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PREPARATION AND CHARACTERIZATION

INFLUENCE OF SUBSTRATE AND TARGET TEMPERATURES ON PROPERTIES OF TRANSPARENT AND CONDUCTIVE DOPED ZnO THIN FILMS PREPARED BY R.F. MAGNETRON SPUTTERING

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The dependence of electrical and optical properties on the temperatures of substrate and target has been studied for aluminium-doped zinc oxide (AZO) and silicon-doped zinc oxide (SZO) thin films prepared by r.f. magnetron sputtering. The AZO and SZO films with the lowest resistivity, which is due to the increased mobility resulting from the improvement of the crystallinity of films, can be prepared at a substrate temperature of 180–220 °C. An excessive cooling of the target is undesirable, because it causes an increase in the resistivity and a decrease in the transmittance of the deposited AZO and SZO films.

1. INTRODUCTION

Undoped and doped zinc oxide (ZnO) films have been actively studied in recent years[1–5] because of their potential applications as low cost transparent conducting oxide (TCO) films. We have reported that doped ZnO films with a resistivity of the order of 10^{-4} Ω cm, prepared by r.f. magnetron sputtering under an applied external d.c. magnetic field, are realized by doping impurities of group III or IV elements[4–6].

In this paper, we describe the influence of substrate temperature on the various properties of aluminium-doped ZnO (AZO) and silicon-doped ZnO (SZO) TCO films prepared by r.f. magnetron sputtering. The influence of the temperature of the target surface on these properties of these TCO films is also investigated.

2. EXPERIMENTS

Films were prepared by r.f. magnetron sputtering in a plasma-focusing magnetic field of 5×10^{-3} T using an external solenoid coil. A sintered disk of a powder mixture of ZnO with a purity of 99.9% and dopant Al_2O_3 or SiO_2 with a purity of 99.99% was used as the target (supplied by Mitui Mining and Smelting Co. Ltd.). The content of Al_2O_3 or SiO_2 added to the ZnO target was about 2 wt.%. Sputter deposition was carried out at a pressure of 8×10^{-1} Pa in pure argon gas with an r.f. power of 50 W. Corning 7059 glass substrates mounted on the holder were placed at an angle of about 45° to the target surface. The substrate temperature

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T_s was controlled by heating and/or cooling of the holder in the range from room temperature (RT) to 400 °C. The temperature of the target surface was varied by water cooling on the backing plate of the target and/or the thermal radiation from heaters placed around the target.

3. RESULTS AND DISCUSSION

3.1. Dependence of the properties on T_s

Figure 1 shows the resistivity ρ of the AZO and SZO films as a function of the substrate temperature. Figure 2 shows a typical substrate temperature dependence of carrier concentration n and Hall mobility μ of the AZO films. T_s was controlled to be as constant as possible during the sputter deposition. It has been reported that the ρ value of AZO films deposited on heated substrates is increased with increasing T_s if T_s is not controlled[7]. However, it was found in this experiment that the gradual decrease in ρ of the AZO and SZO films with increasing T_s in the range from RT to about 200 °C is mainly related to the increase in μ. Above $T_s \approx 250$ °C, the increase in ρ with T_s was related to decreases in both μ and n, as shown in Fig. 2. In order to understand the dependence of the electrical properties on T_s, the crystallographic properties of the films shown in Fig. 1 were investigated by X-ray diffraction analysis. The X-ray diffractions were measured using Cr Kα radiation. All films shown in Fig. 1 were polycrystalline ZnO which is preferentially oriented perpendicular to the substrate surface (c axis orientation). Figure 3 shows a typical substrate temperature dependence of the intensity, full width at half-maximum (half-width (HW)) and angle 2θ of the (00.2) diffraction peak for the AZO films shown in Fig. 1. The 2θ value of the AZO films deposited on low temperature substrates was shifted to lower angles with increasing content of Al_2O_3 dopant in the target. In the AZO films measured here, the 2θ value with increase in T_s approached the value of undoped ZnO films, or of powder ZnO (indicated by broken line in Fig. 3). Above $T_s \approx 250$ °C, the crystallinity of the films was drastically lowered with increasing T_s, whereas the 2θ value of the films recovered to that of stress-free ZnO. It should be

