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Investigations on impact of post-heat temperature on structural, optical and electrical properties of Al-doped ZnO thin films prepared by sol-gel method

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Abstract

Aluminum doped ZnO (AZO) thin films have been prepared by spin coating route on glass substrate. The structural, optical and electrical thin films have been characterized in different post-heat temperatures between 450 and 600°C. X-ray diffraction analysis has revealed hexagonal wurtzite structure with (002) preferred orientation which increased in crystallite size by increasing post-heat temperature. The optical spectra of the films showed the transmittance higher than 90% within the visible wavelength region. Our results show that optical gap and surface resistance of the films are decreased by increasing post-heat temperature.

Keywords: Sol-gel method, optical spectra, post-heat temperature, spin coating.

Introduction

Al, In or Ga-doped ZnO thin films are one of the most promising transparent conductive oxides for advanced applications such as displays, solar cells, optoelectronic devices, electrochromic devices, etc. Non-toxic, low cost, with high thermal/chemical stability and resource availability, doped ZnO thin films are intensively studied to replace ITO (what is ITO) thin films in the above mentioned applications (Albrecht *et al*., 1998).

Earlier studies indicate that various techniques have been used to deposit ZnO films (undoped and doped conditions) on different substrates, including spray pyrolysis (Jacoboni & Reggiani, 1983) organometallic chemical vapour deposition (Brennan *et al*., 1983), pulsed laser deposition (Kane, 1957), sputtering (Fischetti *et al*., 1991), and sol-gel process (Ghani *et al*., 2003).

Among these, the sol-gel technique is credited with several advantages such as deposition of high purity, homogeneous, cheaper and large-area films at relatively low temperatures. There are scarcely any reports on the transport parameters of Al-doped in ZnO films prepared by the sol-gel technique. In the present study, Al-doped in ZnO films were prepared on glass substrate by the sol-gel spin coating method using homogeneous and stable zinc acetate dehydrate,2-ethanolamin, monoethanolamine sol doped with 1% Al with respect to Zn. The crystal orientation and electrical and optical properties with post-deposition heating temperature were investigated.

Experimental method

Methoxy ethanol and monoethanolamine were used as the solvent and stabilizing agent, respectively. The dopant source for aluminium was aluminium chloride. Zinc acetate dihydrate and the source of dopant were first dissolved in a mixture of 2-methoxy ethanol and monoethanolamine at room temperature. The concentration of zinc acetate was 0.8 mol/l and the molar ratio of monoethanolamine to zinc acetate was kept as 1:1. The solution is stirred for 1 h at 343 K to yield a clear homogeneous and transparent solution using a magnetic stirrer, which served as the coating solution. The coating was made after 2 days after the solution is prepared, then the solution is dropped onto glass substrates. The substrates were cleaned using methanol and acetone and then rinsed with distilled water before the deposition of the films. The substrates are spinned at 3000 rpm for 25 sec while coating. After spin coating the substrates were kept at 573 K for 12 min to evaporate the solvent and to eliminate the organic component in the film. This procedure is repeated for 12 times. The films are then annealed at 450, 500, 550 and 600°C for 1h. The crystallinity of each film was measured using Bruker D8 advance instrument with Cu_{Ka} radiation of wavelength 1.54 A^{O}. The crystallite size has been calculated from XRD data using Scherrer's formula. The optical transmittance is measured using a UV-VIS spectrophotometer in the wavelength range from 300 to 1200 nm and calculated the optical band gap energy. The electrical resistivity of the films is measured by two electrode method.

Results and discussion

Al-doped in ZnO films were fabricated by the sol-gel technique on corning glass substrates and the XRD spectra of the films annealed in the temperatures up to 600°C.

Fig.1 shows the XRD patterns of the films deposited at different annealing temperature from 450 to 600°C with an interval of 50°C. The films exhibit a dominant peak at $2\theta = 34.34°$ corresponding to the (002) plane of ZnO and other peaks corresponding to (100) and (101) and

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indicating the polycrystalline nature of the films. The relative intensity of the (002) peak increases with increasing annealing temperature to 600°C.

The increase in peak intensity indicates an improvement in the crystallinity of the films. The crystallite size of the films is calculated from the Scherrer formula (Foutz, 1997):

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos\theta}$$

where D is the crystallite size, λ is the X-ray wavelength, θ, the Bragg's angle in degrees and β is the full width at half maximum of the (002) plane. The crystallite size increases from 27 to 42 nm with increasing the post-deposition heating temperature from 450 to 600°C (Table 1) which can be understood by considering the merging process induced from thermal treatment. For ZnO nanoparticles, there are many dangling bonds related to the zinc of oxygen defects at the grain boundaries. As a result, these defects are favorable to the merging process to form larger grains while increasing the annealing temperature.

