Indium-Tin-Oxide Thin Films Prepared by Dip Coating Using Ethanol and Water Solution of Indium Chloride and Tin Chloride.

Ryoko Ota, Shigeyuki Seki, Yutaka Sawada,
Toshikazu Nishide* and Azusa Shida**
Department of Industrial Chemistry, Graduate School of Engineering, Tokyo Institute of Polytechnics,
1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan
Fax: 81-46-242-3000, e-mail: sawada@chem.t-kougei.ac.jp
* Department of Materials Chemistry and Engineering, Collage of Engineering, Nihon University,
Tamura-machi, Koriyama, Fukushima 963-8642 Japan.
Fax: 81-24-956-8862, e-mail: nishide@ce.nihon-u.ac.jp
** Yokohama City Center for Industrial Technology and Design,
1-1-1 Fukuura, Kanazawa-ku, 236-0004 Yokohama, Japan
Fax: 81-45-788-9555, e-mail: azusash@blue.plala.or.jp

Formation of indium-tin-oxide (ITO) transparent conducting films were attempted on Corning #7059 glass substrate by dip coating using indium (III) chloride, tin (II) chloride and tin (IV) chloride dissolved in ethanol, water and mixture of ethanol and water. The glass substrate repelled the coating solutions containing indium (III) chloride with and without tin (IV) chloride. Transparent conducting films were obtained when using solutions containing high concentration of tin (II) chloride. Addition of surfactant into the solution improved the contact; transparent oxide films were obtained without exception. Transparent conducting ITO films were obtained; the lowest resistivity achieved in the present work was 6.1×10^{-3} ohm·cm for a film (thickness, 13 nm; Sn/(In+Sn), 5.4 at.%) prepared using ethanol solution with indium (III) chloride and tin (II) chloride (Sn/(In+Sn); 5 at.%) after annealed at 600°C for 1 h in a nitrogen flow. Lower resistivity was obtained by repeating the dipping and the heating; resistivity of 3.5×10^{-3} ohm·cm was achieved for the four-layer film (total thickness, 41 nm; 4.4 at.%Sn) after annealed at 600°C for 1 h in a nitrogen flow. Addition of surfactant expanded successfully the variety of coating solutions.
Key words: ITO transparent conducting films, dip coating, ethanol solution, water solution, surfactant

1. INTRODUCTION

Thin films of tin-doped indium oxide (indium-tin-oxide, ITO) are deposited often by physical vapor deposition such as sputtering method in order to obtain highly conducting transparent films at relatively low substrate temperature. Dip coating is advantageous for preparation of large area ITO films with less production cost although the conductivity is rather insufficient in most cases. Solutions of indium chloride and tin chloride in alcohol and/or water are possibly the simplest and the cheapest raw materials for dip coating of ITO films. However, little was known of the dip coating process using these solutions although spray hydrolysis using these solutions were reported [1-7]. The lack of the dip coating process should be attributed to the contact between the solutions and the glass substrate; in fact, the glass substrate such as Corning #7059 repelled ethanol and/or water containing indium chloride remarkably. This let us expect the possibility to form ITO transparent conducting films only if the contact is improved by any method.

In the present study, applicability of dip coating using the solutions of indium (III) chloride and tin chloride in ethanol and/or water was investigated systematically. Influence of tin (II) chloride and tin (IV) chloride was compared. Then, surfactant (surface-active agent) was added into the solution to improve the contact. Transparent conducting films were obtained successfully although the resistivity was higher compared with the minimum values of the dip-coating films (in the order of 10^{-4} ohm·cm) reported [8-11] and those deposited by PVD process such as Nath et al. [12] (7×10^{-5} ohm·cm), Ray et al. [13] (6.8×10^{-5} ohm·cm) , Rauf [14, 15] (4.4×10^{-5} ohm·cm) and Ohta et al. [16] (7.7×10^{-5}ohm·cm). Clarification of the contact was abandoned in the present work.

