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Preparation of aluminum doped zinc oxide thin films by using RF sputtering equipment with asymmetric electrodes

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The transparent and conductive thin films of aluminum doped zinc oxide (ZnO:Al) were prepared by using the conventional radio frequency (RF) sputtering method. The deposition rate to the glass was increased with decrease of the grow discharge gap between the both electrodes under the condition of higher argon pressure. The heat treatment after deposition gave good effect on these characterization. The film characteristics, such as transmission loss of light, conductivity, and adhesion behavior to the based glass, were improved by heat treatment after the deposition.

1. INTRODUCTION

The conductive thin film of aluminum doped zinc oxide (ZnO:Al) is transparent in visible region and reflective in infrared region[1]. Thus the film might be applied to the high energy efficient windows. For this purpose, RF spattering method is considered to scale up the easy process for the large area on glass surface, and to go down the cost for the equipment.

In this work, the characteristics of ZnO:Al thin films prepared by various RF spattering condition, such as RF power, argon pressure, electrode distance, the setting angle of the substrate and annealing temperature were investigated. Up to date, the resistivity was improved to the order of 10^{-3} Ω·cm at the film thickness in the region of 600 to 950nm.

2. EXPERIMENTAL

Our equipment is a conventional type of RF sputtering system with asymmetric electrodes as shown in Fig.1. The excited electrode (target) coupled capacitively to RF generator (13.56MHz) is smaller than grounded electrode including the substrate holder and the chamber wall. High voltage is generated between the excited electrode and the plasma. High density area of RF plasma is produced at the interface of ion sheath and bulk plasma near the excited electrode[2]. To evaluate ion acceleration voltage, sheath voltages crossing from the target to the bulk plasma were calculated from measured

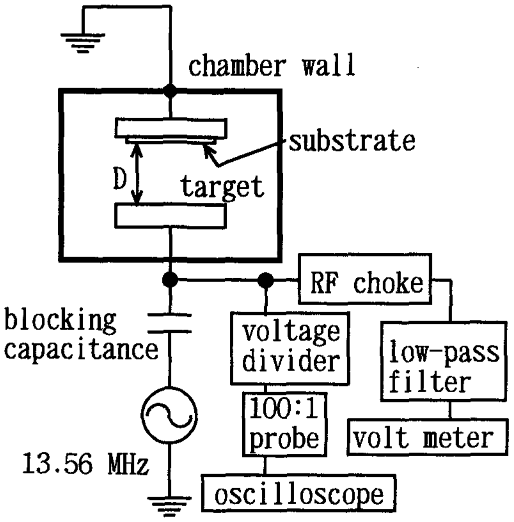

Fig.1 Schematic of experimental apparatus.

amplitudes of RF voltages and self biases at the conductor feeding RF power to the target[3].

Pure argon was introduced in the process chamber and the pumping system consisted of a diffusion pump and a rotary pump. Electrode distance was variable from 13 to 50mm. Hot pressed powder mixture of ZnO with a purity of 99.9% and Al_2O_3 with a purity of 99.99% was used as the target (diameter:80mm). The content of Al_2O_3 as the dopant source was 3mass%. Slide glass was used as the substrate. The substrates set parallel and vertical to the target surface. The temperature of the substrate was not controlled during the deposition.

The film thickness was calculated from maximum and minimum points in wave-lengths in optical transmittance curve. The optical transmittance in visible range, (300~800nm), was measured by the spectro photometer. The four-point probe and the van der Pauw technique were used to measure the resistivity and the electron density. The vacuum electric furnace was evacuated to a pressure of 1.3×10^{-3}Pa for the heat treatment. The adhesion behavior was examined by using the scratch tester with the stylus oscillated mecanically.

3. RESULTS AND DISCUSSION

3.1. Parallel setting

It was considered that characteristics of the films on substrates set parallel to the target surface strongly depend on the sheath voltage because degradation of film's conductivities would be caused by plasma damage, for example, by high energy ions.

The sheath voltage of the RF grow discharge was decreased by about 300V with increasing argon pressure from 1.3 to 13Pa and almost independent of the electrode distance as shown in Fig.2. These results suggest that increasing pressure would reduce the plasma damage and shortening the electrode distance would not give the films significant damage. It is obviously that decrease of electrode distance gives higher deposition rate. Thus, it was supposed that the

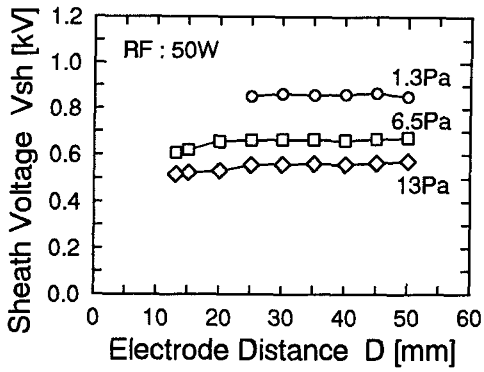

Fig.2 Sheath voltage dependence on electrode distance at different pressures.

