



Influence Of Oxygen Flow Rates On Structural, Optical And Electrical Properties Of Nano Structured Azo Thin Films By Rf Magnetron Sputtering

P.Parhana¹, Prof.M.V.Lakshmaiah^{2,*}

1. Research Scholar, Department of Physics, Sri Krishnadevaraya University, Ananthapuramu-515003, A.P.,India.
2. Professor, Department of Physics, Sri Krishnadevaraya University, Ananthapuramu-515003, A.P.,India.

Abstract

Aluminium doped Zinc Oxide (AZO) thin films were deposited on glass substrate at various oxygen flow rates from 1 to 4 sccm while Ar flow rate was constant by using RF magnetron sputtering technique. The effects of structural, optical and electrical properties of AZO films were investigated by X-ray diffractometer, Scanning electron microscope, UV-visible spectrometer and Hall Effect measurements. XRD patterns revealed that all deposited films exhibit (0 0 2) preferential orientation along c-axis and have hexagonal wurtzite crystal structure. SEM images of AZO thin films reveal columnar grains that are perpendicular to the substrate, along with some granular grains. A maximum optical transmittance of 92% and the lowest resistivity of $3.01 \times 10^{-4} \Omega \cdot \text{cm}$ are achieved for AZO film deposited at an oxygen flow rate of 3 sccm. The optical band gap values of AZO films increases with the increase of oxygen flow rates.

Keywords: AZO thin films, RF magnetron sputtering, oxygen flow rates, structural, optical and electronic properties.

Introduction

Zinc oxide (ZnO) thin films have shown promise as a material for use in optoelectronic devices due to its low resistivity, high electron mobility, and excellent transparency for visible light. Transparent conducting ZnO films doped with a donor impurity like Al or Ga can effectively increase the resistivity stability at high temperatures, as first reported by Minami et al. [1]. Indium tin oxide may be replaced by the promising transparent conductive oxide (TCO) considered as Al doped zinc oxide (AZO). Al doping can maintain transparency within the visible range while also significantly increasing the concentration of free charge carriers. Both of these are required for transparent conduction [2, 3]. Particularly, transparent and conductive Al:ZnO (AZO) films are being considered for the production of transparent electrodes in solar cells, organic light emitting diodes, and flat panel displays because of their high optoelectric quality, abundant supply of materials, and affordable cost for large-area applications [4-6]. Aluminum zinc oxide films have been deposited using various methods such as direct current (DC) and radio frequency (RF) magnetron sputtering [7], Sol-gel [8], chemical vapor deposition [9], spray pyrolysis [10], and pulsed laser deposition [11]. Sputtering is one of the most promising of these methods since it produces uniform films on a variety of large-area substrates at a moderate deposition temperature, has a high packing density of grown film, good interfacial adhesion to the substrate, and simple apparatus than the other methods [12, 13]. The structural, electrical, and optical characteristics of AZO films at various oxygen flow rates have been discussed in detail in this paper.

Experimental details

Aluminum Zinc Oxide (AZO) thin films were prepared by RF magnetron sputtering technique. Metal targets with high purity of Zn (99.999%) and Al (99.99%) with 2 inch diameter and 4 mm thickness are used for deposition on glass substrates. The glass substrate was placed parallel to target surface with a distance of about 60 mm. After ultrasonically cleaning the glass substrates in detergent diluted with deionized water and then ultrasonically bathing them in isopropyl alcohol, the substrates were cleaned and dried in hot placed on the sample holder after air flow. To prevent contamination on the target surface, pre- sputtering was carried out for 10 minutes prior to thin film deposition. High purity (99.99%) Ar and was fed into chamber at a flow rate of 8 sccm through mass flow controller. Another mass flow controller allows pure oxygen introduced into the chamber at different oxygen flow rates from 1 to 4 sccm. At a frequency of 13.56 MHz, the RF power was fixed at 65 W, substrate temperature was kept at 100 °C and deposition time is 30 min. The sputtering pressure was 6.6×10^{-3} mTorr, and the chamber was evacuated using a turbo molecular pump at a vacuum of 4×10^{-6} mbar. Film thickness was measured by Talysurf Profilometer. The resulting thickness of all the films is in the range of 300-350 nm. Surface morphology of the samples has been studied using Hitachi SU 6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectroscopy (Horiba, EMAX, 137eV) and AFM (Park XE-100: Atomic Force Microscopy). The electrical resistivity of the film was measured with Hall Effect system (Ecopia, HMS 7000). The optical transmittance measurements were recorded as a function of wavelength in the range of 300-1200 nm using JASCO Model V-670 UV-VIS-NIR spectrophotometer (Tokyo, Japan).

