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Effect of Aluminum concentration on structural and optical properties of DC reactive magnetron sputtered Zinc Aluminum Oxide thin films for transparent electrode applications

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Abstract. Zinc Aluminum Oxide(ZAO) thin films were deposited on glass substrates by DC reactive magnetron sputtering in an $Ar+O_2$ gas mixture using commercial available Zn metal (99.99% purity) and Al (99.99% purity) targets of 2 inch diameter and 4 mm thickness. The films were characterized and the effect of aluminum (Al) concentration (2 at %-6 at %) on the structural and optical properties was studied. The average crystallite size obtained from Scherer formula is in the range of 32-44nm. Microstructural analysis using Scanning Electron Microscope (SEM) supplemented with EDS is carried out to find the grain size as well as to find the composition elemental data of prepared thin films. Optical study is performed to calculate the extinction coefficient (k), absorption coefficient (α), optical band gap (E_g) using transmission spectra obtained using UV-VIS-NIR spectrophotometer. There was widening of optical band gap with increasing aluminum concentration. ZAO film with low resistivity 3.2×10^{-4} Ω cm and high transmittance of 80% is obtained for 3at% doped Al which is crucial for optoelectronic applications.

1. Introduction

Doped Zinc Oxide thin films such as Zinc aluminum oxide (ZAO) are being widely used as transparent conductive oxide films in many applications due to their numerous advantages over indium tin oxide (ITO) films [1-4]. ZAO films have many industrial applications, such as in the fabrication of thin films solar cells, smart windows, silicon, hetro-junction, high transparency and wide band-gap. Various deposition techniques have been utilized for ZAO films such as direct current(DC) and radio frequency(RF) magnetron sputtering[5], pulsed laser deposition[6], chemical vapor deposition[7], spray hydrolysis[8], and sol-gel[9]. In order to satisfy the demands of good film quality, high–rate and large-area deposition, and low cost of equipment for commercialization of all transparent conductive oxide films, DC magnetron sputtering has been regarded as one of the most attractive and effective fabrication techniques in the mass production of ZAO films. The main purpose of this work is to demonstrate the feasibility of using these ZAO films in photovoltaic devices as front electrode.

2. Experimental details

Zinc Aluminum Oxide (ZAO) thin films were prepared by DC reactive magnetron sputtering. High purity of Zinc (99.999%) and Alumina (99.99%) targets with 2 inch diameter and 4mm thickness are used for deposition on glass substrates. The base pressure in chamber was $3X10^{-4}$Pa and the distance between target and substrate was set at 60mm. 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 was introduced into the chamber and was metered by mass flow controllers for a total flow rate fixed at 25sccm. Deposition was carried out at a working pressure of 1Pa after pre-sputtering with argon for 10min. The depositions were carried out at different doping concentrations of aluminum (Al). Film thickness was measured by Talysurf thickness profilometer. The resulting thicknesses of the films were found to be ~300nm respectively. XRD (Philips: PW1830) was used to analyze the crystalline orientation and structure of ZAO thin films. The sheet resistance (R_s) of the film was measured with a four-point probe method. The resistivity of the film (ρ) was calculated using the simple relation $\rho = R_s.d$, where d is the film thickness. Surface morphology of the samples has been studied using HITACHI S-3400 Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectrum (EDS). EDS is carried out for the elemental analysis of prepared thin films. Optical transmittance measurements were carried out using Cary 5E UV-VIS-NIR spectrophotometer.

3. Results and discussion

XRD measurements were performed to investigate the structural properties of the deposited films. Figure 1 shows the XRD pattern of the thin films deposited at 2, 3, 4 and 6 at % of Al doped ZnO (ZAO) films. As it can be observed, the patterns were clearly dominated by a peak around 34.4^o, corresponding at the (0 0 2) reflection. The position of the peak was very close to the preferred orientation of the standard d powder ZnO crystal ($2\theta=34.45^o$). This fact confirms the preferential c-axis orientation as reported by other authors [10]. It is observed that all XRD peaks were influenced by doping process where the peaks intensity reduced with doping concentrations. The peaks at doping concentration of 4 and 5 at% were more reduced to indicate higher doping concentration heavily affects ZAO thin film structural properties. The result suggested that the crystallinity of ZAO thin films decreased with increase of dopant concentrations. The aggravation of ZAO crystallinity with doping concentration might be from the formation of stress by the difference in ion size between Zn and Al. At higher doping concentration, due to nuclear charge of Al^{3+} is larger than Zn^{2+}, extrinsic Al^{3+} will captured more oxygen in completion of Zn^{2+} which decrease crystallinity and hexagonal structure of the thin films. The average crystallite size obtained from Scherer formula [11] is in the range of 32-44nm.

