

Indium-Tin-Oxide Transparent Conducting Films Deposited by Spray Method Using Ethanol Solution of Indium Chloride and Tin Chloride

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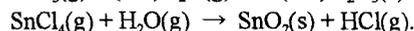
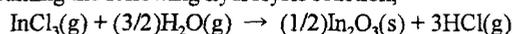
Transparent ITO films were deposited on glass substrate heated at 350°C in air by spraying ethanol solution of indium (III) chloride and tin (II) chloride. The films showed strong (4 00) diffraction peak. Dependence of electrical properties on the tin concentration was systematically investigated between 0-20 at.% as indicated by Sn/(In+Sn). The resistivities of the as-deposited ITO films were in the order of 10⁻⁴ ohm·cm; the minimum resistivity was 1.9×10⁻⁴ ohm·cm. Annealing at 600°C in N₂-0.1%H₂ atmosphere reduced the minimum resistivity to 9.5×10⁻⁵ ohm·cm (thickness, 190nm; composition, approx. 4.4 at.%Sn; carrier concentration, 1.8×10²¹ cm⁻³; mobility, 40 cm²/V·s); this resistivity is probably the lowest among the films prepared by chemical process.

Key words: ITO, spray method, transparent conducting films, indium(III) chloride, tin(II) chloride

1. INTRODUCTION

When thinking indium tin oxide (tin-doped In₂O₃) transparent conducting films, one may often pay attention to recent progress of PVD process such as sputtering method. However, it should be remembered that ITO films with relatively low resistivities were deposited successfully by spray method using solution of InCl₃ and SnCl₄ with much lower production cost since the early stage in the history of ITO thin films. Groth[1] reported 2.3×10⁻⁴ ohm.cm using solution of InCl₃ and SnCl₄ in butylacetate. Frank and Köstlin [2] reported 1.3×10⁻⁴ ohm.cm after the optimized annealing at 500°C using the same spray solution. Blandenet et al. [3,4] reported 2.2×10⁻⁴ ohm.cm by what they called pyrosol method; whose solution was not described in their papers.

When using InCl₃ and SnCl₄, addition of water into the spray solution was thought to be necessary if assuming the following hydrolysis reaction;



Ishikawa[5] reviewed the patents and introduced an example of ITO film with the resistivity of 5.4×10⁻⁴ ohm.cm (10 ohm.sq., 542 nm thick) prepared from water solution of InCl₃ and SnCl₄. Low-resistivity (2×10⁻⁴ ohm.cm) film was reported by Nagatomo et al.[6] who used InCl₃ and SnCl₄ dissolved in hydrochloric acid. Kulaszewicz et al. also reported the water solution[7] but they changed to alcoholic solution later[8] to obtain ITO film with the sheet resistivity of 85 ohm.cm.

The spray solutions of water plus methanol were reported; 15 ohm.sq. by Manificier et al.[9], 2×10⁻⁴

ohm.cm by Pommier et al.[10] and 1.23×10⁻³ ohm.cm by Kaneyasu et al.[11] and Adachi et al.[12]. The spray solutions of water plus ethanol were reported; 5×10⁻⁴ ohm.cm by Manificier et al.[13], 3×10⁻⁴ ohm.cm by Bisht et al.[14] and 5×10⁻⁵ ohm.cm by Benamar et al.[15]. The value by Benamar et al. (substrate temperature; 500°C) is probably the lowest among the spray-deposited films and compatible with the lowest values obtained by PVD process such as Nath [16] (7×10⁻⁵ ohm.cm), Ray[17] (6.8×10⁻⁵ ohm.cm), Rauf [18,19] (4.4×10⁻⁵ ohm.cm) and Ohta et al.[20] (7.7×10⁻⁵ ohm.cm). However, the authors doubt the minimum resistivity by Benamar et al.[15] since higher value (4.5×10⁻⁴ ohm.cm) was obtained when calculating from their sheet resistivity (5 ohm/sq.) and their thickness (900 nm when deposited using 250 ml solution). Hydrochloric acid was added into the solution to increase the solubility of the chlorides and/or prevent the hydrolysis in the solution in case of Nagatomo et al.[6], Manificier et al.[13], Kulaszewicz et al.[8] and Bisht et al.[14].

