

Indium-Tin-Oxide Transparent Conducting Films Prepared by Thermal Decomposition of Solution Containing Indium Formate and Tin Chloride

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Tin-doped In_2O_3 (ITO) films were prepared by the dip-coating method using a novel solution, indium formate $\text{In}(\text{OCHO})_3$, and tin dichloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in the ethanol containing 2-aminoethanol (monoethanolamine) $\text{H}_2\text{NC}_2\text{H}_4\text{OH}$. The influence of the tin concentration on the electrical properties of the as-deposited films was investigated between 0 and 20 at.%. The composition of the films (thickness, ~295 nm) approximately agreed with that of the solution when the dipping and the heating at 600 °C for 30 min in air were repeated thirty times. The ITO films were highly transparent in the visible range. The maximum carrier concentration ($1.0 \times 10^{21} \text{ cm}^{-3}$) and minimum resistivity ($2.1 \times 10^{-4} \Omega \cdot \text{cm}$) were obtained at 6.4 at.%Sn with relatively high mobility ($28 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) after annealing at 600°C for 1 h in $\text{N}_2\text{-}0.1\% \text{H}_2$.

Key words: indium-tin-oxide, indium formate, dip coating, transparent conducting films, tin dichloride

1. INTRODUCTION

Indium-Tin-Oxide (tin-doped In_2O_3 - ITO) has been used as transparent conducting films. The dip coating method has the following advantages: low costs, little material loss, applicability to a large area and step-coverage on complicated surfaces. Resistivities in the order of $10^{-4} \Omega \cdot \text{cm}$ were reported for the dip-coated films; $(6\text{-}8) \times 10^{-4} \Omega \cdot \text{cm}$ [1], $4.23 \times 10^{-4} \Omega \cdot \text{cm}$ [2], $3.3 \times 10^{-4} \Omega \cdot \text{cm}$ [3] for example. However, they were still higher than those deposited by other processes such as CVD ($1.3 \times 10^{-4} \Omega \cdot \text{cm}$ [4]), sputtering ($6.8 \times 10^{-5} \Omega \cdot \text{cm}$ [5]), ion plating ($7 \times 10^{-5} \Omega \cdot \text{cm}$ [6]), pulsed laser deposition ($7.4 \times 10^{-5} \Omega \cdot \text{cm}$ [7]). Therefore, a novel solution was developed in the present study to achieve low-resistivity films by the dip-coating process; indium formate $\text{In}(\text{OCHO})_3$, and tin dichloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in ethanol containing 2-aminoethanol (monoethanolamine), $\text{H}_2\text{NC}_2\text{H}_4\text{OH}$.

Ethanol was selected as the solvent because it is inexpensive and environmentally safe. Indium formate was selected as the indium source, because of the lower number of carbon atoms in the molecule than other indium salts of organic acids such as indium 2-ethylhexanoate by Tsunashima et al. [8], Matsushita et al. [9] and J. J. Xu et al. [10] and indium acetate by Takahashi et al. [3] and R. Bel Hadj Tahar et al. [11]. Indium formate is easily synthesized and stable in the solid form at room temperature. Tin dichloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, was selected for its high solubility in ethanol. In order to lower the resistivity, annealing in a reducing atmosphere was executed in a simple and inexpensive way under flowing $\text{N}_2\text{-}0.1\% \text{H}_2$ gas in the present study. The minimum resistivity ($2.1 \times 10^{-4} \Omega \cdot \text{cm}$) in the present work is probably the lowest those among of the dip-coated films reported.

2. EXPERIMENTAL

Corning 7059 glass substrates ($39 \times 24 \times 0.8$ mm³) were ultrasonically cleaned in water with detergent (Semicoclean 56, Furuuchi Chemical Co., Ltd.) for 10 min, rinsed with water and boiled in acetone (purity 99.0 %, Wako Pure Chemical Industries, Ltd.) for 10 min. Indium formate was synthesized by refluxing indium oxide, In₂O₃ (purity 99.999%, Kojundo Chemical Laboratories Co, Ltd.) in formic acid (purity 99.0%, Wako Pure Chemical Industries, Ltd.) for 2 weeks.

