Structural and Optical Studies of Sol-Gel Deposited Nanostructured ZnO Thin Films: Annealing Effect

Sanjeev Kumar[1,2,a)], Fouran Singh[2] and A. Kapoor[1]

[1]*Department of Electronic Science, University of Delhi South Campus, New Delhi - 110023, India*

[2]*Materials Science Group, Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi- 110067, India*

E-mail: sanjeevkumarphy@gmail.com

***Abstract*— Zinc oxide (ZnO) thin films were deposited by sol–gel spin coating method on the glass substrate and then the film was annealed at 350, 450, 550 ^{0}C for 1 h. Effect of annealing temperature on the structural and optical properties of the film was investigated. Annealed ZnO thin films are polycrystalline with (002) preferential orientation. The information on Crystalline size is obtained from the full width-at half- maximum (FWHM) of the diffraction peaks. The surface morphology of the films was investigated by atomic force microscopy (AFM). Surface roughness was found minimum (8.4 nm) for ZnO sample annealed at 450°C. The maximum transmittance of 87% is observed for the film annealed at 450 °C. The optical band gap value decreased and crystalline size increased with increasing the annealing temperatures.**

***Index Terms*— ZnO thin films, sol-gel, annealing temperature, X-ray diffraction, UV-spectrometer.**

I. INTRODUCTION

In this work, we have chosen ZnO, which is an n-type material having high chemical and thermal stability, high mechanical strength and large exciton binding energy (60 meV), which is quiet larger than GaN (21 meV) and ZnS (20 meV) [1]. ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications [2]. ZnO is transparent to visible light and can be made highly conductive by doping. Zinc oxide is a remarkable material with direct band gap having band gap value of 3.37 eV [3]. It exhibits a variety of properties as UV emission [4], transparent conductivity [5].

ZnO is an alternative material which has most used today for many application, So that ZnO is a technologically important material exhibiting multifunctional properties for various applications in optoelectronic devices, such as solar cell transparent conducting electrodes, heat mirror [6-8], Light emitting diodes and light extraction enhancement [9]. Nowadays, ZnO thin films can be grown by using many deposition techniques such as spray pyrolysis [10], sputtering [11], chemical vapor deposition (CVD) [12], pulsed laser deposition (PLD) [13], sol-gel technique [14].

The sol-gel technique is preferred because of its simplicity, low cost, safety and can be used for large-area applications for smooth as well as curved surfaces. The optical properties of ZnO have their genesis in both intrinsic and extrinsic effects. Intrinsic optical transitions take place between the electrons in the conduction band and the holes in the valence band, including excitonic effects caused by the Coulomb interaction. Excitons are classified into free and bound excitons [15].

In this present work of investigation, ZnO thin films annealed at different temperature have been prepared by sol-gel spin coating technique The films were annealed with different temperature and characterization have been carried out by glancing angle X-ray diffraction (GAXRD), optical (transmittance, band gap), atomic force microscopy (AFM) films have been reported and discussed. The purpose of this work is to determine the optimum annealing temperature that can produce films for optoelectronic applications.

II. EXPERIMENTAL DETAILS

ZnO thin films at different annealing temperature (350-550°C) were developed on corning (1737) glass substrate by spin coating technique. Zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] (purity 99.95%) (Merck Extra pure chemical Ind. Ltd, India) was used as a source of zinc. Ethanol (AR, Merck chemicals, India) and Monoethanolamine [MEA] (Merck, India) were used as the solvent and stabilizer respectively. The Zn precursor solution was prepared by dissolving zinc acetate dihydrate in ethanol so as prepare concentration of 0.2 mol/l further that MEA was dissolved in solution. The molar ratio MEA/Zn was fixed to 1. The mixture was stirred ultrasonically and also using a magnetic stirrer at 25°C for 2 hours. The clear transparent and homogenous solution thus obtained was left to age for 72 hours. Substrate was cleaned ultrasonically, first in acetone and then subsequently in methanol for 10 min each.

They were further cleaned with deionized water for 20 min. One drop of solution was dropped onto substrate which was rotated at 2500 rpm for 30 sec by a spin coater. After deposition by spin coating, the films were dried in air for 10 min over hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated fifteen times until the desired thickness of the ZnO films was reached.

