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RESEARCH PAPER

STRUCTURAL AND OPTICAL CHARACTERIZATION OF ZINC OXIDE FILMS PREPARED BY TWO STAGE; SPIN COATING AND HYDROTHERMAL PROCESS

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ABSTRACT

Thin films of Zinc Oxide (ZnO) of average thickness 364 nm were deposited on glass substrates via hydrothermal process using a mixture of 25 mM aqueous solutions of zinc nitrate and hexamethylenetetramine at a constant temperature of 75 ± 5°C. The structure of ZnO film was analyzed by using X-ray diffraction (XRD). Our result showed that ZnO film is of polycrystalline nature with preferential orientation along (002) perpendicular to the substrate. Average crystallite size of prepared ZnO film was found to be 18 nm. The Scanning Electron Microscope (SEM) image clearly showed the growth of nano-plate structure with an average thickness and breadth of 90 nm and 390 nm respectively. The band gap of ZnO was determined from transmittance spectrum captured in the visible wavelength. The calculated value of direct band gap was 3.24 eV.

Keywords: Thin film, Zinc oxide, Band gap, XRD, SEM

INTRODUCTION

Thin films of binary compound zinc oxide (ZnO) have potential in the fabrication of future generation nanoscale electronic and optoelectronic devices due to possession of high transmittance in the visible range and high absorption coefficient (Benny *et al.* 2006). Generally ZnO exists as n-type wide band gap semiconductor which possesses greater mechanical and chemical strength. ZnO with various morphology such as nanorods, nanowires, nanoflakes are of great interest for the design of new generation dye-sensitized solar cells (Baxter & Aydil 2006). ZnO has also been used in the large number of applications such as thin film transistors, gas sensors, plaster material in medicine (Alver *et al.* 2007, Xiaodan *et al.* 2007, Agnieszka & Tcofil 2014). Its electrical, structural and optical properties can be modified by doping with elements such as Al, Mn, In (Shrestha *et al.* 2010, Yoshino *et al.* 2007, Ilican *et al.* 2007).

The synthesis of high quality ZnO thin film is very important for the development of numerous optoelectronic devices. Several efficient methods such as spray pyrolysis (Gomez-Pozos *et al.* 2007), chemical bath deposition (Cao & Cai 2008), spin coating (Xu *et al.* 2006), reactive magnetron sputtering (Li & Wang 2009), and dip coating (Djouadi *et al.* 2009) are widely used to prepare good thin films of ZnO. According to the application desired of ZnO thin films, we have prepared ZnO thin films using a cost effective hydrothermal process at mild conditions of low temperature, atmospheric pressure as well as allowing for the tuning of the band gap of ZnO film via changes in the thickness of seed layer. We adopted two step, spin coating and hydrothermal method to prepare thin film of ZnO as described by Zhang *et al.* in 2012. The structural, morphology and optical properties of prepared samples were investigated using X-ray Diffraction, Scanning Electron Microscope and Ultra-violet Visible spectrophotometer.

MATERIALS AND METHODS

First of all, a thin seed layer of Al doped Zinc Oxide (AZO) was deposited on a glass substrate using a spin coating method from a 0.3 M precursor solutions of Zinc Acetate (analytical grade Merck 99%) ethanol with diethanolamine (Shrestha *et al.* 2010). The hexahydrated Aluminum Chloride was added into the solution for Al doping. The Al doping percentage used here was of 2%. A homemade spin coater of about 3000 rpm and spinning time of 30 seconds per coat was used during preparation of the AZO film. The spin coated layer was then heated at 100±5°C for 10 minutes for soft baking followed by high heating at 400±5°C for 15 minutes in each coat. Ultimately, the samples were annealed at 400±5°C for another 30 minutes. These AZO substrates were then dipped into the aqueous mixtures of 25mM Zinc Nitrate and hexamethylentetratamine solution for 2 hours at constant temperatures of 75 ± 5 °C to facilitate the growth of zinc oxide nanostructure via hydrothermal process (Zhang *et al.* 2012). Finally, the samples were rinsed with distilled water several times and annealed at 400°C in air for 30 minutes to remove any residues. The structural investigation of prepared film (sample C8) was performed using X-ray diffraction. The surface morphology of prepared film was studied by scanning electron microscope. Additionally, the effect of thickness of AZO coating on band gap of ZnO was also studied. For this experiment we prepared samples with different number of AZO coatings on glass substrates and band gaps were measured using the transmittance data measured using an Ocean Optics, USB 2000 spectrophotometer, Singapore.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of ZnO thin film grown on glass substrate at 75±5°C (sample C8) using a conventional hydrothermal process. The X-ray scan was run in the 2θ range of 10° to 81°. It shows three prominent peaks at 2θ = 32.80°, 35.49° and 37.28°. The strong peak observed at 2θ = 35.49° corresponds to d = 2.52Å shows the orientation of (002) planes. Other two peaks at 2θ = 32.80° (d = 2.72Å), and 2θ = 37.28° (d = 2.40Å) shows the (hkl) plane orientation along (100), and (101) respectively. Other small intensity peaks are observed at 2θ= 48.57° (d = 1.87Å), 2θ = 57.58° (d = 1.59 Å) and 2θ = 63.87° (d = 1.45 Å) which show orientation along (102), (110) and (103) planes respectively. The indexing of (hkl) planes were made with reference to JCPDS card no. 361451 (Shrestha *et al.* 2010). The c-axis lattice constant of the ZnO thin film was calculated to be of 5.21 Å. The XRD pattern of the film shows that the ZnO film is polycrystalline hexagonal system. The crystallite size D, was estimated using Debye Scherrer's formula, $D = 0.9\lambda/\beta \cos\theta$ where λ is the X-ray wavelength and β measures the full width half maximum (FWHM) of the peak and θ is the braggs angle respectively (Shakti 2010). The average crystallite size was estimated by consideration of FWHMs of first three major peaks of Fig.1 which is found to be about 18 nm.