In the present work, ethanol solution of indium chloride and tin chloride was used by a slightly different way; SnCl₂ was used instead of SnCl₄. Addition of SnCl₂ in the spray solution was not found in the literature. Hydrochloric acid was not added into the solution in the present work. Less chlorine content in the solution was expected to lower the vapor pressure of HCl which would restrain the oxide formation. Small amount of solution (approx. 0.25 ml) was sprayed at once in order to reduce the vapor pressure of HCl and prevent the substrate temperature from dropping down by the heat of vaporization. Extra addition of water was refrained in

the present work since the authors thought sufficient water necessary for the oxide formation was contained in the solution because of the hygroscopic nature of the chlorides and ethanol. The as-deposited films were annealed in N_2 - H_2 mixture to lower the resistivity in the present work.

2. EXPERIMENTAL

Indium (III) chloride $InCl_3 \cdot 3.5H_2O$ (purity, 99.99%) and tin (II) chloride $SnCl_2 \cdot 2H_2O$ (purity, 99.9%) were dissolved in ethanol (purity, 99.5%) and stirred for 5 h. The concentration of the total metal ions in the solution was fixed at ~ 0.2 mol/l. The solutions with 0, 5, 10 and 15 at.%Sn were prepared. The solution was sprayed manually in air with an inexpensive atomizer for cosmetic purpose. Corning # 7059 glass substrates ($2.5 \times 3.5 \times 0.7$ mm³) were cleaned ultrasonically for 10 min in deionized water with detergent (Semicoclean 56, Furuuchi Chemical Co. Ltd.) and rinsed several times with deionized water. The glass substrates were boiled in acetone for 10 min and picked up quickly into the air. The substrate was heated on a hot plate (Corning PC-400) at $\sim 350^\circ C$. The substrate temperature was monitored with a thermocouple which was pressed on the upper surface of the glass substrate.

The spraying in air was repeated 100 times to consume ~ 20 ml solution. The substrate temperature was lowered by $\sim 5^\circ C$ by the heat of evaporation so that the spray operation was conducted after recovering the temperature. Some films were annealed in N_2 - $0.1\%H_2$ atmosphere (gas flow rate; 300 ml/min) at $\sim 600^\circ C$ for 60 min in order to increase the conductivity.

The thickness and the composition (Sn/(In+Sn) ratio) of the oxide films were determined by X-ray fluorescence analysis (model JSX-3200, JEOL). The crystalline state of the film was evaluated by X-ray diffraction analysis (model RINT-2500V, Rigaku) with a Cu target (40kV, 300mA) and a graphite monochromator. The lattice constant was calculated from the 622 peak whose diffraction angle was calibrated using silicon standard. The optical transmission was measured with a conventional spectrometer (model UV-1200, shimadzu). The resistivity of the film was measured by four-point-probe method (probe distance of 0.65 mm, probe current 1 mA) with a multimeter (model 34401A, Hewlett Packard). The Hall coefficient was measured by van der Pauw method (model MI675, Sanwa Radio Measurement Works Co., Ltd., probe current 1 mA).

3. RESULTS AND DISCUSSION

Dependence of film composition (at.%) as indicated by Sn/(In+Sn), on the solution composition is shown in Fig. 1. Composition of the oxide film was $\sim 65\%$ of that of the solution. Film thickness (113-214 nm) was independent of the solution composition.