2. EXPERIMENTAL

Indium (III) chloride (InCl₃·3.5H₂O, purity 99.99%) and tin (II) chloride (SnCl₂·2H₂O, purity 99.9%) and tin (IV) chloride (SnCl₄·5H₂O, purity 98%) were supplied from Kojundo Chemical Lab. Co., Ltd. and used without further purification. The chlorides were dissolved into ethanol (purity 99.5 vol.%, Wako Pure Chemical Industries, Ltd.) and stirred for 5 hours to prepare the solution (0.1 mol/l, 50 ml) of indium (III) chloride, tin (II) chloride, tin (IV) chloride, indium (III) chloride plus tin (II) chloride (Sn/(In+Sn); 5, 10 and 15 at.%) and indium (III) chloride plus tin (IV) chloride (Sn/(In+Sn); 5, 10 and 15 at.%) . The chlorides were also dissolved into de-ionized water and stirred for 5 h to prepare the respective solutions (50 ml). When preparing the solution (50 ml) of ethanol and water, the chloride was dissolved into ethanol (25 ml) and stirred for 5 h before adding de-ionized water and further stirring for 7 h.

Corning #7059 glass substrate (25 mm×37 mm×0.7

mm) was cleaned ultrasonically for 10 min in detergent (Semicoclean 56, Furuuchi Chemical Co., Ltd.) and rinsed several times with de-ionized water. The glass substrate was boiled in acetone for 10 min and picked up quickly into the air. The substrate was dipped into the coating solutions for 1 min and pulled up in air at the rate of 28 cm/min so that the both surfaces of the substrate were coated simultaneously. For evaluation of the oxide film, the substrate was held horizontally in order to wipe with ethanol the coating on the lower surface of the substrate. A specimen was placed in an alumina tube (inner diameter, 42 mm) and heated in air at the heating rate of 10°C/min to hold at 600°C for 1 h before cooling by switching off the power of the furnace. Some specimen was then heated in the same furnace by the same heating program but in a nitrogen flow (purity 99.9995%, flow rate 2.0 l/min); the specimen was picked out from the nitrogen flow into air at approximately 100°C.

Approximately 0.06 g of a detergent (K-soft, University Cooperative; sodium alkyl ether sulfuric esters and fatty acid alkanol amide) was added as a surfactant to the above mentioned 50 ml solutions for the purpose of enhancing the contact with the glass substrate; the EPMA analysis of the residue after heated at 500°C in air showed approximately equal molar amount of sodium and sulfur (0.99:1.00). Approximately 6 specimens were inserted quickly into an electric furnace (inner dimension; 19 cm×15 cm×25 cm) preheated at 600°C; the specimens were heated for 30 min in air and picked out quickly. The dip coating and the heating were repeated for some specimens in order to increase the film thickness. Then, the specimen was heated at the heating rate of 10°C/min to anneal at 600°C for 1 h in a nitrogen flow (purity 99.9995%, flow rate 2.0 l/min) in an alumina tube; the cooling was executed in the nitrogen flow until approximately 100°C when the specimen was picked out.

The thickness and the composition of the oxide films were determined by X-ray fluorescence analysis (model JSX-3200, JEOL) with Rh radiation (30kV). The crystalline state of the film was evaluated by X-ray diffraction analysis; model RINT-2500V, Rigaku Co. with thin-film optics (incident angle; 0.5°) and a graphite monochrometer using Cu radiation (40 kV, 300 mA). The optical transmission was measured with a conventional spectrometer (model UV-1200, Shimadzu Co., Ltd.). The resistivities of the films were measured by four-point-probe method; probe distance 0.65 mm, probe current 1 mA using a multimeter (model 34401A, Hewlett Packard Co., Ltd.). The compositional analysis of the residue after heating in air was performed by EPMA (model 8705, Shimadzu Co., Ltd.) with the electron beam accelerated by 15 kV.

3. RESULTS AND DISCUSSION

3.1 Precipitation from the water solution of tin (II) chloride

Results of the dip coating with and without the surfactant are presented in Table I. In case of water solution of tin (II) chloride, dip coating was abandoned

because precipitation occurred. The X-ray diffraction spectrum of the precipitation is shown in Fig. 1. This figure also shows the result after heating the precipitation at 1000°C in air. The spectrum of the heated precipitation agreed with that of tin(IV) oxide SnO_2 [17]. The as-dried precipitation showed the similar spectrum with broader peaks; formation of SnO_2 or a precursory compound with SnO_2-like structure was suggested.

