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Preparation and properties of antimony-doped SnO_2 films by thermal decomposition of tin 2-ethylhexanoate

A. TSUNASHIMA
Mining College, Akita University, Akita 010, Japan
H. YOSHIMIZU*, K. KODAIRA, S. SHIMADA, T. MATSUSHITA
Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Transparent Sb-doped SnO_2 films were prepared at 600° C on glass substrates by thermal decomposition of tin 2-ethylhexanoate and antimony tributoxide. The films 100 to 300 nm thick, which are composed of fine particles, were very smooth. The films showed no preferred orientation. The minimum resistivity ($2.1 \times 10^{-2}\,\Omega$ cm) was attained at a concentration of 8 at% Sb on the substrate precoated with SiO_2. The transmission of these films was about 80% over a wavelength range from 0.4 to 2.0 μm.

1. Introduction

Sb-doped tin oxide films which have high mechanical and chemical stabilities have been widely used as transparent electrodes, infrared mirrors or photothermal conversion cells of solar energy [1].

The films have generally been prepared by spray pyrolysis [2–4], chemical vapour deposition [5, 6], vacuum deposition [7] and sputtering [8, 9]. Selection of the processes for a given application is quite complex, since the properties of the films have been found to depend on the preparation processes. Both technical and economical factors must be considered to obtain a film having high optical transmission and low resistivity. As one of the simplest and least expensive preparation methods, the authors have tried to prepare the films on glass substrate by thermal decomposition of stannous capryrate containing di-isoamyloxy ethoxy antimony [10]. The minimum resistivity of the film was 1 Ω cm.

We modified the method to prepare the films with low resistivity by using tin 2-ethylhexanoate and antimony tributoxide as starting materials. The effects of antimony addition on electrical and optical properties of these films are described in relation to preparation conditions.

2. Experimental details

Reagent grade tin 2-ethylhexanoate, $Sn(C_7H_{15}COO)_2$, and antimony tributoxide, $Sb(C_4H_9O)_3$, were used as sources of tin and antimony organometallic compounds. These two reagents were well mixed in various compositions from 0 to 30 in terms of Sb/Sn + Sb atomic ratio, to which butanol was added to obtain alcoholic solutions containing 50 to 80% organometallic compounds.

The application of solution on a substrate was made by dipping the substrate into the solution and withdrawing it at a controlled rate of 0.5 to 5.8 cm min^{-1}. The applied solution was dried at room temperature for 1 h, and then at 110° C for 30 min. The dried substrate was put into an electric furnace which was kept at desired temperatures ranging from 400 to 600° C to obtain SnO_2 films. The duration varied from 10 min to 2 h. The substrate used was soda-lime glass with a size of 25 mm × 75 mm which was previously coated with about 30 nm layer of TiO_2, SiO_2 or SnO_2 (with 8 at % Sb) by thermal decomposition of organometallic compounds. The precoating conditions are listed in Table I.

The electrical properties of the films were analysed using a d.c. four-probe measuring unit, and the optical

TABLE I Precoating conditions of various oxides

Precoating	Reagent	Heat treatment	
		Temperature (° C)	Time (min)
TiO_2	TAT*, butanol	600	10
SiO_2	Atlon NSi-10†	450	30
SnO_2	Sn 2-ethylhexanoate, butanol	600	10
SnO_2 (8 at % Sb)	Sn 2-ethylhexanoate, Sb tributoxide, butanol	600	10

*$Ti(OC_4H_9)_2[OC_2H_4N(C_2H_4OH)_2]_2$.
†Trade name of reagent for the preparation of SiO_2 film by Nippon Soda Company, Ltd, Japan.

* *Present address*: Research and Development Division, Japan Victor Co Ltd, Yokohama 221, Japan.

