Effect of Annealing Temperature on the Structural and Optical Properties of Zinc Oxide (ZnO) Thin Films Prepared by Spin Coating Process

Sandeep Sanjeev and Dhananjaya Kekuda
Department of Sciences, Manipal University, Manipal-576 104, Karnataka, INDIA

E-mail: sandeepssanjeev@gmail.com
Telephone: 09844488973

ABSTRACT: ZnO thin films were deposited onto the glass substrates by spin coating method. Zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine (MEA) were used as starting materials for the thin film preparation. Films were obtained by spin coating at 4000 rpm for 30 sec at room temperature and were annealed at different temperatures ranging from 200°C to 400°C. The effect of annealing temperature on the structural and optical properties of the ZnO thin films was investigated. Surface morphology of thin films was studied using atomic force microscope (AFM). The optical absorbance and transmittance measurements were recorded by using a single beam spectrophotometer in the wavelength range 300 nm to 900 nm. Evaluated optical band gap value agrees approximately with that of bulk ZnO. It is observed that band gap decreases as the annealing temperature is increased from 200°C to 400°C.

1. Introduction
Zinc oxide is an inexpensive n-type semiconductor having direct band gap of 3.3 eV which crystallizes in hexagonal wurtzite structure. Due to large exciton binding energy of 60 meV, they have potential applications in Optoelectronic devices such as in solar cells Light emitting diodes (LED) Zinc oxide thin films are applied in Thin Film Transistors (TFT). Thin films of Zinc oxide can be prepared by various techniques; among them are thermal evaporation, Sputtering, Chemical Vapor Deposition (CVD), Spin coating and Spray pyrolysis. Apart from doping, to increase the functionality of ZnO thin film, the effect of preparation conditions on the properties have to be considered for its effective technological applications. In the present work we have used spin coating process for film preparation. Zinc acetate dihydrate was used as the starting material. The Sol-gel process has the advantages of controllability of compositions, simplicity in processing and is cost effective (Shakti, 2010). We have studied the effect of annealing temperature on the structural and optical properties of zinc oxide (ZnO) thin films. Surface morphology of thin films was studied using atomic force microscope (AFM). UV-VIS spectrometry, were used for optical characterization.

2. Experimental details
ZnO thin films were prepared on glass substrates by spin coating method. Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) was used as a starting material, 2-methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer respectively for the solution preparation. Zinc acetate dihydrate was first dissolved in 2-methoxyethanol and then MEA were added, at room temperature. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0 and the concentration of zinc acetate dihydrate was 0.3 M. The solution were stirred at 80°C for 2 hours, thus obtained clear solution was then allowed to cool to room temperature. After the filtration coating was made. The solution dropped onto the pre-cleaned glass substrate, which were rotated at 4000 rpm for 30 sec using spin coater at room temperature. After depositing by spin coating, the films were dried at 150°C for 10 min over a hot plate to evaporate the solvent. The process from coating to drying was repeated to obtain the workable thickness of the film. Thus obtained multilayer films annealed in muffle furnace at 200°C, 300°C and 400°C for 1hr were prepared to study the effect of annealing.
Surface morphology of thin films was studied using atomic force microscope (AFM). The optical absorbance and transmittance measurements were recorded by using a single beam spectrophotometer in the wavelength range 300 nm to 900 nm.

3. Results and discussion

3.1 Surface Morphology Of The ZnO Thin Film

Surface morphology of thin films was studied using atomic force microscope (AFM). AFM images of the thin films annealed at 250°C, 350 °C and 400°C are shown in fig.1, fig.2 and fig.3 respectively. The thin film prepared by spin coating is uniform; this was observed by AFM images taken at two different regions of the same film. By comparing the image of thin films annealed at 250°C, 350°C and 400°C it is observed that film roughness increases as increase in annealing temperature. This is due to increase in grain size with increase in annealing temperature.

3.2 Optical Properties of The ZnO Thin Films

The optical absorbance and transmittance measurements were recorded by using a single beam spectrophotometer in the wavelength range 300 nm to 900 nm. Absorption and transmission spectra are shown in Fig.4 and Fig.5 respectively, for ZnO thin films annealed at different temperatures. Figures show the increase in absorption of photon energy as increase in annealing temperature. Transmission increases with increases in wavelength and decreases with increase in annealing temperature. The transmission of the film is above 80% in this visible region.
Refractive index of ZnO thin film was calculated from equation (1) (Hussein et al., 2011)

\[ n = \left[ 1 + \left( \frac{R}{1-R} \right)^{0.5} \right] \] (1)

The reflectance \( R \) was calculated using the following equation (2)

\[ R = 1 - \left( \frac{T}{e^{-\alpha t}} \right)^{0.5} \] (2)

The variation of refractive index with wavelength is shown in fig.6. From fig.6 it is observed that refractive index decreases as wavelength increased.