Table I: Results of dip coating

solute		surfactant	solvent		
			EtOH	H₂O	EtOH + H₂O
InCl₃		free	×	×	×
		added	△	△	△
SnCl₂		free	○	—	○
		added	○	—	○
SnCl₄		free	△	△	△
		added	○	○	○
InCl₃ + SnCl₂	5 at.%Sn	free	×	—	×
		added	△	—	△
	10 at.%Sn	free	△	—	△
		added	○	—	○
	15 at.%Sn	free	○	—	○
		added	○	—	○
InCl₃ + SnCl₄	5 at.%Sn	free	×	×	×
		added	△	△	△
	10 at.%Sn	free	×	×	×
		added	△	△	△
	15 at.%Sn	free	×	×	×
		added	○	○	○

addition of surfactant (K-soft); approx. 1.2 g/l
○: solution coatable and oxide film conductive, △: solution coatable and oxide film nonconductive, ×: uncoatable, —: coating abandoned because of the precipitation.
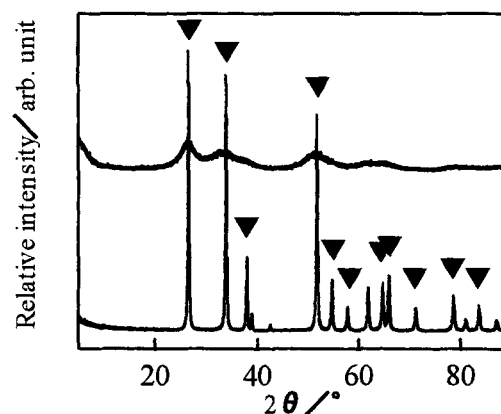

Fig. 1: X-ray diffraction spectrum of the precipitation formed in water solution of tin (II) chloride.
A and B; as-dried precipitation and that after heating at 1000°C in air.

3.2 Dip coating without surfactant

Precipitation did not occur when ethanol was used as solvent. Difference resulting from the solvent was undistinguished in the present study except the precipitation mentioned above.

As indicated in Table I, the glass substrate (Corning #7059) repelled the solution of indium (III) chloride without the surfactant. Transparent oxide films were obtained when dip-coated with other chloride solution i.e. the solution of tin (II) chloride or tin (IV) chloride. Transparent and conducting films were obtained only when coated using the tin (II) chloride solution. These results indicated the priority order of the solute for obtaining transparent conducting films as tin (II) chloride > tin (IV) chloride > indium (III) chloride. Addition of tin (II) chloride offset the repellence caused by indium (III) chloride. Among the indium (III) chloride solutions, transparent conducting film was obtained only in case of the highest concentration of tin (II) chloride, i.e. 15 at.%Sn in the present study. Solutions containing both indium (III) chloride and tin (IV) chloride repelled the glass substrate without exception; tin (IV) chloride seems insufficient to offsets the repellence caused by indium (III) chloride.

3.3 Dip coating with surfactant

Addition of the surfactant into the solution improved remarkably the contact between the solution and the substrate; transparent oxide films were obtained successfully without exception in the present experiment. Transparent conducting films were achieved when using the solution containing tin (II) chloride (10, 15 and 100 at.%Sn) or tin (IV) chloride (15 and 100 at.%Sn). Thus, the surfactant enhanced the formation of transparent conducting film remarkably. The lowest resistivity (4.8×10^{-1} ohm·cm) was obtained for the film (thickness, 12 nm; 6.0 at.%Sn) prepared using ethanol solution of $InCl_3$ and $SnCl_2$ (5 at.%Sn) with the surfactant (1.2 g/l). The annealing in a nitrogen flow reduced the resistivity to 4.0×10^{-2} ohm·cm.

