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Properties of ITO Films Deposited with Different Conductivity ITO Targets

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Characterizations were performed for ITO films deposited using different erosion ratios for the target surface and different conductivity targets. The ITO films were deposited on unheated substrates using dc magnetron sputtering with different conductive targets, and then the films were post-annealed in a H_2 atmosphere in a vacuum chamber. By increasing the target erosion ratio, the optimal O_2 addition ratio to obtain the lowest resistivity was decreased. For the post-annealed films, the resistivity of the ITO films consistently deceased with an increasing T_a, which can be attributed to the increase of the carrier density. By increasing the target erosion ratio, the XRD patterns of the post-annealed ITO films showed a higher peak intensity on the (222) plane than that on the (400) plane, implying that the oxidation of the ITO films was enhanced.

Keywords: ITO, microstructure, post-annealing, magnetron sputtering, erosion ratio

1. INTRODUCTION

Indium tin oxide (ITO) film has been widely used as transparent electrodes for liquid crystal displays (LCDs), plasma display panels (PDPs), organic light emitting diodes (OLEDs), and solar cells [1,2] because it has a high electrical conductivity and optical transmittance in visible light. The preparation processes of ITO thin films include spray [3], chemical vapor deposition [4], and magnetron sputtering [5]. Among these processes, the most preferred method is dc magnetron sputtering using the ITO ceramic target because it has several advantages such as high controllability, high deposition rates, and large area uniform deposition [5]. The sintered high density ITO target is widely used to deposit transparent conductive thin film for various kinds of flat panel displays. In the dc magnetron sputtering process, nodule formation on the target surface is increased with an increasing sputtering time. Nodules formed on the surface of the ITO target degrade the film properties, i.e. resistivity, transmittance, crystallinity, etc. [6]. In order to reduce nodule formation, the ITO target density has been improved [7]. Nakashima *et al.* [8] reported that nodule formation by the ITO target was reduced using a fine raw powder and a modified mixing process.

In this study, ITO films are deposited using dc magnetron sputtering with high density ITO targets which have different conductivities. The correlation between the film properties and target erosion ratio was investigated for different ITO targets.

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2. EXPERIMENTAL PROCEDURE

ITO films with thicknesses between 150 nm and 160 nm were deposited on a non-alkali glass substrate (Corning E2000) at a total gas pressure of 0.6 Pa by dc magnetron sputtering. The depositions were performed using ITO ceramic sintered disks (Samsung Corning Co., Ltd.) with different conductivities. In order to optimize the resistivity of the ITO films, oxygen gas was added to Ar gas [$O_2/(O_2+Ar)$] with a flow ratio of 0 % to 3.0 %. The water partial pressure of the residual gas was maintained at less than 9×10^{-4} Pa to guarantee high reproducibility of the film properties. The depositions were performed without substrate heating at a constant dc power of 100 W. ITO films were also post-annealed under various conditions, such as different annealing temperatures (170 °C and 250 °C) and introducing H_2 gas (0.05 %) in a vacuum chamber for 1 h.

The film thickness was measured using a surface profiler (DekTak[3], Veeco). Resistivity, carrier density, and Hall mobility were measured using Hall Effect measurements (HMS-3000, ECOPIA) at room temperature. Transmittance was measured using a UV-Vis spectrophotometer (200 nm - 2000 nm); X-ray diffraction (XRD) was performed using 40 kV-30 mA CuK_α radiation (X'Pert-Series PW 3040, Philips).

