ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

Influence of Growth Time on Zinc Oxide Nano Rods Prepared By Dip Coating Method

P.Thamarai selvan[1], M.Venkatachalam[2], M.Saroja[2], P.Gowthaman[2], S.Ravikumar[3], S.Shankar[2]

Department of Electronics & Communication, Selvamm Arts and Science College, Namakkal, India[1]

Thin film Centre, Erode Arts and Science College, Erode, India[2]

Department of Electronics & Communication, Sengunthar Arts and Science College, Thiruchengode, India[3]

ABSTRACT: The Dip coating method was used for the preparation of ZnO nano rods and their structural, morphological, optical and photoluminescence properties were taken for study. ZnO seed layer thin films were prepared by dip coating method on well cleaned glass substrates. ZnO seed-coated glass substrates were immersed in aqueous solution of zinc nitrate and hexamethylenetetramine (HMT) at three different growth time of 3, 4 and 5 hours at low temperature of 90°C. 0.02 mol of Zinc nitrate and 0.2 mol of Hexamethylenetetramine (HMT) on 1:10 molar concentration were used for the growth of Zinc oxide nano rods. The growth time influence on the surface morphology of the films was examined. The structure of the ZnO nano rod was studied with X-ray diffraction. The surface morphology was studied with Scanning Electron Microscope. The absorption and transmittance was studied with UV-Vis spectrophotometer. The excitation studies were examined with photoluminescence spectroscopy. Experimental results have shown that prepared ZnO nano rods by this method have increase in c-axis orientation due to increase in growth time.

KEY WORDS: ZnO nanorods, Chemical bath deposition, XRD, SEM, UV and PL properties.

I. INTRODUCTION

Due to the excellent electrical, optical and structural properties, Zinc oxide (ZnO) thin films have wide applications as solar cells [1] gas sensors [2], light emitting diodes (LED's), laser systems [3] and transparent electrodes [4]. Moreover, they can be prepared by different techniques, such as magnetron sputtering [5], dip coating method [6], atomic layer deposition [7], and thermal evaporation [8]. Among the above methods to prepare ZnO, dip coating method is extremely attractive due to its advantages features over other thin film deposition technique, such as its simple low temperature, low cost, easy coating of large surfaces and low evaporation temperature.

In this paper, ZnO nanorod films were prepared by dip coating method at the low temperature of 90°C. Effect of the growth time of ZnO nanorod films structure, morphology, optical and photoluminescence properties were investigated by XRD, SEM, UV-Vis, and PL. A dip coating method was applied to deposit ZnO films on the glass as a seed layers.

II. EXPERIMENTAL

The dip coating method was applied in the present work to prepare ZnO seed layer on glass substrates because of its low cost and easy approach. All the reagents (Merck 99.99) used in the experiment were analytically pure and they were used without further purification. 0.02 mol of Zinc acetate was dissolved into 10ml of ethanol and 0.25 ml of de-ionized water was added drop by drop through syringe. This solution was stirred continuously for 2 hours at room temperature. The resulting solution was used as seed layer and deposited on well cleaned glass substrates by automatic dip coating machine (HO-TH-02). Then the films were annealed in furnace at the temperature of 200°C for 1 hour to crystallize the seed particles.

ZnO nanorods were grown on seed coated glass substrates by hydrothermal technique. Zinc Nitrate ($Zn(NO_3)_2.6H_2O$) and Hexamethylenetetramine($C_6H_{12}N_4$) were employed as precursors on 1:10 molar concentration

DOI: 10.15680/IJIRSET.2014.0309077

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

with de-ionized water as solvent. The above solution was mixed through magnetic stirrer for 2 hours. In the growth process the above solution was taken in a beaker with seed coated substrates and heated in hot air oven at 90°C for three different growth periods of 3 hours, 4 hours and 5 hours. At the end of the growth period, the substrates were removed from the solution and immediately rinsed with de ionized water to remove the residuals from the surface and dried in air at room temperature. Then the above films were annealed in muffle furnace at 500°C for 1 hour.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the product of the thin films with growth solution Zinc nitrate and Hexamethylenetetramine (HMT), with different growth periods of 3 hours, 4 hours and 5 hours at 90°C. All the diffraction peaks can be indexed as hexagonal ZnO phase (Wurtzite-structure) which matches with the JCPDS card no: 036-1451.

