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Low temperature synthesis of radio frequency magnetron sputtered gallium and aluminium co-doped zinc oxide thin films for transparent electrode fabrication

E. Muchuweni*, T.S. Sathiaraj, H. Nyakotyo

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

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ABSTRACT

Gallium and aluminium co-doped zinc oxide (GAZO) thin films were prepared on glass substrates at low temperatures by radio frequency (rf) magnetron sputtering and their physical properties were investigated. All films possessed a hexagonal wurtzite crystal structure with a strong growth orientation along the (0 0 2) c-axis. The (0 0 2) peak intensity and mean crystallite size increased with substrate temperature from room temperature (RT) to 75 °C and then decreased at 100 °C, indicating an improvement in crystallinity up to 75 °C and its deterioration at 100 °C. Scanning electron microscopy (SEM) micrographs revealed the strong dependency of surface morphology on substrate temperature and energy dispersive spectroscopy (EDS) confirmed the incorporation of Ga and Al into the ZnO films. All films exhibited excellent transmittances between 85 and 90% in the visible region and their optical band gap increased from 3.22 eV to 3.28 eV with substrate temperature. The Urbach energy decreased from 194 meV to 168 meV with increasing substrate temperature, indicating a decrease in structural disorders which was consistent with X-ray Diffraction (XRD) analysis. Films deposited at 75 °C exhibited the lowest electrical resistivity (2.4 Ωcm) and highest figure of merit ($7.5 \times 10^{-5}\ \Omega^{-1}$), proving their potential as candidates for transparent electrode fabrication.

1. Introduction

Zinc oxide (ZnO) has attracted more research attention in the past few decades due to its high optical transparency, low electrical resistivity, low cost, abundance and non toxicity [1]. ZnO has proved to be a potential replacement material for the commonly used indium tin oxide (ITO) which inspite of its excellent electrical and optical properties [2], faces the limitations of high cost, scarcity and toxicity [3,4]. Thin films of ZnO have found enormous applications especially as transparent electrodes in optoelectronic devices such as solar cells and flat panel displays [1,5].

Undoped ZnO has a relatively high resistivity and its electrical and optical properties can be appreciably improved by appropriate doping with group III elements such as aluminium (Al) [5] and gallium (Ga) [6]. However, as compared to Al, Ga is less reactive and hence less prone to oxidation during film deposition [7]. Also the atomic radius of Ga which is close to that of Zn allows it to substitute for Zn in the ZnO lattice with very little strain [8]. Furthermore, Ga-doped ZnO (GZO) has better electronic stability as compared to Al-doped ZnO (AZO) when exposed to moisture [9]. Co-doping ZnO with both Ga and Al has been reported to be more favourable since the shortcomings of Al will be redeemed by Ga [10].

Doped ZnO thin films have been deposited by various techniques such as rf magnetron sputtering [1], pulsed laser deposition [11], electron beam evaporation [12], spray pyrolysis [5,6] and spin coating [13]. RF magnetron sputtering is more preferable to others because of its simplicity, less expensive equipment, production of highly uniform films and suitability for large area deposition [14,15]. Sathiaraj [2] reported that sputtering is being frequently used due to its high deposition rate, strong adhesion of the films to the substrate and good reproducibility.

The substrate temperature has been reported as an important parameter which when optimized can improve the optical and electrical properties of rf magnetron sputtered thin films [16]. However, Zhang et al. [17] reported that studies of ZnO thin films prepared at low temperatures have remained limited so far. Also to the best of our knowledge, only a few detailed studies have reported on GAZO thin films [18] prepared by low temperature rf magnetron sput-

* Corresponding author.
E-mail address: muchuweniedigar1@gmail.com (E. Muchuweni).

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tering. Therefore in this study, we report the effect of substrate temperature on the structural, optical and electrical properties of GAZO thin films prepared by rf magnetron sputtering, for transparent electrode fabrication.

2. Experimental details

Thin films of GAZO were prepared by low temperature rf magnetron sputtering on glass substrates using a 99.99% purity Ga/Al/ZnO (1.14/0.62/98.24 wt%) target (HHV, UK) measuring 76.2 mm and 3 mm in diameter and thickness, respectively. The substrates were initially cleaned with acetone, isopropanol and finally with deionized water for 15 min in each step with the help of an ultrasonic bath and dried before loading them to the work holder of the HHV TF500 Thin Film Deposition System at a fixed target-substrate distance of 13 cm. Before deposition, the sputtering chamber was evacuated to a base pressure of about 1.13×10^{-5} mbar, after which the GAZO thin films were deposited at substrate temperatures from RT up to 100 °C. During deposition, the rf power was maintained at 250 W, the flow rate of pure argon was kept constant at 12 sccm and the working pressure was maintained at about 1.20×10^{-2} mbar. Film thickness was varied from 360 nm to 500 nm by varying the deposition time.

