Effect of Annealing Temperature on Optical and Electrical Properties of Sol-Gel ZnO Thin Films

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Abstract. Zinc oxide (ZnO) is a multifunctional material having unique physical properties as well as chemical and photo-stability. In the present work, ZnO thin films were synthesized on indium tin oxide (ITO) coated glass substrates by the sol-gel process using spin coating. The precursor sol was prepared by mixing 2-methoxyethanol and zinc acetate dihydrate and using mono-ethanolamine as stabilizer. After annealing at temperatures of 350 ºC, 450 ºC or 550 ºC, structural, optical and electrical studies were carried out. X-ray diffraction patterns showed the crystalline hexagonal wurtzite structure of the ZnO thin films, while the relative peak intensities showed the formation of a *c*-axis preferential orientation as the annealing temperature increased. Scanning electron microscopy results revealed that a wrinkle-like morphology obtained when annealing at 450 ºC was transformed into a fine grain structure after annealing at 550 ºC. Optical transmittance of the thin films was about 80% obtained in the range 400-800 nm measured using a UV-vis spectrophotometer. The optical bandgap varied from 3.26 eV to 3.28 eV as calculated using Tauc's plot method. The photoluminescence extended from the UV near band edge emission over the blue region and was influenced by the ITO substrate. The current-voltage characteristics of ZnO films show Ohmic behaviour and the resistivity decreased with increasing annealing temperature. These highly transparent and conducting ZnO thin films can be used in solar cells and optoelectronic devices.

1. Introduction

Zinc oxide (ZnO) is a wide direct bandgap semiconductor with an energy gap of 3.3 eV and a high free exciton binding energy of 60 meV at room temperature which has great applications in the information age [1,2]. Zinc is a cheap and abundant raw material, and ZnO thin films possess unique optical, electrical and semiconducting properties used extensively in applications such as transparent conducting contacts, solar cells, gas sensors, laser diodes, ultraviolet lasers and thin film transistors, etc. ZnO is also attractive for high frequency surface acoustic wave device applications [3]. Despite several approaches adopted for fabricating ZnO thin films, controlling the crystallinity as well as grain size and shape still needs to be further investigated. Therefore, it is essential to investigate optimum conditions for fabrication of highly oriented and transparent ZnO thin films.

ZnO thin films can be produced by different methods such as the sol-gel technique [4,5], chemical vapour deposition [6], pulsed laser ablation [7], spray pyrolysis [8], magnetron sputtering [9] and thermal evaporation [10]. The sol-gel technique has many advantages in preparing ZnO films, such as strong *c*-axis orientation, ease of compositional modifications, large films, simplicity of working principle, low cost, and low annealing temperature. The sol-gel method is therefore prevalent today and ideal for exploratory research. In this work we have used the sol-gel method to deposit ZnO thin films but, regardless of the deposition technique, the annealing effects still remain an open subject for

research. It is interesting to study how the physical properties change with annealing temperature. Bouhssira *et al.* [10] have studied the influence of annealing temperature on the properties of ZnO thin films deposited by thermal evaporation and inferred that the annealing of ZnO thin films allowed obtaining layers with optical transmittance close to 80%. Mosbah *et al.* [11] deposited ZnO thin films by RF sputtering and observed annealing effects on the structural and optical properties. In the present work we have deposited ZnO thin film by the sol-gel method on indium tin oxide (ITO) covered glass substrates. We have focused on the influence of the annealing temperature on the structural, morphological, optical and electrical properties of the ZnO thin films.

2. Experimental details

ZnO thin films were deposited on ITO coated Corning glass substrates by the sol-gel process. The sol was prepared by dissolving 2.195 g of zinc acetate dihydrate (99% purity) in 50 ml of 2-methoxyethanol (solvent) and mixed with mono-ethanolamine (stabilizer) in a 1:1 molar ratio. The solution was stirred using a magnetic stirrer at room temperature for 2 h and then at 60 ºC for 1 h. This resulted in a clear solution which was found to be stable and transparent with no precipitate or turbidity after cooling to room temperature. The sol was aged for 72 h at room temperature in order to make it more viscous before using it for spin coating. The ITO covered glass substrates were degreased with acetone by ultrasonic agitation for 10 min and then washed several times by distilled water, and finally methanol. The sol was dropped onto the substrate which was then spun at 2500 rpm for 30 s. The coated substrate was dried at 230 ºC for 10 min in air, and the coating process repeated 15 times to increase the thickness. The resulting material was divided into three pieces and annealed in air at a temperature of 350 ºC, 450 ºC or 550 ºC for 1 h to complete the formation of the ZnO thin film. The flow chart of the entire process for synthesis of the ZnO films is schematically drawn in figure 1.