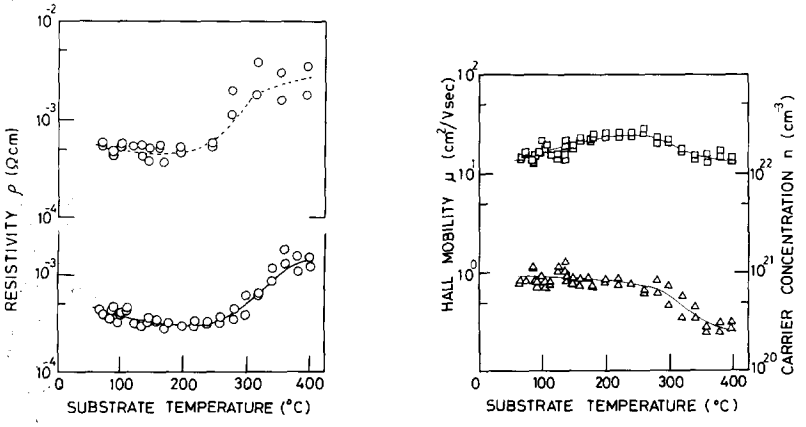


Fig. 1. Dependence of ρ of the AZO (——) and SZO (– – –) films on the substrate temperature.

Fig. 2. Dependence of n (△) and μ (□) of the AZO films on the substrate temperature.

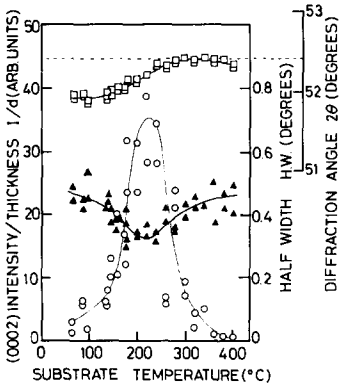


Fig. 3. Intensity (○), HW (▲) and 2θ (□) of the (00.2) X-ray diffraction peak for the AZO films as a function of the substrate temperature. The intensity was normalized by the film thickness.

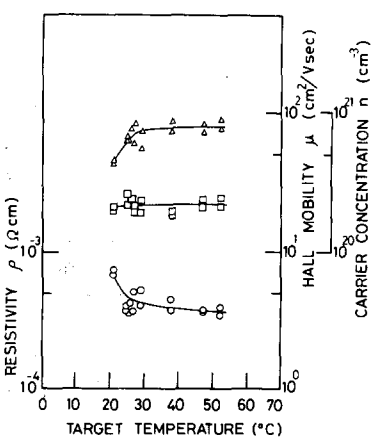
noted from Figs. 2 and 3 that the decrease in both n and μ with increasing T_s above 250 °C is related to the drastically lowered crystallinity. In contrast, the crystallinity of undoped ZnO films prepared by r.f. magnetron sputtering is improved with increasing T_s below 400 °C. This is understood in terms of the approach to stoichiometric ZnO resulting from the enhancement of oxidation on the substrate surface as T_s increases. Thus it seems that the poor crystallinity in AZO films prepared above $T_s \approx 250$ °C is caused by the doping of aluminium impurity. In order to evaluate the amount and electronic state of aluminium introduced in AZO films, X-ray photoelectron spectroscopy (XPS) analysis was performed. XPS analysis showed that the aluminium is always introduced with the form of Al^{3+} and the aluminium content doped in the films is independent of T_s below 400 °C. It is likely that the aluminium which does not substitute to the zinc site is introduced in the form of Al_2O_3 in the AZO films. Thus, the poor crystallinity of AZO films above $T_s \approx 250$ °C may be attributed to the segregation of the Al_2O_3 at grain boundaries in the films, resulting from the enhancement of oxidation on the substrate surface and the increase in T_s. The decreases in n and μ of the AZO films are also related to the enhancement of oxidation on the substrate surface. It can be seen from the results as shown in Figs. 1 and 2 that the AZO films with a low resistivity or high mobility have crystallinity of high quality. The increase in μ with increasing T_s up to about 250 °C is attributed to the improvement in the crystallinity. It is pointed out that the films with the highest n are prepared at a low T_s from RT to 150 °C, and the films with the highest μ are prepared at $T_s = 180$–220 °C. It was also found that the dependences of the crystallographic and electrical properties on T_s in the SZO films are similar to those in the AZO film.

