Effect of Annealing on Structural and Electrical Properties of ZnO Thin Films Prepared by Chemical Bath Deposition Technique

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Abstract. In thin film technology, Chemical Bath Deposition could be the most cost-effective method, especially the double dip technique. Even though this method suffers from limitations such as high resistivity and comparable quality of films, it is widely used for the fabrication of thin films. Zinc Oxide thin films were prepared on glass substrate by Chemical Bath Deposition (CBD) using ammonium Zincate precursor solution. Investigations on effect of annealing the Zinc Oxide (ZnO) films at 400^oC were also carried out. Structural characterization performed using X-ray diffraction technique confirmed the polycrystalline nature for all films with predominant diffraction line along (002) orientation. FE-SEM images showed uniform films with flower like structure and agglomerated grain size of the order of 900nm. The as-grown films with high resistivity which is characteristic of this preparation technique exhibited a decrease on annealing. The temperature dependent conductivity in high temperature range showed the semiconducting nature of ZnO thin films. In this study, results of annealing clearly indicated the improved crystallinity of ZnO films which would be useful in optoelectronic applications and the flower-like structure which affirms increased surface area makes it suitable for gas sensor applications.

Key Words: Thin film, Zinc Oxide, Chemical Batch Deposition, Double Dip Technique

I. INTRODUCTION

Being one of the most prominent metal oxide semiconductors, ZnO exhibits wide range of applications. As thin films, ZnO finds potential applications in electronic and optoelectronic devices like UV photo detectors, gas sensors, solar cells etc. (Ganesh *et al*, 2012; Shelake *et al*, 2008). ZnO which is an n-type semiconductor can be produced by techniques such as spray pyrolysis, chemical bath deposition, sol-gel and thermal evaporation. Solution based chemical deposition method has drawn attention due to the reasons that they are inexpensive, reliable and facilitate large area deposition (Olvera *et al*, 2007). ZnO is a semiconducting crystallite material with large bandgap of 3.37 eV that exhibits hexagonal wurtzite structure (a=0.32nm, c=0.52nm). Heat treatment at high temperature can improve the crystallinity of ZnO films (Gowthaman *et al*, 2011; Xu *et al*, 2012).

In this study, ZnO thin films are prepared by Chemical Bath Deposition (CBD) Technique and their structural, morphological and electrical properties have been discussed. Also effect of annealing ZnO films has been observed and compared with the results obtained for un-annealed films.

II. EXPERIMENTAL METHOD

ZnO thin films are deposited on cleaned soda lime glass substrate using 0.1M $ZnSO_4$ and 1M NH_4OH as reagents. The films are grown in double dip method in which the bath temperature is maintained at 85 ^{0}C (Gao *et al*, 2005). The ZnO films are prepared varying the deposition parameters to get optimal conditions.

The possible chemical reaction mechanism involved is according to the equations given below:

$ZnSO_4 + NH_3 + 2H_2O \rightarrow [Zn(NH_3)_4](OH_2) + (NH_4)_2SO_4$ ....(1)

$[Zn(NH_3)_4]^{2+} + 4\,H_2O \rightarrow Zn(OH)_2 + 4NH_4^{+} + 2OH^{-}$ ....(2)

$Zn(OH)_2 \rightarrow ZnO + H_2O$ ....(3)

Strongly adherent ZnO thin films are deposited onto the substrate after ~30 cycles. For air annealing the ZnO samples, a muffle furnace is employed and annealing carried out for optimized time at the temperature of 400^{0}C.

The structural properties are investigated by X-ray diffraction technique (XRD), morphological studies performed using FESEM and electrical properties recorded through resistivity measurement using four probe technique.

III. RESULTS AND DISCUSSION

a. Structural Characterization

XRD spectra of as-deposited un-annealed and annealed ZnO thin films at 400^{0}C in Fig. 1 indicate that the as-deposited films are polycrystalline in structure with preferential orientation along (002) direction. On air annealing, the XRD pattern of the films exhibit emergence of the characteristic peak of ZnO corresponding to (100) and the peak at (103) is found eliminated. Also increased intensity of the peaks for the annealed films indicates improved crystallinity (Zhang and Kerr, 2007). The crystallite size is calculated from the prominent peaks of both un-annealed and annealed ZnO films using Scherrer formula $\mathbf{D=0.9\lambda/\beta\cos\theta}$ where λ the wavelength of X-ray, β the FWHM and θ the diffraction angle. On annealing, the crystallite size is found to be slightly increased as reported by many researchers (Yogamalara *et al*, 2009; Gowthaman *et al*, 2011). Table 1 depicts FWHM, crystallite size and characteristic d values of both un-annealed and annealed ZnO films. The values of crystallite size indicate the formation of nano-structured ZnO thin films.

Table 1. Structural data of as-prepared ZnO thin films

ZnO Sample	FWHM	Average Crystallite Size D nm	Observed d values A°	hkl values
Un-annealed	0.42 at 35.53°	18.02	2.5244 1.4609	(002) (103)
Annealed at 400^0C	0.36 at 32.84° 0.40 at 35.56° 0.49 at 37.35°	20.36	2.7245 2.5229 2.4058	(100) (002) (101)

