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Preparation of ZnO thin film using sol-gel dip-coating technique and their characterization for optoelectronic applications

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ABSTRACT

ZnO thin film with an aim to employ in opto-electronic applications was prepared using sol-gel dip-coating route and thereafter sintered at temperature 500 ºC. The film has been investigated by XRD pattern, SEM, UV-Vis and photoluminescence spectroscopy for physical and optical characterization of ZnO thin film. X-Ray diffraction pattern analysis reveals the polycrystalline nature with hexagonal wurtzite structure having orientation along the plane (002). Scanning electron micrograph shows symmetrical dense ZnO rod throughout the surface. The diffuse reflectance spectrum is studied in the range of wavelength 300-800 nm. A band gap of 3.21 eV is calculated using Kubelka-Munk function. PL spectrum shows strong peak at 380 nm due to oxygen vacancy of ZnO.

Keywords**:** ZnO, XRD, SEM, Band gap, dip coating

1. INTRODUCTION

In recent years, semiconductor ZnO has intrigued as one of the prominent material for the purpose of opto-electrical devices. ZnO a group II-VI metal oxide semiconductor having a wide direct band gap value of 3.2 to 3.37 eV along with a large excitation binding energy (B.E) of 60 meV at room temperature [1-3]. ZnO films are constantly studied because of interesting

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properties they have, such as having control over resistivity up to 10^{-3}-10^{-5} Ω·cm along with high infrared reflectivity and transparency in the visible region. Because of all these characteristics ZnO films have many applications as antibacterial, cancer treatment, gas sensors [4-6] and piezoelectric films in surface acoustics wave devices [7].

Physical properties of ZnO greatly depend on the method and condition of depositing films. ZnO films has been prepared by various methods such as electrochemical deposition [8], chemical bath deposition (CBD) [9], molecular beam epitaxy [10], pulsed laser deposition [11], magnetron sputtering [12], MOCVD [13] and spray pyrolysis [14]. Sol-gel dip-coating method for depositing ZnO thin film is used in this paper because of its simple procedure; and it require no costly vacuum systems. It has broad advantage of large area deposition with uniform thickness. The sol-gel technique for fabrication of films using various inorganic and organic precursors has been accounted in literature [15-16]. In this research ZnO thin film is fabricated by sol-gel dip-coating route and a detailed investigation is given by analysing its structural and optical characterization of the film for various opto- electronic applications.

2. EXPERIMENTAL MEASUREMENTS

All the chemicals used in this work were of AR grade with 99.9% purity. Sol-gel dip-coating method has been used for the fabrication and deposition of ZnO thin film. A measured quantity of zinc acetate di-hydrate was dissolved in 20 ml ethylene glycol with continuous stirring and then 10 ml monoethanolamine (MEA) is added drop wise. It turned heterogeneous solution to a clear transparent solution. This preparation was done at room temperature (RT). The pH of the solution was maintained to value 7-8 by adding acid and base solution. This clear solution was kept on magnetic stirrer at steady temperature of 80 ºC for 2-3 hours to obtain gel. This gel was kept undisturbed for 24 hours at room temperature. Before dip coating glass substrate was first cleaned with water and then with acetone.

Pre-cleaned glass substrate was dipped into solution vertically at a speed of 120 mm/min. The coated films were dried at 100 ºC for 20 minutes on a hot plate. This procedure was repeated for 9-10 times to obtain the film of desired thickness. After this, coated film is sintered at a temperature of 500 ºC in a furnace to stabilize the film and for combustion of undesirable organic substances. For the crystal structure of prepared ZnO film, Rigaku Diffractmeter (ULTIMA-IV) was employed. Surface morphology was carried out using ZEISS electron microscope (special edition model EV018). Diffuse reflectance spectra (DRS) were performed by UV-Visible (U-3900, model no. 2116-010) spectrophotometer in the range of wavelength 300-800 nm. Gravimetric weight difference method was used to calculate the thickness of the film. The average thickness of the film was 300 nm. PL spectrum was scanned on Perkin Elmer make LLS PL spectrometer at room temperature.

