

## STRUCTURAL AND OPTICAL ANALYSIS OF SPRAY DEPOSITED ZINC OXIDE FILMS

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The zinc oxide films have been obtained by spray pyrolysis technique on to the glass substrates kept at different temperature (380- 480<sup>0</sup>C) .The conditions have been optimized to obtain quality films. Films have been characterized for their structure through XRD analysis and for optical parameters through optical absorption studies by UV-Visible spectroscopy in the spectral range 300 -1100 nm. Effect of substrate temperature on the structure, extinction coefficient, optical band gap and refractive index of these films has been studied.

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### 1. Introduction

Zinc oxide (ZnO) thin films are being extensively studied due to their interesting electro-optical properties, high electro-chemical stability, a large band gap (between 3.2 and 3.4 eV at room temperature), abundance in nature and absence of toxicity. With such characteristics ZnO has been proven to be a very good transparent conductive oxide and as a window material for solar cell applications. ZnO has wide range of technological applications as sensors [1, 2], heat mirrors[3], transparent electrodes [4], solar cells [5-7] and piezoelectric devices [8]. These films can be deposited by several techniques including, sputtering [9], metal organic chemical vapor deposition [10], sol gel [11] and spray pyrolysis [12,13]. Among these, the spray pyrolysis method has the advantage of being simple, easy-to-use and low cost process. Accurate knowledge of the absorption coefficient, optical band gap and refractive index of semiconductors is indispensable for the design and analysis of various optical and optoelectronic devices. It is possible to determine indirect and direct transition occurring in band gap of the materials by optical absorption spectra. The data transmittance can be analyzed to determine optical energy gap and other optical constants.

In this work, spray deposited ZnO thin films have been obtained onto glass substrate. The effect of substrate temperature on optical band gap and other optical constants of the films so obtained have been discussed.

### 2. Experimental

The spray pyrolysis method used here is basically a chemical deposition method in which fine droplets of the desired material are sprayed onto a heated substrate. Continuous films are formed on the hot substrate by thermal decomposition of the material droplets. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally they were rinsed with distilled water and dried. 0.3M solution of zinc acetate dehydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) in

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deionized water was taken as precursor solution for all the films. The solution was continuously stirred for an hour with the help of magnetic stirrer in an air tight container. The resulting solution was allowed to get settled for 24 hours. The spray deposited ZnO films were obtained onto chemically cleaned glass slides kept at 380, 430 and 480<sup>o</sup>C. Dry air was used as the carrier gas. Fixed ratio of the precursor solution and air was made to spray in form of mist from ultrasonic nebulizer on to the open air heated substrates. The ultrasonic nozzle to substrate distance and deposition time was kept 1.5 cm and twenty minutes respectively for each deposition. The films were then cooled down to room temperature in open air. The substrate temperature was measured using an Iron-Constantan thermocouple.

The UV-visible-IR optical transmission spectra of ZnO thin films were recorded by using Shimadzu UV-VIS-2450 scanning spectrophotometer in the range of 300-1100 nm. The measurements were taken at a normal incidence using a reference blank glass substrate. The transmittance and absorbance spectra were used to calculate the absorption coefficient and optical band gap of the films. The thickness of the thin films were estimated using max-min method, using the formula:  $t = \lambda_1 \lambda_2 / 4n (\lambda_2 - \lambda_1)$ , where 't' is the thickness of the film,  $\lambda_1$  and  $\lambda_2$  are the wavelengths which corresponds to the maxima and minima of the transmittance spectra and 'n' is the refractive index to ZnO. Thickness has also been verified by microbalance technique and has been recorded to be around 57 nm.

### 3. Results and discussion

#### 3.1 Structural analysis of ZnO films:

The X-ray diffractogram of ZnO films grown at different substrate temperatures has been shown in figure 1.

