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The Effect of Growth Temperatures on Structural, Morphological and Optical Properties of Sprayed ZnO Thin Films

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ABSTRACT

Transparent conducting ZnO thin films were deposited on glass substrate by Spray Pyrolysis Technique (SPT) using precursor Zinc acetylacetonate at different substrate temperature in the range of 325-400°C. The structural properties, optical properties and surface morphology of the deposited films were studied using X-ray diffraction (XRD), UV-Visible spectroscopy, Photoluminescence and Scanning Electron Microscopy (SEM) attached with Energy Dispersive Detector (EDS). The X-ray diffraction analysis revealed that the films had preferred orientation along (100) direction with a hexagonal wurtzite type crystal structure. The optical properties were investigated by measuring the transmittance curves which were used to find the optical band gap energy, refractive index and extinction coefficient. The photoluminescence spectrum (PL) was studied at room temperature with a wavelength of 275 nm as the excitation source. The surface morphology was observed using scanning electron microscope.

Key words: Zinc acetylacetonate, spray pyrolysis, optical constants, photoluminescence

INTRODUCTION

Zinc oxide (ZnO), a II-VI group of semiconductor material, has attracted considerable attention in recent years due to the potential application in various fields such as solar cell. Liquid Crystal Display (LCD) (Goodman, 1974), Light Emitting Diodes (LED) (Yoo *et al*., 2005), gas sensors (Michel *et al*., 1998), acoustic wave transducers (Chang *et al*., 1995) and multilayer photo thermal conversion systems (Chopra *et al*., 1983). ZnO has a direct band gap of 3.37 eV with high exciton binding energy (60 meV) (Lieber, 1998). It exhibits n-type conductivity and the electrical properties can be improved by using different dopants such as in, Sn, Al, Ga, Ge and Pb (Wang *et al*., 1996). In addition, the constituent elements of ZnO are non-toxic and abundant in nature leading to the development of devices that are environmentally safe and have public acceptability (Major *et al*., 1986; Jin *et al*., 1988).

Zinc oxide thin films have been grown by different techniques including chemical deposition (Khallaf *et al*., 2009; Kathirvel *et al*., 2009), sol-gel (Ohyama *et al*., 1997), spray pyrolysis (Muiva *et al*., 2011), sputtering (Guillen and Herrero, 2006), pulsed laser deposition (Choi *et al*., 2001) and molecular beam epitaxy (Bagnal *et al*., 1997; Nakahara *et al*., 2002). Among these techniques, spray pyrolysis is a simple, cost-effective technique for large area deposition and also

excellent method for the deposition of metallic oxides thin films. This work discusses about the results of the structural and optical properties of zinc oxide thin films prepared by microcontroller based spray pyrolysis technique using precursor solution of zinc acetylacetonate.

MATERIALS AND METHODS

The ZnO films were deposited on microscopic glass substrates using spray pyrolysis technique. For deposition, 0.1 M of Zn(acac) was dissolved in ethanol and sprayed onto microscopic glass substrates with dimensions of 75×25 mm^2 at different substrate temperatures (T = 325, 350, 375 and 400°C). The substrates were first cleaned with water bath, followed by dipping in con. HCl, acetone and ethanol successively. Finally the substrates were rinsed in deionised water and allowed to dry in a hot air oven. In spray unit, the substrate temperature was maintained with help of heater, controlled by a feedback circuit. During the spray, the substrate temperature was kept constant with an accuracy of ±5°C. Spray head and substrate heater were kept inside a chamber, provided with an exhaust fan, for removing gaseous by-products and vapors from the solvent. The spray head was allowed to move in the X-Y plane using the microcontroller stepper motor, inorder to achieve a uniform coating on the substrate. The spray head could scan an area of 200×200 mm with X-movement at a speed of 20 mm sec^{-1} and Y-movement insteps of 5 mm sec^{-1} simultaneously. The spray unit had the provision for controlling the spray rate of the solution as well as the pressure of the carrier gas. The microcontroller device was communicated with PC through the serial port in which the data of each spray could be stored.

The values of optimized parameters are given below:

Spray time	= 15 min
Solution flow rate	= 3 mL min^{-1}
Air flow rate	= 1 kg cm^{-2}
Spray nozzle to substrate distance	= 20 cm

After the deposition, the films were allowed to cool slowly to room temperature and washed with deionized water and then dried.

