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Study of Structural and Morphological Properties of ZnO Thin Films Prepared by Chemical Bath Deposition Technique

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Abstract

ZnO thin films have been deposited on glass substrates by chemical bath deposition technique using aqueous solution of Zinc Sulphate ($ZnSO_4$) as a starting material and triethylamine ($N(CH_2CH_3)$)as a complexing agent. The thickness of the films was found to be about 1.02 μm. The XRD analysis of the thin film revealed that the ZnO films are of polycrystalline nature with grain size in the order of nanometers and has hexagonal structure with orientation of c- axis. The average particle size of the film as estimated from XRD peaks were found to be 28.3687nm. SEM studies indicate that the grains are not uniformly distributed and not well connected to each other. The EDAX spectrum shows that the films are nearly phase pure containing a few other impurities.

Keywords: Chemical bath deposition, SEM, Thin films, XRD.

Introduction

Nanostructure materials possess unique physical and chemical properties which provide great interest in recent years in the field of research. Among nanocrystalline semiconductors group II-VI nanocrystalline materials have attracted a great deal of attention because of their size dependent properties and wide range of applications. ZnO is one of the most important semiconducting materials with a band-gap around

3.2- 3.37 eV at room temperature 300 K. Among different physical forms, the thin films of ZnO find important applications in electronic and optoelectronic devices such as transparent conductors, gas sensors, chemical sensors, solar cell windows, ultra violet laser diodes, heat mirrors, piezoelectric transducers and surface acoustic wave (SAW) devices etc. [1 - 6].

Many techniques have been used for deposition of ZnO thin films. These includes molecular beam epitaxy [7], ion implantation [8], sol- gel deposition [9], spray prolysis [10], sputtering [11], pulsed laser deposition[12], cathodic electrodeposition [13-14] and other solution phase techniques. Among different techniques Chemical Bath Deposition (CBD) [15-20] technique is one of the solution phase technique useful for the synthesis of compound semiconductors from aqueous solutions. In recent times, much interest has been generated around the CBD technique as this technique has many advantages such as no requirement for sophisticated instruments, minimum material wastage, and economical way of large area deposition. In this technique, thin films are deposited on substrates immersed in dilute solutions containing metal and chalcogenide ion sources. The technique may allow to easily control the growth factors such as film thickness, deposition rate and quality of crystallites by varying the solution pH value, temperature and concentration [21].

In this paper, we carried out the deposition of ZnO thin films glass substrates using CBD technique. The structural characterisation, particle size analysis, surface morphology and composition have been studied by XRD, SEM and EDX.

Experimental Details

Substrate preparation:

The commercial microscope's ordinary glass slides (GEMS) of size 75mm x 25mm x 1.25mm were used as a substrate for film deposition. The substrate were submerged into acqua riga (1: 3; NHO_3: HCl) for about 48 hours to dissolve the maximum amount of impurities. Next, the substrates were washed with clean tap water and then submerged in detergent solution for 30 min. The substrates are then rinsed with clean tap water and then with double distilled water. Finally the substrates were washed with acetone to remove oily content and then rinsed with double distilled water for two times and dried in oven.

Sample preparation:

Chemicals of analytical reagents grade are used for the sample preparation. Acqueous solutions of 2ml $ZnSO_4$ (1M), [SDFCL, India] and 2 ml Triethylamine (100%) [CDH, India] and 8 ml of NH_3 (25%) [SDFCL] are taken in a beaker (150 ml capacity) and add double distilled water up to 100 ml to make a mix solution in the beaker. The solution was stirred at room temperature for hours to get a homogeneous mix solution. The pH value of the final solution at room temperature was measured to be 12.2. Glass substrates were then immersed vertically into the solution and then heated the solution up to 85°C so that reaction starts and kept for 30 min with constant heating at 85^oC. After cooling down, the slides are taken out and washed with double distilled water and dried in the oven at room temperature.

The reaction of the above process is as follows:
$ZnSO_4 + NH_3 \rightleftharpoons [Zn(NH_3)]^{2+} + SO_4^{2-}$
$[Zn(NH_3)]^{2+} \rightleftharpoons Zn^{2+} + NH_3$
$Zn^{2+} + 2OH \rightleftharpoons Zn(OH)_2 \downarrow$
$Zn(OH)_2 \rightarrow ZnO(S) + H_2O$

Measurements:
The film thickness was determined by the gravimetric method using electronic precision balance (Model: MAB – 182). The crystal structure and orientation of the prepared ZnO films were investigated by X-ray diffraction method. The X-ray diffraction patterns were recorded using X- ray diffractometer (Model: Pan Analytical X- Pert) with CuK_α radiation (λ= 1.54056Å) and the analysis of the surface morphologies were performed with a scanning electron microscope (Model: FEI Quanta -250). The composition of the ZnO films was determined by studying the energy dispersive X- ray fluorescence of the samples using EDAX-SL, Ametek.