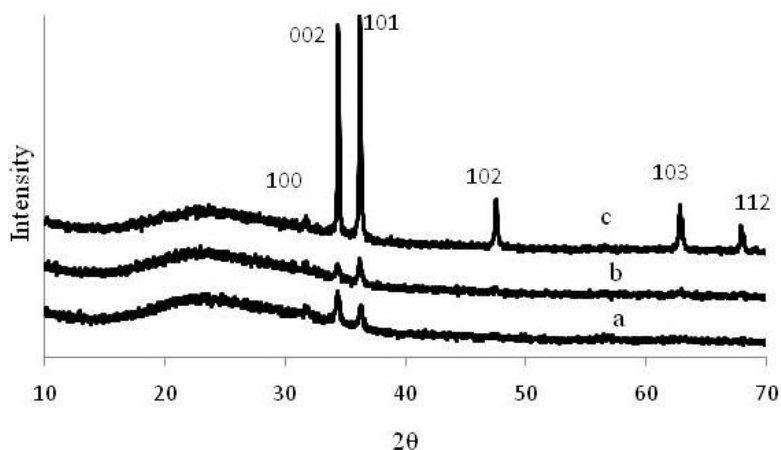


Fig.1 XRD pattern of spray deposited ZnO films at (a) 380<sup>o</sup>C (b) 430<sup>o</sup>C (c) 480<sup>o</sup>C.

The d values of the films have been compared with the literature data to confirm the structure of ZnO and found to be in good agreement ( Table 1)with the Joint Committee of Powder Diffraction Standards (JCPDS) card data for ZnO [14] , thus confirming the formation of ZnO film on the substrate with hexagonal wurtzite geometry .

Table I. XRD parameters of spray deposited ZnO films 480 °C.

h k l	ZnO films (Ts = 480°C)		JCPDS 36-1451	
	2θ (deg)	d-Value (Å)	2θ (deg)	d-Value (Å)
1 0 0	31.726	2.8204	31.770	2.8143
0 0 2	34.384	2.6083	34.422	2.6033
1 0 1	36.175	2.4831	36.253	2.4759
1 0 2	47.492	1.9145	47.539	1.9111
1 0 3	62.806	1.4783	62.864	1.4771

The films are observed to have a preferential crystallographic texture in the [101] direction corresponding to the Bragg angle  $2\theta = 36.2^\circ$  and along [002] with  $2\theta = 34.3^\circ$ . However, X-ray diffractogram shows the presence of weak intensity peaks with orientation along [102], [103] and [112] direction with  $2\theta$  values  $47.5^\circ$ ,  $62.8^\circ$  and  $67.9^\circ$  respectively that is also in agreement with the previously reported values [15]. The films deposited at higher substrate temperature show comparatively intense peaks. Also the decrease in full width measured at half maxima (FWHM) of diffraction peaks has been noticed, thus suggesting a high degree of crystallinity with increase in substrate temperature. The crystallite size for the films deposited at 380, 430 and 480 °C was estimated using the (101) diffraction peaks from the XRD data in accordance with the Debye-Scherrer formula [16]:  $D = 0.9\lambda / (\beta \cos \theta)$ , where  $D$  is the crystallite size in nanometers,  $\lambda$  is the wavelength value of the Cu  $K\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) line,  $\theta$  is the Bragg diffraction angle and  $\beta$  is the FWHM of the diffraction peak measured in radians. Crystallite size have been found to be  $7.29 \text{ \AA}$ ,  $9.24 \text{ \AA}$ ,  $12.46 \text{ \AA}$  for the films obtained at temperature 380, 430 and 480 °C respectively.

### 3.2 Optical properties of ZnO films

The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. The absorption and percentage transmission spectra of ZnO thin films deposited at different temperature is shown in figs.2&3 respectively. In order to determine the optical band gap of the films, the absorbance spectra of the films were recorded at room temperature. The absorption coefficient ( $\alpha$ ) was calculated from the absorbance spectrums using the formula:  $\alpha = 2.3026 (A/d)$ , where  $d$  is the film thickness and  $A$  is the optical absorbance. The absorption edge of the ZnO has been examined in terms of a direct transition using the equation of Bardeen et al [17], stating that:  $\alpha h\nu = B(h\nu - E_g)^n$ , where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $E_g$  is the optical band gap,  $B$  is a constant which does not depend on photon energy and  $n$  is respectively 1/2 and 2 for direct and indirect transitions.

