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SYNTHESIS AND CHARACTERIZATION OF IN DOPED ZnO THIN FILMS

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ABSTRACT :

ZnO thin films were deposited on the pre-heated glass substrates by simple and cost effective spray pyrolysis technique. It is observed from XRD spectra that the preferential (101) peak intensity increases with increasing In dopant concentration. It is found that the crystallite size has increased as the dopant increased up to 4 at%. Then, as the doping concentration increased to 5 at%, reduction in the crystallite size is observed.

From SEM the film consists of grains with uniform coverage of the substrate surface and the grain size is increased from 80 nm to 150 nm as In concentration increased from 1 at% to 4 at%. The presence of Indium in the selected area EDAX analysis is confirmed.

KEYWORDS : *Spray pyrolysis; In doped ZnO films; structural properties; morphological properties.*

INTRODUCTION

A precise study on the properties of doped film is essential to control the doping parameters, and this is indispensable for optoelectronic device applications. Again the technique we used for film preparation is very simple viz CSP technique. It is rather easy to vary the doping concentrations in this technique and hence to adjust the properties of the films. Several reports are available on the properties of indium doped ZnO thin films. Indium was proved to be one of the best candidates for making ZnO low resistive. When ZnO is doped with group III elements, such as Al, Ga or In, it is expected that the dopants act as singly charged donors by substituting Zn. The excess carriers supplied by the impurities to the conduction band contribute to the increase of the electrical conductivity of ZnO [1-11].

Structural and electrical characterization of indium doped ZnO thin films prepared using spray pyrolysis technique were reported by Maldonado et al [1]. They used zinc acetate and indium nitrate as precursors and substrate temperature was varied from 675 to 800 K. By using indium nitrate instead of indium chloride for doping, the unintentional doping of chlorine in the film was avoided. The lowest resistivity value of 6x10-3 ohm cm was obtained for the sample prepared at 775 K and these films showed an average transmittance of around 85% in the visible region. Both doped and undoped films were polycrystalline with preferential orientation along (101) plane except at lower substrate temperature [<700 K]. At those temperatures, there was significant contribution in the (002) direction [12-20].

EXPERIMENTAL DETAILS

ZnO thin films were deposited on the pre-heated glass substrates by simple and cost effective spray pyrolysis technique. The precursor used laws Zinc acetate dehydrated ($Zn(C2H3O2)_2.2H_2O$). The Indium chloride was the doping source. The mixture was dissolved in methanol (75%) + double distilled water (25%). The concentration of zinc acetate was 0.5 M and the In /Zn ratio in the solution was varied from 1 at% to 5 at% in the starting solution. The prepared solution is then sprayed on the heated glass substrates which transforms the solution (mixture) to a stream formed with uniform land fine droplets. The temperature of the substrates was kept constant at 450 ^{0}C throughout the experiment. Characterization techniques used, were XRD, SEM measurements.

RESULTS AND DISCUSSIONS

X-ray diffraction analysis

X-ray diffraction data were analyzed in order to identify the crystal structure and also the various phases present in the samples. Fig. 1 shows the XRD patterns of In-doped films with different doping levels. As seen in Fig. 1, IZO films have polycrystalline nature with a wurtzite structure. The films exhibit a dominant peak at $2\theta = 36.44$ corresponding to the (101) plane of ZnO. Other peaks corresponding to (100) and (002) planes are also presents in the spectra indicating polycrystalline nature. It is observed from XRD spectra that the preferential (101) peak intensity increases with increasing In dopant concentration. This indicates an

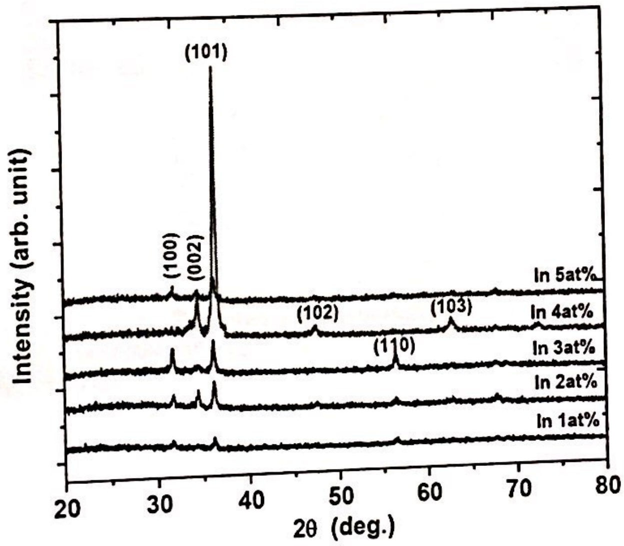


Fig. 1: X-ray diffraction spectra of In-doped ZnO thin films.