The film thickness was measured using a 2D surface profilometer (Alpha-step D-100, KLA-Tencor, USA). The crystal structure and orientation of the film were examined by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) using Cu Kα radiation (λ = 1.5418 Å). The surface morphology and elemental composition were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7100F, Japan) and EDS, respectively. The optical transmission spectra were obtained using a UV/Vis/NIR spectrophotometer (Lambda-750, Perkin-Elmer, USA) in the wavelength region 300–800 nm. The electrical resistivity was determined at RT from Current–Voltage (I–V) measurements using the Keithley Four-point probe equipment.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD spectra of GAZO films deposited at four different substrate temperatures (RT, 50, 75 and 100 °C). A strong (0 0 2) diffraction peak was detected in all films, suggesting that they grow perpendicular to the substrate. The (0 0 2) peak intensity increased with substrate temperature from RT to 75 °C indicating an improvement in crystallinity due to the settling of atoms in stable positions as the substrate temperature rises [15]. However, the appearance of (1 0 0) and (1 0 1) secondary peaks of ZnO in films deposited at 100 °C, caused their relatively low (0 0 2) peak intensity [19]. This was consistent with Cho [16] and Singh et al. [20] who also obtained low (0 0 2) peak intensities at 100 °C and 150–250 °C, respectively, due to the appearance of (1 0 0) and (1 0 1) reflections of ZnO. Another possible cause for the observed decrease in the (0 0 2) peak intensity of our GAZO thin film at 100 °C may be its relatively smaller film thickness because thinner ZnO films are known to have low (0 0 2) intensities than thicker ones [21,22]. In a similar study, Ondo-Ndong et al. [23] reported of an increase in the (0 0 2) peak intensity of ZnO thin films with the substrate up to 100 °C, afterwhich it started to decrease, suggesting an improvement in crystallinity up to 100 °C and its deterioration above 100 °C. Contrary to their findings, Cho [16] observed the crystallinity of ZnO thin films to be poor at 100 °C and then increased with substrate temperature above 100 °C. Neither Zn, Ga and Al characteristic peaks nor Ga_2O_3 and Al_2O_3 peaks were observed on the XRD spectra indicating that the incorporation of Ga and Al dopants did not affect the ZnO lattice structure since no new phase formation occurred.

Table 1
The dependence of *FWHM*, *D* and d_{hkl} with substrate temperature.

Substrate Temperature (°C)	β (°)	D (nm)	d_{hkl} (Å)
RT	0.905	9.20	2.591
50	0.844	9.86	2.590
75	0.650	12.81	2.587
100	0.897	9.28	2.587

The mean crystallite size (D) shown in Table 1 was calculated using the Debye-Scherrer formula [2]:

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

where λ, β and θ are the X-ray wavelength (1.5418 Å), full width at half maximum (FWHM) of the (0 0 2) peak in radians and Bragg's diffraction angle, respectively. The FWHM of the (0 0 2) peak decreased and the mean crystallite sizes increased with substrate temperature from RT to 75 °C as shown in Table 1, indicating an enhancement of the film's crystalline nature. However, a slight increase in FWHM values and decrease in mean crystallite sizes occurred in films deposited at 100 °C and this was ascribed to their relatively smaller thickness and the appearance of the (1 0 0) and (1 0 1) crystallographic orientations. This behaviour is in close agreement with Rosa et al. [24] who observed an increase in the mean crystallite size of rf sputtered ZnO thin films from 9 to 12 nm with increasing substrate temperature up to 100 °C and a brief decrease thereafter.

Fig. 2 shows the (0 0 2) peak position and lattice parameter c as a function of substrate temperature. The (0 0 2) peak positions for all films were slightly higher than the bulk ZnO value (34.467^0) and they shifted to higher values with increasing substrate temperature. This

produced relatively smaller lattice parameter c values as compared to $c = 5.2$ Å for bulk ZnO (Crystallography Open Database, COD 10 11 258). This observation was consistent with Wu et al. [1]. The lattice parameter *c* was calculated using the equation [25]:

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

where *a* and *c* are the lattice parameters, d_{hkl} is the interplanar spacing (shown in Table 1) obtained from Bragg's law and *h*, *k* and *l* are the Miller indices denoting the plane. The existence of very small amounts of compressive strain and tensile stress in the films originating from the substitution of Zn^{2+} ions with relatively smaller Ga^{3+} and Al^{3+} ions [26,27] and the thermal mismatch between substrates and films [28] may be the possible causes for the shift in (0 0 2) peak positions and subsequently lower d_{hkl} and c values. Interestingly, the values for the (0 0 2) peak position and lattice parameter c for our GAZO thin films were closer to those of bulk ZnO thin films as compared to those for GZO thin films in our previous study [6]. This shows that GAZO thin films can be prepared with very slight distortions of the ZnO lattice when compared to the GZO thin films.

3.2. Surface morphology and elemental composition

Fig. 3 shows the FE-SEM micrographs of the GAZO thin films deposited at (a) RT, (b) 50 °C, (c) 75 °C and (d) 100 °C. From Fig. 3(a) and (b), uniformly covered surfaces with small and near spherical grains of an estimated size of 30 nm and 50 nm were respectively observed in RT and 50 °C deposited films and these tended to coalesce forming larger grains. However, at 75 °C there was a structural transition in the surface morphology as evidenced by the forma-