Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S239-S242

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Structural, Optical and Surface Properties of Sol-Gel Spin Coated Al Doped ZnO Thin Films†

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AJC-12842

Undoped and aluminium doped zinc oxide (ZnO:Al, AZO) thin films have been prepared at different heat treatment temperatures (300 to 400 ºC) onto mineral glass substrates by sol-gel spin coating method. The XRD profile of all the films confirm the hexagonal wurtzite structure with preferred orientation along the (002) plane. The average particle size evaluated from the XRD profile lies in between 15 nm and 25 nm. The other crystallographic parameters namely, lattice strain, dislocation density, texture coefficient and standard deviation have been estimated and reported. The optical transmittance of the aluminium doped zinc oxide film heat treated at 350 ºC exhibits a maximum of 85 % at the wavelength 800 nm. The band gap energy of the aluminium doped zinc oxide films evaluated from the optical transmittance measurement lies between 3 and 3.1 eV. The AFM image of the aluminium doped zinc oxide film heat treated at 350 ºC shows uniform surface pattern with nano sized particles. The effect of heat treatment temperature on the properties of spin coated aluminium doped zinc oxide thin films has been analyzed and elaborated.

Key Words: Aluminium doped zinc oxide thin films, Sol-gel spin coating, Particle size, Transmittance, Band gap.

INTRODUCTION

Recent developments in the semi-conductor industry have depicted an increased interest in zinc oxide (ZnO) and zinc oxide based semi-conducting crystalline materials because of their current and potential applications. Zinc oxide is a versatile material with unique properties finds application in various photonic associated technologies. It is an *n*-type semiconductor of wurtzite structure with a direct energy wide-band gap of about 3.37 eV at room temperature. As a consequence, it absorbs UV radiation due to band-to-band transitions has a larger exciton binding energy (60 meV). Doped zinc oxide films have a number of attractive applications, such as gas sensor devices[1], piezoelectric devices and transparent conducting electrode materials for various electronic devices such as solar cells[2] and electroluminescence displays.

Pronounced electrical and optical properties were obtained by Al doping of ZnO thin films as reported by Srinivasan *et al.*[3]. Various techniques employed for the fabrication of doped and undoped ZnO thin films are pulsed laser deposition[4], magnetron sputtering[5], chemical vapour deposition[6], spray pyrolysis[7] and spin coating process[8]. Due to its compatibility sol gel spin coating process was chosen for coating ZnO film. Sol gel process has been comparatively low cost and yields high quality thin films of purity, homogeneity and adopted for wide area coating. In this study, ZnO thin films have been prepared with aluminum dopant to search for the improved properties. In this paper the results of the characterization studies on the thinfilms of ZnO doped with aluminum prepared by sol-gel process and spin coating have been reported.

EXPERIMENTAL

Zinc oxide thin films doped with aluminium have been prepared by sol gel spin coating method. The sol solution was prepared by dissolving zinc acetate dihydrate in the solvent mixture ethanol and monoethanolamine. The molar ratio of monoethanolamoine to zinc acetate was 1:1 and the concentration of zinc acetate dihydrate was 0.36 mol/L. Aliminium chloride with concentration of 0.006 mol % was dissolved in the sol solution. The resultant solution is refluxed at 60 ºC for 1 h and then allowed for aging in the ambient. The coating was made on the third day of aging which was the optimized critical time for coating. The sol solution was spin coated on glass substrate at spin rate 3500 rpm with coating time 10 s. The films were subjected to heat treatment at different temperature *viz.*, 300, 350 and 400 ºC for 5 min duration to evaporate the solvent and to remove the organic residuals. All the thin films were prepared up to 10 layers of coating to obtain the uniform thickness of ZnO thin films. All the prepared films were then annealed at 475 ºC in air furnace for 1 h. The

†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

structural properties of the films prepared were analyzed by the XRD studies using PW 1840 X-ray diffractometer with CuK_α radiation source. The optical transmittance of the prepared films were recorded in the wavelength region between 325-800 nm using UV-visible Perkin-Elmer spectrophotometer and optical properties of the aluminium doped zinc oxide films have been studied. The surface properties of the films were analyzed using the images obtained by atomic force microscopy.

