Print ISSN: 0974-2115
www.jchps.com Journal of Chemical and Pharmaceutical Sciences

Effect of Solution Molarity on the Structural, Morphological and Optical Properties of Nanostructured Zinc Oxide Thin Films

A. Sales Amalraj[1]*, G. Senguttuvan[2]

[1]Department of Physics, PSNA College of Engineering & Technology, Dindigul- 624 622, India

[2]Department of Physics, Anna University, BIT Campus, Tiruchirappalli- 620 024, India

***Corresponding author: E-Mail: salesamalraj@gmail.com, Phone: 9976115563**

ABSTRACT

Zinc oxide (ZnO) nanorods have been deposited onto glass substrates by integrating inexpensive successive ionic layer adsorption and reaction (SILAR) at room temperature. The concentration of precursor solution was varied in order to study its effect on structural, morphological and optical properties. The X- ray diffraction (XRD) patterns showed that the films deposited are polycrystalline with preferential orientation along (101) plane. Scanning electron microscopy (SEM) images show the formation of vertical ZnO nanorods with diameter and length of ~120 nm and ~400 nm respectively. The optical study showed that films are highly transparent in the visible region with an average transmission of about ~85%. The optical band gap degreased from 3.30 eV to 3.075 eV on increase in molar concentration.

KEY WORDS: SILAR, ZnO, Thin Films, Molar value, SEM, Optical.

1. INTRODUCTION

Transparent conductive oxide (TCO) thin films occupy an important place in the domain of the microelectronics and the optoelectronics. Among the family of TCO, Zinc oxide (ZnO) thin films are attractive in the semiconductor field due to their good optical characteristics, high stability and excellent electrical properties, among others (Krunks and Mellikov, 1995). They have been frequently used in several electronic applications such as transparent conducting materials, piezoelectric transducers, solar cells, surface acoustic wave filters, heat mirrors, and liquid crystal displays (Major, 1986). In addition to their potential in optoelectronic devices, nowadays they are being used as gas chemical sensors due to their high surface sensitivity (Shishiyanu, 2005). Therefore, investigation on ZnO films is of great importance for the above applications. Over the past few years, many methods have been developed for the growth of ZnO semiconductors (Kumar, 2008). The techniques used to deposit ZnO films include chemical vapor deposition (Jih-Jen Wu and Sai-Chang Liu, 2002), ultrasonic spray pyrolysis (Turan, 2007), pulsed laser deposition (Ianno, 1992) and successive ionic layer adsorption and reaction (SILAR) method (Nicolau, 1985) which is also known as modified version of chemical bath deposition. Among these, SILAR method is simple, inexpensive and involves the growth of nanocrystals from solution phase at room temperature and normal pressure. The aim of the present work is to apply the SILAR method for preparing ZnO films and to investigate the structural and optical properties of the samples.

2. MATERIALS AND METHODS

In the present work, analytical reagents of $ZnSO_4$ and ammonia were used as starting precursor. Initially $ZnSO_4$ were made dissolved in diluted ammonia to get zinc ammonium complex solution, which then served as zinc cation precursor and double distilled water (DDW) as anionic precursor. The SILAR growth is a four step process involving subsequent immersion of cleaned substrate in cationic and anionic solution along with rinsing the substrate in between in DD water kept at room temperature. In the first step, the substrate was immersed in a beaker containing $Zn(SO_4)$ and ammonia solution, where Zn^{2+} with ammonia formed zinc ammonia complex ($[Zn(NH_3)_4]^{2+}$). Detailed experimental process is described in previous reports (Sales Amalraj, 2014). In this present work, The ZnO nanorods were prepared by using an aqueous zinc ammonium complex solution with different molarities (0.025M, 0.05M, 0.075M, 0.1M and 0.125M). Thickness of the annealed films was calculated by weight gain method. The structural, surface morphological, and optical characterization of the ZnO nanostructured films was analyzed by X-ray diffraction (XRD) using PAN analytical diffractometer (model X'per PRO) with Cu Ka (λ=0.1542 nm) radiation, Scanning electron microscopy (SEM) using Hitachi S-3000H, and room temperature optical spectrum using Perkin Elmer UV–VIS spectrophotometer (Model: Lambda 35).