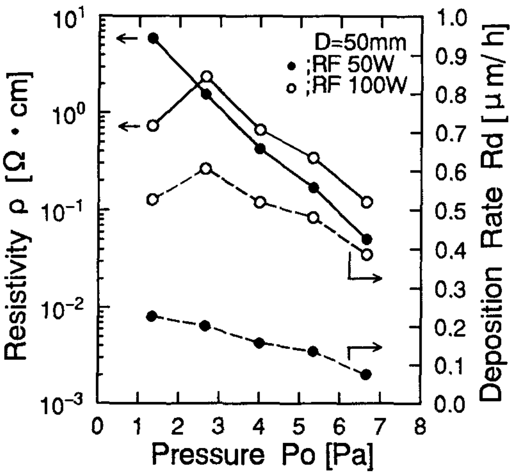

Fig.3 Dependence of resistivity and deposition rate at a power of 50 and 100W on pressure.

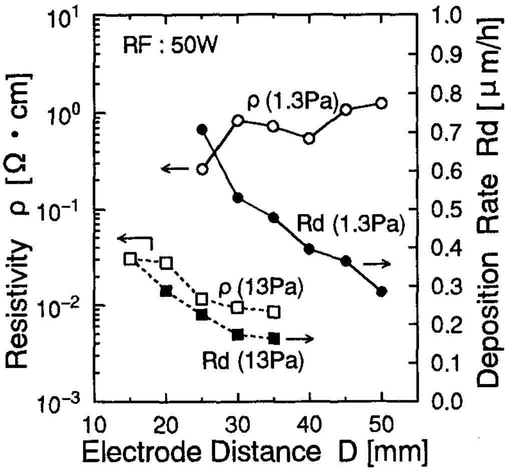

Fig.4 Resistivity and deposition rate along electrode distance at a pressure of 1.3 and 13Pa.

conductivity could be increased by rising argon pressure with keeping the deposition rate by adjusting the electrode distance.

Figure 3 shows that the resistivity decreases with increasing the pressure, but the deposition rate also decreases. When more RF power is introduced to the chamber to keep the deposition rate, the resistivity will go up. Figure 4 indicates that the deposition rate more than 0.15 μm/h can be obtained even at high pressure of 13Pa by shortening electrode distance, where the resistivity attained to as low as $8\times10^{-3}\,\Omega\cdot$cm at a electrode distance of 35mm.

Heat treatment in the evacuated electric furnace after the deposition could improve the film's characteristics such as conductivity, optical transmittance and adhesion behavior to the based glass. Figure 5 shows that the resistivity reduced to $4\times10^{-3}\,\Omega\cdot$cm at a temperature of 673K and heating period of 14.4ks(4hours). On the other hand, the electron density increased with the annealing temperature. Therefore, the reduction in the resistivity was carried out by increase in the electron density in the film. The optical transmittance after the heat treatment was improved in the wave-length range from 350 to 510nm as shown in Fig.6. Faint yellow coloring of the film disappeared after the heat treatment. The X-ray diffraction pattern was sharpened after the heat treatment as shown in Fig.7. It was considered that residual stress in the film was released.

Figure 8 shows the results of adhesion test. In this figure, critical load represents a load from the stylus at which the thin film begins peeling off from the substrate. The critical load profile increased rapidly at about 600K and went down

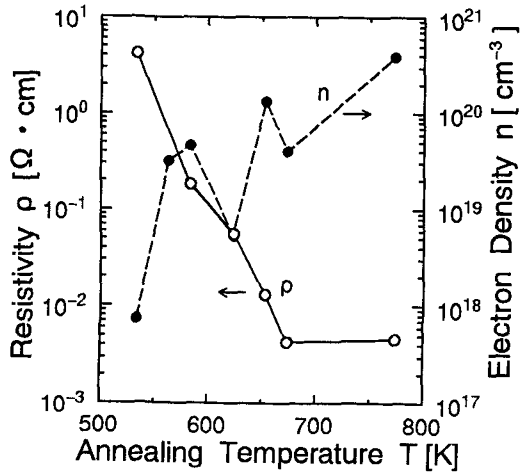

Fig.5 Variation both of resistivity and electron density with annealing temperature for 14.4ks. The samples were deposited under the condition of 1.3Pa, 50W and a electrode distance of 50mm.

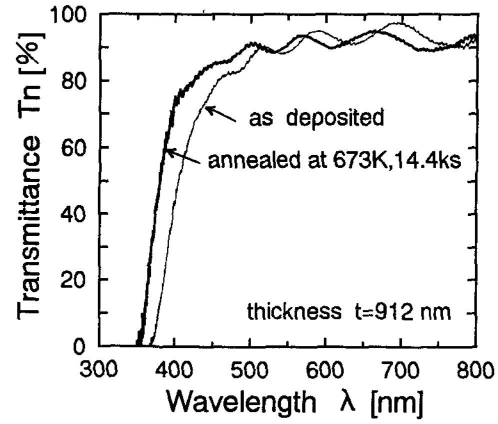

Fig.6 Normal transmission spectra as deposited and after annealed. The processing condition of the samples was 1.3Pa, 50W and a electrode distance of 50mm.

