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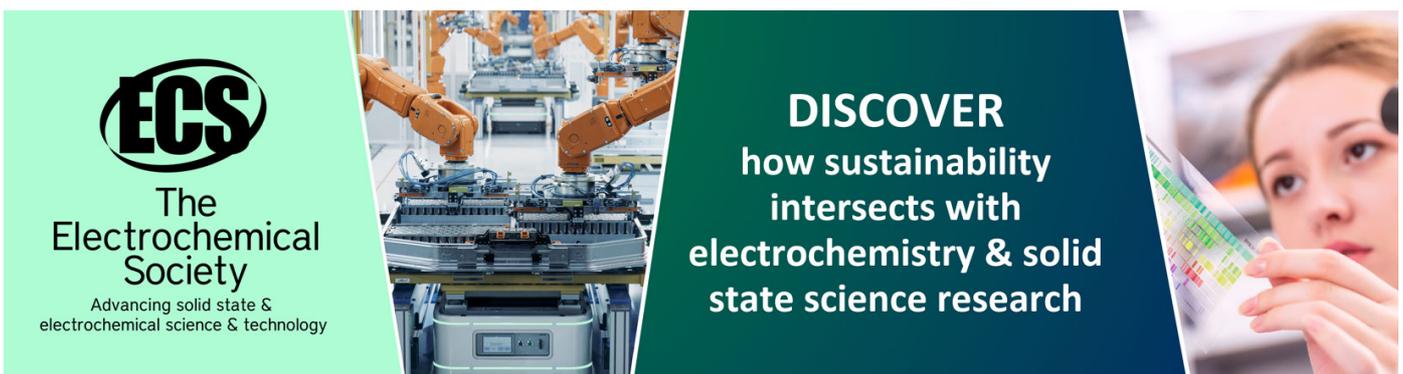
Effect of Spin Rate on the Properties of $\text{Zn}_{0.98}\text{Al}_{0.02}\text{O}$ Transparent Films

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Effect of Spin Rate on the Properties of $Zn_{0.98}Al_{0.02}O$ Transparent Films

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Abstract. $Zn_{0.98}Al_{0.02}O$ thinfilms were deposited onto glass substrate through spin coating technique with different chuck rotation rates (rpm's) and the effect of rpm on their structural, optical and photoluminescence properties were investigated. The structural results confirm the good adhesive nature of the films with glass substrate and formation of hexagonal wurtzite crystal phase with an average crystallite size of 20 nm. Small significant effect on the crystallinity was observed with increase in the chuck rotation speed (rpm), whereas the thickness of the films found to decreases. The optical absorbance and transmittance measurements were recorded in the wavelength range 250 - 1000 nm. Optical studies confirm the films with > 85% transparency in the visible wavelength region were achieved. Photoluminescence (PL) excitation spectra of films were recorded under the emission wavelength of 450 nm. It reveals the distinct peak at 329 nm and it also shows distinct emission peaks at 408, 450, 483 and 530 nm for excitation wavelength of 329 nm and these emission peaks are assigned to the defects induced by the Al^{3+} substitution.

1. Introduction

In recent years zinc oxide is the most widely explored material for many potential applications by virtue of its extra-ordinary properties in the fields of opto-electronics [1], spintronics [2-3], electroluminescence displays [4] and gas sensors [5]. Recently, group III elements doped ZnO films, in particular Al doped ZnO (AZO) thin films are showing great promise as the alternative material to costlier Indium Tin Oxide (ITO), due to high abundance, non-toxicity and low cost when compared to ITO films. Substitution of trivalent ion, Al^{+3} at Zn^{2+} site in ZnO induces optical transparency in the visible region (400 – 800 nm) and offers good electrical conductivity. In addition, AZO films show good chemical, mechanical and thermal stability. In particular, Al doped ZnO (AZO) shows an excellent transparency over the entire visible spectrum [6]. Numerous chemical and physical methods are reported in the literature to deposit AZO thin films, such as sputtering [7], spin coating [8], spray pyrolysis [9], pulsed laser deposition [10], molecular beam epitaxy [11], etc. Among all the methods, spin coating technique is more advantageous due to its simplicity, cost effective and non-vacuum technique. Recently, the effect of Al concentration on the properties of spin coated ZnO thin films is reported [12-13]. In addition, it is interesting to study the effect of chuck rotation rate (rpm's) on the



