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Quality improvement of high-performance transparent conductive Ti-doped GaZnO thin film

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ABSTRACT

Ti-doped GaZnO transparent conductive oxide films were deposited at various substrate temperatures by radio-frequency magnetron sputtering to examine the effects of crystalline quality on thin-film optoelectronic properties. The results show a low resistivity of 2.97×10^{-4} Ω-cm and a high optical transmittance of 94.15% (wavelength region of 400–800 nm) in 300-nm-thick Ti-doped GaZnO thin films grown at the substrate temperature of 300 °C, with a post-annealing temperature of 400 °C. To evaluate the performance of Ti-doped GaZnO transparent conductive oxide films, this study employed the figure of merit (Φ_{TC}), expressed as $\Phi_{TC} = T^{10}/R_S$ (T: transmittance R_S: sheet resistance), and calculated as 55.2×10^{-3} Ω^{-1}, which is suitable for high-performance optoelectronic device applications.

1. Introduction

Transparent conductive oxide (TCO) thin films have been extensively studied in recent years because of their high transmittance and electrical conductivity in various optoelectronic devices. Indium tin oxide (ITO) is the most used transparent conducting oxide film in the industry [1]. Recently, concerns regarding the availability of the indium element have arisen, causing increased fabrication cost of ITO thin-film based applications. Zinc oxide (ZnO) thin films have been regarded as one of the most competitive TCOs because of their low material cost, high stability, ease of doping, non-toxicity and optical/electrical properties that are comparable to those of ITO [2–4].

Among the potential candidates of Group III-doped ZnO, gallium-doped ZnO (GZO) seems to be the most advantageous and favorable. The low reactivity of gallium dopant with oxygen atoms and high electron carrier concentration make GZO-based optoelectronic devices highly reliable. Compared with the Group III elements, TiO_2-doped ZnO (TZO) exhibits Ti^{4+} (ionic radius: 0.68 Å) substitution for Zn^{2+} (ionic radius: 0.72 Å) ions; hence, it behaves as a donor providing an extra two free electrons, thus increasing the thin-film conductivity [5]. Although the Ti atoms may be interstitially incorporated into the ZnO hexagonal crystal lattices, a moderate concentration of Ti atoms not only reduces the number of Ti^{4+} carrier scattering centers but also increases the preferential c-axis orientation and optical transmittance in ZnO-based thin films [6,7]. Therefore, in this study, we propose a combination of the advantages of Ga and Ti elemental doping in ZnO as a high performance Ti-doped GaZnO (GTZO) for future applications in optoelectronic devices.

Numerous approaches have been adopted to prepare TCO film, including chemical vapor deposition, pulsed laser deposition, radio-frequency (RF) magnetron sputtering, molecular beam epitaxy and the sol–gel method [8,9]. Among these deposition methods, RF magnetron sputtering is extensively used in industry; it is regarded as an effective technique for preparing TCO films because it is relatively inexpensive, provides a high deposition rate, has strong adhesion and maintains a highly uniform thickness over a large wafer area [10].

However, the substrate temperature during thin-film deposition plays an important role in regard to the crystalline quality. Furthermore, the migration length of the absorbed atoms on the thin-film surface is closely related to the substrate temperature. Surface adatoms on thin films deposited on low-temperature substrate typically exhibit short migration length, and tend to form a crystal structure with high porosity and rough surface properties. On the other hand, thin films deposited at high substrate temperatures provide energy for surface atoms, thereby enhancing the ability of diffusion that could improve thin-film smoothness and crystal quality [11,12]. Therefore, this study reports on high-performance Ti-doped GZO thin film deposited by RF magnetron sputtering techniques with optimized substrate and post-growth annealing temperatures (Ta), demonstrating high potential for employment in displays and lighting applications.

