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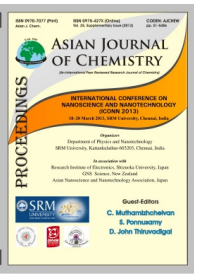

Study of ZnO Thin Films Prepared by Chemical Bath Deposition†

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Zinc oxide thin films were deposited on glass substrates by chemical bath deposition. Thin films were prepared from a solution of zinc acetate, triethanolamine and sodium hydroxide with different stirring times for zinc acetate and triethanolamine. The stirring times were 1, 2 and 3 h. The deposition temperature was 80 ºC. The deposited films were annealed at 200 ºC for 1 h. The effect of stirring time on structural properties of the film as well as composition, surface morphology was studied. ZnO thin films are widely used for optoelectronic and sensor applications.

Key Words: Thin films, ZnO, Chemical bath deposition, Surface morphology.

INTRODUCTION

With growing technological advancements, there is a continuous demand for semiconducting materials. Researchers are trying to prepare new materials or improve the properties of already known materials by doping or other methods. Zinc oxide is one of the semiconducting material having potential applications in numerous fields. The bad gap of ZnO is 3.37 eV and has large exciton binding energy of 60 meV[1]. The use of ZnO has been explored in solar cells[2], gas sensors[3], LEDs[4], piezoelectric devices[5], thin film transistors[6], *etc*. The morphology of ZnO has a wide variation. Apart from nanoparticles[7] and thin films[8], other morphological structures include nanorods[9], dendritic nanowires[10], flowers[11]. A number of physical and chemical methods have been reported for the synthesis of ZnO thinfilms which include metal-organic chemical vapour deposition[12], pulsed laser deposition[13], molecular beam epitaxy[14], sputtering[15], sol-gel deposition[16], spray pyrolysis[17].

Wet chemical routes are gaining accelerated usage due to their inherent advantages like low temperature, low cost, variety of precursors, high efficiency and process control. Due to the wide applications of thin films in almost all spheres of technology, there is a high demand for cost effective and industrially applicable fabrication techniques.

Chemical bath deposition[18-25] is one such technique. This is a solution phase technique in which desired substrates are coated with thin films by dipping it into the chemical bath solution at elevated temperatures. The chemical reagents present in the solution react and form precipitates resulting in thin film over the substrate. The major advantage of this process is the control of the film formation by regulating the pH, concentration and temperature of the chemical solution[26].

In this paper we report the preparation of ZnO thin films on glass substrates by using chemical bath deposition technique. The effect of stirring time of Zinc acetate and triethanolamine on properties of the film were studied. To the best of our knowledge this is the first time when the dependence of film properties on stirring time of zinc acetate and triethanolamine is being studied. The properties of the prepared thin films were studied using X-ray diffraction technique, scanning electron microscope and energy-dispersive X-ray spectroscopy.

EXPERIMENTAL

ZnO thin films were prepared using aqueous solution of $Zn(CH_3COO)_2{\cdot}2H_2O$, triethanolamine and sodium hydroxide. Micro corning glass was used as substrates. The glass substrates were washed with liquid detergent and treated first with a mixed solution of potassium dichromate and concentrated sulfuric acid and then with 2 M sodium hydroxide solution for several hours[27] and then washed with deionized water. Three different set of deposition solutions were prepared with varying time of stirring of zinc acetate and triethanolamine. 0.02 M of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 2 drops of triethanolamine in water to a volume of 80 mL were stirred for 1, 2 and 3 h using a magnetic stirrer. After stirring, the solution was placed in a water bath with a constant temperature of 80 ºC. The glass substrates were placed in the solution after 5 min of placing

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the deposition solution in the water bath so as to stabilize the temperature of the solution. The substrates were held in the solution using a suitable holder. Then NaOH solution was added to the deposition solution till the pH was 11. When the ionic product becomes more than the solubility product, precipitation occurs and this results in the deposition of ZnO on the substrates. During the whole deposition time (2 h), the solution was continuously stirred. At the end of the deposition time, the substrates were taken out and rinsed with deionized water and dried in hot air (60 ºC). The substrates were coated with milky white deposition. The equation of deposition reaction[28] is:

$$Zn(CH_3COO)_2{\cdot}2H_2O + TEA \rightarrow [Zn(TEA)]^{2+} + 2CH_3COO^-$$

$$[Zn(TEA)]^{2+} \rightarrow Zn^{2+} + TEA$$

$$2NaOH \rightarrow 2Na^+ + 2OH^-$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \uparrow$$

The substrates were then annealed at 200 ºC for 1 h. The structural properties were studied using X'pert high score diffractometer (XRD). Film morphology and composition were analyzed using scanning electron microscope and energy-dispersive X-ray spectroscopy (EDS) respectively.

