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Effect of Annealing on Optical Properties of Zinc Oxide Thin Films Prepared by Homemade Spin Coater

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Abstract
Zinc oxide (ZnO) thin films were deposited on the ordinary glass substrates by spin coating method. The precursor solution was prepared by mixing zinc acetate dihydrate in appropriate proportions with ethanol and diethanolamine (DEA). The obtained thin films were dried at 200°C for 15 minutes in hot air oven. Crystalline ZnO thin films were achieved following annealing process at temperatures 300°, 400° and 500°C for 2 hours. Thin films as- prepared were studied by X-ray diffraction and UV-visible spectroscopy. The films were transparent from near ultraviolet to infrared region. Optical band gap energy of ZnO was obtained 3.22 eV at 300°C. On annealing at 400° and 500°C, band gap energy was shifted at 3.14 eV and 3.05 eV respectively.

Key words: sol-gel method, zinc oxide, absorption spectra, annealing, band gap energy

Introduction
Semiconducting devices are mostly based on advancement of thin film technology. Thin film is a two dimensional material deposited by either atom-by-atom or molecule-by-molecule condensation method. The thin film technology is deposition of molecules. On the other hand, the thick film is deposition of particles. Oxide semiconductors have drawn much attention because of their wide range of potential device applications, from transistors to optical detection and emission. In this context, ZnO is of a particular interest because of its wide direct band gap energy of 3.37 eV and a large binding energy of 60 meV (Liang & Yoffe 1968) that makes it one of the best candidates for transparent field effect transistors, gas sensors and solar cells (Djurišiæ *et al.* 2010). Moreover, ZnO is a promising material for short wavelength optoelectronic devices, especially for ultraviolet light-emitting diodes (UV LEDs) and laser diodes (LDs). This exciton binding energy (60 meV) is much larger than the room temperature thermal energy (26 meV), suggesting that the electron-hole pairs are stable even at room temperature. Therefore, efficient UV LEDs and LDs operating at room temperature can be expected, provided that high-quality p-type ZnO is available. A great effort has been brought out to improve the electrical and optical properties of ZnO films through a diversity of material synthesis techniques, substrates, doping and processing. Up to now, several methods have been used to fabricate high quality ZnO thin films such as pulsed laser deposition (Craciun *et al.* 1994), molecular beam epitaxy (Heo *et al.* 2006), metal organic chemical vapor deposition (Tan *et al.* 2005), direct current and radio-frequency magnetron sputtering (Cho 2009), sol-gel (Ghodsi *et al.* 2010), and spray pyrolysis (Ayouchi *et al.* 2003 and Godbole *et al.* 2011). Among the growth methods, the sol-gel method shows many advantages over other deposition techniques, such as its simplicity, ease of control of the chemical composition of the thin films, and low equipment cost. In addition, it deposits films with large areas and good thickness uniformity. However, the crystalline quality of the ZnO prepared by sol–gel process might be inferior to other methods (Borgogno *et al.* 1982). This effect is caused by the low temperature annealing performed in the sol-gel process that affects the structural and optical characteristics of the thin films. The present study deals with preparation of ZnO thin films by Sol-gel method using homemade spin coater. Also this work reports structural and optical characterization of ZnO thin films by varying temperature.

