Title	Preparation and Properties of Sb-doped SnO_2 Films by Reactive Evaporation (Commemoration Issue Dedicated to Professor Toshio TAKADA On the Occasion of His Retirement)
Author(s)	Muranaka, Shigetoshi; Bando, Yoshichika; Takada, Toshio
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1986), 64(4): 227-234
Issue Date	1986-12-06
URL	http://hdl.handle.net/2433/77158
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 64, No. 4, 1986

Preparation and Properties of Sb-doped SnO_2 Films by Reactive Evaporation

Shigetoshi MURANAKA*, Yoshichika BANDO** and Toshio TAKADA**

Received June 2, 1986

Tin oxide films doped with Sb or In were reactively evaporated. The influence of the dopant concentration on the film structure, electrical resistivity and optical transmission was investigated. It was found that films doped with (1–2) mol%Sb exhibited the lowest resistivity (about 3×10^{-3} Ωcm) and the high optical transmission in the visible region (about 95%). All the Sb-doped films showed the good crystallinity with a rutil-like SnO_2 structure, but the film texture changed with the Sb concentration. The resistivity of In-doped films drastically increased with increasing In concentration, while the optical transmission in the visible region was not so sensitive to the dopant concentration. Films doped with below 6 mol%In showed the good crystallinity with a rutil-like SnO_2 structure. Beyond this concentration, the crystallinity of films deteriorated.

KEY WORDS: Thin films/ SnO_2 films/ Transparent conductors/

1. INTRODUCTION

Tin oxide films (SnO_2) are n-type semiconductors and optically transparent in the visible region. The electro-conductive nature of this film is generally accepted to be due to oxygen vacancies in the film. Because of the good conductivity and light transmission, tin oxide films have been widely deposited for the application of transparent conductors such as the transparent electrode.[1] Films have been prepared by various methods, *e.g.* vacuum evaporation, chemical vapour deposition (CVD) and sputtering. The resistivity and optical transmission of films have been found much to depend on the deposition technique adopted, deposition conditions and the doping of impurities. Undoped films have resistivities of the order of (10^0–10^{-2}) Ω cm. The appropriate doping of group V atoms such as Sb in films reduces the resistivity to the order of (10^{-3}–10^{-4}) Ω cm without deteriorating the film transparency.[2,3,4,5,6] For example, the resistivity of films produced by CVD is 8×10^{-4} Ω cm with about 1 mol%Sb[2] and that of films by sputtering is 3×10^{-3} Ω cm with about 7 mol%Sb.[5]

In a previous paper,[7] we reported the preparation and properties of undoped tin oxide films by reactive evaporation. The deposition conditions to produce SnO_2 films with a good crystallinity were clarified. This paper describes the influence of doping of impurities on electrical and optical properties of the films.

* 村中重利：Department of Chemistry, College of Liberal Arts and Science, Kyoto University, Kyoto 606.

** 坂東尚周，高田利夫：Laboratory of Solid State Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

2. EXPERIMENTAL PROCEDURES

The deposition apparatus used and the main deposition procedure were almost the same as those described elsewhere.[7] An only different point was that the dopant evaporation was added to the deposition process. The dopant source was placed by the Sn source with a distance of about 5 cm in the vacuum chamber. The dopant was evaporated from an Al_2O_3 crucible which was heated with a tungsten wire heater. The tungsten wire was coated with an Al_2O_3 cement in order to avoid the oxidation of the wire. The purities of Sn and Sb were 99.999% and that of In was 99.99%.

The Sn and the dopant were simultaneously evaporated. Both evaporation rates were kept constant by controlling their source temperatures with electrically feed-back circuit. The total evaporation rate was monitored by a quartz crystal oscillator, which was previously calibrated by the interferometric method. It was in the range of (1.5–2.0) A/sec. The concentrations of the dopant in films were nominally calculated from the evaporation rates of the Sn and the dopant.

