

Investigation on the Evolution of Structural, Electrical and Transmitting Properties of Aluminium Doped Zinc Oxide Thin Film as a function of substrate temperature

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Abstract. Improved electrical conductivity of aluminium doped zinc oxide (AZO) thin films deposited by chemical spray pyrolysis method at various substrate temperatures is reported. Detailed investigation on the structural, electrical and optical properties were carried out using XRD, four point probe and UV-Vis-NIR measurements. The films deposited at 450 °C shows better conductivity and transparency as compared to the films grown at lower temperatures. Electrical conductivity, determined using four point probe measurements, is $6.271 \times 10^2 \Omega \cdot \text{cm}$ with an average transmittance of 70 % in the visible and IR region.

1. Introduction

Over the past decades, ZnO attracted considerable attention of the optoelectronics research community as a transparent conducting oxide (TCO) replacing comparatively expensive tin oxide which is widely used in various devices. Highly conducting and transparent ZnO films have been already realized by doping with F[1], Al[2], and Sn[3] through various deposition techniques like RF Magnetron sputtering[4], chemical vapour deposition[5], molecular beam epitaxy[6], pulsed laser deposition[7], sol-gel[8] and electrodeposition[9]. Because of the complexity in the deposition processes the cost of production is still not under control. Spray pyrolysis, different from other deposition techniques, is really promising in terms of large area deposition in a cost-effective way [10]. Al doped ZnO film based devices like Solar cells [2], LEDs [11], Transistors [12], etc. have been realized with very good efficiency.

Here, we investigate the influence of substrate temperature on the structural, electrical and optical properties of Al doped ZnO films deposited by Chemical Spray pyrolysis technique.



2. Experimental Details

We have adopted chemical spray pyrolysis technique to deposit Al (2 at.%) doped ZnO on soda lime glass substrates. The 0.2 M spray solution was prepared from zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2$, MERCK, $\geq 98\%$) and aluminium chloride (AlCl_3 , MERCK, $\geq 98\%$) as source material and dopant respectively. The solvent used was a mixture of propanol and distilled water in the ratio 7:3. 3ml acetic acid was added to suppress the precipitation of zinc hydroxide. Soda lime glass substrates were cleaned using soap solution and then immersed in chromic acid for 2 hours which were then ultrasonically cleaned in distilled water for 30 minutes and further washed with acetone, propanol and distilled water, respectively. The substrate temperature was varied from 300 to 450 °C. The spray rate was kept as 6 ml/min and the spray head was kept at a distance of 10 cm from the surface of glass substrate. The prepared solution was sprayed on to glass substrates for 10 minutes. After deposition, the films were removed immediately from the hot plate to a wooden surface. It was then allowed to cool in the atmosphere which was then covered and stored in air tight bags.

The structural, electrical and optical properties of all the samples were carried out in detail to analyse the quality of films to use them as transparent electrode in various optoelectronic devices. Structural properties of the samples were examined by X-ray diffractometer (Bruker D8 Advance) using CuK_α radiation ($\lambda = 0.15406$ nm). A four point probe setup (Keithley Source Measure Unit, Model 2450) was employed to measure the conductivity of the samples. UV-Vis-NIR spectroscopy (SCHIMADZU) was used in order to evaluate the transmittance properties.

3. Results and Discussion

3.1. Structural Analysis

Investigation on the main crystalline phases of the AZO thin films were carried out using X-Ray diffraction measurements. The diffraction patterns were recorded from 20° - 80° for all the samples prepared at various substrate temperatures and are shown in figure 1. The XRD patterns revealed the single phase of the ZnO films with hexagonal wurtzite structure. The major peaks (100), (002), (101) and (110) were observed at 31.8° , 34.4° , 36.2° and 56.5° respectively. All the peaks are in match with the JCPDS file no: 89-0510.