Methodology

The precursor solution can be deposited on a suitable substrate by various coating techniques. The mainly used techniques for thin film preparation from the Sol-gel route are either spin coating or dip coating. Spin coating allows the preparation of thin films on flat substrates. An adequate amount of solution is dropped on a rotating substrate. The solution spreads on the surface and forms a film. In second step, the speed of rotation increases and not required rest of the solution will be removed by centrifugal forces. In this step, the volatile solvent evaporates and a dry, thin, metal organic film is formed. The thickness of the film depends on the viscosity, the concentration of the solution and on the angular speed of the spin coater. With increasing angular speed the film thickness decreases. Zinc oxide thin films were deposited on glass substrates by spin coating method. As a starting material, 0.5 M of zinc acetate dihydrate $[(CH_3COO)_2Zn.2H_2O]$ was used. The precursor solution was prepared by mixing zinc acetate dihydrate in appropriate proportions with ethanol and diethanolamine (DEA). Here ethanol and DEA were used as solvent and stabilizer respectively. The glass substrate (often used as a slide in microscope) was first cut into two equal pieces using a diamond glass cutter and washed by detergent, and cleaned in distilled water and acetone, and then dried in oven at 200°C for 2 hours. The coating solution was dropped using a syringe as shown in Fig. 1(a) onto the glass substrate. Then the substrate with the solution was rotated at 3000 rpm for 30 sec by using homemade spin coater as shown in Fig. 2(b) and 2(c). After depositing by spin coating, the film was dried at 200°C for 15 mins in a hot air oven in order to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated six times. The film was then inserted into a muffle furnace and annealed in air at 300°, 400° and 500°C for 2 hrs. The process of thin film growing could be well understood from the flow chart as shown in Fig. 2.

Fig. 1. Steps involved in homemade spin coating process.
(a) a medical syringe is used to drop the coating solution on the glass substrate

(b) a sample holder made from plastic ice cream box

(c) a centrifuge machine is modified as a homemade spin coater

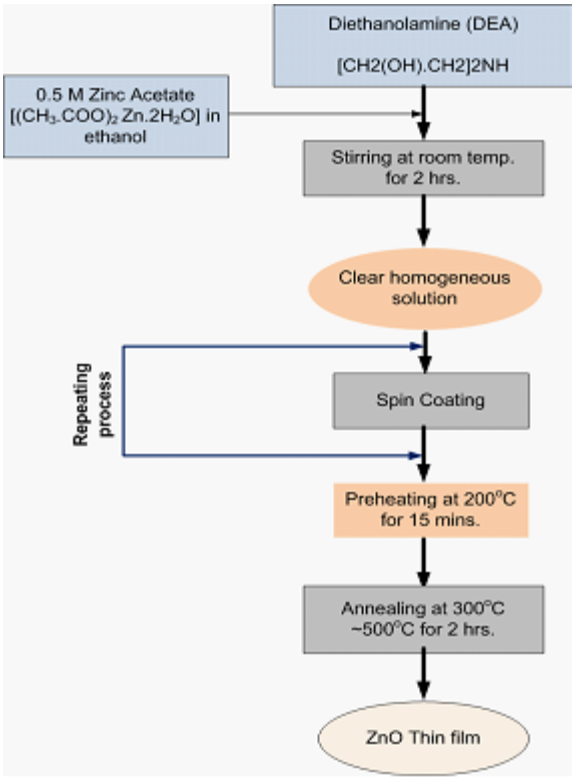

Fig. 2. Flow chart showing the procedure of ZnO thin films preparation

Results and Discussion

Structure characterization

X-ray diffraction (XRD) patterns of the sample were taken with a D2 phaser Bruker X-ray diffractometer at room temperature using CuKα radiation wavelength of λ = 1.542 Å. The peak position and intensity were obtained between 0 and 80°. Fig. 3 shows the powder X-ray diffraction pattern of the as-grown ZnO thin films. The diffraction lines are consistent with the values reported in the database of ZnO (JCPDS card no PDF 89-1397) providing clear evidence for the formation of hexagonal Wurtzite-type structure of the synthesized ZnO. The as-grown ZnO thin films were of pure sample and no diffraction peaks from any other impurities were detected. All the diffraction peaks are rather sharp which indicate that the ZnO sample has high degree of crystallanity. From the XRD data, the crystallite size (*D*) of the as-grown ZnO thin films was calculated to 39.54 nm, using the Debye-Scherrer equation (Khan *et al*. 2011),