The structural characterization of the deposited films were carried out by X-ray diffraction technique on JEOL JDX-803 a diffractometer (monochromatic CuKα radiation, λ = 1.5406 Å). The XRD patterns were recorded in 2θ interval from 10 to 80° with the steps of 0.05°at room temperature. The surface morphology was studied by using SEM (JEOL-JES-1600) with a magnification of 10 K. Optical absorption spectrum was recorded in the range 350-900 nm using Varian-Cary 500 scan double-beam spectrophotometer. The photoluminescence spectrum (PL) was studied at room temperature with a wavelength of 275 nm as the excitation source.

RESULTS AND DISCUSSION

The XRD profiles of ZnO films deposited at different substrate temperatures are shown in Fig. 1. The diffraction peaks indicated two strong peaks at 31.91 and 36.38° corresponding to the (100) and (101) planes of the ZnO wurtzite structure and other reflections exist at 34.62 and 56.69° which also coincide with the ZnO lattice planes. The films exhibited hexagonal crystal structure and the peak intensities are in agreement with the JCPDS data (No. 75-0576). The intensity of the diffraction peaks gradually increases with increase in substrate temperature and the observed peaks are in agreement with the reported values of Prasada Rao *et al.* (2010) and Abou-Helal (2011).

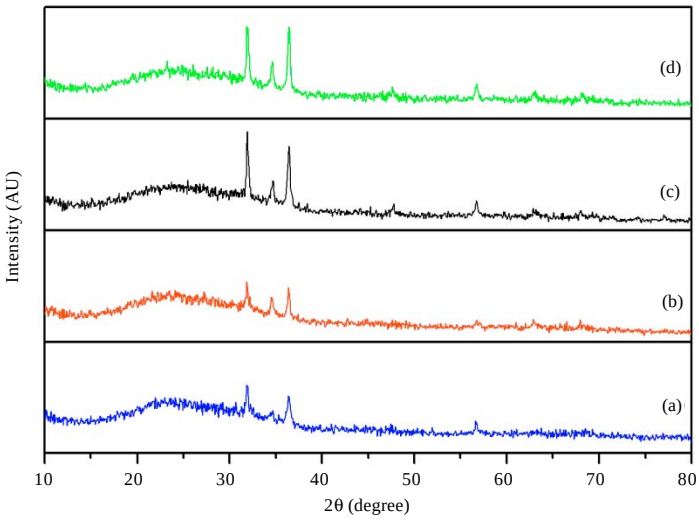

Fig. 1: X-ray diffraction patterns of ZnO films deposited at (a) 325°C, (b) 350°C, (c) 357°C and (d) 400° C

The crystallite size is evaluated from the FWHM of the (100) plane using the Scherrer's formula (Klung and Alexandar, 1974):

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where, K = 0.94 is the shape factor, λ is the X-ray wavelength of CuKα radiation, θ is the Bragg's angle and β is the full width at half maximum of the peaks. The lattice strain (ε) is calculated using the relation (Kathirvel *et al*., 2009):

$$\varepsilon = \frac{\beta\cos\theta}{4}$$

The value of dislocation density (δ) is calculated using the relation (Kathirvel *et al*., 2009):

$$\varepsilon = \frac{1}{D^2}$$

The effect of substrate temperature on the micro-structural parameters of ZnO films are summarized in Table 1. The crystallite size of ZnO can be tuned between 32 to 39 nm by varying the substrate temperature. Generally, it is observed that strain and dislocation density decreases as there is increase in the crystallite size which is well-known phenomenon (Edelestein and Camarata, 1998).

SEM image of the samples gave a more general view of the morphology in confirming the uniformity of the sample. Figure 2 shows the surface morphology of the ZnO thin films deposited at various substrate temperatures. From SEM image, it is evident that surface morphology of the

