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EFFECT OF PRECURSOR SOL CONCENTRATION ON THE PROPERTIES OF ZnO THIN FILMS GROWN BY SOL-GEL SPIN COATING TECHNIQUE

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ABSTRACT

In the present study nano crystalline zinc oxide (ZnO) thin films were deposited onto ultrasonically cleaned quartz substrates by the sol–gel spin-coating technique. Effect of sol concentration on the structure and micro structure of the grown thin films were investigated. Experimental results indicate that the concentration of precursor sol strongly affected the surface morphology of the film. It was found that films with higher sol concentration (~ 0.6 M) exhibits polycrystalline nature with agglomerated grains whereas reducing sol concentration (~ 0.4 M) leads to the growth of textured thin films with a preferred orientation along (002) plane along with uniformly distributed grains. It was argued that either poly crystalline or textured ZnO thin films as desired can be grown by tailoring the concentration of the precursor sol, which in turn can be used for specific device applications.

Keywords- Micro structure, Spin coating technique, Sol concentration, Textured films, ZnO

I. INTRODUCTION

ZnO is one of the most attractive semiconducting metal oxides. It has a direct and wide band gap (3.37 eV) in the near-UV spectral region [1], and a large free-exciton binding energy of 60 meV (sufficiently larger than the thermal energy at room temperature (26 meV)) [1], this makes the excitonic emission possible at or even above room temperature [2]. It is a promising material for its potential application in many devices, such as semiconductor devices [3]-[4], transparent conductors [5], solar cell [6], varistors [7], liquid-crystal displays [8], spintronic applications [9], gas sensors [10]-[11], and so on. Owing to the above cited applications and hence the motivation of device miniaturization, large effort has been focused on the synthesis and characterization of ZnO nanomaterials. These nanostructures of ZnO, particularly ZnO thin films have been successfully grown via a variety of methods including chemical vapor deposition, sol-gel spin coating technique, spray pyrolysis, and so on [12], [13]-[14]. Among them sol-gel method is simple and inexpensive. In particular, the most important advantage of this method over conventional deposition methods is that the microstructure of the deposited films can be tailored as desired. However, the controlling factors for this include type of the precursor materials, heat treatment, aging time of the sol, number of coatings, concentration of the precursor material in the sol, and so on.

In the present work, only by varying the sol concentration and keeping all other parameters invariant both polycrystalline and (002) oriented textured ZnO thin films were successfully grown using sol-gel spin coating technique. The variation in structural and micro structural properties with the sol concentration are studied from the results of XRD pattern and FESEM micrographs, respectively and the underlying mechanisms are discussed.

II. EXPERIMENTAL PROCEDURE

First the precursor sol with varying concentration (~ 0.4 M to 0.6 M) was prepared by dissolving zinc acetate dihydrate [Zn $(CH_3CO_2)_2 \cdot 2H_2O$] in 2-methoxyethanol. Mono-ethanolamine (MEA) was added as stabilizer. The molar ratio of MEA to zinc acetate was kept at 1: 1. The solution was stirred at 60^{o}C for 2 h to get it in homogeneous form which served as precursor sol. The precursor sol was spin coated over ultrasonically cleaned quartz substrate at 3000 rpm for 30 s using a commercial spin coating unit (SCU 2007, Apex Instruments Co, Kolkata). After deposition, the film was put in a furnace kept at 300^{o}C, for 5 min and then brought to room temperature. The coating and drying cycles were repeated to obtain the film. After final coating and drying cycle the film was annealed at 600^{o}C for 1 h in air and cooled down to room temperature.

The phase formation behavior of the grown ZnO thin films was studied by X-ray diffraction (Ultima III, Rigaku, Japan) analyses using Cu Kα radiation. The micro structural characteristics of the films were investigated using field emission scanning electron microscope (FESEM) (SUPRA-40, Carl Zeiss, Germany).

III. RESULTS AND DISCUSSION

1.1. Structural Characterization

The XRD patterns of the thin films grown by the sol–gel spin coating technique on quartz substrates using different sol concentration are shown in Fig.1.

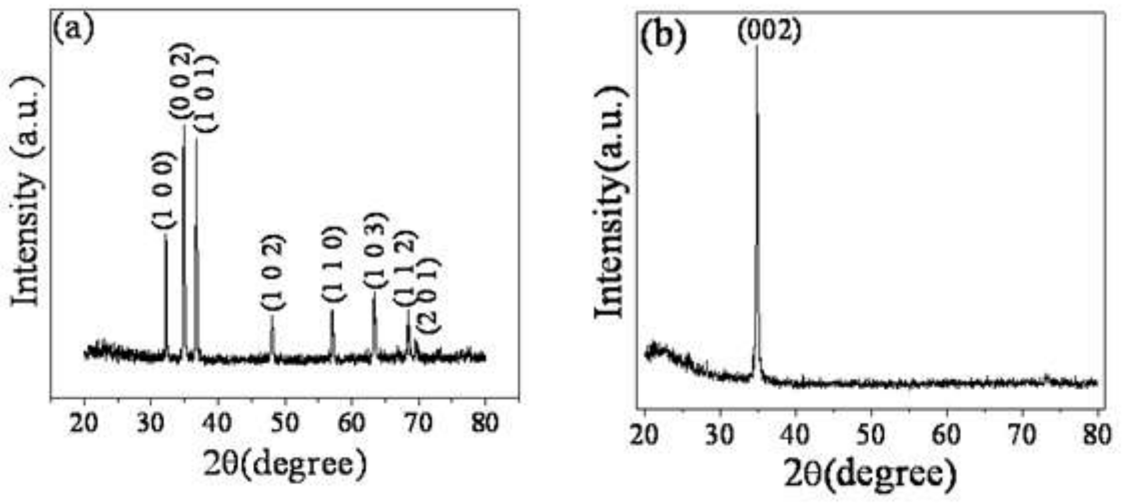

Fig. 1: Xrd Pattern Of Zno Thin Films Grown By Sol-Gel Spin Coating Method On Quartz Substrates Using Various Sol Concentrations (A) 0.6M And (B) 0.4M