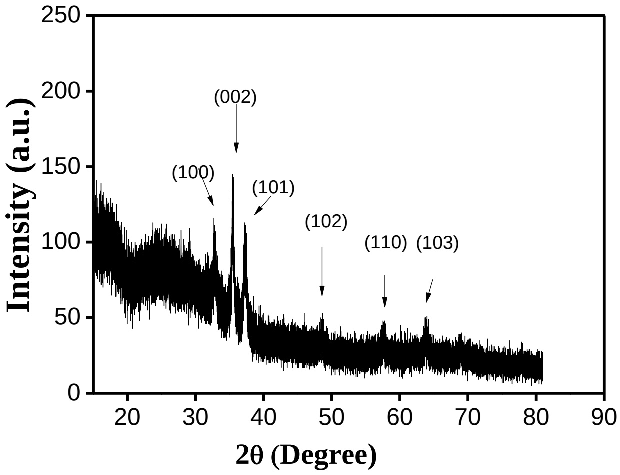

Fig.1. X-ray diffraction pattern of ZnO film grown on glass substrate at 75 ± 5 °C (sample C8).

Fig. 2 shows the scanning electron microscope image of ZnO film grown on glass substrate at 75 ± 5°C. It clearly shows the growth of nano-plates of ZnO film. The average thickness and breath of these sheets were estimated, according to the scale bar provided at the bottom of image, to be 90 nm and 390 nm respectively.

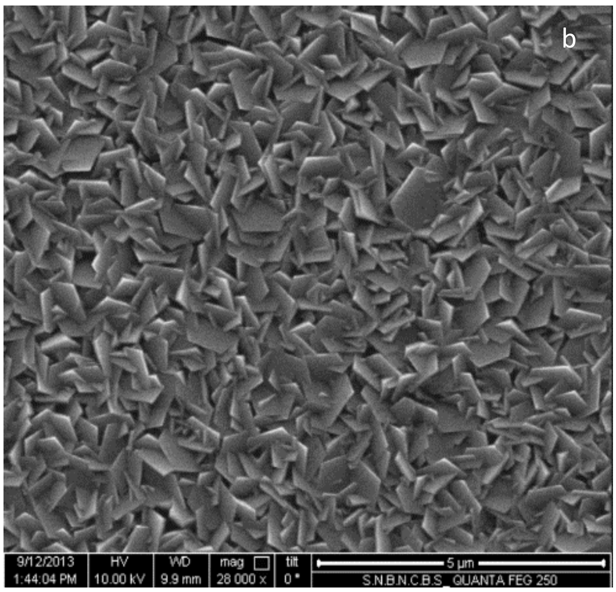

Fig. 2. Scanning Electron Microscope image of ZnO thin film prepared on glass at 75 ± 5°C (sample C8).

Fig. 3 shows the recorded optical transmittance spectrum of ZnO thin film in the wavelength range from 300 nm to 1000 nm. The maximum transmission of the film was more than 80% in the visible range with a sharp cut-off at approximately 380 nm.