On the basis of the previous results,[7] the substrate temperature during deposition was kept at about 420°C, and the oxygen pressure was at about 5×10^{-3} Torr. These were the optimum conditions to produce the crystalline SnO_2 films. Films were deposited on quartz glass and borosilicate glass, both of which gave quite the similar results. The thickness of the films was about 5500 Å.

The dopant concentrations in several films were determined by X-ray fluorescence analysis. The accuracy was within ±0.4 mol%. The crystal structure of films was studied by X-ray diffraction analysis using Cu K_α radiation. The resistivity and Hall effect measurements were made by van der-Pauw method. The optical transmission was measured using a double-beam spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Sb-doped films

Table 1 shows the Sb concentrations in films determined by X-ray fluorescence analysis. Since measured values are accurate within ±0.4 mol%, the nominal concentrations below 7 mol% are in good agreement with the measured values. This indicates that the Sb concentration below 7 mol% can be determined from the evaporation rates of Sn and Sb. The measured value for the film with 54.0 mol%, however, was much reduced to about 11 mol%, and that for the film with

Table 1. Sb concentrations in films (mol%)

Calculated	Measured
2.7	2.6
4.9	5.1
6.2	7.4
14.9	10.0
54.0	11.4

14.9 mol% to about 10 mol%. This indicates that the doping of Sb by reactive evaporation method is substantially limitted to about 11 mol%.

Figure 1 shows examples of X-ray diffraction patterns for typical films. Table 2 shows relative intensities of major diffraction lines, (110), (101) and (211), and lattice parameters, a and c. All the films were composed of a rutil-like SnO_2 structure. The lattice parameters, a and c, were insensitive to the Sb concentration,

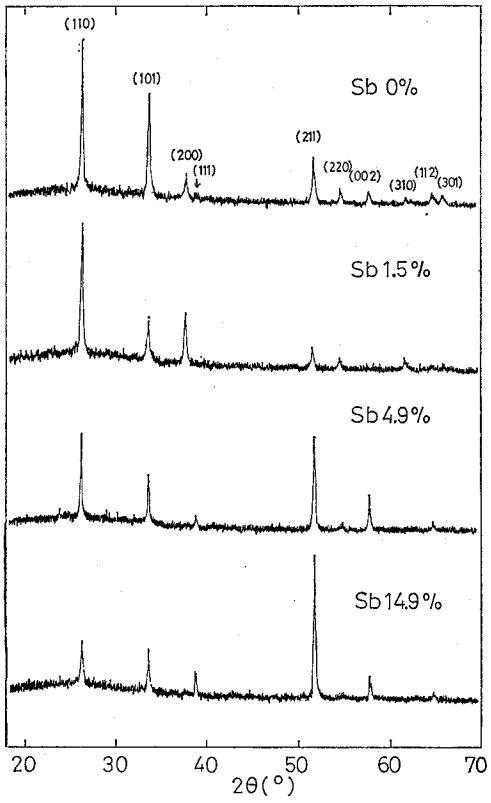

Fig. 1. X-ray diffraction patterns for films with various Sb concentrations.

Table 2. Intensities of (110), (101) and (211) diffraction lines and lattice parameters, a and c, for Sb-doped films.

Sb concentration (mol%)	Intensity			Lattice parameter (Å)	
	(110)	(101)	(211)	a	c
0	100	68	31	4.736	3.183
1.5	100	33	17	4.734	3.184
2.7	100	56	44		
4.9	90	52	100	4.736	3.188
6.2	80	36	100		
14.9	29	29	100	4.738	3.189
54.0	30	19	100	4.736	3.191
ASTM SnO_2(5-467)	100	81	61	4.738	3.188

and were in good agreement with the values in ASTM (5-467). However, the intensities of diffraction lines varied with the Sb concentration. With increasing Sb concentration, the (211) line became much stronger, while the (110) and the (101) lines weaker. The intensity of the (211) line for films with 14.9 mol% and 54.0 mol% was about three times larger than that of the (110) line. This indicates that films with higher Sb concentrations have a strong tendency toward a preferred orientation with a (211) plane parallel to the substrate.

