

Low resistivity ITO films by Ag addition

M. Suzuki^{a,b} and Y. Sawada^b

^aDevelopment Division, Kojundo Chemical Laboratory Co., Ltd., 5-1-28 Chiyoda, Sakado-shi, Saitama 350-02 (Japan)

^bDepartment of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi-shi, Kanagawa 243-02 (Japan)

Ag-added ITO films were deposited using conventional rf magnetron sputtering with an ITO target on which Ag chips were placed. The resistivity and transmittance of these films were investigated and compared to the ITO films. The resistivity of the ITO films was lowered by adding Ag up to ~ 1.5 at.%. This tendency was independent of the substrate temperatures or Sn concentration. The visible transmittance of $>80\%$ was obtained for the film with below 1 at.% Ag. The resistivity of $1.9 \times 10^{-4} \Omega \cdot \text{cm}$ was obtained for the film with 0.6 at.% Ag at a substrate temperature of 250°C , whereas it was $2.6 \times 10^{-4} \Omega \cdot \text{cm}$ for the ITO film. The deposition temperature can be lowered by $\sim 50^\circ\text{C}$ and achieve the same resistivity. Improvement in the conductivity by Ag addition is explained by crystallinity enhancement.

1. Introduction

Tin-doped indium oxide (Sn-doped In_2O_3 , ITO) films have been widely used as transparent electrodes for liquid crystal displays (LCDs). Low resistivity ITO films have been successfully deposited at relatively high temperature ($\sim 400^\circ\text{C}$) on a glass substrate by physical vapor deposition processes, e.g. evaporation^{1,2}, sputtering³ and ion plating⁴. Because the polymer substrate (polymer filters or PET films) for color-LCDs can not survive at above 200°C in a vacuum, the low temperature deposition of ITO films was achieved using special techniques, e.g. low-voltage sputtering^{5,6} and highly dense plasma-assisted EB evaporation^{6,7}. On the other hand, we successfully made low resistivity ITO films using a conventional rf magnetron sputtering apparatus with the simple addition of silver. The addition of various

metals (Au, Pd and Pt) and oxide (TiO_2 , ZrO_2 , Nb_2O_5 , MoO_3 , Sb_2O_3 , TeO_2 and HfO_2) in the ITO films have been reported by Higuchi⁸. In addition, the ZnO films with adding silver⁹ and the ITO ceramics with adding TiO_2 and ZrO_2 ¹⁰ have also been reported. However, the ITO films with added silver have not yet been reported. We report the resistivities, transmittance and X-ray diffraction analysis of Ag-added ITO films on which no previous report was found.

2. Experimental

The Ag-added ITO films were prepared by rf magnetron sputtering using an ITO target on which Ag chips ($1\text{mm} \times 1\text{mm} \times 14\text{mm}$) were placed. Sputter deposition was carried out at a pressure of 0.67Pa in Ar gas with an rf power of 200W . The 6-inch diameter targets used were the sintered ITO

containing 5 and 10 wt.% SnO₂ with a relative density of about 73 and 71 %, respectively. The films were deposited on a glass substrate (Corning 7059, 52mm×32mm×0.7mm), which was placed 40mm above and parallel to the target surface. The substrate temperature was varied within the range from room temperature (~50°C) to 250°C. The ratio of Ag was controlled by varying the number of chips. The deposition rate was independent of the number of Ag chips and substrate temperature. The rates were 73 and 69 nm/min for the ITO target containing 5 and 10 wt.% SnO₂, respectively.

The film thickness was measured using a conventional stylus surface profilometer (Talystep Instrument). The resistivity was measured at room temperature by the four-point probe method. The optical transmission through the films was measured in the wavelength range of 200-1100 nm with a conventional spectrometer (Shimadzu UV-1200). The crystallinity of the films was investigated by X-ray diffraction using monochromated 50kV-300mA CuK α radiation (Rigaku Rint 2500V System). The concentration of Sn and Ag in the films was analyzed using an induced coupled plasma (SPS1200A Plasma Spectrometer, Seiko Instruments Inc.) with 1.09 kW of rf power after being electrochemically dissolved in 10 % H₂SO₄ solution.

3. Results and discussion

The Sn content in the films was constant in the present study, i.e., 4.3 or 8.1 at.%, when an ITO target containing 5 or 10 wt.% SnO₂ was used, respectively. Therefore, the influence of Ag addition was successfully investigated without the influence of

the Sn concentration.

The resistivities of the ITO and Ag-added ITO films with a thickness of about 309-385 nm deposited at various substrate temperatures are shown in Fig. 1. The addition of Ag lowered the resistivity of the ITO films at all Sn concentrations and substrate temperatures. Fig. 2 shows the resistivity of the films deposited at 200°C with various thicknesses as a function of Ag content. The thicker films showed lower resistivities. The minimum resistivity was observed at approximately 1.5 at.% Ag, independent of the thickness.

