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Preparation and Characterization of Nanostructured Zinc Oxide Thin Films

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Abstract. Thin films of Zinc Oxide (ZnO) were deposited on slide glass substrates by the chemical bath deposition technique (CBD). The formation of nanostructured ZnO thin films have been confirmed through XRD, TEM, and SEM. The structure properties were investigated by XRD. The optical properties were measured by UV-VIS spectrophotometer. The absorption coefficient is calculated from recorded data and it is best fitted for direct band gap. The direct band gap was in range 3.8-4.0 eV.

Keywords: ZnO Nanoparticles Thin Films, CBD Method, XRD, (WBGS), Optical Properties
PACS: 73.63.Bd.

INTRODUCTION

ZnO nanoparticles thin films have attracted immerse interest because of their unique properties and potential applications in optoelectronics devices. ZnO is a wide band gap semiconductors (WBGS) that displays high optical transparency and luminescent properties in the UV and VIS region, good transparency, high electron mobility, strong room temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, thin-film transistor and light-emitting diode. ZnO is promising material for electronics and optoelectronic application such as solar cells [1] , gas sensors [2], UV photo detectors [3] heat mirrors , wave devices and bulk acoustic wave resonators [4] etc. In this work, simple, low-cost technique is the chemical bath deposition (CBD) method to deposit ZnO nanoparticle thin films on the glass substrates has been investigated. The crystalline structure of the samples was evaluated by X- ray diffraction (XRD). The optical band gap of high quality thin films obtained by using optical transmission measurements in the wavelength range 300 to 1500 nm at room temperature was found to be in the range of 3.8-4.0 eV.

METHODOLOGY

ZnO nanoparticle thin films were deposited on glass substrates (12×25 mm^2) cleaned with detergent, degreased with trichloroethylene, acetone, and ethanol and rinsed with deionized water in an ultrasonic cleaner and finally etched in a 10 % HF solution just before use for the depositions. The chemical bath deposition was formed by 0.45 M aqueous solution of zinc nitrate (Zn $(NO_3)_2.6H_2O$) and 0.9 M aqueous solution of Potassium hydroxide (KOH) were prepared in distilled water. Then, the beaker containing KOH solution was heated at the temperature of about 60 ºC. The Zn $(NO_3)_2$ solutions were added drop wise (slowly up to pH 8) to the above heated solution under speed stirring. For stopping agglomeration we have used (polyvinylpyrrollidone) PVP as capping agent after few hours of reaction, the white precipitate deposited on glass substrate. The samples and holders were retired from the chemical bath after 60 min deposition time. The films obtained by this method, after ultrasonic cleaning, were smooth, uniform, adherent, clear and transparent. X-ray diffraction (XRD) measurements using Cu K_α radiation of wavelength λ = 0.15406 nm in the scan range 2θ = 20-90º. Surface morphology was examined by JEOL model JSM – 6380 LA Scanning Electron Microscope (SEM with EDS) for compositional analysis of the prepared ZnO nanoparticle thin films. The formation of ZnO nanoparticle was confirmed using transmission electron microscope (TEM, JEOL 1010). Optical transmission measurements were performed with UV/VIS Jasco 7800 spectrophotometer. The incidence photon flux was normal to the film surface. The investigated wavelength ranges from 300 to 1500 nm. The optical band gap (E_g) of the transparent films was

determined by using the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ where α is the absorption coefficient, A is a constant and $h\nu$ is the light energy.

CHARACTERIZATION

The low-dimensional structures can be grown to restrict the degree of free movement of charge carriers in zero, one and two dimensions. The associated structures are referred to as quantum dots, quantum wires and quantum layer. The wave-like behavior of carriers exhibits new physical properties in low-dimensional structures when their de Broglie wavelength is comparable to the dimensions of the structure. Hexagonal Wurtzite is most stable structure of ZnO at ambient conditions. X-ray diffractograms of ZnO nanostructured thin films is shown in figure 1. All the XRD peaks are indexed by hexagonal wurtzite phase of ZnO (PDF file no 80-0075). An electron diffraction result confirms XRD. Selected area electron diffraction pattern exhibiting several uniform bright rings suggests that the ZnO nanostructured have preferential instead of random orientation are shown in fig 2a and fig 2b respectively. The particle size distribution as obtained from the TEM micrograph of ZnO nanoparticles is demonstrated in Fig.2c.Table 1 summarizes the difference between XRD, PDF file and TEM. The following Eqn. (1) derived using the effective mass model [5] describe the particle size (r, radius) as a function of peak absorbance wavelength (λ_p) for ZnO nanoparticle thin films.

$$r(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \dfrac{10240.72}{\lambda_p(nm)}}}{-6.3829 + \dfrac{2483.2}{\lambda_p(nm)}} \quad . \quad (1)$$

