Influence of Concentration on Structural and Optical Characteristics of Nanocrystalline ZnO Thin Films Synthesized by Sol-Gel Dip Coating Method

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***Abstract*- Zinc Oxide thin films (ZnO) were deposited successfully on glass substrate by sol-gel dip coating method by varying precursor concentrations. The structural properties of ZnO thin films were investigated by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) techniques. The optical properties of ZnO thin films were also characterised using UV visible Spectrophotometer, Fourier Transform Infrared Spectrometer (FTIR) and Photoluminescence (PL) studies. The XRD analysis of all ZnO films showed hexagonal structure with c-axis orientation along (002) plane, whereas SEM image of ZnO thin films showed granular surface. The UV visible spectral study showed a higher transmittance in the visible region with a direct band gap value in the range of 3.2 eV to 3.3 eV for prepared Zinc Oxide thin films. FTIR spectra indicated a ZnO stretching mode at 480 cm^{-1}. The PL spectra of ZnO sample gave an intense visible strongest ultraviolet emission peak centred at 380 nm and weak blue emission peak around 480 nm.**

Keywords- ZnO; Sol-gel Method; XRD; SEM; Optical; FTIR

I. INTRODUCTION

Zinc oxide is an ideal material for fabrication of short-wavelength optoelectronic devices since it has wide bandgap (E_g=3.37 eV n-type semiconductor) at room temperature with large exciton binding energy of 60 meV. Due to its high refractive index and chemical stability, ZnO is also considered as an appropriate material for the fabrication of photonic crystals [1, 2]. So far, ZnO has been studied mainly in the form of thin films. ZnO thin film is a transparent and able to conduct electricity. It can be applied in optical waveguides [3], Light Emitting Diodes (LED) [4], Thin Film Transistor (TFT) [5] and various gas, chemical and bio-molecule sensors. Thin films of Zinc oxide can be prepared by various techniques, such as sputtering [6], Chemical Vapour Deposition (CVD) [7], Sol-gel [8] and Spray pyrolysis [9].

Among the various techniques, sol-gel dip coating method is most preferable for this type of study since it has many advantages like simplicity, easy for control of composition, fabrication of large area films and better homogeneity. Hence it has made possible the fabrication of ZnO thin films with reproducible and desired properties. It is known that the physical properties of ZnO material strongly depend on the deposition method. Many factors like concentration, aging time and pH value of the solution, including the kinds of substrate and annealing treatment, affect the quality of the prepared films. In the present investigation, the sol-gel dip-coating technique has been employed to prepare ZnO thin films on glass substrates with various concentrations, to elucidate the structural and optical properties of ZnO thin films.

II. EXPERIMENTAL WORK

In the preparation of ZnO thin films, Zinc acetate dihydrate ($Zn(CH_3COO)_2 2H_2O$), ethanol and mono ethanolamine (MEA) were used as starting material, solvent and sol stabilizer respectively. Zinc acetate (0.2M) was first dissolved in ethanol at room temperature, the resulting mixture was stirred at 60℃ for an hour and MEA was added into the solution drop by drop (molar ratio of MEA and zinc acetate was maintained at 1.0). Finally, a clear homogeneous solution was obtained. The ZnO solution was aged for 24 hours at room temperature and then ZnO thin films were prepared by dip-coating method on cleaned and dried glass substrates. Every time the substrate was withdrawn from the ZnO solution and kept in furnace, and allowed to dry and subjected for pre-heat treatment at 300℃ for 5 minutes. The procedure from dip-coating to drying was repeated six times. At last, ZnO thin film was annealed at 550℃ in air for an hour. Two more samples were also prepared by varying the molarities of zinc acetate as 0.3M and 0.4M.