For the preparation of undoped In₂O₃ films, 0.01 mol of indium formate was dissolved in ethanol (75 ml, purity 99.5%, Wako Pure Chemical Industries, Ltd.) that contained 0.04 mol of 2-aminoethanol (purity 97%, Wako Pure Chemical Industries, Ltd.). For preparation of the ITO films, indium formate and tin dichloride (SnCl₂·2H₂O, purity 99.9 %, Kojundo Chemical Laboratories Co., Ltd.), whose total amount was fixed at 0.05 mol, were dissolved in the ethanol solution (75 ml) containing 2-aminoethanol. Tin dichloride was soluble in ethanol while indium formate was insoluble; therefore, 2-aminoethanol was added. The molar ratio of indium formate and 2-aminoethanol was fixed at 1:4; the ratio was experimentally determined. The glass substrate was dipped into the solution for 1 min and pulled up in air at a rate of 10 cm/min. Since both surfaces of the substrate were simultaneously coated with the solutions, one of the surfaces was wiped with ethanol. The specimens were directly heated at 600 °C for 30 min in air. The dipping and the heating were repeated thirty times. The specimens were then annealed at 600 °C for 1 h at a heating rate of 10 °C/min in flowing N₂-0.1%H₂ gas (flow rate 300 ml/min) in an alumina tube (42 mm inner diameter) then cooled to 100 °C before being removed.

All oxide films were examined by energy dispersive X-ray fluorescence analysis (Model JSX-3200, JEOL Ltd.) with Rh radiation (30 kV) to determine the thickness and the composition. The film thickness determined by X-ray fluorescence analysis agreed with those by the profilometer (DecTak Surface Profile Measuring System). The crystalline state of the oxide film was evaluated by X-ray diffraction analysis (Model RINT-2500V,

Rigaku Co., Ltd.) with a high-power X-ray source (Cu, 40 kV, 300 mA) at a scan speed of 2.0 deg./min. The optical transmission of the film was measured in the wavelength range between 200 and 1100 nm using a UV-Vis. spectrometer (Model UV-1200, Shimadzu Co., Ltd.). The resistivities of the films were measured by the four-point-probe method (0.6 mm probe distance, 0.5 mm probe diameter, 1 mA probe current) with a digital multimeter (Model 34401A, Hewlett Packard Co., Ltd.). The carrier concentrations and mobilities were measured by the van der Pauw method (3.0×10^3 G DC magnetic field, 1 mA probe current) with a Hall coefficient analyzer (Model MI-675, Sanwa Radio Measurement Works Co., Ltd.).

3. RESULTS AND DISCUSSION

The film composition Sn/(In+Sn) approximately agreed with the composition of the solution. All X-ray diffraction peaks were assigned to In₂O₃ [12] for the films prepared from solutions with various at.%Sn. The (222) diffraction peak was remarkably strong; the preferred orientation was suggested. The peak intensities (peak areas) decreased with increasing tin concentration.

The film thickness (average 300 nm) was approximately independent of the film composition and the annealing atmospheres.

Typical examples of the optical transmittance of the as-deposited and the annealed films are shown in Figs. 1 and 2, respectively. A high visible transmittance (average 82%) was achieved for the as-deposited films with 0 and 6 at.%Sn. The transmittance decreased on annealing in a reducing atmosphere. A brown film was obtained by annealing the film without Sn. In case of 6 at.%Sn film, the visible transmittance decreased slightly (average 74%). In Fig.2, the reflectance of 6 at.%Sn film is indicated for reference. The decrease in transmittance at the near infrared region should be attributed to the absorption because an increase in reflectance was not observed.

