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Effects of substrate temperature on the structural, morphological, electrical and optical properties of Al and Ga co-doped ZnO thin films grown by DC magnetron sputtering

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ABSTRACT

In this work, Al and Ga co-doped zinc oxide (AGZO) thin films were deposited on glass substrates by DC magnetron sputtering under different substrate temperatures. Evolutions of the structural, morphological, electrical and optical properties of the AGZO thin films as a function of substrate temperature were analyzed. Results showed that the average transmittance in the visible range (400–800 nm) for all the thin films was over 82%, which did not change obviously with the substrate temperature. The average grain size increased from 20.6 nm to 51.4 nm and the RMS surface roughness decreased from 21.1 nm to 4.0 nm with substrate temperatures ranging from 150 °C up to 450 °C. The carrier concentration, Hall mobility of the thin films increased when the substrate temperature was increased from 150 °C to 350 °C, and then decreased with a further increase of substrate temperature. The film deposited at 350 °C exhibited a lowest resistivity of $3.0 \times 10^{-4}\,\Omega$ cm with the highest carrier concentration of 5.0×10^{20} cm^{-3} and Hall mobility of 42 cm^2 V^{-1} s^{-1}.

1. Introduction

Doped-ZnO transparent conductive thin films are widely applied in optoelectronic devices such as flat panel displays and thin-film solar cells, because of their excellent optoelectronic properties, non-toxicity, low material cost, and stability in hydrogen plasma processes [1–3]. In singly-doped ZnO, Al doped ZnO (AZO) has good conductivity and chemical stability, while Ga doped ZnO (GZO) has superb humidity durability and more resistant to oxidation compared to AZO [4–7]. Thus, improvements in various properties can be expected for Al and Ga co-doped ZnO (AGZO) thin film, which make it promising and attractive for device applications. Previously, Lin et al. reported that an AGZO thin film grown by pulsed direct current magnetron sputtering had a low resistivity of $8.2 \times 10^{-4}\,\Omega$ cm and an average transmittance above 80% [8]. Ebrahimifard et al. synthesized AGZO thin films with different doping contents of 0.5–4 at% via sol–gel route using a dip coating method and demonstrated that samples with 1 at% Al and 1 at% Ga had the lowest resistivity [7]. Seo et al. investigated the effects of thickness on the properties of AGZO thin films and obtained a sheet resistance of 63.2 Ω and an average transmittance of 94.8% in the visible range with an optimized thickness of 200 nm [9]. Despite the progress in the growth of AGZO thin films; however, the properties of AGZO thin films are still not sufficiently good enough for the application of optoelectronic devices.

In this paper, AGZO thin films were deposited on glass by DC magnetron sputtering at various substrate temperatures. The effects of substrate temperature on the structural, morphological, electrical and optical properties of the AGZO thin films were investigated in detail. Finally, a high-quality AGZO thin film with a low resistivity of $3.0 \times 10^{-4}\,\Omega$ cm and a high average visible transmittance over 82% was obtained at a moderate substrate temperature (350 °C).

2. Experimental details

AGZO thin films were deposited on glass substrates from a home-made AGZO (98 wt%-ZnO, 1 wt%-Al_2O_3, 1 wt%-Ga_2O_3) ceramic target. The substrate temperature varied from 150 °C to 450 °C. Prior to deposition, the substrates were sequentially cleaned in an ultrasonic bath with acetone, ethanol, and deionized water, and then blown dried with nitrogen gas. The

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distance between the target and substrate was fixed at 90 mm, while the base pressure in the chamber was kept below 5×10^{-4} Pa and the sputtering pressure was 0.6 Pa. The sputtering process was carried out in pure Ar atmosphere and the sputtering DC power was 200 W.

The phase structure of the films was analyzed by X-ray diffraction (XRD) with Cu Kα radiation in θ–2θ Bragg–Brentano geometry (Bruker, AXSD8 Advance, USA). The thickness of the films was determined by a spectroscopic ellipsometry (M2000-DI, JA Woollam, USA) operated in the wavelength range of 300–800 nm with Cauchy model for optical simulation. The surface morphology was observed by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4800, Japan), and the surface roughness was examined over a scan area of $5 \times 5\ \mu m^2$ for 5 repetitions by an atomic force microscope (AFM, CSPM5500, China) in contact mode. The optical transmittance and reflection of the films were measured using an UV/vis/NIR spectrophotometer (Perkin-Elmer, Lambda 950, USA). The resistivity, carrier concentration and mobility of the films were measured usi ng a Van der Pauw method by Hall measurements (Accent, HL5500PC, UK).