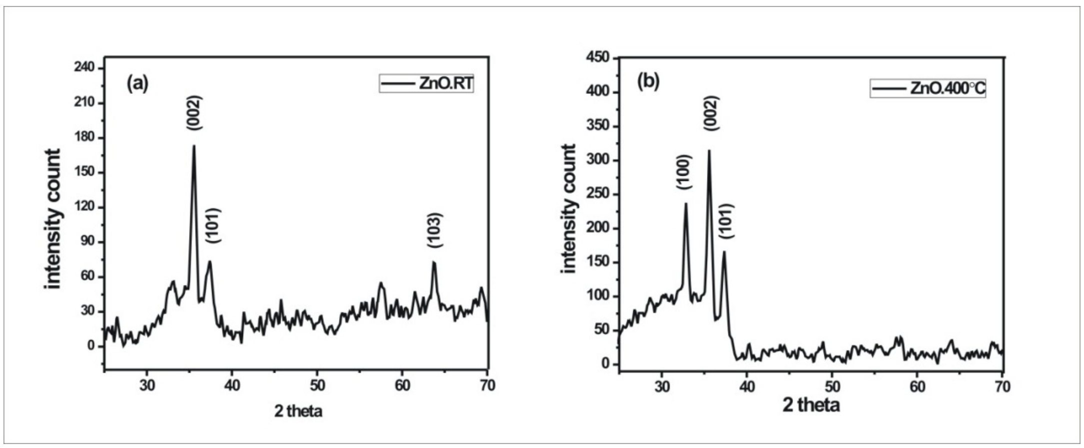

Fig 1. XRD pattern of un-annealed and annealed as-grown ZnO thin films

b. Surface Morphology

Field Effect Scanning Electron Microscopy FE-SEM has been used to study the microstructure of thin films and are illustrated in Fig. 2. The FE-SEM images of un-annealed ZnO films clearly show the formation of flower-like structure with large petal to petal size. On air annealing, size of the flowers appears to be reduced, but assembling of nanograins leads to uniform distribution with particles crowded together more closely. A slight increase in agglomerated particle size also can be observed on annealing which is in agreement with the results from X-ray diffraction studies. The flower-like structure which affirms increased surface area makes it suitable for gas sensor applications (Sheeba *et al.*, 2015).

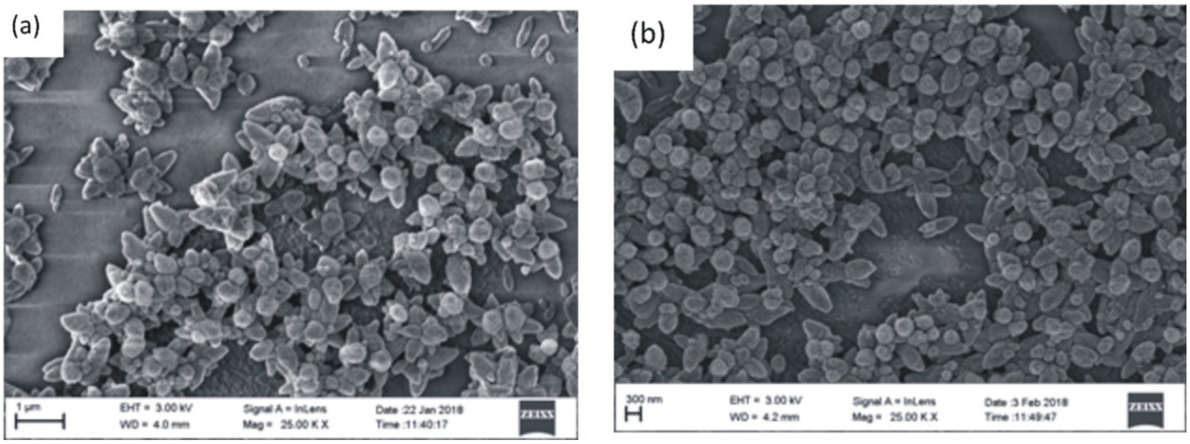

Fig 2. FESEM micrographs of (a) as-prepared un-annealed ZnO film (b) annealed at 400^{o}C

c. Electrical properties

It is observed that there is a significant effect of annealing on the electrical properties of the films. The resistivity of as-deposited un-annealed ZnO thin film is determined to be 62 Ωm which reduces to 9 Ωm on annealing. The decrease in resistivity may be due to the fact that on annealing, the particles come closer together which leads to increase in grain size (Chandramohan *et al.*, 2011). Fig 3 shows ρ vs T plot for the un-annealed and annealed ZnO films and the decrease in resistivity of the films with increase in temperature clearly indicates the semiconducting nature of the films (Mondal *et al.*, 2008).

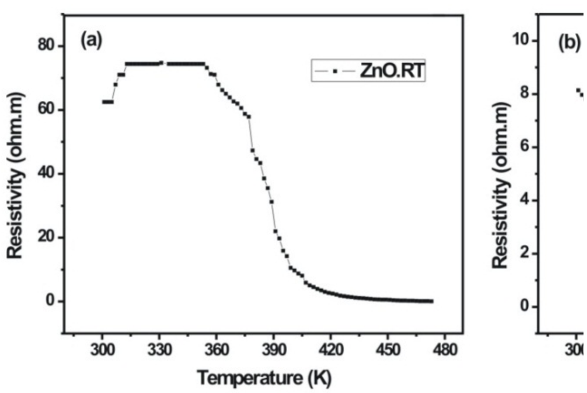

Fig 3. Resistivity Vs Temperature graph of (a) Un-annealed and (b) annealed ZnO thin film

IV. CONCLUSION

ZnO thin films are grown over glass substrates by cost effective chemical bath deposition technique. The XRD results reveal that the deposited thin films have polycrystalline hexagonal structure. The as-grown films with high resistivity which is characteristic of this preparation technique exhibit a decrease on annealing as from 62Ωm to 9Ωm. The temperature dependent resistivity in high temperature range shows the semiconducting nature of the ZnO films. In this study, the flower-like structure shown by FESEM images suggest the suitability of the films in gas sensor applications and results of annealing that indicate the improved conductivity of ZnO films make it useful in opto-electronic applications.

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