The films were annealed in air at temperature range 350-550°C for 1 hour in a microprocessor controlled furnace by a heating rate 5°/min. Crystalline nature of the ZnO films was confirmed by PAN alytical X'pert PRO diffractometer using the CuK_{α} radiation having a wavelength 1.5140°A. The band gap of ZnO films were measured by optical transmittance using a Shimadzu Solid Spec 3700 double beam spectrophotometer.

V. K. Jain and A. Verma (eds.), *Physics of Semiconductor Devices*, Environmental Science and Engineering, DOI: 10.1007/978-3-319-03002-9_183,

III. RESULTS & DISCUSSIONS

Structural Properties

The structural properties of the films were investigated by X-ray diffraction studies. The X-ray 2θ scan pattern of ZnO thin films deposited on glass substrate at different annealing temperature is shown in Fig.1. These scans were carried out at a step size of 0.5 s with continuous scan mode and 1° glancing angle. It is evident from the XRD patterns that the films are well crystallized with preferred orientation along (002) plane and maximum intensity is obtained for ZnO at temperature 450 °C. That means enhanced crystallization of ZnO thin films. The lattice constant c of ZnO thin film is 5.138 ˚A calculated from the peak position of (002) plane using Bragg's law. This value is small in comparison with the bulk value of 5.206 ˚A. The difference in lattice parameter between ZnO film and the bulk is −0.068 ˚A, which indicates that the film is under compression stress along c- direction

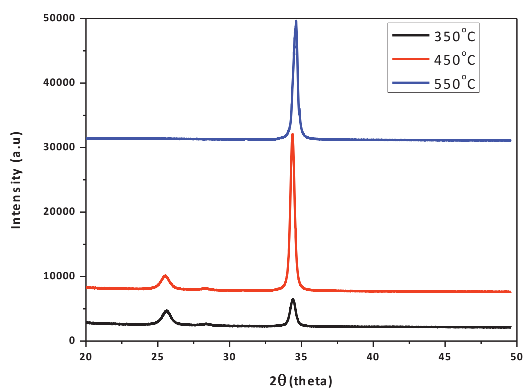

Figure. 1. XRD pattern of ZnO films as a function of annealing temperature.

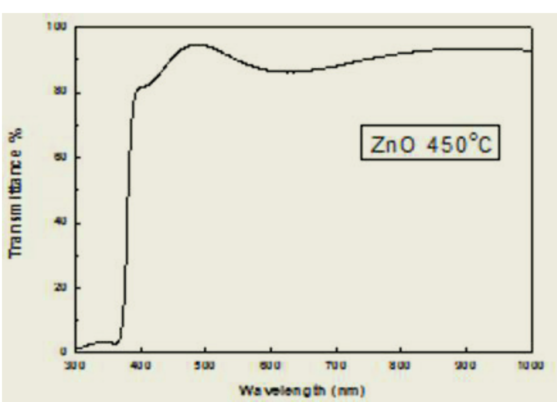

Figure. 2. Optical transmittance spectra of ZnO films at 450°C

Crystallite size of ZnO films is calculated using Debye Scherrer's formula [16]

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, k is shape factor, λ is wavelength of CuK_α line (1.5406°A) and β is the full width half maximum (FWHM) of (002) reflection peak and θ is the Bragg's angle about (002) peak. For the main peak the calculated values of the average size of the crystallites varies from 24 nm to 30 nm. It is observed that Crystallite size is increasing continuously with increase in annealing temperature and the peak position angle shifts towards the higher θ value. The value of crystallite size for different temperature is shown in table.

Table -1 Variation of crystallite size and band gap with different temperature.

ZnO (Temperature °C)	Crystallite size (nm)	Band gap (eV)
350°C	24	3.26
450°C	27	3.24
550°C	30	3.23

Optical properties

Transmittance measurements were carried out in 300-1000 nm range of spectrum. The effect of film temperature on the optical properties such as transmittance and band gap of ZnO films is investigated. Figure 2 shows the transmittance curves of ZnO film with temperature (450°C). The samples showed high and constant transparency higher than 84% in the visible range. Maximum transmittance was found to be 88% for 450 °C as shown in Fig. 2. The transmittance remains constant for all the samples, in this range of spectra. Increase in transmittance from 85–88% has been observed with increase in temperature. Increase in transmittance can be explained with the help of relation

$$I = I_O e^{-\alpha d} \quad (2)$$

Where, α is the absorption coefficient and d is the film thickness. Optical absorption coefficient (α) is calculated using [17]

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (3)$$

Where, T is the transmittance of the film and d is the thickness of film.