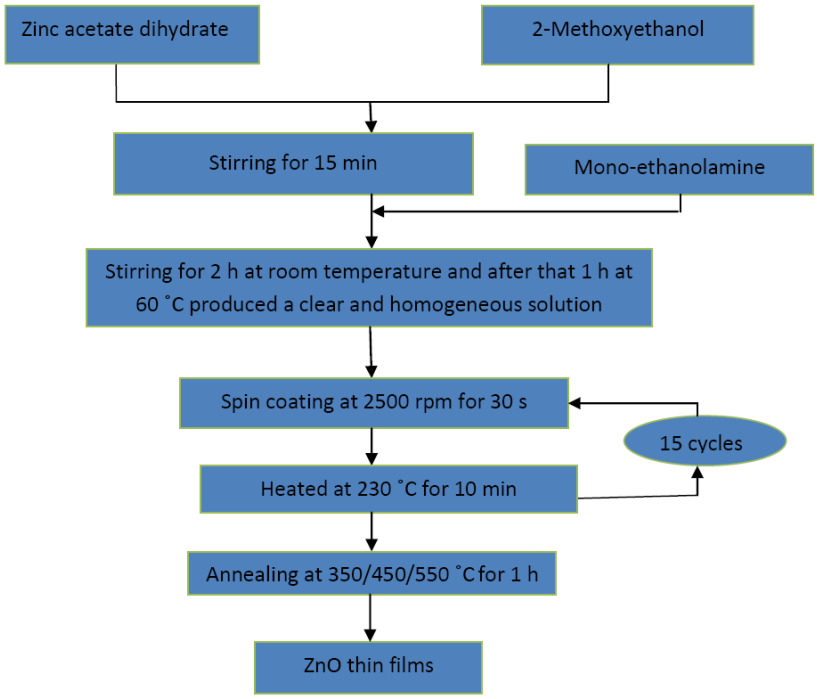

Figure 1. Flow chart for the preparation of ZnO thin films by spin-coating.

Structural, optical and electrical characterization of the ZnO thin films followed. X-ray diffraction (XRD) using a PANalytical X'pert Pro system was used to analyze the crystallographic structure and crystallite size of the films. Scanning electron microscopy (SEM) performed with a Zeiss EVO-40 instrument was used to assess the surface morphology, while a UV-vis spectrophotometer (Schimadzu-3600) was used to measure the transmittance of the samples. The bandgap was determined using Tauc's plot method. Photoluminescence (PL) data was recorded using a

spectrofluorophotometer (Shimadzu RF-5301 pc) and current-voltage (I-V) measurements were made using a Keithley 4200 Semiconductor Characterization System.

3. Results and discussion

3.1. X-ray diffraction analysis

The structure and crystalline quality of the deposited ZnO thin films on ITO coated glass substrates annealed at different temperatures of 350 ºC, 450 ºC or 550 ºC were studied by XRD and the patterns are shown in figure 2(a). The (100), (101), (102) and (002) peaks of ZnO (JCPDS file No. 36-1451) are observed, in addition to several peaks corresponding to ITO occurring at 21.58º, 30.69º, 35.57º and 51.17º which are marked with an asterisk (*) in figure 2(a). The ZnO peaks result from interplanar spacings d_{hkl} given by [12]

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

for the hexagonal wurtzite structure, where a and c represent the lattice parameters and hkl are the Miller indices. The (100) peak had maximum intensity relative to the (002) peak for the sample annealed at 350 ºC, but showed a relative decrease as the annealing temperature was increased. The (002) peak was dominant for the ZnO thin film which was annealed at 550 ºC, showing a preferential orientation and indicating that the c-axis of the crystallites is generally perpendicular to the surface of the film.