2. Experiment

Ti-doped GZO films were grown with a 3-in. $ZnO/Ga_2O_3/TiO_2$ (96/3/1 wt.%, purity 99.99%) target. All Ti-doped GZO films were deposited by RF magnetron sputtering on glass substrates. Prior to deposition, the targets were pre-sputtered for 3 min. The sputtering chamber was evacuated with a high-vacuum pressure of approximately 5.3×10^{-4} Pa, and a working pressure of 6.7×10^{-1} Pa was maintained with an argon (Ar)

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gas flow of 30 sccm. The RF sputtering power was 150 W. The GTZO films were then deposited at substrate temperatures (Ts) from room temperature (RT = 25 °C) to 500 °C. The schematic illustration of the substrate heating system within the sputtering system is shown in Fig. 1. During deposition, the chamber was cooled using a water-cooled chiller system, and the thickness of the deposited GTZO film was maintained at 300 nm for preferable TCO optoelectronic properties and reduced fabrication cost [13,14]. The GTZO samples were then thermally post-annealed for 3 min in nitrogen ambient at temperatures of 400 (Ta 400) and 500 °C (Ta 500) in a rapid thermal annealing (RTA) system.

The electrical resistivity, electron mobility and carrier concentration were measured using a Hall measurement system by employing the van der Pauw configuration at RT. The crystallite structural properties were examined using X-ray diffraction (XRD) with operational voltage and current of 40 kV and 40 mA, respectively, and a Cu-Kα (λ = 1.54052 Å) irradiation source in a configuration of grazing incident X-ray diffraction scan with 2theta scanning angle from 30 to 50°. The optical transmittance was determined using a UV–VIS spectrophotometer with reference to a glass substrate over a range of optical wavelengths from 300 to 800 nm. The photoluminescence (PL) measurements were performed under 200 mW He–Cd laser excitation at a wavelength of 325 nm at RT. The chemical states of the Ti-doped GZO were analyzed at a base pressure of 1.0×10^{-8} Pa by X-ray photoelectron spectroscopy (XPS) with a Microfocus Monochromatic Al Kα radiation (1486.6 eV) source operated at 108 W. The surface of all samples was cleaned for 5 min with an Ar ion beam with a size of 1 mm generated using voltage and current of 3 kV and 1 μA, respectively. The XPS signals were calibrated using 285.3 eV for C1s as a reference element. The optoelectronic characteristics of as-grown GTZO thin films were also adopted as a reference sample for comparison in subsequent analysis. All of the samples were measured under the same conditions to ensure reliable results.

3. Results and discussion

Fig. 2(a) shows the XRD patterns of 300 nm-thick Ti-doped GZO films with substrate temperatures from room temperature (RT = 25 °C) to 500 °C. The diffractogram patterns of the Ti-doped GZO films show that all of the XRD patterns exhibit a prominent (002) peak (JCPDS No.89-1397 (ZnO)). Fig. 2(b) shows a summary of the XRD results of the Ti-doped GZO thin film with different substrate temperatures from room temperature (RT = 25 °C) to 500 °C. All of the GTZO films exhibit a prominent ZnO (002) peak, which indicates a wurtzite structure preferentially oriented along the c-axis, perpendicular to the

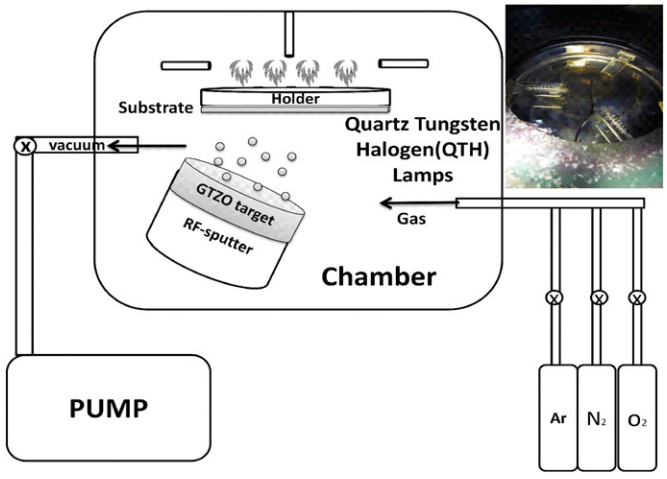

Fig. 1. The schematic illustration of the substrate heating system in the sputtering system; the picture of the heating system with the quartz tungsten halogen lamps is shown as the inset.