AZO film properties. Hence, in the present investigation, we have deposited 2% Al doped ZnO transparent films by sol-gel spin coating method onto glass substrates and the effect of chuck rotation rate on the structural, optical and luminescent properties are studied.

2. Experimental

2 mol % Al doped ZnO (AZO) thin films were prepared using the conventional spin coating method using zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), Aluminum Chloride Hydrate ($\text{AlCl}_3 \cdot x\text{H}_2\text{O}$), 2-methoxyethanol and Di-ethanol-amine (DEA) as a source, dopant, solvent and stabilizer, respectively. The flow chart of synthesis procedure is shown in the Fig. 1. The stoichiometric amounts of zinc acetate dihydrate, Aluminum Chloride Hydrate were dissolved independently in 2-methoxyethanol at room temperature to get source solution (A) and dopant solution (B) respectively. The mixture was stirred at 60 °C and di-ethanol-amine (DEA) was added drop wise to the mixture A as a stabilizer until clear solution was appeared. The solution B is added drop wise to the solution A in order to obtain the 2 mol% Al doped ZnO. . The resulting mixture was then stirred at 60 °C for 2 h to form a clear and transparent homogeneous mixture. The precursor solution was aged for 48 h at room temperature and then filtered and stored in a container. The concentration of the solution was 0.8 mol / L and molar ratio of DEA to zinc acetate was maintained at 1:1. Prior to the spin coating, conventional cleaning procedure was followed to clean the glass substrates (microscope slides, Borosil)(reference). Finally the substrates were baked at 350 °C for 10 min and cooled down to room temperature before deposition. AZO thin films were obtained by spin coating the sol-gel with different chuck rotation rates, 2000, 3000, 4000 and 5000 rpm's for 60 sec. Then the films were heated at 350 °C for 10 min. The process of coating to subsequent drying at 350 °C was repeated for 10 times to get the desired thickness of the film. Finally, the as-prepared films were post annealed at 550 °C for 2 hr and cooled down to room temperature in a muffle furnace.

Pure and Al substituted ZnO thin films were characterized through PXRD (Rigaku, ULTIMA, 40 kV, 30 mA) using Cu K α radiation of wavelength 1.5418 Å. Optical properties were investigated through room temperature optical absorbance and transmittance spectra recorded in the 300 - 1000 nm wavelength range using UV-Visible spectrophotometer, Ocean Optics, USB 4000-XR. The Photoluminescence measurements were carried out at room temperature with a PerkinElmer LS55 spectrophotometer.