3. RESULT AND DISCUSSIONS

3. 1. Structural analysis

XRD pattern of ZnO film is presented in Figure 1. This pattern shows three prominent peaks corresponding to (100), (002) and (101) planes along with some less prominent peaks corresponding to (102), (110), (103) (200), (112) and (201) planes. XRD pattern shows that film is strongly oriented in the (002) direction. All the peaks in the XRD pattern correspond to standard ZnO (JCPDS 36-1451). XRD pattern reveals the polycrystalline nature and has a hexagonal wurzite structure. Mean size of crystallites were estimated using Debye-Scherrer formula [17]:

$$D = 0.94\lambda/\beta\cos\theta$$

where D is average size of crystallites particles
λ is wavelength of X-Rays
β is full width half maxima
θ is angle of diffraction

In present work the average crystallite size of grain is found to be 20 nm.

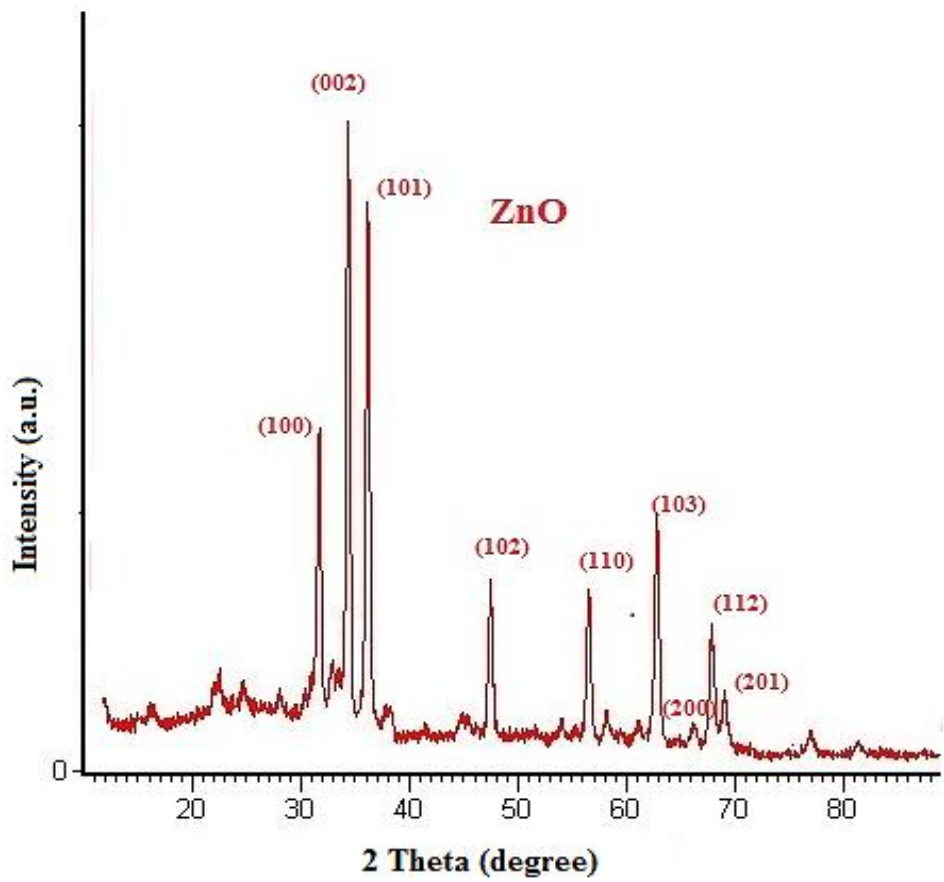

Figure 1. X-Ray diffraction (XRD) spectra of ZnO thin film.

3. 2. Scanning electron microscope analysis

SEM is an easy method to study the microstructure of thin films. Figure 2 depicts the SEM image of ZnO thin film. Symmetrical ZnO rod growth in large surface area can be seen in SEM image. Such type of rod shaped thin films of ZnO is reported by L. Znaidi et al. [18].