Result and Discussion

Physical properties of film growth:
In the process of film preparation, when the temperature of the homogeneous mix solution reach 85^0C the solution turned milky due to the formation of ZnO particles by homogeneous nucleation and starts deposition to glass substrates. The non deposited particles soon settled on the bottom of the beaker, as a non – adherent powder.

Film thickness measurement:
The thickness of the films was determined gravimetrically by measuring the change in weight of the substrate due to film deposition and the area of deposition with known density of ZnO (5.6 gm/cm^3). The thickness of the films is calculated using the following equation.

$$t = \frac{W_1 - W_2}{\rho A} \times 10^{-4} \mu m$$

where W_1 is the weight of the substrate before the deposition of film, W_2 is the weight of the substrate after the deposition of film, A is the area of the film deposition in cm^2 and ρ is the density of ZnO.
The average thickness of the prepared films is found to be 1.05 μm

Structural Characterisation and Particle size analysis:
The X-ray diffraction pattern of one film of the prepared samples is presented in figure 1. The diffraction peaks of ZnO exhibited a hexagonal plane with preferred grain orientation s along (100), (002), and (101k). All of the peaks are in slightly non-standard as compared with the Joint Committee on powder diffraction standard (JCPDS) data belonging to the hexagonal Wurtzite structure [22-23]. The XRD

pattern of the sample suggested that enhanced intensities for the peaks corresponding to (002) plane imply preferred orientation along the c-axis.

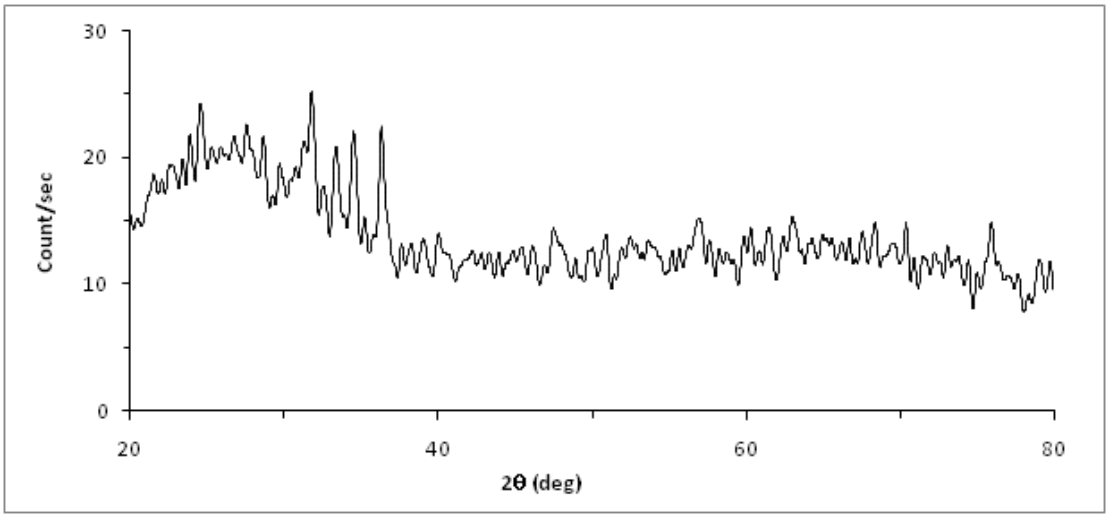

Figure 1 : XRD pattern of ZnO thin film of 1M.

The grain size or particle size (D) of the particles was estimated from the Debye-Scherrer's
Formula [24]

$D = \frac{0.94\lambda}{\beta\, Cos\theta}$ (for spherical crystallites)

where θ is the Bragg's angle, λ is the X-ray wavelength used (1.5406Å for CuK_{α}) and β (in radian) is the full width at half maximum (FWHM) of the diffraction peak for which the particle size is to be calculated. The dislocation density was calculated by the relation [25]:

$\delta = \frac{1}{D^2}$ where D is the grain size.