3. Results and discussion

Fig. 1 shows the XRD patterns of the AGZO thin films with different substrate temperatures. All the thin films showed a pronounced diffraction peak (2θ) around 34°, indicating the typical hexagonal wurtzite structure with (002) preferred orientation. In Fig. 1(a), it was observed that the peak positions were shifted to larger angles and the peak intensity was gradually increased with increasing substrate temperatures to 450 °C. Shifted peak positions to higher diffraction angle indicated that the inter-planar distance between the (002) planes decreased. This result revealed that more Al and Ga atoms replaced Zn substitutionally at high substrate temperature since the ionic radius of Al^{3+} (53 pm) and Ga^{3+} (62 pm) were smaller than that of Zn^{2+} (72 pm) [10–13]. Increasing peak intensities implied that the enhancement of the orientation of the AGZO grains. From Fig. 1(b), one can notice that the full-width at half-maximum (FWHM) of the (002) diffraction peak decreased from 0.40° to 0.16° when the substrate temperature increased from 150 °C to 450 °C, accordingly, the average grain size calculated through the Scherrer equation was increased from 20.6 nm to 51.4 nm. The increase of the grain size with substrate temperature was attributed to the improvement of the thin film crystallinity by the coalescence of small crystallites [14].

The SEM and AFM images of the AGZO thin films are shown in Fig. 2. As seen from the SEM micrographs, the film surface became more compact and continuous with increasing substrate temperature. The RMS roughness of the AGZO thin films decreased from 21.1 nm to 4.0 nm when the substrate temperature increased from 150 °C to 350 °C, then remained unchanged for a further increase in the substrate temperature. This dependence was ascribed to an improved surface diffusion for higher substrate temperature and thus an improved crystalline quality [14,15]. The decrease in surface roughness reduced the absorption of oxygen and thus contributes to improve the electrical properties [14].

Fig. 3 shows the electrical properties of the AGZO thin films deposited at different substrate temperatures. The carrier concentrations increased moderately with increasing substrate temperature up to 350 °C although the sputtering target had the fixed Al and Ga concentration of 2 wt%. This can be explained by the fact that the increase of temperature promotes the substitution of Al^{3+} and Ga^{3+}

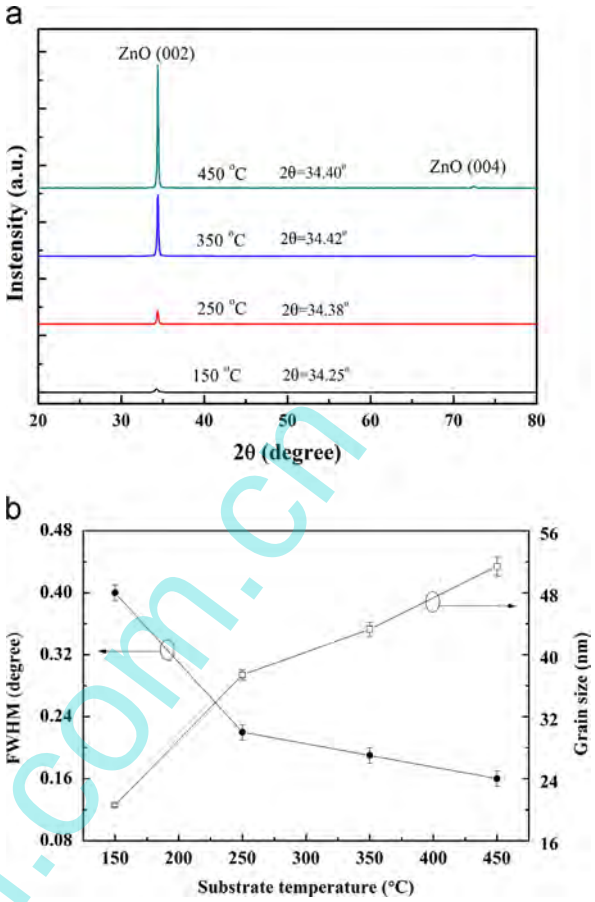

Fig. 1. (a) XRD patterns and (b) FWHM and grain size of the AGZO thin films deposited at different substrate temperatures.