$$D = \frac{B\lambda}{\beta\cos\theta} \quad \text{.....} \quad (1)$$

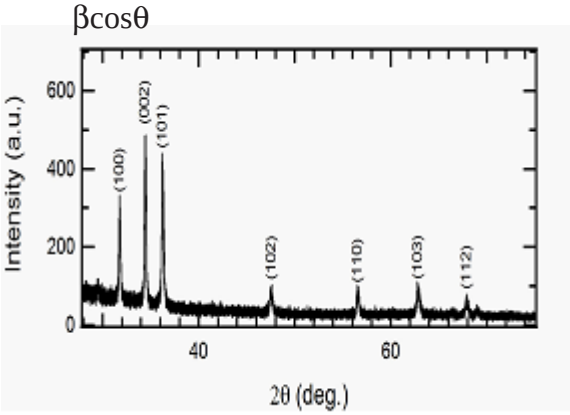

Fig 3. XRD patterns of ZnO thin film on glass substrate at room temperature

In this equation, *D* is the crystallite size (nm) of the phase under investigation, B is the Scherrer constant (0.9), λ is the wavelength of X-ray of Cu Kα = 0.154 nm, β is the full width half maximum (FWHM) of (002) reflection peak as shown in Fig. 4 and θ is the Bragg's angle. The calculated crystallite size in the present study was very close to that reported by Kumar *et al.* (2011). Peaks corresponding to the (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal ZnO were observed. No other peaks were observed, suggesting that only single-phase ZnO was formed.

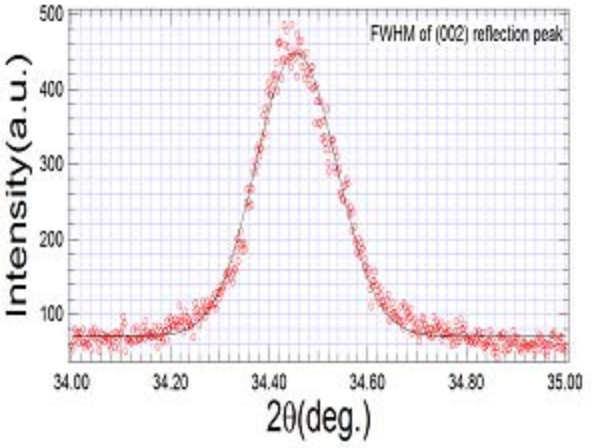

Fig 4. Full width at half maximum of (002) reflection peak used for the calculation of the crystallite size. The circles and line represent the experimental values and curve fitting respectively

Optical properties of ZnO

Band gaps are one of the most important properties of modern semiconductors. With applications in photovoltaic, visual display and lighting sources, the band gap of a semiconductor is an essential property for designing and discovering new applications for semiconductors. The most common method of determining the band gap of a semiconductor was by optical absorption or transmission measurements. For measuring the band gap energy of a material, the optical absorption method was applied using *USB 2000* spectrophotometer of Ocean Optics. In this measurement, photons of selected wavelength fell on the sample and the transmitted photons were measured. This experiment could calculate an exact value of the band gap energy because photons with energies higher than the band gap energy were absorbed and photons with energies lower than the band gap were transmitted. The experimental assembly provided electromagnetic radiation in the wide range of 200 nm to 1100 nm. In the long wavelength limit, radiation could excite free charge carriers to oscillate causing reflection. In short wavelength limit, radiation had enough energy to interact with inner shell electrons. The room temperature optical absorption of ZnO thin films annealed at different temperatures has been shown in Fig.5. The films showed a sharp absorption around 400 nm and almost transparent in the visible range.

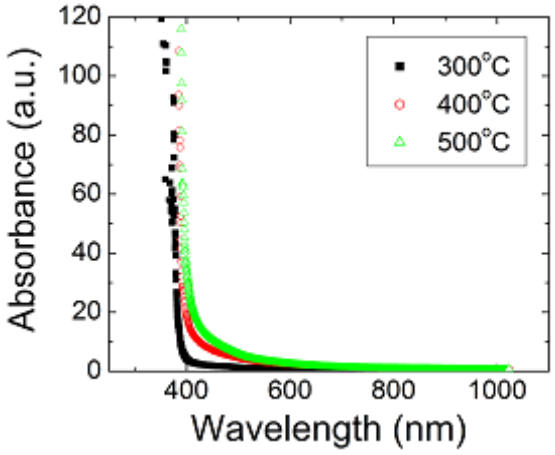

Fig. 5. The room temperature optical absorption of ZnO thin films annealed at different temperatures

