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Microwave Assisted Single Deposition Spin Coating Chemical Synthesis of ZnO Thin Film on Glass Slide

Deepesh Bhardwaj

Institute of Information Technology and Management, ITM GOI, ITM Universe Campus, Gwalior 474001, India.
Author Email id: bhardwajdeepesh@gmail.com, Mobile No.9977672671

Abstract: **ZnO thin films (thickness ~441nm, crystal size ~19.6nm) were synthesized by a single deposition method using zinc-ammonia complex as main precursor. Effect of synthesis temperature on the morphology and phase purity crystallization was studiesdat three different temperatures (70, 80 and 90 °C)for fixed time (20 sec)using microwave oven. Phase identification, morphology and structural properties of the ZnO thin films were studied using diffraction, microscopic and spectroscopic techniques. The ZnO thin films prepared at 70ºC show amorphous character while 90ºC films are crystalline as indicated by sharp diffraction peak in X-ray diffraction (XRD) pattern. Moreover, the surface morphology of the ZnO thin films strongly depend on deposition temperature. The optical characteristics of the samples were obtained by UV-Visible spectrophotometer at 200–900 nm wavelengths. The absorption at wavelength <370 nm indicates that the nano size ZnO nanoparticles have band gap energy of ≈3.4eV.**

Keywords: **Low thickness, Microwave, Spin coating, Band gap energy, Amorphous.**

I. INTRODUCTION

Thin films of ZnO are also applied to the transparent conductive films and on the solar cell windows because of the high optical transmittance in the visible region. Studies on the application of ZnO thin film to the surface acoustic wave device and film bulk acoustic resonator filter have also been reported, because of their excellent piezoelectric properties[1] [2] [3] [4] [5]. The ZnO thin film is prepared using various methods such as spray pyrolysis, sputtering, sol-gel, spin coating, pulsed laser deposition, chemical vapor deposition [6] [7] [8] [9].

As reported by Reeja-Jayan et al., and many other researchers that thermodynamic and kinetic parameters control the growth of thin film in solution phase, whereas microwave radiation can initiate favorable kinetics for thin film growth [10] [11] [12] [13] [14]. While particles generally initiate in embryonic nuclei within a solution ‘‘homogeneous nucleation’’, thin film growth requires preferential nucleation at interfaces ‘‘heterogeneous nucleation’’. It was expected that the microwave heating creates sites for ZnO nucleation and grow in a single step [10].

II. EXPERIMENTAL

A. Synthesis of ZnO thin film

For ZnO thin film synthesis 0.001M $ZnSO_4$ solution prepared in ammonia was used as ZnO precursor solution and normal laboratory glass slides were chosen as substrate. Prior to use, the glass substrates were placed in a boiling sulfuric acid diluted with water (1:10 v/v) for 45min and then thoroughly washed withDDW and subsequentlyrinsed with ethanol. After this the glass slides were sonicated for 10 min in DDW, dried and placed in an air tight moisture free container for

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further use.The 25 mL 0.001M $ZnSO_4$ solution was then added drop wise into a 25 mL DDW at room temperature with constant stirring and 2-3 drops of thisobtained homogeneous solution of $Zn(OH)_2$were placed over 25x25 mm pretreated glass slide. This glass slide was then allowed to stand for 20sec and subjected to spin with a speed of 1500rpm for 10sec in a spin coating machine (NXG-M1, Apex Instrument Company). Finally, the $Zn(OH)_2$coated substrate was immersed into the microwave heated distilled water for 20sec which was maintained at three different temperatures viz., 70, 80 and 90 °C. $Zn(OH)_2$was then converted into solid ZnO films at these temperatures. The glass slides were then allowed to sonicate in distilled water for 60sec to remove the loosely bound particles, kept out, air dried and stored in air tight container till further use. The present method is the modified form of method described by Kumar et.al and Bhardwaj et.al.[15] [16] Reported work is in continuation with our previously published work and followed the same method and precursors except heating which is done by domestic microwave oven [17].

