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Microstructure and Electrical Properties of Yb- or Sm-Doped Indium–Tin-Oxide Films Prepared by DC Magnetron Sputtering

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Indium–tin-oxide (ITO) films and Sm- or Yb-doped ITO films were deposited by DC magnetron sputtering using sintered ceramic ITO targets containing 3.0 wt % of Sm or Yb. The depositions of the films were carried out in pure Ar inert gas under a total gas pressure of 0.5 Pa and without substrate heating. The as-deposited films were post annealed at various temperatures, *viz.*, 170 and 250 °C, in an Ar gas atmosphere at 1.0 Pa for 1 h. The effect of the doped Sm- or Yb-impurities on the microstructure and electrical properties of the ITO films was investigated. It was confirmed that the microstructure, electrical properties, and surface morphology of the Sm- or Yb-doped ITO films were strongly dependent on the content of impurity atoms in the films. The crystallization of the films during deposition was interrupted owing to the large radii of the Yb^{3+} and Sm^{3+} ions doped into the In_2O_3 matrix. The surface roughness of the films was improved by the doping of Yb- or Sm-impurities, as compared with that of the undoped ITO film. The resistivity of the films gradually decreased with increasing annealing temperature. The minimum resistivity of the films was obtained at an annealing temperature of 250 °C owing to the increase in carrier concentration and Hall mobility.

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1. Introduction

Indium–tin-oxide (ITO) films are widely used as transparent conductive electrodes for flat panel displays (FPDs). However, their physical and chemical properties must be improved to produce high quality FPDs. Amorphous ITO films are highly attractive as advanced transparent conducting oxide (TCO) films owing to their superior surface morphology and etching behavior. In general, the properties of amorphous ITO films were found to mainly depend on their microstructure.[1)] To deposit amorphous ITO films, it is necessary to control the deposition parameters,[2)] such as the amount of additional gas injected and the deposition temperature, because the crystallization temperature for general ITO films is about 170 °C.[3)] However, it is still difficult to produce amorphous ITO films because the injection of additional gases deteriorates the properties of the film owing to the increase in the number of target nodules.[4)]

To achieve the easy deposition of amorphous ITO films without the need to control these complicated deposition parameters, we conducted a thorough investigation focusing on the addition of Yb_2O_3 or Sm_2O_3 to the ITO target bulk. The ionic radii of Yb^{3+} (0.81 nm) and Sm^{3+} (0.97 nm) are larger than that of In^{3+} (0.80 nm). Therefore, their addition led to a decrease in the crystallization temperature of the ITO films owing to the effects of the added impurities. Moreover, the use of a sintered quaternary oxide target should make it possible to easily control the deposition system. In this study, the microstructure and electrical properties of ITO, ITO:Yb, and ITO:Sm films deposited at various substrate temperatures were investigated.

2. Experimental Procedure

ITO, ITO:Yb, and ITO:Sm films with thicknesses of 150–160 nm were deposited on unheated non alkali glass substrates (Corning E2000) by DC magnetron sputtering using high-density ceramic targets consisting of ITO (10 wt % SnO_2), Yb_2O_3-doped ITO (3 wt % Yb_2O_3), and Sm_2O_3-doped ITO (3 wt % Sm_2O_3), respectively. The distance between the target and the substrate was 50 mm and the DC power was maintained at 100 W for all the depositions. The as-deposited films were post annealed at various temperatures (170 and 250 °C) in an Ar (99.9999% purity) gas atmosphere at 1.0 Pa for an hour. The thickness and electrical properties of the films were measured using a surface profilometer (Veeco DekTak[3]) and Hall effect measurements (ECOPIA HMS-3000), respectively. The X-ray diffraction (XRD) patterns of the films were measured with Cu Kα radiation (40 kV–20 mA) (BRUKER GADDS). The transmittance of the films was measured using a spectrophotometer (Cary 4E UV–Vis). The atomic force microscopy (AFM; PSIA XE-120) measurement was performed in the non contact mode. The average roughness of the films R_a, was estimated by calculating the average of five R_a values measured at different points on their surfaces.