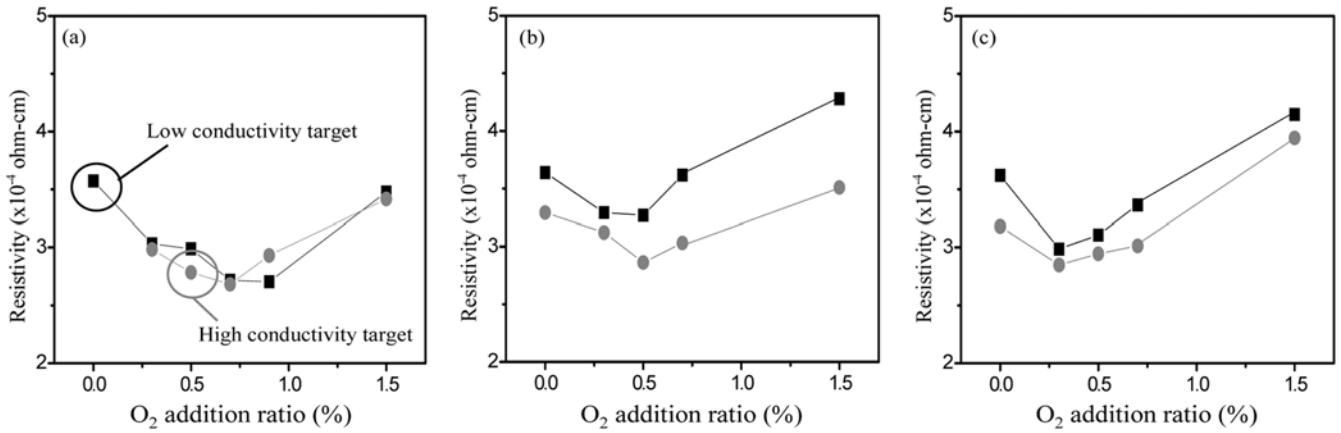

Fig. 1. The change of resistivity of ITO films deposited using different conductivity targets with an increasing O_2 gas addition ratio in relation to the target erosion ratios: (a) 5 %, (b) 15 %, and (c) 30 %.

3. RESULTS AND DISCUSSION

Figure 1 shows the change of resistivity of ITO films with an increasing O_2 gas addition ratio in relation to the target erosion ratios: (a) 5 %, (b) 15 %, and (c) 30 %. Deposition was performed with a low conductivity target and a high conductivity target without substrate heating. For each target erosion ratio (5 %, 15 %, 30 %), despite different target conductivities, relatively low resistivities were obtained for the films deposited at O_2 addition ratios of 0.7 %, 0.5 %, and 0.3 %, respectively. The optimum resistivity using the O_2 addition was generally observed in the manufacturing line of the sputtered ITO films. The sputtered atoms should experience collision scattering with sputter gases between the target and substrate before they arrive at the substrate surface in the sputtering process [9]. Sputtered oxygen atoms with small masses can be scattered widely compared with sputtered In or Sn atoms. Therefore, it is possible that the composition of the ITO film is different from that of the ITO target.

It was also found that the optimum O_2 addition ratio to obtain the lowest resistivity decreased with an increasing target erosion ratio. This result can be attributed to the change in the chemical composition of the target surface with an increased sputtering time. With an increase of the target erosion ratio, the high conductivity target showed relatively low resistivity of ITO film compared with the low conductivity target. It is therefore considered that the high conductivity ITO target led to the decrease in micro-nodule formation on the target surface due to its high cooling efficiency.

Figure 2 shows the transmittance of the ITO films deposited without substrate heating for different O_2 addition ratios (0 % and 3.0 %) and target erosion ratios (5 % and 30 %). The as-deposited films showed high transmittances (above 85 %) in the visible light region. A red-shift was also observed at the absorption edge with an increasing O_2 addition ratio

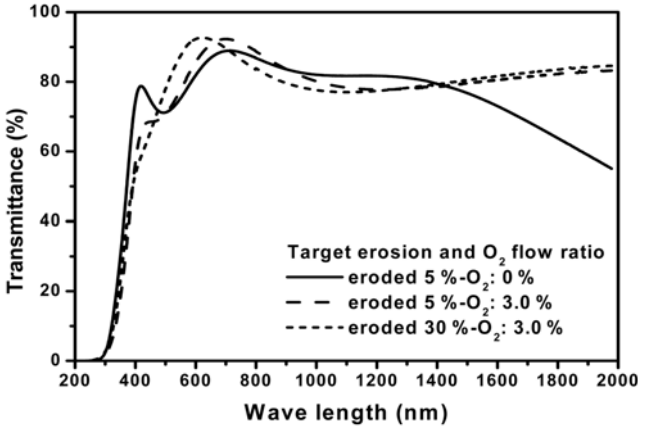

Fig. 2. Transmittance of the ITO films deposited using high conductivity targets with O_2 addition in relation to the target erosion ratio.