The X-ray diffraction spectrum of the oxide film is shown in Fig. 2. The spectra agreed with that of In_2O_3 ; strong (400) peak was observed. Integrated intensity of the (400) peak to the (222) peak (I_{400}/I_{222}) is shown in Fig. 3 as a function of the film composition in order to evaluate the preferred orientation. Preferred orientation at $350^\circ C$ in the present films was more remarkable than that ($I_{400}/I_{222} = 1$) by Benamar et al. [15].

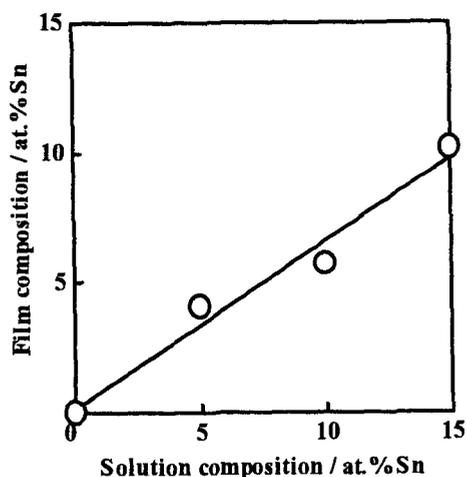


Fig. 1 Dependence of the film composition on the solution composition.

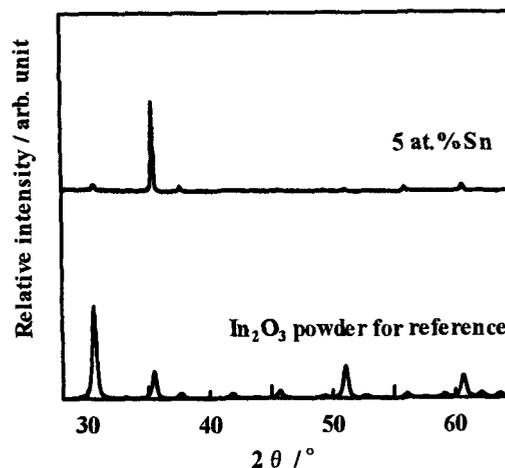


Fig. 2 The X-Ray diffraction spectra of the as-deposited films.

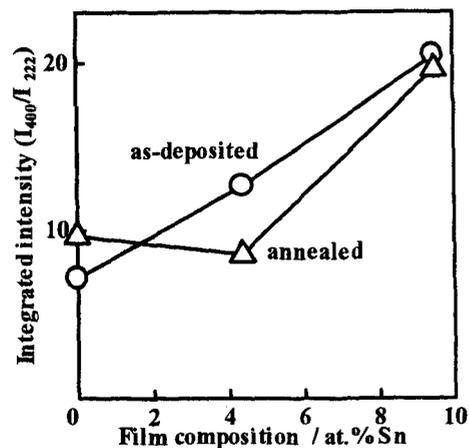


Fig. 3 The integrated intensity of the (400) peak to the (222) peak (I_{400}/I_{222}) for as-deposited ITO films as a function of film composition.

Lattice constant of the films is shown in Fig. 4 as a function of the film composition. In case of the undoped In_2O_3 film, the lattice constant was smaller than the reported value (1.0118 nm) for the bulk In_2O_3 [20]; the lattice constant approximately unchanged after the annealing in reduced atmosphere. The lattice constant of ITO films increased with increasing the tin concentration. Annealing in the reduced atmosphere seemed to expand slightly the lattice constant of the ITO films. The dependence on tin concentration and the reduction agreed with the results reported by Frank and Köstlin[2].

