



SPRAY DEPOSITED Ga DOPED ZnO THIN FILMS: SYNTHESIS AND CHARACTERIZATION

E. U. Masumdar^a and M. A. Barote^{b*}

^aThin Film Physics Laboratory, Department of Physics, Rajarshi Shahu Mahavidyalaya - Latur-413512, Maharashtra, India.

^bDepartment of Physics, Azad college, Ausa-413520, Maharashtra, India. (*Corr. Author)

ABSTRACT :

The ZnO:Ga thin films were deposited on preheated amorphous glass substrates using P C controlled spray pyrolysis technique. The structural properties of Ga doped ZnO thin films produced by the spray pyrolysis method at 450 °C substrate temperature are studied. The films exhibit a dominant peak at $2\theta = 34.44$ corresponding to the (002) plane of ZnO. A uniform grain growth in all the film samples is observed from the SEM micrographs.

KEYWORDS : Spray pyrolysis; Ga-doped ZnO films; structural properties, SEM.

INTRODUCTION

Ga-doped ZnO (GZO) has drawn attentions recently because it has some advantages over AZO. Whereas AZO and GZO TCOs have comparable electrical properties [1-5], Ga dopant is less reactive with oxygen compared with Al dopant meaning that it can function as better dopant within ZnO [6]. In addition, the Ga-O covalent bond length of 1.92\AA , which is smaller than that of Zn-O (1.97\AA), is expected to cause smaller deformation of ZnO lattice when Ga^{3+} ions substitute Zn^{2+} site in case of high doping concentration [6]. Concerning the use of Ga as the dopant to enhance electrical properties, it has been reported that resistivity of GZO films decreased with increasing film thickness where as the transmittance of films decreased as the film thickness increased [7]. On the practical side, increasing the thickness of the GZO TCO film would result in rising cost and reduced throughput. Further, as in the case of the AZO films, it would be possible to improve the electrical properties of GZO films by post-annealing treatment in hydrogen atmosphere [8-12].

EXPERIMENTAL DETAILS

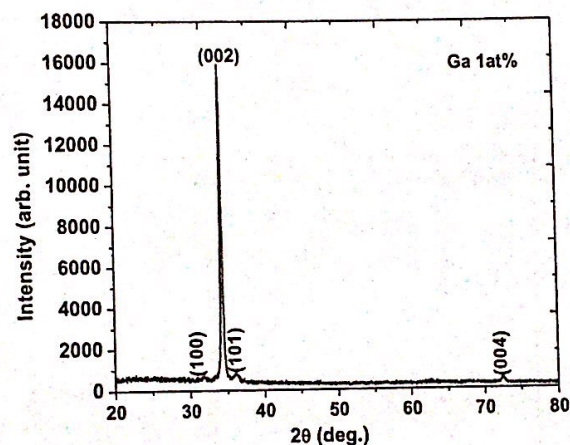
In this investigation, the ZnO:Ga thin films were deposited on preheated amorphous glass substrates using P C controlled spray pyrolysis technique supplied by Holmark (Cochin, India). A solution of zinc acetate in a mixed solvent of 75% methanol and 25% double distilled water was used as a precursor. Compressed air was used as the carrier gas. The GZO films were deposited at optimized temperature of 450 °C by varying the gallium concentration from 1 to 5 at%. The precursor solution was atomized into the fine droplets and carried to the preheated glass substrates.

XRD (Rigaku Mini- II) was used to analyze the crystalline orientation and the crystalline plane spacing of the films. The XRD measurements were performed in a standard θ - 2θ scan using a Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$) over the range of 200 to 800. The microscopic features were observed through a scanning electron microscope (JEOL-JSM-5600).