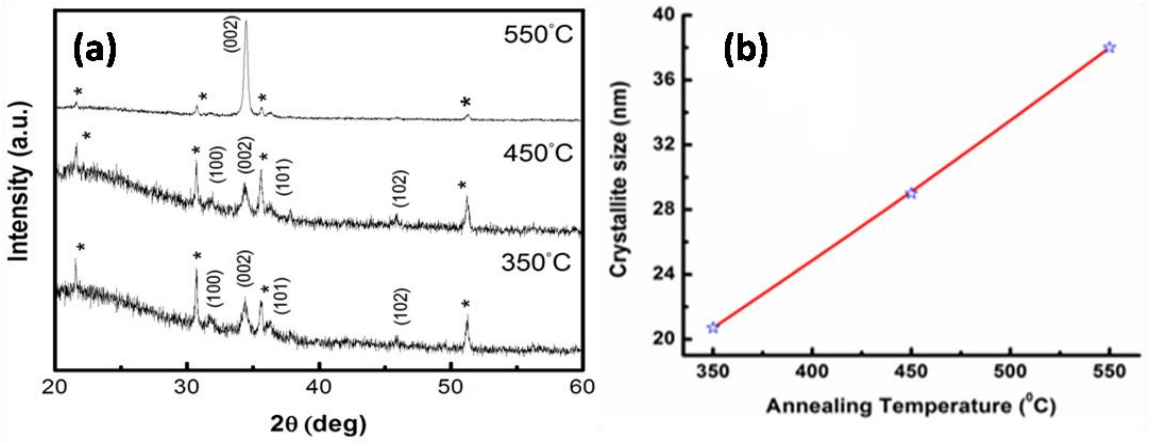

Figure 2. XRD patterns of ZnO thin films annealed at different temperatures. (b) Crystallite size as a function of annealing temperature.

The crystallite size was determined by Scherrer's equation [13]

$$D = \frac{K\lambda}{\beta \sin\theta} \tag{2}$$

where K is a constant taken to be 0.94, λ is the wavelength of X-rays used (0.154 nm for Cu Kα) and β is the full width at half maximum. The crystallite size was calculated using the (002) peaks which were dominant in all the samples, and it increased from 21 nm to 38 nm with increasing annealing temperature as shown in figure 2(b). A similar result was obtained by Rattana *et al.* [14] on NiO/ZnO heterojunction thin films prepared by the sol-gel method and the increase of the crystallite size with annealing temperature can be explained by the atoms have enough energy to diffuse. The direction perpendicular to the c-axis is the most favourable growth plane for the hexagonal ZnO structure because it has the lowest surface energy [15].

3.2. Surface morphology

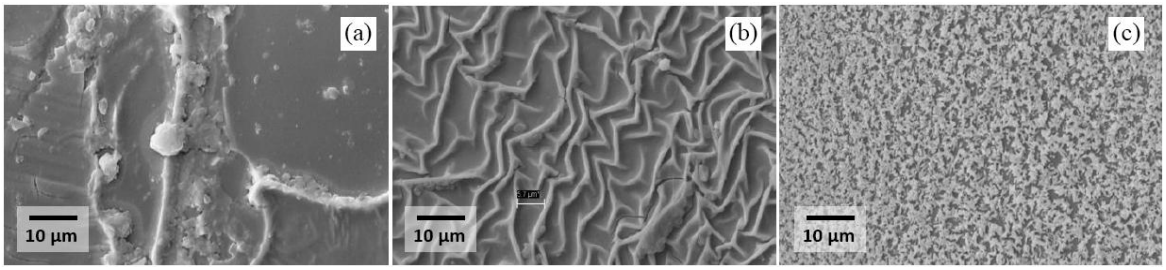

Figure 3. SEM images of the ZnO thin films annealed at (a) 350 ºC, (b) 450 ºC and (c) 550 ºC.

The microstructure and surface morphology of the ZnO thin films were observed using SEM micrographs recorded using an electron accelerating voltage of 20 kV at an original magnification of 4000 times and are shown in figure 3. An irregular morphology is obtained when the annealing temperature is low (350 ºC). The microstructure of the film annealed at 450 ºC has a wrinkle-like morphology. In contrast, the higher annealing temperature of 550 ºC results in a surface of fine grains which is similar to the morphology of Sn doped ZnO thin films observed by Zegadi *et al.* [16]. This is consistent with the improved XRD spectrum for ZnO, suggesting grain growth found for the sample annealed at this temperature.