Figure 2 shows the dependence of the electrical resistivity, carrier concentration and carrier mobility on the Sb concentration. In this figure, the resistivities of films with 14.9 mol% and 54.0 mol% are plotted against the measured concentrations of 10.0 mol% and 11.4 mol%, respectively. The resistivity initially decreased with increasing Sb concentration and took the minimum value of about 3×10^{-3} Ω cm in the range of (1–2) mol%. Beyond about 2 mol%, the resistivity increased rather steeply with increasing Sb concentration. The carrier concentration initially increased with increasing Sb concentration, took the maximum value of about 2×10^{20} cm^{-3} at around 2 mol%, and then decreased at higher concentrations. The

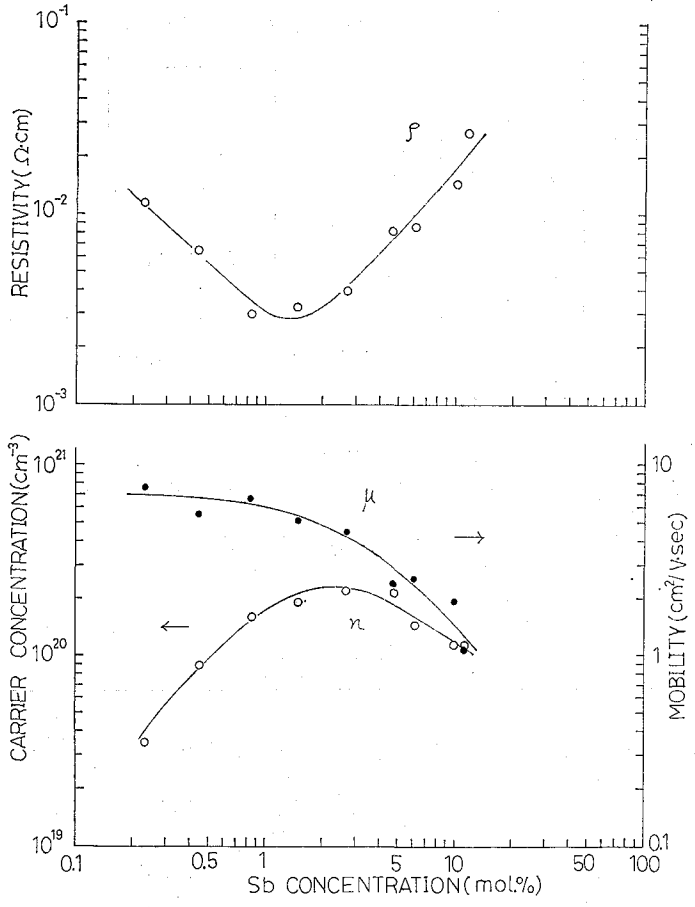

Fig. 2. Dependence of the electrical properties on the Sb concentration: ρ, resistivity; n, carrier concentration; μ, carrier mobility.