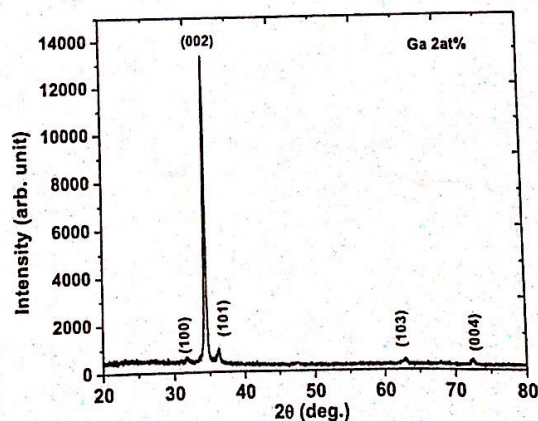
RESULTS AND DISCUSSIONS

5.3.1 X-ray diffraction analysis

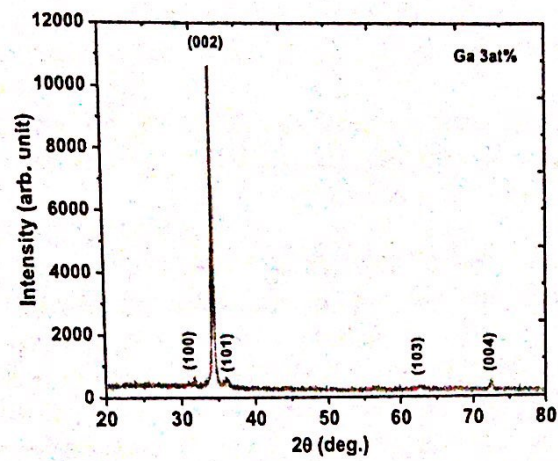
The structural properties of Ga doped ZnO thin films produced by the spray pyrolysis method at 450 °C substrate temperature were investigated by XRD and the results for all doping levels of Ga are shown in Fig. 1. The XRD patterns of these samples are in good agreement with the JCPDS standard (No. 75-0576) data of wurtzite hexagonal ZnO. As seen from Fig. 1, the films exhibit a dominant peak at $2\theta = 34.44^\circ$ corresponding to the (002) plane of ZnO. However, weaker ZnO peaks like (100), (101), (103) and (004) are also observed, suggesting that during the material depositing some grains grow with another orientation [13]. Apart from ZnO characteristic peaks, no peaks that correspond to either gallium, zinc or their complex oxide could be detected. Similar results were also obtained by T. Prasad Rao [14]. This observation suggests that the film do not have any phase segregation or secondary phase formation. Meanwhile, it was apparent that



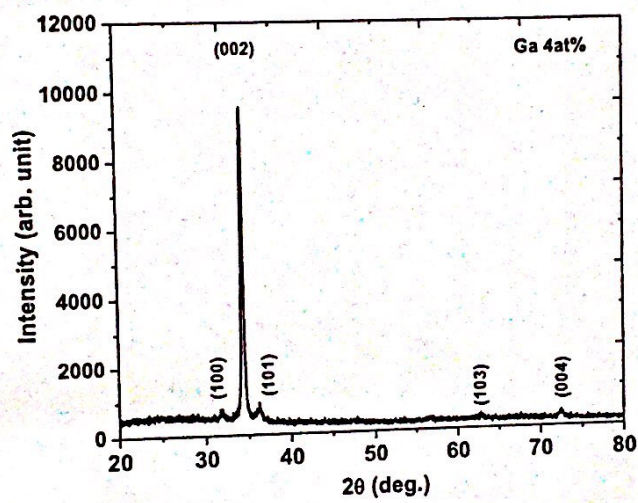
(a)



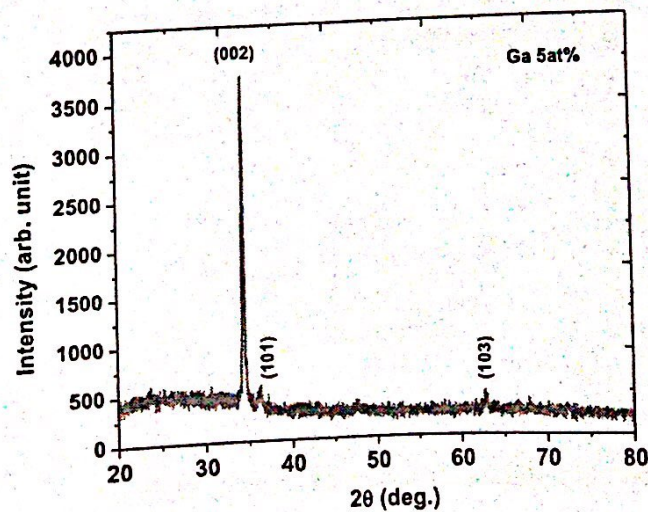
(b)



(c)



(d)



(e)