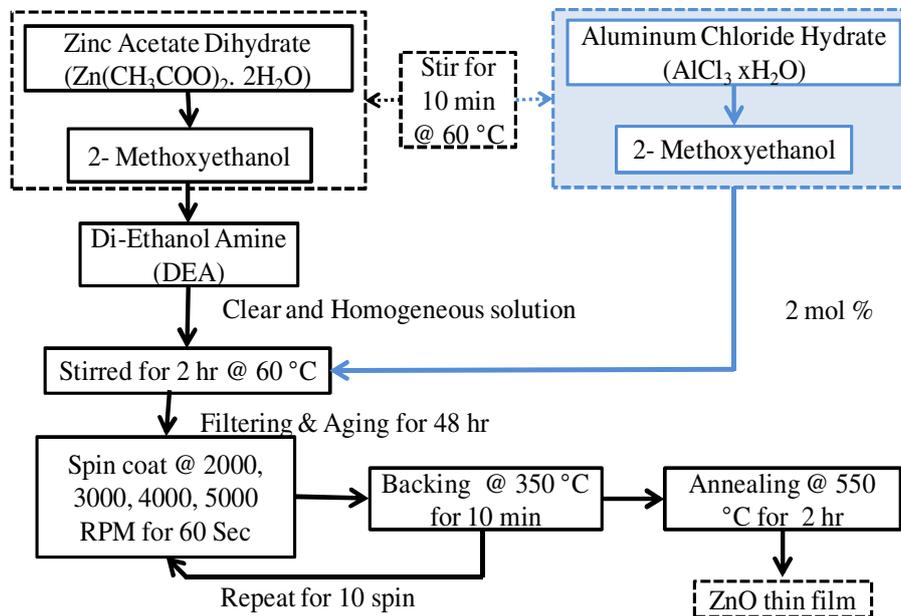


Figure 1 Flow chart showing the synthesis procedure of spin coating technique.

3. Results and discussion

To study the effect of chuck rotation rate on the structure, AZO samples were characterized through powder x-ray diffractometer. PXRD patterns of AZO thinfilms with different chuck rotation rates are depicted in the Fig. 2. From figure, it is observed that, all the films exhibits multiple crystalline reflections and are indexed to the JCPDS card no. 36-1451, belongs to hexagonal wurtzite crystal structure with P63mc space group. That is, all the samples exhibit polycrystalline in nature with majority of the crystallites orienting along (002) plane. It can be seen that, chuck rotation rate has significant effect on the crystallinity of the films as evidenced from the variation in the intensity of the (002) peak. With increase in the chuck rotation rate, the thickness of the films gets reduced, hence the intensity of the peaks. It is also observed that, peaks related to the impurity phases are not seen within the detection limit of XRD with 2% Al doping, which confirms Al substituting at Zn site. The crystallite size was calculated using Scherer’s formula (1) for highest intensity peak, i.e. (002) peak.

$$D = \frac{k \lambda}{\beta \cos\theta} \dots\dots\dots (1)$$

Where, β is the full width at half maximum of (002) peak. It is found that, the crystallite size of AZO films is in the nano range (20 – 25 nm).

Fig. 3 (a& b) respectively shows the optical absorption spectra along with the transmittance spectra were recorded for AZO films using UV-Vis spectrophotometer. From the absorbance spectra (Fig. 3(a)), no significant shift in the absorption edge of AZO films is observed with chuck rotation rate. As a result of Al (2%) substitution into ZnO, > 85% transmittance of the films has been achieved (Fig. 3(b)). Indeed which is needed to address for their potential applications as TCO materials. Though Al substitution induces transparency in the films, chuck rotation rate has not affected the transparency of the films. Further to estimate the optical band gap of AZO films, optical absorption spectra was used.