ions and thus improves doping efficiency. The Hall mobility increased substantially from 15 $cm^2\ V^{-1}\ s^{-1}$ to 42 $cm^2\ V^{-1}\ s^{-1}$ as the substrate temperature increased to 350 °C, which could be understood in terms of the enhanced orientation of the AGZO grains and the improved crystallinity. At the higher temperature of 450 °C, the carrier concentration decreased from $5.0 \times 10^{20}\ cm^{-3}$ to $4.3 \times 10^{20}\ cm^{-3}$ and the Hall mobility decreased from 42 $cm^2\ V^{-1}\ s^{-1}$ to 34 $cm^2\ V^{-1}\ s^{-1}$. These could be related to the segregation of Al_2O_3 and/or Ga_2O_3 at the grain boundaries at high temperature, which reduced the doping efficiency and increased the grain barrier scattering. Similar results were reported for AZO thin films [15–17]. As a result, the resistivity of the AGZO films reached the minimum value of $3.0 \times 10^{-4}\ \Omega$ cm at the substrate temperature of 350 °C.

Fig. 4 shows the optical transmission spectra of the AGZO thin films deposited at different substrate temperatures. It was observed that the average transmittance in the visible range (400–800 nm) for all the films was over 82%, which did not change obviously with the substrate temperature. As the substrate temperature increased, the fundamental absorption edge of the thin films shifted to the short wavelength region while it shifted back when the substrate temperature was higher than 350 °C. The movement of the absorption edge to the shorter wavelength region was the Burstein–Moss effect, which was due to the Fermi level moving into the conduction band with the increase of carrier concentration [18,19]. The Burstein–Moss theory predicts that the optical band gap widening is proportional to $N^{2/3}$, where N is the carrier concentration. This was in good agreement with electrical measurement showing that carrier concentration of the AGZO thin films increased with increasing substrate temperature up to 350 °C.