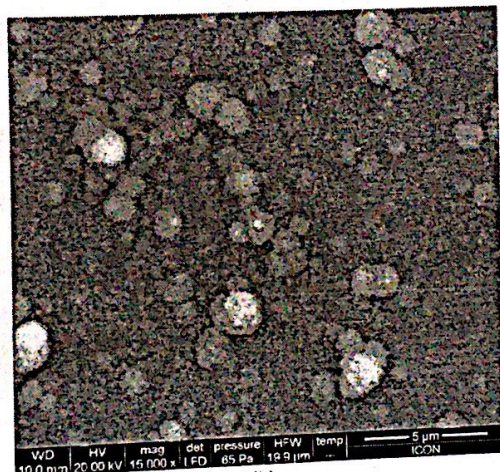
Figure 1: X-ray diffraction spectrum for the ZnO:Ga films with different Ga at%.

intensity of (002) diffraction peak decreased and the full width at half maximum (FWHM) of (002) peak decreased with increase in Ga concentration, indicating that the more the Ga concentration in ZnO films the worse the crystal quality. This might be due to the lattice disorder and strain induced by interstitial Ga atoms of the substitution of Ga for Zn.

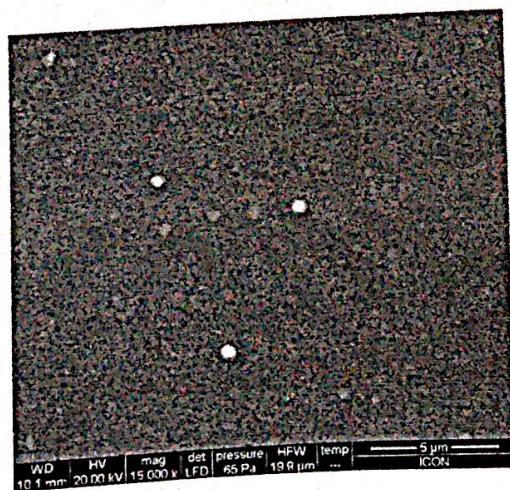
The average crystallite size for (002) peak has been calculated using Deby-Sherrer's equation [15]. It is observed that as Ga doping increases the crystallite size decreased. It is decreased from 29 nm to 21 nm.

SURFACE MORPHOLOGICAL STUDIES

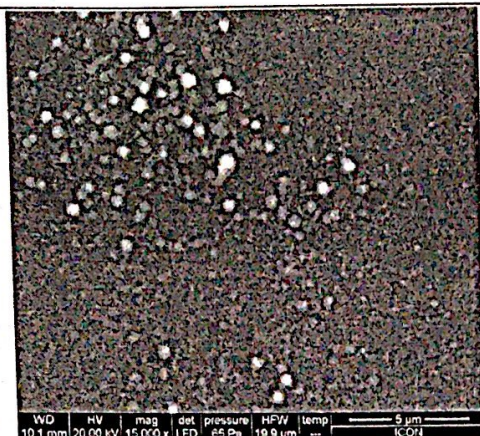
It is known that the surface properties of the TCO films influence their optical and electrical properties which are important factors for application in optoelectronic devices. The two-dimensional surface morphologies of as-deposited GZO thin films were carried out using SEM images are shown in Fig. 2. A uniform grain growth in all the film samples is observed from the SEM micrographs. It is also observed that grains are small and distributed uniformly throughout the surface. The uniformity and compactness presented by the films is a result of the specific deposition and solution conditions. In this case, the surface is covered by round and small-size grains, and seems to be a smoother and more uniform surface, whereas, films with a higher content of Ga show an irregular surface, which is covered by different size grains and some big features that seems to be agglomerates of smaller-grains. As Ga doping concentration increases, a



(a)



(b)



(c)

Figure 2(a-c): SEM micrographs of the GZO films at various Ga at%.

gradual decrease in grain size occurred due to an increasing number of nucleation centers during incorporation of the dopant into the host material [17].

CONCLUSION:

- The GZO films were deposited at optimized temperature of 450 °C by varying the gallium concentration from 1 to 5 at%.
- It is observed that as Ga doping increases the crystallite size decreased from 29 nm to 21 nm.
- It is observed that as Ga concentration increases, the ZnO films the worse the crystal quality.
- Films with a higher content of Ga show an irregular surface.

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