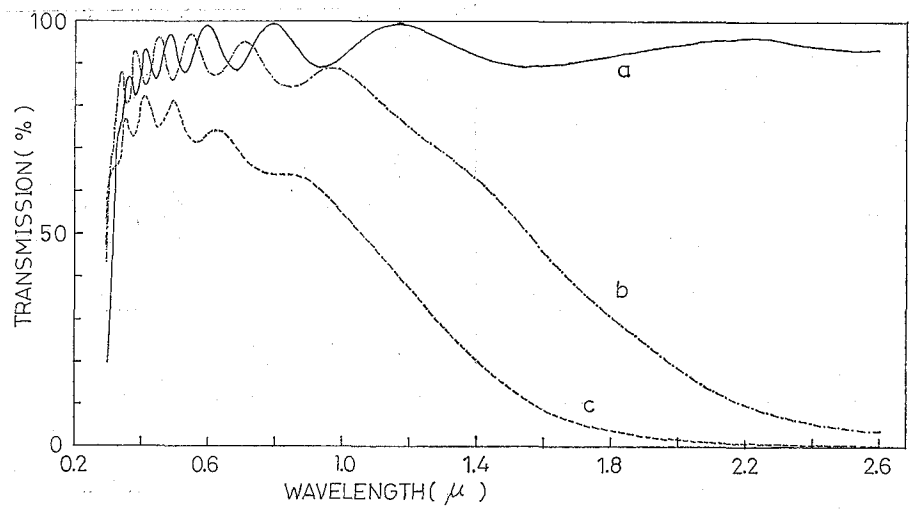

Fig. 3. Optical transmission curves for films with various Sb concentrations: (a) 0 mol%; (b) 2.7 mol%; (c) 14.9 mol%.

carrier mobility decreased slightly with increasing Sb concentration upto about 2 mol%, and then decreased steeply at higher concentrations. These results indicates that the initial decrease in the resistivity is due to an increase in the carrier concentration. The increase in the resistivity beyond about 2 mol% is due to a decrease in both the carrier mobility and the carrier concentration.

The decrease in the carrier mobility at Sb concentrations above about 2 mol% is assumed to be caused by an increase in the number of carrier scattering centers from the substitutional Sb or oxygen vacancies. Besides this, the carrier mobility may be decreased by the enhancement of the carrier scattering mechanism by the grain boundary. As revealed by X-ray diffraction analysis, the microstructure of films changed to the (211) texture at higher Sb concentrations, and this might result in enhancing the grain boundary scattering of free carriers. The carrier concentration of films with above about 2 mol%Sb decreased with increasing Sb concentration. This suggests that the doping of Sb atoms above about 2 mol% is ineffective to liberate free carriers, and that excessively doped-Sb atoms only act as carrier scattering centers.

Figure 3 shows examples of optical transmission curves for typical films. The films doped with below 2 mol%Sb exhibited the high transmission of about 95% in the visible region. Beyond 2 mol%Sb, the transmission of films in the visible region gradually decreased with increasing Sb concentration and much decreased in the infra-red region.

3.2 In-doped films

Table 3 shows the results of X-ray fluorescence analysis. The nominal concentrations are all in good agreement with the measured values. This indicates that the In concentration can be determined over the wide range from the evaporation rates of Sn and In.

Table 3. In concentrations in films (mol%)

Calculated	Measured
2.5	2.1
8.7	10.0
50.0	47.2

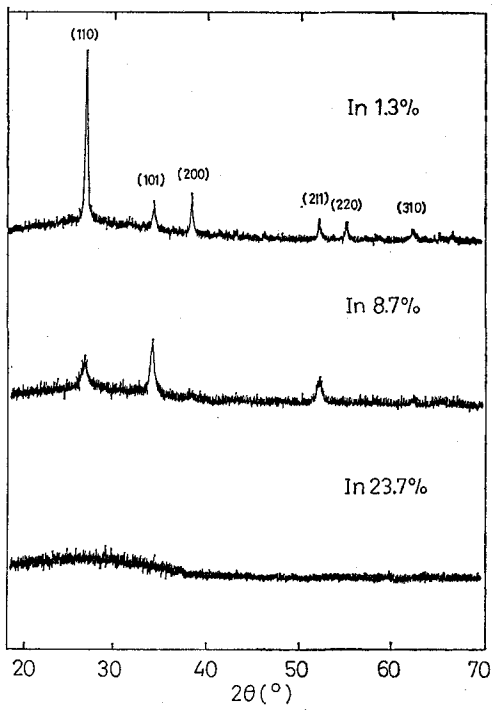

Fig. 4. X-ray diffraction patterns for films with various In concentrations.