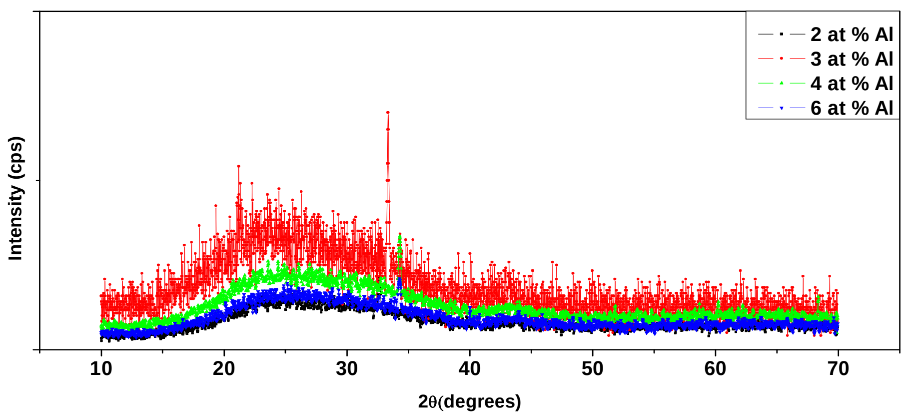

Fig. 1. XRD patterns of ZAO thin films at different Al doping concentrations.

Figure 2(a)-2(d) shows Scanning electron microscopy (SEM) images of ZAO thin films deposited on glass substrate doped with 2, 3, 4 and 6 at % of Al. The SEM images reveal that the films are uniformly deposited with nanoscale particles. It could be observed that grain size tends to reduce with increment of Al doping. The average grain size from SEM images have 53nm, 42nm, 34nm and 28nm for 2 at %, 3 at%, 4 at % and 6 at % Al doped ZnO. Energy Dispersive Spectrum (EDS) of ZAO thin films with its compositional elemental data are shown in figure 3(a)-3(d).

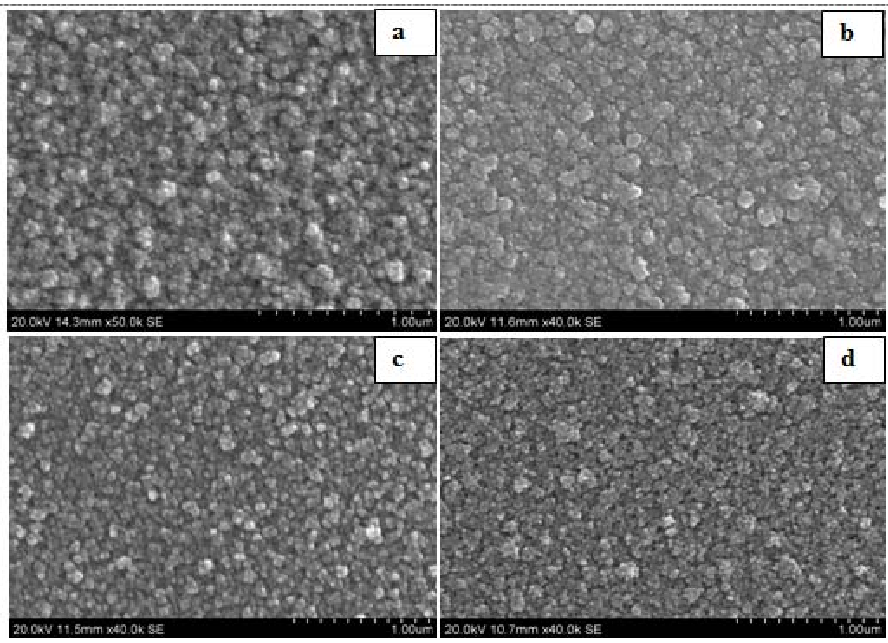

Fig. 2. Surface morphology of ZAO thin films doped with (a) 2 at %, (b) 3 at % (c) 4 at % and (d) 6 at % of Al.