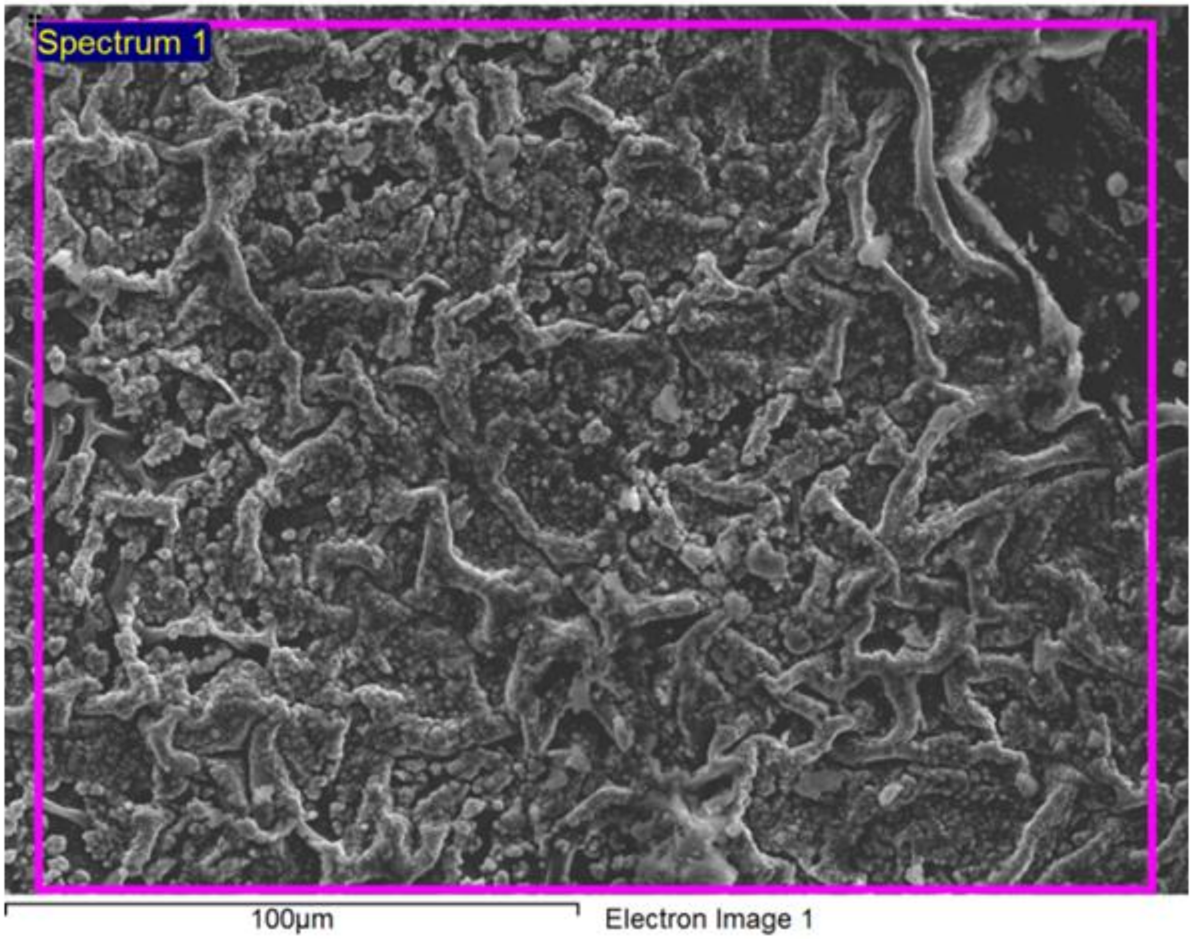

Figure 2. SEM Image of ZnO thin film

3. 3. Optical properties

Energy band gap (E_g) of prepared ZnO film can be estimated using diffuse reflectance spectroscopy. Figure 3.presents the reflectance spectrum of ZnO thin films studied in the wavelength range of 300-800 nm.