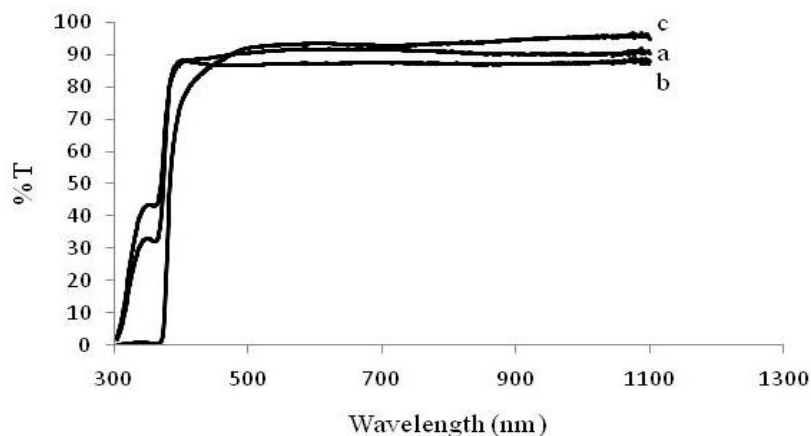


Fig. 2 Optical transmittance spectra of ZnO films deposited at (a) 380 °C (b) 430 °C (c) 480 °C.

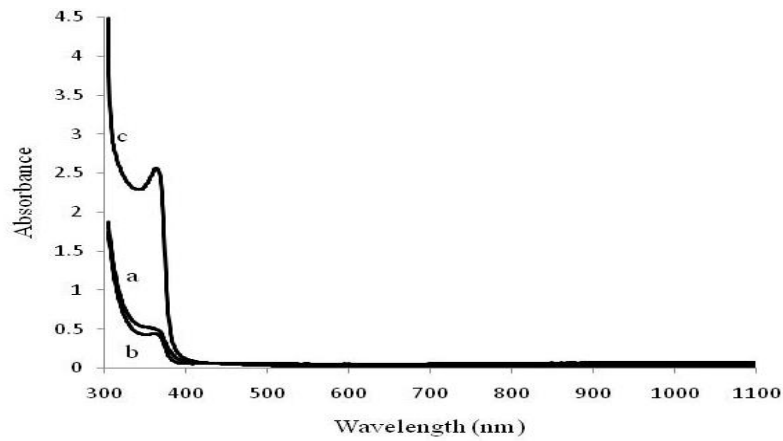


Fig. 3 Optical absorbance spectra of ZnO films deposited at (a) 350 °C (b) 400 °C (c) 450 °C.

The direct and indirect band gap was determined by plotting  $(\alpha h\nu)^2$  vs.  $h\nu$  and  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  curves and have been shown in figs.4 (a,b,c) and 5(a,b,c) respectively. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the optical energy band gaps. It has been observed that both direct and indirect optical band gap increases from 3.282 eV to 3.301 eV and from 3.17 eV to 3.22 eV respectively with the increase in substrate temperature. This increase in band gap energy may be attributed to the improvement of crystallinity of the films with the increase in substrate temperature and due to the fact that high substrate temperature favours the growth of larger crystallite size and exhibit more ordered structure, which gives comparatively less contribution to the absorption [18]. Results are in good agreement with the findings of Yakuphanuglu et al [19], Caglar et al [20] and Senadim et al [21].