Fig. 1. XRD patterns of the Al-doped in ZnO thin film

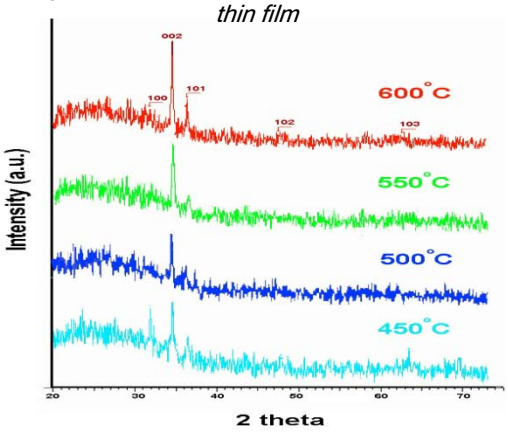


Table 1 shows the change in thickness with the heat treatment temperatures, thickness of the films were calculated using transmittance spectra (Izuka *et al*., 1990). As it can be seen, the thickness continually decreased with increasing in annealing temperature which is due to the organics reducing and film crystallization (Bhuiyam *et al*., 2000).

Table 1. Structural information from the XRD pattern

Sample	2θ (deg)	D (Å)	FWHM (θ)	Mean grain size(nm)	Thick-ness (nm)
AZO-450	34.55	2.59	0.314	27	425
AZO-500	34.57	2.59	0.314	32	415
AZO-550	34.56	2.59	0.218	38	391
AZO-600	34.52	2.59	0.201	41	372

Figure 2 shows the optical transmittance spectrum for the samples. The transmittance within the visible and the near infrared region is always higher than 90% (including the glass substrate), which reveal the superior optical properties exhibited by the Al-doped in ZnO thin films produced in this work by the sol-gel method.

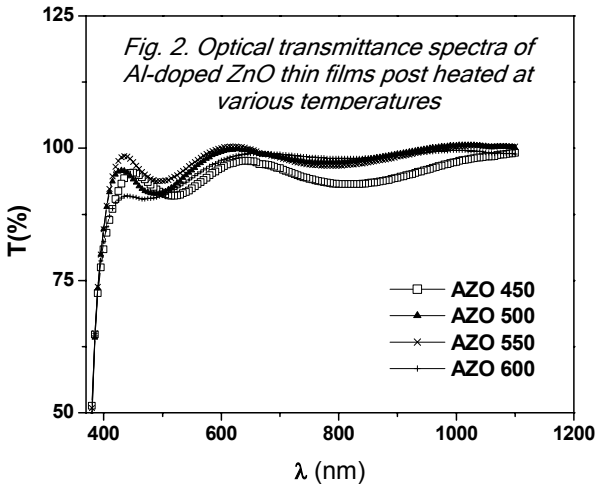
When the annealing temperature is increased from 450°C to 600°C the transmittance of the films increases. The transmittance of the films annealed at 550 and 600°C is higher than 95% for wavelengths between 600 to 700 nm. As mentioned before, particle size and number of voids present in the film increase with increasing annealing temperature and may lead to a decrease in optical scattering.

The optical band gap is calculated using Tauc's plot as shown in figure 3. The value of α is determined from transmittance spectra. It can be noticed from the Fig. 3, that the energy gap was obtained by extrapolating the linear absorption edge part. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents. In all cases the films present a sharp absorption edge at wavelengths of about 360 nm, which is higher than the intrinsic band gap of ZnO.

Figure 4 shows electrical resistivity in the Al-doped ZnO films with post deposition heating temperature by four terminal method at room temperature. The resistivity of the films decreases with increasing the annealing temperature from 450 to 600°C, because increasing of crystallite size results in decreasing of grain boundary which leads to higher conductivity (Martienssen *et al*., 2005).

Figure 5 shows photo-conductance effect in the films. The resistivity decreased while increasing time from 0 to 10 min at constant light intensity of 40000 Lux. It is well known that the n-type conductivity in nonstoichiometric ZnO is due to the presence of oxygen vacancies and interstitial zinc. This is because the electrical conductivity of ZnO is directly related to the electron density. The electrons formed by the ionization of the interstitial zinc and the oxygen vacancies will affect the electrical conductivity of ZnO. The decrease in electrical resistivity might result from the increase in electron concentration in the film structure.