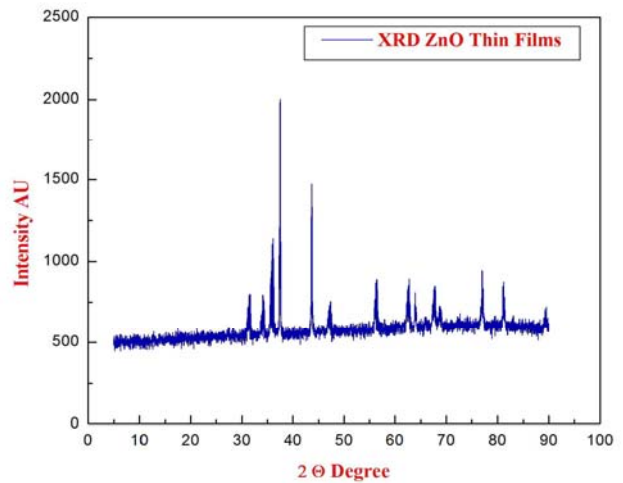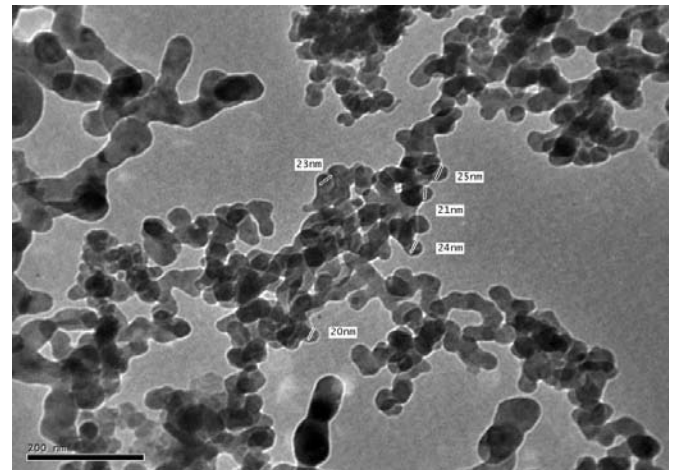**FIGURE 1.** XRD of ZnO nanoparticles thin films.
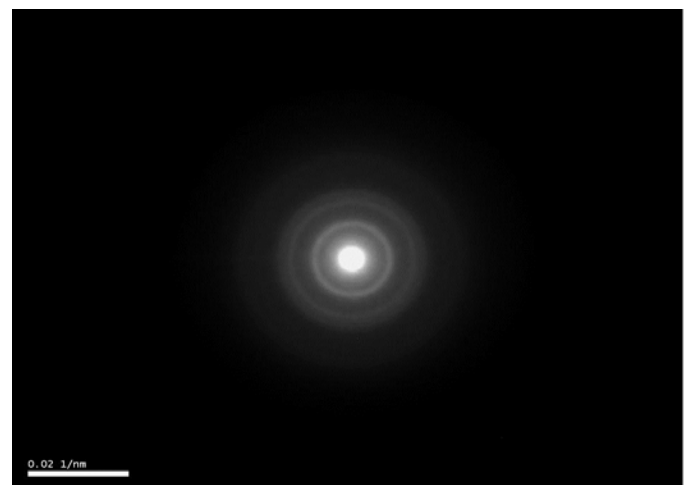

FIGURE 2A. TEM picture of ZnO thin films.

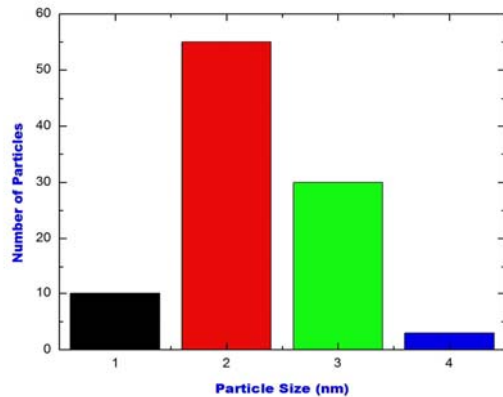**FIGURE 2B** Electron Diffraction patterns of ZnO.

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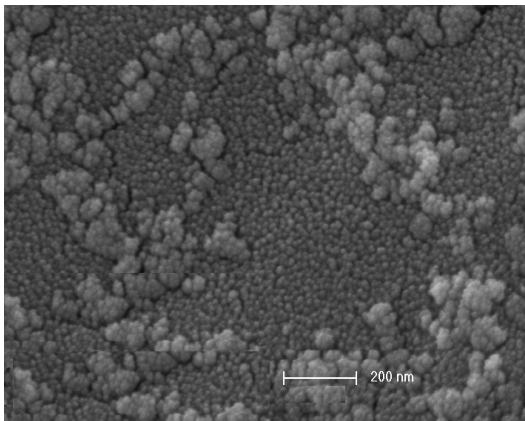**FIGURE 2C.** The particle distribution of ZnO.

