etc. Among all TCO thin films Fluorine doped tin oxide (FTO), and Indium tin oxide (ITO) are commercially available for different device applications and the others are under lab scale development stage. TCO thin films have wide applications such as in micro-electronic devices, displays, thin film transistor, light emitting diodes (LEDs), solar cells and other photonic devices [4-9]. Though indium tin oxide (ITO) film is extensively applied to photovoltaic devices and flat panel display because of its good electrical and optical properties, it has some problems such as high cost, low stability to H_2 plasma and toxicity. Aluminum-doped zinc oxide thin films are make a compete as transparent conductive oxide (TCO) films prepared materials due to the advantages of ZnO:Al films are cheap and abundant elements [10]. In addition, AZO thin films have an excellent chemical stability and specific electronic/optical properties of a wide band gap (Eg=3.4 to 3.9) semiconductor. Therefore, AZO thin films are usually used as transparent conducting electrodes in solar cells. Several studies using different deposition methods have been reported, such as sol-gel processes [11], pulsed laser deposition [12], sputtering [13] and molecular beam epitaxy [14]. RF (Radio-Frequency) Sputtering method is an effective technique due to its ability to produce reasonable quality thin films at a high deposition rate [15]. Based on the progress in the previous works, it is important to better understand the influences of rf magnetron sputtering at different Ar flows and sputtering power to obtain the optimum conductivity and transmittance.

In this study ZnO: Al thin films were prepared by using the rf magnetron sputtering at different Ar flows (from 30 to 60 sccm) with sputtering power 150W to examine the optical and electronic properties. Transmittance of all films is about 80 - 90 % in the visible range. The lowest resistivity of 3.7×10^{-4} Ω-cm (18.5Ω/sq) and highest transmittance of 90 % was obtained at sputtering power of 150 W and Ar flow of 40 sccm. The observed property of the ZnO:Al thin films is suitable for transparent conductive electrode applications.

II. EXPERIMENTAL

ZnO:Al thin films were deposited by dual-target RF magnetron (powered at 13.56 MHz radio frequency) sputtering system (Hind High Vacuum Co. (P) Ltd) on glass substrate at substrate temperature $T_s=250^0C$ under environment with different Ar ambient. Sintered ceramic disc of Al doped ZnO (ZnO:Al 98:2 wt%) with a purity of (99.99%) having 2 inch diameter and 5mm thickness were used as sputtering target. The process chamber is evacuated up to a base vacuum of 3.5×10^{-6} mbar. The RF power was 150W. Target to substrate distance was kept at 8 cm for all experiments. The modified chamber design is helpful for uniform ZnO thin film growth with high deposition rate and good adhesion with the substrate material.

The electrical properties of ZnO:Al thin films such as Carrier concentration and mobility have been measured attached by using highly sophisticated Hall measurement (Ecopia-HMS-3000) set-up by 4-probe van-der-Pauw technique. Optical transmittance (specular, diffuse and total) and absorbance data of ZnO thin films was measured using microprocessor controlled UV-VIS (Perkin-Elmer Lamda-35) spectrophotometer (Integrating sphere attached). The thickness of the deposited films was measured DTM incorporate with the rf magnetron sputtering system (Hind High Vac Ltd.). Structural characterization of ZnO films was carried out by Crystallographic phase analysis X-ray diffraction (XRD) (Philips PW 1710 diffractometer) (Cu K_α, λ=1.54178 Å, 2θ scan mode).Surface topography of ZnO:Al films was studied by Atomic Force Microscopy (AFM) (Tap 300 G).

III. RESULTS AND DISCUSSIONS

The crystalline structure and preferential orientation of ZnO:Al thin films were examined by X-ray diffraction(XRD).The XRD spectrum is quite similar for all the ZnO films shown in Fig.1. ZnO:Al films shows polycrystalline nature with (002) preferred orientation along C-axis with hexagonal wurtzite structure. With the variation of the Ar flow the peak position of the diffraction peak were not changed it indicates that the structure of ZnO:Al thin films are maintained. As the Ar flow was increased to 40 sccm, the peak intensity increased to a maximum and then decreased at 60 sccm. The results show the good crystallinity with large grain size of the Ar flow at 40 sccm due to the smallest full width at half maximum (FWHM) [16].

