

Preparation of Indium-Tin-Oxide Transparent Conducting Films: Influence of the Concentration of Dip-coating Solutions and the Withdrawal Rate on the Films Thickness and Resistivity.

Shigeyuki Seki, Yutaka Sawada and Toshikazu Nishide*

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, College of Engineering, Nihon University,
Tamura-machi, Koriyama 963-8642, Japan

Fax: 81-24-956-8862, e-mail: nishide@ce.nihon-u.ac.jp

ITO films were prepared with novel solutions; indium diacetate monohydroxide, tin chloride ($\text{Sn}/(\text{In}+\text{Sn}) = 5$ at.%) and 2-aminoethanol in ethanol solvent. The glass substrates were dip-coated using solutions with different concentration C ($\text{In}+\text{Sn}$; 0.19, 0.37 and 0.65 mol/dm³) whose densities d and viscosities η were 0.82, 0.87 and 0.93 g/cm³ and 1.29×10^{-3} , 1.72×10^{-3} and 3.22×10^{-3} kg·m⁻¹·s⁻¹, respectively. The thickness of the oxide film x was approximately in proportion to $C^{3/2}$ and $u^{1/2}$, where u is the withdrawal rate. The results agreed with the model assuming laminar flow except in case of the lowest concentration (0.19 mol/dm³). The film compositions C_{Sn} ($\text{Sn}/(\text{In}+\text{Sn})$) were approximately the same as the composition of the solutions. Some of the films were cross-checked by XPS; the depth profiles of the these films showed homogeneous composition along the thickness direction of the films. Tin concentration and the resistivity was discussed referring to the results of mono-, triple- and ten-layer films. The resistivity ρ ($\sim 1.2 \times 10^{-2}$ - 1.4×10^{-3} Ω·cm) decreased by increasing the film thickness x (~ 10 -286 nm). The ten-layer films were annealed at 600 °C for 1 h in N₂-1.0%H₂ gas (flow rate, 0.3 dm³/min); the lowest resistivity obtained was 2.7×10^{-4} Ω·cm with the carrier concentration and the hall mobility 9.4×10^{20} cm⁻³ and 24 cm²·V⁻¹·s⁻¹, respectively. This value was probably the lowest as the ITO films prepared by dip coating.

Key words: ITO, dip coating, withdrawal rate, density, viscosity

1. INTRODUCTION

Thin films of tin-doped indium oxide (Indium-Tin-Oxide) are used for transparent electrodes of display devices [1]. As a new application of ITO films, heat shielding of windows is expected. Dip coating process can achieve large-area films with low production cost. The various dip-coating solutions are reported [2-15]. However, dip-coated ITO films were generally less conductive than those deposited by PVD process such as sputtering deposition [16] and ion plating [17]. Therefore, deposition parameters of dip coating process should be carefully examined in order to enhance the conductivity. Film thickness is one of the important parameters to affect the film properties. Brinker et al. [18] discussed the influence of porosity, pore radius, surface area and refractive index of the sol-gel derived SiO₂ films. They reported that the thickness of the solution layer h could be expressed as $h = \alpha(\eta u/dg)^{1/2}$ where α , η , u , d and g are the constant, the viscosity of the dip-coating solution, the withdrawal rate of the substrate and the acceleration of the gravity, respectively; the equation was derived on the assumption of the laminar flow. They did not indicate the thickness of the oxide film but used instead the multiplication of the refractive index and the optical thickness. Ogihara and Kinugawa [19] reported the effect of withdrawal rate u on thickness of ITO films x using dip-coating solutions prepared from indium nitrile acetylacetonate and tin metal with nitric acid, acetylacetonate and acetone solvent; the thickness x was

approximately proportional to withdrawal rate u . Yamamoto and Sasamoto [20] reported the effect of rotation rate on thickness of ITO films x prepared by spin coating using indium chloride (InCl₃) and tin chloride (SnCl₄) with ethylene glycol. They also reported the viscosity of the solutions. Influence of the withdrawal rate for other solutions were not found in the literature in case of ITO films. In the present study, a novel solution was investigated to clarify the influence of the coating parameters on the thickness of ITO films; indium diacetate monohydroxide (In(OH)(CH₃COO)₂), tin dichloride (SnCl₂·2H₂O), 2-aminoethanol (monoethanolamine H₂NC₂H₄OH) and ethanol. Tin concentration and the resistivity was discussed referring to the results of triple- and ten-layer films.