RESULTS AND DISCUSSION

Structural properties: The X-ray diffraction pattern of the ZnO thin film at 350 ºC and Al doped ZnO thin films at different heat treatment temperatures 300, 350 and 400 ºC are shown in Fig. 1. The diffraction peaks indicates the films are poly crystalline in nature. The XRD pattern of all the films shows the presence of diffractive peaks[9] (100), (002), (101) with varying intensity matches with hexagonal ZnO Wurtizite structure. The intensity of (002) plane was more stronger than that of other planes in the pure and aluminium doped films indicates the formation of preferred c-axis orientation[10] and in particular the film coated at heat treatment temperature 350 ºC shows highly intense (002) plane than the other films which implies the formation of good crystallinity of this film. In the aluminium doped film (002) plane has less intensity than the pure zinc oxide film[10,11]. It indicates that dopant incorporation leads to the deterioration of the crystallinity of films, which may be due to the formation of stresses by ion size difference between zinc and dopant as discussed by Chen *et al.*[12]. The reason is due to Al ion replaces Zn ion or inserts into the interstitial site of ZnO lattice which resulted in change of original lattice as discussed by Lee and Park[13]. The values of lattice constants calculated for the aluminium doped zinc oxide film spin coated at 350 ºC are a = 3.2519, c = 5.2012 found to have good agreement with standard values of JCPDS file No. (05-0664). But Al doping slightly increased a value and decreased c value. The lattice parameters calculated for other heat treatment temperatures are shown in the Table-1 and plotted in Fig. 2. The crystallite size D was estimated from the Scherer's formula:

$$D = 0.94\lambda/\beta \cos \theta \quad (1)$$

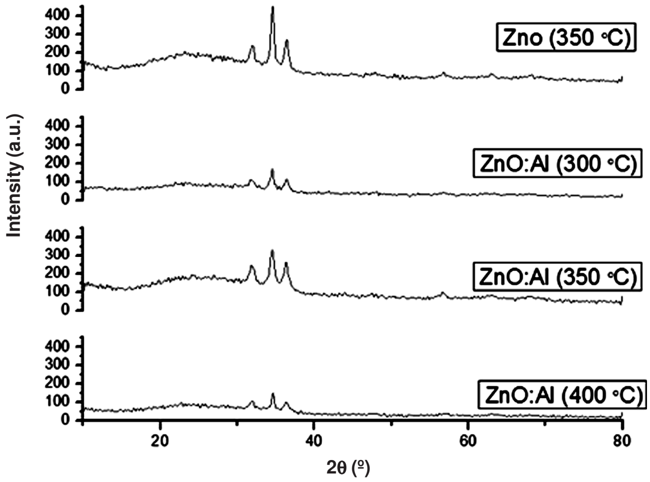

Fig. 1. XRD pattern of ZnO and aluminium doped zinc oxide thin films at different heat treatment temperatures

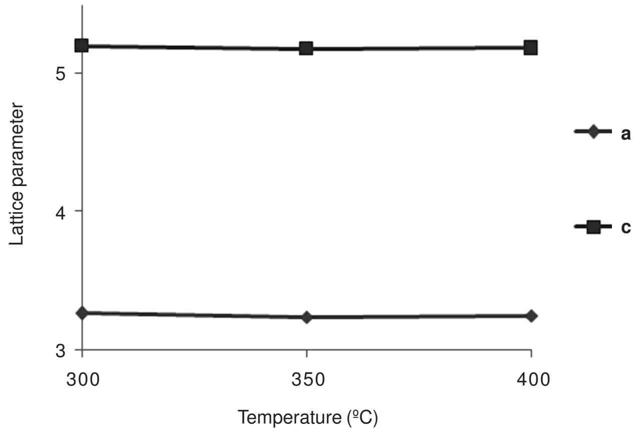

Fig. 2. Variation of lattice constants at different temperatures

where, D, λ, θ, β are the mean crystal size, the X-ray wavelength, Bragg diffraction angle, FWHM of the diffraction peak respectively.