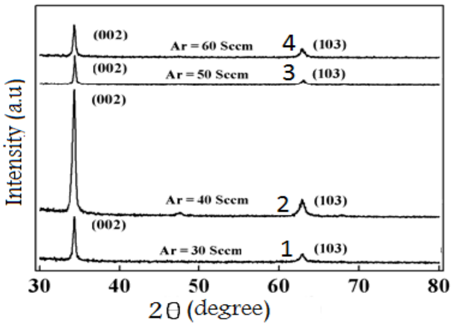

Fig. 1: XRD spectrum of ZnO:Al film deposited under different Ar flow.

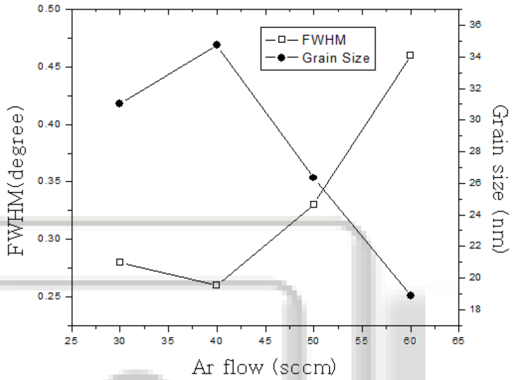

Fig. 2: Variation of grain size of ZnO:Al thin films with FWHM of XRD

Variation of grain size of ZnO: Al thin films with FWHM of XRD (002) peaks shown in Fig.2 as a function of Ar flow. The grain size of the AZO thin films was calculated using Scherrer's formulation [17]:

$$D = 0.9\lambda/\beta\cos\theta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where $\lambda = 1.54$ and β = FWHM, θ=Braggs diffraction angle.

The maximum grain size is around 34 nm at sputtering power of 150 W with Ar flow of 40 sccm. Increasing the crystallite size of the AZO films can decrease grain boundary scattering and increase the carrier lifetime for achieving the lower resistivity of the AZO thin films.

The improvement of crystallinity can cause a decrease in grain boundary scattering and an increase of carrier lifetime [18,19].The increase in both carrier concentration and Hall mobility would consequently lead to an increase of conductivity. Fig. 3 shows the transmission spectra of ZnO:Al thin films deposited at various Ar flows(1-4 for Ar flow 30-60). Optical transmittance was about 80-90 % in the visible range. This means that the Ar gas pressure does not have a significant effect on the transparency of the thin films over the visible light wavelength range. However, the short wavelength cut-off in transmittance of ZnO:Al thin films has a clear shift towards to the long wavelength range with increasing the Ar gas pressure, indicating that the optical energy gap is reduced [20]. Maximum transmittance of around 90 % was observed for the prepared ZnO:Al films with sputtering power of 150 W at Ar flow of 30 sccm.

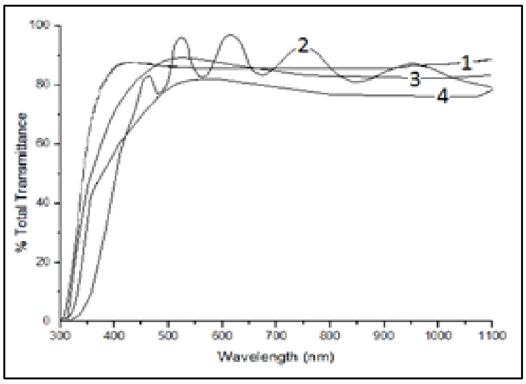

Fig. 3: Optical transmittance of ZnO:Al thin film in different Ar flow.

Table-1 shows the electrical resistively (ρ), Hall mobility (μ) and carrier concentration (n) of the ZnO:Al thin films thickness is fixed as 200 nm with sputtering power of 150 W at various Ar flows of 30, 40, 50 and 60 sccm. Resistivity of the ZnO:Al thin films increases from 1.6×10^{-3} Ω-cm with a sheet resistance of 80 Ω/sq to 3.7×10^{-4} Ω-cm with sheet resistance of 18.5 Ω/sq at Ar flow of 40 sccm as the sputtering power was at 150 W. The decrease in resistivity AZO thin films reduced grain boundary scattering, thus forming the continuous and decreasing the interface scattering.