3. Results and Discussion

3.1 Microstructure of the films

Figures 1(a)–1(c) show the XRD patterns of the ITO, ITO:Yb, and ITO:Sm films deposited using a commercial ITO target, 3 wt % Yb_2O_3 doped ITO target, and 3 wt % Sm_2O_3 doped ITO target at room temperature and annealed at different temperatures, respectively. As shown in this figure, the ITO films annealed at temperatures above 170 °C have a crystalline structure with strong peaks for (222) and relatively weak peaks for (400). The films composed of ITO:Yb and ITO:Sm annealed at 170 °C are amorphous; they are crystallized when the annealing temperature is increased above 200 °C. The crystallization temperature of amorphous ITO films has been reported to be about 170 °C.[3)] The formation of the amorphous structures of ITO:Yb and ITO:Sm annealed at 170 °C is most likely due to the size effects of the Yb^{3+} and Sm^{3+} ions doped into the ITO films. The crystallization of the films during their deposition may be interrupted because the ionic radii of Yb^{3+} and Sm^{3+} are larger than that of In^{3+}. There were no peaks observed in addition to the typical peaks corresponding to the ITO phases in the films.

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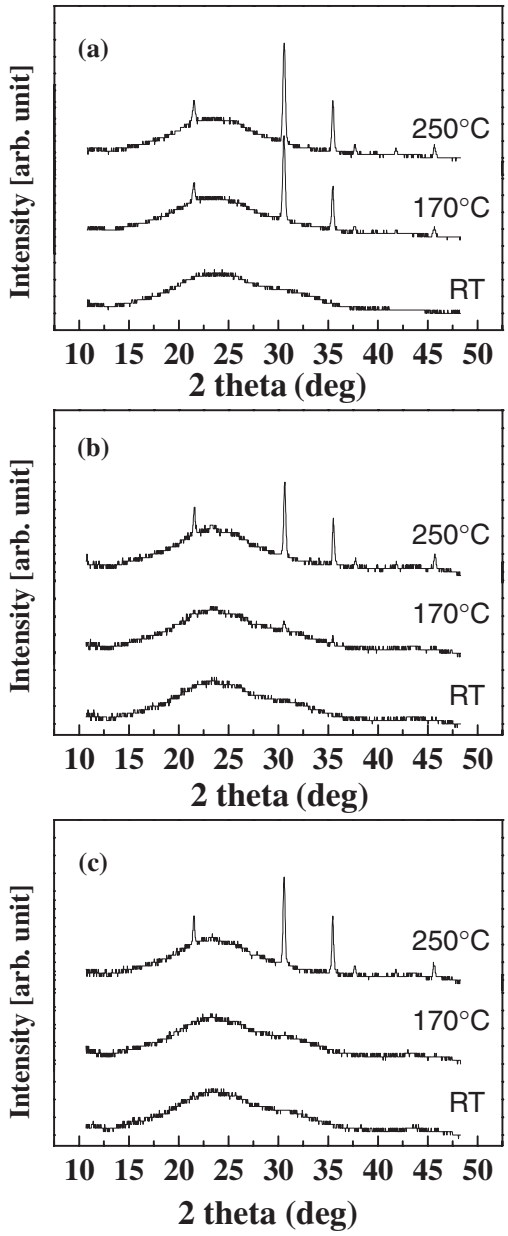

Fig. 1. XRD patterns of (a) ITO, (b) ITO:Yb, and (c) ITO:Sm films annealed at different temperatures.

3.2 Electrical properties of the films

The electrical properties, *viz.*, resistivity, carrier density, and Hall mobility, of the ITO, ITO:Yb, and ITO:Sm films annealed at different temperatures are shown in Fig. 2. The resistivity of the films decreased with increasing annealing temperature and the lowest resistivities of 1.65×10^{-4} (ITO), 2.78×10^{-4} (ITO:Yb), and $2.63 \times 10^{-4}\,\Omega\,\mathrm{cm}$ (ITO:Sm) were obtained by annealing the films at 250 °C. It is well known that the resistivity of the films is related to the concentration of carriers and their mobility. Shigesato *et al.*[5] reported that the carrier concentration in ITO films arises from oxygen vacancies and activated Sn^{+4} ions. They also reported that Sn does not generate any carriers in amorphous ITO films.[6] Therefore, the carrier concentration of the ITO, ITO:Yb, and ITO:Sm films increased with increasing annealing temperature, owing to the improved solubility of the doped impurities and generated oxygen vacancies. The amorphous ITO:Yb and ITO:Sm films have