The crystallinites of the ZnO thin films were studied by an X-ray diffractometer (RIGAKU, Japan) with CuK_α radiation. The surface morphologies of the films were observed using Scanning Electron Microscope (Shimadzu S-3000N). The optical transmittance and band gap of ZnO thin films were found out at room temperature using Spectrophotometer (Shimadzu UV-Vis 1800). The Photoluminescence spectra of ZnO thin films were evaluated by Spectrofluorometer (Perkin Elmer LS55). In addition the thickness of the films was also determined by Stylus Profilometer (Mitutoyo SJ-301).

III. RESULTS AND DISCUSSION

A. *Structural Properties*

1) XRD Analysis:

The X-Ray diffraction patterns of the ZnO thin films with different Zinc acetate concentrations (0.2M, 0.3M and 0.4M) were indicated in Figure 1. The prominent peak was obtained (002) which exhibited as hexagonal wurtzite structure, and was preferentially orientated along the c-axis. The other peaks observed were recorded as (100), (102) and (110) (JCPDS, 36-1451). It was found that an increase in the zinc acetate concentration resulted in an increase in the intensity of the (002) peak. The XRD spectra indicated that the films were of polycrystalline in nature. The lattice constants are calculated from the prominent peaks using the Equations 1 and 2.

$$a = \sqrt{\frac{1}{3}}\left(\frac{\lambda}{\sin\theta}\right) nm \tag{1}$$

$$c = \left(\frac{\lambda}{\sin\theta}\right) nm \tag{2}$$

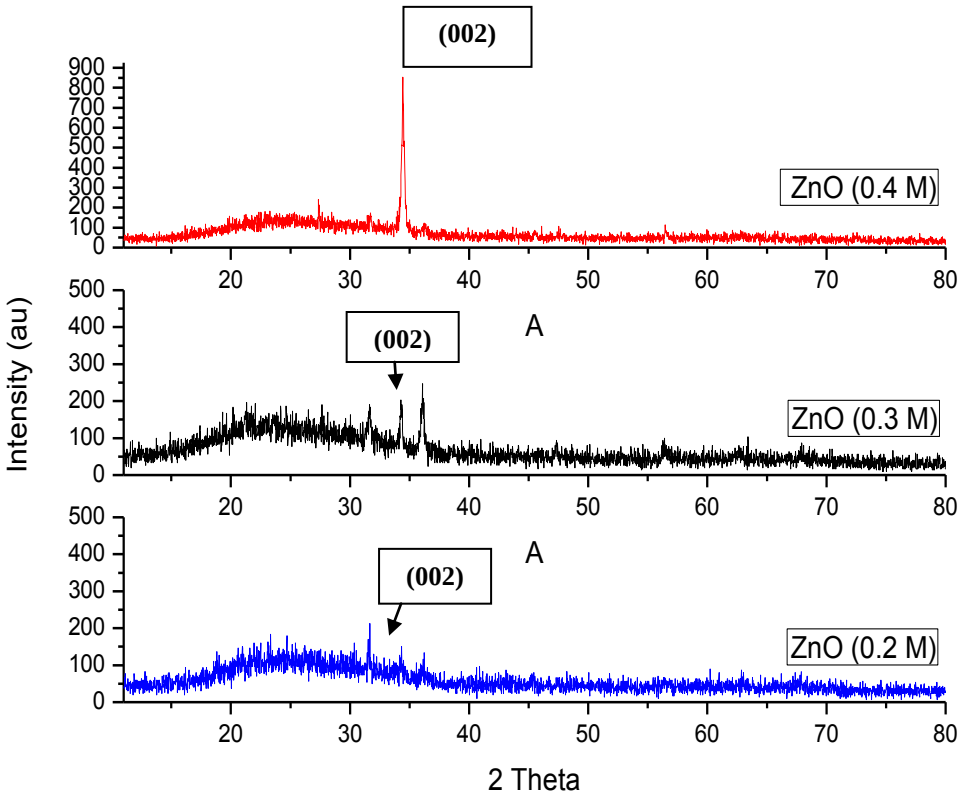


Fig. 1 X-Ray diffraction spectra of ZnO thin films for 0.2M, 0.3M and 0.4M concentrations

The lattice constants calculated for ZnO thin films were shown in Table 1. The 'a' and 'c' values were in concordance with the standard values of ZnO single crystals (a=0.3250 nm and c=0.5207 nm) which indicated that the quality of ZnO films was good crystalline in nature. The grain sizes (D) of crystallites were calculated using the Debye-Scherer's formula.