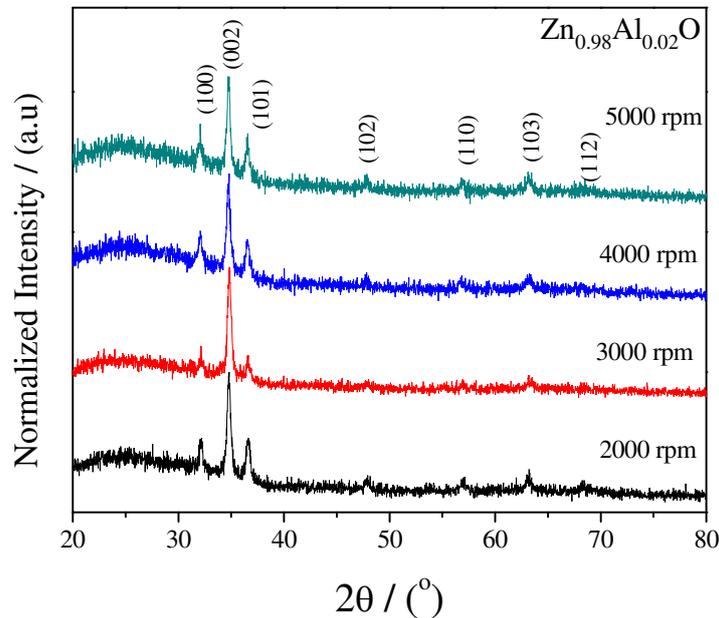


Figure 2 XRD patterns of Zn_{0.98}Al_{0.02}O thinfilms deposited at different chuck rotation rates.

The optical band gap energy (E_g), is calculated using the Tauc’s equation (2),

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

Where, B is a constant, ' $h\nu$ ' is the photon energy, ' E_g ' is the optical energy band gap and ' n ' is a number which characterizes the transition process. The exponent ' n ' takes the values; 2, 3, 1/2 and 3/2 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. And $\alpha(\lambda)$, is the optical absorption coefficient, which is determined using the following equation (3);

$$\alpha(\lambda) = 2.303 \frac{A}{t} \quad \dots\dots\dots (3)$$

Where, A is the absorbance and t is the thickness of the film,

The experimental optical absorption data was well fitted to the above equation (2) for $n = 1/2$ (direct allowed transition). The Tauc’s plots, $(\alpha h\nu)^2$ vs $(h\nu)$ of AZO films are depicted in the Fig. 4. From the Tauc’s plots, the optical band gap (E_g) values were estimated by extrapolating the linear region of curve to intercept to x -axis i.e. for $(\alpha h\nu)^2 = 0$. It is found that, the estimated band gap values are in agreement with the bulk band gap of ZnO. It is also seen that, a small significant variation in the band gap is observed with chuck rotation rate due to the variation in the thickness and crystallite size.

