

# Effect of gallium doping on the structural, optical and electrical properties of zinc oxide thin films prepared by spray pyrolysis

E. Muchuweni\*, T.S. Sathiaraj, H. Nyakoty

Department of Physics and Astronomy, Botswana International University of Science and Technology (BIUST), P. Bag 16, Palapye, Botswana

## ARTICLE INFO

### Article history:

Received 26 January 2016

Received in revised form

7 March 2016

Accepted 15 March 2016

Available online 16 March 2016

### Keywords:

A. GZO thin films

C. Electrical properties

C. Optical properties

Spray pyrolysis

## ABSTRACT

Gallium-doped zinc oxide (GZO) thin films were deposited onto glass substrates by the spray pyrolysis technique and the effect of gallium (Ga) doping on their structural, optical and electrical properties was investigated by X-ray Diffraction (XRD), Spectrophotometry and Current–Voltage ( $I$ – $V$ ) measurements, respectively. XRD studies revealed that all films were polycrystalline in nature, with a hexagonal wurtzite crystal structure and a predominant (002)  $c$ -axis orientation. Ga doping resulted in deterioration of the film's crystallinity, increase in full width at half maximum (FWHM) and reduction in the mean crystallite sizes. All GZO thin films had relatively higher average transmittances, approximately 70–85% in the visible region as compared to the undoped ZnO thin films. Introduction of Ga led to a blue shift in the optical band gap from 3.26 eV to 3.30 eV and an increase in the Urbach energy from around 67 meV to 100 meV. Ga doping induced a decrease in sheet resistance leading to a minimum electrical resistivity of  $1.2 \Omega \text{ cm}$  and a maximum figure of merit of  $1.02 \times 10^{-4} \Omega^{-1}$  for the 1 at% GZO thin film, indicating its suitability for optoelectronic applications, especially transparent electrode fabrication.

© 2016 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

## 1. Introduction

In the past few years, there has been much research interest on transparent conducting oxide (TCO) thin films due to their wide use as transparent electrodes in flat screen displays [1], photovoltaic devices [2], light emitting diodes [3] and heat mirrors [4]. The most commonly used TCO material is indium tin oxide (ITO), due to its excellent optical and electrical properties [5,6]. However, due to indium's scarcity, high processing cost and toxicity, there has been much emphasis on finding suitable alternatives [7].

ZnO is a promising alternative material to ITO due to its competitive optical and electrical properties [8,9], low deposition temperature, high chemical and thermal stability [10] combined with zinc's abundance in nature, low cost and non-toxicity [11]. However, undoped ZnO has a relatively low transparency and high resistivity, so it is commonly doped with aluminium (Al) to enhance its electrical and optical properties [12,13]. However, compared to Ga, Al has a relatively poor thermal stability and its high reactivity causes degeneration problems when exposed to ambient air for a long time [14]. Therefore, doping ZnO with Ga is favourable due to its less reactivity and more stability with respect to oxidation [14,15] and its capability of creating a more uniform structure with few lattice defects due to the closer atomic radius of

Ga (0.062 nm) to Zn (0.060 nm) than Al (0.052 nm) [8]. Muiva et al. [10], reported that doping plays a significant role in lowering the electrical resistivity through charge carrier multiplication and defect population reduction.

Several synthesis routes, such as spin coating [16], dip coating [17], rf magnetron sputtering [18], electron beam evaporation [19] and spray pyrolysis [20] have been successfully used to deposit GZO thin films. Among these methods, spray pyrolysis has the advantages of safety, simplicity, cheap cost, no high vacuum requirement and well adaptation for large area coatings. To the best of our knowledge, GZO thin films have been relatively less studied than Al doped ZnO thin films [20].

In this work, we report the effect of Ga doping on the structural, optical and electrical properties of GZO thin films prepared on glass substrates by spray pyrolysis. The optimum Ga concentration yielding the best optical and electrical properties is revealed for possible transparent electrode fabrication.

## 2. Experimental details

GZO thin films were deposited onto glass substrates (Corning NY 14831, USA) of size (75 mm × 25 mm × 1 mm) using the spray pyrolysis technique. A 0.1 M spray solution was prepared by dissolving zinc acetate dihydrate in a mixture of methanol and deionized (DI) water. The ratio of methanol to DI water was maintained at 13:7. To achieve Ga doping, four different

\* Corresponding author.

E-mail address: [muchuweniedigar1@gmail.com](mailto:muchuweniedigar1@gmail.com) (E. Muchuweni).

concentrations (1, 2, 3 and 5 at%) of Ga nitrate hydrate were added into the spray solution. A few drops of acetic acid were also added to the spray solution to prevent the formation of zinc hydroxide. Just before deposition, the glass substrates were ultrasonically cleaned with acetone, isopropanol and finally with DI water for 10 min in each step. After cleaning, the substrates were dried at room temperature using compressed air.

Thin films were then deposited by spraying the solution onto clean glass substrates placed on a hot plate stove set at 723.15 K. The solution flow rate was maintained at 3 ml/min throughout the coating process and compressed air was used as the carrier gas to atomize the precursor solution through a nozzle held at 25 cm directly above the substrate. After deposition, the samples were left to cool down to room temperature and then taken for characterization.

The thickness of the films was measured using a 2D surface profilometer (Alpha-step D-100, KLA-Tencor, USA). Crystal structure and orientation of the films were examined using an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), in the  $2\theta$  scan range from  $10^\circ$  up to  $70^\circ$ . The average grain sizes were evaluated using the Debye–Scherrer equation from broadening of diffraction peaks. Optical transmittance was measured between 300 and 800 nm range of wavelengths using a UV/Vis/NIR spectrophotometer (Lambda-750, Perkin-Elmer, America). The optical band gap and Urbach energy were obtained from transmission spectrum data. The electrical properties were determined from the sheet resistance using the four point probe equipment comprising of a Signatone probe station, an EZ GP-4303 d.c. source and two Keithley 197 digital multimeters for voltage and current measurements.