The full width at half maximum (FWHM) of ZnO (002) peaks of pure and Al:ZnO films are 0.2460 and 0.3444, respectively. The average crystallite size calculated form the XRD data found to range between 13 and 37 nm, as shown in Fig. 3. The crystallite size of aluminium doped zinc oxide thin

TABLE-1
STRUCTURAL PROPERTIES OF ZnO AND ALUMINIUM DOPED ZINC OXIDE THIN FILMS COATED AT DIFFERENT HEAT TREATMENT TEMPERATURES

Sample/ Temperature	Lattice orientation hkl	Texture coefficient (TC)	Lattice constant		Standard deviation (σ)	Crystallite size (D) (nm)	Dislocation density, $\delta \times 10^{15}$ $Line^{-2}$ m^{-1}	Micro strain, $\varepsilon \times 10^{-4}$ $Line/m^2$
			a (Å)	a (Å)				
ZnO (350 ºC)	1 0 0	0.5230	3.2329	5.1966	30.537	19.93	2.51	18.15
	0 0 2	2.0392				30.44	1.07	11.88
	1 0 1	0.4375				26.11	1.46	13.86
ZnO:Al (300 ºC)	1 0 0	0.9579	3.2634	5.2024	14.900	3.85	67.57	94.07
	0 0 2	1.8642				22.21	2.02	16.29
	1 0 1	1.4787				14.77	4.58	24.49
ZnO:Al (350 ºC)	1 0 0	0.6648	3.2376	5.1826	19.690	16.24	3.79	22.28
	0 0 2	1.1454				46.48	0.46	7.7857
	1 0 1	0.5859				46.69	0.45	7.74
ZnO:Al (400 ºC)	1 0 0	0.5992	3.2466	5.1871	25.760	6.43	24.17	56.26
	0 0 2	1.8455				26.25	1.45	13.78
	1 0 1	0.5437				15.56	4.12	23.25

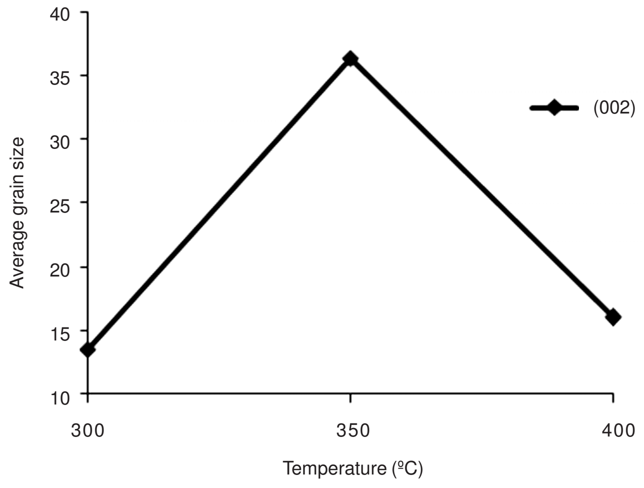

Fig. 3. Variation of mean crystallite size at different temperatures

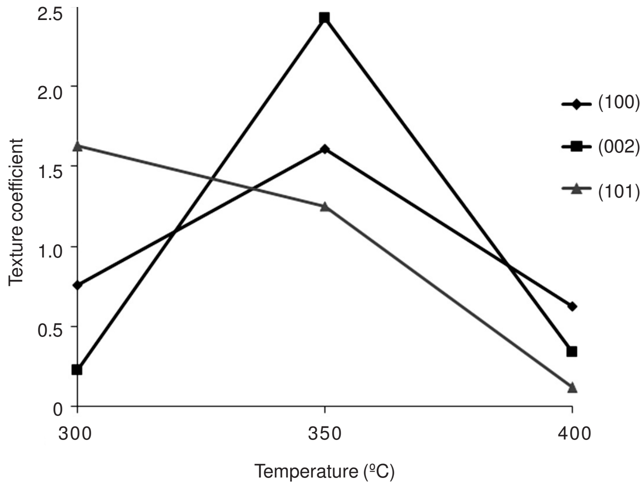

Fig. 4.Variation of texture co-efficient with different temperatures

film at 350 ºC for (002) orientation has been found to be 46.48 nm, highest among the films heat treated at other temperatures. This value of crystallite size agreed with the result of Paraguay *et al.*[1]. Table-1 showed that the micro strain value was lower for (002) orientation of each coated film for all the heat treatment temperatures. It revealed that the probable growth of ZnO crystals with fewer defects in this preferred orientation, which leads to larger crystallite size. The dislocation density (δ) defined as the length of dislocation per unit volume which gives the amount of defects in a crystal was estimated. The lower values of dislocation density along (002) orientation exhibits the good crystallinity of aluminium doped zinc oxide thin films. To analyze the preferred orientation, the texture coefficient (TC) of the films had been calculated using the following relation:

