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Preparation of transparent conducting ZnO thin films by excimer laser ablation method

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Transparent conducting Al-doped ZnO (AZO) thin films have been deposited on quartz glass substrate using XeCl excimer laser ablation technique. The effects of substrate temperature and oxygen gas pressure on the electrical and optical properties of the films deposited in an oxygen atmosphere were investigated. Optical transmittance above 85% was observed in the visible region of the spectrum for the 450 nm-thick film deposited from the ZnO target doped with 1 wt% Al_2O_3. Resistivity of 1.34×10^{-4} Ω·cm was obtained at low substrate temperature of 200 °C.

1. INTRODUCTION

Al-doped ZnO (AZO) thin films have attracted considerable attention for transparent conducting films in place of indium tin oxide (ITO) [1-2], because of their high conductivity, good optical transmittance, and low cost. AZO films have been prepared by several kinds of deposition techniques such as sputtering and chemical vapor deposition (CVD) [3-4]. On the other hand, the laser ablation method has been successfully applied to deposition of superconducting thin films and ferroelectric thin films[5-6]. Ogasawara *et al.* have demonstrated the preparation of ZnO thin films by the laser ablation using KrF excimer laser[7]. Recently, Suzuki *et al.* have carried out the preparation of transparent conducting ZnO thin films by the laser ablation using ArF excimer laser[8]. From the practical point of view, it is necessary to lower the process temperature while improving the quality and growth rate of the AZO thin films.

In this article, transparent conducting AZO thin films have been prepared using laser ablation method employing XeCl excimer laser (308 nm). The effects of substrate temperature and oxygen gas pressure on the electrical and optical properties of the films are described.

2. EXPERIMENTAL PROCEDURE

A schematic diagram of the experimental apparatus is shown in Figure 1. A XeCl excimer laser was used for ablation of AZO bulk target. The excimer laser beam was focused onto the target in the deposition chamber through a quartz lens and a quartz window. The power density of excimer laser beam at the target surface was maintained at 1.5 J/cm² and the repetition

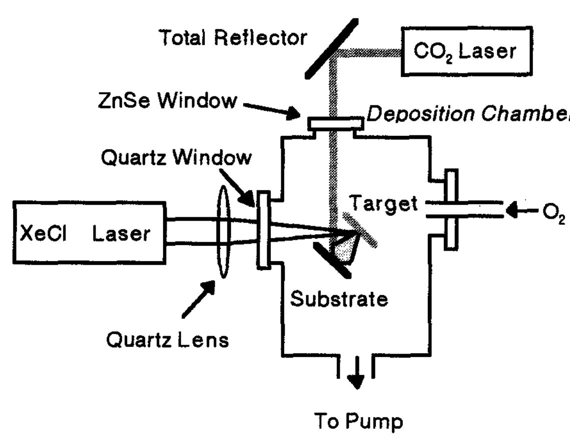

Figure 1. Schematic diagram of film deposition system using excimer laser ablation method.

rate was 5 Hz. The laser pulse duration was 20 ns. A substrate-target distance was 15 mm. The target was a sintered ZnO disc of 12 mm in diameter and 1.5 mm in thickness, containing excess Al_2O_3 of 0-5 wt%. Typical deposition rate of AZO film was 10 nm/min. The substrate heating was carried out using a continuous wave (cw) CO_2 laser (10.6 μm). The CO_2 laser was introduced into the deposition chamber through a ZnSe window and irradiated the surface of the substrate directly during deposition. The surface temperature of the substrate was controlled by varying the irradiation power density of the cw-CO_2 laser and was monitored by a Chromel-Almel thermocouples in contact with the surface of the substrate. Substrates used for AZO film deposition were quartz glass and single crystal Si (100). Deposition was carried out in an oxygen atmosphere. The pressure was changed from 10 to 200 mTorr. The substrate temperature was varied in the range from room temperature to 300 °C. The surface morphology of the film was investigated using scanning electron microscopy (SEM). The crystal orientation of the film was examined by X-ray diffraction (XRD). The resistivity of the deposited film was measured at room temperature by the Van der Pauw method. The optical transmittance through film was measured in the wavelength range from 350 to 800 nm using a spectrophotometer.

3. RESULTS AND DISCUSSION

The Al_2O_3 dopant content of the AZO target was changed from 0 to 5 wt%. AZO films were prepared from these targets at a substrate temperature of 300 °C and an oxygen pressure of 10 mTorr. Figure 2 shows the Al_2O_3 content dependence of the resistivity of AZO films. The film with the lowest value in resistivity was obtained from the target with Al_2O_3 content of 1 wt%. Hereafter, the AZO target with 1 wt% Al_2O_3 was used for the preparation of AZO thin films using excimer laser ablation.

