Blue Shift of Optical Band Gap in ZnO Thin Film Grown by Spin Coating Process

Santhosh Prabhu[1]
prabhusanthoshmsc@gmail.com

Dr. Dhananjaya Kekuda[2]
kekuda@gmail.com

Department of Physics,
Manipal University, Manipal,
Karnataka, India

***Abstract*- Optical band gap of ZnO thin films deposited on glass substrate by spin coating process was studied. The optical band gap of as-grown ZnO blue shifted from 3.11eV to 3.69 eV as the annealing temperature decreased from 300 to 100 °C. Also observed that there is a variation in the transmittance of ZnO thin film. X-ray diffraction measurements showed that samples deposited at 100^{0}C, 200^{0}C and 300^{0}C consisted of amorphous phases without any prominent diffraction peaks. The AFM images showed that there is a decrease in the grain size, which is the evidence for the decrease in the transmittance.**

***Index Terms*- Spin coating, UV-visible, XRD, AFM, Optical properties**

I. INTRODUCTION

Metal oxides exhibit a wide range of functional properties depending on their crystal structure and bonding between the metal cat ion and oxygen. Indeed, the electrical properties of metal oxides range from insulating to highly conducting like a metal, or even superconducting. Some metal oxides also exhibit magnetic properties such as ferromagnetism or ferrimagnetisms. Because of this diverse functionality, metal oxides have become one of the most fascinating inorganic materials in device applications such as light emitting diodes, field effect transistors, solar cells and spintronic devices.

Among the metal oxides, ZnO is attractive because the metals are abundant on earth, inexpensive and non-toxic. Moreover, these oxides have useful optical and electrical properties suitable for a wide variety of electrical devices. As synthesized ZnO is almost always an n-type semiconductor with high mobility (10 ~ 200 cm^2 / V sec) in thin high quality films at room temperature. This is due to the oxygen vacancies in the grown films. ZnO is a wide band gap (3.3 eV) semiconductor and therefore, it has been considered as a potential material for transparent electrode and electronics and widely used in solar cells as window layer and transparent thin film transistors.

II. EXPERIMENT

The ZnO thin film used in this study are grown on the glass substrate by spin coating process. The glass substrates were cleaned with acid (con.H_2SO_4), then soap solution followed by ultra-sonication in distilled water for 1 hr and subsequently dried. For sol preparation **Zinc** acetate di-hydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was first dissolved in a 2-methoxyethanol ($(CH_2)2CHOH$) with mono ethanolamine (MEA: $H_2NCH_2CH_2OH$) which was used as a stabilizer. The molar ratio of MEA to zinc acetate was kept to 1.0 and concentration of zinc acetate was 0.8 mol/l. The resultant solution was stirred at 60˚C for 1 hr to yield a clear and homogeneous solution ready for coating. The spinning rate was kept at 1000rpm. The wet films were dried at room temperature for 10 min. The process was repeated to obtain the desired thickness of the film. Multilayer films were post annealed at 100^{0}C, 200^{0}C and 300^{0}C for 1hr to study the effect of annealing. The structural properties of the prepared films were studied by X-ray diffraction measurements (Rigaku-miniflex600). The Atomic Force Microscopy (Innova SPM) was used to find the surface morphology of the grown films.

III. RESULT AND DISCUSSION

A. *Optical Properties*

Fig. (1) Shows the representative transmittance spectra of 0.8 M ZnO thin films, annealed at different temperatures. It is observed that as annealing temperature increases there is increase in the transmittance.

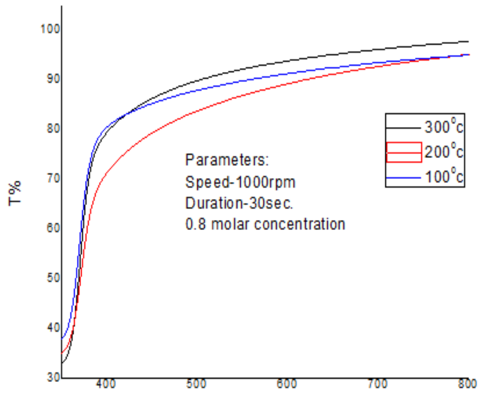

Fig:1 Effect of annealing temperature on optical transmittance

It is probably due to the decrease in the grain size of the ZnO thin films [1]. In this experiment 0.8M concentration solution is used. The transmittance is observed between 91% to 95%. for all the films. The highest transmittance is obtained for the film which was annealed at 300^{0}C and lowest in the case of the film which was annealed at 200^{0}c.

