Thin Solid Films, *124* (1985) 43–47
PREPARATION AND CHARACTERIZATION

HIGHLY CONDUCTIVE AND TRANSPARENT ZnO THIN FILMS PREPARED BY R.F. MAGNETRON SPUTTERING IN AN APPLIED EXTERNAL D.C. MAGNETIC FIELD*

T. MINAMI, H. NANTO AND S. TAKATA
Department of Electrical and Electronic Engineering, Kanazawa Institute of Technology, 7-1 Oogigaoka, Nonoichi-machi, P.O. Kanazawa-South, Ishikawa 921 (Japan)
(Received August 13, 1984; accepted October 4, 1984)

Highly conductive films of undoped and aluminium-doped ZnO were prepared by r.f. magnetron sputtering in an applied external magnetic field in pure argon gas. Films with a resistivity as low as $2 \times 10^{-4}\ \Omega$ cm and a transmittance above 80% at wavelengths between 400 and 800 nm can be produced on a non-intentionally heated substrate by the sputtering of a ZnO target to which 2 wt.% Al_2O_3 had been added. The characteristic features of aluminium-doped ZnO films are their high carrier concentration, low mobility and blue shift in the absorption edge in comparison with the properties of undoped ZnO films.

1. INTRODUCTION

At present, indium tin oxide (ITO) films with a low resistivity of the order of $10^{-4}\ \Omega$ cm and with stable electrical and optical properties are generally used as a transparent electrode for optoelectronic devices. ITO films have the disadvantage that the indium source material is expensive, although the properties of ITO films as transparent electrodes are excellent. Highly conductive films of ZnO have been actively investigated in recent years because of their potential applications as transparent and conductive coatings and as IR reflective coatings. The constituent elements of ZnO are abundant and the material has a low cost. If highly conductive films of ZnO with a high optical transmission can be prepared using an inexpensive thin film deposition technique, ZnO would be useful as a less expensive coating material than ITO. In as-deposited ZnO films prepared by the sputtering technique, a low resistivity of the order of $10^{-3}\ \Omega$ cm has been achieved in recent years[1–3]. More recently, we have reported that highly transparent films with a resistivity of the order of $10^{-4}\ \Omega$ cm could be produced by r.f. magnetron sputtering in an external d.c. magnetic field[4–6]. In this paper we report a detailed study of the electrical and optical properties of aluminium-doped and undoped ZnO thin films prepared by r.f. magnetron sputtering.

* Paper presented at the Sixth International Conference on Thin Films, Stockholm, Sweden, August 13–17, 1984.

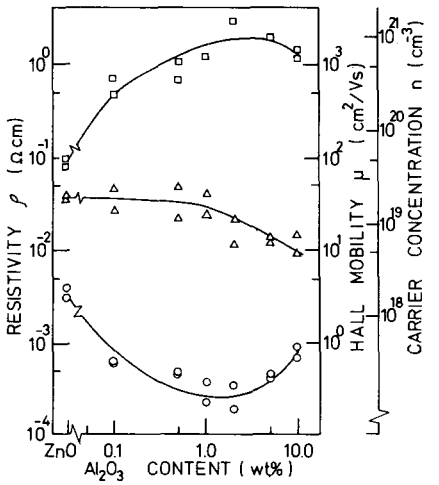
0040-6090/85/$3.30

2. EXPERIMENTAL PROCEDURE

Films were obtained by r.f. magnetron sputtering in a d.c. magnetic field of up to about 70 G using an external solenoid coil. Details of the sputtering system have been described elsewhere[4–6]. Sputter deposition was carried out at a pressure of $(6.0–60) \times 10^{-3}$ Torr in pure argon gas with an r.f. power of 25–80 W. A disc of sintered ZnO 80 mm in diameter and ZnO powder with a purity of 99.999% were used as targets. In the preparation of aluminium-doped ZnO films, a powder mixture of ZnO with a purity of 99.9% and the dopant Al_2O_3 with a purity of 99.99% was used as the target using a stainless holder. Substrates of Corning 7059 glass were placed perpendicular to the target surface[5]. The deposition rate was independent of the content of Al_2O_3 (up to 2 wt.%) added to the ZnO powder target, but it decreased rapidly as the Al_2O_3 content was increased above 5 wt.%. The film thickness was measured using a conventional surface roughness detector with a stylus. The electrical resistivity and Hall mobility were measured at room temperature by the van der Pauw method. The optical transmission through the film was measured in the wavelength range 300–800 nm.