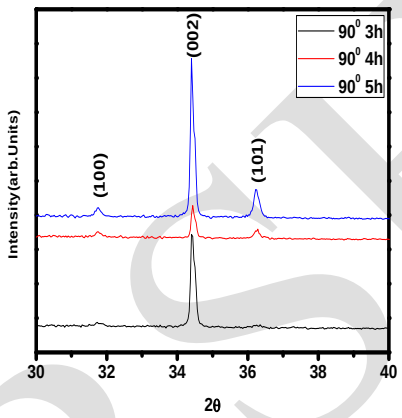


Fig. 1: XRD pattern of ZnO thin films at different growth time.

The strong and narrow diffraction peaks indicate that the material has a good crystallinity. The XRD patterns of the films at growth time of 3 hours at annealing temperature of 500°C shows that, it has a moderate (002) peak and no (101) and (100) peak. The XRD at growth time of 4 hours indicates low (100), (002) and (101) peak. The XRD pattern of growth temperature of 90°C at 5 hours annealed at 500°C has a very strong (002) peak and weak (100) and (101) peak. From the above XRD patterns it is clearly seen that, at the growth time of 5 hours the diffraction peaks were oriented strongly along the (002) peak. This implies that the grown nanorods show perfect c-axis orientation which is in accordance with SEM images. The average size of the ZnO particle is calculated using Debye Scherer formula,

$$davg = 0.9\lambda / \beta \, Cos\theta$$

where *davg* = average crystal size, λ = Wavelength of incident beam (1.5406A) , β = FWHM in radians and θ = scattering angle in degree. The grain size of the nano particles is found to be 100.56nm, 104.18nm and 109.70nm for growth temperatures of 3 hours, 4 hours and 5 hours respectively. This implies that growth temperature influences the particle size.

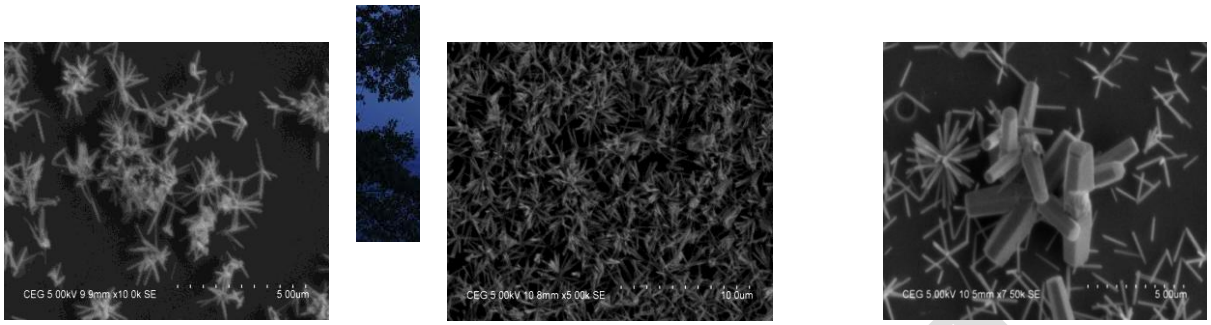
The SEM images of the products are given in Fig.2(a), Fig.2(b) and Fig.2(c). Many rod-like hexagonal structures can be clearly seen. The sizes of the products are homogeneous and the mean size is about 100 - 110 nm.

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014



(a) (b) (c)

Fig 2 .SEM image of ZnO nanorods(a) 90°C 3 hour(b) 90°C 4 hour (c) 90°C 5 hour

The images can be indexed as hexagonal Wurtzite-structural ZnO, which is very consistent with the analysis of XRD. As stated in the XRD patterns, the SEM images of the ZnO nano rods indicates that the length of the ZnO nano rods is maximum when the growth time is at 5 hours. It indicates that the samples grown in same solution experienced different growth rate of nano rods at 3 hours and 4 hours. The growth rate is defined along with growing length per growth time. Fig.2a and Fig.2b shows SEM images of ZnO nanorods grown at 3 hours and 4 hours in which rods have grown in all directions in a flower like pattern, which reveals the XRD patterns, where all three peaks are moderately reflected. Fig.2c shows SEM image of ZnO nanorod grown for 5 hours at 90°C. These rods show hexagonal structure with increase in diameter and its length towards c-axis orientation. This result relates with the peaks as indicated in the XRD pattern.