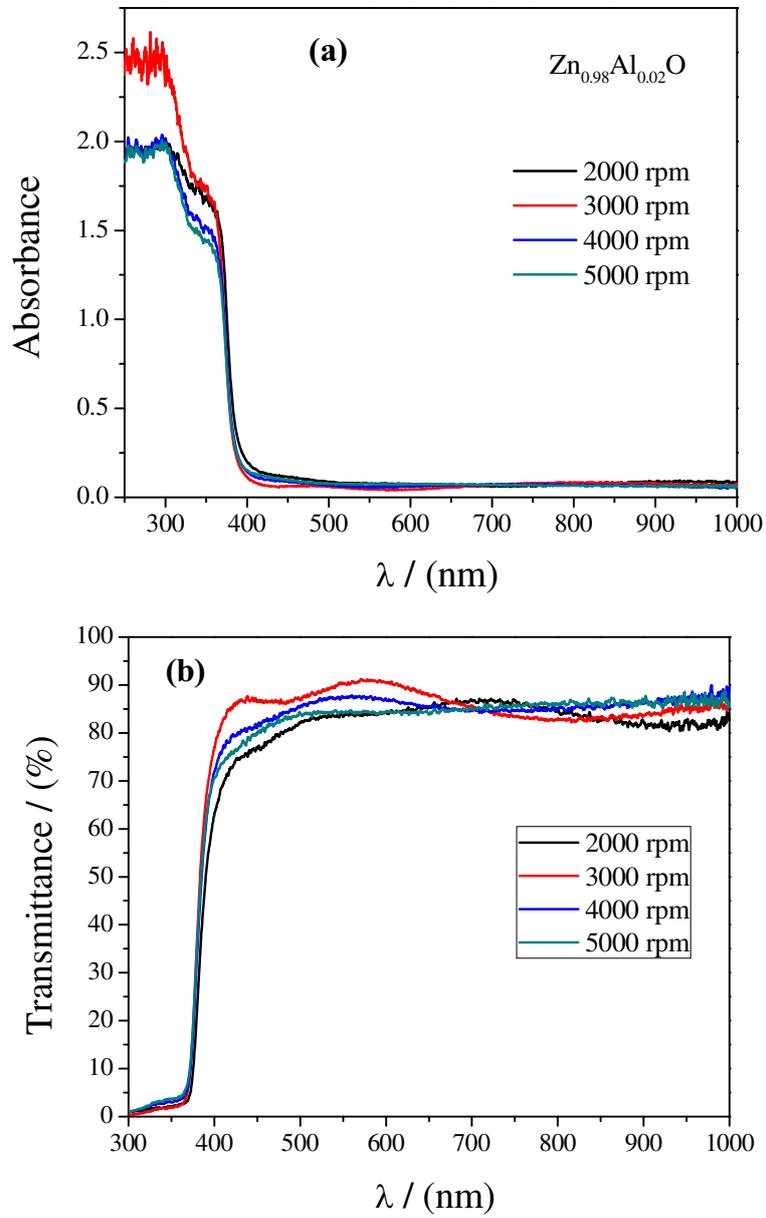


Figure 3 UV-Visible (a) absorbance and (b) transmittance spectra of AZO thinfilms prepared for different chuck rotation rates.

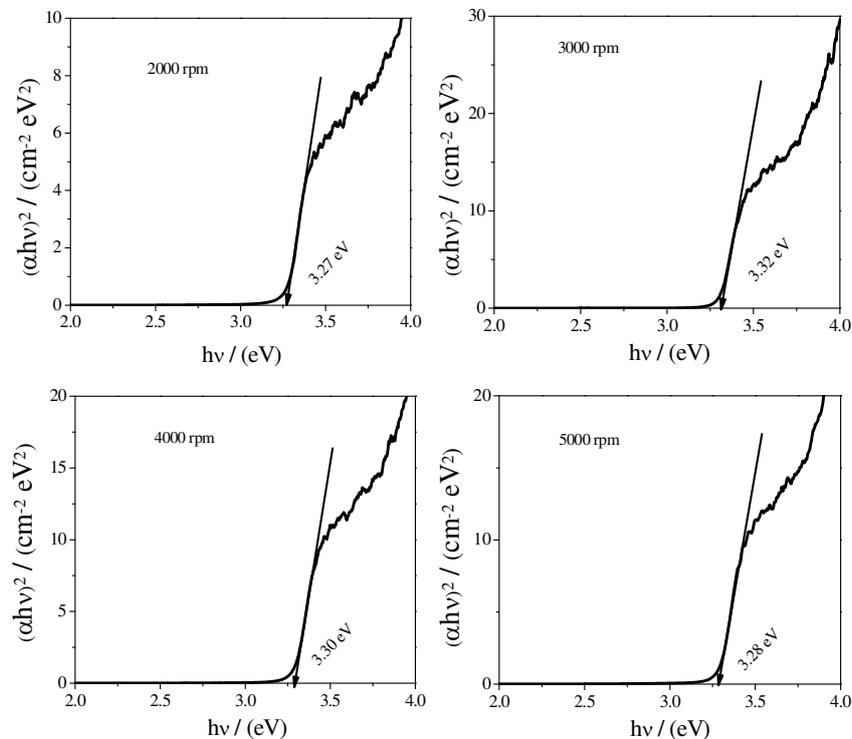


Figure 4 $(\alpha hv)^2$ vs hv plots of AZO thinfilms prepared for different spin rate.

