International Journal of Materials Science
ISSN 0973-4589 Volume 12, Number 1 (2017), pp. 9-16

http://www.ripublication.com

Synthesis and Characterization of Nanocrystalline Zinc Oxide Thin Films for Optoelectronic Applications

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Abstract

Metal oxide is highly important material which possesses many unique optical and electrical properties for applications in many areas such as Solar cells, Gas sensors and so on. With the development of research and applications of Metal oxide thin films, research results are verified that the morphology of Metal oxide thin films are plays an important role in applications of these films. Variety of morphologies, complex structure has been developed by physical or chemical methods. However the work on controlled growth of these films is still in developing state. Therefore in present work we deposited ZnO metal oxides thin films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited films were investigated by XRD, SEM, and UV-VIS Spectrophotometer. The band gap is also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the films. We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases.

Keywords: Metal Oxide Thin films, Nanostructure, Chemical bath Deposition.

INTRODUCTION

The Metal oxides such as CdO, ZnO thin films have been studied extensively as a result of wide range of technical applications [1, 2]. It is also a gifted semiconductor material due to its direct wide energy band gap with a large exciton binding energy at ambient temperature [3– 5]. Because of its excellent optical, chemical, electrical and luminescent properties it has potential applications in light-emitting diodes (LEDs), solar cells, sensors, photo catalytic degradation and drug delivery [6–11].

A series of methods have been adopted for the synthesis of Metal Oxide nanostructures such as thermal evaporation and thermal decomposition [12], electro spinning [13], sonochemical [14], sol-gel method [15] and chemical bath deposition technique (CBDT), etc. Among them, chemical bath deposition technique CBDT is most common but inexpensive and convenient and controllable method for large preparation of thin films at low temperatures [16, 17].

Therefore in present work we deposited ZnO metal oxides thin films on different substrates by Chemical Bath Deposition Technique and study its Structural, Surface Morphology and Optical properties of as deposited films by XRD, SEM, FTIR and UV-VIS Spectrophotometer. We also study the influence of the change in preparative parameters on the deposition rate of thin films.

MATERIAL AND METHODS

To prepare Metal Oxide films, aqueous solutions of Zinc Source and Thiourea with calculated proportion was added in 130 ml of de-ionized water. Complexing agent ammonia was added slowly to adjust the pH of the solution. The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at 70±2ºC for 1 hour. The substrate used is commercial glass slide. Cleaning of substrate is important in fabrication of thin films, cleaning steps and growth procedure is reported elsewhere [18-22]. After 20-30 minutes the bath solution in beaker turned whitish, thus indicating the onset ZnS deposition on the glass slide, After a reaction time of 1 hour the glass slides were taken out and dried in air for 15 minutes. Then for the post annealing treatment in air, the prepared ZnS films were kept in the oven at various temperatures between 400ºC and 750ºC for 10 hours. The ZnS films get oxidized in the oven to form thin films of ZnO.

The crystallographic structure of films was analyzed with x-ray diffractometer (EXPERT-PRO) by using Cu-Kα lines (λ= 1.542Å). The average grain size in the fabricated films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM). The optical transmission spectra for a range of samples were obtained in UVVIS-NIR region using Perklin-Elmer UV-VIS lambda-35 spectrometer. [21]

RESULTS AND DISCUSSION:

XRD Studies:

Figure1. shows the X-ray diffraction pattern of ZnS thin films and ZnO thin films obtained from post annealing treatment over ZnS films at various temperatures. The XRD pattern confirms that the ZnS films get oxidized in the oven to form ZnO thin films. It was found that cubic structured ZnS is completely oxidized at higher annealing temperature to form a hexagonal ZnO. The film shows reflections from (100), (002) and (101) planes at 600°C, indicating the formation of ZnO nano particles having pure hexagonal structure (matches with JCPDF data).