TABLE 1 THE LATTICE CONSTANTS AND GRAIN SIZE AND DISLOCATION DENSITY OF ZNO THIN FILMS WITH DIFFERENT CONCENTRATIONS, CALCULATED FOR PEAK (002)

Concentrations Mol/Lit	Peak Position (2θ)	a (nm)	c (nm)	D (nm)	δ (nm)	Thickness (nm)
0.2M	34.720	0.3081	0.5164	59	2.872	98
0.3M	34.440	0.3004	0.5204	62	2.601	100
0.4M	34.320	0.3014	0.5222	64	2.441	122

$$\mathbf{D} = \mathbf{0.94}\left(\frac{\boldsymbol{\lambda}}{\boldsymbol{\beta}\cos\boldsymbol{\theta}}\right) \tag{3}$$

Where,

D is the crystallite size

λ is the wavelength of the X-ray used (λ=1.5406 Å)

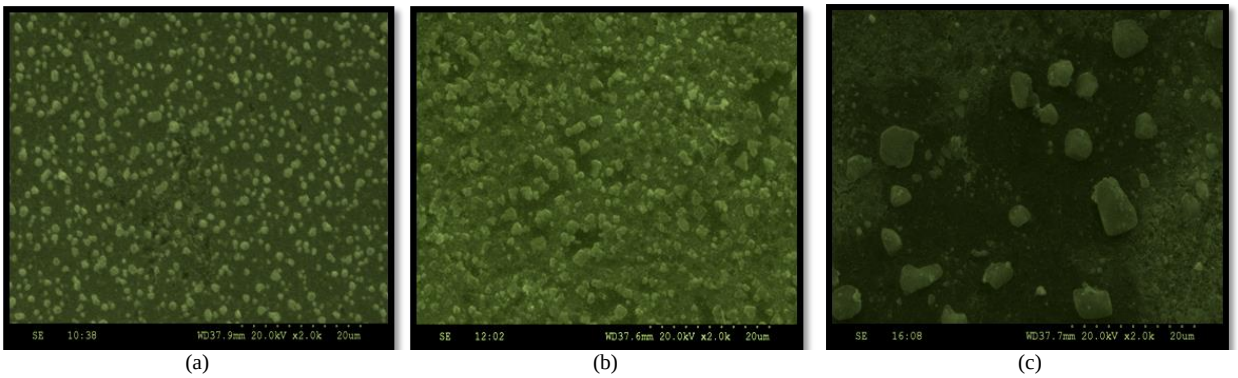
β is the broadening of diffraction line measured at the half of its maximum intensity in radians

θ is the angle of diffraction.

The dislocation density was determined using the formula $\delta=1/D^2$. It can be observed that the grain size increases and the dislocation density decreases with increase in Zn concentration in precursor solution which showed that the Zn^{2+} concentration plays an important role in grain size. The result of the present study corroborated with reports of Dharmendra Mishra et al., [10, 11]. They have stated that the XRD intensity of (002) peak increases with respect to increase in molarities of ZnO thin films prepared by sol-gel method.

2) SEM Analysis:

The surface morphology of ZnO film prepared with 0.2M, 0.3M and 0.4M of Zinc acetate was carried out using Scanning Electron Microscope (SEM). The surface morphology of the ZnO film at different concentrations was depicted in Figure 2. All the ZnO films have granular and uniform grains of the order of nm. It can be seen that the grain size of ZnO film increases with increase in Zinc acetate concentration. As the concentration increases, the crystal grain grows up continuously. J. Lu et al. (2010) have also investigated that the particle size increases with increase in concentration of ZnO thin films [12].