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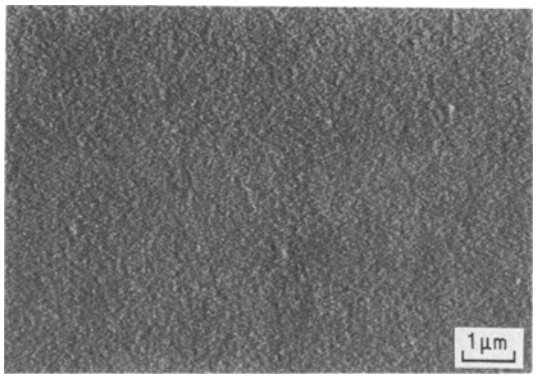

Figure 1 An electron micrograph of SnO_2 (with 8 wt % Sb) film prepared at 600° C for 10 min.

transmittance was measured as a function of wavelength in the range 0.2 to 2.0 μm.

3. Results and discussion

3.1. Structural properties

Clear and transparent SnO_2 films with thicknesses ranging from 100 to 300 nm were obtained at 600° C on glass substrates. The thickness of the films depended on the concentration of organometallic compounds in the alcoholic solution and the withdrawal rate of the substrates from the dipping solution, when the thickness was less than 300 nm. The surface morphology of the films with 8 wt % Sb was found to be very smooth by transmission electron microscope observation, as shown in Fig. 1. Very fine particles can be recognized in the figure.

X-ray diffraction patterns of undoped and Sb-doped films prepared at 600° C for 30 min are shown in Fig. 2. The diffraction peaks were not so sharp, but were assigned to cassiterite. Since the relative intensities for each peak agreed with those of the ASTM data, the films which have polycrystalline structure consisting of very fine particles exhibited no preferred orientation. Any Sb_2O_3 phases were not recognized in the X-ray diffraction patterns up to 30 at % Sb. However, with increasing antimony concentration, the diffraction peaks became broader. The broadening is due

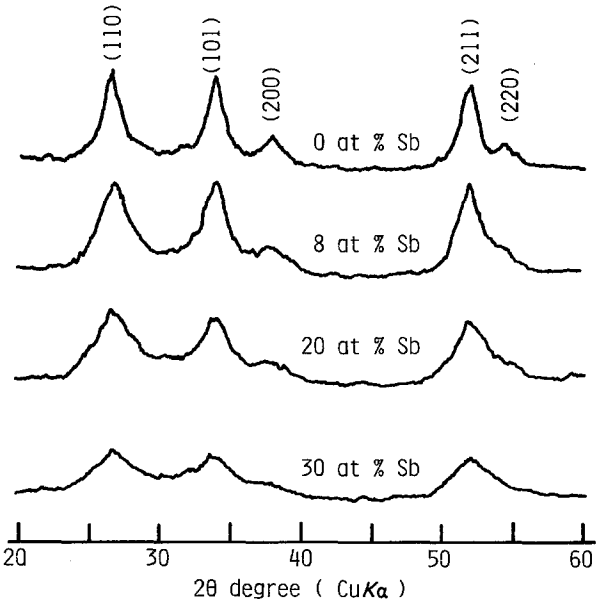

Figure 2 X-ray diffraction patterns of SnO_2 films with various antimony concentrations prepared at 600° C on a precoated SiO_2 layer.

to an increase in the amount of amorphous Sb_2O_3 by increasing antimony concentration.

3.2. Electrical properties

The soda-lime glass substrate used in the present study interacts readily with Sb-doped SnO_2 films to give a larger resistivity. Therefore, the effects of precoating on conductivity were examined for TiO_2, SiO_2, SnO_2 and SnO_2 (with 8 at % Sb) layers, on which Sb-doped SnO_2 films were prepared at 600° C. Table II shows the resistivity of the films on glass substrates with a 30 nm layer. Resistivities decreased depending on the type of precoating layers in the order uncoated > TiO_2 > SnO_2 > SnO_2 (with 8 at % Sb) > SiO_2. The resistivity of the film with a precoating of SiO_2 was two orders of magnitude lower than that on the uncoated glass substrate. Substrates precoated with SiO_2 were therefore used for measurement of electrical properties. Fig. 3 shows the variation of resistivity, ϱ, carrier concentration, n, and Hall mobility, μ, of free carriers