Figure 4 shows examples of X-ray diffraction patterns for typical films. Table 4 shows the results of X-ray diffraction analysis. Films doped with 8.7 mol%In or below were composed of a rutil-like SnO_2 structure. The lattice parameters, a and c, were almostly in good agreement with the values in ASTM (5-467). The doping of In or Sb to the level of about 10 mol% gave little influence on the lattice dimension. This is because the ionic radius of In^{3+} or Sb^{5+} is nearly equal to that of Sn^{4+}. The intensities of diffraction lines for films with (1–6) mol%In, however, noticeably deviated from those expected from the ASTM. The (110) line was much stronger than that in the ASTM. This indicates that the films with (1–6) mol%In have a strong tendency toward a preferred orientation with a (110) plane parallel to the substrate. This tendency of the In-doped films is quite different

Table 4. Intensities of (110), (101) and (211) diffraction lines and lattice parameters, a and c, for In-doped films.

In concentration	Intensity			Lattice parameter (Å)	
(mol%)	(110)	(101)	(211)	a	c
0.24	100	61	40	4.735	3.185
1.3	100	14	11	4.737	3.187
3.1	100	18	12		
5.6	100	16	14	4.734	3.188
8.7	100	18	73	4.743	3.187

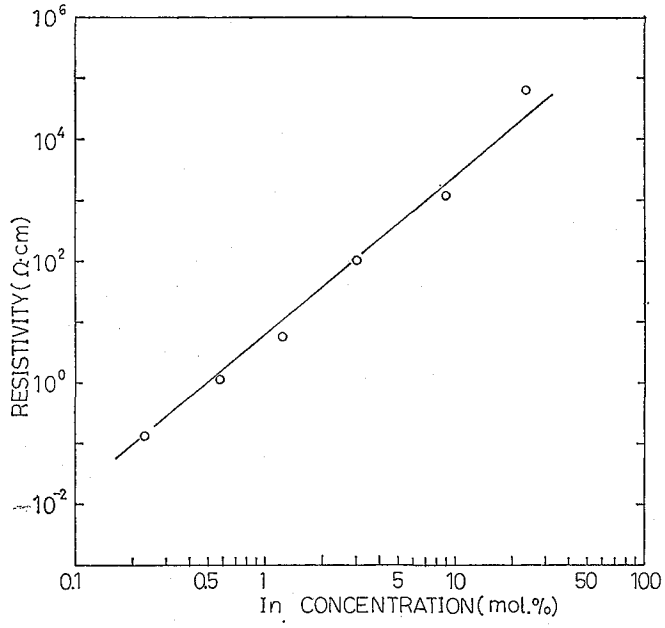

Fig. 5. Dependence of the resistivity on the In concentration.

from that of the Sb-doped films (which have a tendency to the (211) texture). Thus, the film texture have a marked dependence on the kind of the dopant as well as its concentration. Diffraction patterns of films with 8.7 mol%In consisted of rather diffuse lines and those of films with 23.7 mol%In were halo. These results indicate that the crystallinity of films gradually deteriorates as the In concentration increases from 8.7 mol% to 23.7 mol%. Films with 50 mol%In were composed of the mixture of two phases; an amorphous and a crystalline In_2O_3.

Figure 5 shows the dependence of the resistivity of films on the In concentration upto 23.7 mol%. The resistivity drastically increased with increasing In concentration. Thus, the doping of In and Sb had an opposite effect on the resistivity of films. The similar increase in resistivity by doping of In has been reported for films produced by CVD.[3] The Hall coefficient was measured for two films with 0.24 mol%In and 0.58 mol%In. The carrier mobility was insensitive to the In concentration. It was about 7 $cm^2/V \cdot sec$, nearly equal to the value for undoped films or Sb-doped films with the low concentration. The carrier concentration, however, decreased remarkably with increasing In concentration. The carrier concentration for undoped films was 2×10^{19} cm^{-3}, and those for films with 0.24 mol%In and 0.58 mol%In were 3×10^{18} cm^{-3} and 6×10^{17} cm^{-3}, respectively. Therefore, the increase in the resistivity with increasing In concentration can be ascribed to a decrease in the carrier concentration. The doping of In in films is assumed to reduce the number of oxygen vacancies and result in the decrease in free carriers.