The absorption coefficient can be calculated from the relation [2]

$$T = A \exp(-\alpha d)$$

Where T is the transmittance of thin film, A is a constant, and d is the film thickness. The constant A is approximately unity, as the reflectivity is negligible and insignificant near the absorption edge. The optical band gap of the films is determined by applying the Tauc model [3] and the Davis and Mott model [4] in the high absorbance region

$$\alpha h\nu = D\,(h\nu - E_g)^n$$

Where h is the photon energy, Eg is the optical band gap, and D is a constant. For a direct transition, n=1/2 or 2/3 and the former value was found to be more suitable for ZnO thin films since it gives the best linear curve in the band-edge region [2][5] In Fig. (2) The relationship between $(h\nu\alpha)^2$ and hν is plotted. The Eg value can be obtained by extrapolating the linear portion to the photon energy axis in that figure. The optical band-gap values obtained are summarized in Table I. As the annealing temperature was reduced from 300 to 100 °C, the optical band gap blue shifted from 3.11 to 3.69 eV

Samples	Annealed temperature(0c)	Estimated optical band gap(eV)
1	100	3.69
2	200	3.20
3	300	3.11

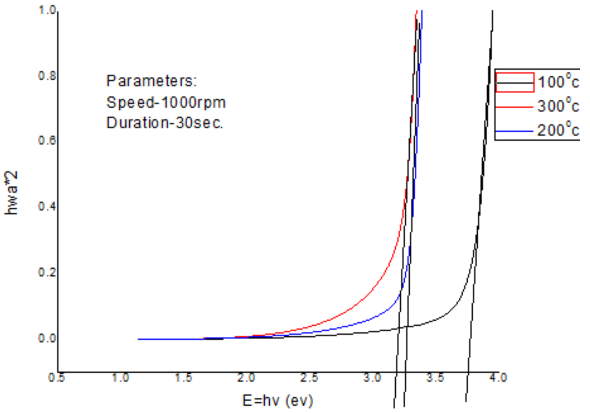

Fig. (2) Effect of annealing temperature on Band gap of ZnO thin film of 0.7 and 0.8 molar concentration

The experiment is carried out by keeping all other parameters are constant i. e. A spin speed is kept at 1000 rpm, the duration of spin coating cycle was 30 sec. and the molar concentration of the sample is 0.8

The blue shift is clearly shown by zooming the absorption tail, which is shown in fig. (3) Bellow

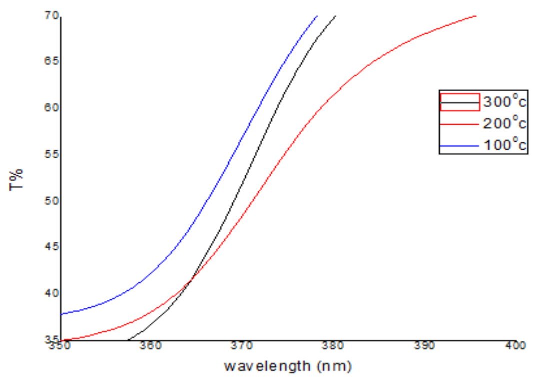

Fig. (3) Absorption tail moving towards lower wavelength as annealing temperature decreases

From the XRD results fig. (4), we propose that the absorption edge blue shift is due to the poor crystallinity of ZnO thin films grown at low temperature. The crystalline of the ZnO thin films grown below 400 °C was poor and exhibits an amorphous character. The physical model of the structure can be viewed as various nanocrystalline islands embedded in a matrix of amorphous ZnO, which is seen in the AFM image fig. (5). Qualitatively, the interatomic spacing of amorphous structure would be relatively long and more disordered than crystalline structure due to the absence of long-range translational periodicity. As the fraction of amorphous ZnO phase increases in the films grown at low temperature, the extended localization in the conduction and valence bands increases [2]. As a result, the absorption of photon is mainly contributed by amorphous ZnO and hence the absorption edge blue shifted.

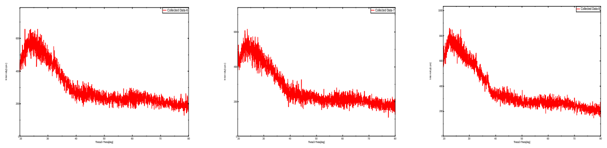

Fig. (4) XRD measurement for 0.8 mol concentration ZnO thin film at 100^0C, 200^0C and 300^0C

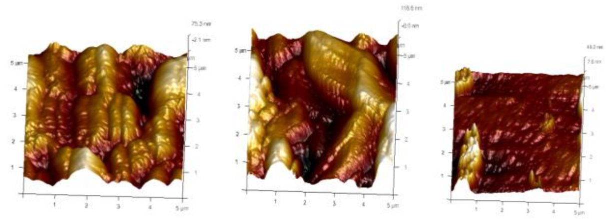

Fig (5) AFM images of the ZnO thin film annealed at different temperature

IV. CONCLUSION

In conclusion, the optical band-gap blue shift of ZnO thin films made of amorphous phases was studied. The amorphous phase in ZnO films obtained in films annealed at low temperature is believed to be the main reason for the blue shift of optical band gap. The estimated optical band gap of ZnO thin film blue shifts from 3.11eV to 3.69 eV as the annealing temperatures decreased from 300 to 100 °C.

V. ACKNOWLEDGMENT

This study was supported by Manipal University

REFERENCE

[1] S. T. Tan et al "Blue shift of optical band gap in ZnO thin films grown by metal-organic chemical-vapor deposition" S. T. Tan et al; School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

[2] J. Tauc, Amorphous and Liquid Semiconductors Plenum, London, 1974.

[3] J. G. Lu, Z. Z. Ye, L. Wang, J. Y. Huang, and B. H. Zhao, "Mater. Sci. Semiconductor Process" 2003.

[4] Somnath C. Roy, G.L. Sharma and M.C. Bhatnagar " Large blue shift in the optical band-gap of sol–gel derived $Ba_{0.5}Sr_{0.5}TiO_3$ thin films" Volume 141, Issue 5, February 2007.