Fig.3 shows the absorption spectra of ZnO nanorods. The optical absorption edge has a tendency to shift to an upper wavelength with increase in growth temperature. It is well identified that the optical absorption determines the optical band gap of ZnO films which has a direct band gap. The optical band gap of ZnO films at growth temperature of 90°C for 3 hours, 4 hours and 5 hours growth time was found to be 3.34 eV, 3.31 eV and 3.23 eV respectively. With the increase of growth temperature from 80°C to 90°C, the band gap decreases from 3.34 eV to 3.23 eV.

Considering the results, it is clearly indicated that as growth time increases the band gap decreases. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size.

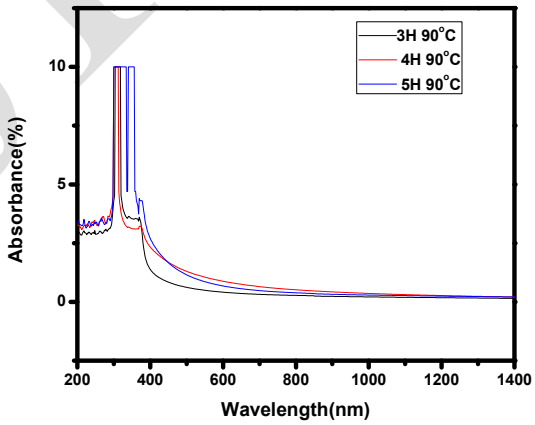


Fig.3 UV-Vis absorption spectra of ZnO at three different growth time

DOI: 10.15680/IJIRSET.2014.0309077

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

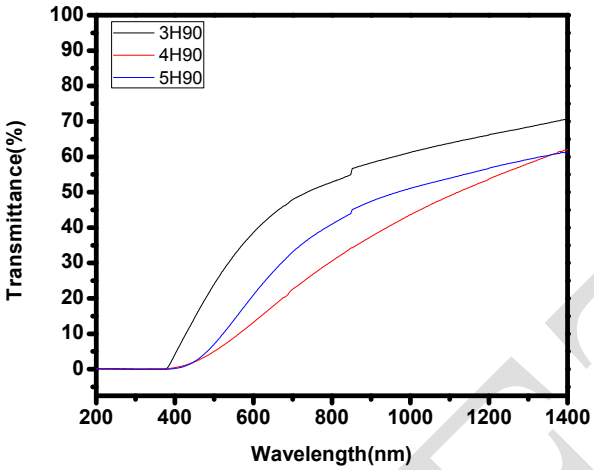


Fig.4 UV-Vis transmission spectra of ZnO at three different growth time

Fig 4 shows the optical transmittance spectra of samples with three different growth time of 3 hour, 4 hour and 5 hour, annealed at constant temperature of 500°C for 1 hour. The transmittance spectra are in the visible range nearer to infrared wavelength region. The effect of change in the growth time on the optical transmittance was investigated. A slight decrease in average transmission was observed with the increase of growth layer molar concentration and was attributed to the increase of surface roughness. The optical transmittance of ZnO films was found to decrease from 65%, 55%, to 52% with the increase of growth time.

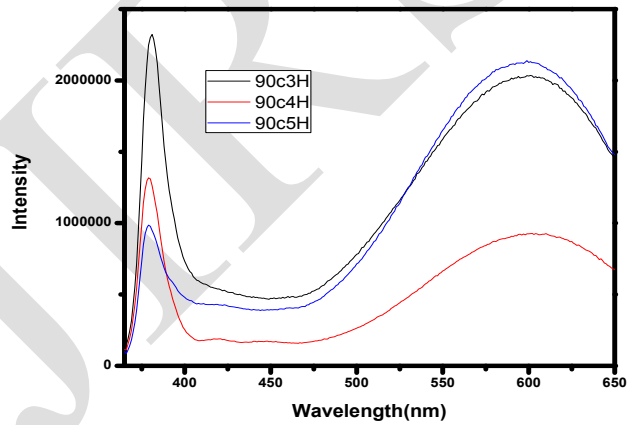


Fig.5 Photoluminescence spectra obtained at three different growth time

The Photoluminescence (PL) spectra of ZnO samples obtained with an excitation wavelength of 350nm for three different growth time of 3 hour, 4 hour and 5 hour is shown in the fig.5. The Ultraviolet (UV) emission peak in the range of 340-390 nm dominates all the PL spectra, the only difference being the relative intensity of peaks. The UV emission also called the near band edge emission (NBE) may originate from free excitonic emission in the ZnO materials as ZnO has a high exciton binding energy of 60meV at room temperature. Besides the strong UV emission peak, PL spectrum covers the surface related visible PL emission in the wavelength range of 550-650nm. The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nano particles [9].