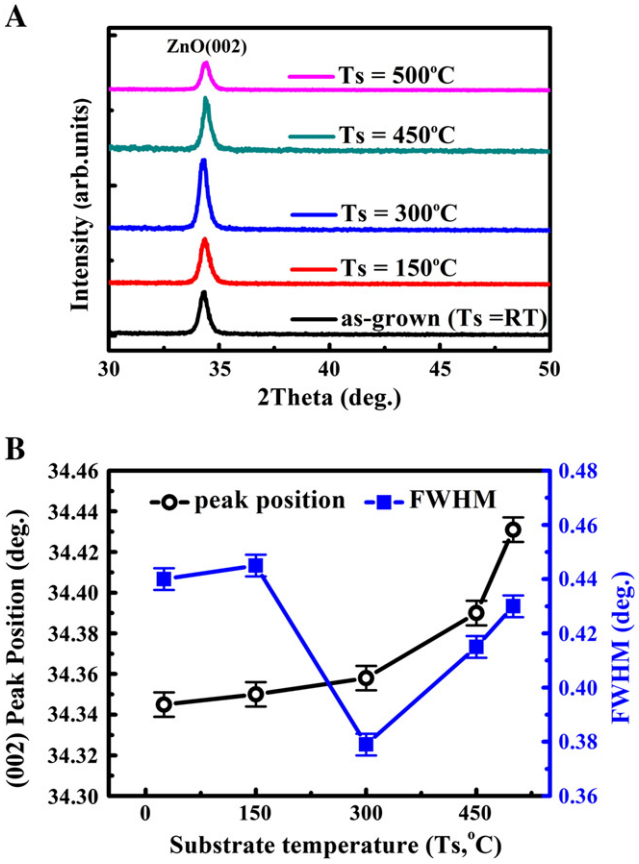

Fig. 2. (a) XRD patterns of Ti-doped GZO films deposited at various substrate temperatures from room temperature (RT = 25 °C) to 500 °C. (b) Peak position and FWHM of the (002) X-ray diffraction peak as a function of substrate temperature (Ts, °C). The error bars represent the measurement error range.

substrate surface. In this study, an optimum substrate temperature of 300 °C (Ts 300) was obtained because of the strongest (002) peak intensity and a reduced XRD full width at half maximum (FWHM), which indicates that the crystallite quality of the ZnO thin films improved with the increased grain size [15]. When the substrate temperature increases to 300 °C, the sputtered particles have enough energy to diffuse, which results in the formation of a more dense and compact grain. This is attributed to the increased surface diffusion at higher substrate temperatures and the improved crystallinity in GTZO films [16]. When the temperature of a substrate was higher than 300 °C, the XRD intensity decreased. Such behavior at high substrate temperature can be ascribed to the decomposition or desorption of Zn and O atoms from the GTZO films, leading to crystallinity deterioration [17,18]. The XRD results indicate that the increase of the substrate temperature up to the optimum condition of 300 °C enhanced the crystallinity of GTZO films.

Fig. 3(a) and (b) shows the measured surface morphology utilizing an atomic force microscope (AFM) over an area of 1000 nm × 1000 nm of the 300-nm-thick GTZO films deposited at an RF power of 150 W with substrate temperature at RT and 300 °C, respectively. The mean grain size of the GTZO films increased as the substrate temperature from RT to 300 °C. The increased grain size was ascribed to the enhanced migration length of surface adatoms, and the coalescence of adjacent grains, with the contribution of high thermal energy at elevated substrate temperatures [19].

Fig. 4 shows the electrical resistivity (ρ), mobility (μ) and carrier concentration (n) of the GTZO films as functions of the substrate temperature. The resistivity of GTZO films decreased from 1.16×10^{-3} Ω-cm to 4.98×10^{-4} Ω-cm with the increased temperature of the substrate from as-grown to 300 °C. At a substrate temperature of 300 °C, there is the