Results and Discussions

Structural Properties

Figure.1 shows the XRD patterns of AZO thin films deposited on glass substrate at different oxygen flow rates. It is observed that all deposited films exhibit (0 0 2) diffraction angle shifts from 34° to 33.76° towards lower angles as the oxygen flow rate changes from 1 to 4 sccm. An increasing peak width indicates more micro stress, the presence point defects and smaller grain sizes Furthermore, the lattice parameter of c is greater than the ASTM value of 5.20 Å for bulk ZnO and increases with increasing oxygen flow rate, indicating that the film has residual stress along the c-axis and that the stress value increase with increasing oxygen flow rate. There have been prior reports of similar behavior in the literature [14, 15].

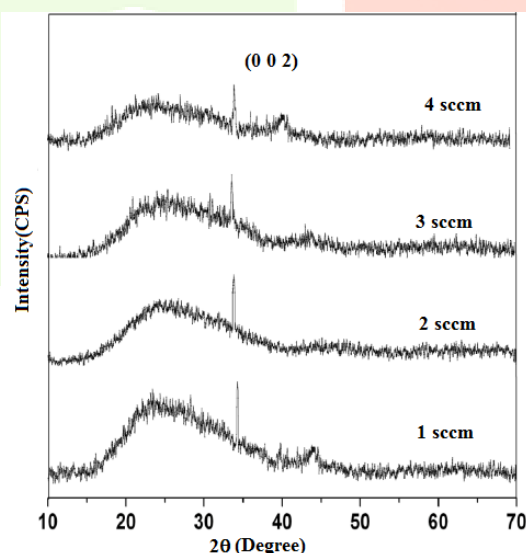


Fig.1. XRD patterns of AZO thin films deposited at different oxygen flow rates

For a hexagonal crystal system, the lattice parameters were determined by using following formula [16]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

Where d_{hkl} is the crystalline plane distance for indices (h k l) and a and c are the lattice constants. It was found that all d values are greater than that of standard ZnO powder d_o , which is equal to 0.2603 nm. According to equation (1), for the (0 0 2) diffraction peak, the lattice constant c is equal to 2d. The addition of Al atoms, which are found at the interstitial site rather than the Zn site, is most likely the cause of the

increase in the lattice constants because the radius ($0.53 \text{ \AA}$) of Al^{3+} is less than that ($0.74 \text{ \AA}$) of Zn^{2+} . As the oxygen flow rate increased from 1 to 4 sccm, the crystallite size measured using the Scherrer formula [17] decreased from 37 to 18 nm.

