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Effects of thickness and annealing on the properties of Ti-doped ZnO films by radio frequency magnetron sputtering

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ABSTRACT

Ti-doped ZnO (TZO) thin films were prepared by radio frequency magnetron sputtering with a target containing 1.5 wt% TiO_2 on glass substrates at 300 °C and then thermally annealed in a hydrogen ambient. The structural, electrical, and optical properties of TZO films were investigated with respect to the variation of film thickness and annealing condition. X-ray diffraction analysis exhibited that all TZO films had a (0 0 2) peak at 2θ ~34°, indicating that the films were hexagonal wurtzite structure and showed a good c-axis orientation perpendicular to the substrate. As film thickness increased from 30 to 950 nm, the crystallite size increased from 11.9 to 36.8 nm and the surface roughness increased from 0.57 to 1.78 nm. The film resistivity decreased from 3.94×10^{-2} to 1.06×10^{-3} Ω cm. To enhance the characteristics of TZO films for transparent conductive oxide applications, the films were subsequently annealed at temperatures ranging from 300 to 500 °C in hydrogen or argon ambient for various times. The results indicated that hydrogen annealing made film resistivity decrease more than argon annealing. The resistivity of the hydrogen-annealed film monotonically decreased with increasing annealing time up to 90 min. At the optimal annealing condition (400 °C, 60 min), the film resistivity decreased by 57% and the average optical transmittance in the visible wavelength range (400–700 nm) increased slightly as compared to the as-deposited films. The enhanced characteristics of the annealed TZO film are attributed to desorption of negative charged oxygen species and passivation of surface and defects at grain boundaries.

1. Introduction

Transparent conducting oxide (TCO) films such as indium tin oxide (ITO), tin oxide (SnO_2) and zinc oxide (ZnO) have been widely studied for applications such as solar cells, flat panel displays, and other optoelectronic devices [1–10]. Among these TCOs, ZnO is one of the most favorable materials because of its abundant, relatively low cost, good stability in hydrogen plasma process, and non-toxicity [5–10]. However, undoped ZnO thin films have unstable electrical properties because the sheet resistance of the films varies under either oxygen chemisorption or desorption. There is a considerable interest in understanding the electrical and transport properties of doped ZnO films. Many studies have found that the trivalent element-doped ZnO exhibits marked electrical conductivity [3–10]. Besides, Ti-doped ZnO (TZO) thin films are also possible alternative and have been reported previously [11–16]. Ti^{4+} has a radius of 0.68 Å, which is smaller than that of Zn^{2+}, 0.74 Å, and could be incorporated as an interstitial and acted as a scattering site. However, only a small amount of doped Ti^{4+} could induce more electrons and avoid acting scattering centers. Chung et al. [13] investigated the properties of Ti-doped ZnO films doped with different TiO_2 contents and reported that the lowest resistivity of TZO films was achieved as the Ti addition was 1.34%. Lin et al. [14] studied the effects of substrate temperature on the properties of TZO films by simultaneous RF and DC magnetron sputtering. Among these literatures, few studies report the influence of annealing on the characteristics of TZO thin films.

In this study, transparent conducting Ti-doped ZnO thin films were deposited on glass substrates by RF magnetron sputtering. The dependence of film thickness and annealing treatment on the structural, electrical, and optical properties of TZO thin films were investigated.

2. Experimental procedures

TZO thin films were deposited on glass substrates (Corning 1737) in a RF magnetron sputtering system with a ceramic target made of 98.5 wt% ZnO (99.999%) and 1.5 wt% TiO_2 (99.999%)

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powders. The substrates with an area of 33 × 33 mm^2 were cleaned with isopropyl alcohol (IPA) and deionized (DI) water, and then dried under blown nitrogen gas. The working distance was fixed at 10 cm. The base pressure was 5 × 10^{-6} Torr and the working pressure was maintained at 5 × 10^{-3} Torr. The deposition temperature was kept at 300 °C and the RF power was 100 W. The thickness of TZO thin films varied from 30 to 950 nm. The as-deposited TZO films with a thickness of 330 nm were subsequently annealed in a hydrogen or argon atmosphere at temperatures of 300–500 °C for different times using a horizontal furnace.

Film thickness was measured using a spectroscopic ellipsometer (Nano-view SE MF-100). Films crystallinity was analyzed using X-Ray diffraction (XRD) (PANalytical) with Cu-Kα radiation ($\lambda = 1.54056$ Å). Morphology of films was observed using field emission scanning electron microscopy (FE-SEM) (JEOL, JSM-6700) and atomic force microscopy (AFM) (Digital Instrument, NS4/D3100CL/Multimode). Electrical resistivity was determined by a four-point probe (Napson RT-70). Carrier concentration and Hall mobility were obtained from Hall-effect measurement by the Van der Pauw method (Ecopia, HMS-3000). Optical transmittance was measured by a UV/VIS/IR spectrophotometer (Jasco, V-570) in the 220–2500 nm wavelength range. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the deposition rate of the TZO thin films for various thicknesses. When the film thickness ranged from 30 to 220 nm, the deposition rate decreased rapidly with increasing film thickness. As the film thickness increased beyond 220 nm, the deposition rate decreased slightly and finally saturated at about 8.3 nm/min. This phenomenon may be attributed to that the structure of the film tends to be porous and loose at the initial deposition stage; as the film thickness increases, the grains become densely packed [17].