A sudden fall in spectrum indicates about the presence of optical band gap in the film. To calculate the energy band gap (E_g) of ZnO film, a graph between Kubelka-Munk (K-M) function $[F(R)\, h\upsilon]^2$ and photon energy ($h\upsilon$) is plotted in Figure 4. The optical band gap (E_g) can be calculated by the extrapolating the linear part of this plot. The Kubelka- Munk function is given by [19]

$$[F(R)\, h\upsilon] = A\,(h\upsilon - E_g)^{1/2}$$

where $F(R) = (1-R)^2/\ 2R$ is Kubelka-Munk (K-M) function. R is the magnitude of the reflectance as function of energy.

The direct band gap is estimated at 3.21 eV which is found to be in good agreement with the reported value [20].

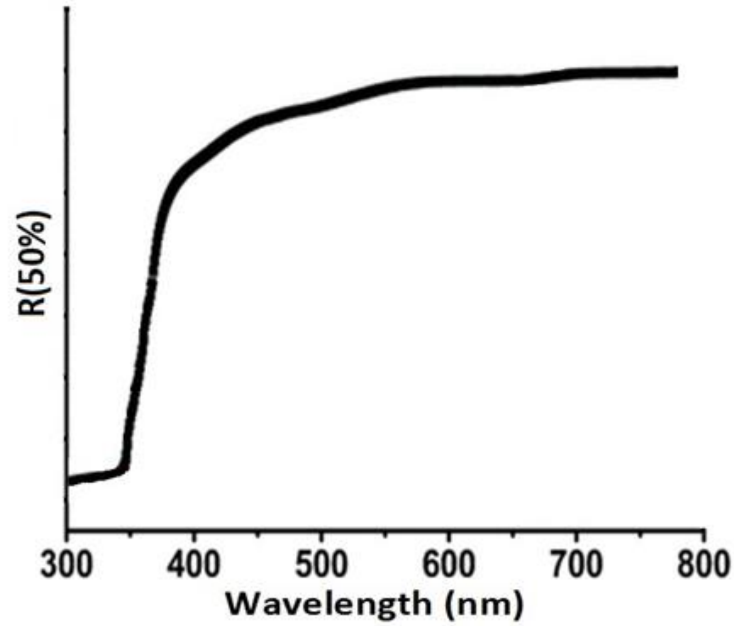

Figure 3. Diffuse reflectance spectra of ZnO thin film.

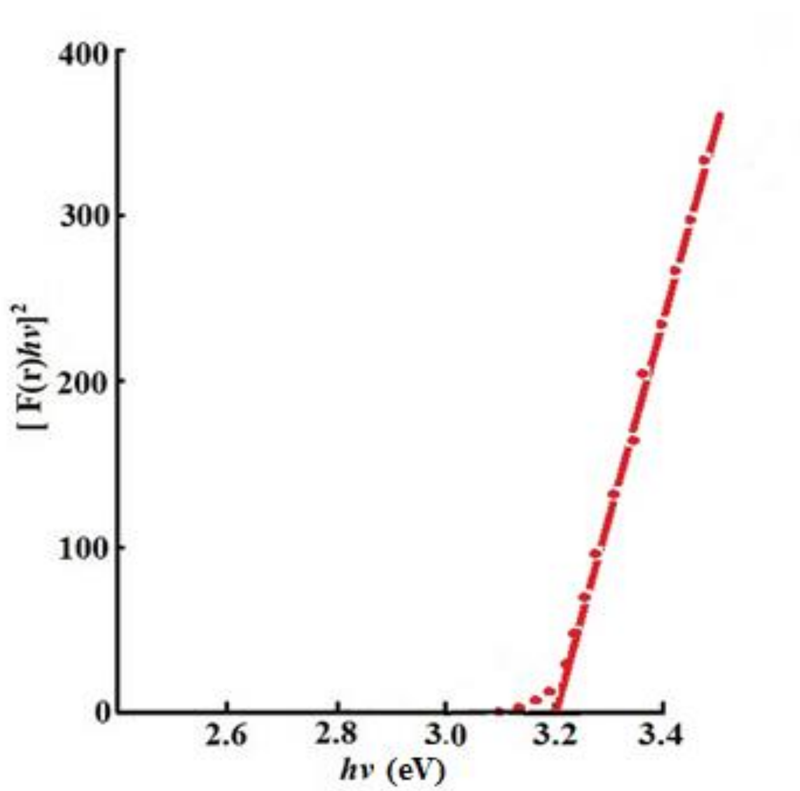

Figure 4. Plot of $[F(R)\ h\upsilon]^2$ versus photon energy ($h\upsilon$) for ZnO thin film