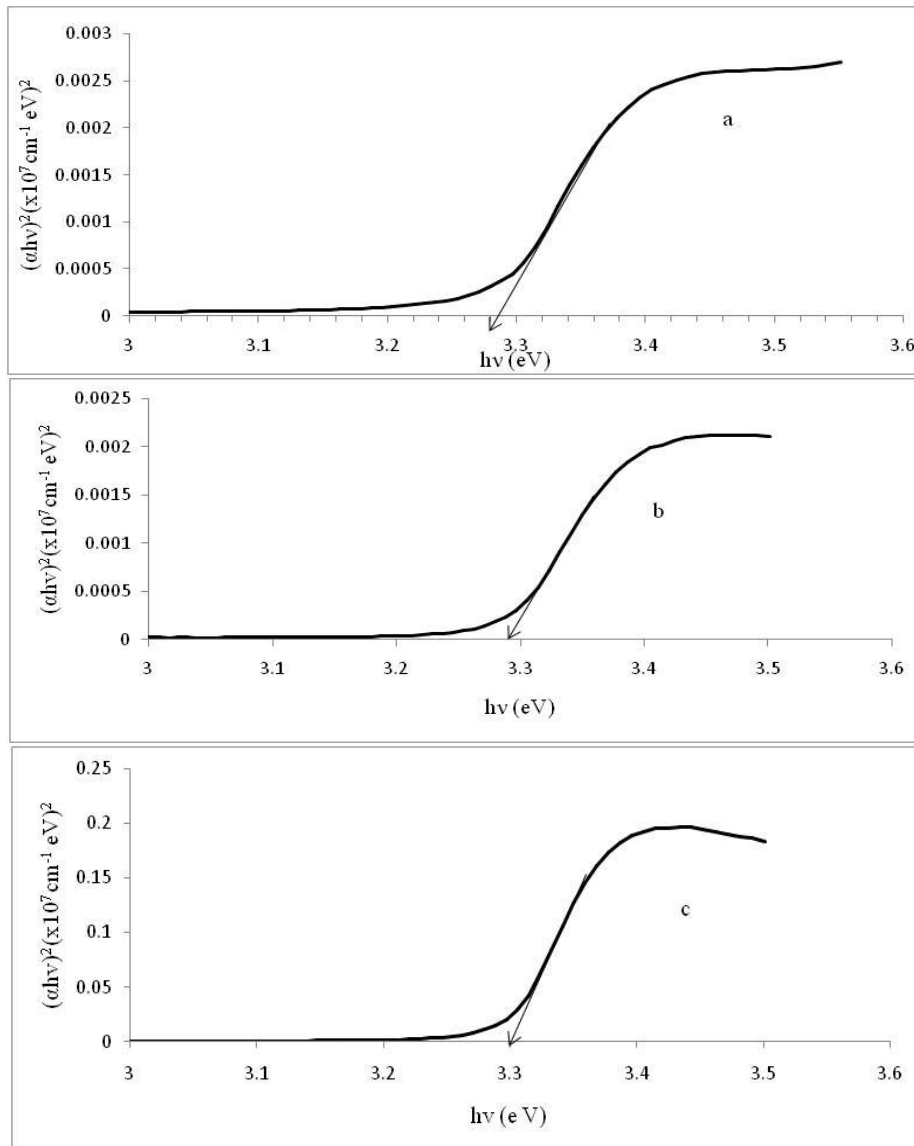


Fig.4 Variation of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ) of ZnO films deposited at (a) 380 °C (b) 430 °C and (c) 480 °C.