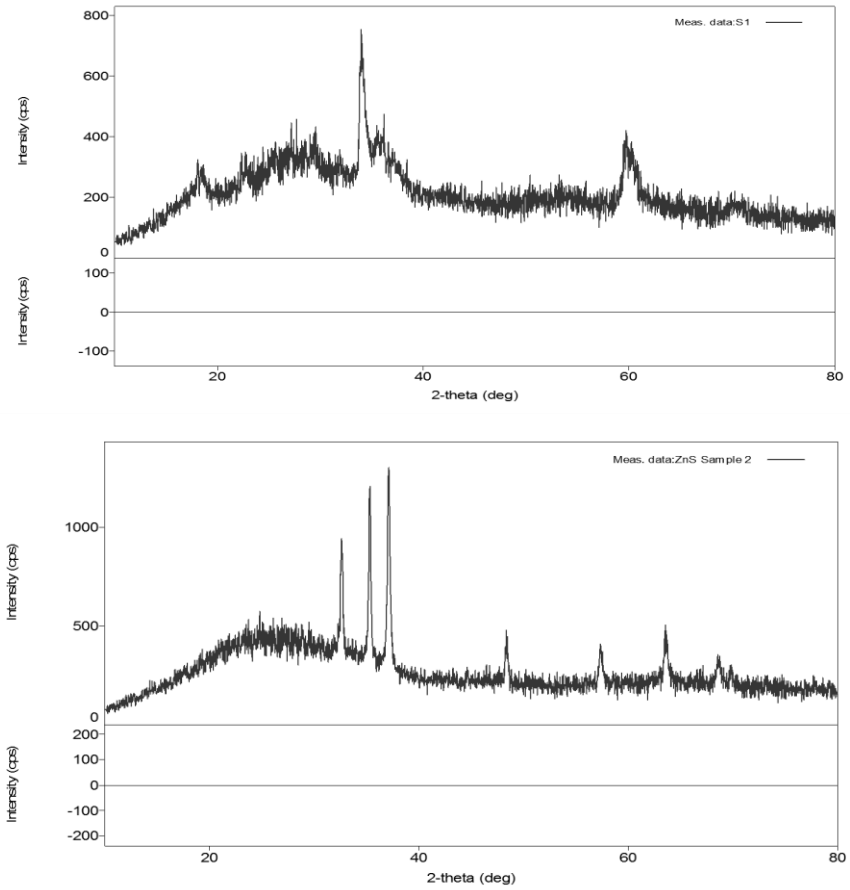

Figure 1. XRD patterns of ZnS and ZnO thin film fabricated at 600ºC

The average size of grain (g) have been obtained from the XRD patterns using Debye-Scherrer's formula, [22-24]

$$g = K\lambda / \beta \cos\theta \quad (1)$$

Where,

K = constant taken to be 0.94, λ = wavelength of X-ray used (1.542Å), β = FWHM of the peak and θ = Bragg's angle. The grain sizes were found to be within the range from 16 to 157nm. This confirms the good crystallinity of the samples.

Surface Morphology Studies:
The surface morphology of deposited ZnO thin films were investigated by SEM at different magnifications as shown in Figure 2.