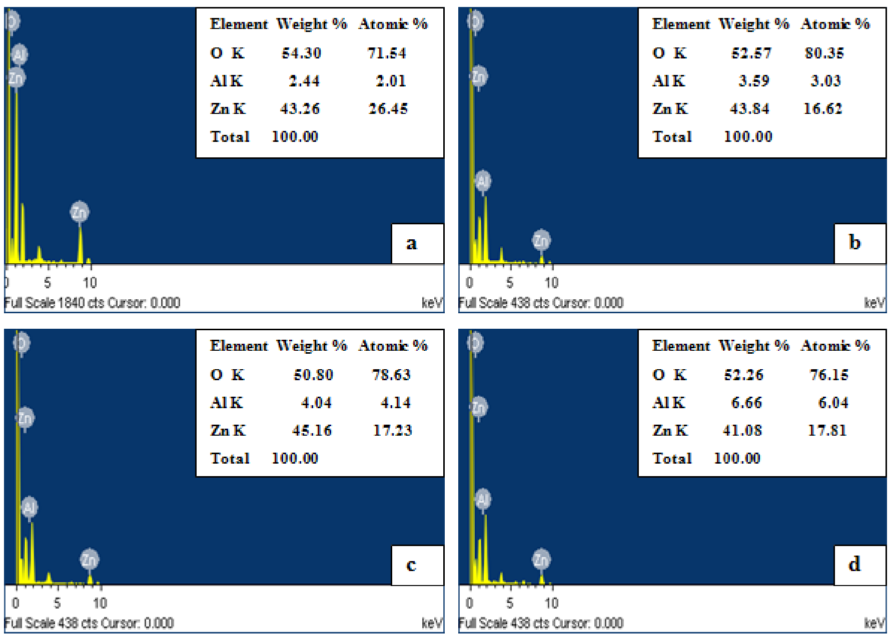

Fig. 3. EDS of ZAO thin films doped with (a) 2 at %, (b) 3 at % (c) 4 at % and (d) 6 at % of Al.

The electrical resistivity of the ZAO films was investigated by four-point probe method at room temperature. The electrical resistivity is in the range of $3.48X10^{-4}$ Ω cm – $5.2X10^{-4}$ Ω cm. The lowest resistivity of 3.2X 10^{-4} Ω cm is obtained for 3 at % doped Al. The electrical properties of ZAO films were analyzed because of the strong influence of Al dopant, as they exert on the final performance of the optoelectronic devices such as solar cells.

The transmittance spectra of ZAO thin films are shown in figure 4. The film deposited with 3 at% doped Al exhibits maximum transmittance of 80%. Optical parameters such as absorption coefficient (α), extinction coefficient (k) and optical band gap (E_g) were determined from the transmission data. The extinction coefficient (k) can be calculated by using the relation [12].

$$k = \frac{\alpha\lambda}{4\pi} \quad (1)$$

where α is the absorption coefficient and is calculated from the relation

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (2)$$

where d is the thickness of the film and T is the transmittance [13].

