Transparent Conductive Thin Films of Aluminum-doped Zinc Oxide Prepared by Magnetron Sputtering

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Abstract. Transparent conductive thin films of aluminum-doped zinc oxide (ZAO) were prepared by radio-frequency magnetron sputtering with ZAO (98 wt% ZnO, 2 wt% Al_2O_3) as the ceramic target. The visible transmittance was investigated by ultraviolet–visible spectroscopy, the carrier concentration and Hall mobility were measured by the Van der Pauw method, and the phase composition was characterized by X-ray diffraction. The results show that the substrate temperature was a dominant factor of the properties, with the ZnO film deposited at a substrate temperature of 200 °C and a pure-argon gas pressure of 1 Pa exhibiting optimal performance. The resistivity and average transmittance in the wavelength range of 300–760 nm were 2.0×10^{-4} Ω cm and 90.6%, respectively.

Introduction

Aluminum-doped zinc oxide (ZAO) films are especially attractive materials among different oxide materials because of the abundance of raw materials, low cost, environmental friendliness, and stability in hydrogen plasma. The effects of the substrate temperature on the properties of ZnO thin films have been reported by many research groups [1-3]. ZAO film's quality and its photoelectric performance are affected by process parameters such as substrate temperature [4], sputtering time [5], sputtering power [6], target-substrate distance, working pressure [7], annealing temperature and annealing time [4, 8]. B.L.Zhu et al [9]discovered that ZnO films grown at room temperature suffer compressive stress and the tensile stress exists in films grown at a substrate temperature of 200–500 °C. Zhiyun Zhang et al[10] discovered that all the films deposited at different substrate temperature from RT to 350°C exhibited residual tensile strain. In our study, ZAO thin films were deposited on glass substrates by RF magnetron sputtering, with the substrate temperature ranging from room temperature (RT) to 300 °C. The crystalline, microstructure, optical and electrical properties of the films were investigated.

Experimental procedures

ZAO thin films were deposited by a radio-frequency (RF) magnetron sputtering system (JSD-300, JS Vacuum, China). The ceramic ZnO: Al2O3 (2 wt %) was 50 mm in diameter and 99.99% in purity. Soda-lime glass sheets were used as the substrates cleaned successively in an ultrasonic bath with acetone, alcohol and deionized water for 10 min before being loaded into the chamber. The target-base distance is 60 mm. The base pressure of the chamber was kept at 6×10^{-4} Pa. Pure Ar gas was supplied into the sputtering chamber maintained at 1 Pa in pressure at 100 W's sputtering power. The substrate temperatures (*ST*) was set at 25, 100, 200 and 300 °C, respectively, and samples were obtained and rapidly cooled to RT in air. An X-ray diffractometer (XRD; D8 Advance, Bruker AXS, Germany) with Cu K_α as the radiation source was used to identify the film's

phase composition. The film's surface was observed by a cold-field-emission scanning electron microscope (JSM-6700F, JEOL, and Japan) operated at 5 kV. The electrical properties of the films were measured using the van der Pauw method at room temperature with Hall Effect measurement system (HMS3000, Ecopia, Korea).

Results and discussion

Structural characterization

Fig.1 shows XRD diffraction patterns of the ZAO films deposited at different substrate temperatures. Weak (002) peak and a stronger (100) peak were emerged at *ST* = 25°C. When *ST* was raised to 100 °C, the (002) peak became stronger. As *ST* was further increased to 200 and 300 °C, only (002) dpeak was observed in the deposited film, indicating that the atoms had sufficient energy to settle in stable positions and had the tendency to adopt the orientation of the (002) plane to minimize the surface energy at higher *ST*. The (100) peak deposited at *ST* < 100 °C in ZAO films indicating that the number of crystals oriented along the *c*-axis decreased. In addition, it was also observed that no Al_2O_3 phase was present, which implies that most of the Al atoms were in substitutions for Zn atoms in the ZnO lattice or Al interstitial atoms between the lattices.