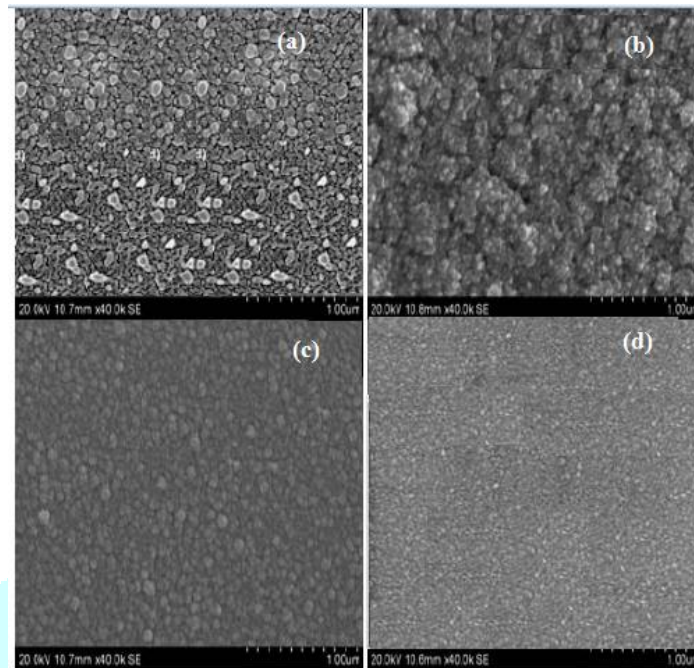


Fig.2. SEM images of AZO films deposited at oxygen flow rates of (a) 1 sccm, (b) 2 sccm, (c) 3 sccm and (d) 4 sccm.

Fig. 2 shows Scanning electron microscopy (SEM) images of AZO thin films deposited at different oxygen flow rates. All the deposited film grows mostly with columnar grains that are perpendicular to the substrate, though some granular grains are also exist. Aggregation of nanoscale crystallites forms the domains in the films deposited at oxygen flow rate of 2 sccm. The average grain size of the films is range from 18-41 nm.

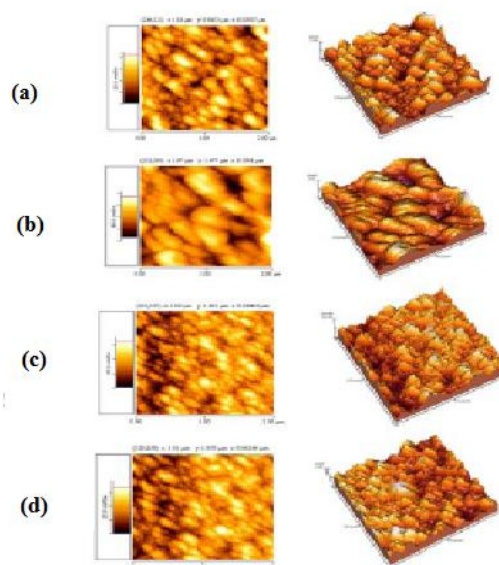


Fig.4 . AFM images of ZAO thin films at oxygen flow rates of (a) 1 sccm, (b) 2 sccm, (c) 3 sccm and (d) 4 sccm.

Fig. 4 shows two and three dimensional AFM images of the films deposited at different oxygen flow rates with scanned over an area of $2 \mu \times 2 \mu$. AFM images indicate that the film surface's sharp hill-and-valley structure was the reason for the surface roughness increase produced by oxygen flow rate. However, no particularly sharp peak develops in the domain, and the surface of the film deposited at an oxygen flow rate of 2 sccm is very flat. The film deposited at an oxygen flow rate of 2 sccm yields the greatest RMS surface roughness value. We found that films deposited at higher oxygen flow rates had a homogeneous grain distribution and were smaller than films produced from a metallic target. The addition of oxygen to the plasma, which may also produce high energy oxygen neutral atoms, could be the cause of these results. It is generally

believed that the resputtering of high energy neutral oxygen atoms may be the cause of grain agglomerates in the film produced after oxygen gas was introduced [18]. The re-sputtering impact of high energy neutral oxygen atoms may increase as the amount of oxygen gas in plasma gas increases. At the initial stage of the film growth process, it may then accelerate grain growth or particle aggregation, changing the film's surface topography.

Electrical Properties

Doping or a non-stoichiometric composition are the main causes of films' high conductivity. Electrons for these films were obtained from donor sites associated with oxygen vacancies in high-valence metal ions. Therefore, the oxygen flow rate has a major impact on the electrical properties of AZO thin films. The conduction properties of AZO thin films are dominated by the electrons that are broken down from the Al^{3+} ion substitutional sites. Using a Hall Effect measurement method, an electrical resistivity AZO film was calculated. As shown in Fig. 5, oxygen flow rates increase, the resistivity will be decrease. The oxygen flow rate of 3 sccm yields the lowest resistivity, $3.01 \times 10^{-4} \Omega\cdot\text{cm}$.