improvement in film crystallanity with In doping. This is due to the fact that the In incorporation in film network enables more nucleation sites. It should be noted that no any secondary phases, In clusters or other oxide phases within the precision limit of XRD measurement were found, which confirms that it is highly pure and single ZnO phase. When the doping level is increased the (101) diffraction peak becomes progressively strong and at 4 at% of In doping level it is more strong. However, as doping raised to 5 at% the intensity of (101) peak suddenly decreased. The orientation of (101) is the dominant plane in the doped films. A weak peak of (100), (102), (110) and (103) were also detected in XRD pattern.

Surface morphological and compositional studies

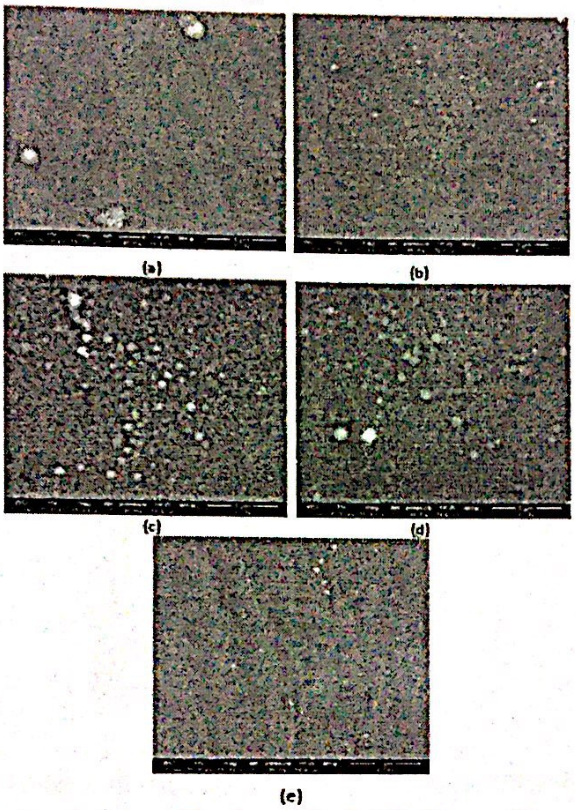
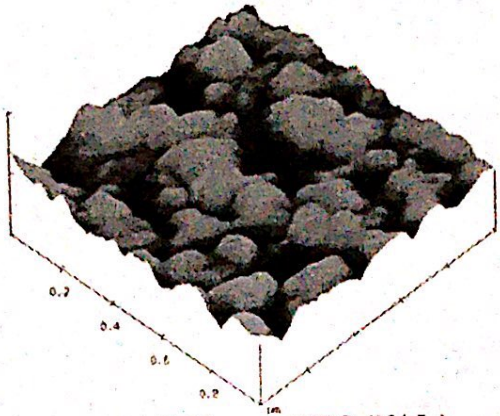


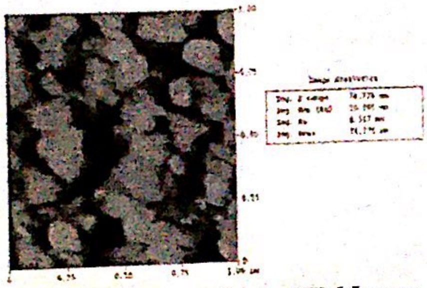
Fig. 2: The surface SEM morphology of In-doped ZnO thin films with various concentrations of In dopant.

The two dimensional surface morphologies of IZO thin films deposited at 450 ^{0}C were carried out using SEM images are shown in Fig. 2(a-e). From the micrographs, it is seen that the film consists of grains with uniform coverage of the substrate surface and the grain size is increased from 80 nm to 150 nm as In concentration increased from 1 at% to 4 at%.