3.3. Optical and photoluminescence studies

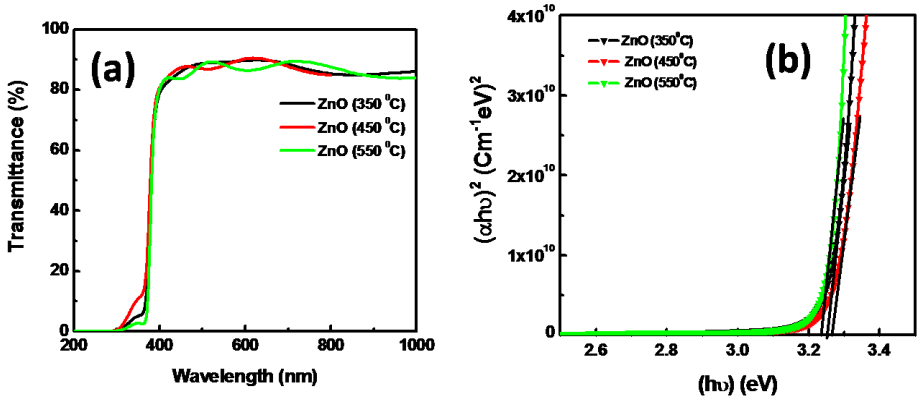

Figure 4. (a) Transmittance, and (b) Tauc's plot of annealed ZnO thin films.

The transmittance measurements were carried out in the range 200 nm - 1000 nm and are shown in figure 4(a). The maximum transmittance, greater than 80%, is observed over the whole visible range and it does not vary greatly with annealing temperature. The dramatic decrease in transmittance in the UV region below 400 nm is due to exciton-related band-to-band absorption of ZnO. The optical bandgap was calculated by considering that for a direct bandgap material the absorption coefficient α can be modelled by [17]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{3}$$

where A is a constant, E_g is the bandgap energy, h is Planck's constant and ν is the frequency of the incident radiation. Therefore the optical bandgap can be estimated by extrapolating the experimental data in a Tauc's plot, figure 4(b), to the horizontal axis. The bandgap has a maximum value 3.28 eV for the sample annealed at 450 ºC and is slightly smaller for the sample annealed at 550 ºC. This decrease in the bandgap is attributed to the reduction in oxygen vacancies in the thin films when annealed at the higher temperature. Chaabouni *et al.* [18] and Saleh *et al.* [19] found similar results in ZnO thin films deposited by sol-gel and RF sputtering methods respectively.

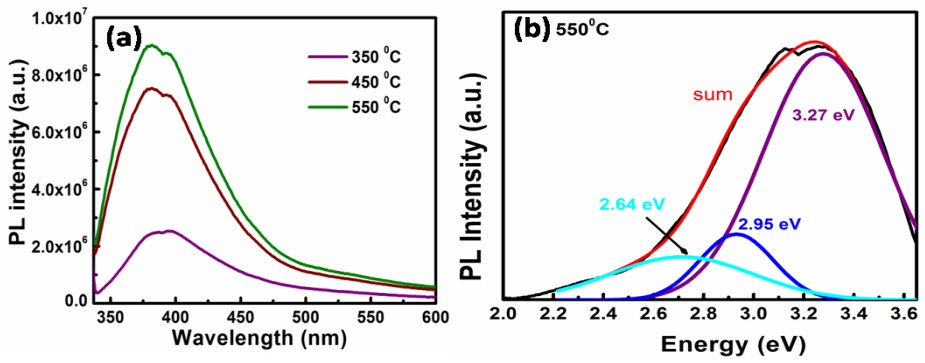

Figure 5. (a) PL spectra of ZnO thin films produced with different annealing temperatures. (b) Deconvolution of the PL emission for the sample annealed at 550 ºC.

