

# Preparation and study of doped and undoped tin dioxide films by the open air chemical vapour deposition technique

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## Abstract

Highly transparent and conducting undoped and doped (Mo, Sb, F) tin dioxide films have been prepared by the open air chemical vapour deposition technique. The electrical and optical properties have been studied in detail for films deposited on glass substrates. Surface morphology study by scanning electron microscope shows that for films deposited on glass substrates, Sb- and F-doped films have a larger grain size than undoped ones. Mo-doping, in contrast, produces smaller grains. Films deposited on mica and Al sheet substrate have also a larger grain size compared to those on glass substrate. Films of very high quality in terms of crystallinity, electrical conductivity and optical transmission were obtained when deposited at a substrate temperature of 400°C. The optimum concentration for each dopant, at which the sheet resistance is a minimum, has been determined. 4.5 at.% F-doped SnO<sub>2</sub> films show the lowest resistivity,  $\sim 4 \times 10^{-4} \Omega \text{ cm}$ , and an average optical transmission of 80% at a thickness of 3500 Å. © 1997 Elsevier Science S.A.

**Keywords:** Transparent conducting oxide; SnO<sub>2</sub> thin films; CVD

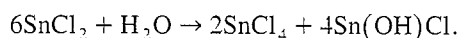
## 1. Introduction

Tin dioxide has been widely used as a transparent conducting thin film material for application in a number of solid state devices such as solar cells, opto-electronic devices, liquid crystal displays, heat mirrors, photo-thermal converters, thin film resistors and gas sensors [1–4].

The films are also very useful because of the stability of their mechanical, optical and electrical properties. Tin dioxide is a wide band gap electron degenerate semiconductor, whose properties largely depend on the deviation from stoichiometry (oxygen deficiency) as well as on the dopants used. Usually antimony or fluorine is used as a dopant to substitute tin or oxygen atoms, respectively.

Tin dioxide films have been prepared by a large variety of techniques which include spray pyrolysis [5–12], chemical vapour deposition [13–17], sol-gel method [18–20], reactive evaporation [21] and reactive r.f. sputtering [22]. The properties of these films crucially depend on the deposition technique and post deposition treatment.

In a previous report [23] we described an extremely simple and low-cost chemical vapour deposition method for tin dioxide films. In this method, the starting material is SnCl<sub>2</sub> · 2 H<sub>2</sub>O crystals which are ground with water into a paste and the paste applied in the form of a 4–5 mm wide band near, and parallel to, the lower edge of a substrate positioned vertically. On heating in air the paste decomposes according to the equation



SnCl<sub>4</sub>, which is generated as one of the reaction products, rises upward due to convection and hydrolyses on the heated substrate to produce a tin dioxide film. Doping with antimony can be achieved by mixing the requisite amount of SbCl<sub>3</sub> with SnCl<sub>2</sub> paste. Considering the simplicity of the method, films of reasonably good quality can be obtained. Details are given in Ref. [23].

This so-called ‘paste-heat’ method, however, suffers from the following disadvantages: (i) the portion of the substrate where the SnCl<sub>2</sub> paste is applied must be subsequently cut away before the films can be used, (ii) because of the geometry of the arrangement, the films are non-uniform, being thickest near the paste-coated area and becoming thinner away from it, and (iii) non-planar substrates, as also those with small sizes cannot be used.

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In this report, we describe a modification of the above method, which employs the same principle, and maintains essentially the same simplicity, at the same time enabling one to obtain films free from the above defects. The preparation of undoped and doped (Sb, Mo, F) tin dioxide thin films by this method and the study of their electrical and optical properties as well as their surface morphology and crystal structure are described.

## 2. Experimental details

A 75 cm long glass tube with an internal diameter of 5 cm was placed vertically as shown in Fig. 1. The tube was heated from the outside in atmospheric condition by winding a heater coil on its outer surface over a length of 70 cm. The substrate was placed vertically in the central region of the tube. The starting material was taken in a conical flask placed at the bottom of the tube and heated separately. The temperature of the substrate was measured by a thermocouple placed close to the substrate. The starting material was prepared by mixing crystals of  $\text{SnCl}_2$ ,  $2\text{H}_2\text{O}$  with a few drops of water along with any dopant material that might be added and was stirred mechanically to convert it to a paste.

In the film forming process, the substrate was initially heated to attain the desired temperature after which the  $\text{SnCl}_2$  paste was heated. White fumes were given off by

the paste and were seen to deposit  $\text{SnO}_2$  films where they came into contact with the hot substrate.