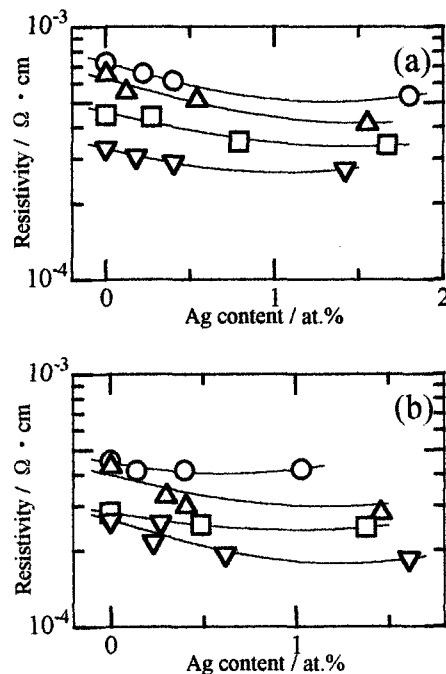


Fig. 1 Resistivity of the Ag-added ITO films deposited at various temperatures. a and b : 4.3 and 8.1 at.% Sn, ○, △, □ and ▽ : room temperature, 150, 200 and 250°C, respectively.

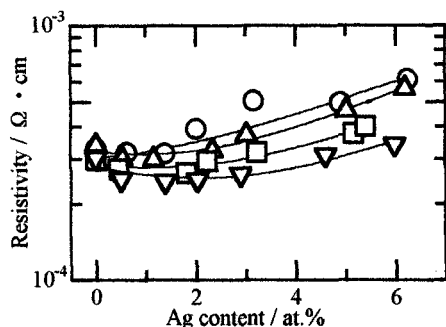


Fig. 2 Resistivity of the Ag-added ITO (8.1 at.% Sn) films deposited at 200°C with various thicknesses.
○, △, □ and ▽ :67-71, 107-115, 217-239 and 323-373nm, respectively.

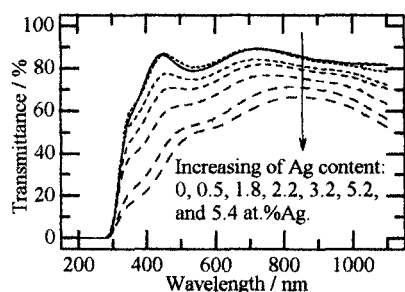


Fig. 3 Transmittance of the Ag-added ITO (8.1 at.% Sn) deposited at 200°C with a thickness of 217-239nm as a function of Ag content.

Fig. 3 shows the transmittance of the films (thickness of 217-239 nm) deposited at 200 °C. The transmittance of the films decreased with increasing Ag concentration. Ag concentration must be below 1 at.% in order to obtain an 80 % transmittance or above in the visible range. At 250°C, the resistivity of the films with 0.6 at.% Ag ($1.9 \times 10^{-4} \Omega \cdot \text{cm}$) was about 26 % lower than that of the ITO films ($2.6 \times 10^{-4} \Omega \cdot \text{cm}$). The deposition temperature can be lowered by $\sim 50^\circ\text{C}$ to achieve the same resistivity,

as shown in Fig. 1.

The X-ray diffraction patterns of the films deposited at 200°C with thicknesses of 309-373 nm are shown in Fig. 4. All the peaks can be assigned to the cubic bixbyite structure of In_2O_3 ¹¹⁾, though they were

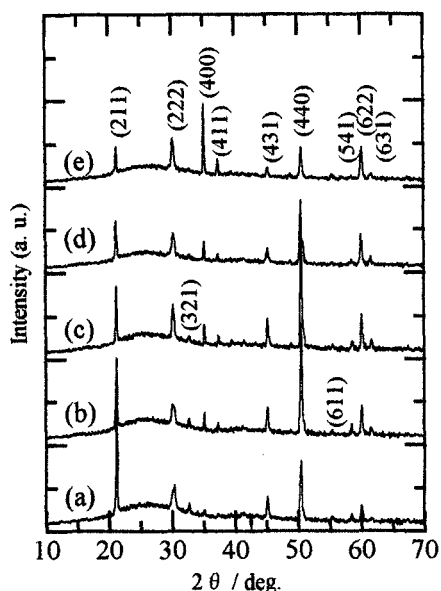


Fig. 4 X-ray diffraction patterns of the ITO (8.1 at.% Sn) films deposited at 200°C as a function of Ag content.
a, b, c, d, and e : 0, 0.5, 1.4, 2.9 and 6.0 at.%Ag, respectively.

Table 1. X-ray diffraction data and the resistivities of Ag-added ITO films deposited at 200°C.

Ag content [at.%]	Σ Int.* [cps]	Lattice constant [10^{-1}nm]	Resistivity [$\Omega \cdot \text{cm}$]
0.0	3285	10.2033	2.82×10^{-4}
0.5	3674	10.1945	2.51×10^{-4}
1.4	3836	10.1932	2.46×10^{-4}
2.9	2519	10.2072	2.62×10^{-4}
6.0	2575	10.1961	3.43×10^{-4}

*: total intensities of (211), (400), (431), (440) and (622) peaks.

shifted to the lower angles. Peaks of SnO₂ and Ag were not observed. Only the (222) peak was notably broader which indicated a small grain size and/or random strains. The diffraction data are listed in Table 1 with the resistivities. The maximum total intensity and minimum lattice constant were observed for the films with 1.4 at.% Ag, which had the minimum resistivity. Therefore, the efficiency of low resistivity by Ag addition is tentatively interpreted by the improvement in crystallinity.

4. Conclusions

Ag-added ITO films were deposited by conventional rf magnetron sputtering using an ITO target on which Ag chips were placed. The following results were obtained.

(1) The resistivity of the ITO films was lowered by adding Ag up to ~1.5 at.%. This tendency was independent of the substrate temperatures or Sn concentrations.

(2) A visible transmittance of >80% was obtained for the film with less than 1 at.% Ag.

(3) The crystallinity of the films was improved by Ag addition.

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