For the allowed direct transition, the variation of α with photon energy (hυ) obey Tauc's plot that form [18]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (4)$$

Where, A is a constant, E_g is optical band gap, h is plank constant and α is the absorption coefficient.

Fig. 3 shows the Tauc's plot for optical band gap as a function of temperature for the ZnO films. The band gap was observed to decrease from 3.26 to 3.23 eV as the film temperature increase from 350°C to 550°C. Beyond this temperature (450 °C), increase in the band gap is observed to be 3.24 eV.

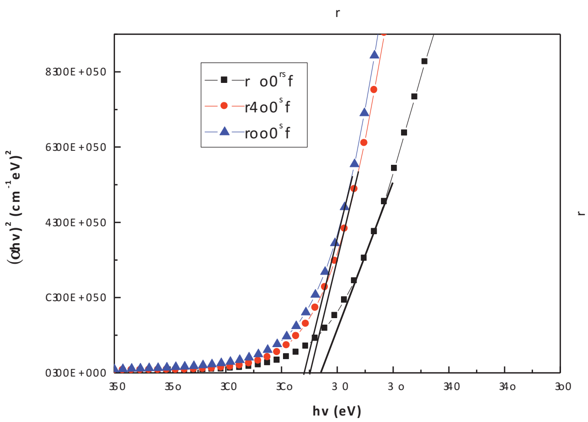

Figure. 2. Band gap variation of ZnO films as a function of annealing temperature.

The variation in the band gap of ZnO thin film can also be evaluated from the effective mass model expression [19] as

$$E = E_g + \frac{h^2}{8m^* R^2} - \frac{e^2}{4\pi\varepsilon_o \varepsilon R} \quad (5)$$

Where, E_g = band gap of the bulk semiconductor, h = Planck's constant, R = crystallite size

ε = dielectric constant of the semiconductor. m* (effective mass) = $(m_e \times m_h)/(m_e+m_h)$. m_e = effective mass of electron m_h = effective mass of hole. It is noticed that the band gap measured from absorption spectra closely coincides with the theoretical results.

Surface morphology

The surface morphology of the annealed films was observed by atomic force microscopy (AFM) in the tapping mode. Fig. 5 shows the AFM images of ZnO films scanned over an area of 1.0 μm^2 annealed at different temperature. It shows hexagonally faceted columnar grains that dominate the surface morphology. It can be observed that with the increase in annealing temperature, the surface roughness of the film decreases.

The increase in the smoothness of the ZnO thin films annealing at 450 °C may originate from a decrease in the grain boundaries. The further increase in annealing temperature shows a process of coalescence resulting in the occurrence of grain growth. Several mechanisms like Ostwald ripening, sintering and cluster migration have been proposed to explain the coalescence phenomena [20]. At high temperature, the atoms have enough diffusion to occupy the correct site in the crystal lattice and the grains with the lower surface energy will become large at high temperature, resulting in the increase in root mean square deviation. Sharma et al. [21] have also reported an increase in surface roughness as the annealing temperature was further increased after 400 °C in scandium doped ZnO.

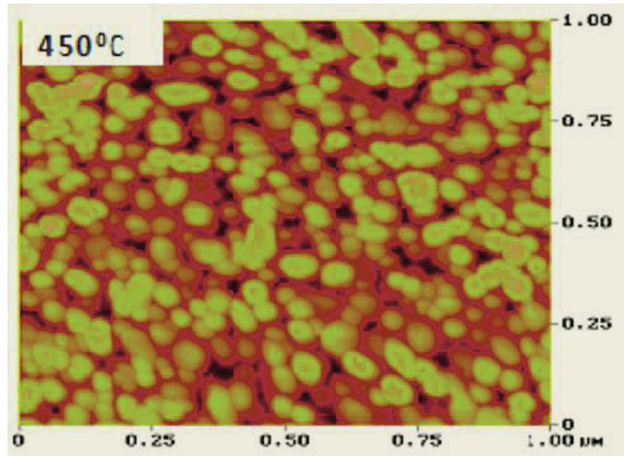

Figure. 4. Atomic Force Microscopy image of ZnO thin film at 450°C.

