Densification and Grain Growth of Indium-Tin-Oxide and Indium Oxide Thin Films Fabricated by Dip Coating Process

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Indium oxide and tin-doped indium oxide (ITO) films were fabricated by repeating dip coating and heating at various temperatures in air for 30 minutes before annealed in N₂-0.1%H₂ at 600°C for 30 minutes. The heating at 300°C resulted in porous nanostructure composed of small grains and crystallite size. Densification and growth of grain and crystallite size were remarkable when heated at 800°C. Resistivity of the film decreased by increasing the heating temperature until 700°C. The resistivity increase at the higher heating temperature was attributed to the crack formation of the films. The lowest resistivity (5.5 × 10⁻⁴ ohm cm) was obtained when the ITO film was prepared at 500°C.

Key words: ITO, transparent conducting films, dip coating, crack formation, thermal expansion

1. INTRODUCTION

Tin-doped indium oxide (Indium-Tin-Oxide) is used for transparent conducting films which are applied to flat panel displays including touch panels, solar cells, heat-shielding windows, transparent heaters, shielding of electromagnetic waves etc. The ITO films are often fabricated by physical vapor deposition such as sputtering process. Dip coating is a process wherein a substrate is pulled up from the solution of the precursory material prior to heating. Dip coating process can provide large area deposition of transparent conducting films easily without material loss. The electrical properties for the reported ITO films fabricated by dip coating process were listed in Table 1. The lowest resistivity was approximately 3×10⁻⁴ ohm cm. These values were compatible with those fabricated by sputtering process.

The dip-coated films were composed of minute grains and pores⁴ and resulted in higher resistivity compared with the lowest reported value (7.7×10⁻⁵ ohm cm) for dense films with large grains fabricated via pulsed laser deposition on a single-crystal yttrium-stabilized zirconia substrate by Ohta et al.⁵ and via spray chemical vapor deposition on a glass substrate by Sawada⁶. Densification and grain growth of dip coated ITO and In₂O₃ films were attempted in the present study by heating at higher temperature to investigate the relationship between the nanostructure and the resistivity.

2. EXPERIMENTAL

Substrates were Corning #1737 glass (50 mm × 30 mm × 0.7 mm) and silica glass (60 mm × 30 mm × 0.8 mm). The substrates were ultrasonically cleaned for 10 minutes using Semicolean 56 (Furuch Ichemical Co., Ltd.). The substrates were rinsed three times using de-ionized water before being boiled for 10 minutes in acetone.

The coating solutions were supplied from ADEKA Co., Ltd. The In₂O₃ films were fabricated using Indium 2-ethylhexanate monohydroxide, dissolved in xylene : ethanol : butyl acetate = 9 : 1 : 1 (viscosity, 47-55 mPa s). The ITO films were fabricated using indium 2-ethylhexanate monohydroxide and tin 2-ethylhexanate, (In : Sn = 90 : 10) dissolved in xylene : butyl acetate = 9 : 1 (viscosity, 52 mPa s).

The substrate was dipped into the solution and pulled up at the rate of 10 cm/min before heating in air with a furnace for 30 minutes in air at 300, 400, 500, 600, 700 or 800°C. The dip coating and the heating were repeated four or five times before annealing (thermal reduction) in N₂-0.1%H₂ atmosphere at 600°C for 30 minutes.

The film thickness (mass thickness) was determined by X-ray fluorescent analysis (fundamental parameter method) assuming the specific densities of In₂O₃ and ITO were 7.121 g/cm³ and 7.121 g/cm³ at 600°C, respectively. The XRF was measured using a model JX-3200 (JEOL) with Rh X-ray source and energy dispersive type detector.

The crystal state was evaluated by X-ray diffraction analysis using a copper rotating target (the acceleration voltage, 40 kV; the target current, 300 mA) and a graphite monochromator (model Rint 2500V, (Rigaku)).