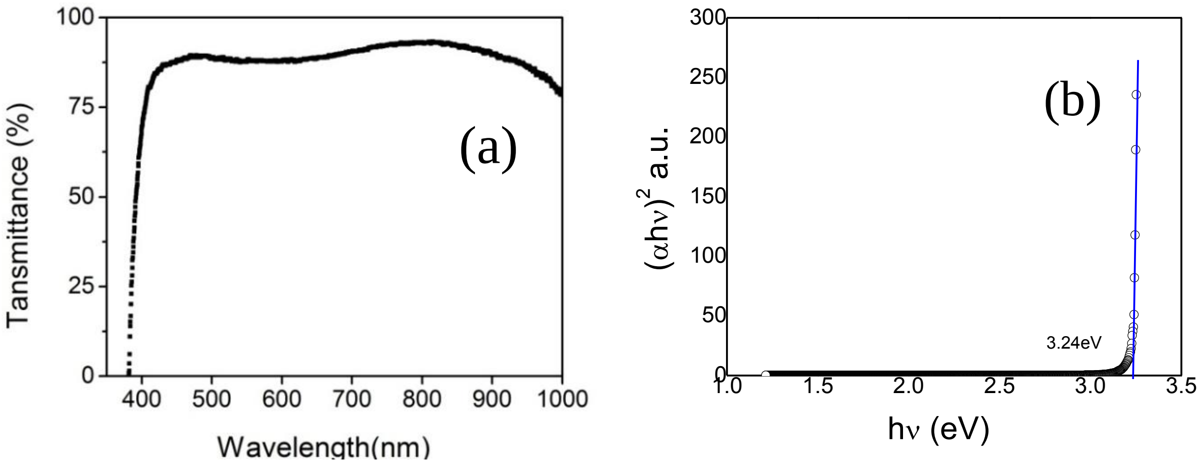

Fig. 3. (a) Transmission spectrum (b) corresponding $(\alpha h\nu)^2$ versus hν plot of ZnO film grown on glass substrate at 75 ± 5°C (sample C8).

The thickness (t) of the film was calculated using the swanepoel method (Dorranlan *et al.* 2012) for which t is given by:

$$t = \frac{\lambda_1 \lambda_2}{2[n_1(\lambda_1)\lambda_2 - n_2(\lambda_2)\lambda_1]} \qquad (1)$$

where n_1 and n_2 are the refractive indices at wavelengths λ_1 and λ_2 respectively. Using the transmittance of adjacent maxima and minima observed in the spectrum, n_1 and n_2 were calculated as described by (Dorranlan *et al.* 2012). The average calculated value of film thickness using above equation is found to be about 364 nm. We calculated the direct band gap of prepared ZnO film by extrapolating the linear portion of the curve of $(\alpha h\nu)^2$ versus hν on x-axis. The direct band gap of ZnO is obtained using the equation

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

where α, hν, E_g and A represent the absorption coefficient, photon energy, band gap, and a constant respectively (Joshi *et al.* 2015). The calculated value of band gap from above curve (Fig. 3b) after extrapolation of the linear portion of the curve of sample C8 is Eg = 3.24 eV. Here, in this report we have also studied the effect of thickness of seed layer of AZO on band gap of ZnO growth in hydrothermal process. Fig. 4 shows the graphs of ZnO films prepared from same molar concentration of growth solution but with different number of coats of seed layer of AZO film on glass substrate. The samples made from 3 coats and 4 coats of seed layer were named as S3 and S13 respectively. The results showed that as we increase the thickness of seed layer in the growth of ZnO film the band gap only ranges from 3.22 eV to 3.24 eV(shown in Table 1 below).

Table 1. The seed layer thickness, concentrations of zinc acetate and growth solution, and band gap of ZnO.

S. No.	Sample Name	No. of coats	Precursor Solution Concentration (M)	Al doping (at. %)	Growth Concentration (mM)	Band gap (eV)
1	S3	2	0.3	2	25	3.22
2	C8	3	0.3	2	25	3.24
3	S13	4	0.3	2	25	3.21

The estimated band gap of ZnO films from 2, 3, and 4 coatings of seed layer were 3.22eV, 3.24 eV, and 3.21 eV respectively. It showed no significant change in band gap of ZnO for changing the number of coats of seed layers prior to grow ZnO film in hydrothermal process.

CONCLUSIONS

Thin films of zinc oxide were prepared using a hydrothermal process from a spin coated seed layers of Al doped zinc oxide. The SEM image shows nano-plate structure of ZnO. The average thickness and breadth of these plates of ZnO were found to be of about 90 nm and 390 nm respectively. The X-ray diffraction result showed the ZnO film's polycrystalline nature with (002) preferential orientation. The crystallite size was estimated to be 18 nm. Optical transmission data captured in the visible wavelength range shows band gap of hydrothermally grown ZnO films with 3 coats of AZO seed layer was found to be of about 3.24 eV. The study on effect of number of coatings of seed layer on band gap of ZnO film developed by hydrothermal process shows no significant change.

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