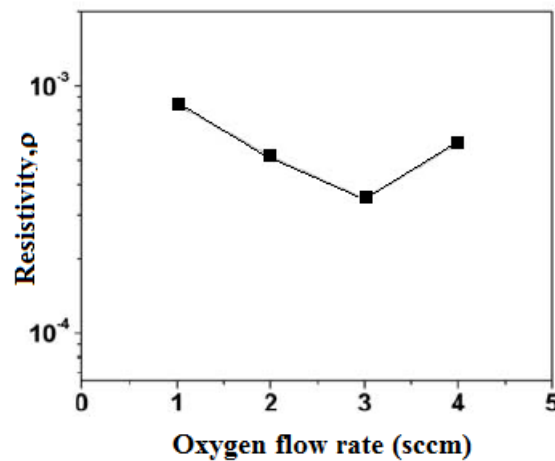


Fig.5. Electrical resistivity of AZO films as a function of Oxygen flow rates

Mobility of AZO films at various oxygen flow rates is shown in Fig. 6. When the oxygen flow rate increases from 1 to 3 sccm, the mobility value increases from $11.6 \text{ cm}^2/\text{Vs}$ to $27.7 \text{ cm}^2/\text{Vs}$, and when the oxygen flow rate increases from 1 to 4 sccm, then decreases to $24.6 \text{ cm}^2/\text{Vs}$ when the oxygen flow rate reaches to 4 sccm. The highest mobility of AZO films is attained when AZO is deposited at 3 sccm. The mobility of AZO thin films with carrier concentrations of 10^{19} and 10^{20} cm^{-3} is influenced by both grain boundary scattering and ionized impurity scattering [19]. The increase in mobility is caused by improved oxygen release and reduced grain boundary scattering due to thin film densification and improved crystallization.

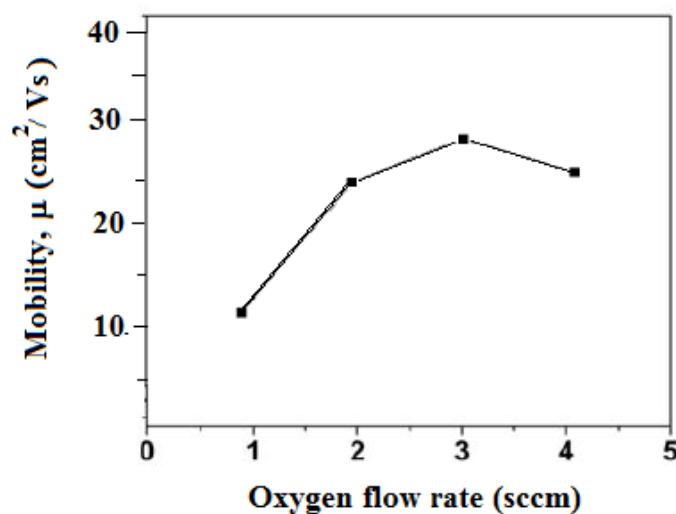


Fig.6. Variation of mobility of AZO films at various Oxygen flow rates.

Optical properties

Fig. 7 shows the transmission spectra of AZO thin films deposited at different oxygen flow rates. According to optical transmission measurements, it was observed that the all films were highly transparent in the range of 84 – 92% is obtained in the UV-Visible region. The absorption edge of all the films is around 352 – 365 nm. As the oxygen flow rate increases, the absorption edge is slightly shifts to the shorter wavelength. Since the absorption edge of the degenerate semiconductor shifts to a shorter wavelength with increasing carrier concentration, this is mainly attributed to Burstein-Moss effect.