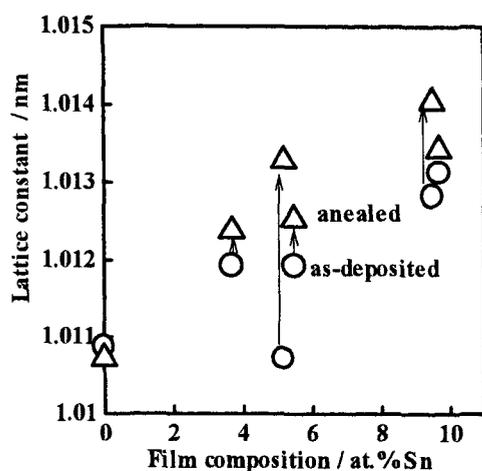


Fig. 4 Dependence of lattice constant as a function of the film composition

Dependence of resistivity on the film composition is shown in Fig. 5. As-deposited ITO films showed the resistivities in the order of 10^{-4} ohm.cm; the minimum resistivity in the present case was 1.9×10^{-4} ohm.cm for the films with Sn 5.8 at.% (thickness; 215 nm). This value was compatible with those deposited by PVD such as sputtering. In this figure, the resistivities after annealing in N_2 -0.1% H_2 atmosphere were also plotted. The resistivity decreased by annealing in reduced atmosphere. The minimum resistivity (9.5×10^{-5} ohm.cm) was obtained for the film with 4.4 at.%Sn (thickness; 189 nm); this value is probably the lowest among the films fabricated by chemical process. The result of Ohta et al.[20] (7.7×10^{-5} ohm.cm) is plotted for reference in this figure. Their value is slightly lower but they needed expensive pulsed-laser depositon apparatus and zirconia single crystal substrate. The resistivity at $\sim 1.0 \times 10^{-4}$ ohm.cm was reproducible easily at ~ 4 -7 at.% Sn.

Dependence of carrier concentration on the film composition is shown in Fig. 6. As-deposited film showed the highest carrier concentration (4.6×10^{20} cm^{-3}) at 6.7 at.%Sn. Carrier concentration increased drastically by the annealing; the highest value (1.3×10^{21} cm^{-3}) was observed also at 7.4 at.%Sn. This value was equal with that by Ohta et al.[20] Carrier concentration for the the above-mentioned ITO film with the lowest resistivity was 1.8×10^{21} cm^{-3} . All annealed ITO films

showed high carrier concentration ($>1.9 \times 10^{21}$ cm^{-3}) in the present work.

Dependence of carrier mobility on the film composition is shown in Fig. 7. Relatively high values were obtained. Mobility for the above-mentioned ITO film with the lowest resistivity was $40 \text{ cm}^2/\text{V}\cdot\text{s}$ which was approximately equal with that ($42 \text{ cm}^2/\text{V}\cdot\text{s}$) by Ohta et al.[20]. Slight increase was observed after the annealing. The averaged mobility for ITO films was $31 \text{ cm}^2/\text{V}\cdot\text{s}$; slight decrease was observed by increasing the tin concentration. Undoped In_2O_3 films showed higher mobility (average; $64 \text{ cm}^2/\text{V}\cdot\text{s}$).

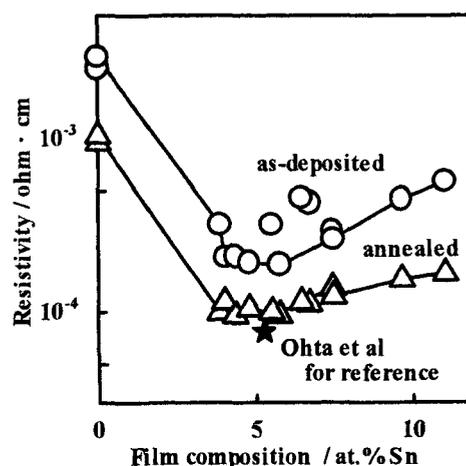


Fig. 5 Dependence of resistivity on the film composition.

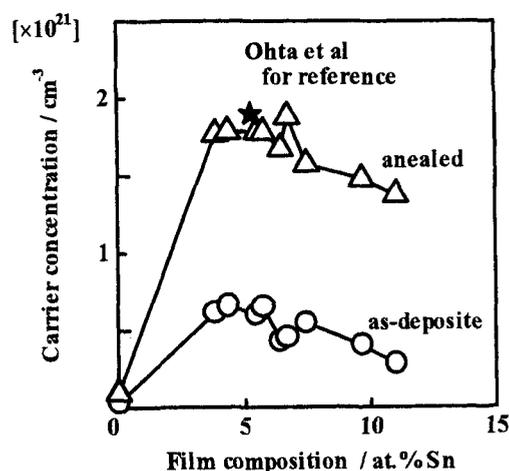


Fig. 6 Dependence of carrier concentration on the film composition.