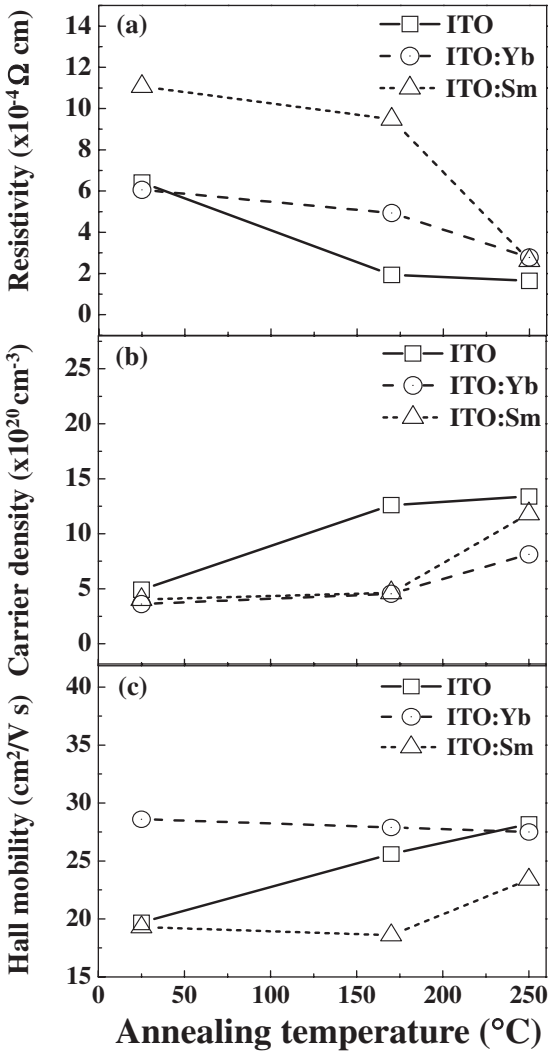

Fig. 2. (a) Resistivity, (b) carrier density, and (c) Hall mobility of ITO, ITO:Yb and ITO:Sm films as a function of annealing temperature.

lower mobilities than the ITO film at annealing temperatures below 170 °C. This is in agreement with the result show in Fig. 1(b). On the other hand, Fig. 2(c) shows that the mobilities of the ITO:Yb and ITO:Sm films remain almost constant, despite the increase in annealing temperature from room temperature to 170 °C. This tendency was attributed to the amorphous microstructure of the ITO:Yb and ITO:Sm films. The doped atoms, including Sn, Yb, and Sm, acted as neutral scattering agents in the amorphous films.[6] The thermal energy induced by annealing in the range from room temperature to 170 °C was less than the activation energy required to substitute the doped ions into the In matrix. Therefore, the mobilities of the ITO:Yb and ITO:Sm films annealed at temperatures below 170 °C were decreased. The increased mobility at a higher annealing temperature of 250 °C was considered to be due to the effects of grain growth. Therefore, the minimum resistivity of the films was obtained at an annealing temperature of 250 °C, owing to the increase in the carrier concentration and Hall mobility.

3.3 Optical properties

Figure 3 shows the optical transmission measured over the wavelength range of 200–1100 nm for the ITO, ITO:Yb, and ITO:Sm films annealed at 250 °C. As shown in this figure,

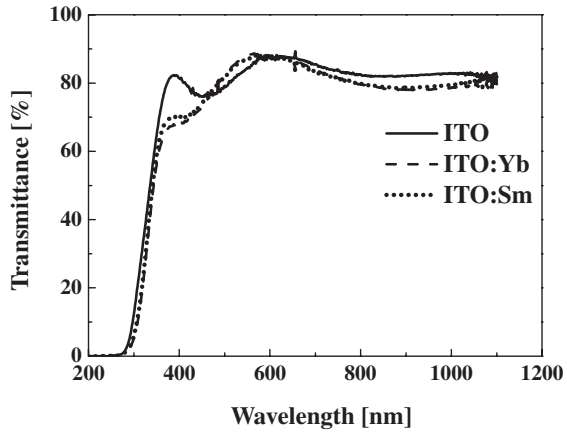

Fig. 3. Optical transmission spectra of ITO, ITO:Yb, and ITO:Sm films annealed at 250 °C.