(a) (b) (c)

Fig. 2 SEM Images of ZnO thin films (a) 0.2M (b) 0.3M (c) 0.4M

B. *Optical Properties*

1) UV Analysis:

UV-Visible transmittance spectra of ZnO thin films prepared for various concentration were shown in Figure 3. All the ZnO films showed transmittance higher than 70% at 500 nm in the visible region. It was observed that the 0.2M ZnO thin film has the highest transmittance and 0.4M ZnO thin film has lowest transmittance in the visible region. The optical transmittance decreases (oriented to c-axis) with increase in the concentration of Zinc. The transmittance of ZnO thin film has much do to with its crystallination quality. J. Lu et al. have reported that the increase of grain boundaries increases the light scattering, which in turn will lead to a decrease in transmittance [12].

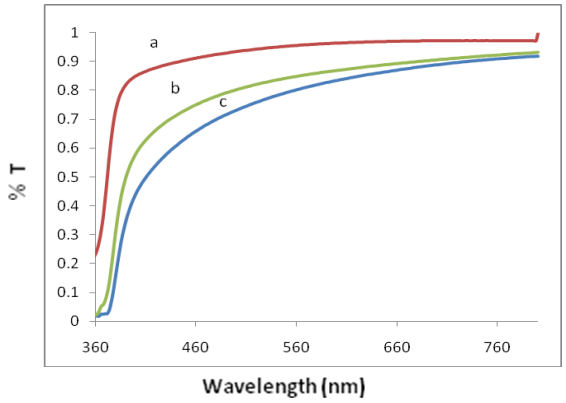


Fig. 3 Optical transmittance spectra of ZnO thin films for 0.2M,0.3M and 0.4M

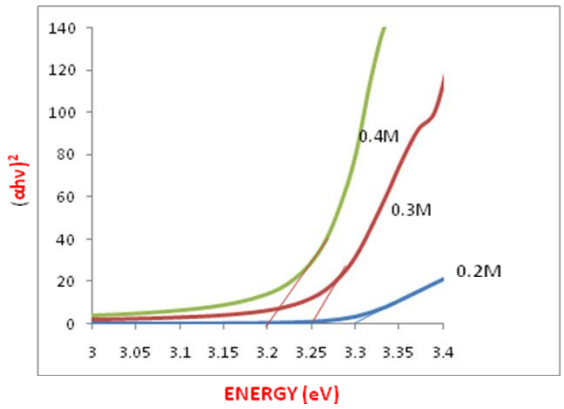


Fig. 4 Plots of $(\alpha h\nu)^2$ and $(h\nu)$ for ZnO thin films for 0.2M,0.3M and 0.4M

The optical absorption coefficient can be calculated using the Lambert law relation

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \tag{4}$$

Where,

t is the thickness of the film

T is the transmittance

The relation between absorption coefficient and incident photon energy can be written as,

$$\alpha h\nu = A\,(h\nu - Eg)^{1/2} \tag{5}$$

Where,

α is the absorption co-efficient

hν is the photon enegy

A is constant for direct transition.

E_g is the direct bandgap

Figure 4 showed that the plot of $(\alpha h\nu)^2$ versus $(h\nu)$, indicates the direct bandgap nature of the films. By extrapolating the linear portion of the curve onto the X-axis the energy bandgap of the films is determined. The optical band gap energy values decrease as 3.3 eV, 3.25 eV and 3.2 eV with increase in the molarity of the precursor solution as 0.2M, 0.3M and 0.4M respectively. These results were consistent with the conclusions arrived by Shinde et al., [13] who reported that the larger optical bandgap of ZnO thin film was due to high crystalline quality.

2) FTIR Analysis:

FTIR spectra of the ZnO samples (Figure 5) recorded at room temperature with different concentration and the peak positions were tabulated in Table 2. Three broad bands were observed for all ZnO thin films at 480.27 cm^{-1}, 1579 cm^{-1} and 2952 cm^{-1} which correspond to ZnO, C=O symmetric group and asymmetric O=C=O group. Similar results were observed also by Ziaul et al. [14].