3. RESULTS AND DISCUSSION

The resistivities of the sputtered films are considerably dependent on the sputtering conditions such as the gas pressure, the external magnetic field and the position and temperature of the substrates. It should be noted that the difference between films sputtered using the sintered and the powder ZnO targets is manifested in the dependence of the resistivities on the sputtering conditions. Figure 1 shows the dependence on the Al_2O_3 content of the electrical resistivity ρ, the Hall mobility μ and the carrier concentration n of aluminium-doped ZnO films. The results for the non-intentionally doped (undoped) ZnO powder target are also plotted on the left-hand side of Fig. 1. The Al_2O_3 content shown is the content of Al_2O_3 powder added to the ZnO powder target. The sputtering was carried out at a pressure of 6×10^{-3} Torr with a power of 50 W in an applied d.c. magnetic field of 50 G. The substrates were not intentionally heated. It is seen that aluminium-doped ZnO films exhibit a high carrier concentration and a low mobility in comparison with those of undoped films. The high carrier concentration in aluminium-doped ZnO films is attributed to the contributions from Al^{3+} ions on substitutional sites of Zn^{2+} ions and from interstitial aluminium in the ZnO lattice. The mobility in highly conductive films of polycrystalline ZnO is limited by scattering from grain boundaries and ionized impurities. The decrease in mobility with increasing Al_2O_3 content may be ascribed to the enhancement of these scattering mechanisms resulting from disorder introduced into the ZnO lattice. Figure 2 shows the dependence of ρ, μ and n for aluminium-doped (Al_2O_3 content, 2 wt.%) ZnO films on the substrate temperature T_s. Data at T_s values of about 150 and 160 °C correspond to the results for films sputtered onto non-intentionally heated substrates, because the surface temperature of the substrates during the sputter deposition for about 30 min at an r.f. power of 50 W was estimated to reach about 150 °C. It should be noted that ρ increases rapidly with increasing T_s because both μ and n decrease with



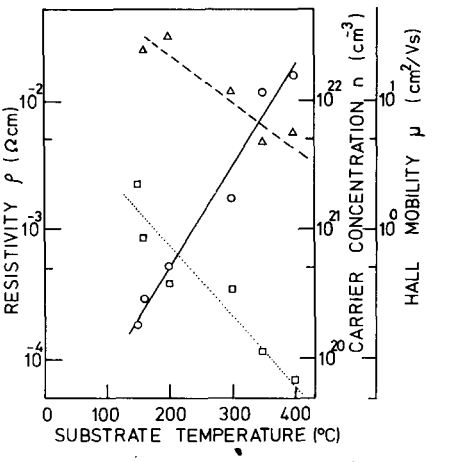


Fig. 1. Resistivity ρ (○), Hall mobility μ (△) and carrier concentration n (□) of sputtered ZnO films as a function of the Al_2O_3 content.

Fig. 2. ρ (○), n (□) and μ (△) in aluminium-doped ZnO films as a function of the substrate temperature.

T_s. It was also found that the substrate temperature dependence of resistivity for undoped ZnO films was similar to that for aluminium-doped films, as shown in Fig. 2. We believe that n decreases because of a decrease in the number of effective native donors and μ decreases as a result of an increase in the grain boundary barrier, because a more complete compound on the substrate surface yielding a more stoichiometric film is produced by the increase in substrate temperature.

The following deposition conditions have to be fulfilled simultaneously in order to obtain highly conductive films.

(1) The films are deposited onto substrates placed perpendicular to the target surface.

(2) The substrates are not heated intentionally.

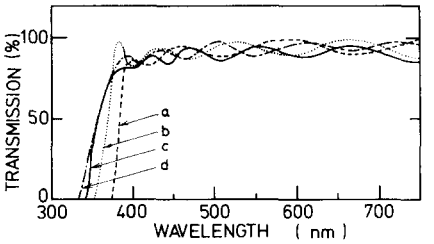
(3) The argon gas pressure during the sputter deposition is about 6×10^{-3} Torr.

(4) The applied d.c. magnetic field is about 50 G.

(5) The Al_2O_3 content of the target is about 2 wt.%.