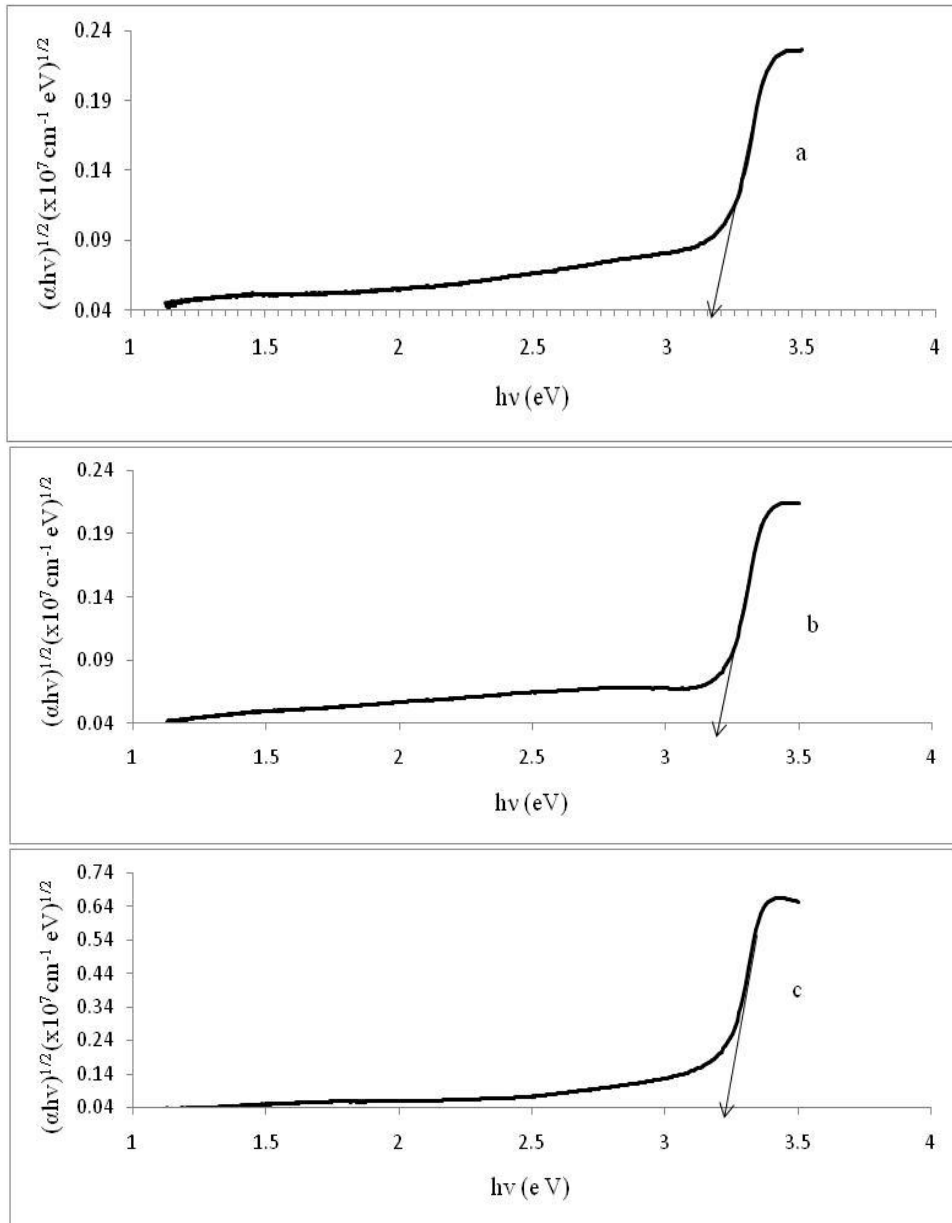


Fig. 5 Variation of  $(\alpha h\nu)^{1/2}$  as a function of photon energy  $h\nu$  of ZnO films deposited at (a) 380 °C (b) 430 °C and (c) 480 °C.

The direct and indirect band gap energy of zinc oxide films deposited on glass substrate at different substrate temperatures has been listed in table 2.

Table 2. Band gap energy of spray deposited zinc oxide films on glass substrate kept at different temperature.

Substrate Temperature (°C)	Direct Band Gap (eV)	Indirect Band Gap (eV)
380	3.282	3.17
430	3.290	3.20
480	3.301	3.22

The extinction coefficient is an optical parameter that measures the fraction of light that is lost per unit distance of the penetration medium due to both scattering and absorption and is estimated using the relation [22] :  $K = \alpha\lambda/4\pi$ , where  $\alpha$  is the absorption coefficient and  $\lambda$  is incident wavelength . Variation of  $K$  with wavelength  $\lambda$  for the ZnO films has been shown in fig. (6).