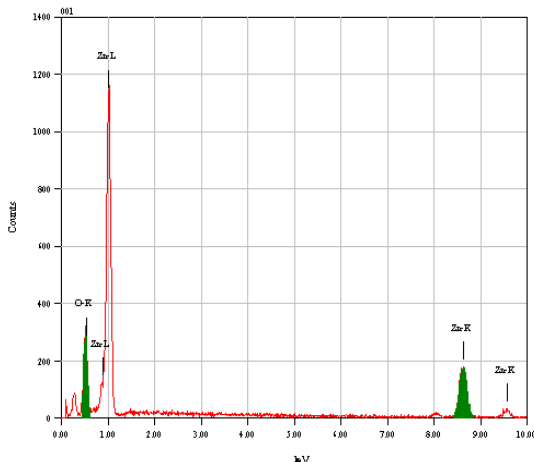
FIGURE3A. SEM of ZnO nanoparticles thin films.

FIGURE 3B. EDS of ZnO nanoparticles thin films.

The grain size value of the as-deposited films evaluated from SEM micrographs, as shown in Fig. 3, is less than 50 nm. From EDS technique, the Zn and O content is equal to 57 and 43 % respectively.

OPTICAL PROPERTIES

The measured absorption characteristics are shown in Fig. 4a. At 262 nm the excitonic absorption peak is observed which lies much below the bandgap wavelength (shown in Fig. 4a) of 388 nm (E_g = 3.2 eV) of bulk ZnO. The absorption of ZnO is very sharp, which indicates the monodispersed nature of the nanoparticle distribution [6-7]. The transmittance (T) at different wavelengths (λ) are measured and then absorbance (α) at the corresponding wavelengths λ are calculated using the Beer-Lambert's relation.

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right), (2)$$

Where, d is thickness of the film. The absorption edge for ZnO is very sharp and is determined by the nature of the electronic transition between the valence band and conduction band. The absorption edge for nanoparticles thin films is much broader and is determined by the distribution of particle size [8]. Particles with smaller sizes contribute more at the region of smaller wavelength range so the average particle size can be determined from the absorption data spectrum. [8].
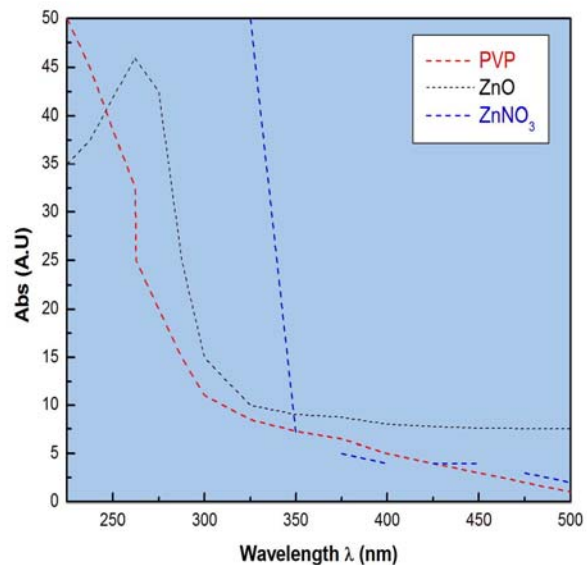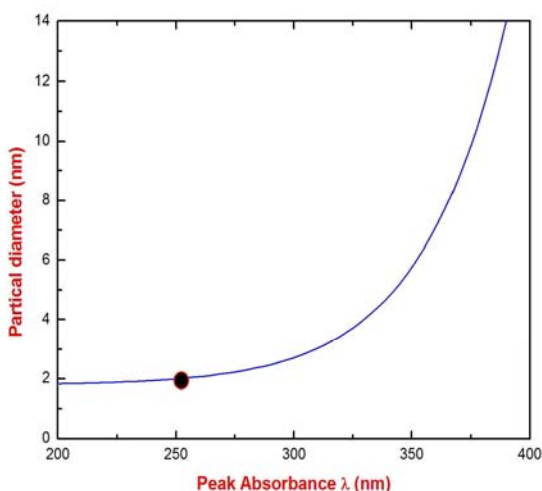

FIGURE 4A. UV-VIS absorption of ZnO.

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FIGURE 4B. Particle diameter of ZnO calculated.

TABLE 1. Interplanner spacing (d_{hkl}) from TEM, XRD and PDF data file and corresponding (h k l) values

d_{PDF} (A^0)	d_{XRD} (A^0)	d_{TEM} (A^0)	(hkl)
2.82	2.80	2.84	(100)
2.60	2.63	2.58	(002)
2.48	2.51	2.45	(101)
1.91	1.92	1.88	(102)
1.63	1.61	1.6	(110)
1.38	1.39	1.42	(112)

CONCLUSIONS

In this work, we have reported the synthesis of ZnO nanoparticles thin films with average size of 1.9 nm by chemical method with PVP as capping agent and double distilled water as solvent. The nanostructures of the prepared ZnO nanoparticles thin films have been confirmed using XRD, TEM and UV-VIS absorption analysis. ZnO nanoparticles thin films average sizes have been determined from the absorption data using the effective mass model [5]. TEM analysis supported that ZnO nanoparticles nearly monodisperse. Due to the smaller crystallites the density of surface would increase with a decrease in the size and the probability of excitonic emission [9-10].

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