The AFM data have been found consistent with XRD results. Among these samples, the ZnO (450 °C) sample morphology shows a smoother surface in comparison to other samples. The smoothness of this sample can predict less scattering of light corresponding to good transparency.

The optical transmission spectra in Fig. 2 shows that the ZnO (450 °C) sample is the most transparent sample as compared to other samples and thus confirm that less light is scattered from the smooth surfaces.

Conclusion

The ZnO thin film was deposited by sol–gel spin-coating method. The structural and optical properties of the ZnO film were influenced by annealing process. XRD results showed that as grown and annealed ZnO thin films have (002) preferred orientation. The optical band gap values were found to decrease and increase the crystalline size with increasing of the annealing temperature. We can say from both the structural and optical results that 450 °C annealing temperature is suitable for production of good ZnO thin film. In addition, it is important to note down that a specific annealing temperature (in our case 450 °C) is sufficient to get the improved properties of ZnO film for solar cell applications.

References

[1] D. C. Look, D. C. Reynolds, J. R. Sizelove, R L Jpnes, C. W Litton, G. Cantwell, W.C. Harch, Solid state comm., **105**, 399 **(1998)**.
[2] SunH, Zhang Q F and Wu J L Acta Phys. Sin. **56** 3479 **(2007)**
[3] Kulkarni A. J. and Zhou M Appl. Phys. Lett. **88** 141921 **(2006)**
[4] Liu D F,Tang D S,Ci L J,Yan X Q,Liang Y X,Zhou Z P, Yuan H J, Zhou W Y and Wang G Chin. Phys.Lett. **20** 928 **(2003)**.
[5] Wen Q,Li Q H,Chen Y J,Wang T H,He X L,Li J P and Lin C L Appl. Phys. Lett. **84** 3654 **(2004)**
[6] A. J. Ronovich, D. Golmoya, H. R. Bube, J. Appl. Phys., **51**, 4260 **(1980).**
[7] V. Srikant, D. R. Clarke, J. Appl. Phys., **81**, 6357 **(1997)**.
[8] T. Minami, H. Nato, S. A. Takata, Thin Solid Films, **124**, 43 **(1985)**.
[9] M. D. McCluskey and S. J. Jokela, J. Appl. Phy, **106**, 071101 **(2009)**.

[10] O,vigil, F. Cruz, G.santana et al material chemistry and physics **68** 249-252 **(2001).**
[11] S. Muthukumar, C.R. Gorla, N.W. Emanetoglu, S. Liang, Y. Lu, J. Cryst. Growth **225** 197–201 **(2001)**
[12] B.J. Jin, S.H. Bae, S.Y. Lee, S. Im, Mater. Sci. Eng. B **71** 301–305 **(2000)**.
[13] B.J. Jin, S. Im, S.Y. Lee, Thin Solid Films **366** 107–110 **(2000)**.
[14] F.singh, Sanjeev kumar A.Kapoor et al. J.Appl.phys **112**, 73101 **(2012).**
[15] D. C. Look, D. C. Reynolds, J. W. Hemsky, R. L. Jones and J. R. Sizelove, Appl. Phys. Lett. **75**, 811 **(1999)**.
[16] V. L. Azaroff, Elements of X-ray Crystallography, McGraw Hill, New York **(1968).**
[17] X. Jiang, F. L. Wong, M. K. Fung, S. T. Lee, Appl. Phys. Lett. **83** 1875, **(2003)**.
[18] A. E. Jimenez-Gonzalez, J. A. S. Urueta, R. J. Suarez-Parra, Cryst. Growth **192** 430 **(1998)**.
[19] K. F. Lin, H. M. Cheng, H. C. Hsu, W. F. Hsieh, Chem. Phys. Let **409**, 208 **(2005)**.
[20] M. Ohring: Material Science of Thin Films: Deposition and Structure, 2nd edn, Academic, San Diego, 386 - 400 **(2001)**
[21] R. Sharma, K. Sehrawat, A. Wakahara and R.M. Mehra: Appl. Surf. Sci. **255**, 5781**(2009)**.