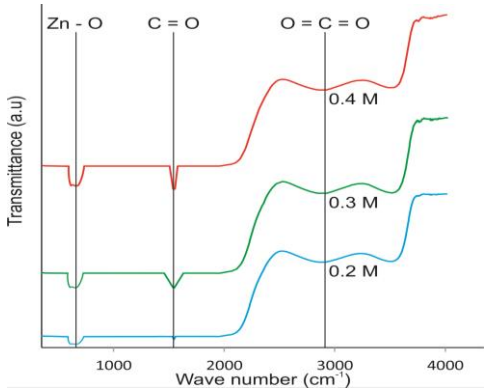


Fig. 5 FTIR spectra of ZnO thin films for 0.2M,0.3M and 0.4M

TABLE 2 FTIR SPECTRA OF PEAK POSITION AND MODE OF VIBRATION FOR ZNO THIN FILMS WITH DIFFERENT CONCENTRATIONS

Molarity Concentration (Mol/Lit)	Peak position (cm^{-1})	Mode of Vibration
0.2, 0.3 and 0.4	480	ZnO Stretching vibration
	1579	C=O
	2952	O=C=O

3) PL Analysis:

All the ZnO thin films (Figure 6) showed ultraviolet emission peak at 380 nm, and they also have a weak blue emission peak located at 480 nm. The blue emission peak intensity gradually increases with increase in the molarities. The increase in zinc acetate concentration might lead to increase in structural defects, mainly oxygen vacancies which cause increase in the intensity of PL emission peak [15-17].

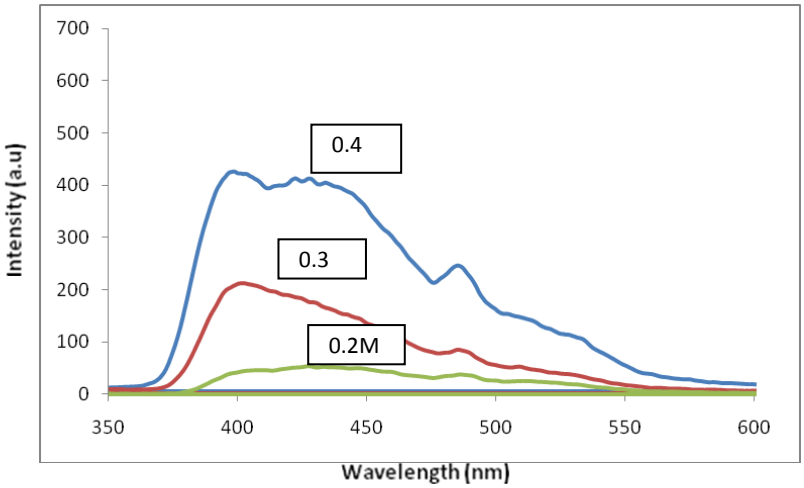


Fig. 6 The PL Spectra of ZnO thin films for 0.2M, 0.3M and 0.4M

The increased intensity of UV emission depends on the grain size and crystal orientation of ZnO thin films. The XRD study of ZnO diffraction peak (002) and UV emission (380 nm) intensity increases by increase in the concentration. It can be noted that the PL spectra very much closely agreed well with result of XRD spectra. The PL results showed that the characteristics of ZnO thin film depend on the precursor concentrations [18].

IV. CONCLUSIONS

The ZnO thin films were successfully prepared by the cost effective sol-gel method and their structural and optical properties were investigated. The XRD spectra confirmed that the films were of hexagonal in structure. The grain size of crystallites increases with increase in Zn concentrations. SEM images revealed the formation of granular surface in ZnO thin films. The optical band gap of ZnO thin films estimated was 3.2eV to 3.3eV using UV spectra. The ZnO peak was identified by FTIR spectra. PL spectra of ultraviolet and blue emission peak were located at 380 nm and 480 nm and hence the ZnO thin films prepared in the present study can be utilized for preparing optoelectronic devices, because of their desirable qualities.

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