DOI: 10.15680/IJIRSET.2014.0309077

ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 9, September 2014

The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as growth time increases and particularly at 5 hours, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials [10].

IV. CONCLUSION

ZnO nano rods had been successfully synthesized in a dip coating method at low growth temperature of 90°C for three different growth periods of 3, 4 and 5 hours and annealed at 500°C. The prepared ZnO nanorods were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) UV-Visible spectrophotometer (UV) and photoluminescence spectroscopy (PL). From the XRD results, it is clearly seen that, at the growth time of 5 hours the diffraction peaks were oriented strongly along the (002) peak. The grain size of the nano particles are found to be increasing as growth time increases. SEM results clearly show that nanorods grown at 5 hours have hexagonal structure with increase in diameter and length towards c-axis orientation when compared to 3 hours and 4 hours. The UV-Vis Absorption spectra show that band gap of the grown rods decreases from 3.34 eV to 3.23 eV as growth time increases. The optical transmittance was found to decrease from 65%, 55%, to 52% with the increase of growth time. The PL spectrum shows two emission bands, near band edge emission in the UV region and high intensity broad emission in the visible region. Experiments showed that the different growth time would influence the properties of the prepared ZnO nano rods.

REFERENCES

1. U. Rau and M. Schmidt, '*Electronic Properties of ZnO/CdS/Cu(In, Ga)Se2 Solar Cells -Aspects of Heterojunction Formation*', Thin Solid Films, Vol. 387, N°1, pp. 141 – 146, 2001.
2. S.T. Shishiyanu, T.S. Shishiyanu and O.L. Lupan, '*Sensing Characteristics of Tin-Doped ZnO Thin Films as NO2 Gas Sensor*', Sensors and Actuators B Chemical, Vol. 107, N°1, pp. 379 – 386, 2007.
3. J.M. Szarko, J.K. Song, C.W. Blackledge, I. Swart, S.R. Leone, S. Li and Y. Zhao, '*Optical Injection Probing of Single ZnO Tetrapod Lasers*', Chemical Physics Letters, Vol. 404, pp. 171 –176, 2005.
4. T. Ootsuka, Z. Liu, M. Osamura, Y. Fukuzawa, R. Kuroda, Y. Suzuki, N. Otogawa, T. Mise, S. Wang and Y. Hoshino, '*Studies on Aluminium-Doped ZnO Films for Transparent Electrode and Antireflection Coating of β-FeSi2 Optoelectronic Devices*', Thin Solid Films, Vol. 476, N°1, pp. 30 – 34, 2005.
5. D.Y. Ku, I.H. Kim, I. Lee, K.S. Lee, T.S. Lee, J. Jeong, B. Cheong, Y.J. Baik, W.M. Kim, '*Structural and Electrical Properties of Sputtered Indium–Zinc Oxide Thin Films*', Thin Solid Films, Vol. 515, N°4, pp. 1364 – 1369, 2006.
6. J.Deenadathayalan, M.Soroja, M.Venkatachalam, P.Gowathaman, T.S.Senthil, *Effect of Growth layer solution concentration on the structural and optical properties of hydrothermally grown Zinc Oxide nana rods*. Chaloogenide letters, Vol 8, No.9: 549-554(2011) .
7. M. Lim and C. M. Lee: *Thin Solid Films* 515, 3335 (2007).
8. Q. Wan, K. Yu, and T. H. Wang: Appl. Phys. Lett. 83, 2253 (2003).
9. Ghosh M, Raychaudhuri A. K. Nanotechnology 19, 445704 (2008).
10. Tian Yu, Lu Hong-Bing, Liao Lei, Li Jin-Chai, Wu Yun, Fu Qiang, Physica E 41, 729 (2009).