The optical transmission of a typical film (4.3 at.%Sn, thickness 189 nm is shown in Fig. 8. The average in the visible range (380-780 nm) was $\sim 83\%$ for all as-deposited and annealed films in the present work. The result of the glass substrate without the film was indicated for reference in this figure. The result of the annealed film (the transmittance and the reflectance) was also indicated in this figure. The averaged transmittance in the visible range was 81%. Decrease of

transmittance and the increase of reflectance at $> \sim 1000$ nm should be attributed to the high carrier concentration ($1.8 \times 10^{21} \text{ cm}^{-3}$).

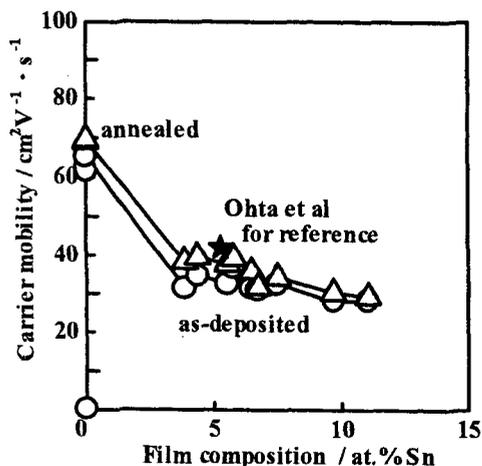


Fig. 7 Dependence of carrier mobility on the film composition.

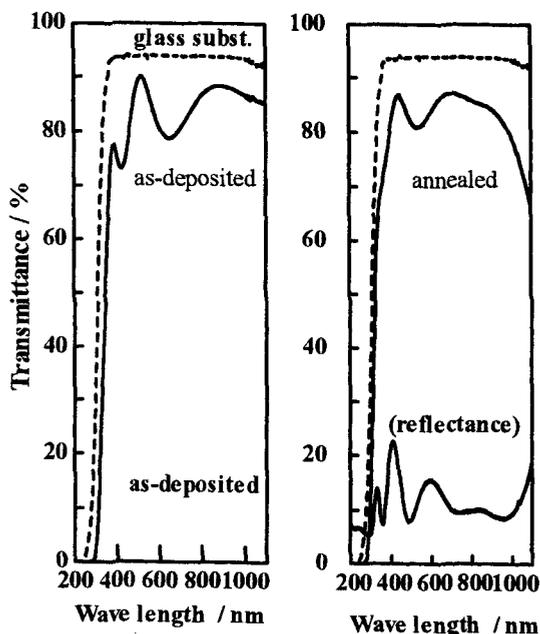


Fig. 8 Optical transmission and reflectance of the film.

(4 0 0)-oriented with the minimum resistivity of $1.9 \times 10^{-4} \text{ ohm} \cdot \text{cm}$. Films annealed at 600°C in $\text{N}_2\text{-}0.1\text{H}_2\%$ atmosphere showed lower resistivities; the lowest resistivity in the present work was $9.5 \times 10^{-5} \text{ ohm} \cdot \text{cm}$ (carrier concentration and mobility; $1.8 \times 10^{21} \text{ cm}^{-3}$ and $40 \text{ cm}^2/\text{V} \cdot \text{s}$, respectively) for the film with 4.4 at.%Sn (thickness, 189 nm).

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4. CONCLUSION

Ethanol solution of indium (III) chloride and tin (II) chloride was sprayed onto a Corning #7059 glass substrate heated at 350°C . Films as-deposited in air were