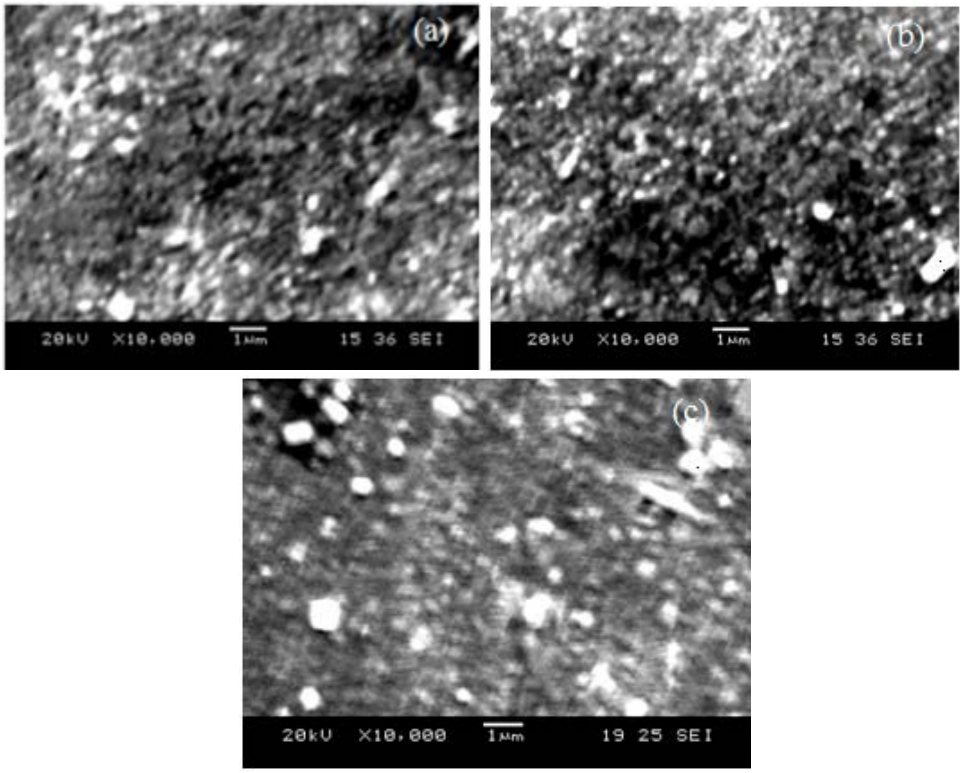

Fig. 2: SEM micrographs of ZnO films prepared at a substrate temperatures; (a) 350°C, (b) 375°C and (c) 400°C

Table 1: Micro-structural parameters of ZnO films deposited at (a) 325°C (b) 350°C (c) 357°C and (d) 400° C

Substrate temperature (°C)	Crystallite size (D) nm	Lattice strain (ε) $\times 10^{-4}$	Dislocation density (δ) $\times 10^{14}$ lines m^{-2}
325	32	11.0	9.76
350	33	11.0	9.18
375	37	9.6	7.30
400	39	9.2	6.57

films strongly dependent on the substrate temperature. It is clearly seen from the micrographs that the surface smoothness, uniformity and grain size increase with increasing substrate temperature. Average grain size for all the films is observed about <0.5 μm. A representative EDS spectrum of the ZnO film deposited at 400°C is shown in Fig. 3. It is found that zinc and oxygen are present in near stoichiometric ratio (Zn:O = 52:48 at%).

The optical transmission spectra of ZnO films are measured in the wavelength range 350-900 nm at room temperature and are shown in Fig. 4. The value of transmittance in the visible region increases with increase in substrate temperature which indicates that the films had less defects and better crystalline structure. The better crystalline structure with increase in substrate temperature is established through XRD analysis.

The energy band gap of the film is evaluated from the relation (Mott and Gurney, 1964):