$$TC\ (hkl) = \frac{I_i(hkl)/I_0(hkl)}{1/N\sum_{i=1}^{N} I_i(hkl)/I_0(hkl)} \quad (2)$$

where, TC (hkl) is the texture coefficient of the (hkl) plane, I_i (hkl) is the measured intensity, I_0 (hkl) is the standard intensity of JCPDS power diffraction pattern of the corresponding peak and N is the number of reflection considered for the analysis.

Values of texture coefficient greater than unity indicate the preferred orientation of the crystallites in that particular direction. The variation of texture coefficient corresponding to the observed peaks in the XRD pattern is shown in Fig. 4. The values of texture coefficient observed for (002) plane found to be more than 1 for all the films showed the preferred orientation[12]. The calculated structural parameters for aluminium doped zinc oxide thin films coated at different heat treatment temperatures are compared with undoped ZnO thin film and the values are presented in Table-1. It showed relatively high texture coefficient value, low dislocation density and micro strain values for the Al doped ZnO film at 350 ºC. The above results indicated the better structural properties of doped thin films.

Optical properties: The transmittance spectra of ZnO and Al doped ZnO thin films are shown Fig. 5. The measured transmittance percentge of the aluminium doped zinc oxide films initially increases as the heat treatment temperature increases

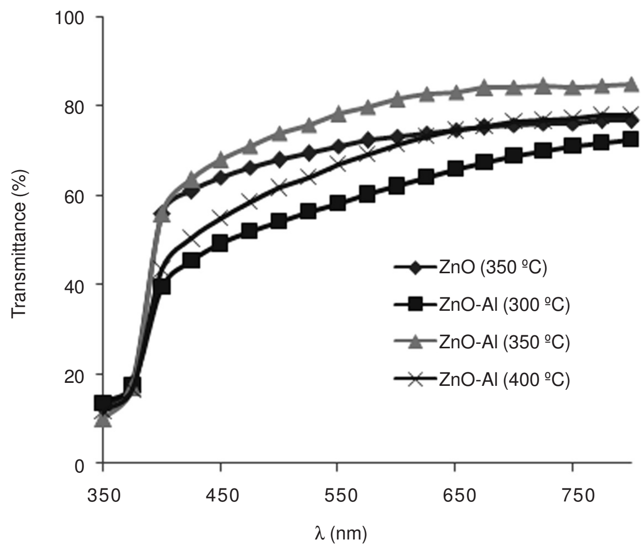

Fig. 5. Transmittance spectra of aluminium doped zinc oxide thin films

up to 350 ºC and decreases with the further increase in temperature as shown in the figure. Therefore the maximum transmittance of 85 % was observed in the visible region for the aluminium doped zinc oxide thin film heat treated at the temperature of 350 ºC. This increase in transparancy of the doped film as compared to the transparancy of undoped film at 350 ºC may be due to the formation of good crytallinity of this film and increase in grain size as found from XRD data. The value of absorption coefficient was determined and the band gap energy of aluminium doped zinc oxide thin films were determined using the plot between square of absorption coefficient and energy (α^2 *versus* hν) as shown in Fig. 6. The measured band gap energy of the films varies between 3.0 eV to 3.1 eV and is well in agreement with reported results[14]. It was also observed that there is an increment in the band gap energy value of doped thin film while compared with undoped ZnO thin film as reported by previous studies.