### 3. Results and discussion

#### 3.1. Structural properties

Fig. 1 shows XRD patterns of undoped ZnO and GZO thin films of almost similar thicknesses ranging between 350 and 400 nm, prepared on glass substrates at 723.15 K. Weak (100), (002), (101), (210) and (103) diffraction peaks were observed in most samples, except the absence of the (100) peak in undoped ZnO thin films. All films were polycrystalline with a hexagonal wurtzite structure and a strong orientation along the (002) plane, regardless of the

amount of Ga doping. This was in agreement with sprayed GZO thin films by Rao and Kumar [21]. Contrary to our findings, Lohkhande and Uplane [22] obtained sprayed ZnO thin films with a preferred growth orientation along the (100) plane. The (002) plane's intensity was observed to decrease for films with higher Ga content and Babar et al. [23], attributed this crystallinity deterioration to crystal reorientation effect emanating from incorporation of more Ga atoms. Winer et al. [8], reported that mechanical stresses caused by differences in the ionic radii of the dopant and Zn may be the possible cause of degradation in crystallinity at higher doping concentrations. Reddy et al. [24] observed a relative decrease in the (002) peak intensity for films with smaller thicknesses, so the slight reduction of thickness values in our films may also be responsible for the decrease in intensity. No extra peaks corresponding to neither Zn or Ga nor Ga<sub>2</sub>O<sub>3</sub> were observed indicating the absence of secondary phase formation in our films. This shows that Ga managed to substitute Zn and can reasonably reside on zinc site in the hexagonal lattice [25].

The mean crystallite size for each sample was calculated according to broadening of the dominant peak corresponding to the (002) diffraction plane using Debye–Scherrer's formula [18]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (1)$$

where  $D$ ,  $\lambda$ ,  $\beta$ , and  $\theta$  are the mean crystallite size, X-ray wavelength (1.5418 Å), FWHM in radians and Bragg's diffraction angle, respectively. The dislocation density  $\delta$  was also calculated using [26]:

$$\delta = \frac{1}{D^2}, \quad (2)$$

where  $D$  is the mean crystallite size. The (002) peak positions, FWHM, mean crystallite sizes and dislocation densities with respect to Ga doping are shown in Table 1.

Ga doping led to the increase in FWHM values and a decrease in the mean grain sizes. From Table 1, it is clear that an increase in Ga content leads to an increase in the dislocation density, which in turn results in the observed reduction of the films' crystallinity qualities. The (002) peak position of GZO thin films showed a slight shift towards a higher Bragg angle relative to that of undoped ZnO thin films. This may be due to a slight increase in relative strain [23] originating from the substitution of Zn<sup>2+</sup> ions with relatively smaller Ga<sup>3+</sup> ions [7].

The lattice parameters  $a$  and  $c$  were calculated using the equation [27,28]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}, \quad (3)$$

where  $d_{hkl}$  is the interplanar spacing obtained from Bragg's law, and  $h$ ,  $k$  and  $l$  are the Miller indices denoting the plane. Ga doping did not produce a significant change in the lattice parameters since the undoped ZnO and all GZO films had approximately equal lattice parameters,  $a = 3.21 \text{ \AA}$  and  $c = 5.14 \text{ \AA}$ . These values are slightly less than those for bulk ZnO,  $a = 3.22 \text{ \AA}$  and  $c = 5.2 \text{ \AA}$ ,

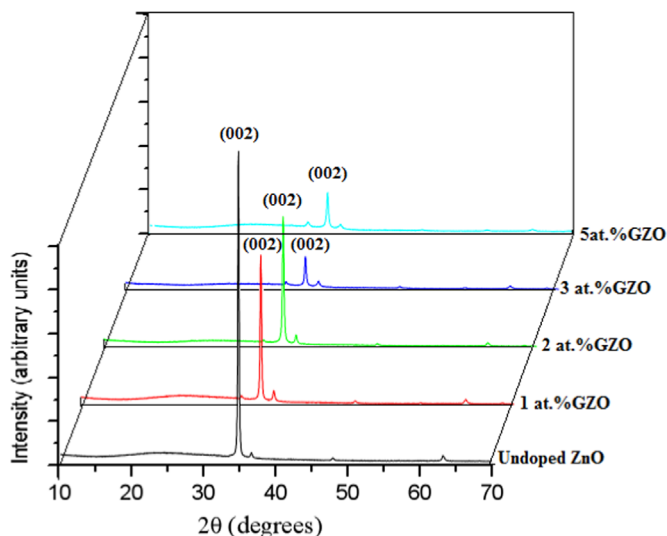


Fig. 1. XRD patterns of undoped ZnO and GZO thin films deposited on glass substrates at 723.15 K.

Table 1

The (002) peak position, FWHM, grain size and dislocation density of undoped ZnO and GZO thin films.

GZO (at%)	(002) peak position $2\theta$ ( $^\circ$ )	$\beta$ ( $^\circ$ )	$D$ (nm)	$\delta$ ( $\times 10^{-4} \text{ nm}^{-2}$ )
0	34.899	0.198	42.04	5.66
1	34.899	0.207	40.20	6.19
2	34.917	0.244	34.12	8.59
3	34.917	0.251	33.21	9.07
5	34.899	0.290	28.68	12.16

Download English Version:

<https://daneshyari.com/en/article/1459091>

Download Persian Version:

<https://daneshyari.com/article/1459091>

[Daneshyari.com](https://daneshyari.com)