B. Mechanism

The mechanism of ZnO thin film synthesis can be understood by following reactions [17];

$$ZnSO_4 + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + SO_4^{2-} \quad (1)$$

$$(Zn(NH_3)_4)^{2+} + 2H_2O \rightarrow Zn(OH)_2 + 4NH_3 \quad (2)$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O \quad (3)$$

These chemical reactions (1-3) reveal that when $ZnSO_4$ is dissolved in ammonia to prepare a 0.001M ZnSO4 solution it gets converted into $[Zn(NH_3)_4]^{2+}$ (zinc-ammonia complex) which forms $Zn(OH)_2$on reaction with water. At last on heating$Zn(OH)_2$converted into ZnO.

C. Characterization

To study the crystalline nature and to identify the ZnO phase, X-ray diffraction (XRD) patterns were collected. Morphology of the ZnO thin films were obtained by scanning electron microscope (JEOL JSM 6390LV). The band gap calculation has been done by using data obtained from UV-visible Spectrophotometer (UV-VIS, Systronics 114 spectrophotometer).

III. RESULT AND DISCUSSION

The ZnO thin film synthesized at 90°C shows a major diffraction peaks at 2θ equal to 34.8, which is corresponding to (002) orientation of wurtzite hexagonal structure of ZnO (JCPDS no. 36-1451). The $Zn(OH)_2$ phase has higher intensity at low temperature i.e. 70 and 80°C which is clearly observed from the broad and low intensity peaks shown in XRD patterns (Figures 1 and 2). This indicates 20 sec thermal treatment at 70 and 80°C is not sufficient for the conversion of hydroxide form of zinc to its oxide form.

The crystallite size of ZnO sample particle (Figure. 3) was calculated from the XRD data using Debye–Scherrer formula [18] [19] [20] [21] from the full-width at half maximum (FWHM) as given below:

$$D = 0.9\lambda/\beta\cos\theta \quad (4)$$

Where, *D* is the particle size of the crystallite, λ (1.54059 Å) is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction. The value calculated for the crystallite size was~19.6 nm.The thickness of the films was then calculated using the following equation:

$$t = \lambda_1\lambda_2/ 2(\lambda_1 n_2 - \lambda_2 n_1) \quad (5)$$

where, $n_1$and $n_2$are the refractive indices corresponding to wavelengths $\lambda_1$and λ_2, respectively [6]. The thickness of the ZnO thin film sample was found to be ~441 nm.

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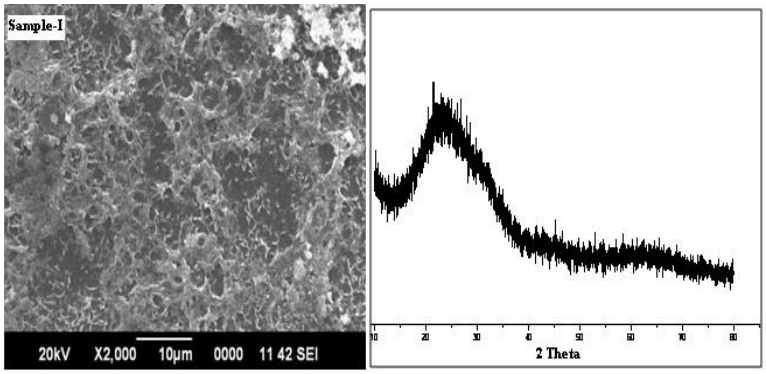

Fig. 1 SEM micrograph and XRD pattern of ZnO thin film prepared at 70°C (ZnO^{70}).