3.4 Influence of the surfactant concentration

Influence of the surfactant concentration in the dip-coating solution was investigated for the ethanol solution with indium (III) chloride and tin (II) chloride (5 at.%Sn). Tin concentration in the oxide film (average, 5.0 at.%) was independent of the surfactant concentration (0.6-8.0 g/l) and higher than that of the solution (5 at.%Sn). Sodium and chlorine was not detected in the oxide films by the X-ray fluorescence analysis. Degradation of the film conductivity by sodium ion seems negligible in the present case. Absence of chlorine was interpreted as complete formation of oxide. The thickness of the oxide films (average, 14.8 nm) was independent of the surfactant concentration in the solution. The resistivity of the oxide film is indicated in Fig. 2 as a function of the surfactant concentration in the coating solution. Drastic decrease in the resistivity was observed at a narrow range of the surfactant concentration. The minimum resistivity in the present case was 1.2×10^{-1} ohm·cm for a film (thickness, 17 nm; 19 at.%Sn) prepared using ethanol solution with indium (III) chloride and tin (II) chloride (5 at.%Sn) with the surfactant concentration 0.87 g/l. The resistivity was reduced to 6.1×10^{-3} ohm·cm by annealing at 600°C in a nitrogen flow for 1 h.
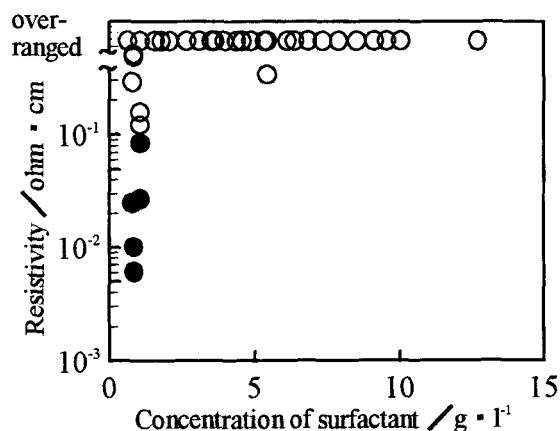

Fig. 2: Resistivity of the oxide films as a function of the surfactant concentration in the dip-coating solution. $\bigcirc$; heated at 600°C in air for 30 min, and $\bullet$; annealed at 600°C in nitrogen for 1 h after heating in air. Ethanol solution of inidium (III) chloride, tin (II) chloride (5 at.%Sn; metal ion, 0.1 mol/l) and surfactant (K-soft).

3.5 Multi-layar coating

The dip coating and the heating in air were repeated several times to obtain thicker films. The surfactant was necessary even when dip coating was executed on the oxide films. Resistivity is indicated in Fig. 3 as a function of the number of the layers. The resistivity decreased with increasing the layer thickness; this should be attributed to the increased coverage of the substrate surface and the enhanced crystal growth by prolonged total heating time. The minimum resistivity in the present case was 1.5×10^{-2} ohm·cm for the four-layer film with the total thickness of 41 nm when heated at 600°C in air. Tin concentration (4.4 at.%) in the film was slightly lower than those of the mono-layer films but approximately equal to that of the solution (5 at.%). The resistivity after annealed in a nitrogen flow at 600°C for 1 h is indicated also in Fig. 3 for reference; 3.5×10^{-3} ohm·cm was obtained. This value is higher by approximately one order than the minimum values (approximately 4×10^{-4} ohm·cm [8-11]) reported for much thicker films (thickness, approximately 300 nm) by dip coating process.

The X-ray diffraction spectrum of the film is shown in Fig.4. The spectrum was assigned to ITO (cubic In_2O_3 [18]). Optical transmission of the film is shown in Fig. 5 wherein the spectrum of the glass substrate without the film is indicated for reference. Average in the visible range (87 %) for the four-layer film should be sufficiently high for the most application.

Thus, addition of surfactant proved to be effective to produce transparent conducting films in case of dip coating process using one of the cheapest solution, i.e. ethanol solution of indium (III) chloride and tin (II) chloride. It should be emphasized that application of surfactant will expand the variety of the coating solution which was abandoned in the past. Although the resistivity in the present case may be slightly high, the authors believe improvement is possible by selecting the surfactant and optimizing the process parameters.