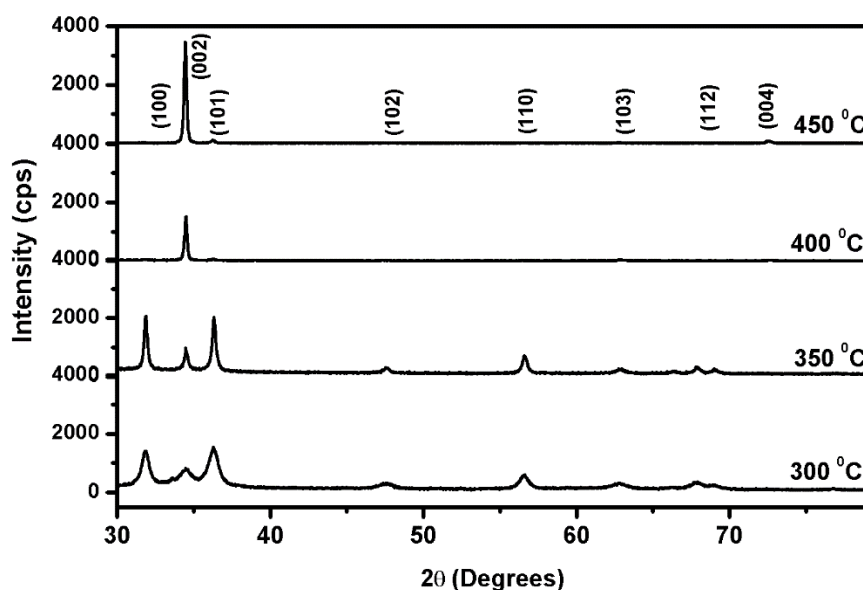


Figure 1. XRD patterns of AZO films prepared at various substrate temperatures of 300°C, 350°C, 400°C and 450 °C.

The XRD patterns reveals that the Al^{3+} ions are incorporated into the structure of ZnO without changing hexagonal wurtzite structure and no other phases from other oxides are observed. It is observed that the AZO films prepared at lower temperatures (300 and 350 °C) have a preferential orientation along (100) and (101) directions. At higher temperatures the intensity of (100) and (101) peaks were reduced and the preferential orientation changes to (002) direction at 400 and 450 °C. At higher temperatures (002) plane possesses lower surface free energy as compared to other planes, hence prefers growth along that direction [13]. The increased intensity of (002) peak shows the improved crystallinity of the samples along c-axis at higher substrate temperatures as a result of the relaxation in the strain. Figure 2 shows the texture coefficient of the films determined by using the equation [14] and its variation with temperature is plotted in figure 2.

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(N)^{-1} \sum I(hkl)/I_0(hkl)} \quad (1)$$

$I(hkl)$ – Intensity of (hkl) peak in AZO film, $I_0(hkl)$ – Intensity of (hkl) peak in bulk ZnO.

The size of the crystallites were calculated from Scherer's formula [15],

$$D = \frac{k \lambda}{(\beta \cos \theta)} \quad (2)$$

Where λ is the wavelength of X-ray ($\text{Cu } K_{\alpha} = 1.5406 \text{ \AA}$), β is the full width at half maximum, θ is the Bragg's angle. The crystallite size of the samples increases from 13 nm to 47 nm with the increase in substrate temperature. Growth of the grains with lowest surface free energy is more favoured at higher temperatures [13]. The lattice parameters of the hexagonal structured ZnO can be calculated from the relation [16],

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

Where, d_{hkl} = interplanar distance, (hkl) – Miller indices, a, c – lattice parameters. Figure 3 shows the calculated lattice parameters as a function of substrate temperature.

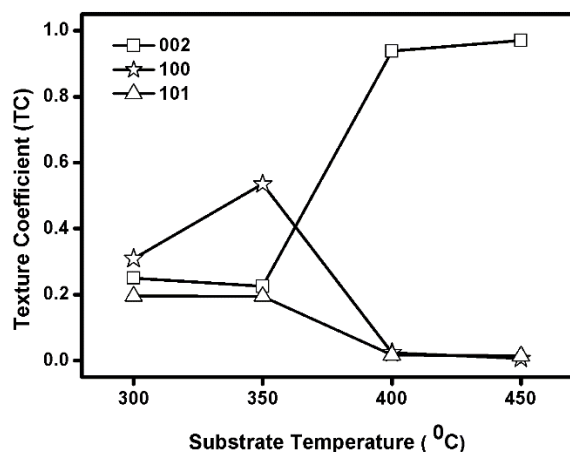


Figure 2. Texture coefficient of (002), (100) and (101) planes of AZO samples at various substrate temperatures.