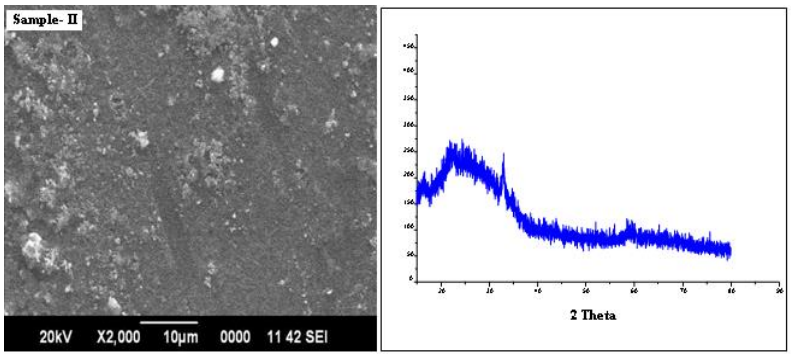

Fig. 2 SEM micrograph and XRD pattern of ZnO thin film prepared at 80°C (ZnO^{80}).

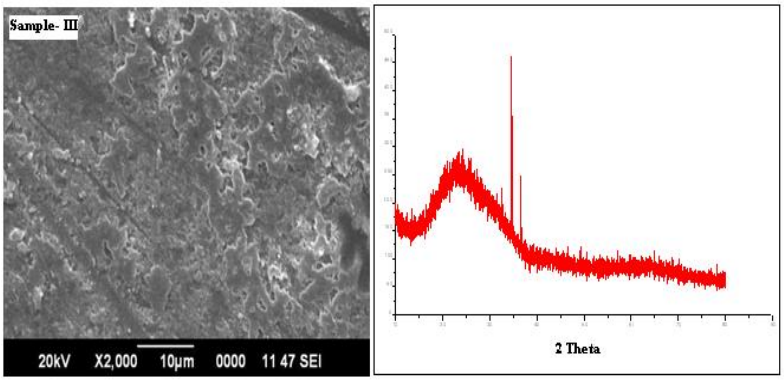

Fig. 3 SEM micrograph and XRD pattern of ZnO thin film prepared at 90°C (ZnO^{90}).

The refraction index*n* at different wavelengths was calculated using the envelope curve for *Tmax*(T_M) and *Tmin*(T_m) in the transmission spectra [6].

The expression for refractive index is given by:

$$n= [N + (N^2 – n_s^2)^{1/2}]^{1/2} \quad (6)$$

1) *Where,*

$$N = [2n_s(T_M-T_m/T_MT_m) + (n_s^2 + 1/2)] \quad (7)$$

And n_s is the refractive index of the substrate (for glass *ns* =1.52).

The surface morphology of ZnO thin films grown at three different temperature conditions are shown in FigureS 1, 2 and 3. The ZnO^{70}thin film surface shows a rough and porous structure[22] which may be due to the presence of $Zn(OH)_2$ indicated by XRD analysis. The porous structure is uncharacteristic for ZnO^{80}thin film (Figure 2) however, its high surface roughness. Figure 3 shows that in case of ZnO thin film sample, the roughness and porous structure disappears and a smoother surface with a few micro-cracks is obtained.

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The FTIR spectrum (Figure 4) of the ZnO thin film synthesized at 90°C was taken in the range of 450-4000 cm^{-1}. The broad absorption at 3200-3600 cm^{-1} corresponds to the existence of hydroxyl mode of vibration on the surface of ZnO sample. The band between 450-550 cm^{-1} is correlated to metal oxide bond (ZnO). The adsorption band around 1600cm^{-1} is assigned O-H bending vibrations and other 1396cm^{-1} corresponds to O-H bending**.** A strong band at around 538cm^{-1} is attributed to ZnO stretching mode[17, 21].