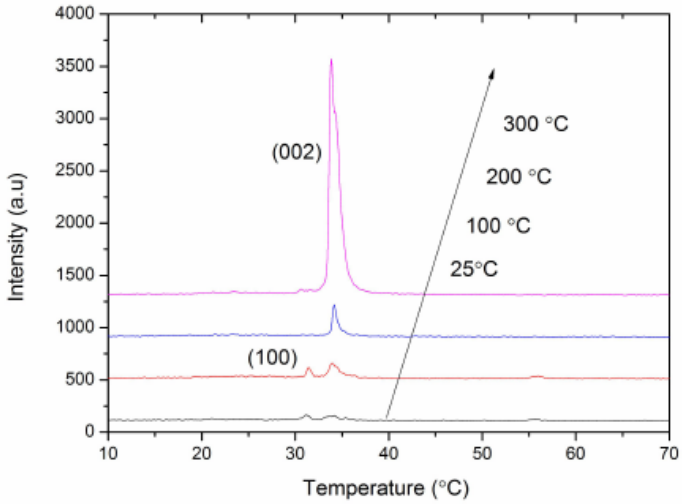

Figure 1 XRD diffraction curves of samples at different substrate temperature

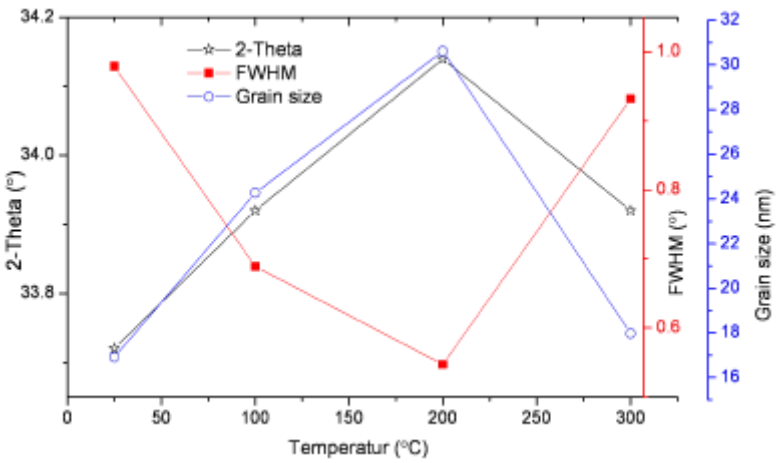

Figure 2 Theta, FWHM, and grain size of the samples

Variations of 2θ, full width at half maximum (*FWHM*), and the grain size of the (002) diffraction peak were also investigated, as shown in Fig.2. When *ST* increased from 25 to 200 °C, *FWHM* decreased and the peak position of (002) gradually moved from 33.72 to 34.14°, particularly,

FWHM decreased sharply with ST increasing from 100 to 200 °C. Then when ST increased from 200 to 300°C, FWHM increased and the position of the (002) diffraction peak slightly decreased from 34.14 to 33.92°. Compared 2θ of 34.42° for the (002) diffraction peak to bulk ZnO, the decrease in the diffraction peak angle corresponds to an increase in the interplanar spacing of (002), indicating that there was compressive stress in the ZAO thin films. The reason is that the prepared films were rapidly cooled to room temperature and substrate shrinks faster than the film, because the thermal expansion coefficient of ZnO is 6.5×10^{-6} °C^{-1}, which is lower than that of the glass substrate (8×10^{-6} °C^{-1}). This is different from the report of residual tensile strain in ZAO thin films by Zhang et al.[10]. Although it could cause the decrease in the interplanar spacing of (002) when Zn atoms were replaced by Al atoms at their lattice sites which brought tensile stress in the films, because Al^{3+} has a smaller ionic radius than Zn^{2+}. Obviously, the the prepared films rapidly cooled could not eliminate effectively compressive strain caused by crystal defects in the films.