Band gap energy of ZnO

Determination of band gap energy (E_g) was often necessary to develop the electronic band structure of a thin film material. Absorption coefficient *á* was related to the energy *h í* of incident photons by the relation called Tauc's plot method (Ding *et al.* 2010):

$$\alpha h\nu = B(h\nu - E_g)^p \qquad (2)$$

where *B* was a constant and *p* was an index that characterized the optical absorption process and was theoretically equal to 1/2, 2, 3/2 or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. In the present study of ZnO, the value of *p* of Eq. (2) was taken as 1/2 (Gümü *et al.* 2006). Absorption coefficient, *á*, was mainly influenced by two factors: (i) scattering losses and (ii) fundamental absorption. At shorter wavelengths close to the optical band gap, the influence of fundamental absorption on *á* was more prominent than to scattering losses and *á* might be obtained by (Kumar *et al.* 2011):

$$\alpha = \left[\frac{1}{d}\, ln\left(\frac{1}{T}\right)\right] \ldots \qquad (3)$$

The band gap variation of ZnO with annealing temperature has been shown in Fig. 6. The optical band gap (Eg) was obtained by extrapolating the linear part of the Tauc's plot to intercept the energy axis at $(á hí)^2 = 0$. The optical band gap energies versus temperature as determined from the obtained optical spectra have been shown in Fig.7. The optical band gap for the ZnO film grown at 300°C was 3.22 eV. As the growth temperature was increased to 400° and 500°C, the optical band gap shifted to 3.14 and 3.05 eV respectively. It was found that there was a narrowing of the band gap of about 170meV between the two samples deposited at 300° and 500°C. These results were consistent with those observed for the mechanical assisted thermal decomposition method (Zhang *et al.* 2014).

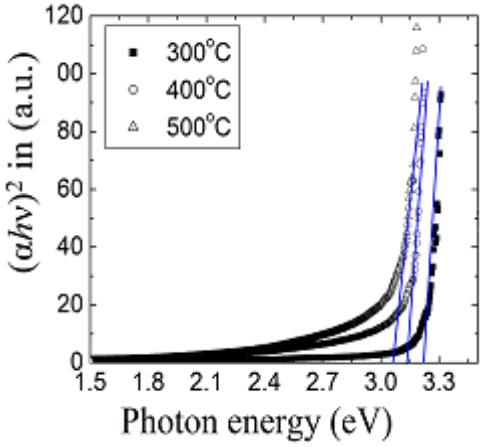

Fig.6. Graph between $(á hí)^2$ and photon energy

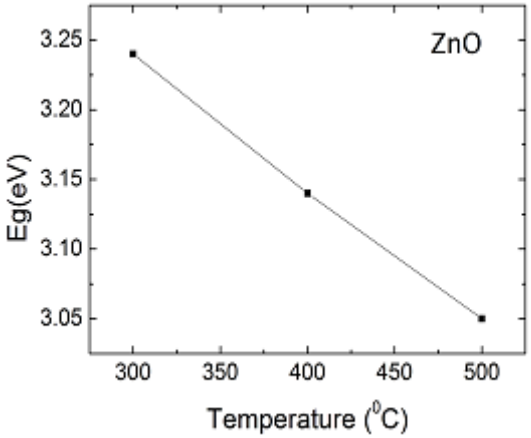

Fig.7. Band gap energy of ZnO annealed at different temperatures

The band gap energy of the ZnO thin films decreased with temperature. Compared with the band gap energy of ZnO single crystal (3.3 eV), the band gap energy of the ZnO thin film (3.22 eV) was somewhat smaller. The small variation of the band gap energy might be originated from the defects in ZnO thin films.

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