3. RESULTS AND DISCUSSION

Structural analysis: The structural quality of prepared ZnO nanostructured samples were examined using XRD analysis. Fig.1, shows the XRD pattern of ZnO nanostructure thin films grown on glass substrate with different molarity. XRD pattern of all the ZnO deposited nanostructure thin films shows a dominant peak at 36.2° which indexed to the ZnO (101) orientation and confirms the hexagonal wurtzite structured ZnO with good crystallinity, which is close agreement with the standard card (JCPDS 36- 1451).

In addition to this, a strongest detected (hkl) peaks are at 2θ values around of 31.4°, 34.4°, 47.5°, 56.6°, 62.8°, 67.96° and 72.56° corresponding to the following lattice planes of (100), (002), (102), (110), (103), and (112)

respectively. No other peaks of impurity phases such as Zn, or Zn (OH) were observed. From the XRD patterns as shown in Fig.2, the 2θ value corresponding to the position of (101) ZnO diffraction peak shifts towards higher angles as the concentration of the cation solution increases. The thickness of the film is observed to increase, as increase in annealing duration could have been caused by growth of grains. The crystalline size was calculated for (101) orientation ZnO nanostructured films by using Debye Scherrer's formula (Sales Amalraj**,** 2015). The particle sizes of the ZnO nanostructured thin films deposited at different molarities are given in table.1. The lattice constants a and c have been computed by using the relation (Ahmet Taner, 2011), and the result are given in table 1. The values for the c/a ratio have been computed and found to be quite close to the standard value.

Surface morphology analysis: The variation of the surface morphology of ZnO nanostructured thin films deposited with different molarity was analyzed by scanning electron microscopy. Fig.3a-e, shows the SEM morphologies of ZnO films deposited at different molarities. The micrograph clearly illustrates the uniform distribution of hexagonal shaped grains for 0.025M molar concentration (Fig.3a). The films prepared at 0.05M and 0.075M (Fig.3b, c) shows hexagonal shaped nano rods. The well aligned and uniformly shaped ZnO nano rods are observed for films that were prepared by 0.1M concentration (Fig.3d). Further, increase in molar concentration to 0.125M shows a surface morphology with vertically grown perfect hexagonal shaped rods (Fig.3e), with diameters ranging from 100 to 450 nm. No further oriented growth of ZnO nanorods were observed when the molar concentration increased beyond 0.125M. At the molarity of 0.125M, the growth of vertical ZnO nanorods is more prominent when compared to other molar concentrations. Energy dispersive X- ray (EDAX) spectra for ZnO nanostructures are shown in Fig.3f. The characteristic peaks for Zn and O are clearly observed. This spectrum clearly indentified that the material synthesized was ZnO. No impurity peaks were observed, which is a clear indication of the purity of grown ZnO nanostructures.

Optical analysis: Fig.4, shows the optical transmittance spectra of ZnO films deposited at five different molar concentrations of anionic precursor. The optical transmittance of the films decreases from 65 to 40% as the molar concentration of the films increases. This decrement of the transmittance might be due to the enhanced surface scattering, surface roughness and thickness induced absorption (Revathi, 2009).

The optical band gap of the ZnO films has been evaluated using the relation (Sales Amalraj, 2015). The (αhν) versus photon energy (hν) plots for the ZnO films are linear in the region where the fundamental absorption is concerned. This linearity as seen in Fig.5 indicates the direct nature of the optical transition. The straight portion is extrapolated to the energy axis at α=0, which gives the optical band gap of ZnO films.

The optical band gap values determined from Fig.5 are plotted in Fig.6 with the molar condition. We observe that the band gap decreases as the molar concentration increases. The probable cause for this red shift could be attributed to the structural changes of the films as observed from the XRD results (Kalandaragh, 2007).