Ar Flow	Resistivity (Ω.cm)	Sheet Resistance (Ω/□)	carrier concentration /cm^3	Mobility (cm/V-s)
30	1.6×10^{-3}	80.0	1.9×10^{21}	2
40	3.7×10^{-4}	18.5	5.6×10^{21}	3
50	6.2×10-4	31.0	4.0×10^{21}	2.5
60	8.7×10-4	43.5	3.1×10^{21}	2.3

Table 1: Electrical Parameters

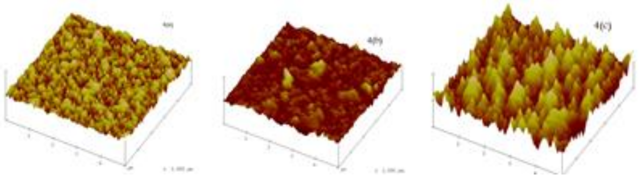

Fig. 4: AFM of ZnO:Al (a).at Ar flow 50sccm, 4(b). at Ar flow 40sccm (c).Ar flow at 60sccm

Fig.4 shows the AFM images of the AZO thin films with sputtering power of 150 W deposited at various Ar flow of 40, 50 and 60 sccm. Surface roughness is one of the important properties of the AZO thin films for many opto-electronics applications, because the level of surface roughness will dominate the carrier mobility and light scattering [21] also contribution to increase the transmittance [22]. Surface roughness can more affect the carrier mobility [23]. The morphologies of the ZnO:Al thin films were affected by the Ar flow.

Ar flow can be attributed to an decrease in the grain size of the AZO thin films from 30 to 34 nm and high plasma dense with the increasing the growth Ar flow, therefore, reducing the grain boundary scattering and decreasing the resistivity. The increase in resistivity of the ZnO:Al thin films growth at higher Ar flow above 40 sccm may be due to contamination of the alkali ions from the glass substrate [21]. The doping effect of some Ar^+ into the thin films might cause the higher resistivity with higher deposition pressure [24].

IV. CONCLUSION

The ZnO:Al thin films have been successfully deposited on glass substrate by rf sputtering. The prepared AZO thin films show the optical transmittance greater than 90 % in the visible range, the lowest electrical resistivity of 3.7×10^{-4} Ω-cm (18.5Ω/sq) at sputtering power of 150 W and Ar flow of 40 sccm. For the XRD analysis, the results show the good crystallinity and large grain size of the Ar flow of 40 sccm due to the smallest full width at half maximum. Such results indicated that these ZnO:Al thin films are good candidates for transparent conductive electrode applications.

ACKNOWLEDGEMENT

The authors acknowledge Department of Science and Technology, Govt. of India [DST/TM/SERI/2K10/67(G)] for financial support for pursuing the R&D activity.

REFERENCES

[1] B. Nasr, S. Dasgupta, D. Wang, N. Mechau, R. Kruk, H. Hahn. “Electrical resistivity of nanocrystalline Al-doped zinc oxide films as a function of Al content and the degree of its segregation at the grain boundaries,” J Appl Phys, vol. 108, no. 10, pp. 103721, Nov. 2010.

[2] Z. A. Wang, J. B. Chu, H. B. Zhu, Z. Sun, Y. W. Chen, S. M. Huang.“ Growth of ZnO: Al films by RF sputtering at room temperature for solar cell applications,” Sol St Electr ,vol. 53, no. 11, pp. 1149-53, Nov. 2009.

[3] W. Beyer, J. Hupkes, H. Stiebig. “Transparent conducting oxide films for thin film silicon photovoltaics.,” Thin Solid Films,vol. 516, no. 2-4, pp.147-54, Dec. 2007.

[4] J Rodriguez Baez, A Maldonado, G Torres Delgado, R Castanedo Perez, and M de la L Olvera “Influence of the molar concentration and substrate temperature on fluorine-doped zinc oxide thin films chemically sprayed” Mater. Lett. Vol 60,1594, 2006.

[5] H Gomeza, A Maldonado, M de la L Olvera, and D R Acosta “Gallium-doped ZnO thin films deposited by chemical spray” Sol. Energ. Mater. Sol.Cell Vol 87 107, 2005.

[6] Z Liu, Lei E, J Ya, and Y Xin **“**Growth of ZnO nanorods by aqueous solution method with electrodeposited ZnO seed layers” Appl. Surf. Sci.Vol 255,6415, 2009.

[7] M A Lucio Lopez, M A Luna Arias, A Maldonado, M de la L Olvera, and D R Acosta Sol. Energ. Mater. Sol. Cell Vol.90, 733, 2006.

[8] R Martins, R Igreja, I Ferreira, A Marques, A Pimentel, A Gonçalves, E Fortunato “Room temperature dc and ac electrical behaviour of undoped ZnO films under UV light ”Mat.Science and Eng. B Vol.118,135, 2005.

[9] P P Sahay and R K Nath “Al-doped zinc oxide thin films for liquid petroleum gas (LPG) sensors,” Sensors and Actuators B, vol. 133, no. 1, pp. 222–227, 2008.