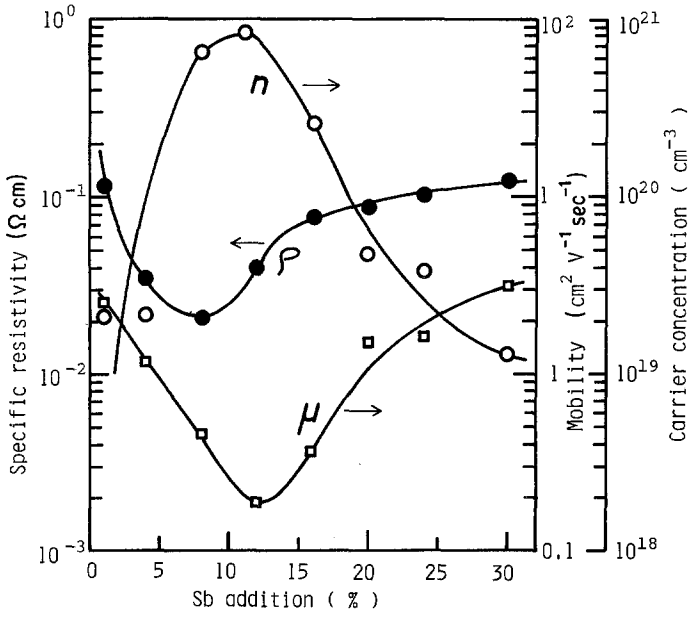

Figure 3 The electrical properties of SnO_2 films as a function of antimony concentration. The films were obtained at 600° C for 10 min.

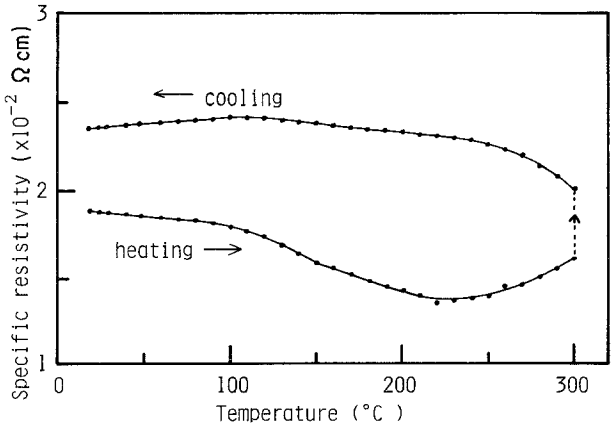

Figure 4 Variation in resistivity of SnO_2 (with 8 wt % Sb) films with temperature on heating and cooling in air.

measured at room temperature as a function of antimony concentration. The resistivity of the films decreases up to a concentration of 8 at % Sb and increases for higher antimony concentrations. The minimum resistivity was $2.1 \times 10^{-2}\,\Omega$cm, a value which is higher than those of films prepared by the spraying method and CVD (10^{-4} to $10^{-3}\,\Omega$cm) [2–6]. Resistivity variations up to 300° C in air are shown in Fig. 4 for the film with 8 at % Sb. The resistivity showed a hysteresis curve for the increasing and decreasing temperatures. However, it was reversible up to approximately 200° C. On the other hand, the carrier concentration showed an increase initially up to 10 at % Sb and a gradual decrease thereafter. The maximum concentration was $6.5 \times 10^{20}\,\text{cm}^{-3}$. Hall mobility also indicated an analogous pattern to that of resistivity. The lowest value was $0.5\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$.

3.3. Optical properties

Fig. 5 shows the transmittance and reflectance spectra of the films with various antimony concentrations. The measurements were performed on 270 nm thick films with a double-beam spectrometer in the wavelength range 0.2 to 2 μm. The transmission of these films remained more than 80% in the visible region. However, the sum of transmittance and reflectance was very close to 100% and then, the absorption of spectra was very low for these films. The effect of the free-carrier was clearly observed as reduced transmittance and increased reflectance in the near infrared region.