The optical band gap, E_g is calculated from the dependence of absorption coefficient values (α) and the incident photon energy, using Tauc's relation [20]

$$(\alpha h\nu) = B (h\nu - E_g)^n \quad (2)$$

where B is a parameter that depends on electron-hole mobility, E_g is the optical band gap energy of the material, $h\nu$ is the photon energy and n is an index that characterizes the optical absorption process and is theoretically equal to 2 and $\frac{1}{2}$ for indirect and direct allowed transitions respectively. Fig. 7 shows the plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$. The optical band gap energy (E_g) of the films was obtained by extrapolating the linear absorption edge part. The optical band gap increases with increase of oxygen flow rate. The optical band gap of thin films deposited at different oxygen flow rates are 3.44 to 3.57 eV, The widening of band gap was caused by increase in carrier concentration after doping with Al^{3+} ions, which is attributed to Burstein – Moss effect [21]. The Fermi energy level shifts to the higher energy level. The condition is confirmed by the increase in the carrier concentration.

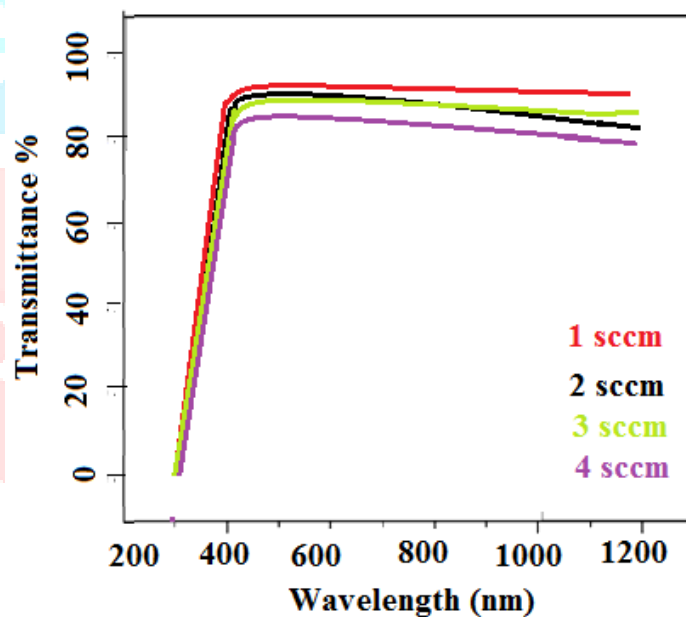


Fig.7. Transmission spectra of AZO thin films prepared at different Oxygen flow rates

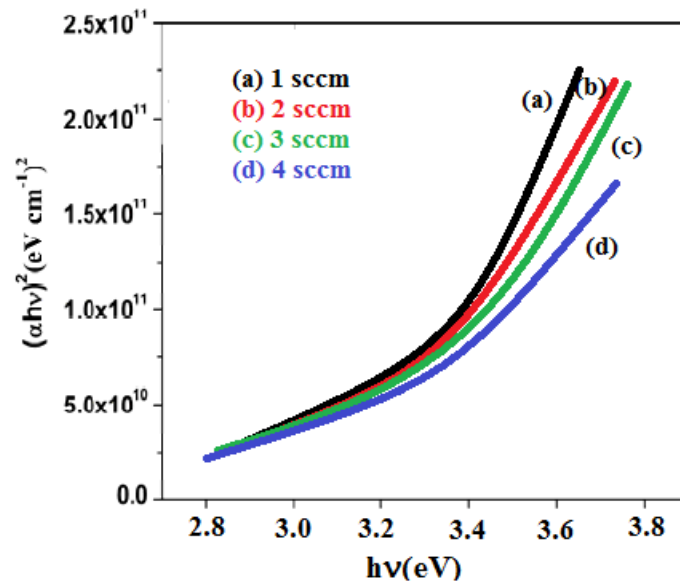


Fig.8. Variation of $(\alpha h\nu)^2$ versus photon energy $h\nu$ of AZO thin films deposited at various Oxygen flow rates.

The energy band gap widening ΔE_g is related to carrier concentration through the following equation [24]

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

Where h is the Planck's constant, m^* is the electron effective mass in conduction band, and n is the carrier concentration. The carrier concentration of AZO thin films is determined from equation (3) and is found to be in the range of $2.98 \times 10^{20} \text{ cm}^{-3}$ – $8.72 \times 10^{20} \text{ cm}^{-3}$. The maximum carrier concentration is obtained for the AZO film deposited at oxygen flow rate of 3 sccm.