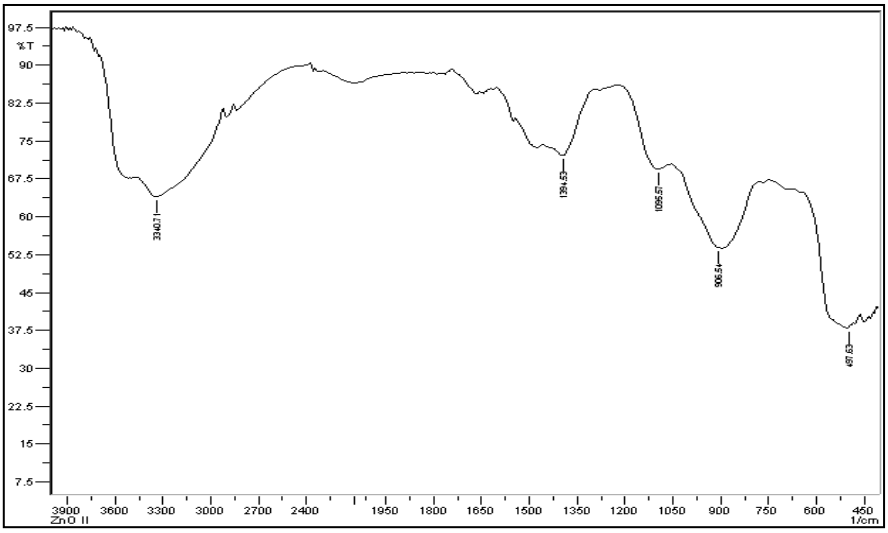

Fig. 4 FTIR Spectrum of ZnO[90]thin film

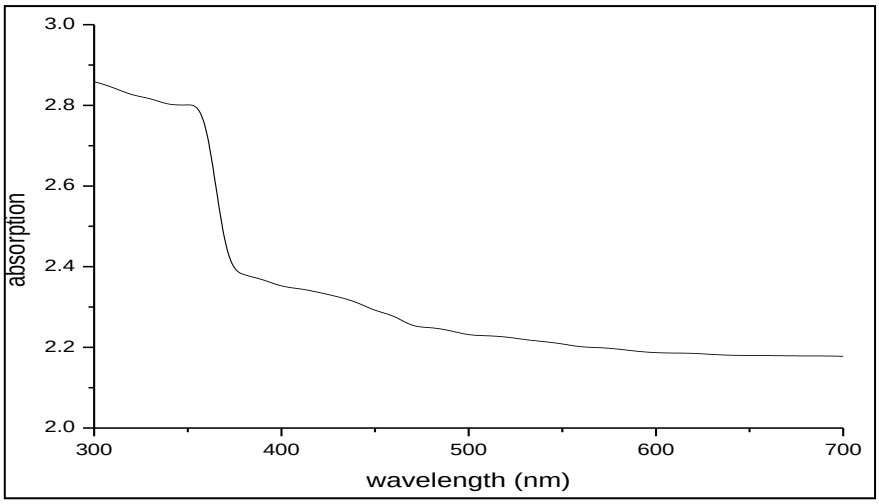

Fig. 5 UV-Vis optical absorption spectrum ZnO[90] thin film

The optical absorption spectrum (Figure 5) for ZnO thin film displaysexcitonic absorption peak around 365 nm which implies the lower particle size ZnO. A photon of wavelength 365 nm would have energy of approximately 3.43 eV and this estimated band gap value(3.43eV) is slightly higher than that of bulk ZnO (3.37eV).

IV. CONCLUSION

The Synthesis of ZnO thin film with a single deposition cycle is successfully achieved by a simple chemical synthesis route. The XRD results reveal that low temperature is not favorable for the synthesis of crystalline ZnO thin films.

It has been clearly indicated by the XRD and SEM analysis that a porous ZnO thin films can be obtained at low synthesis temperature (70°C). The optical and morphological properties of these ZnO thin films strongly depend on the preparation conditions. The morphology of the ZnO thin films were changed with increase in temperature. In this study the structure of the ZnO thin films was initially amorphous (Sample-I and II) as shown by XRD and SEM analysis. At temperature of 90°C a thin, Transparent and crystalline film of thickness 441nm and crystal size 19.6nm can be obtained in a single deposition cycle.

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