Fig. 2. Optical transmittance spectra of Al-doped ZnO thin films post heated at various temperatures



Conclusion

Transparent and conductive Al-doped ZnO thin films on glass substrate were prepared by a sol-gel method using zinc acetate and aluminium chloride, 2-methoxyethanol as solvent. The effects of different annealing temperature on the

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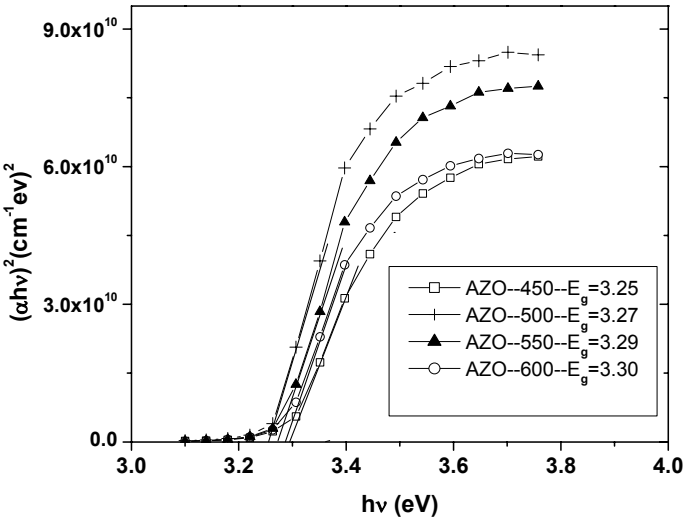
structural properties, electrical resistivity and optical transparency of the films were studied.

Fig. 3. Plot of $(\alpha h\nu)^2$ versus hν for Al-doped ZnO thin films with different annealing temperature.



All the films were polycrystalline with a hexagonal structure and had a preferred orientation with the c-axis perpendicular to the substrate. The crystallite size increases from 27 to 42 nm with increasing the annealing temperature from 450 to 600°C while the resistivity decreased. The optical transmittance spectra of the annealed films show a transmittance over than 90% within the visible and near infrared wavelength region and more than 95% for the 550 and 600°C post-heated samples. Electrical resistivity of the films is also decreased by increasing in annealing temperature.

Fig. 4. Electrical resistivity of the films annealed from 450 to 600° C

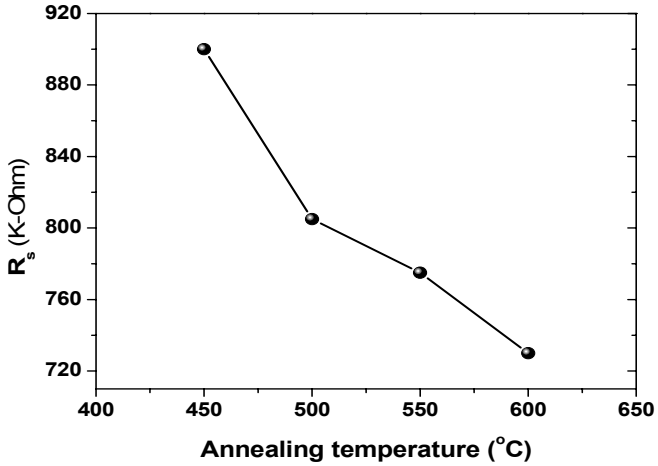
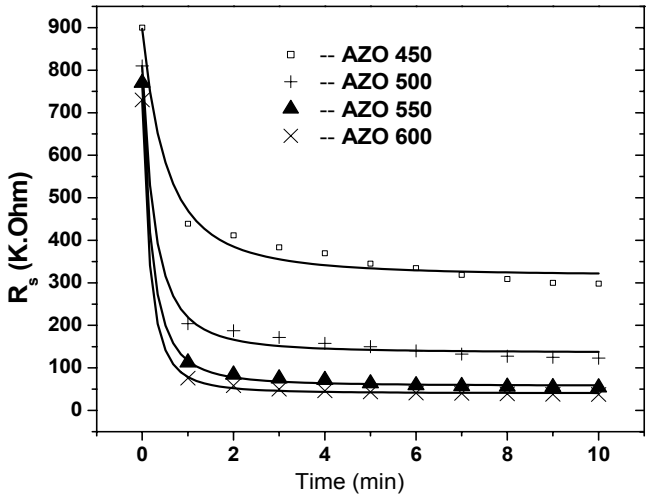


Fig. 5. Electrical resistivity vs time of the films annealed from 450 to 600° C.



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