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Crystal, optical, and electrical characteristics of transparent conducting gallium-doped zinc oxide films deposited on flexible polyethylene naphthalate substrates using radio frequency magnetron sputtering

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ABSTRACT

Gallium-doped zinc oxide (GZO) thin films were deposited on flexible polyethylene naphthalate substrates using radio frequency (RF) magnetron sputtering. The resulting GZO thin films were polycrystalline, displaying a hexagonal wurtzite-type crystal structure with a preferred grain orientation in the (002) direction. The covalent bond length of the films decreased as the RF deposition power increased, an inverse trend to that of the residual stress. In the transmission spectra, the absorption edge was about 380 nm, and the optical transmittance decreased from 93.2% to 88.6% in the visible range as the RF deposition power increased from 75 to 150 W. A minimum resistivity of $2.994 \times 10^{-3}\ \Omega$-cm was obtained for the film deposited at 125 W, with a Hall mobility of $8.652\ cm^2\ V\ s^{-1}$ and a carrier concentration of $6.3417 \times 10^{19}\ cm^{-3}$. The figure of merit results indicated that the film deposited at 125 W possessed satisfactory optical and electrical properties for potential applications.

1. Introduction

Indium tin oxide (ITO) is the best choice of transparent conducting (TCO) thin film for its low resistivity ($10^{-4}\ \Omega$-cm) and high transmittance (90%), and it is widely used in solar cell applications, flat panel displays, and light-emitting diodes [1–3]. However, the limited availability of indium makes ITO relatively expensive [4]. To overcome this drawback, researchers have been studying other TCO materials as potential alternatives [5–7]. Zinc oxide (ZnO) seems to be the most promising contender for a wide variety of TCO applications because it is nontoxic, inexpensive, and has good stability. Undoped ZnO thin films typically exhibit *n*-type conduction, with a background electron concentration as high as $10^{21}\ cm^{-3}$ [8,9]. Many studies have found that trivalent element-doped ZnO exhibits marked electrical conductivity [10–12]. The conductivity of a ZnO thin film can be improved by adding dopant elements such as aluminum (Al) [13], gallium (Ga) [14], indium (In) [15], molybdenum (Mo) [16], fluorine (F) [17], and co-doped In and Ga [18]. Ga-doped ZnO (GZO) films have certain merits in comparison with Al-doped ZnO films (AZO); for example, the atomic radii and covalent bond lengths of Ga—O and Zn—O are very similar [19], and Ga is less reactive and more resistant to oxidation than Al [20].

Recently, it has become increasingly necessary to study the deposition process of TCO thin films on polymer substrates, as these substrates are suitable for flexible electronic devices [21,22]. Glass substrates are too heavy, fragile, and brittle for manufacturing, whereas polymer ones are remarkably flexible, light, and easy to handle. TCO thin films prepared on flexible substrates of polyethylene terephthalate (PET), polyimide (PI), or polyethylene naphthalate (PEN) have been reported [23–25]. PI and PEN generally possesses higher transparency, melting point, and mechanical strength than PET.

Several studies using different deposition methods have been reported, such as sol–gel processes [26], pulsed laser deposition [27], sputtering [28], evaporation [29], and atomic layer deposition [30]. The radio frequency (RF) sputtering method is an effective technique due to its ability to produce reasonable quality thin films. In this work, GZO thin films with high transmittance and low resistivity were grown on flexible PEN substrates using an RF magnetron sputtering technique at various RF deposition powers. The crystallographic, optical, and electrical properties of the films were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), UV–vis spectroscopy, and Hall measurement.

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2. Experimental procedures

GZO thin films were deposited on flexible PEN (Teonex®, Teijin DuPont Films) substrates with a 2 in. $ZnO:Ga_2O_3$ (97:3 wt%) ceramic target (Summit-Tech., Co.), using an RF magnetron sputtering system. The area of flexible PEN substrate is 2×2 cm. The flexible PEN substrates were ultrasonically cleaned sequentially in acetone, alcohol, and deionized water, then dried with nitrogen (N_2) gas. The working distance between the flexible PEN substrate and target was fixed at 12 cm. The base pressure was 8×10^{-6} Torr, and then, argon (Ar) gas was introduced into the sputtering chamber through a standard mass flow controller. The working pressure was set to 5×10^{-3} Torr. The deposition temperature of the GZO thin films was kept at room temperature, and the RF power was varied from 75 to 150 W. The surface morphology and thickness of the films were measured using FE-SEM (JEOL-6700). The crystalline structures were determined by grazing incidence X-ray diffraction (GIXRD) (Bede D1) using CuKα radiation (Kα = 1.5418 Å). The resistivity (ρ), carrier concentration (n_e), and carrier mobility (μ) were obtained from Hall-effect measurements (HMS-3000) using the Van der Pauw method. Optical transmittance was measured with a UV–vis spectrophotometer in the wavelength range of 200–1100 nm.

3. Results and discussion

The crystal structure and orientation of the GZO thin films grown at various RF deposition power levels on a flexible PEN substrate were investigated via their XRD patterns, which are presented in Fig. 1. All the films exhibited a dominant (002) peak with slight (100) peak in the diffraction angle (2θ) range of 25–55°. The XRD patterns showed the characteristic peaks of ZnO (JCPDS no. 36-1451), and only the hexagonal wurtzite structure was found; no secondary or unknown phases were detectable. Neither the peaks characteristic of metallic zinc and gallium nor a gallium oxide peak were observable, implying that Ga atoms substituted for the Zn atoms in the hexagonal lattice. These Ga atoms may have occupied the interstitial sites in ZnO; more likely is that the Ga atoms were segregated in the non-crystalline region in the grain boundaries and formed Ga—O bonds.