The absorption coefficient of thin film is calculated from the expression (3) (Kumar et al., 2011)

\[ \alpha = 2.303 \left( \frac{A}{t} \right) \] (3)

Where, \( A \) is absorbance and \( t \) is the thickness. Shakti (2010) notes that the absorption coefficient \( \alpha \) and the extinction coefficient \( k \) are related by the formula (4) (Shaaban E.R., 2006).

\[ k = \frac{\alpha \lambda}{4\pi} \] (4)

Where, \( \lambda \) is the wavelength. The variation of extinction coefficient with wavelength is shown in Fig.7.

It is well known that ZnO is a direct-gap semiconductor. The Optical band gap energy \( E_g \) and absorption coefficient \( \alpha \) is related by the equation (5) (Tauc, 1970)

\[ (\alpha h\nu)^2 = h\nu - E_g \] (5)

Where, \( \alpha \) is absorption coefficient and \( h\nu \) is the incident photon energy. The variation of \( (\alpha h\nu)^2 \) with \( h\nu \) is plotted, for the ZnO thin films, were annealed at different temperature, which is shown in Fig.8. The band gap energy \( E_g \) of the films was evaluated from the intercept of the linear portion of the each curve for different annealing temperature with the \( h\nu \) in X-axis. The value of Band gap energy \( E_g \) as calculated above agrees nearly with band gap of bulk ZnO (3.37 eV). It is observed that band gap value decreases from 3.28eV to 3.16eV as the annealing temperature is increased from 200˚C to 400˚C. The effect annealing time on optical band gap were studied by annealing the thin film for different time intervals. The variation of \( E_g \) with annealing time is shown in fig.9 it is observed that band gap value decreases linearly as the annealing time interval increases.
4. CONCLUSIONS

Zinc Oxide thin films prepared on glass substrate by spin coating process and annealed at different temperatures (200ºC to 400ºC). It is investigated that annealing temperature affects the structural and optical properties of the ZnO thin film. The transmission spectrums of the films were recorded by UV–VIS Spectrophotometer. The films showed high transparency (>80%) in the visible region. The refractive indices, extinction coefficients were calculated. The refractive index and extinction coefficient showed some variation with rise in annealing temperature of ZnO film. The Optical energy band gap values were evaluated by plot of \((\alpha h\nu)^2\) versus \(h\nu\). The value of band gaps agrees approximately with that of bulk ZnO. Band gap value decreases as the annealing temperature increases. AFM image of the samples results the increase in roughness as annealing temperature increases, this is possibly because of increase in grain size, so that band gap energy \(E_g\) decreases.

5. ACKNOWLEDGEMENTS

Authors are grateful to Innovation Centre and Center for Atomic and Molecular Physics (CAMP), Manipal Institute of Technology, Manipal University for helping to do the project.

6. REFERENCES

Hussein ¹H.F., Ghufran Mohammad Shabeeb ², S.Sh. Hashim ³. Preparation ZnO Thin Film by using Sol-gel-processed and determination of thickness and study optical properties. J. Mater. Environ. Sci. 2 (4) (2011) 423–426
ISSN : 2028-2508.http://www.jmaterenvironsci.com

ILICAN*, S., Y. CAGLAR, M. CAGLAR, 2008. Preparation and characterization of ZnO thin films deposited by sol-gel spin coating method. JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10. 2578 – 2583.

Kumar1*, K. Balachandrananda P. Raji2, 2011. SYNTHESIS AND CHARACTERIZATION OF NANO ZINC OXIDE BY SOL GEL SPIN COATING. Recent Research in Science and Technology 2011, 3(3): 48-52
ISSN: 2076-5061 www.recent-science.com

Shakti, Nanda and P. S. Gupta, 2010. Structural and Optical Properties of Sol-gel Prepared ZnO Thin Film. Applied Physics Research Vol. 2, No. 1. 19-28
Tauc, J., 1970. The optical properties of solids (North-Holland, Amsterdam, 1970).