The FE-SEM used was a model S-5000 (Hitachi) with the acceleration voltage of 20 kV for the nanostructure observation.
3. RESULTS AND DISCUSSION

3.1 Crystal state
All X-ray diffraction peaks for the present films agreed with those for In$_2$O$_3$. No other phase was detected. The crystals oriented randomly. The (222) diffraction peak was the strongest as well as that of the powders. The half width at half maximum (HWHM) for (222) peak was plotted as a function of the heating temperature in Figure 1. Decrease of the width at high temperature indicated growth of the crystallite size. Tin doping suppressed the growth.

3.2 Nanostructure
The FE-SEM photos for the fractured surface of the In$_2$O$_3$ films are shown in Figure 2. The film fabricated at 300°C was porous and consisted of small grains whose sizes were a several or 10 nm. From the thickness determined from the photo (660 nm) and the mass thickness determined by the X-ray fluorescent analysis (400 nm) the relative density was calculated as 60.6%.

Table 1. Reports on electrical properties for ITO films fabricated by dip coating process

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The film fabricated at higher temperature (800°C) was denser and consisted of grains equal to or larger than approximately 20 nm. The relative density calculated from the FE-SEM photo (500 nm) and the mass thickness accelerated remarkably the densification and grain growth.

Fig. 2. FE-SEM photos of Indium oxide films.

The fractured surfaces for the ITO films are shown in Figure 3. In case of the film fabricated at 300°C the relative density calculated from the FE-SEM photo (970 nm) and the mass thickness (387 nm) was 37.8%. This value was much lower than that of the In$_2$O$_3$ film. The (404 nm) was 80.8%. Thus heating at higher temperature thickness of the film fabricated at 800°C were 840 nm and 507 nm, respectively determined by the FE-SEM photo and XRF. The relative density (60.4%) was higher than that fabricated at 300°C although much lower than that of In$_2$O$_3$ film fabricated at the same temperature. Thus tin doping restrained grain growth and the densification.

3.3 Optical properties

Optical transmittances for In$_2$O$_3$ films are shown in Figure 4. The transmittance for the uncoated glass substrate is shown for reference. The average transmittances in the visible range are 82.4% for the films fabricated at 600°C. The lower values (75.2, and 75.7%) were obtained when fabricated at 300 and 800°C, respectively. Periodic fluctuations are attributed to the interference between the substrate and thin film with the higher refractive index. Less fluctuations for the film fabricated at 300°C was interpreted as lower reflective index of the film with lowest density.

Transmittances for ITO films are shown in Figure 5. The average transmittances in the visible range are 87.4, 82.5, and 82.3% for the films fabricated at 300, 700 and 800°C, respectively. Decrease of transmittance at infrared region was due to the absorption by the carrier electron in the film.

3.4 Resistivity

The resistivity of the as-deposited films is shown in Figure 6. The resistivity in the figure was calculated from the mass thickness determined by XRF. Tin doping lowered the resistivity remarkably. Annealing (thermal reduction) lowered the resistivity remarkably in case of tin-doped films. The lowest resistivity after annealing was $5.5 \times 10^{-2}$ and $5.5 \times 10^{-3}$ ohm cm, respectively for In$_2$O$_3$ films (thickness; 431 nm) fabricated at 600°C on a silica glass and ITO films (thickness; 450 nm) fabricated at 700°C on was on a silica glass. High values at higher temperature was attributed to the cracks in the films. Figure 7 shows a photo of digital microscope for the ITO films fabricated at 800°C on a silica glass. The cracks would be formed during the cooling process by the difference of the thermal expansion coefficients of ITO film (1.02×10$^{-5}$/K) and silica glass (0.05×10$^{-5}$/K).
4. Conclusions
Densification and grain growth of In$_2$O$_3$ and ITO films was accelerated by increasing the heating temperature. Resistivity of the films decreased by increasing heating temperature until at 500-700°C. Increase of the resistivity at higher temperature was attributed to crack formation of in the film.

Acknowledgements
The authors thank to Ms. A. Iwasawa (TOTO Ltd.) for FE-SEM and digital microscope observation, Dr. A. Yajima, Mrs. A. Yoshinaka and H. Kameda (Asahidenka Co. Ltd.) for providing the dip coating solutions.

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(Received March 15, 2009; Accepted April 20, 2009)