The PL spectra of the ZnO thin films annealed at different temperatures are shown in figure 5(a). The small cusp-like feature near 390 nm in all the spectra is due to the instrument. Although there is no significant change in the form of the emission, its intensity increased with annealing temperature. Generally the luminescence from ZnO consists of a narrow excitonic emission in the UV region and broad intrinsic defect emission in the visible region, but in this case it consists of a broad emission extending from the UV over to the blue region. In figure 5(b) the emission of the sample annealed at 550 ºC is redrawn with a horizontal energy axis and fitted with three Gaussian peaks, namely a high energy peak in the UV region at 3.27 eV (~380 nm) attributed to near band edge emission, a violet peak at 2.95 eV (~420 nm) due to O dangling bonds, together with a weak blue emission at 2.64 eV (~470 eV) originating from Zn and O intrinsic defect emission. Teng *et al.* [20] reported that the near band edge emission of ZnO deposited on ITO by magnetron sputtering was broadened by an unusual (anomalous) component at 410 nm (similar to the violet peak reported here) and suggested this was as a result of O dangling bonds on the ITO surface layer or the interface between the ZnO and ITO. As the annealing temperature was increased, the crystallinity of the ZnO films improved which enhanced the PL intensity.

3.4. Electrical Characterization

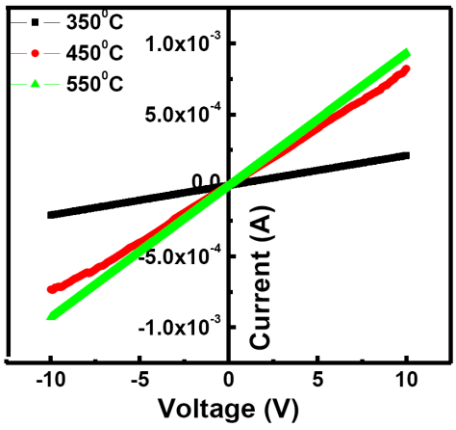

Figure 6. Electrical characterization of ZnO thin films produced at different annealing temperatures.

Few studies have been done of the electrical characterization of ZnO thin films with respect to annealing temperature. In the present work the electrical characteristics of sol-gel ZnO thin films on ITO coated glass substrates produced at different annealing temperatures were measured using a Keithley 4200 semiconductor characterization system. The effect of annealing temperature on the I-V results of the ZnO films is shown in figure 6. The I-V characteristics show good linear (Ohmic) behaviour. Aoun *et al.* [21] deposited ZnO thin films by spray pyrolysis for different substrate temperatures and reported a decrease in resistivity with increasing temperature. In the present work the ZnO thin film annealed at 550 ºC showed minimum resistivity and a current of close to 1 mA is obtained for an applied 10 V potential difference, which is larger than for the thin films annealed at

350 ºC and 450 ºC. The decrease in electrical resistivity may be due to the improved cystallinity and increased crystallite size, as well as the possible reduction in defect concentrations, of the thin films with increased annealing temperature. From the XRD and SEM results it is evident that the films annealed at higher temperature have better crystallinity. As a result of the enhancement of both morphological and structural characteristics of ZnO films, the electrical properties are also improved. Therefore sol-gel ZnO thin films on ITO glass are suitable for optoelectronic devices and buffer layers in solar cells, but require proper annealing at moderate temperature.

4. Conclusion

ZnO thin films were deposited on ITO coated Corning glass substrates using the sol-gel technique and annealed at different temperatures between 350 ºC and 550 ºC. The films have the hexagonal wurtzite crystalline structure and the (002) diffraction peak was dominant in the ZnO film annealed at 550 ºC, indicating preferential orientation of the hexagonal axis perpendicular to the substrate surface. The crystallite size increased from 21 nm to 38 nm with increasing annealing temperature. The transmittance of the films were above 80% in the visible region and the bandgap had a maximum value of 3.28 eV for the sample annealed at 450 ºC, which decreased slightly when the maximum annealing temperature of 550 ºC was used. The PL emission consisted of near band edge emission near 380 nm, violet emission near 420 nm associated with the ITO/ZnO surface/interface O dangling bonds and a weak blue defect emission at ~470 nm. The I-V characteristics of ZnO films show Ohmic behaviour and the resistivity decreases with increasing annealing temperature. These highly transparent ZnO thin films can be used as a window layer in solar cells and optoelectronic devices.

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