Room temperature PL emission spectra were recorded for AZO films using an excitation wavelength of 329 nm and the spectra are shown in Fig. 5. The inset of Fig. 5 shows the PL excitation spectra taken at 450 nm. It is seen from Fig. 5, all the films exhibit four distinct and characteristic emission bands at 408, 450, 483 and 530 nm. A prominent high intense peak observed at 408 nm (near UV-region) is attributed to near band edge emission (NBE) due to an excitonic transition from the localized states below the conduction band (C.B) to the valence band (V.B). The NBE emission peak is remains unaltered with increase in chuck rotation rate. This is due to the combined effect of an optical transition to the excitonic state of ZnO and electronic transitions involving in crystal-field splitting [5]. On the other hand, the peak positions of other emissions at 450, 483 and 530 nm are also remains unaffected. The emission peaks observed at 450 and 483 nm are corresponds to blue emissions and are assigned as follows; the band emissions around 450 nm is assigned to the transition between exciton level (E) and interstitial oxygen (O_i) [14]. The emission band at 483 nm assigned to electron transition from Zn_i level to top of the valence band. The green emission peak at 530 nm is attributed to the presence of Oxygen vacancies results due to the trivalent ion (Al^{+3}) substitution at divalent ion (Zn^{+2}) site. Hence, at room temperature, the PL intensity of the blue emissions is related to the defect states correspond to the substitution of Al^{3+} ion. In particular, the significant variation in the intensities of the peaks at 450, 483 and 530 nm emissions may be related to O_i centers, which induces the chemisorption oxygen which intern increases the density of electronic states in the film [14].

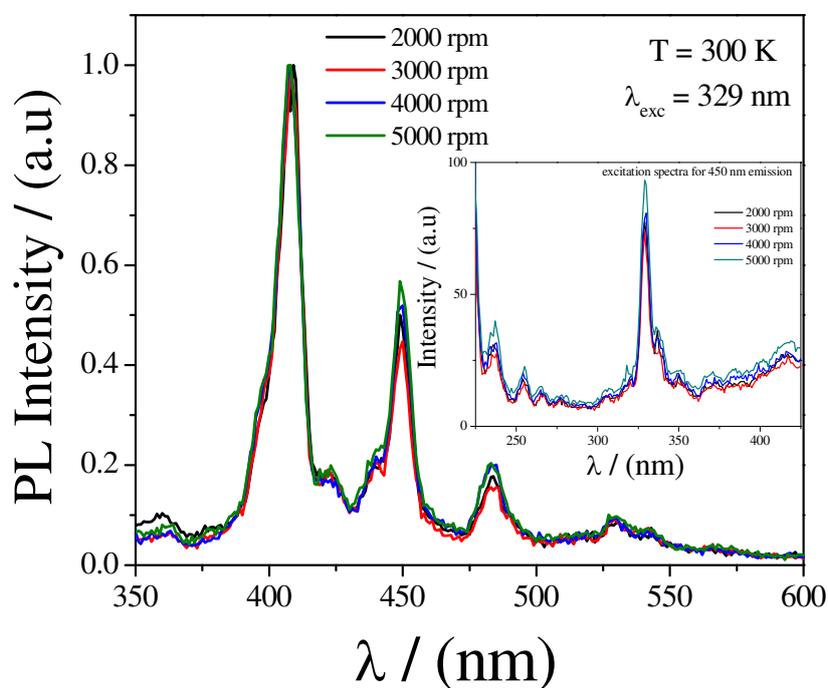


Figure 5 PL emission spectra of AZO thin films for different chuck rotation rates.

4. Conclusions

2% Al doped ZnO thinfilms were prepared onto glass substrate using sol-gel spin coating method at different chuck rotation rates and their effect on the structural, optical and luminescent properties were investigated. XRD results show the polycrystalline nature AZO films and less significant effect on the crystallinity of the films. Also, no traces of impurities were observed confirming the substitution of Al at Zn site without formation of impurities. The crystallite size was found to be in the range of 20-25 nm. The optical studies confirms, the films are highly transparent with transparency > 85% in the visible wavelength region. The estimated band gap energy (E_g) found in comparable with the band gap of bulk ZnO. PL studies shows four distinct peaks in the blue and green wavelength regions related to the defect states being induced due to the substitution of Al^{3+} ion in ZnO host matrix.

Acknowledgments

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