TABLE II Resistivities of SnO_2 (with 8 at % Sb) films of 270 nm thickness prepared at 600° C on glass substrates precoated with various layers

Precoating	Resistivity	
	($10^3\,\Omega\text{cm}^{-2}$)	(Ωcm)
None	18.1	0.49
TiO_2	16.3	0.44
SiO_2	0.62	0.017
SnO_2	7.4	0.20
SnO_2 (8 at % Sb)	1.4	0.037

4. Conclusion

Transparent and clear antimony-doped SnO_2 films of 100 to 300 nm thick were prepared by thermal decomposition of butanol solution of tin 2-ethylhexanoate and antimony tributoxide. The application of a solution on a substrate was made by dipping the substrate into the solution and withdrawing it.

The lowest resistivity of about $2 \times 10^{-2}\,\Omega$cm was attained by using substrates precoated with an SiO_2 layer of 30 nm thickness, and the films had a transmittance of over 80%.

Electrical properties were more or less poor, compared with those of films obtained by the other methods such as spraying, chemical vapour deposition and r.f. sputtering. However, advantages of the present process lie in the simplicity of film preparation, which will make it possible to use these films in a number of electronic devices.

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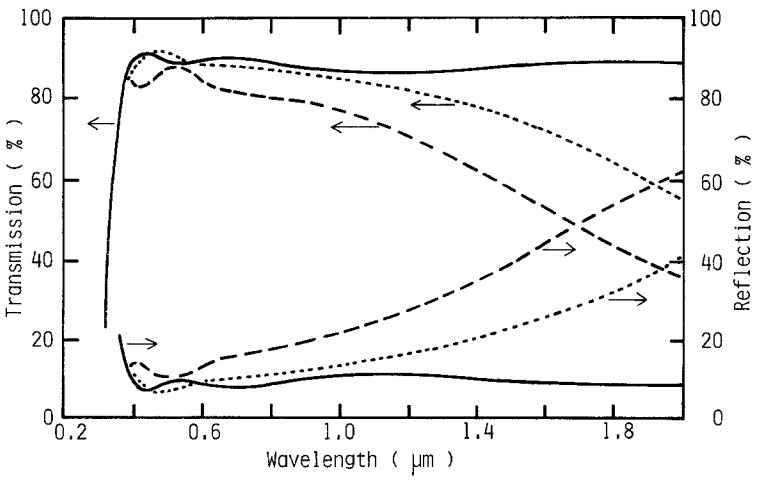

Figure 5 Transmittance and reflectance spectra of SnO_2 films with various antimony concentrations. (—) 0 at % Sb; (-----) 4 at % Sb; (——) 8 at % Sb.

References

1. J. L. VOSSEN, *Phys. Thin Films* **9** (1977) 1.
2. J. P. MARTON and D. A. LEPIC, *J. Electrochem. Soc.* **123** (1976) 234.
3. E. SHANTHI, A. BANERJEE and K. L. CHOPRA, *Thin Solid Films* **88** (1982) 93.
4. J. C. MANIFACIER, J. P. FILLARD and J. M. BIND, *ibid.* **77** (1981) 67.
5. R. MUTO and S. FURUUCHI, *Oyo Butsuri* **41** (1972) 134.
6. J. KANE, H. P. SCHWEIZER and W. KERN, *J. Electrochem. Soc.* **122** (1975) 1144.
7. Y. KATSUBE and S. KATSUBE, *Shinku Kagaku* **9** (1966) 443.
8. H. W. LEHMANN and R. WIDMER, *Thin Solid Films* **27** (1975) 359.
9. K. SUZUKI and M. MIZUHASHI, *ibid.* **97** (1982) 119.
10. T. MATSUSHITA, T. SEKIYA and I. YAMAI, *J. Jpn. Chem. Soc.* **1972** (1982) 880.

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