Conclusion

AZO THIN FILMS HAVE BEEN PREPARED BY RF MAGNETRON SPUTTERING TECHNIQUE ON GLASS SUBSTRATES BY VARYING OXYGEN FLOW RATES FROM 1 TO 4 SCCM. THE DEPOSITED AZO FILMS HAVE A PREFERRED CRYSTALLINE ORIENTATION OF (0 0 2) DIRECTION. THE LOWEST RESISTIVITY OF $3.01 \times 10^{-4} \Omega \cdot \text{cm}$ AND A MAXIMUM OPTICAL TRANSMITTANCE OF 92% ARE OBTAINED FOR THE OXYGEN FLOW RATE OF 3 SCCM. THE CONDUCTION CHARACTERISTICS OF AZO FILMS ARE DOMINATED BY O^{2-} VACANCIES, ZN INTERSTITIAL ATOMS, AL IONS ON SUBSTITUTIONAL SITE OF ZN IONS AND AL INTERSTITIAL ATOMS. THESE RESULTS INDICATE THAT THESE FILMS ARE SUITABLE FOR THE TCO FILMS FOR DISPLAY AND SOLAR CELL APPLICATIONS.

References

- [1] T. Minami, H. Sato, H. Nanto, S. Takata, Jpn. Appl.Phys. **24**, L781 (1985).
- [2] S. Takata, T. Minami, H. Nanto, Thin Solid Films **135**,183 (1986).
- [3] Jiaheng Wang, Lei Meng, Yang Qi, Maolin Li, Guimei Shi, Meilin Liu, J. Cryst. Growth, **311**, 2305 (2009).
- [4] X.T. Hao, F.R. Zhu, K.S.Ong, L.W.Tan, Semicond. Sci.Technol. **21**, 48 (2006).
- [5] C.G.Granqvist, Sol. Energy Mater.Sol.Cells, **91**, 1529 (2007).
- [6] T.Minami, Thin Solid Films **516**, 5822 (2008).
- [7] C. Agashe, O. Kluth, G. Schope, H. Siekmann, J. Hupkes, B.Rech, Thin Solid Films **442**,167 (2003).
- [8] A.E.Jimenez-Gonzalez, J.A.S.Urueta, R.Suarez-Parra, J.Cryst.Growth, **192**, 430 (1998).
- [9] H. Sato, T. Minami, S. Takata, T. Miyata, M. Ishii, Thin Solid Films, **236**, 14 (1993).
- [10] P.Nunes, E.Fortunato, R.Martins, Thin Solid Films, **383**, 277 (2001).
- [11] H. Agura, A. Suzuki, T. Matushita, T. Aoki, M. Okuda, Thin Solid Films, **445**, 263 (2003).
- [12] Abdul kader Jazmati, Bassam Abdullah. Materials Research 21(3): e20170821, 2018.
- [13] Huawa Yu, Jing Wang, Yangan Yan, IEEE conference. 2011, 978-1-61284-088-8.
- [14] M. Chen, Z. L. Pei, X. Wang, C. Sun, L. S. Wen, Mat. Lett. **48**, 137 (2001).
- [15] L. J. Meng, M.P.Santos, Vacuum, **46**, 6090 (1995).
- [16] G. J. Fang, D. J Li, B. L. Yao, Phys.Stat.Sol. A, **93**, 139 (2002).
- [17] B.D.Cullity, Editor, Elements of X-ray diffraction, Addition-Wesley, London (1959).

[18] S.Mishra, C.Ghanshyama, N.Rama, R.P.Bajpai, R.K.Bedi, Sens. Actuators, B **97**, 387 (2004).

[19] T.Minami, S.Suzuki, T.Miyata, Thin Solid Films, **53**, 398 (2001).

[20] J. Tauc, R. Grigorovici, A. Vancu, Phys. Stat. Sol. **15**, 627 (1966).

[21] Grilli M L, Sytchkova A, Boycheva S, Piegari , Physica Status Solidi-A-Applications and Materials Science,210,748-754,2013.