and target erosion ratio, which could have originated from the absorption of excess SnO_2 impurities [10].

The change in the electrical properties of the ITO films with an increasing annealing temperature is shown in Fig. 3. These films were deposited using a high conductivity target with different erosion ratios (15 % and 30 %) under O_2 addition ratios of 0 % and 0.7 %; then they were annealed under a H_2 addition ratio of 0.05 % in a vacuum for 1 hour. The resistivity of the ITO films deceased with an increasing T_a, which is attributed to an increase of the carrier density. However, Hall mobility decreased with an increasing T_a, which may be explained in terms of the increase of "ionized scattering centers" [11,12]. A clear increase of resistivity was observed at 250 ^{o}C for the film deposited using the 30 % eroded target at an O_2 addition ratio of 0.7 %. This resulted from the large decrease of the Hall mobility and the small increase of the carrier density, which is related to the oxidation of the ITO film with an increase in the target erosion ratio.

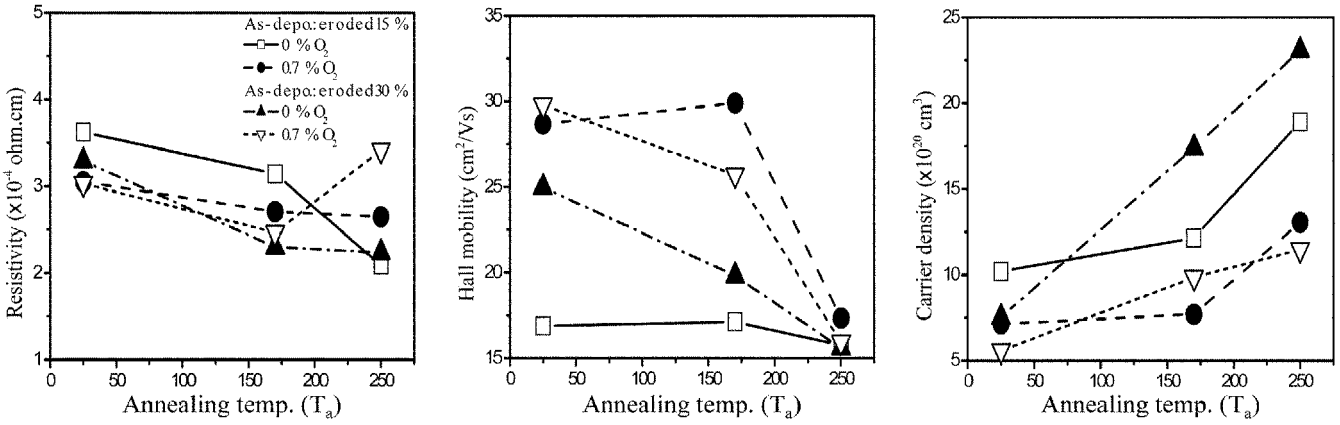

Fig. 3. (a) Resistivity, (b) Hall mobility, and (c) carrier density of ITO films with an increasing annealing temperature (T_a) under a H_2 addition ratio of 0.05 % in a vacuum chamber.