The dependence of the resistivity on the film composition is shown in Fig. 3. Tin doping decreased the resistivity. The minimum resistivity for the as-deposited films was 1.2×10^{-3} Ω·cm at 6.4 at.%Sn (thickness 295 nm). Annealing in a

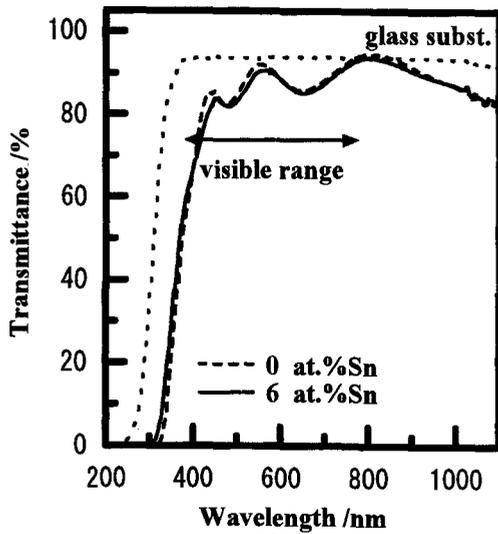


Fig. 1 Optical transmittance of the as-deposited ITO films.

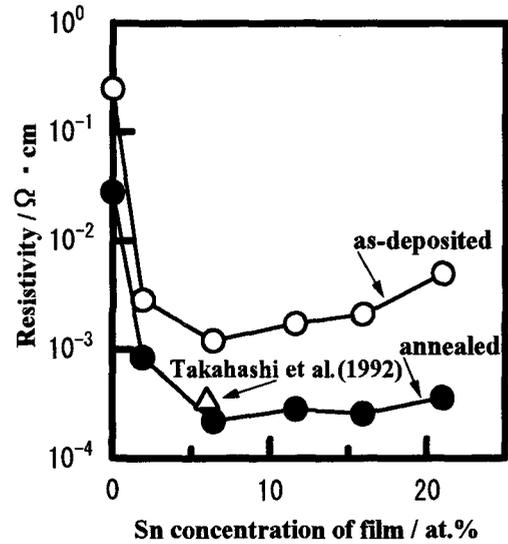


Fig. 3 Dependence of resistivity on the film composition.

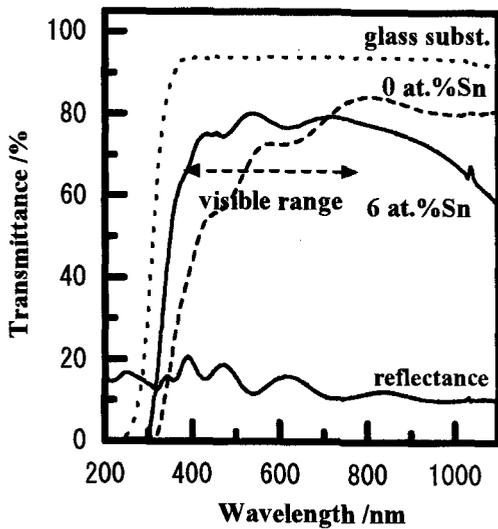


Fig. 2 Optical transmittance of the annealed ITO films.

The dependence of carrier concentration on the film composition is shown in Fig. 4. Carrier concentration increased with tin doping and annealing in a $N_2-0.1\%H_2$ atmosphere. High values were observed at 6-16 at.%Sn. Maximum carrier concentration in the present work was $1.0 \times 10^{21} \text{ cm}^{-3}$ at 6.4 at.%Sn. This result agreed excellently with that by Takahashi et al. [3] ($1.0 \times 10^{21} \text{ cm}^{-3}$ at 6.4at.%Sn).

$N_2-0.1\%H_2$ atmosphere lowered resistivity. Low resistivity was observed at the (6-16) at.%Sn. The minimum resistivity ($2.1 \times 10^{-4} \Omega\cdot\text{cm}$) was obtained at 6.4 at.%Sn (thickness; 295 nm). This value is probably the lowest of the dip-coated films. This figure also shows, for reference, the result ($3.3 \times 10^{-4} \Omega\cdot\text{cm}$, 300 nm thick) by Takahashi et al. [3] that was the lowest found in the literature.