2. EXPERIMENTAL

Indium diacetate monohydroxide was synthesized by refluxing acetic acid (purity 99.7 %, Wako Pure Chemical Industries, Ltd.) with fine powders of indium oxide (In₂O₃, purity 99.999 %, Kojundo Chemical Laboratories Co., Ltd.). Indium diacetate monohydroxide was dissolved in ethanol (purity 99.7 %, Wako Pure Chemical Industries, Ltd.) by adding 2-aminoethanol (purity 97 %, Wako Pure Chemical Industries, Ltd.) whose molar amount was four times of that of the indium. Tin dichloride (purity 99.9 %, Kojundo Chemical Laboratories Co., Ltd.) was also included in the ethanol solution; the tin concentration C_{Sn} was 5 at.% as indicated by Sn/(In+Sn). The

concentrations of the total metal ions in the solutions C were fixed as 0.19, 0.37 and 0.65 mol/dm³. Viscosities of the solutions were measured by Ostwald method at 20 °C using ethanol as a standard.

A glass substrate (Corning #7059, 37 × 25 × 0.7 mm³) was cleaned ultrasonically with Semicoclean 56 (Furuuchi Chemical Co., Ltd.), rinsed several times with ion-exchanged water, boiled and pulled out quickly from boiling acetone (purity 99.7 %, Wako Pure Chemical Industries, Ltd.). Dip coating was executed using a handmade coating machine with withdrawal rate u of 2.0, 5.0, 8.0, 10.0, 12.0 and 20.0 cm/min where the rotation of the DC motor connected with a gear system (ITEM 72001 planetary gear box set, Tamiya Co., Ltd.) was regulated by supplying the constant voltage. One of the coated surfaces was wiped out quickly with a tissue containing acetone. The substrates were inserted into a furnace preheated at 600 °C and held for 30 min before picked out. The coating and the heating were repeated three or ten times for some specimens in order to obtain thicker films. For the purpose of increasing the conductivity some films were annealed at 600 °C for 1 h in N₂ flow (purity, 99.9995%; oxygen partial pressure measured by zirconia oxygen sensor, ~2.0 Pa; flow rate, 3 dm³/min) or N₂-0.1%H₂ or N₂-1.0%H₂ gas (flow rate, 0.3 dm³/min).

The thickness and the composition (at.%Sn, as indicated by Sn/(In+Sn)) was measured by energy-dispersive type X-ray fluorescence analyzer (JEOL JSX-3200, Rh 30 kV); the calibration of the composition was performed using the ITO films whose composition was determined by ICP. The composition C_{Sn} in the ITO film was also investigated by X-ray photoelectron spectroscopy (Rigaku XPS-7100, Mg 10 kV, 30 mA) with cyclic etching by Ar⁺ ions (acceleration voltage 3 kV).

The resistivities of the films were measured by four-point-probe method (probe distance 0.6 mm, probe diameter 0.5 mm, probe current 1 mA) with digital multimeter (34401A, Hewlett Packard Co., Ltd.). The carrier concentrations and mobilities were measured by the van der Pauw method (DC magnetic field 3.0 × 10³ G, probe current 1 mA) with Hall coefficient analyzer (MI-675, Sanwa Radio Measurement Works Co., Ltd.).