Fig. 2 shows the XRD spectra of the TZO thin films deposited at 300 °C as a function of film thickness. All films exhibited a (0 0 2) peak at 2θ ~34°, indicating that the TZO films prepared by RF magnetron sputtering had a hexagonal wurtzite structure and showed a good c-axis orientation perpendicular to the substrate. The c-axis orientation in the TZO films can be explained by the "survival of the fastest" model proposed by Drift [18]. This result is similar with that of ZnO:Al and ZnO:Ga films [7,10,17]. Besides, there was no TiO_2 phase found from the XRD spectra, implying that titanium may replace zinc in the hexagonal lattice or segregate to the non-crystalline region in grain boundaries. When the film thickness increased from 30 to 950 nm, the positions of the (0 0 2) diffraction peaks are within 34.06° ± 0.03°. Moreover, the intensity

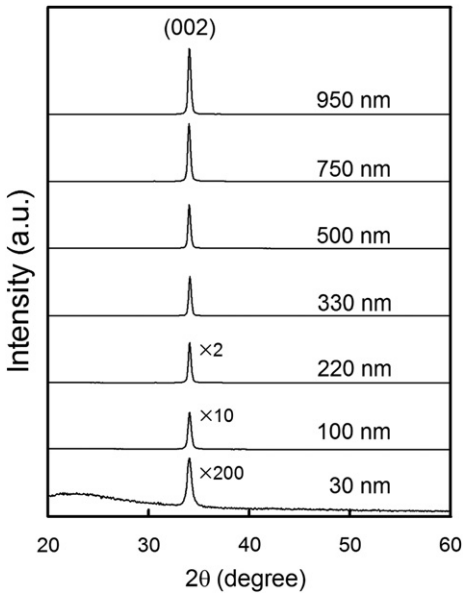

Fig. 2. XRD spectrum of the TZO thin films with various film thickness.

of the (0 0 2) peak increased with the increase of the film thickness. The XRD result indicates that the crystallinity of the TZO films improved as the films thickness increased.

Fig. 3 shows the dependence of the full width at half-maximum (FWHM) and grain size on thickness of the TZO thin films. The grain size can be estimated using Scherrer's formula [19],

$$D(\text{crystal size}) = (0.94\lambda)/(\beta\cos\theta) \quad (1)$$

where $\lambda = 1.54056$ Å and β is the FWHM. As the film thickness increased from 30 to 950 nm, the FWHM decreased from 0.81° to 0.26° and the grain size increased from 11.9 to 36.8 nm. As the film grows thicker, the larger grain is formed via the aggregation of small grains or grain boundary movement [20].

The dependence of the surface roughness on thickness of the TZO thin films was studied by AFM. Fig. 4 displays the AFM micrographs (1 μm × 1 μm) of the TZO films with various thicknesses. When the film thickness was very thin (30 nm), some hillocks occurred obviously, as Fig. 4(a) displayed, due to the film tending towards porous and loose. Ohring [21] has proposed that local mass flux divergences exist throughout the film due to varying grain size and distributions. When atoms come into a grain more than leave it, the pileup or growth of the mass can be expected. The

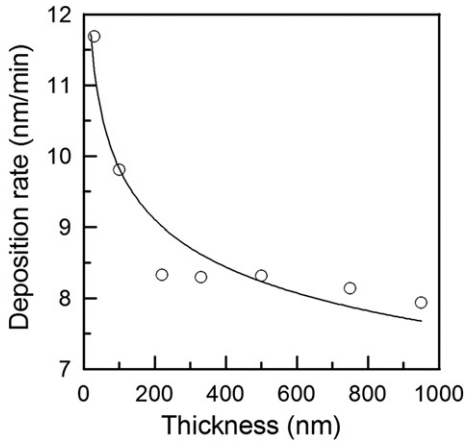

Fig. 1. Deposition rate of the TZO thin films as a function of film thickness.

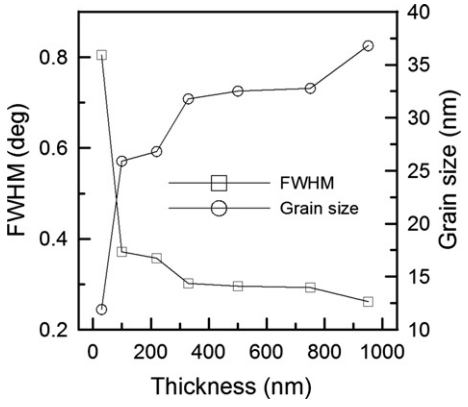

Fig. 3. Full width at half-maximum (FWHM) and grain size of the TZO thin films as a function of film thickness.