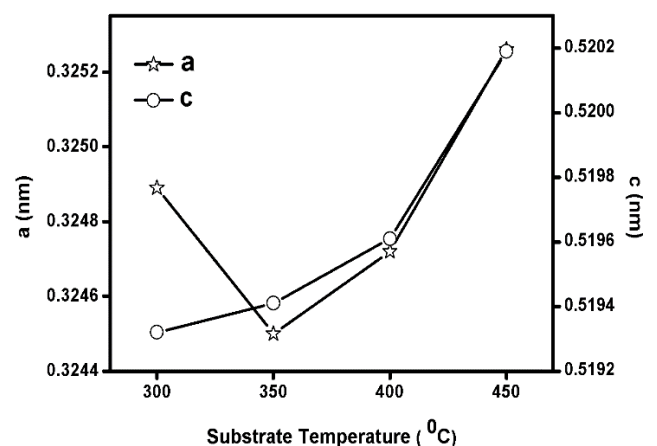


Figure 3. Illustration of lattice parameters as a function of substrate temperature.

The calculated lattice parameter 'c' for all the samples are less than the bulk ZnO which confirms the presence of residual strain in the films due to the substitution of Al^{3+} ions with shorter ionic radius ($\text{Zn}^{2+} = 0.072 \text{ nm}$, $\text{Al}^{3+} = 0.053 \text{ nm}$). The strain present in the thin films were determined by using the expression [17],

$$\varepsilon_{zz} = \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}} \quad (4)$$

Here, c_{bulk} refers to the lattice parameter of bulk ZnO (0.5205 nm) without strain taken from the JCPDS file and c_{film} is the calculated lattice parameter of samples. Figure 3 shows the evolution of stress and crystallite size as the substrate temperature increase from 300 to 450 °C. Stress in the films were calculated from [17],

$$\sigma_{\text{film}} = \left[\frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{C_{13}} \right] \times \varepsilon_{zz} \quad (5)$$

Where, $C_{11} = 208.8$, $C_{12} = 1197$, $C_{13} = 104.2$ and $C_{33} = 213.8 \text{ GPa}$, are elastic stiffness constants of bulk ZnO. Table 1 shows the crystallite size, d-spacing, lattice parameters, texture coefficient, strain and stress as determined from XRD patterns of the AZO films. Figure 4 gives information on the variation of crystallite size and stress as a function of substrate temperature.

Table 1. Details of Structural analysis from X-ray diffraction of samples at various substrate temperatures.

Substrate Temperature (°C)	Crystallite Size (nm)	d_{002} -spacing (nm)	c (nm)	a (nm)	Texture Coefficient (TC_{002})	Strain	Stress (GPa)
300	13	0.2596	0.51932	0.3248	1.0012	-0.00246	1.146
350	22	0.2597	0.51941	0.3245	0.9020	-0.00229	1.065
400	46	0.2598	0.51961	0.3247	3.7516	-0.00190	0.886
450	47	0.2601	0.52019	0.3252	3.8808	-0.00079	0.367

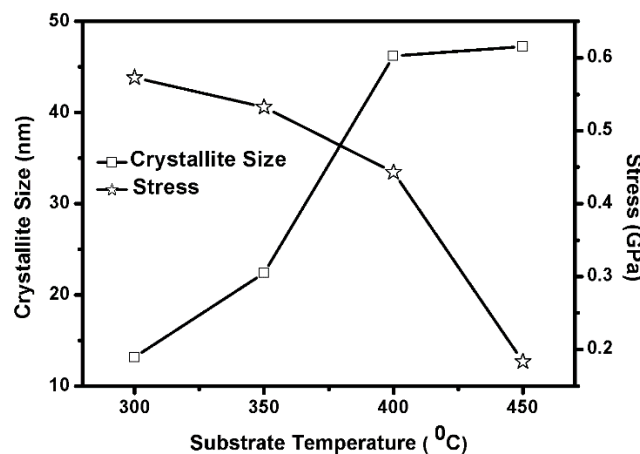


Figure 4. Variation of Crystallite size and stress with an increase in substrate temperature.

3.2. Electrical Studies

Electrical conductivity measurements were carried out by using a Keithley SMU Four probe setup. Table 2 shows the improvement in electrical conductivity when substrate temperature was increased. The increase in the conductivity is due to the improved crystallinity of the samples which reduces the scattering of charge carriers in the crystal lattice.

Table 2. Conductivity measurements of the Samples.