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

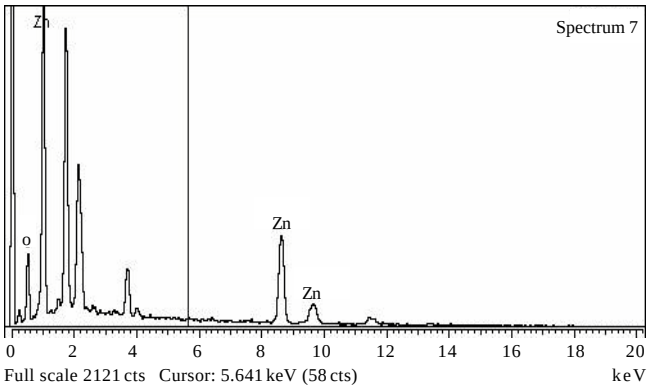

Fig. 3: EDS spectrum of ZnO films prepared at 400°C

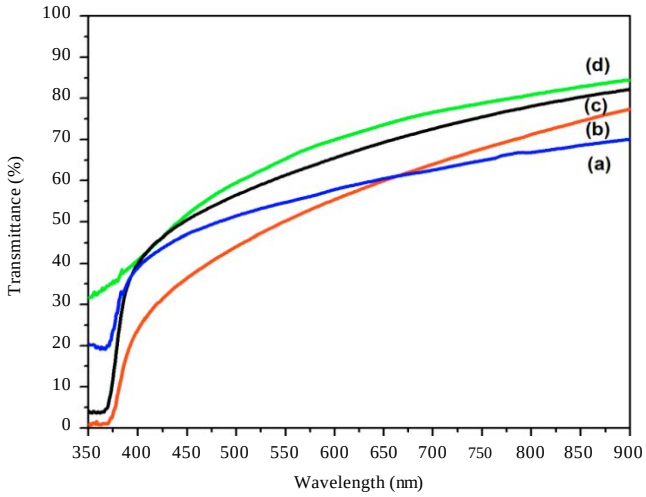

Fig. 4: Transmission spectra of ZnO thin films deposited on glass at (a) 325°C, (b) 350°C, (c) 357°C and (d) 400°C

where, A is a proportionality constant and E_g is the direct transition band gap. From the $(\alpha hv)^2$ vs hv plot, the optical band gap energy is determined by extrapolating the linear portion of the graph as shown in Fig. 5. The optical direct band gap values for different substrate temperatures are tabulated in Table 2. The band gap values are increased from 2.83 to 3.25 eV with increase in substrate temperature and this similar behavior was also observed by Prasada Rao *et al.* (2010). Previous workers (Paraguay *et al.*, 1999; Gumus *et al.*, 2006) also had reported the band gap energy of the direct transitions in the range 2.75-3.31 eV for ZnO films.

The extinction coefficient (k) can be obtained from the relation (Li, 2001):

$$k = \frac{\alpha\lambda}{4\pi}$$

The variation of extinction coefficient with wavelength is shown in Fig. 6. Extinction coefficient is high in the wavelength range of 350-400 nm and low in the

Table 2: Direct allowed band gap values with respect to substrate temperature

Substrate temperature (°C)	Direct energy band gap (eV)
325	2.83
350	3.12
375	3.20
400	3.25

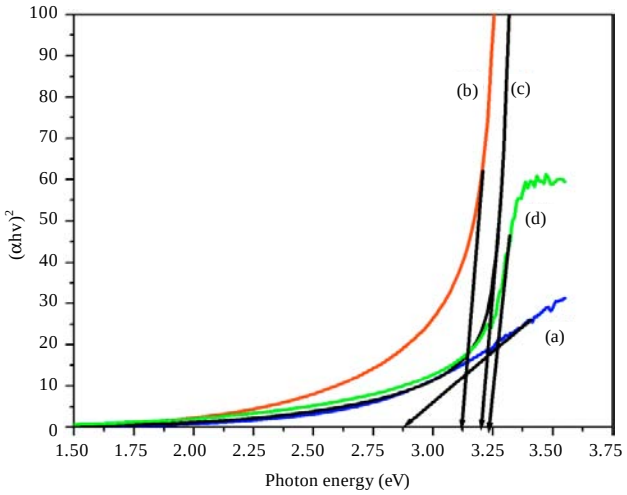

Fig. 5: Optical band gap of ZnO thin films deposited at (a) 325°C, (b) 350°C, (c) 357°C and (d) 400°C

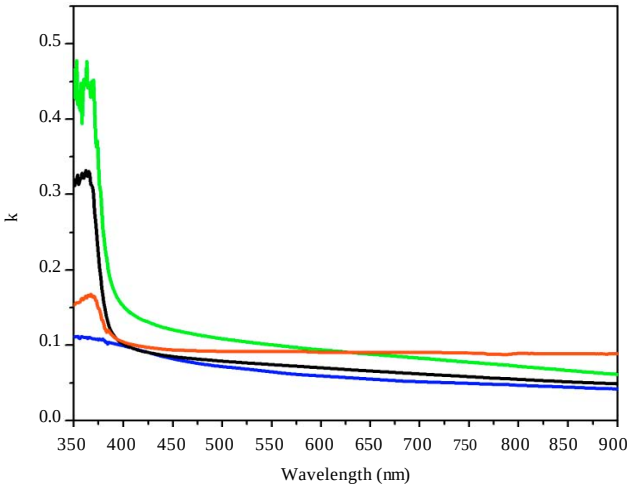

Fig. 6: Variation of extinction coefficient (k) as a function of wavelength for ZnO thin films

wavelength range of 400-900 nm. The rise and fall in the extinction coefficient is directly related to absorption of light (Islam and Podder, 2009).