Because the atoms of the ZAO films had higher energy and the surface mobility to settle at stable positions with the increase of *ST* from 25 to 200 °C, the compressive stress was reduced. As *ST* was further increased from 200 to 300 °C, the atoms had more energy to re-arrange themselves and recrystallize and the compressive stress was increased, showing that more grain boundaries emerged as a result of recrystallization of ZnO at 300°C. The compressive stress decreased as *ST* increased from 25 to 200 °C, indicating that the intrinsic stress related to the defects in the ZAO lattice played an important role.

The crystallite size first increased and then slightly decreased with increasing *ST*. The crystallite size of the film deposited at 200 °C was obviously larger than that at 25, 100, and 300 °C. At 25 °C, the ZAO film's grains grew limitely along the substrate surface. Increasing *ST* from 25 to 200 °C enhanced the growth of grains, but decreased with further increasing of *ST* to 300 °C, which was probably related to grain refinement by the recrystallization of ZnO at 300 °C.

Optical properties

Fig.3 shows the optical transmittance in the wavelength range of 300–760 nm for ZAO films deposited at different substrate temperatures. It can be seen that the spectra had undulating profiles because of the interference originating from the reflection at the films' interfaces. The transmittance decreased rapidly at wavelengths below 400 nm and reached 0 at approximately 370 nm, because the energy below wavelength of 370 nm was higher than the band gap of intrinsic ZnO (3.37eV). Moreover, in the ultraviolet range, the absorption edge shifted towards shorter wavelengths. The average transmittance of samples deposited at 25, 100, 200, and 300 °C were 90.3, 89.6, 90.6, and 87.6%, respectively. The lower transmittance at 300 °C was caused by grain refinement resulting from the recrystallization of ZnO, which led to the increase in scattering, reflection, and optical absorption.

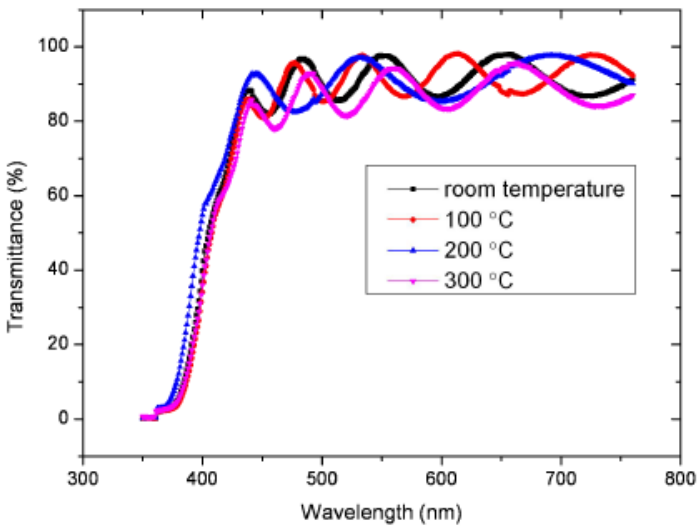

Figure 3 UV-visible light transmittance of samples

Electrical properties

The carrier concentration, Hall mobility, and resistivity are plotted in Fig. 4 as functions of substrate temperature; their values were in the approximate ranges of 1.2–3.0 × 10^{20} cm^{-3}, 3.0–8.0 cm^2 V^{-1} s^{-1} and 9.7–2.0 × 10^{-4} Ω cm, respectively. It was observed that the carrier concentration increased as *ST* increased from 25 to 200 °C, but decreased as *ST* increased from 200 to 300 °C. And the changes in resistivity were opposite. At the room temperature, there was water vapor with higer content in chamber, and it could be lonized as H and O in the plasma. The element H may exist as H^+, H^- and H^0 , but it mainly existed as H^+ in ZnO films proved by the theory and experiments[11, 12]. It was certificated by many groups that the the interstitial H^+ was a shallow donor and contributed a lot to the n-type nature of ZnO. Although H^+ had a high solubility in ZnO film, it was transformed into an acceptor as it was easy to form H-O band combined with O^{2-}, which was also the reason of higher resistivity with low substrate temperature. Furthermore, the formationof H-O bonds also cause relaxation of the surrounding atoms and increase the stress.