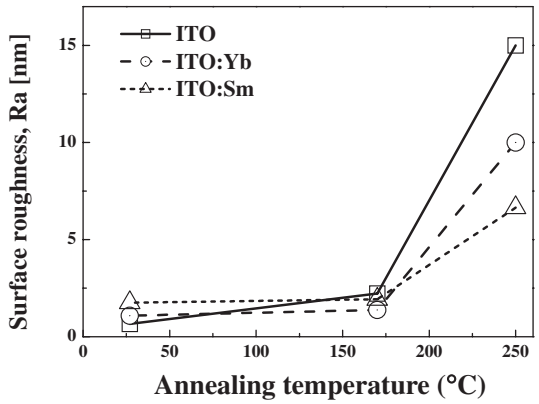

Fig. 4. Surface roughness of ITO, ITO:Yb, and ITO:Sm films annealed at various temperatures.

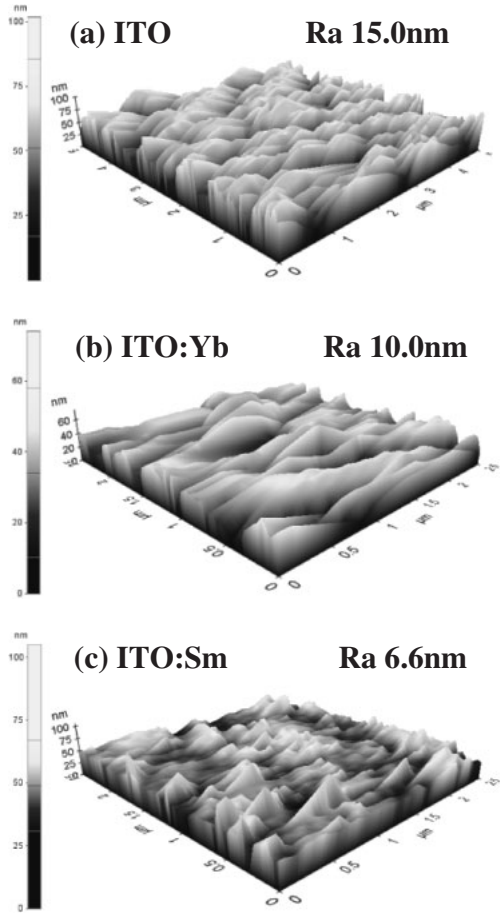

Fig. 5. AFM images of (a) ITO, (b) ITO:Yb, and (c) ITO:Sm films post annealed at 250 °C.

all of films had a high transmittance of more than 80% in the region of visible light. The transmittances of the ITO, ITO:Yb, and ITO:Sm films were 84.4, 87.5, and 88.0% at a wavelength of 550 nm, respectively.

3.4 Surface morphology of the films

The average roughness values (R_a) and surface morphology images obtained by atomic force microscopy (AFM) are shown in Figs. 4 and 5, respectively. As the annealing temperature was increased from room temperature to 250 °C, the surface roughness of the ITO film abruptly increased from 0.66 to 15.00 nm. However, the surface roughness of the ITO:Yb and ITO:Sm films are lower than those of the ITO films. This result may be related to the microstructure of the films determined from the XRD results. The crystallization of the ITO:Yb and ITO:Sm films was interrupted, owing to the additional impurities. Therefore, the surface roughness of the ITO:Yb and ITO:Sm films is lower than that of the ITO film. The improved surface roughness of the ITO:Yb and ITO:Sm films will enable them to satisfy the demand for advanced TCO films in various FPDs fields.

4. Conclusions

The films were deposited using a commercial ITO target, 3 wt % Yb_2O_3-doped ITO target, and 3 wt % Sm_2O_3-doped ITO target at room temperature. The crystallization of the films during their deposition was interrupted owing to the large radii of the Yb^{3+} and Sm^{3+} ions doped into the In_2O_3 matrix. The surface morphology of the ITO:Yb and the ITO:Sm films was improved compared with that of the ITO film. The resistivity of the films decreased with increasing annealing temperature. The minimum resistivity of the ITO ($1.65 \times 10^{-4}\,\Omega\,\mathrm{cm}$), ITO:Yb ($2.78 \times 10^{-4}\,\Omega\,\mathrm{cm}$), and ITO:Sm films ($2.63 \times 10^{-4}\,\Omega\,\mathrm{cm}$) was obtained at an annealing temperature of 250 °C owing to the increase in the carrier concentration and Hall mobility. However, further research is necessary to investigate the effects of the doped Yb and Sm atoms at various contents in ITO films.

Acknowledgments

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