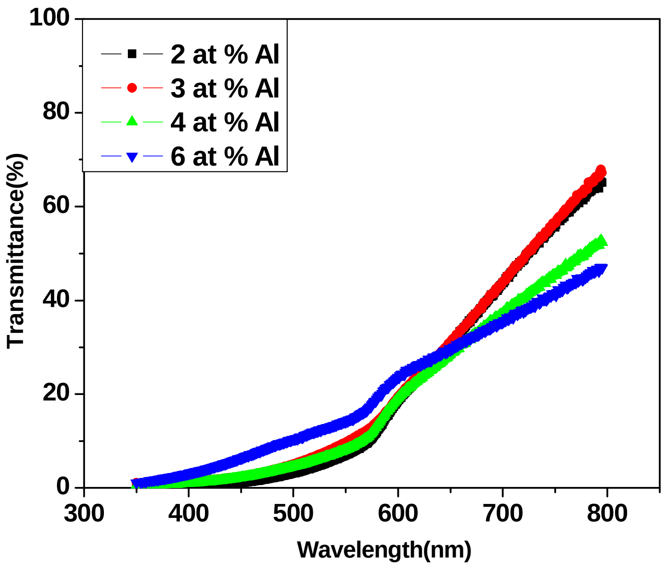

Fig. 4. Optical transmittance spectra of ZAO films deposited at different atomic weight % of Al.

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. The extinction coefficient increases with the increase in energy of the incident beam. The values of extinction coefficient (k) with wavelength (λ) are found to be in the range of 0.02-0.58.

The optical band gap, E_g is determined from the dependence of absorption coefficient values (α) on the photon energy, using Tauc's relation [14]

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

where B is a parameter that depends on the transition probability, E_g is the optical band gap energy of the material, hυ 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 of the films was evaluated from the Tauc's plot of $(\alpha h\upsilon)^2$ versus hυ shown in figure 5. The optical band gap is in the range of 3.2-3.46eV, the contribution from Al^{3+} ions on substitution sites of Zn^{2+} ions and Al interstitial atoms determines the widening of the band gap caused by increase in carrier concentration , which is believed to be Burstein-Moss effect because of doping by Al[15].

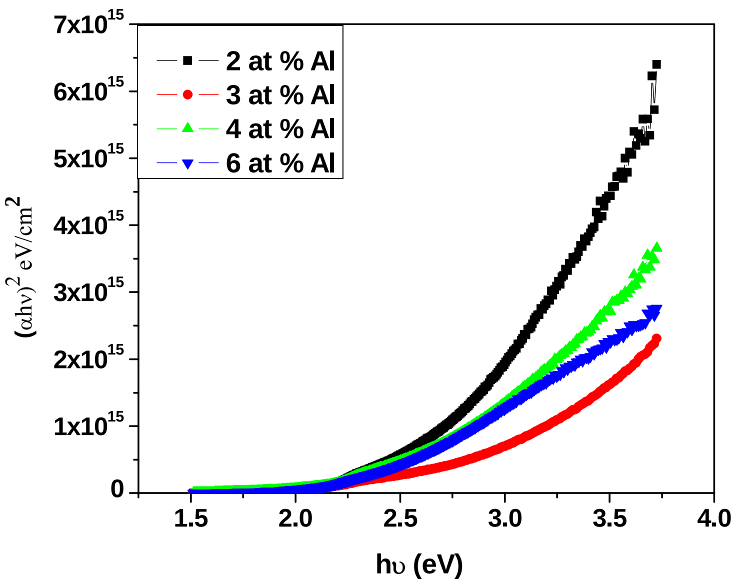

Fig. 5. Tauc's plot of ZAO films deposited at different atomic weight % of Al.

The figure of merit F is introduced in order to quantify the optoelectronic properties of transparent oxides. It is defined as [16]

$$F = \frac{-1}{[R_s . \ln(T_{av})]} \tag{4}$$

where R_s is sheet resistance and T_{av} is average visible transmittance of the films.

The best combination of low resistivity and high transmission, ie., the highest figure of merit F = 4.87 X 10^{-1} Ω^{-1} was obtained for the ZAO thin film doped with 3 at % of Al with R_s = 21.7 Ω/□.

4. Conclusions

ZAO thin films have been grown by DC reactive magnetron sputtering technique on glass substrates at different doping concentrations of Al. The deposited ZAO films have a preferred crystalline orientation of (0 0 1) direction. The conduction characteristics of ZAO films are dominated by O^{2-} vacancies, Zn interstitial atoms, Al ions on substitutional site of Zn ions and Al interstitial atoms. ZAO films with low resistivity 3.2 X 10^{-2} □ cm and high transmittance over 80% is obtained for Al concentration of 3 at %. This indicates that these films satisfy basic requirement as transparent electrodes for display and solar cell applications.

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