3. 4. Photoluminescence analysis

Photoluminescence (PL) spectrum of ZnO thin film is shown in Figure 5. The spectrum shows a strong peak at 380 nm because of free exciton emission in PL spectrum near band edge (NBE). A broad and weak peak is also obtained in PL spectrum centred at 545 nm, it relates to the amount of non-stoichiometric intrinsic defects. This is found to be in good agreement with reported value [21].

A rough idea of optical band gap can also be taken from PL spectrum shown in figure 5. by using the formula:

$$E_g = 1240/\lambda$$

The estimated value of band gap from PL spectrum corresponding to wavelength 380 nm is observed to be 3.26eV, which is slightly greater than the band gap estimated by Kubelka-Munk function.

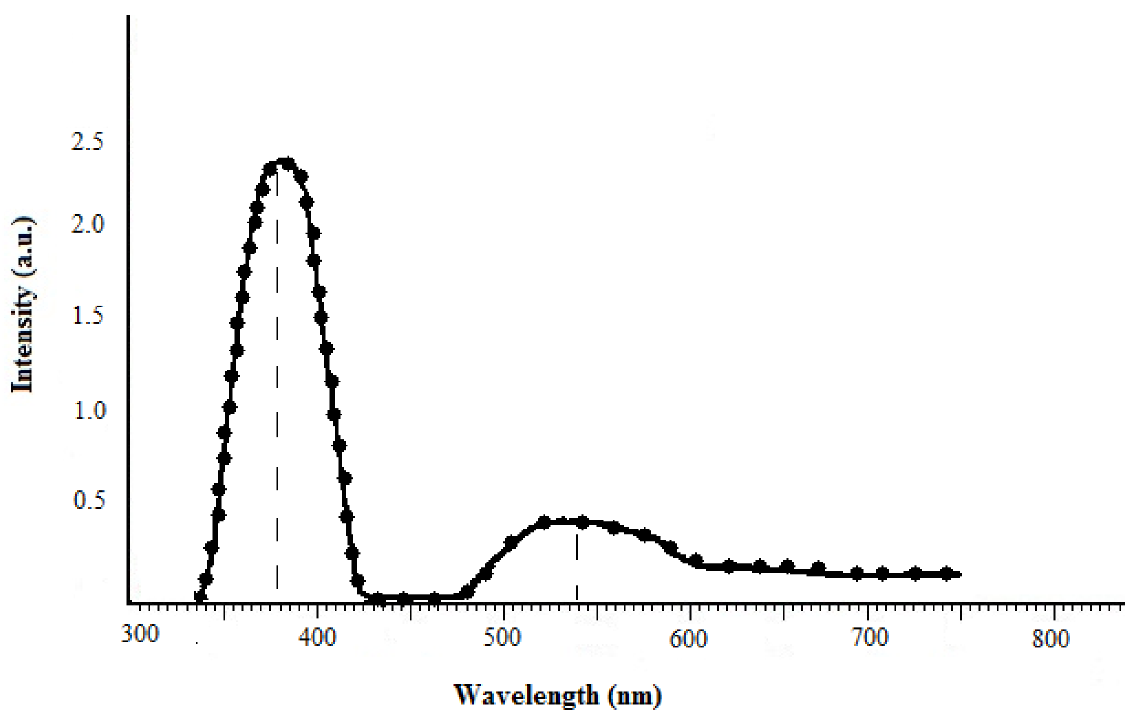

Figure 5. Photoluminescence spectrum of ZnO thin film.

4. CONCLUSIONS

ZnO thin film was fabricated using cost effective sol-gel dip coating technique on glass substrate. The x ray analysis revealed hexagonal wurtzite structure. The film shows the direct energy band gap of 3.21eV. PL measurement shows that ZnO has strong luminescence character. Results obtained of in this study are suitable for opto-electronic devices.

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