RESULTS AND DISCUSSION

The structural properties of the ZnO thin films annealed at 200 ºC for 1 h were analyzed by X-ray diffraction patterns obtained by Glancing Incidence-XRD. The XRD patterns were obtained for annealed ZnO thin films with different stirring time for zinc acetate and triethanolamine. All the diffraction peaks matched with wurtzite hexagonal ZnO. XRD patterns for the three samples are shown in Figs. 1-3.

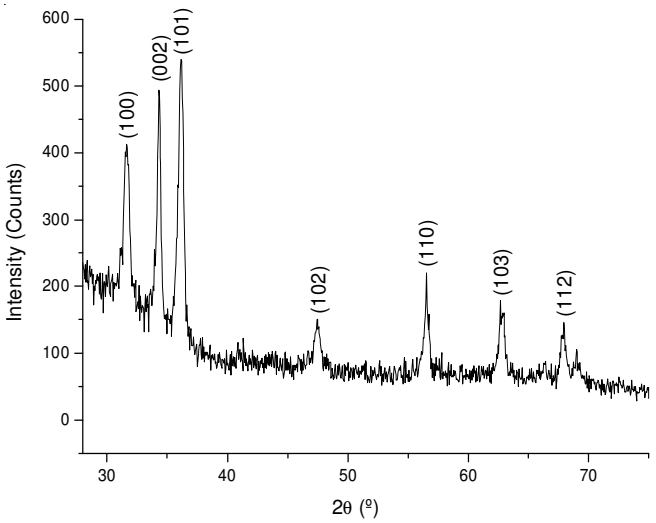

Fig. 1. XRD pattern of annealed ZnO thin film with Stirring time of 1 h for Zinc acetate and triethanolamine

In Figs. 1-3 the patterns corresponds to the annealed ZnO thin film with stirring time of 1, 2 and 3 h for zinc acetate and triethanolamine respectively. The prominent peaks are (100), (002), (101). The other minor peaks suggest that the annealed ZnO films are polycrystalline in nature. The intensity peaks of XRD pattern were matched with JCPDS and confirmed that the annealed samples were crystalline ZnO which are hexagonal

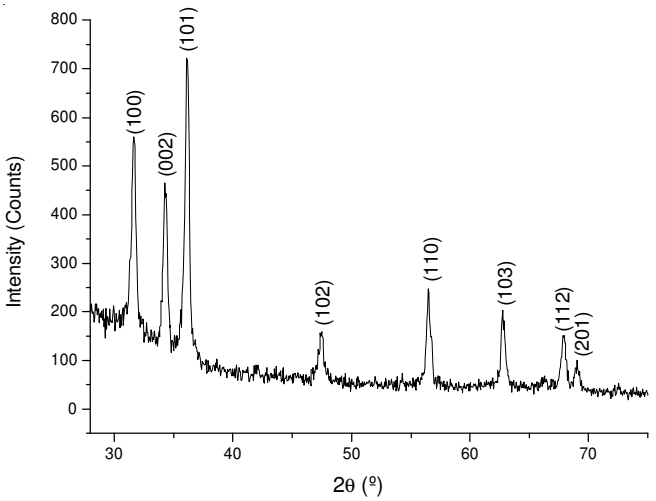

Fig. 2. XRD pattern of annealed ZnO thin film with stirring time of 2 h for zinc acetate and triethanolamine

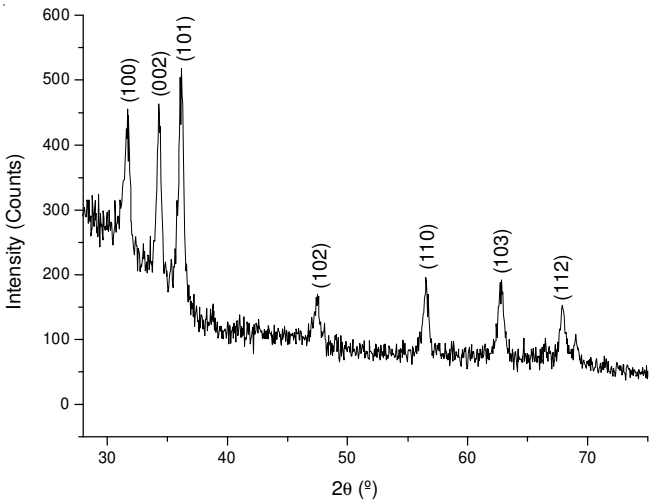

Fig. 3. XRD pattern of annealed ZnO thin film with stirring time of 3 h for zinc acetate and triethanolamine

in structure. The mean crystallite size of the ZnO thin films were estimated by Debye-Scherer formula[29].