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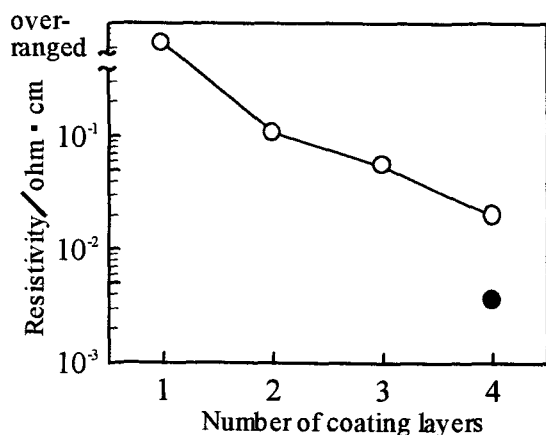
Fig. 3: Resistivity as a function of the layer numbers. The resymbols and the solution are identical with these indicated in Fig. 2.

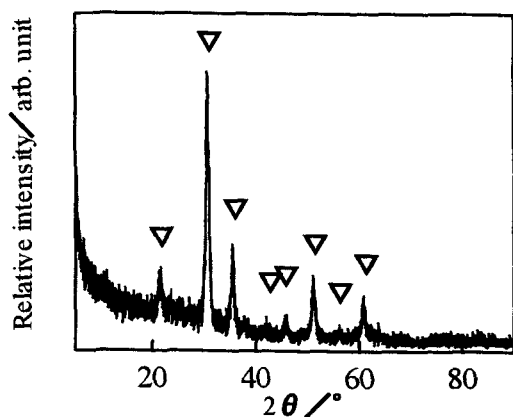Fig. 4: X-ray diffraction spectrum of the oxide films. ∇: In_2O_3. Dip coating and heating at 600°C in air was repeated 3 times.
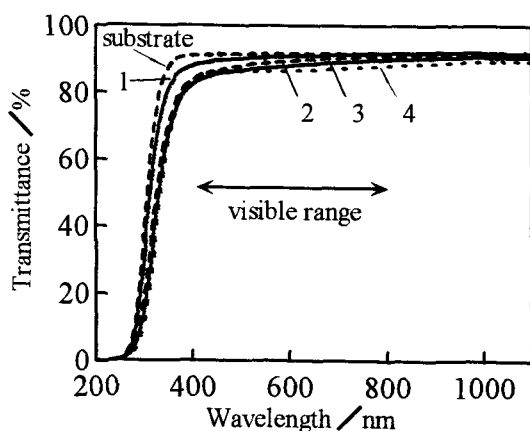

Fig. 5: Optical spectrum of the oxide film.
Numbers in the figure show the cycle of the dip coating and the heating at 600°C for 30 min in air. The solution is described in the caption of Fig. 2.

4. CONCLUSION

Dip coating of ITO films on glass substrate was investigated using indium (III) chloride, tin (II) chloride and tin (IV) chloride dissolved in ethanol, water and mixture of ethanol and water. Contact between the glass substrate and the solution was influenced by the solute; tin (II) chloride was the best and indium (III) chloride was the worst among them.

Addition of surfactant improved the contact to achieve transparent oxide films successfully. Transparent conducing film with the lowest resistivity of 1.2×10^{-1} ohm·cm (thickness, 17 nm; 6.1 at.%Sn) was obtained using ethanol solution with indium (III) chloride and tin (II) chloride (5 at.%Sn) with the surfactant (0.87 g/l) and heated at 600°C in air for 30 min. The registivity was reduced to 6.1×10^{-3} ohm·cm by annealing in a nitrogen flow at 600°C for 1h.

The registivity was reduced by the repeating process of coating and heating; minimum resistivity of 1.5×10^{-2} ohm·cm was achieved for the four-layer film (total thickness, 40 nm; 4.4 at.%Sn). The resistivity after annealed in a nitrogen flow at 600°C for 1 h was 3.5×10^{-3} ohm·cm.

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