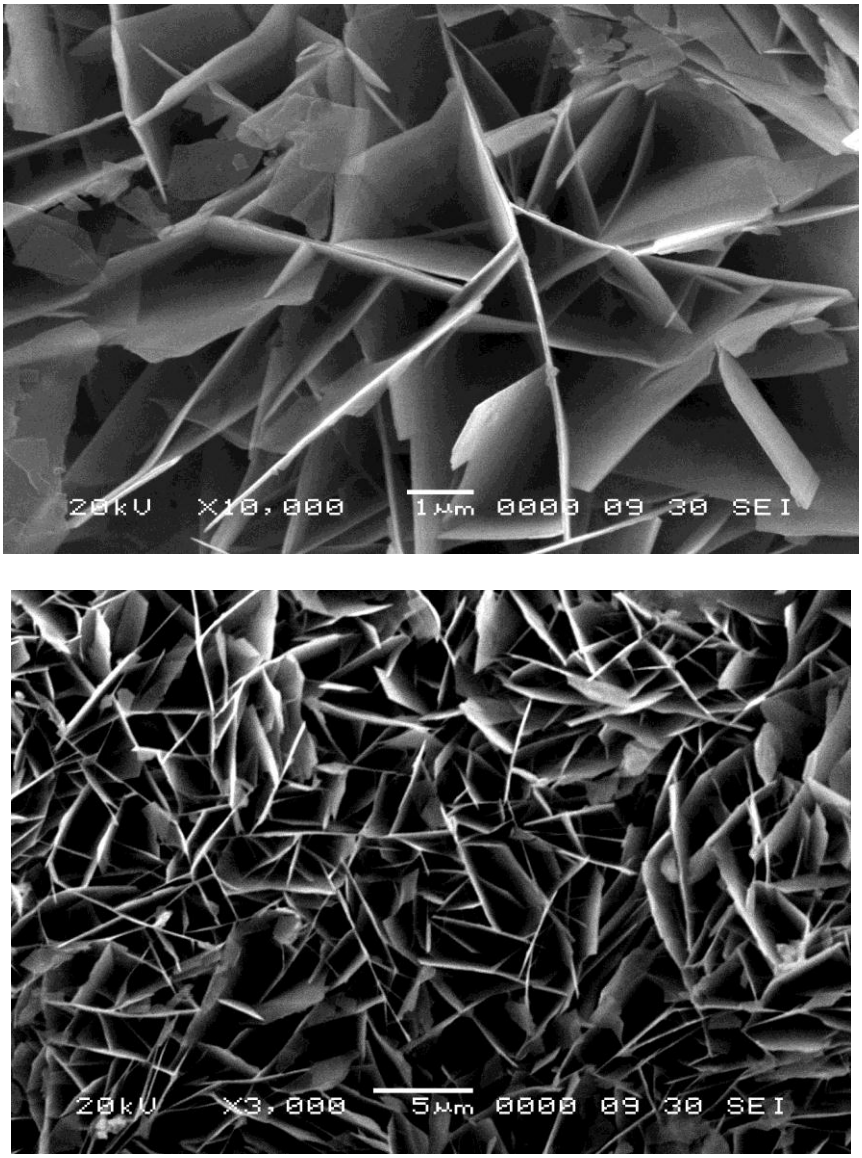

Figure 2: Scanning Electron Micrograph of as deposited ZnO thin film at different magnification.

The deposits are compact, pinhole free with spherical grains from few nanometers up to clusters of 157 nm and the films are well covered on the substrate. From the figure, it is observed that the small nanosized grains engaged in a fibrous- like structure and nanoribbons which clearly indicates the nanocrystalline nature along with some amorphous phase of ZnO thin films. The average grain size of the nanoparticles is about 130 nm. [25-26].

Optical Studies:

The optical energy band gap (Eg) was determined by plotting $(\alpha h\nu)^2$ versus hν and then extrapolating the straight line portion to the energy axis at α =0 (Figure 3(a)). It was observed that the band gap of the film obtained is 3.4eV. Fig. 3(b) shows the absorption spectrum of ZnO nanoparticles at different annealing temperatures and thickness. The exaction absorption at 360 nm is observed in the absorption spectrum at room temperature, which is blue shifted with respect to the bulk absorption edge at room temperature. It is clear that the absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle. This systematic shift in the absorption edge is due to the quantum size effect. Thus the average particle size can be determined from the inflection point in the absorption vs. wavelength spectrum

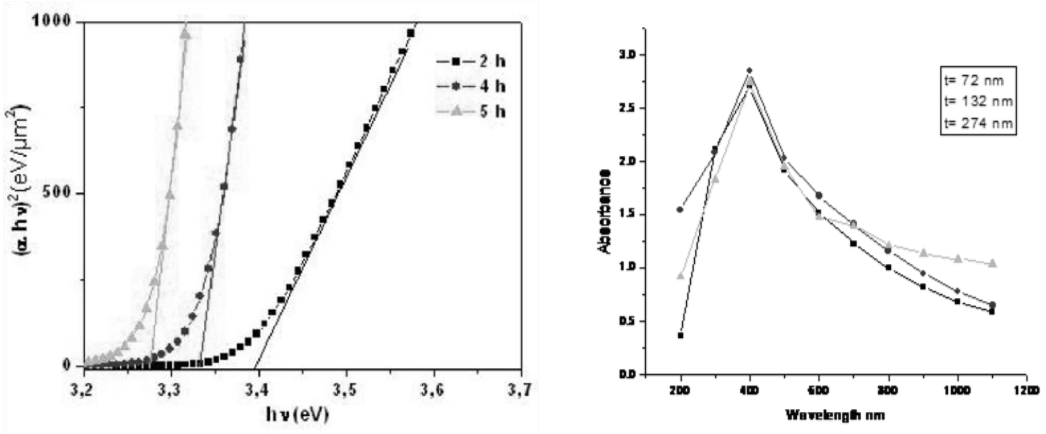

Figure 3 (a) and (b): Plot of $(\alpha h\nu)^2$ vs hν and absorption spectrum of ZnO thin films.

Effect of Deposition Temperature on Film Thickness

Figure 4 shows the variation of film thickness as a function of deposition time at different temperatures. Various temperatures from 313^0K to 345^0K in steps of 10^0K were used in the depositing ZnS & ZnO to obtain the optimal temperature. Figure 4 shows an increase in film thickness as the temperature increases from 313^0K to 363^0K. The rise in the film thickness may be due to the dissociation of the Zinc-complexes (with ammonia and with thiourea) and increase in the hydrolysis of $SC(NH_2)_2$ as the temperature increases. At higher temperatures, the decomposition of thiourea will be faster setting more S^{2-} ions free. Additionally, the Zinc-complex dissociation is greater and gives higher concentrations of free Zn^{2+} in the solution, which in turn results in higher deposition rates or in other words for a constant buffer layer thickness, in shorter deposition times. Also the kinetic energy of the ions in solution is higher at higher temperature, which brings about increased interaction between them and subsequent deposition at volume nucleation centers of the substrate. It can be seen from figure, the average growth rate is high at 363ºK (9.478nm/min) and it is slow at 313ºK (7.622nm/min). The prepared ZnS films were kept in the oven at various temperatures between 400ºC and 750ºC for 10 hours. The

ZnS films get oxidized in the oven to form thin films of ZnO.