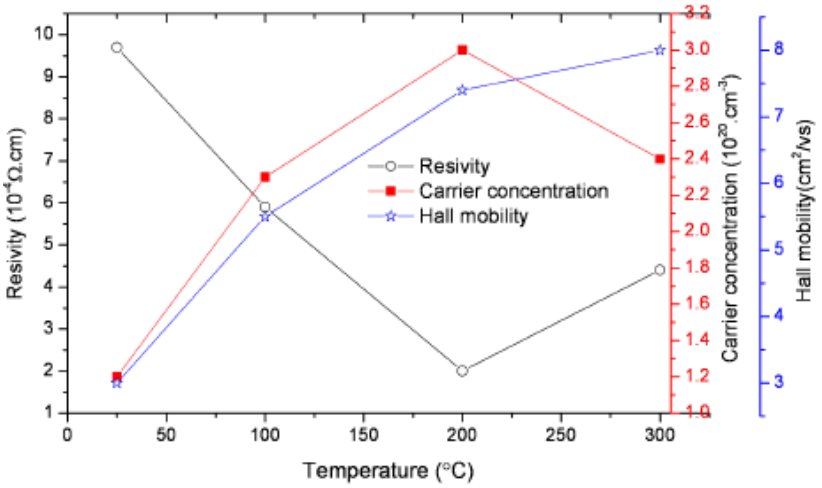

Figure 4 Resistivity,carrier concentration,and Hall mobility of the samples

On the other hand, at lower *ST*, more Al could be easily incorporated into the film since the Al sticking coefficient is inversely related to the exponential of temperature, thus increasing the number of Al, causing the carrier concentration to increase, as shown in the measurements. It has been reported [13] that the energy barrier for self-diffusion of intrinsic defects in ZnO is lowest for Zn^{2+} interstitials, so that the Zn interstitial atoms could readily diffuse through the bulk, especially along the films' grain boundaries, and evaporate from the surface. Zn vacancies would have been left after this process or the extinction of oxygen vacancies, which are acceptors, thereby the net carrier concentration reduced at higher temperatures (*ST*=300 °C). The mobility increased with increasing substrate temperature, which could be attributed to the thermal annihilation of point defects, dislocations and stacking faults, within the grains as well as grain boundaries reduced. Smaller grain size and higer defect density would increase the probability of electron scattering, reducing the Hall mobility. The Hall mobility of the film deposited at 25 °C was low mainly because of the scattering from the grain boundaries as the grain size was smaller. This is supported by XRD results, which indicate that the film grown at 200 °C was more crystalline and the crystallinity decreased with growth temperature increased from 200 to 300 °C.

Conclusion

In conclusion, the microstructure of ZAO films prepared by magnetron sputtering were effected significantly by substrate temperature, and the optical and electrical properties were dependented on the microstructure of the films. When substrate temperature increased from 25 to 200 °C, the grain size of the films changed from 16.92 to 30.62 nm, and the resistivity decreased from 9.7 × 10^{-4} to 2.0 × 10^{-4} Ω cm. As substrate temperature increased from 200 to 300 °C, the grain size decreased to

17.89 nm, and the resistivity increased to 4.2×10^{-4} Ω.cm. From XRD and SEM results of the ZAO films, it showed a crystallinity improvement at *ST*=200 °C. Good quality films, with resistivity that was as low as 2.0×10^{-4} Ω cm and around 91% transmittance in the visible region, were obtained at a substrate temperature of 200 °C.

Acknowledgements

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