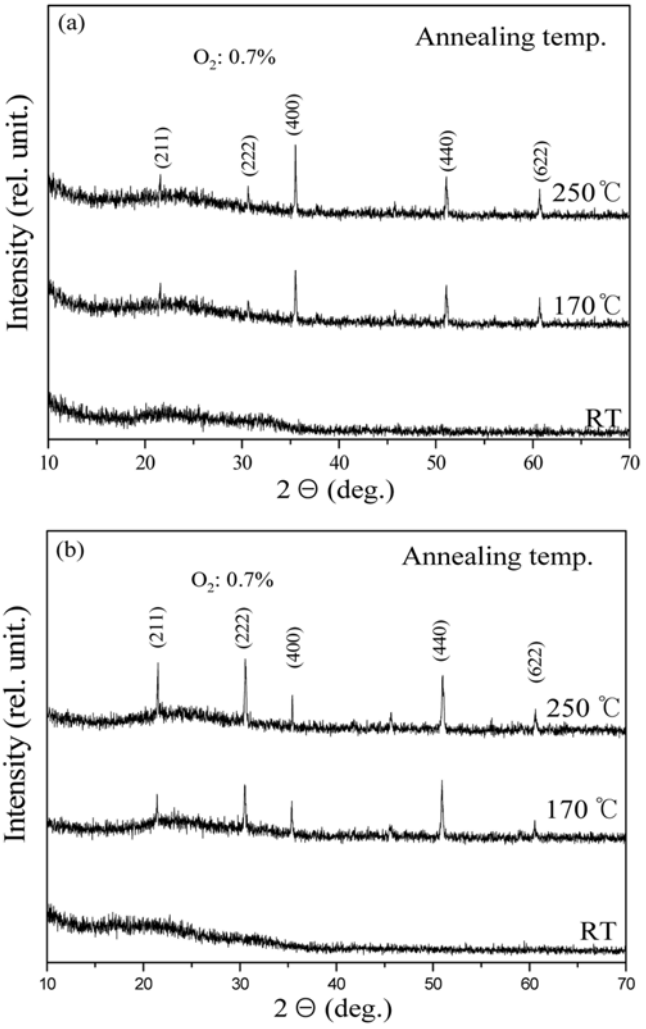

Fig. 4. XRD patterns of the ITO films with an increasing annealing temperature at H_2 = 0.05 %, where (a) and (b) represent ITO films deposited with target erosions of 15 % and 30 %, respectively.

Figure 4 shows the XRD patterns of the ITO films with an increasing T_a under a H_2 addition ratio of 0.05 %, where (a) and (b) films were deposited with a target erosion of 15 % and 30 %, respectively. From the XRD results, the as-deposited films were confirmed to have amorphous structures, whereas the post-annealed films showed a polycrystalline structure above a T_a of 170 °C, indicating that the crystallization temperature of amorphous ITO films was between 150 and 170 °C [13]. For the 15 % eroded target, a preferred crystal growth on the (400) plane was observed with an increasing T_a, compared with the (222) plane in the 30 % eroded target. However, for the 30 % eroded target, the peak intensity of the (222) plane was higher than that of the (400) plane. This result is responsible for the oxygen partial pressure during deposition, which is related to the generation or exhaustion of oxygen vacancies, i.e. carrier density.

4. SUMMARY

ITO films were deposited on unheated glass substrates using dc magnetron sputtering with different conductive targets. There is an optimum O_2 addition ratio to obtain the lowest resistivity for each target which decreased with an increasing target erosion ratio. A red-shift was observed in the visible light region when the target erosion ratio was increased. For the post-annealed films, the ITO film resistivity deceased with an increasing T_a, which is attributed to the increase in the carrier density. The Hall mobility decreased with an increasing T_a, which may be explained by the increase of "ionized scattering centers". However, a clear increase in resistivity was observed at 250 °C for the film deposited using 30 % eroded target at an O_2 addition ratio of 0.7 %. This is responsible for the large decrease of Hall mobility and the small increase of carrier density compared with other films. With an increasing target erosion ratio, the XRD patterns of the post-annealed ITO films showed a higher

peak intensity on the (222) plane than that on the (400) plane, implying that the oxidation of ITO films was enhanced. This result can be related to the variations of carrier density in ITO films.

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