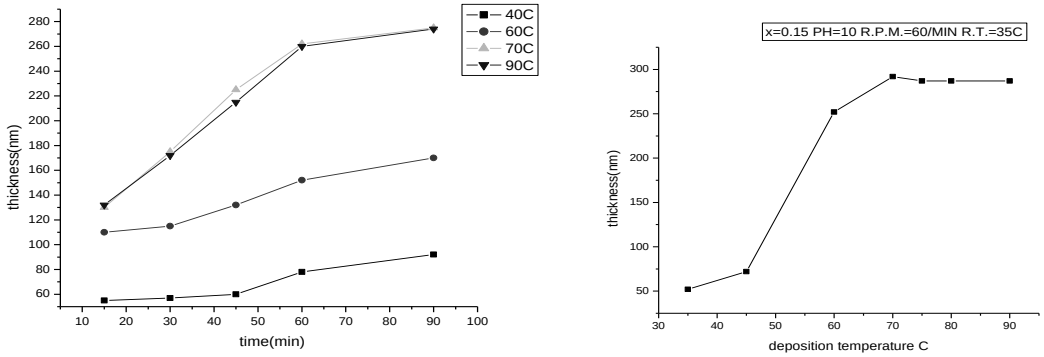

Figure 4: Variation of film thickness as a function of deposition time at different temperatures.

Effect of Deposition Time on Film Thickness:

To study the influence of deposition time on film thickness of ZnS films, the deposition time is taken as 10, 20, 30, 40, 50 and 60 Minute. Figure 5 shows the variation of film thickness as a function of deposition time.

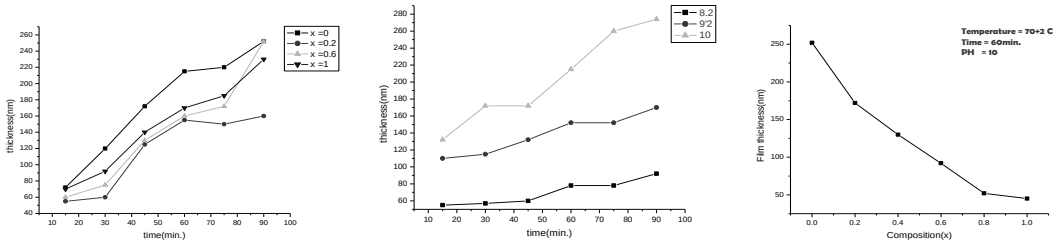

Figure 5: variation of film thickness as a function of deposition time.

The Figure 5 shows an increase in film thickness as the deposition time increases. The deposition process clearly shows two different growth phases: quasi linear phase and saturation phase. Many researchers have observed similar growth rate dependence on temperature for ZnS and Sb_2S_3 film by CBD. It can be seen from this figure that the rate of deposition is high in the initial process of growth due to high concentrations of Zn^{2+} and S^{2-}. As more and more ZnS is formed, solution becomes deficient in ions giving lower rate of deposition and film attains terminal thickness.

Deposition time is optimized by taking a substrate out of bath at regular interval of 10 Minute and film thickness is monitored after each 10 Minute. It is observed in the experiment that the film thickness increases up to 60 Minute deposition time and then remains nearly constant. The average rate of deposition is 6.72 nm/Minute. The maximum film thickness obtained by this method is about 260 nm. The maximum rate of deposition is 7.87 nm/Minute.

CONCLUSION

In present work we deposited ZnO metal oxides thin films on different substrates by Chemical Bath Deposition Technique. Structural, Surface Morphology and Optical properties of as deposited films were investigated by XRD, SEM, and UV-VIS Spectrophotometer. The X-ray diffraction analysis showed that film is polycrystalline with pure hexagonal structure. The grain size estimated is in the range of 16 to 157nm. The band gap is also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the films. The film has a direct band gap with an optical value of 3.4eV which is in good agreement with the standard value.

We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases. This makes the films suitable for various optoelectronic and sensor applications.

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