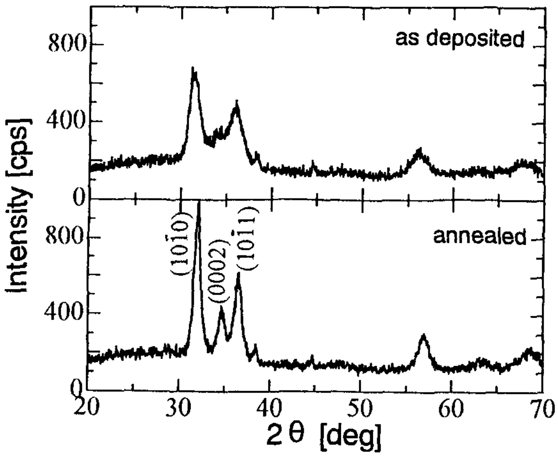

Fig.7 X-ray diffraction patterns (Cu-Kα) of parallel setting sample(1.3Pa,50W,D=50mm) as deposited and after annealed at 673K for 14.4ks.

at about 750K. Increase in the critical load was probably carried out by the diffusion reaction at the interface of the film and the glass.

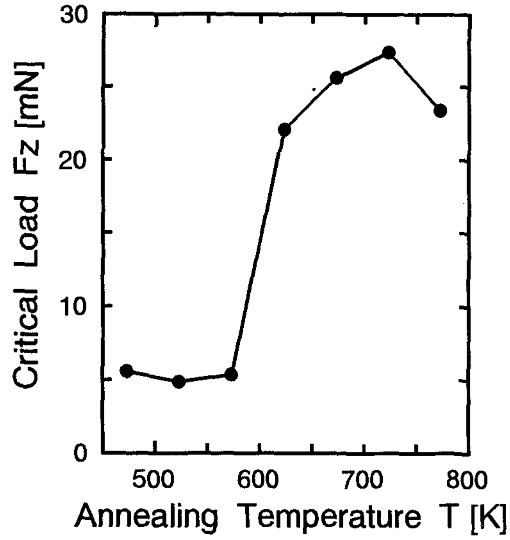

Fig.8 Critical load as a function of annealing temperature. The films were deposited at 1.3Pa, 50W and a electrode distance of 50mm.

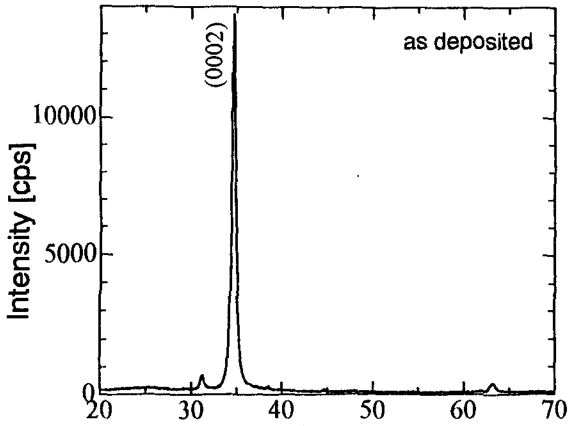

Fig.9 X-ray diffraction pattern (Cu-Kα) of vertical setting sample(1.3Pa,50W) as deposited.

3.2. Vertical setting

The films deposited on vertically set substrates to the target surface showed lower resistivities, about $5\times10^{-3}\,\Omega\cdot$cm, in comparison with those of parallel setting . Their X-ray diffraction pattern consists of only one strong peak from (0002) plane as shown in Fig.9. It seems that incident particles to the substrate with shallow angle enhance crystallization and crystal growth in the direction of c axis orienting to normal direction of the substrate surface.

The resistivity was reduced to $1\sim2\times10^{-3}\,\Omega\cdot$cm under the same heat treatment condition for the samples of parallel setting.

4. CONCLUSIONS

Thin film of ZnO:Al was produced by using RF sputtering system with asymmetric electrodes. Taking into consideration how this deposition technique is applied to large area of glass plate, the substrate should be set parallel to the target. In this parallel configuration, the low resistivity of the order of $10^{-3}\,\Omega\cdot$cm was obtained under the condition of closed electrode distance and high argon pressure during the deposition process. Even though the resistivity was bad condition of the order of $10^{0}\,\Omega\cdot$cm as deposited, it could be reduced to $4\times10^{-3}\,\Omega\cdot$cm by the subsequent heat treatment after deposition. At the same time, optical transmittance and adhesion behavior were improved.

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