We could not detect any marked dependence of the resistivity on the applied r.f. power in the range from 25 to 80 W, although the typical deposition rate varied in the range 6–32 nm min^{-1}.

Figure 3 shows the transmission spectra for undoped and aluminium-doped films. Although the absorption edge was dependent on the Al_2O_3 content, which is related to the change in carrier concentration, the average transmittance in the visible region was approximately the same and above 80%. The considerable blue shift in the absorption edge with increasing carrier concentration is attributed to the Burstein–Moss shift[7]. Figure 4 shows the dependence of the sheet resistance of aluminium-doped (Al_2O_3 content, 1 wt.%) and undoped ZnO films on the film thickness. Although the resistivity of undoped films is independent of the change in



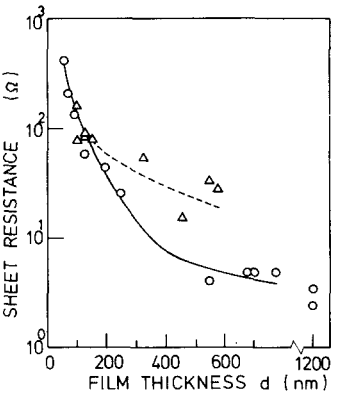


Fig. 3. Optical transmission spectra for an undoped film (curve a) (425 nm thick) and for aluminium-doped films with Al_2O_3 contents of 0.5 wt.% (curve b) (540 nm thick), 1.0 wt.% (curve c) (675 nm thick) and 2.0 wt.% (curve d) (625 nm thick).

Fig. 4. Sheet resistance of undoped (△) and aluminium-doped (1.0 wt.%) (○) films as a function of the film thickness.

film thickness d, it should be noted that the resistivity of the aluminium-doped film increases with decreasing d below about 400 nm. It was found that the change in the resistivity is explained by the contribution of the Hall mobility because the carrier concentration is independent of the film thickness. We also found from X-ray analysis that the increase in the mobility with increasing film thickness can be related to an improvement in the crystallization of aluminium-doped films. The mobility may be limited by scattering from ionized impurities and grain boundaries, which is governed by the crystallization in ZnO films. The crystallization in polycrystalline films grown on glass substrates is determined by the number or types of nucleation on the surface of the substrate, particularly at the beginning of the deposition[4]. Therefore, we believe that the decrease in the mobility is ascribed to the enhancement of the carrier scattering mechanism resulting from disorder introduced in the ZnO lattice by the doping of the aluminium impurity.

4. CONCLUSION

Highly conductive films of undoped and aluminium-doped ZnO with a high transparency on non-intentionally heated substrates were prepared by r.f. magnetron sputtering in an applied external magnetic field in pure argon gas. Films with a resistivity as low as 2×10^{-4} Ω cm can easily be produced by sputter deposition onto substrates placed perpendicular to the ZnO target containing 2 wt.% Al_2O_3 dopant. The characteristic features in the electrical properties of aluminium-doped ZnO films are their high carrier concentration and low mobility in comparison with those for undoped ZnO films. Aluminium-doped ZnO films exhibit a dependence of the resistivity on the film thickness below 400 nm and a blue shift in absorption edge with increasing Al_2O_3 content. Films of ZnO with a high conductivity and transparency should be useful as a less expensive window material for solar cells and display devices.

ACKNOWLEDGMENTS

The authors wish to acknowledge S. Shooji, M. Igarashi, M. Makisawa, T. Kawamura and M. Yamamoto for their technical assistance in the experiments.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES

1 P. S. Nayer and A. Catalano, *Appl. Phys. Lett.*, *39* (1981) 105.
2 J. B. Webb, D. F. Williams and M. Buchanan, *Appl. Phys. Lett.*, *39* (1981) 640.
3 T. Minami, H. Nanto and S. Takata, *Appl. Phys. Lett.*, *41* (1982) 958.
4 K. Ito and T. Nakazawa, *Jpn. J. Appl. Phys.*, *22* (1983) L245.
5 H. Nanto, T. Minami, S. Shooji and S. Takata, *J. Appl. Phys.*, *55* (1984) 1029.
6 T. Minami, H. Nanto and S. Takata, *Jpn. J. Appl. Phys.*, *23* (1984) L280.
7 A. P. Roth, J. B. Webb and D. F. Williams, *Solid State Commun.*, *39* (1981) 1269.