$$D = 0.9\lambda/\beta \cos\theta$$

where λ = wavelength of X-rays (1.5406Å); β = FWHM of the most intense peak; θ = diffraction angle.

The dislocation density was calculated by the formula[30].

$$\delta = 1/D^2$$

where, D is the crystallite size.

The micro strain is calculated from the relation[30].

$$\varepsilon = \beta \cos\theta/4$$

Sample	Crystallite size (nm)	Dislocation density δ (line^2/m^2) $\times 10^{15}$	Micro strain ε
ZnO [(Zinc acetate + TEA)-1 h stirring]	28	1.2755	.07131
ZnO [(Zinc acetate + TEA)-2 h stirring]	24	1.7361	.08185
ZnO [(Zinc acetate + TEA)-3 h stirring]	20	2.5000	.09978

It is evident from the decreasing values of crystallite size that there is a change in the crystallite size with changing stirring time for zinc acetate and triethanolamine. The crystallite

or grain size decreases with increasing stirring time for zinc acetate and triethanolamine. The effect of stirring time on the particle size might be from changes to the rate of nucleation[31]. The dislocation density and micro strain values increase with decreasing crystallite size which is consistent with work of Kathirvel *et al.*[30].

The surface morphologies of the annealed ZnO films were examined using SEM. The deposited films were gray in colour and cover the substrate uniformLy. SEM images for different stirring times of zinc acetate and triethanolamine are shown in Figs. 4-6.

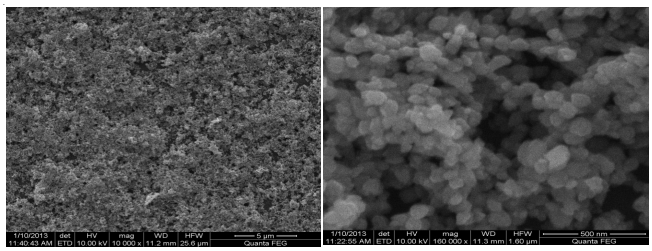

Fig. 4. SEM of the annealed ZnO thin film with stirring time of 1 h for zinc acetate and triethanolamine

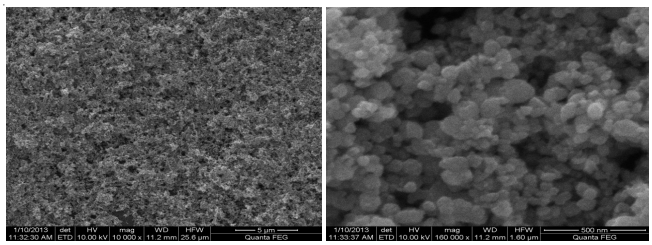

Fig. 5. SEM of the annealed ZnO thin film with stirring time of 2 h for zinc acetate and triethanolamine

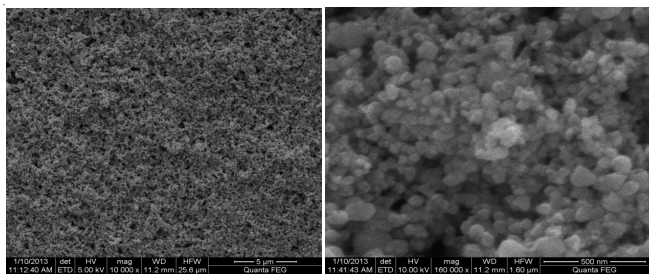

Fig. 6. SEM of the annealed ZnO thin film with stirring time of 3 h for Zinc acetate and triethanolamine

From the SEM images, it was observed that the grain size decreases with increasing stirring time of zinc acetate and triethanolamine. The SEM image Fig. 6 looks more uniform in comparison to the other two SEM images (Figs. 4 and 5) which might be due to the smaller size of the grains in case of the third sample.