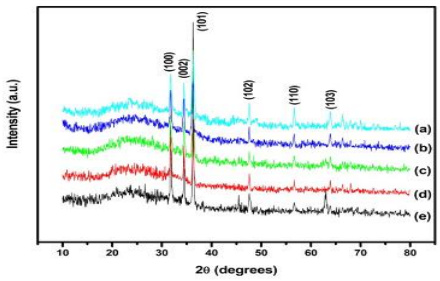

Figure.1. The effect of molarity on the XRD patterns of ZnO thin films (a) 0.025M, (b) 0.05M, (c) 0.075M, (d) 0.1M, (e) 0.125M

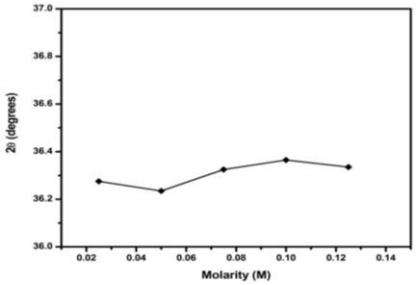

Figure.2. The variation in peak position along (101) plane as a function of molarity

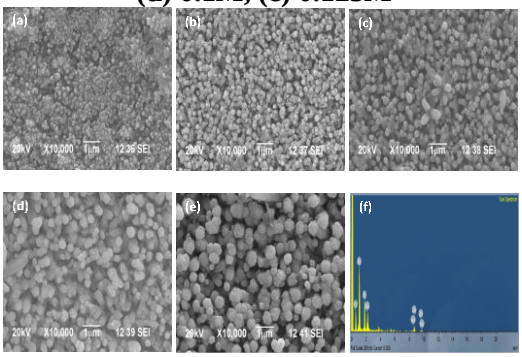

Figure.3. The effect of molarity on the transmittance spectrum of ZnO thin films (a) 0.025M, (b) 0.05M, (c) 0.075M, (d) 0.1M, (e) 0.125M

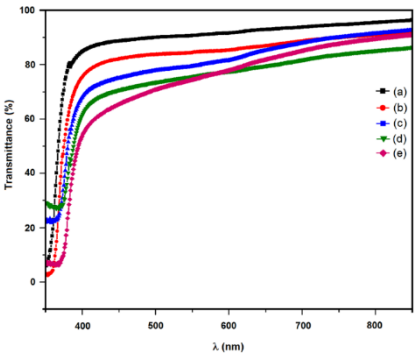

Figure.4. The effect of molarity on the transmittance spectrum of ZnO thin films (a) 0.025M, (b) 0.05M, (c) 0.075M, (d) 0.1M, (e) 0.125M

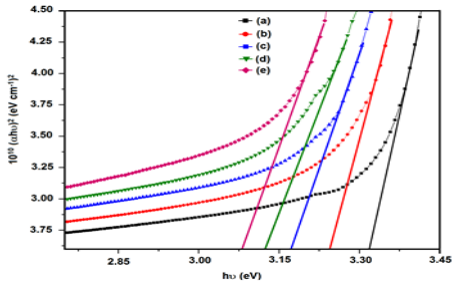

Figure.5. The effect of molarity on the band gap determination of ZnO thin films (a) 0.025M, (b) 0.05M, (c) 0.075M, (d) 0.1M and (e) 0.125M

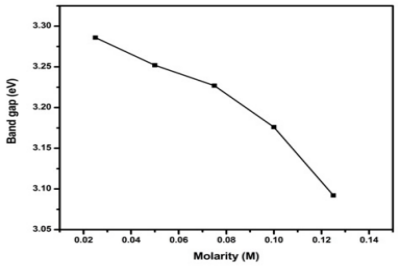

Figure.6. The band gap energy of ZnO thin films changing with increasing the molarity of the cationic precursor

Table.1. The Microstructural parameters of Zinc Oxide thin films on effect of molar concentration

Molarity (M)	d- Value (Å)	Thickness t (nm)	Cell Parameters (Å)		c/a ratio	Crystallite size (nm)
			a = b	c		
0.025	2.5343	0.33	3.2684	5.3034	1.6226	41.7909
0.05	2.4946	0.51	3.2303	5.2381	1.6216	46.6373
0.075	2.4681	0.77	3.3034	5.2630	1.5932	51.1818
0.1	2.5172	0.95	3.2678	5.2188	1.5970	68.5339
0.125	2.4682	1.13	3.2693	5.2835	1.6161	82.6508