As reflected from Fig. 1 (a) films with higher sol concentration (~0.6M) exhibit polycrystalline behavior. It shows prominent peaks at 32.32^o, 34.93^o, 36.67^o, 47.93^o, 56.93^o, 63.32^o, 68.45^o and 69.42^o corresponding to (100), (002), (101), (102), (110), (103), (112), and (201) planes respectively, which corresponds to the diffraction planes of hexagonal ZnO. However, the XRD patterns for films with lower sol concentration (~0.4M), as shown in Fig. 1(b), shows textured behavior with preferred orientation along (002) planes. As stated by Brinker et al. the lack of preferred orientation could be due to densification of sol and crystallization of gel film [15]. The crystallite size D is estimated using the Debye-Scherer formula (1):

$$\mathbf{D = 0.9\lambda / \beta \cos\theta} \quad \mathbf{(1)}$$

Where λ (= 0.154 nm) is the wavelength of the X-ray radiation used, θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) of diffraction peaks measured in radian [16]. The average crystallite size is found to be 30.9 nm and 56.7 nm for the thin films having ~0.4M and ~0.6M sol concentration. The increase in crystallite size is also reflected from the FESEM micrographs shown in the following section.

1.2. Micro structural Characterization

The surface morphologies of all the grown ZnO thin films are investigated using a field emission scanning electron microscope. Fig. 2 (a-b) shows two typical micrographs corresponding to films grown using 0.6 M concentration of sol (Fig. 2a) and 0.4 M concentration of sol (Fig. 2b).

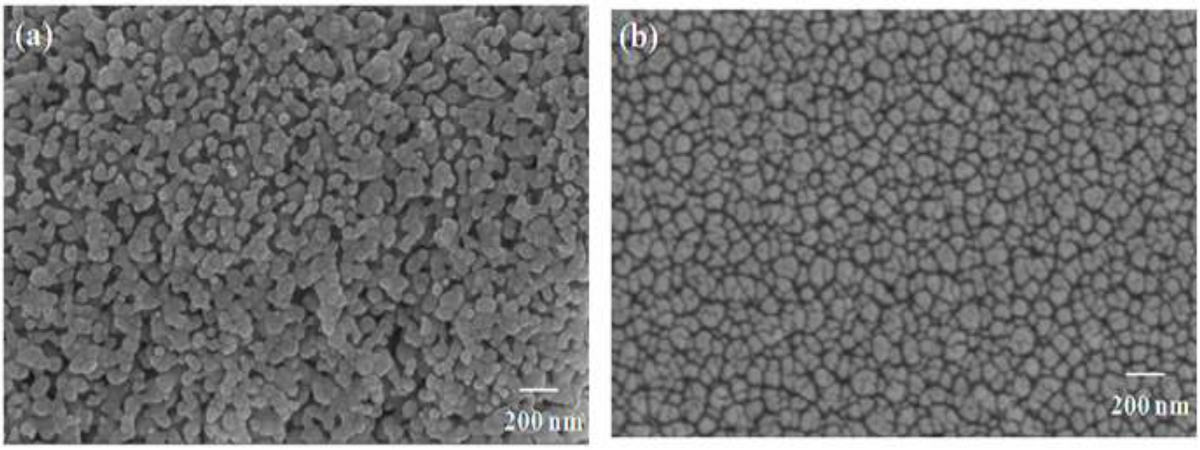

Fig. 2: FESEM Image Of Zno Thin Films Grown By Sol-Gel Spin Coating Method On Quartz Substrates Using Various Sol Concentrations (A) 0.6M And (B) 0.4M

The films prepared from ~0.6 M concentration sol shows polycrystalline structure with agglomerated grains, whereas the film prepared from ~0.4 M sol exhibits smooth, uniform and homogeneous morphology over the entire surface. It clearly reflects the influence of precursor sol concentration on the grain size which is the characteristics of crystal growth in solution phase [17]. The increase in grain size in Fig. 2a can be attributed to the coalescence of small grains owing to the densification of sol. As reported by Znaidi et al. during film deposition the nature of the complexes formed and their degree of dissociation strongly depends on the nature of initial precursor sol [18].

II. CONCLUSION

Two different precursor solutions were used to prepare ZnO thin films, one at sol concentration ~0.4 M and the other at ~0.6 M. The influence of precursor solution on the properties of the films was studied. Both transparent polycrystalline and textured thin films were obtained. Films prepared using ~0.4 M sol was found to be textured along (002) plane and those prepared using ~0.6 M sol shows polycrystalline behavior. The structural properties such as crystallite size and surface morphology strongly depend on the concentration of the precursor solution. Thus, ZnO thin films both polycrystalline and textured, as desired can be tailored by this simple and cost effective wet chemical route which in turn is very useful considering the versatile application of ZnO thin films.

III. ACKNOWLEDGEMENT

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