Surface properties: The AFM images obtained for ZnO and aluminium doped zinc oxide thin films heat treated at 350 ºC is shown in Fig. 7a. It has been observed further the formation of the uniform and smooth surface pattern of the films have

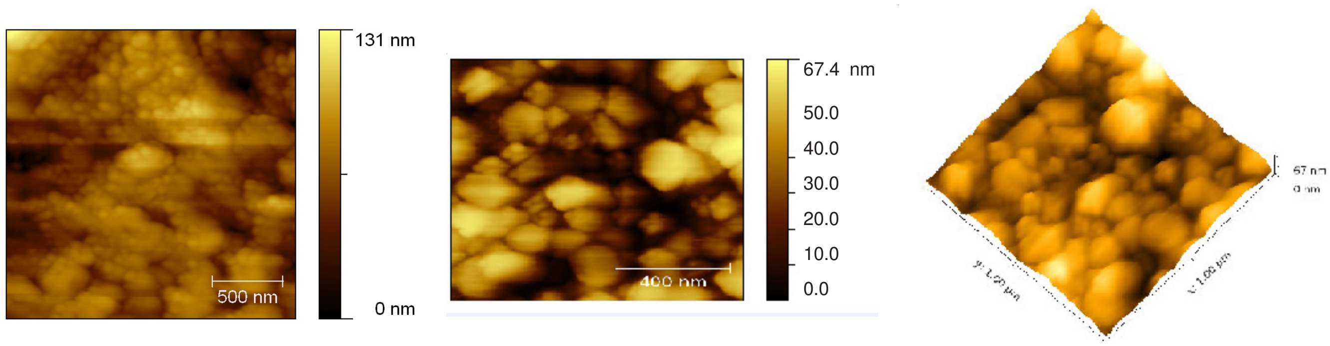

Fig. 7. (a) AFM image of ZnO thin film at heat treatment of 350 ºC; (b & c) 2D and 3D AFM images of aluminium doped zinc oxide thin film at heat treatment of 350 ºC

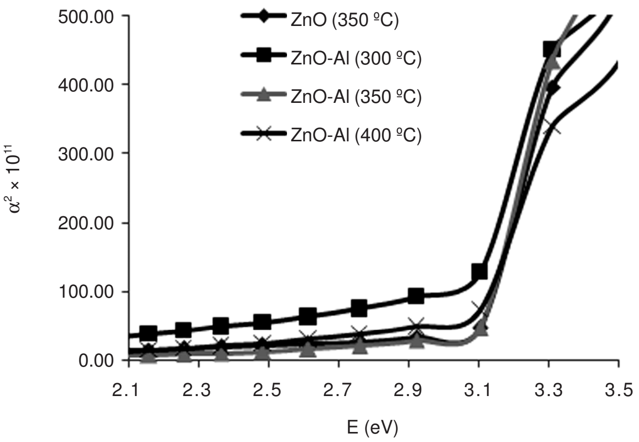

Fig. 6. Determination of band gap energy

evenly distributed grains. The root mean square (RMS) surface roughness of undoped and doped ZnO thin films observed were 2.8 and 2.24 nm[10]. It indicated the reduction of surface roughness on doping. The particle size of films doped with aluminum has been found to be larger than that of the undoped film[15]. It may be due to the cluster formation of smaller grains. The AFM image depicts the ZnO nano structure with grain size in the range of 30 to 40 nm and exhibited a porous structure.

Conclusion

Aluminium doped ZnO thin films had been prepared on the glass substrates by sol-gel spin coating process using zinc acetate as the source material and aluminum chloride as the dopant material. Observed properties of aluminium doped zinc oxide thin films were compared with undoped ZnO thin films. The XRD studies showed that the doping with different heat treatment temperatures affected the crystallinity of the aluminium doped zinc oxide films significantly as inferred from the degree of decrease of c-axis orientation and the hexagonal Wurtzite structure was not modified with the addition of dopant. The XRD pattern for doped thin films prepared at heat treatment temperature of 350 ºC exhibited an increase in grain size up to 40 nm. Higher optical transparency of 85 % had been observed for the aluminium doped zinc oxide thinfilms coated at heat treatment temperature of 350 ºC. Its direct band gap energy evaluated from the optical data was 3.1 eV, which shows increase in the band gap of Al doped thin film than the undoped thin film. The SEM images of aluminium doped zinc oxide thin films showed the crystalline form with smooth morphology and low surface roughness. The above results indicate the aluminium doped zinc oxide films developed under optimized condition could be desirable for solar cell applications.

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