3. RESULTS AND DISCUSSION

Dependence of the solution concentration C on the density d and the viscosity η is shown in Fig. 1. The increment of the density d (0.82, 0.87 and 0.93 g/cm³) was approximately proportional to the solution concentration C (0.19, 0.37 and 0.65 mol/dm³, respectively). The viscosity η (1.29×10^{-3} , 1.72×10^{-3} and 3.22×10^{-3} kg·m⁻¹·s⁻¹, respectively) increased remarkably at high solution concentration. This should be attributed to both the higher viscosity of 2-aminoethanol than ethanol and the influence of indium diacetate monohydroxide and tin dichloride.

Thickness x of the ITO films is plotted in Fig. 2 against the repeating number of the dipping and the heating. The film thickness was approximately proportional to the repeating numbers. The surface of the substrate i.e. whether the glass substrate itself in case of the first layer or the ITO film in case of the following layers did not influence the layer thickness. Etching of

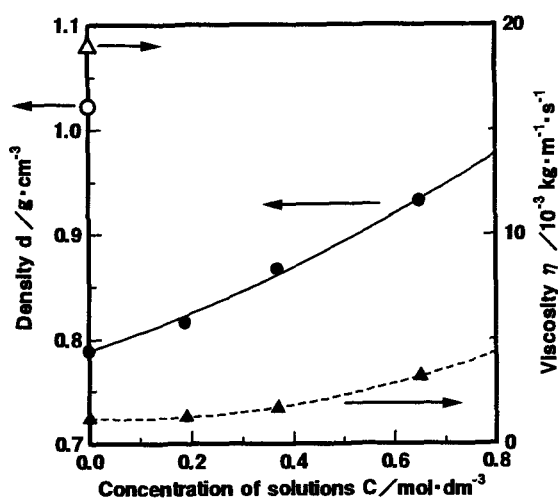


Fig. 1 Dependence of the solution density and viscosity on the solution concentration.

Tin concentration C_{Sn} in the solution; 5 at.% as indicated by Sn/(In+Sn). Measured by 20 °C. O and Δ ; the density and the viscosity of 2-aminoethanol at 20 °C, respectively.

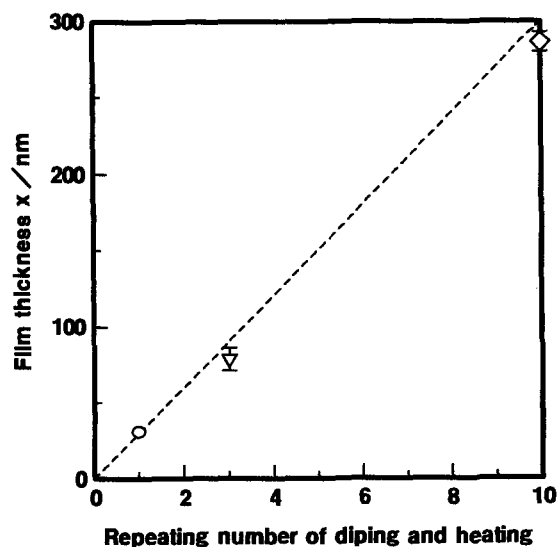


Fig. 2 Dependence of the ITO film thickness on the repeating number of the dipping and the heating.

Tin concentration C_{Sn} in the solution; 5 at.%. \bullet , ∇ and \diamond ; mono-, triple- and ten-layer film, respectively.

the ITO films by the dip-coating solutions was negligible.

Dependence of the film composition C_{Sn} on the film thickness x is shown in Fig. 3. This figure also shows the results of thicker films fabricated by the cyclic dipping and heating. The thinner films (~10–40 nm) were calibrated with the results of ICP. Film composition was approximately constant and independent of the film thickness. Figure 4 shows the XPS results of depth profile. The composition C_{Sn} was approximately homogeneous along the depth direction in the film.