Figure 6 shows examples of optical transmission curves for typical films. Films doped with below 6 mol%In exhibited the high transmission of about 95%. Be-

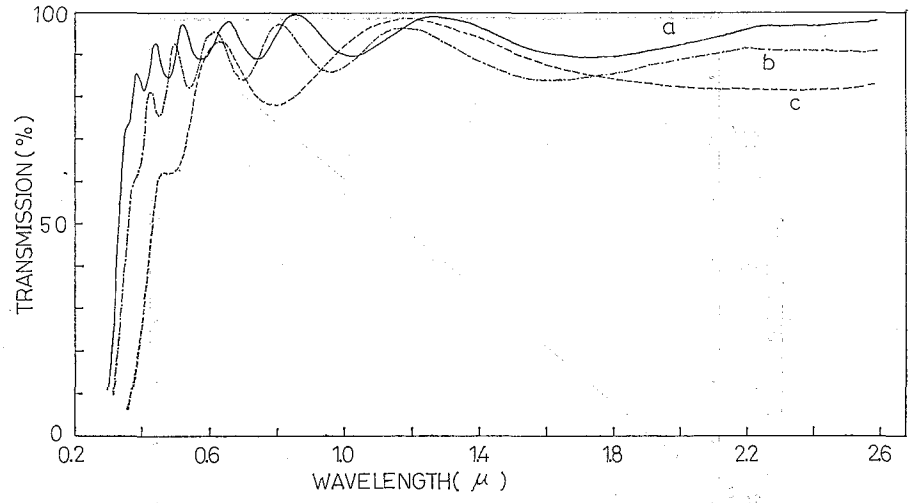

Fig. 6. Optical transmission curves for films with various In concentrations: (a) 3.1 mol%; (b) 8.7 mol%; (c) 23.7 mol%. The film with 23.7 mol% was of about 2370 Å thick.

yond this concentration, the transmission slightly decreased with increasing In concentration, perhaps because of the deterioration of the crystallinity of films.

4. SUMMARY

SnO_2 films doped with Sb or In were reactively deposited by use of two evaporation sources of Sn and Sb or In. Sb atoms could be doped in films upto about 11 mol%. The optimum dopant concentration of Sb for the lowest resistivity was (1–2) mol%. Films with (1–2) mol%Sb exhibited the high optical transmission of about 95% in the visible region. Beyond 2 mol%Sb, the resistivity steeply increased with increasing Sb concentration and the optical transmission gradually decreased. Films doped with In could be produced over the wide range of the concentration, but the crystallinity of films deteriorated with above 8 mol%In. The resistivity of In-doped films drastically increased with increasing In concentration, while the optical transmission was rather insensitive to the In concentration.

ACKNOWLEDGMENTS

The authors wish to thank to Dr. H. Takagi for supplying the opportunity for the use of the X-ray fluorescence equipment and to Dr. Sasaki for the optical transmission measurements.

REFERENCES

(1) J.L. Vossen, *Phys. Thin Films*, **9** (1977) 1.
(2) R. Muto and S. Furuuchi, *Oyo Butsuri*, **41** (1972) 134.
(3) A. Rohatagi, T.R. Viverito and L.H. Slack, *J. Am. Ceram. Soc.*, **57** (1974) 278.
(4) S. Kulaszewicz, *Thin Soiid Films*, **74** (1980) 211.
(5) H.W. Lehamann and R. Widmer, *Thin Solid Films*, **27** (1975) 359.
(6) A.G. Sabnis and L.D. Feisel, *J. Vac. Sci. Technol.*, **14** (1977) 685.
(7) S. Muranaka, Y. Bando and T. Takada, *Thin Solid Films*, **86** (1981) 11.