Figure 3 shows the dependence of the resistivity of the film on the oxygen pressure. All AZO films shown in Figure 3 were prepared at a substrate temperature of 300 °C. The resistivity of the film increased with the increase of the oxygen pressure,

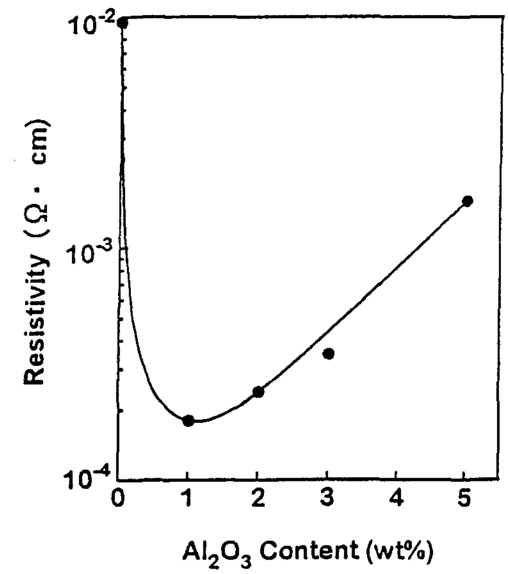

Figure 2. Dependence of resistivity of AZO films deposited at a substrate temperature of 300 °C from the ZnO target with 0-5 wt% Al_2O_3 on Al_2O_3 content.

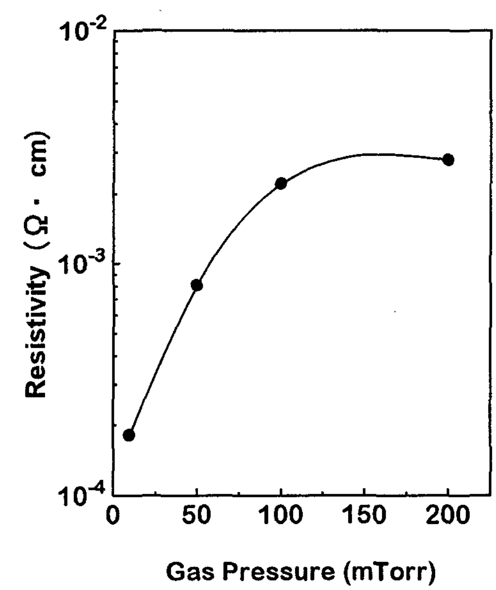

Figure 3. Dependence of resistivity of the AZO films deposited at a substrate temperature of 300 °C from the ZnO target with 1 wt% Al_2O_3 on the oxygen pressure.

and became almost constant at the oxygen pressure of 100 mTorr. The resistivity of $1.81\times10^{-4}\ \Omega\cdot cm$ was obtained for the film deposited at the pressure of 10 mTorr.

Figure 4 shows the XRD patterns of the films deposited at a substrate temperature of 300 ℃ under different oxygen pressures. The XRD patterns of AZO films showed (002) plane exclusively, which indicates that these films were oriented with c axis normal to the surface of quartz glass substrate. The intensity of (002) peak decreased as the oxygen pressure increased.

Figure 5 shows the optical transmittance spectra of the films deposited at a substrate temperature of 300 ℃ under different oxygen pressures. As shown in Figure 5, deposited AZO films have an average optical transmittance above 85% in the visible range. The film with high optical transmittance above 90% in the visible range was obtained at an oxygen pressure of 200 mTorr.

Figures 6 (a) and (b) show the SEM micrographs of the surface of the AZO (1 wt%) films deposited at

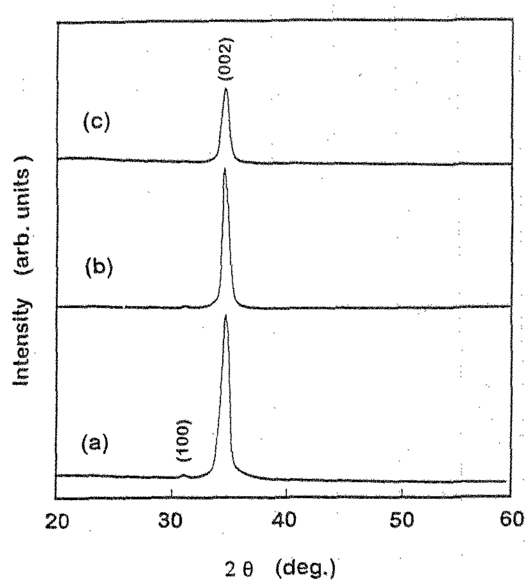

Figure 4. X-ray diffraction patterns of AZO films deposited at an oxygen pressure of (a) 10 mTorr, (b) 100 mTorr and (c) 200 mTorr.