Fig. 3 (a) and (b) shows AFM Images 3D and 2D roughness analysis of IZO thin films deposited under different doping levels. From the surface morphology of the films it is observed that the grain growth is of nanometer size with uniform structure. At higher doping levels of indium the formation of nuclei, resulting in fewer, but larger, nuclei. Growth of these larger nuclei is more three-dimensional than in films prepared at lower doping levels. The coalescence should result in large and irregularly shaped grains [21-22]. To find film uniformity, we measured the surface rms (root mean square) and average roughness of IZO films. It is seen that the films deposited at various In doping levels show different surface roughness. At the In 1%, the average and rms (root mean square) roughness are very low as 10.705 nm and 8.517 nm, respectively. The In at% is further increased, the values of average roughness and rms roughness increases to 24.157 nm and 18.247 nm. The measured size of the particle from the AFM surface images is higher than the values calculated from XRD studies, indicating that these particles are probably an aggregation of small crystallites on the surface of the films [23-24].

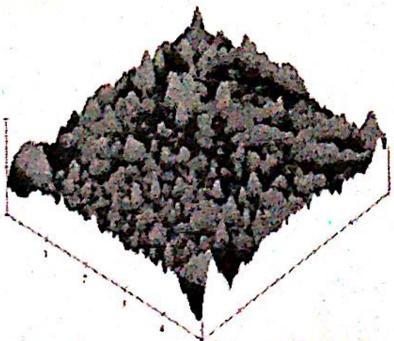


3D AFM image of IZO (1% In)

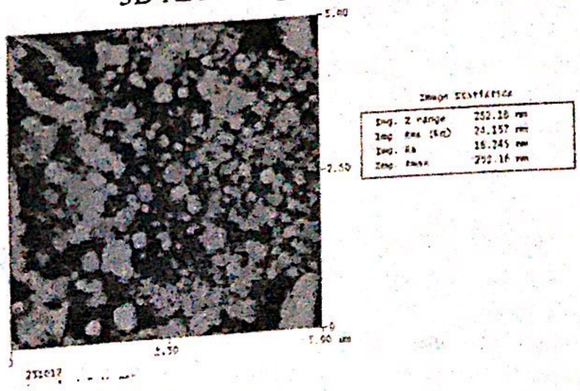


2D roughness analysis AFM Image

Figure 3 (a) AFM Images 3D and 2D roughness analysis of IZO thin films (In 1at%)

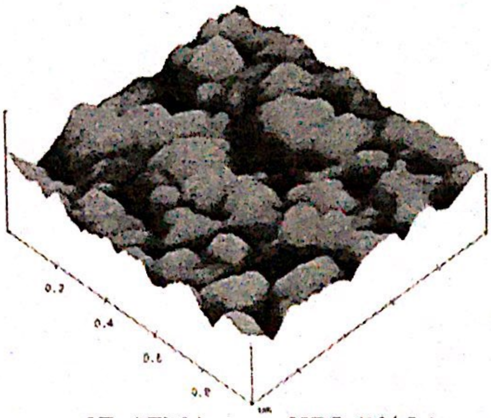


3D AFM image of IZO (4% In)

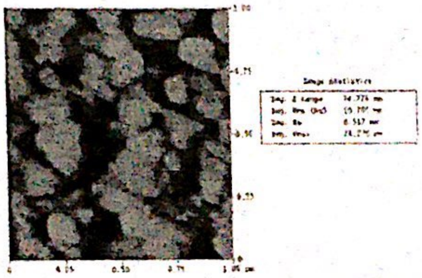


2D roughness analysis AFM Image

Figure 3 (b) AFM Images 3D and 2D roughness analysis of IZO thin films (In 4 at%)

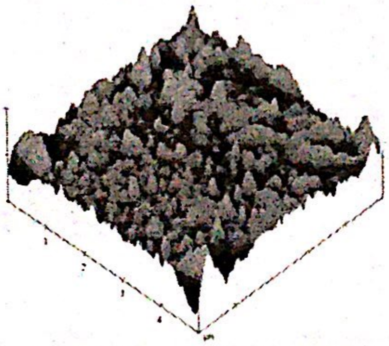


3D AFM image of IZO (1% In)