Sample (Substrate Temp. ⁰ C)	Conductivity (Scm ⁻¹)
300	4.599×10^{-5}
350	3.631×10^{-4}
400	1.919×10^1
450	6.271×10^2

3.3. Transmittance studies

Figure 5 shows the observed transmittance values of the AZO films in the range of 350-1000 nm using a UV-Vis-NIR spectrometer. The films prepared at higher temperatures shows better transmittance due to the decrease the concentration of oxygen vacancies [18]. The films prepared at 450 °C shows an average transmittance of 70% (figure 5). A blue shift was observed for the fundamental absorption edge of ZnO films with substrate temperature, which reveals the broadening of band gap.

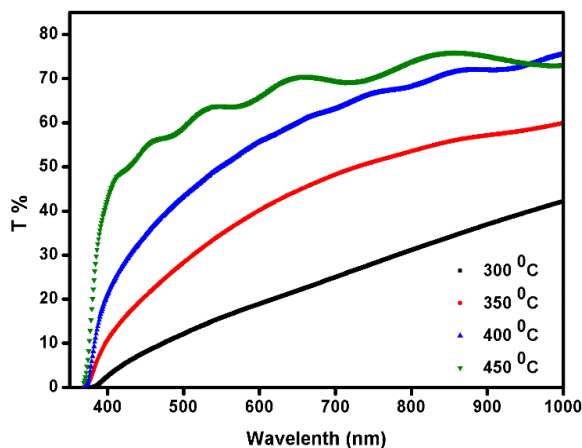


Figure 5. Transmittance spectra of AZO samples with increase in substrate temperature.

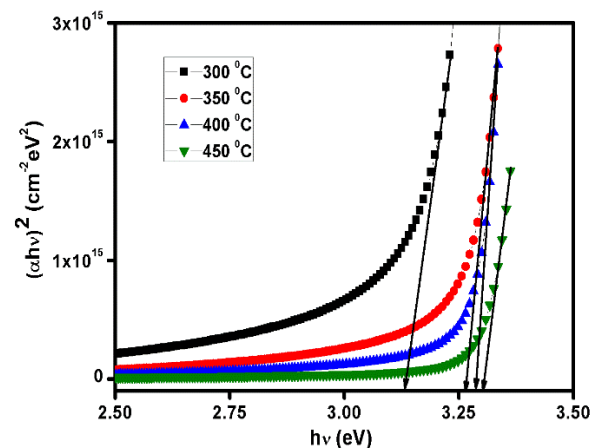


Figure 6. Tauc's plots for the determination of band gap of AZO thin films.

The bandgap of the samples were determined from tauc's plots, as seen in figure 6, drawn by using the formula [8],

$$(\alpha h\nu)^2 = B(h\nu - E_g) \quad (6)$$

Where, E_g is the optical bandgap, $h\nu$ is energy of incident photon and B is a constant. Figure 6 shows the $h\nu$ vs $(\alpha h\nu)^2$ graph whose linear part is extrapolated to x-axis to obtain the optical band gap which is the $h\nu$ value corresponding to zero $(\alpha h\nu)^2$. The observed optical bandgap of the films are shown in the table 3. The bandgap is increased from 3.132 to 3.303eV. This increase is due to the Burstein-Moss band filling effect [15]. The increase in the substrate temperature might have increased the

number of charge carriers which fills the lower energy states in the conduction band leading to an increased Fermi level. Hence the absorption edge should shift to higher energy [19].

Table 3. Bandgap values obtained from the tauc's plot.

Sample (Substrate Temp. ⁰ C)	Bandgap (eV)
300	3.132
350	3.266
400	3.288
450	3.303

4. Conclusion

Aluminium doped ZnO thin films have been deposited by Chemical Spray pyrolysis method at various substrate temperatures. The structural, electrical and transmittance properties of the samples with temperature were investigated by employing XRD, four point probe and UV-Vis-NIR spectroscopy measurements. Highly crystalline sample with improved conductivity and transmittance was obtained at a substrate temperature of 450 ⁰C. The optimum sample shows a conductivity of $6.271 \times 10^2 \text{ Scm}^{-1}$ with an average transmittance of 70 %. These investigations promises the possibility of achieving highly conducting and transparent ZnO thin films doped with aluminium through chemical spray pyrolysis for optoelectronic applications.

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