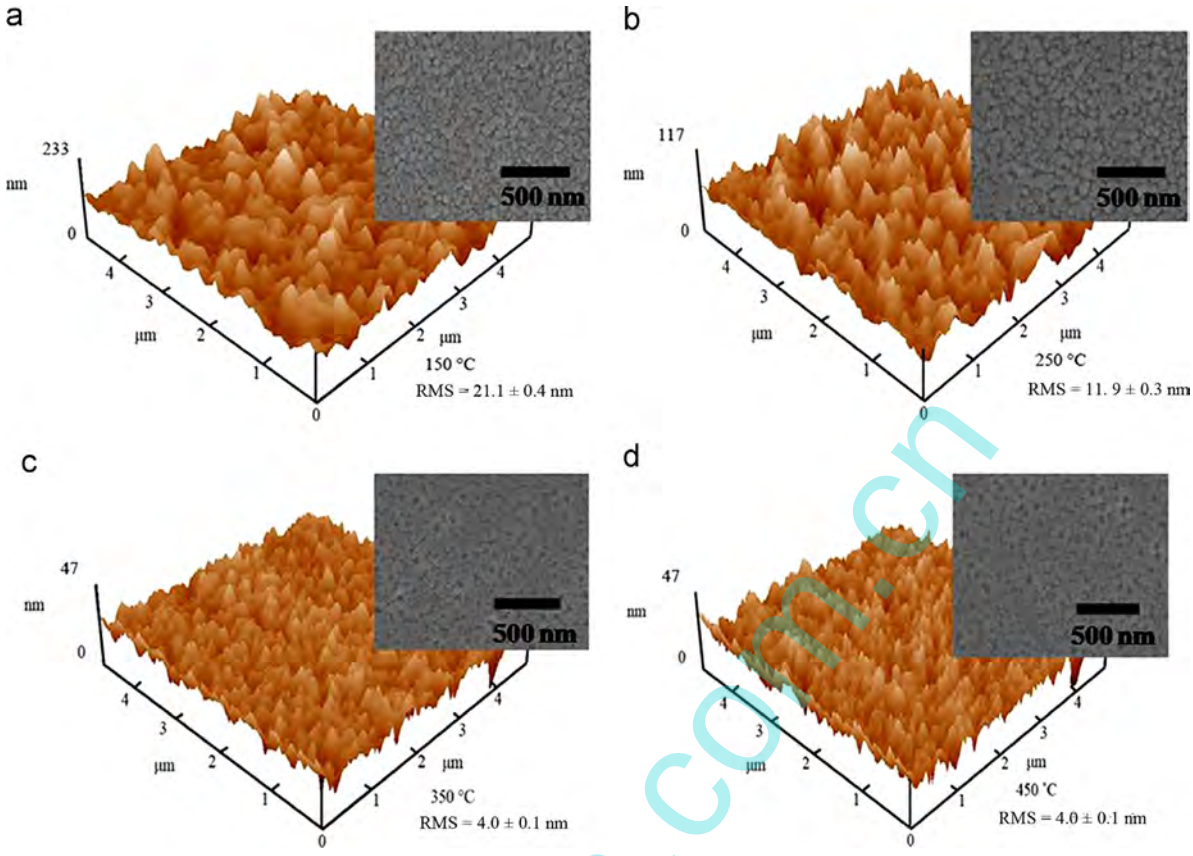

Fig. 2. SEM and AFM images of the AGZO thin films deposited at different substrate temperatures.

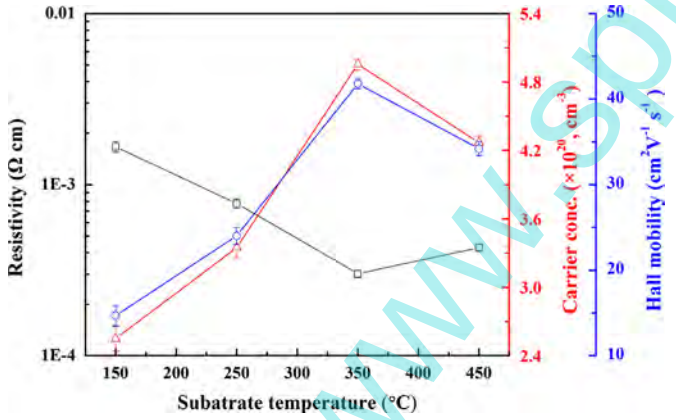

Fig. 3. Electrical properties of the AGZO thin films deposited at different substrate temperatures.

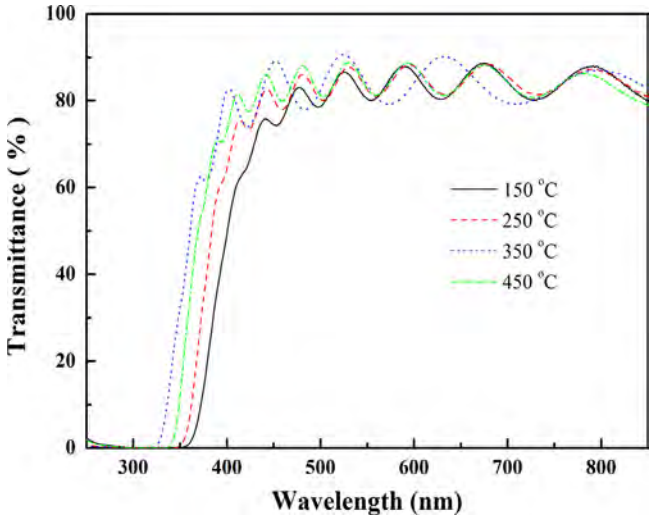

Fig. 4. Optical transmittance of the AGZO thin films deposited at different substrate temperatures.

4. Conclusions

In summary, AGZO thin films were deposited on glass substrates by DC magnetron sputtering and the effects of substrate temperature on the structural, morphological, electrical, and optical properties of AGZO thin films were investigated. All AGZO thin films exhibited a transmittance higher than 82% in visible range. Increasing the deposition temperature to a moderate level (350 °C in this study) accompanied improved crystalline quality, surface roughness and doping efficiency which yielded the lowest electrical resistivity of 3.0×10^{-4} Ω cm with the highest carrier concentration of 5.0×10^{20} cm^{-3} and Hall mobility of 42 cm^2 V^{-1} s^{-1}. This work revealed a possibility of producing high-quality AGZO thin film for futuristic optoelectronic devices by a simple low-cost process.

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