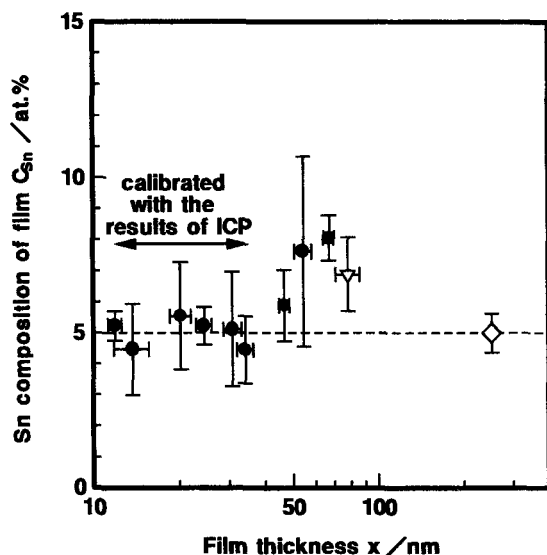


Fig. 3 Dependence of the film composition on the film thickness.

Tin concentration C_{Sn} in the solution; 5 at.%
 ●, ▽ and ◇; mono-, triple- and ten-layer films, respectively.
 The average \pm standard deviation was indicated by error bar.

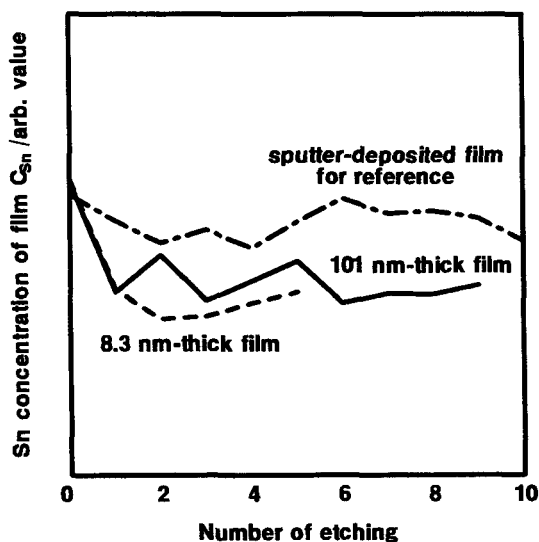


Fig. 4 XPS results of depth profile.

Tin concentration C_{Sn} in the solution; 5 at.%
 - - -; ITO films prepared by sputtering process with $C_{Sn}=7.7$ at.%

Dependence of the film thickness x on the withdrawal rate u is shown in Fig. 5. The thickness was proportional to $u^{1/2}$, these results agreed with the model by Brinker et al. [18] derived from the laminar flow. Deviation from the parabolic law was observed exceptionally in case of the lowest solution concentration ($C = 0.19 \text{ mol/dm}^3$) in the present experiment when the thickness x of the ITO film approached to the minimum value of $\sim 9 \text{ nm}$ which corresponds to the thickness h of the solution layer $\sim 2 \mu\text{m}$ at low withdrawal rate.

Dependence of the film thickness x on the solution

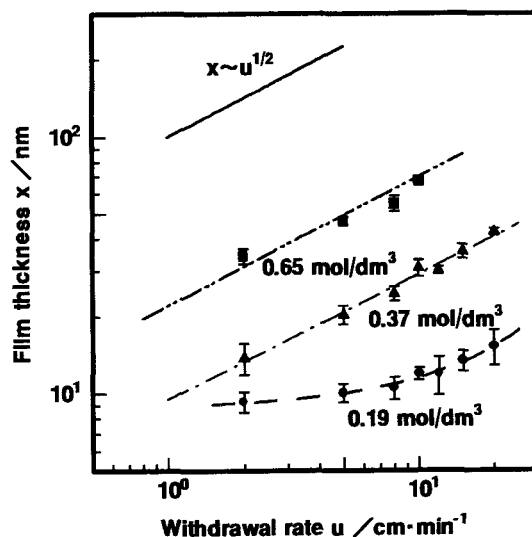


Fig. 5 Dependence of the film thickness on the withdrawal rate.

Monolayer films fabricated using the solution with C_{Sn} 5 at.%
 ●, ▲ and ■; 0.19, 0.37 and 0.65 mol/dm^3 , respectively.