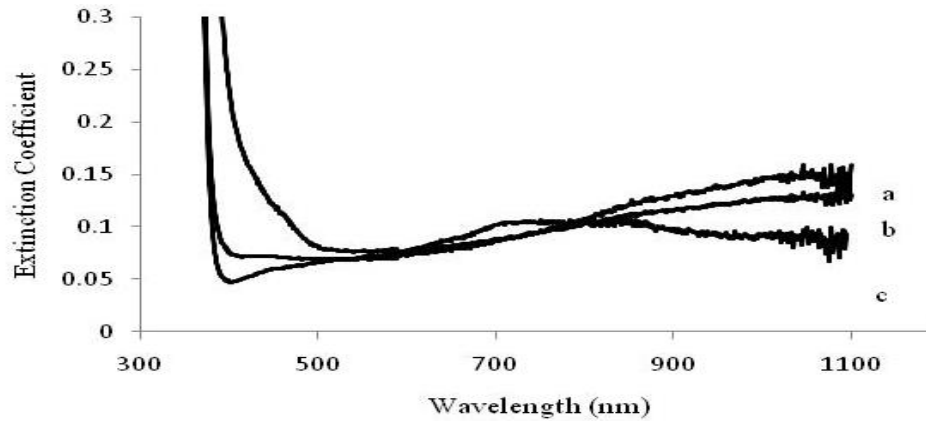


Fig.6 Variation of extinction coefficient Vs wavelength of spray deposited ZnO films at (a) 380<sup>o</sup>C (b) 430<sup>o</sup>C (c) 480<sup>o</sup>C.

Extinction coefficient has been observed to be decreasing with the rise in substrate temperature indicating decrease in scattering and absorption with the increase substrate temperature indicating more ordered structure at higher substrate temperature which is also in accordance with the XRD results.

Refractive index of films has been determined from the transmittance spectra and has been plotted against wavelength in fig.(7).

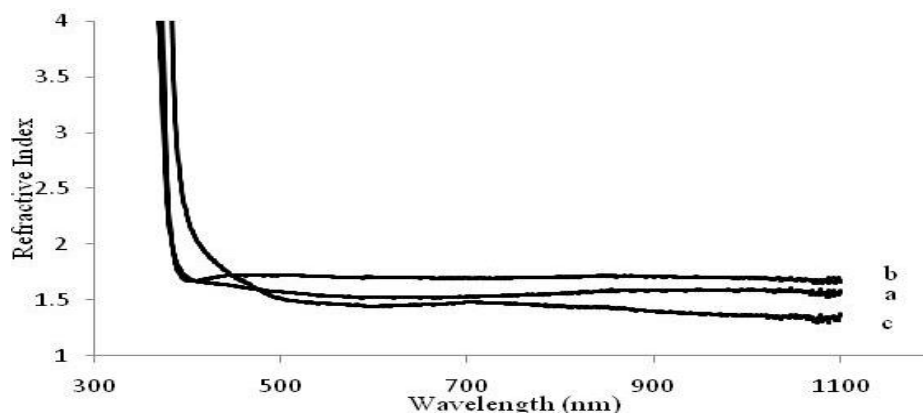


Fig.7 Variation of refractive index Vs wavelength of spray deposited ZnO films at (a) 380<sup>o</sup>C (b) 430<sup>o</sup>C (c) 480<sup>o</sup>C

The decrease in refractive index with the incident wavelength has been observed indicating the normal dispersion behavior of the ZnO films .Also decrease in refractive index with increasing substrate temperature can be attributed to the decrease in optical absorption of the ZnO films with increase in substrate temperature.

#### 4. Conclusion

The spray deposited zinc oxide films have been obtained on glass substrates kept at different temperature. The optical absorbance and transmittance spectra of the films so obtained has been recorded in the wavelength range of 200-100 nm. It has been observed that both the allowed direct and indirect optical band gap increases from 3.282 eV to 3.301eV and from 3.17 eV to 3.22 e V with the increase of substrate temperature respectively. Extinction coefficient of ZnO films decreasing with the rise in substrate temperature. The refractive index has been observed to decreases with the increase in wavelength.

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