[10] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R.Russo, P. Yang, “Room-Temperature Ultraviolet Nanowire Nanolasers,” Science, Vol. 292, no. 5523, pp. 1897-1899, Jun. 2001.

[11] Y. S. Kim, W. P. Tai, “Electrical and optical properties of Al-doped ZnOthin films by sol–gel process,” Applied Surface Science, Vol. 253, no. 11,Mar. 2007.

[12] H. Kim, A. Pique, J. S. Horwitz, H. Murata, Z. H. Kafafi, C. M. Gilmore, D.B. Chrisey, “Effect of aluminum doping on zinc oxide thin films grown by pulsed laser deposition for organic light-emitting devices,” Thin Solid Films, Vol. 377-378, pp. 798-802, Dec. 2009.

[13] W. T. Yen, Y. C. Lin, P. C. Yao, J. H. Ke, Y. L. Chen, “Effect of post-annealing on the optoelectronic properties of ZnO:Ga films prepared by pulsed direct current magnetron sputtering,” Thin Solid Films, Vol. 518,no. 14, pp. 3882–3885, May. 2010.

[14] D. R. Sahu, S. Y. Lin, J. L. Huang, “ Study on the electrical and optical properties of Ag/Al-doped ZnO coatings deposited by electron beam evaporation,” Applied Surface Science. Vol. 253, no. 11, pp. 4886-4890,Mar. 2007.

[15] M. J. Lee, T. I. Lee, J. Lim, J. Bang, W. Lee, T. Lee, and J. M. Myoung,“ Effect of the Deposition Temperature and a Hydrogen Post-Annealing Treatment on the Structural, Electrical, and Optical Properties of Ga-Doped ZnO Films,” Electronic Materials Letters. Vol. 5, no. 3, pp.127-133, Sep. 2009.

[16] X. T. Hao, L. W. Tan, K. S. Ong, F. Zhu, “ High-performance low-temperature transparent conducting aluminum-doped ZnO thin films and applications,” Journal of Crystal Growth. Vol. 287, no. 1, pp. 44-47,Jan. 2006.

[17] B. D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, Reading,Massachusetts, 1978, p. 102.

[18] H. Kim, J.S. Horwitz, G. Kushto, A. Pique´, Z.H. Kafafi, C.M. Gilmore,D.B. Chrisey, “Thickness dependence of structural, optical and electrical properties of ZnO:Al films prepared on flexible substrates, ” Journal of Applied Physics. Vol. 88, no. 10, pp. 6021, Aug. 2000.

[19] X. T. Hao, J. Ma, D. H. Zhang, T.L. Yang, H. L. Ma, Y. G. Yang, C. F.Cheng, J. Huang, “Thickness dependence of structural, optical and electrical properties of ZnO:Al films prepared on flexible substrates, ”Applied Surface Science. Vol. 183, no. 1-2, pp. 137-142 , Nov. 2001.

[20] D. K. Kim and H.B. Kim, “Room temperature deposition of Al-doped ZnO thin films on glass by RF magnetron sputtering under different Ar gas pressure” Journal of Alloys and Compounds. Vol. 509, no. 2, pp. 421-425,Jan. 2011.

[21] M. Suchea, S. Christoulakis, N. Katsarakis, T. Kitsopoulos, G. Kiriakidis,“ Comparative study of zinc oxide and aluminum doped zinc oxide transparent thin films grown by direct current magnetron sputtering,” Thin Solid Films. Vol. 515. no.16, pp. 6562-6566. Jun. 2007.

[22] H. Kim and C. M. Gilmore, J. S. Horwitz, A. Pique, H. Murata, G. P.Kushto, R. Schlaf, Z. H. Kafafi, and D. B. Chrisey, “ Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices,” Applied Physics Letters. Vol. 76, no. 3, pp.259-261, Nov. 1999.

[23] D. Y. Song, A. G. Aberle, J. Xia, “ Optimisation of ZnO:Al films by change of sputter gas pressure for solar

cell application," Applied Surface Science. Vol.195, no.1-4. pp. 291-296. Jul. 2002.

[24] H. Sato, T. Minami, Y. Tamura, S. Takata, T. Mouri, N. Ogawa, "Aluminium content dependence of milky transparent conducting ZnO:Al films with textured surface prepared by d.c. magnetron sputtering," Thin Solid Films. Vol. 246,no. 1-2. pp. 86-91. june. 1994.