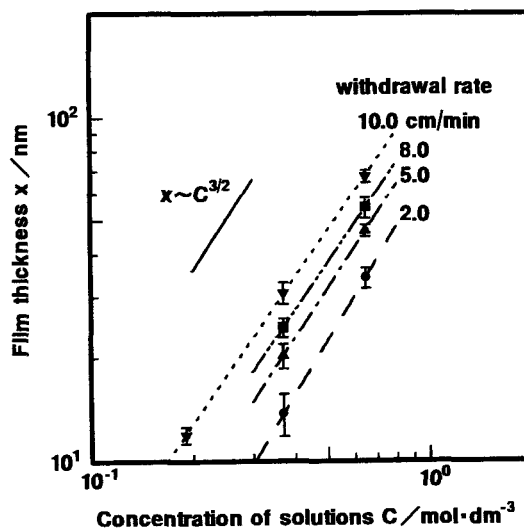


Fig. 6 Dependence of the film thickness on the solution concentration.

Monolayer films fabricated using the solution with C_{Sn} 5 at.%
 ●, ▲, ■ and ▽; 2.0, 5.0, 8.0 and 10.0 cm/min , respectively.

concentration C is shown in Fig. 6. The thickness x was approximately proportional to $C^{3/2}$ although more deviation was observed compared with the case shown in Fig. 5. This correlation agreed with the equation proposed by Brinker et al. [18] if the $[\text{viscosity } \eta] / [\text{density } d]$ is proportional to the solution concentration C since the thickness x of the oxide film is proportional to hC . The $[\text{viscosity } \eta] / [\text{density } d]$ was apparently proportional to the solution concentration C at a limited concentration range between 0.37 and 0.65 mol/dm^3 in the present case.

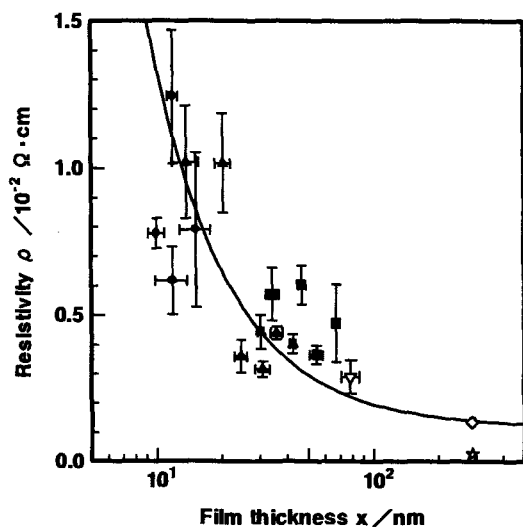


Fig. 7 Dependence of resistivity on the film thickness for as-deposited ITO films.

Tin concentration C_{Sn} in the solution; 5 at.%. The average \pm standard deviation is indicated by error bars.
 ●, ▲ and ■; monolayer films used 0.19, 0.37 and 0.65 mol/dm³ solutions, respectively.
 ▼ and ◇; triple- and ten-layer films using 0.37 mol/dm³ solution, respectively.
 ★; ten-layer films annealed at 600 °C for 1 h in N₂-1.0%H₂ gas flow (0.3 dm³/min.).

Dependence of the resistivity ρ on the film thickness x is shown in Fig. 7. The resistivity ρ ($\sim 1.2 \times 10^{-2}$ – 1.4×10^{-3} Ω·cm) decreased by increasing the film thickness x (~ 10 – 286 nm), especially the decrease at $x < 20$ nm was remarkable. It should be interpreted that the thinner films have higher porosity than the thicker ones. The ten-layer films were annealed at 600 °C for 1 h in N₂-1.0%H₂ gas (flow rate, 0.3 dm³/min). In the present study, the lowest resistivity was 2.7×10^{-4} Ω·cm and the carrier concentration and the hall mobility were 9.4 cm⁻³ and 24 cm²·V⁻¹·s⁻¹, respectively. This value was probably the lowest as the ITO films prepared by dip coating.