The refractive index is calculated using the relation (Di Gielo *et al*., 1987):

$$n = \frac{1+R^{1/2}}{1-R^{1/2}}$$

where, R is the optical reflectance. Figure 7 shows the variation of refractive index with different wavelengths of the ZnO films. From the result, it shows that there is increase in the refractive index in the UV region and the values are decreased gradually from 2.6 to 1.8 in the high transmission range.

Room temperature PL emission spectrum for the samples deposited at different substrate temperature is measured in the wavelength range of 300-450 nm as shown in Fig. 8. The ZnO

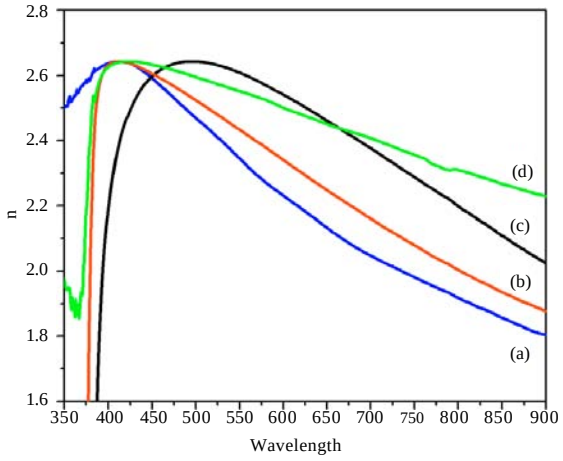

Fig. 7: Variation of refractive index (n) versus wavelength with various substrate temperatures (a) 325°C, (b) 350°C, (c) 357°C and (d) 400°C

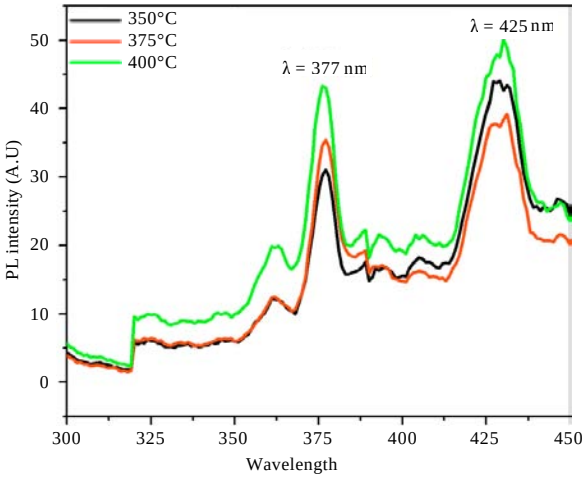

Fig. 8: Photoluminescence spectra of ZnO thin films with different substrate temperatures

emission is generally classified into two categories one is the UV emission of the near band edge in the UV region related to free-exciton recombination and the other is the deep-level (DL) emission in the visible range. From the Fig. 8, there are two emission bands are observed: one sharp UV luminescence at 377 nm and one visible emission at 420 nm in the ZnO thin films has been attributed to structural defects such as oxygen vacancies and interstitial zinc (Vanheusden *et al.*, 1996). The visible emission shift to high energy side with increasing substrate temperature and the intensity becomes gradually strong.

CONCLUSION

Zinc oxide thin films have been prepared by spray pyrolysis technique at different substrate temperature in the range of 325-400°C. XRD pattern shows that the film exhibited a poly crystalline wurtzite hexagonal structure. Maximum crystalline size obtained is 39 nm and band gap energy is found to be 3.25 eV. The optical constants viz., extinction coefficient and refractive index are also calculated. Room temperature PL spectra of the ZnO thin film shows a strong UV emission band located at 377 nm which is ascribed to the near band-edge emission and one visible emission at 425 nm. Finally properties of the ZnO thin films are good and suitable for fabricating the opto-electronic devices.

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