In contrast, the dependence of optical transmission spectra on T_s was not observed for all AZO and SZO films. It was found that the AZO and SZO films prepared at $T_s = 180$–220 °C are more stable than those prepared on unheated substrates[8] for use in high temperature ambients such as vacuum and air. Also, the film thickness dependence of ρ, observed for AZO films prepared on unheated substrates[5], improved considerably for the TCO films prepared at $T_s = 180$–220 °C. It is, therefore, concluded that stable AZO or SZO films with the lowest resistivity

can be prepared at $T_s = 180$–$220\,^{\circ}C$ using the r.f. magnetron sputtering technique under an applied external d.c. magnetic field.

3.2. Dependence of properties on the target temperature

Sputtering with a high deposition rate has been carried out using a sintered target attached to a water-cooled backing plate. The electrical and optical properties of the AZO and SZO film were dependent on the target temperature T_t measured before sputter deposition. Figure 4 shows the ρ, μ and n values of the AZO films prepared at $T_s = 200\,^{\circ}C$ as a function of T_t. The sputtering was carried out with an effective target area of 120 mm × 80 mm at an r.f. power of 50 W. It can be seen that the n value of the films is decreased with decreasing T_t below about 30 °C and consequently the ρ value of the films is increased with decreasing T_t. Figure 5 shows typical transmission spectra for the AZO films prepared by using the target with and without water cooling (the water temperature was about 15 °C). It should be noted that a drastic decrease in transmittance in the UV wavelength region is observed for the films prepared using the target with water cooling. The films prepared using the water cooled target were coloured yellow and the sputtered surface of the target was coloured black. These results suggest that the surface of the target is reduced when the sputter deposition was carried out using the excessively cooled target. Consequently, the AZO films deposited have an oxygen deficiency because of the reduction of the ZnO target surface. The surface of the ZnO target becomes zinc rich as a result of the reduction of ZnO, but Al_2O_3 dopant in the target may not be reduced because of its chemical stability. Therefore, the decrease in n of the films prepared at $T_t = 20\,^{\circ}C$ as shown in Fig. 4 may be attributed to the decreased quantity of aluminium donors in the films. We can point out from the results as described above that excessive cooling of the target causes an increase in ρ and a decrease in the transmittance of the AZO and SZO films when the films are prepared by r.f.



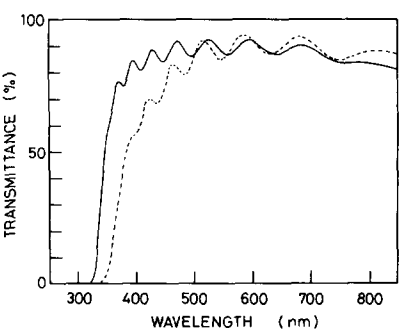


Fig. 4. Dependence of ρ (○), μ (□) and n (△) of the AZO films on the target surface temperature. The films were prepared at $T_s = 200\,^{\circ}C$.

Fig. 5. Typical transmission spectra of the AZO films prepared by using the target with (– – –) and without (——) water cooling.

magnetron sputtering with an r.f. power as low as 50 W using the water-cooled target.

4. CONCLUSIONS

The influence of the substrate and target temperatures on the electrical and optical properties of AZO and SZO thin films prepared by r.f. magnetron sputtering has been investigated. It was found that the optimum substrate temperature required to prepare the AZO and SZO films with the lowest resistivity is 180–220 °C. An improvement in the thickness dependence of the resistivity and the stability for use in high temperature ambients can also be realized by these films prepared on substrates heated at a constant temperature. The improvement in these properties for the AZO and SZO films is related to the improvement in the crystallinity. An excessive cooling of the target during sputter deposition is undesirable, because it causes an increase in ρ and a decrease in the transmittance for deposited AZO and SZO films.

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