KIET IJCE KIET International Journal of Communications & Electronics
Volume. No. 6, Issue No. 2, July-Dec. 2018, ISSN: 2320 – 8996

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 were prepared using sol-gel dip-coating method and thereafter sintered at 500ºC. The film has been investigated by XRD, SEM, UV- Vis and photoluminescence spectroscopy for physical and optical properties ofZnO 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 300-800nm. A band gap of 3.21 eV is calculated using Kubelka- Munk function. PL spectra shows strong peak at 380 nm due to oxygen vacancy of ZnO.

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

INTRODUCTION

In recent years, semiconductor ZnO has intrigued as one of the prominent material for the application in opto-electrical devices. ZnO is a group II-VI metal oxide with a wide direct band gap of 3.2 to 3.37 eV and having a large excitation binding energy of 60 meV at room temperature [1-3]. ZnO films are constantly studied because of interesting properties they have, such as having control over resistivity up to 10^{-3}-10^{-5}Ω-cm and transparency in the visible and high infrared reflectivity. Because of all these characteristics ZnO film 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 film 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], spray pyrolysis [14]. Sol-gel dip-coating method for depositing ZnO thin film is used in this paper because of its simple procedure; require no costly vacuum systems and having wide advantage of large area deposition with uniform thickness. The sol-gel technique for fabrication of film using various inorganic and organic precursors has been reported in literature [15-16].
In the present work ZnO thin film is fabricated by sol-gel dip-coating method and a detailed investigation is given by studying structural and optical properties of the film for various opto-electronic applications.

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 amount of zinc acetate dihydrate 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. The pH of the solution was adjusted to value 7-8 by adding acid and base solution. This clear solution was kept on magnetic stirrer at steady temperature of 80ºC 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 120mm/min. These coated films were dried at 100ºC for 20 minutes in the oven. This process was repeated for 9-10 times to obtain the film of desired thickness. After it coated film is sintered at 500ºC in a muffle furnace to stabilize the films and for combustion of undesired organic substances.
For the crystal structure of prepared ZnO film, Rigaku (ULTIMA-IV) diffractometer was used. Surface morphology was carried out using ZEISS electron microscope (model EV018 special edition). Diffuse reflectance spectra were recorded by UV-Visible spectrophotometer (U-3900, model no. 2116-010) in the wavelength range of 300-800nm. Gravimetric weight difference method was used to calculate the thickness of the film. The average thickness of the film was 300 nm. PL spectra have been scanned on Perkin Elmer make LLS PL spectrometer at room temperature.

Result and discussions

Structural analysis

XRD pattern of ZnO thin film is presented in figure 1. This pattern shows the 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 wurtzite structure. Mean size of crystallites were estimated using Debye-scherrer formula [17]:
$D= 0.94\lambda/\beta\cos\theta$
Here D is Average size of crystallites particles
λ is wavelength of x- rays
β is full width half maxima
θ is diffraction angleIn present work the average size of grain is found to be 20 nm.

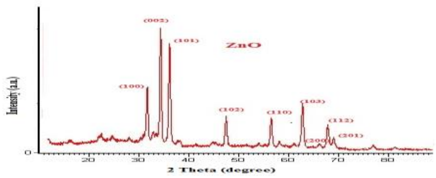


Figure 1. X-ray diffraction (XRD) spectra of ZnO thin film.

Scanning electron microscope analysis

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

Optical properties

Energy band gap of prepared ZnO film can be estimated using diffuse reflectance spectra Figure 3.shows the reflectance spectra of ZnO thin films studied in range of 300-800nm wavelengths. A sudden fall in reflectance spectra indicate about the presence of optical band gap in the film. Energy band gap can be estimated using diffuse reflectance spectra. To calculate the energy band gap of ZnO film a graph between Kubelka-Munk function $[F(R)\ h\upsilon]^2$ and photon energy ($h\upsilon$) is plotted in figure 4. The optical band gap can be calculated by the extrapolation of linear part. The Kubelka- Munk function is given as [19]
$[F(R)\ h\upsilon]=A\ (h\upsilon-E_g)^{1/2}$Here $F(R) = (1-R)^2/\ 2R$ is Kubelka-Munk function. R is the magnitude of the reflectance as function of energy. The direct band gap is estimatedat 3.21 eV which is in good agreement with the reported value [20].

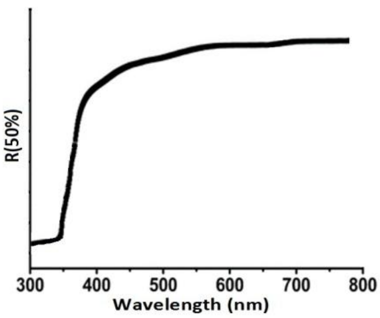


Figure 3. Diffuse reflectance spectra of ZnO thin film.

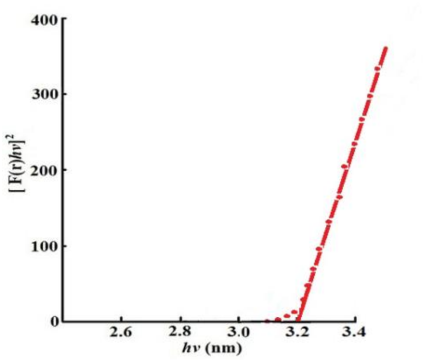
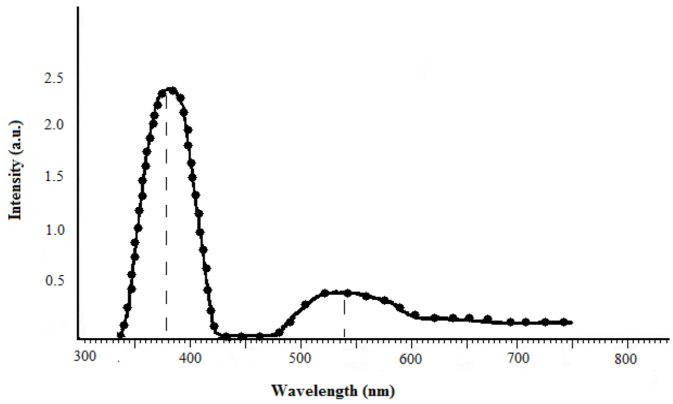


Figure 4. Plot of $[F(R)\ h\upsilon]^2$ versus photon energy ($h\upsilon$) for ZnO thin film

Photoluminescence analysis

PL spectrum of ZnO thin film is shown in figure 5. This spectrum shows a strong peakat 380nm due to free exciton emission in PL spectrum near band edge (NBE). A broad and weak peak is also obtained in PL spectrum centred at 545nm, 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.



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. Result obtained of ZnO sol-gel dip coated film is suitable for opto-electronic devices.

Acknowledgements

The Authors are thankful to Dr. (Col.) Amik K. Garg (Director, KIET Group of Institutions, Ghaziabad) and Dr. Jagannath Sahoo (Principal, KIET School of pharmacy) for their encouragement and providing facilities to carryout work smoothly.

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