The authors thank Mr. H. Yoshida of Geomatec. Co. Ltd. (the standard ITO film), Profs. Y. Shirai (the use of X-ray fluorescence analyzer) and T. Matsumoto (the use of Ostwald viscometer) of our institute.

4. CONCLUSION

The novel solution was investigated to clarify the influence of the coating parameters on the thickness of ITO films; indium diacetate monohydroxide, tin dichloride, 2-aminoethanol and ethanol. The increment of the density d was approximately proportional to the solution concentration C . The viscosity η increased remarkably at high solution concentration C . The film thickness x was approximately proportional to the repeating numbers of the dipping and the heating. Film composition C_{Sn} was approximately constant and independent of the film thickness x . The thickness x was proportional to $u^{1/2}$; these results agreed with the model by Brinker et al. [18] derived from the laminar flow, and was approximately proportional to $C^{3/2}$. The resistivity ρ of the film (~ 10 – 20 nm) was decreased by increasing the film thickness x .

REFERENCES

- [1] Y. Shigesato and I. Yasui, *Oyo Butsuri*, **64**, 1225-29 (1995).
- [2] S. Ogihara, K. Kinugawa and M. Nakayama, *Nihon Kagaku Kaishi*, **9**, 1345-51 (1980).
- [3] S. Ogihara and K. Kinugawa, *Yogyo-Kyokai-Shi*, **90**, 157-63 (1982).
- [4] Y. Takahashi, H. Hayashi and Y. Ohya, *Mater. Res. Soc. Symp. Proc.*, **271**, 401-06 (1992).
- [5] T. Maruyama, *Chem. Eng.*, **8**, 34-37 (1987).
- [6] T. Maruyama, and A. Kojima, *Jpn. J. Appl. Phys.*, **27**, 1829-31 (1988).
- [7] D. Gallagher, F. Scanlan, R. Houriet, H. J. Mathieu, and T. A. Ring, *J. Mater. Res.*, **8**, 3135-44 (1993).
- [8] A. Tsunashima, T. Asai, K. Kodaira, and T. Matsushita, *Chem. Lett.*, **80**, 855-56 (1978).
- [9] T. Matsushita, *Bull. Ceram. Soc. Jpn.*, **21**, 236-42 (1986).
- [10] T. Furusaki, K. Kodaira, M. Yamamoto, S. Shimada, and T. Matsushita, *Mater. Res. Bull.*, **21**, 803-06 (1986).
- [11] J. J. Xu, A. S. Shaikh and W. Vest, *Thin Solid Films*, **161**, 273-80 (1988).
- [12] A. Yoshinaka and K. Onosawa, *New Ceramics*, **4**, 24-29 (1996).
- [13] T. Furusaki, J. Takahashi and K. Kodaira, *J. Ceram. Soc. Jpn.*, **102**, 200-05 (1994).
- [14] R. Bel Hadj Tahar, T. Ban, Y. Ohya and Y. Takahashi, *J. Appl. Phys.*, **83**, 2139-2141 (1998).
- [15] Seon-Soon Kim, Se-Young Choi, Chan-Gyung Park and Hyeon-Woo Jin, *Thin Solid Films*, **347**, 155-60 (1999).
- [16] Y. Shigesato, S. Takaki and T. Haranoh, *J. Appl. Phys.*, **71**, 3356-64 (1992).
- [17] S. Takaki, K. Matsumoto and K. Suzuki, *Appl. Surf. Sci.*, **33/34**, 919-25 (1988).
- [18] C. J. Brinker, G. C. Frye, A. J. Hurd and C. S. Ashley, *Thin Solid Films*, **201**, 97-108 (1991).
- [19] S. Ogihara and K. Kinugawa, *Yogyo-Kyokai-Shi*, **90**, 157-63 (1982).
- [20] O. Yamamoto, T. Sasamoto and M. Inagaki, *J. Mater. Res.*, **7**, 2488-91 (1992).

(Received December 7, 2000; Accepted January 31, 2001)