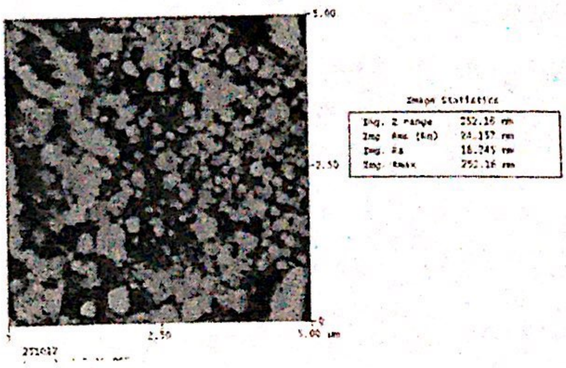


2D roughness analysis AFM Image

Figure 3 (a) AFM Images 3D and 2D roughness analysis of IZO thin films (In 1at%)

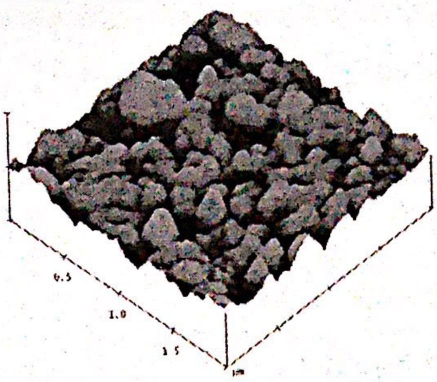


3D AFM image of IZO (4% In)

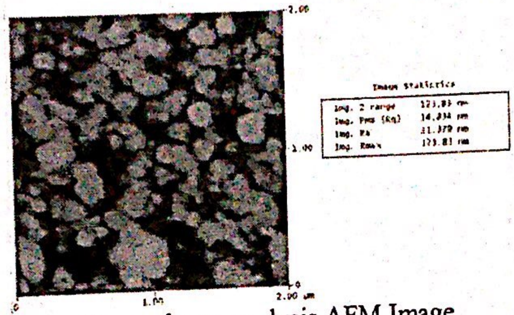


2D roughness analysis AFM Image

Figure 3 (b) AFM Images 3D and 2D roughness analysis of IZO thin films (In 4 at%)



3D AFM image of IZO (5 % In)



2D roughness analysis AFM Image

Figure 3 (c) AFM Images 3D and 2D roughness analysis of IZO thin films (In 5 at%)

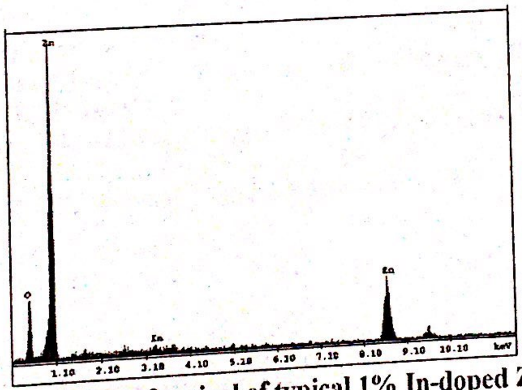


Figure 4.: EDAX spectra of typical of typical 1% In-doped ZnO thin films.

Fig. 4 illustrates the energy dispersive analysis by X-ray (EDAX) spectra of elemental composition of 1 at% In-doped ZnO thin films. The presence of Indium in the selected area EDAX analysis is confirmed. It can be verified from the results of XRD and EDAX that the In is successfully doped in the ZnO crystals.

CONCLUSION

- In doped Zinc oxide films were deposited by spray pyrolysis method using an aqueous zinc nitrate solution.
- IZO films have polycrystalline nature with a wurtzite structure.
- The orientation of (101) is the dominant plane in the doped films.
- The film consists of grains with uniform coverage of the substrate surface and the grain size is increased from 80 nm to 150 nm as In concentration increased from 1 at% to 4 at%.

- . From the surface morphology of the films it is observed that the grain growth is of nanometer size with uniform structure.
- The presence of Indium in the selected area EDAX analysis is confirmed.

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