The XRD patterns also exhibited the (002) diffraction peaks of the GZO crystallization preferential orientation along the c-axis at 2θ near 34.31°. The intensity of the (002) peak increased with the RF deposition power, suggesting that better crystalline quality was obtained by using more power. The c-axis orientation of the films can be explained by the "survival of the fastest" model proposed by Drift [31]. This result is similar to results achieved with Al-doped ZnO (AZO) and Ti-doped ZnO (TZO) thin films [32,33].

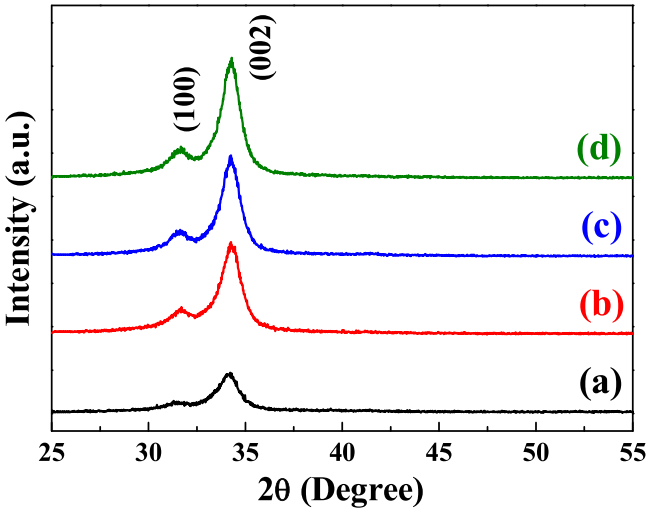

Fig. 1. XRD patterns of GZO thin films deposited using different RF power levels: (a) 50 W, (b) 75 W, (c) 100 W, and (d) 125 W.

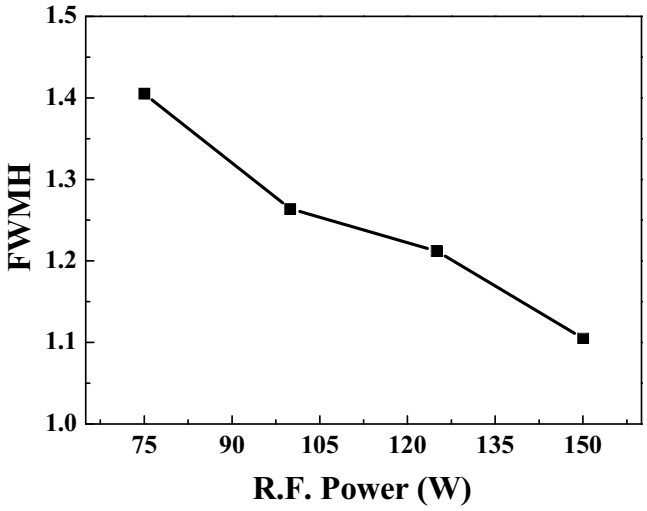

Fig. 2. The FWHM values of GZO thin films deposited using different RF power levels.

One important factor in judging crystal quality is the full width at half maximum (FWHM) of the (002) diffraction peak for GZO thin films. From the FWHM, we could then judge the various films' crystal quality. It used Gaussian fitting to estimate the FWHM values from the XRD diffraction peaks. The FWHM values decreased from 0.360° to 0.198° as the RF deposition power increased from 75 to 150 W. These results indicate that a higher RF deposition power may have improved the crystallinity of the GZO thin films by causing small crystallites to coalesce and make larger crystallites [34]

It is known that all the thin films formed had stress during the deposition process. The residual stress in a thin film depends on the degree of energetic particle bombardment—that is, energy striking the condensing film during sputter deposition with plasma discharge [35,36]. Fig. 3 shows the residual stress (σ) and covalent bond length (L) of the GZO thin films. The residual stress can be expressed as [37]

$$\sigma = \frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{2C_{13}} \times \frac{c - c_0}{c_0} \quad (1)$$

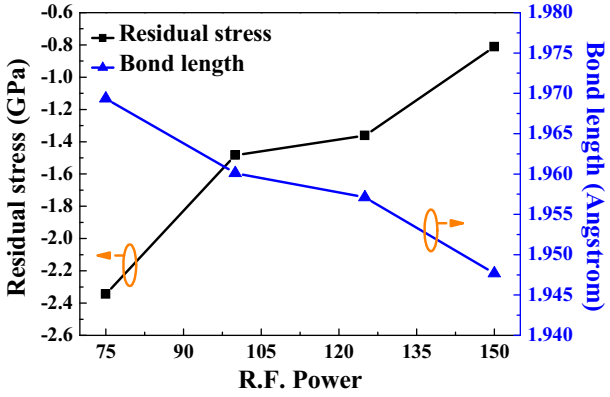

Fig. 3. Residual stress and bond length of Zn—O in GZO thin films deposited using different RF power levels.