4. CONCLUSION

ZnO nanostructured films have been deposited onto the glass substrates by means of SILAR method. This method seems to be a very practical, easy and inexpensive way to deposit semiconducting films. The structural study of the films by X-ray diffraction showed that films have a polycrystalline structure with an orientation according to the (101) crystallographic orientation. With the increase in molarity, the intensity of this peak increases. The crystallinity of ZnO belonging to the hexagonal phase with random orientation observed to improve with increasing molar concentrations. SEM images confirm the growth of vertical ZnO nanorods at optimized annealing conditions. The optical measurements have shown decrease in the transmission T (%) with an increase in the molarity. The direct band gap of the film was found to decrease from 3.37 to 3.22 eV with increasing the concentration of the precursor solution.

REFERENCES

Ahmet Taner, Metin Kul, Evren Turan, Optical and structural properties of zinc oxide films with different thicknesses prepared by successive ionic layer adsorption and reaction method, Thin Solid films, 520, 2011, 1358- 1362.

Ianno NJ, McConVille LC, Shaikh N, Pittal, Snyder PG, Characterization of pulsed laser deposited zinc oxide, Thin Solid Films, 220, 1992, 92- 99.

Jih-Jen Wu, Sai-Chang Liu, Low-Temperature Growth of Well-Aligned ZnO Nanorods by Chemical Vapor Deposition, Avd Mater, 14, 2002, 215- 218.

Kalandaragh YA, Muradov MB, Mammedov RK, Khodayari A, Growth process and investigation of some physical properties of CdS nanocrystals formed in polymer matrix by successive ionic layer adsorption and reaction (SILAR) method, J Cryst Growth, 305, 2007, 175- 180.

Krunks M, Mellikov E, Zinc oxide thin films by the spray pyrolysis method, Thin Solid Films, 270, 1995, 33-36.

Kumar PS, Raj AD, Mangalaraj D, Nataraj D, Growth and characterization of ZnO nanostructured thin films by a twostep chemical method, Appl Surf Sci, 255, 2008, 2382- 2387.

Major S, Kumar S, Bhatnagar M, Chopra KL, Effect of hydrogen plasma treatment on transparent conducting oxides, Appl Phys Lett, 49, 1986, 394-396.

Nicolau YF, Solution deposition of thin solid compound films by a successive ionic-layer adsorption and reaction process, Appl Surf Sci, 22 (23), 1985, 1061- 1074.

Revathi N, Prathap P, Ramakrishna Reddy KT, Thickness dependent physical properties of close space evaporated In_2S_3 films, Solid State Sci, 1, 2009, 1288- 1296.

Sales Amalraj A, Senguttuvan G, Effect of multiple dipping of SILAR deposited ZnO thin films by physico-chemical process, J Mat Scien & Mat Elect, 25, 2014, 2035– 2040.

Sales Amalraj A, Tharani AP, Joseph Prince J, Siva Kumar V, Senguttuvan G, Studies on vertically grown and annealed ZnO nanorods synthesized through aqueous solution process, J Mat Scien & Mat Elect, 26, 2015, 4257–4264.

Sales Amalraj A, Dharani AP, Fermi Hilbert Inbaraj P, Sivakumar V, Senguttuvan G, Influence of pH on structural, morphological and optical properties of chemically deposited nanocrystalline ZnO thin films, J Mat Scien & Mat. Elect, 26, 2015, 8877- 8886.

Shishiyanu ST, Shishiyanu TS, Oleg Lupan I, Sensing characteristics of tin-doped ZnO thin films as NO_2 gas sensor, Sens. Actuators B, Chem, 107, 2005, 379-386.

Turan E, Zor M, Aybek AS, Kul M, Electrical properties of ZnO/Au/ZnS/Au films deposited by ultrasonic spray pyrolysis, Thin Solid Films, 24, 2007, 8752- 8755.