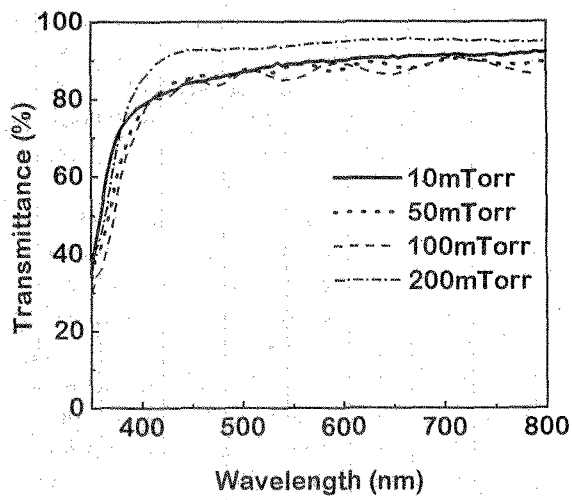

Figure 5. Optical transmittance spectra for AZO films deposited at an oxygen pressures of 10, 50, 100 and 200 mTorr.

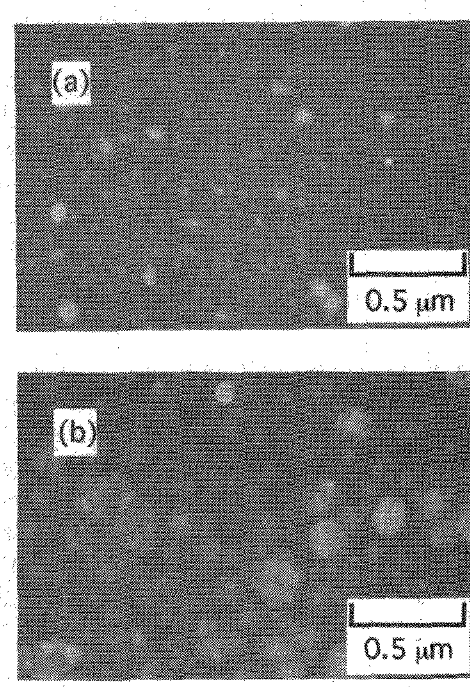

Figure 6. SEM micrographs of the surface of the AZO films deposited at oxygen pressures of (a) 10 mTorr and (b) 200 mTorr.

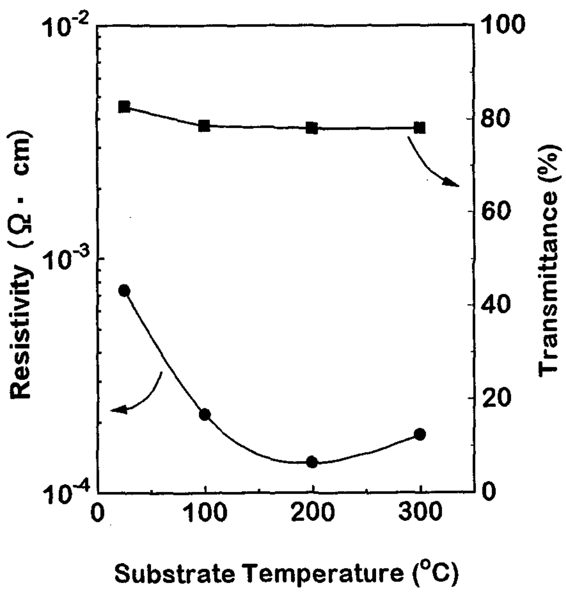

Figure 7. Dependences of resistivity and optical transmittance at the wavelength of 600 nm on the substrate temperature.

a substrate temperature of 300 °C and oxygen pressures of 10 and 200 mTorr, respectively. The surface morphology was strongly dependent on the oxygen pressure. As shown in Figure 6 (a), a smooth surface morphology with microcrystallites was observed for the film deposited at an oxygen pressure of 10 mTorr. In Figure 6 (b), on the other hand, grains with 100 to 300 nm in size were observed on the film deposited at an oxygen pressure of 200 mTorr.

Figure 7 shows the optical transmittance at the wavelength of 600 nm and the resistivity of the AZO films deposited at an oxygen pressure of 10 mTorr as a function of substrate temperature during deposition. The optical transmittance of the film was almost constant at 80% in the range of substrate temperature investigated. On the other hand, the resistivity of the film was significantly dependent on the substrate temperature and the minimum of the resistivity 1.34×10^{-4} Ω·cm was obtained for the film deposited at the substrate temperature of 200 °C.

4. CONCLUSIONS

The AZO (1 wt%) thin films of high conductivity and good transmittance were prepared by excimer laser ablation method. A smooth surface morphology was observed for the film deposited at an oxygen pressure of 10 mTorr. The resistivity of 1.34×10^{-4} Ω·cm and an average transmittance of 80% were obtained for the AZO film deposited at an oxygen pressure of 10 mTorr and a substrate temperature of 200 °C. In the case of the deposition at the oxygen pressure of 200 mTorr, an average transmittance above 90% in the visible range was obtained for the film deposited at the substrate temperature of 300 °C.

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