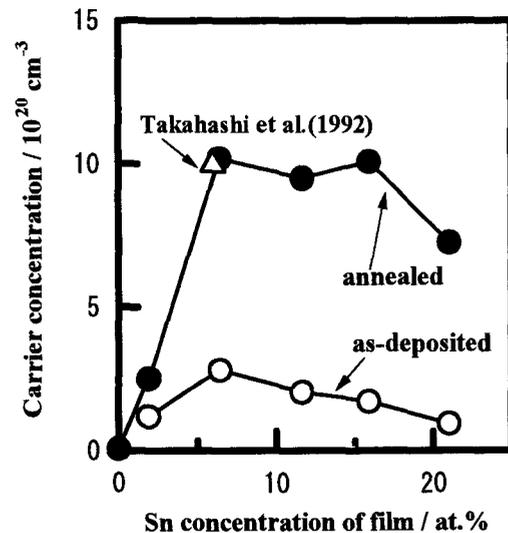


Fig. 4 Dependence of carrier concentration on the film composition.

The dependence of mobility on the film composition is shown in Fig. 5. The films showed a relatively high value compared with those of other ITO films fabricated by the dip-coating process. This should be attributed to the precursors material. Takahashi et al. [13] reported that decreasing the film thickness per coating when repeating the dip-coating and the heating enhanced the crystal growth. The present oxide layer (thickness; ~ 10 nm) fabricated by one cycle was thinner than their films (thickness $> \sim 15$ nm); this supported the higher mobility of the present film. The mobility increased with the annealing. The maximum mobility achieved was $34 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for undoped In_2O_3 films. The mobilities decreased slightly as the tin concentration increased. The mobilities of ITO films were higher than $24 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. High mobility

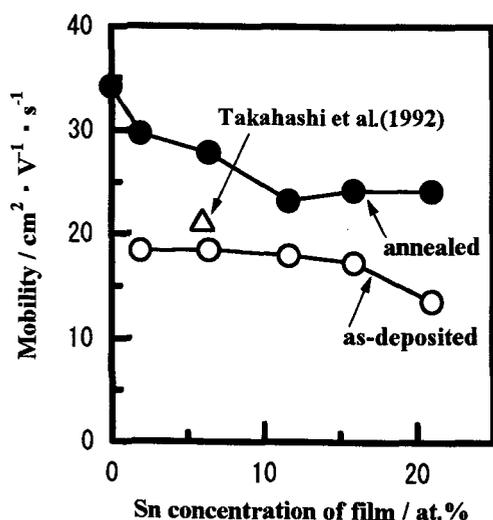


Fig.5 Dependence of mobility on the film composition.

($28 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) was achieved for the ITO film (6.4 at.%Sn) with the lowest resistivity and the highest carrier concentration. This mobility was higher than the value ($21 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) by Takahashi et al. [3] that should be the highest reported for the dip-coated ITO films.

The authors thank Prof. Y. Shirai of our institute for use of the X-ray fluorescence analyzer.

4. CONCLUSION

Glass substrates were coated with the ethanol solutions of indium formate, tin dichloride and

2-aminoethanol. The substrates were heated at $600 \text{ }^\circ\text{C}$ for 30 min in air to prepare ITO films. After repeating the dip coating and the heating thirty times, the ITO films (~ 295 nm thickness) were annealed at $600 \text{ }^\circ\text{C}$ for 1 h in flowing N_2 -0.1% H_2 to enhance the conductivity. The electrical properties of the films were investigated as a function of the tin concentration. The carrier concentration increased with the annealing. The minimum resistivity ($2.1 \times 10^{-4} \Omega \cdot \text{cm}$) was achieved at 6.4 at.%Sn where the carrier concentration was a maximum ($1.0 \times 10^{21} \text{ cm}^{-3}$) with high carrier mobility ($28 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).

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