The microstrain was calculated by the formula [26]:

$\varepsilon = \frac{\beta\, Cos\theta}{4}$

The average value of grain size, the dislocation density (δ) and the microstrain (ε) are presented in table 1.

Table 1: Diffraction peaks, d- values, average particle size, average dislocation density(δ) and average microstrain (ε).

hkl	2θ degree	d (Å)	Average D value (nm)	Average of δ value ($line^2/m^2$)	Average value of ε
(100)	31.774	1.4628	28.3687	1.2425×10^{15}	1.3341×10^{-3}
(002)	34.5478	1.3583			
(101)	36.3073	1.3009			

Surface Morphology Studies:

The morphologies of the deposited material were examined using Scanning Electron Microscopy (SEM) of the prepared ZnO thin films. One of the Scanning electron micrographs of the thin films is presented in figure 2. It shows that grains are distributed with uneven shape and are not well connected to each other.

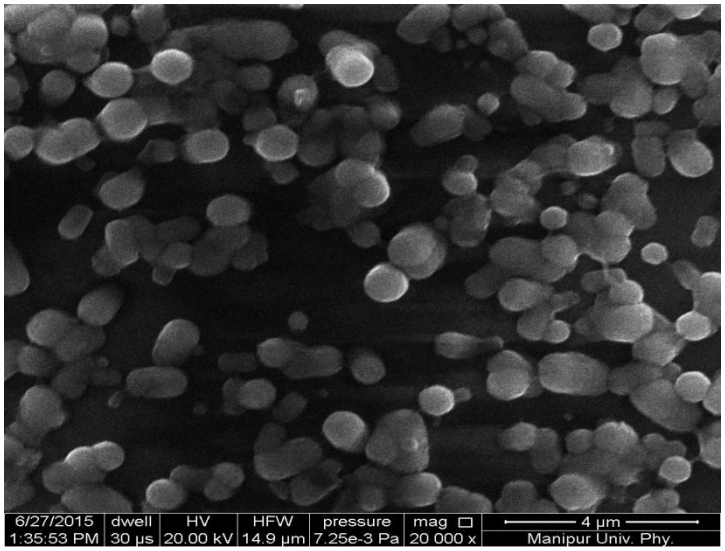

Figure 2: SEM picture of ZnO thin film of 1M.

Compositional Studies:

The spectrum of the ZnO thin films obtained by EDX analysis is presented in figure 3. The EDX analysis indicates that the products consist of Zinc and Oxygen elements. The Silicon signal appears from the glass substrate.

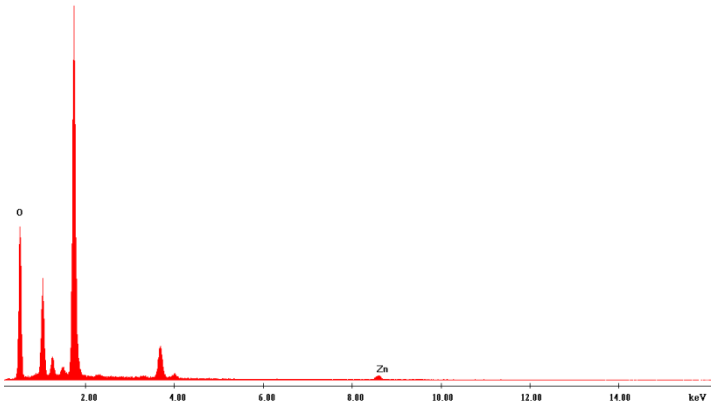

Figure 3 : EDAX spectrum of ZnO thin film of 1M.

The Percentage of the compositional elements present in the ZnO thin film is presented in table 3, which shows that the prepared ZnO nanoparticles is almost free from impurities.

Table 3: Percentage of elements present in the prepared ZnO thin films.

Element	Weight (%)	Atomic (%)	[Z]/[O]
O	84.81	95.81	
Zn	15.19	4.20	0.043836
Total	100	100	

Conclusion:

The chemical bath deposition technique was successfully used to prepare ZnO thin films on glass substrates. Physical, structural, morphological, and compositional studies were carried out. Structural analysis indicates that the prepared films are strong c- axis oriented polycrystalline films. The average particle size estimated from XRD peaks was found to be 28.3687 nm. SEM analysis indicates that the grains are not uniformly distributed and not well connected to each other. The films are nearly phase pure containing few other impurities as revealed from EDX.

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