EDS analysis was performed on the annealed samples to determine the elemental composition. Accuracy of EDS spectrum is affected by a number of factors. Many elements will have overlapping peaks (*e.g.*, Ti Kβ and V Kα, Mn Kβ and Fe Kα). The accuracy of the spectrum can also be affected by the nature of the sample[32]. The main purpose of EDS analysis is to detect the presence of various elements and unwanted impurities in the sample. The EDS spectra for the different samples are shown in Figs. 7-9.

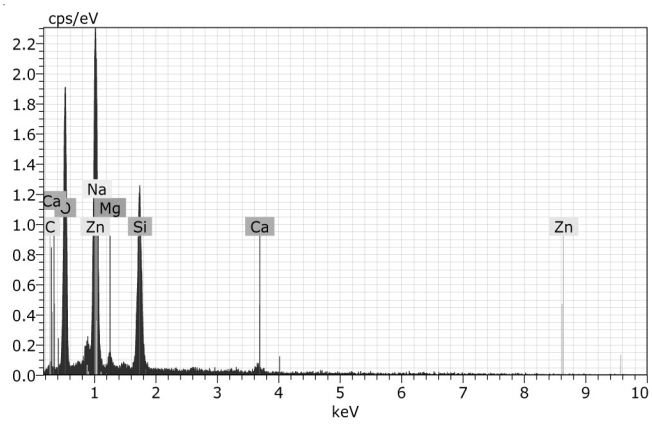

Fig. 7. EDS spectrum of the annealed ZnO thin film with stirring time of 1h for Zinc acetate and triethanolamine

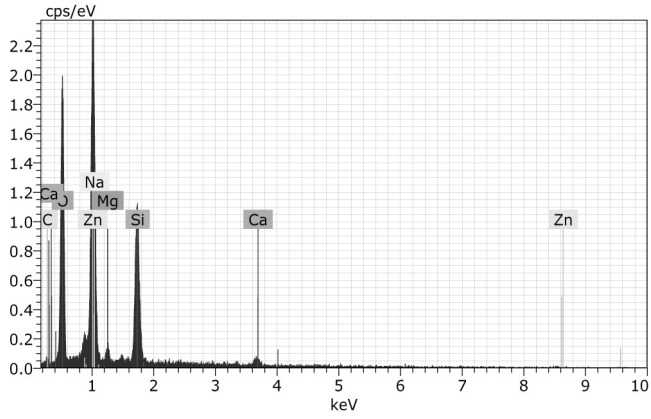

Fig. 8. EDS spectrum of the annealed ZnO thin film with stirring time of 2 h for zinc acetate and triethanolamine

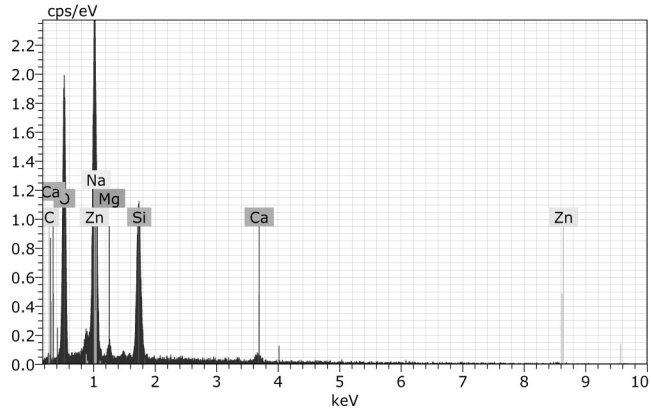

Fig. 9. EDS spectrum of the annealed ZnO thin film with stirring time of 3 h for zinc acetate and triethanolamine

The peak intensity for Zn and O in the EDS spectrum is almost the same for all the three samples. Silicon peak is from the glass substrate. Other elements such as calcium, magnesium. Carbon and sodium are present in trace amounts as impurities which may be from water, substrate cleaning agents or from the chemicals used in the reaction process. The high intensity of the Zn and O peaks suggest that the sample mainly contains ZnO.

The inherent properties of ZnO like direct wide bandgap[1], gas sensitivity[33] and morphological variation[34] make it suitable for optoelectronic and sensor applications.

Conclusion

ZnO thin films have been deposited successfully on glass substrates with varying stirring times for zinc acetate and triethanolamine. Structural and morphological studies were carried out. The ZnO particle size was found to depend on the stirring time. The grain size decreased with increasing stirring times. The pH of 11 was found to be suitable for ZnO thin film deposition by chemical bath deposition. The pre-step stirring is important as it has marked effect on the grain size.

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