It is possible to deposit a number of films in a batch, by attaching them to a holder, which is placed in the central region of the tube. Usually both sides of the substrate are coated by this method, which is advantageous in some special cases [24], but it is also possible to coat one side only by masking the other side, or by fixing two substrates back to back. This method is especially advantageous for inaccessible surfaces and the inside surface of a tube, where one can obtain a coating quite easily, in contrast to the rather complex arrangements required in the usual CVD methods. The films were usually deposited over soda glass substrates ( $7.5\text{ cm} \times 2.5\text{ cm}$ ) and showed a uniform interference colour over their entire area except at the edges. But uniform films could also be routinely obtained, if necessary, over a larger area of 40 cm long by 4 cm wide.

Undoped tin dioxide films of various thicknesses were prepared at substrate temperatures of  $350^\circ\text{C}$ ,  $400^\circ\text{C}$  and  $450^\circ\text{C}$ . Soda glass microslides, mica and Al sheet were used as substrates.

The films were doped with antimony, fluorine and molybdenum by adding antimony trichloride, ammonium fluoride and ammonium molybdate respectively to the  $\text{SnCl}_2$  starting material. Characterization of the films was carried out by optical transmission and electrical conductivity measurements, X-ray diffractometry and scanning electron microscopy.

The electrical properties of the films were measured by the standard four-probe method and the optical properties were studied by a Shimadzu UV-240 double-beam spectrophotometer. Surface morphology and X-ray diffractometric studies were carried out by a Hitachi S-530 scanning electron microscope and a Philips diffractometer (model PW 1390) with  $\text{CuK}_\alpha$  radiation (Ni-filter) at  $1.54\text{ \AA}$ , respectively.

## 3. Results and discussions

The films were smooth, highly uniform and resistant to peeling-off and acids, and also showed long-term stability with respect to their optical, electrical and mechanical properties. They displayed characteristic interference colours. Films of various thicknesses were obtained by varying the amount of starting material, deposition time and substrate temperature. By observing the change in interference colours as a function of time the order of a particular colour could be known, and from the standard value of the mean refractive index of  $\text{SnO}_2$  (taken as 2.0 over the range of 400–800 nm) the thickness could be estimated [25].

It was found that using this process a substrate temperature of  $400^\circ\text{C}$  was necessary to prepare films of very high quality in terms of conductivity, optical transmission, uni-

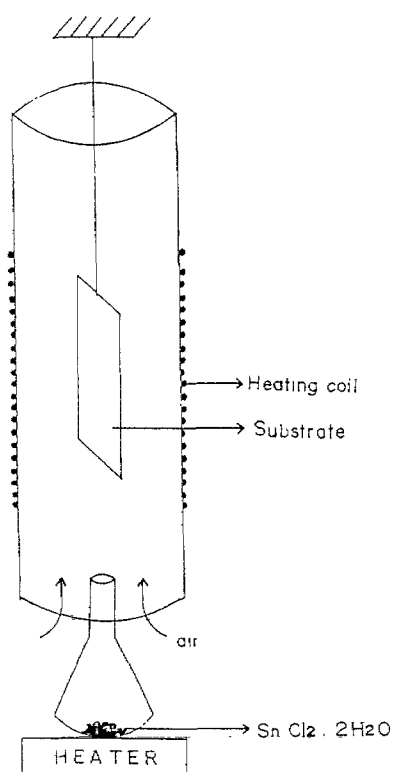


Fig. 1. Experimental arrangement for the deposition of  $\text{SnO}_2$  films.

formity and resistance to peeling-off and acids as well as environmental shocks.

### 3.1. X-ray diffractometric study

X-ray diffractometric studies were carried out on undoped and doped  $\text{SnO}_2$  films deposited at a substrate temperature of  $400^\circ\text{C}$ . Diffraction peaks for undoped  $\text{SnO}_2$  films having two different thicknesses are shown in Fig. 2(a). Fig. 2(b) shows the X-ray diffractograms of Sb and F doped  $\text{SnO}_2$  films. The crystal structure is in accordance with the usual tetragonal form of  $\text{SnO}_2$ .

It is clear from the XRD patterns that there is no amorphous background in the diffractograms of the deposited films. Moreover, none of the undoped films show any preferred orientation, while those doped with Sb and F show a preferred orientation along the (110) planes. Prominent peaks, their  $d$ -values and relative intensities ( $I/I_0$ ) for a typical F-doped  $\text{SnO}_2$  film are listed in Table 1.

### 3.2. Surface morphology

Surface topographies of undoped, 6 at.% Mo-doped, 1.5 at.% Sb-doped, and 4.5 at.% F-doped  $\text{SnO}_2$  films de-

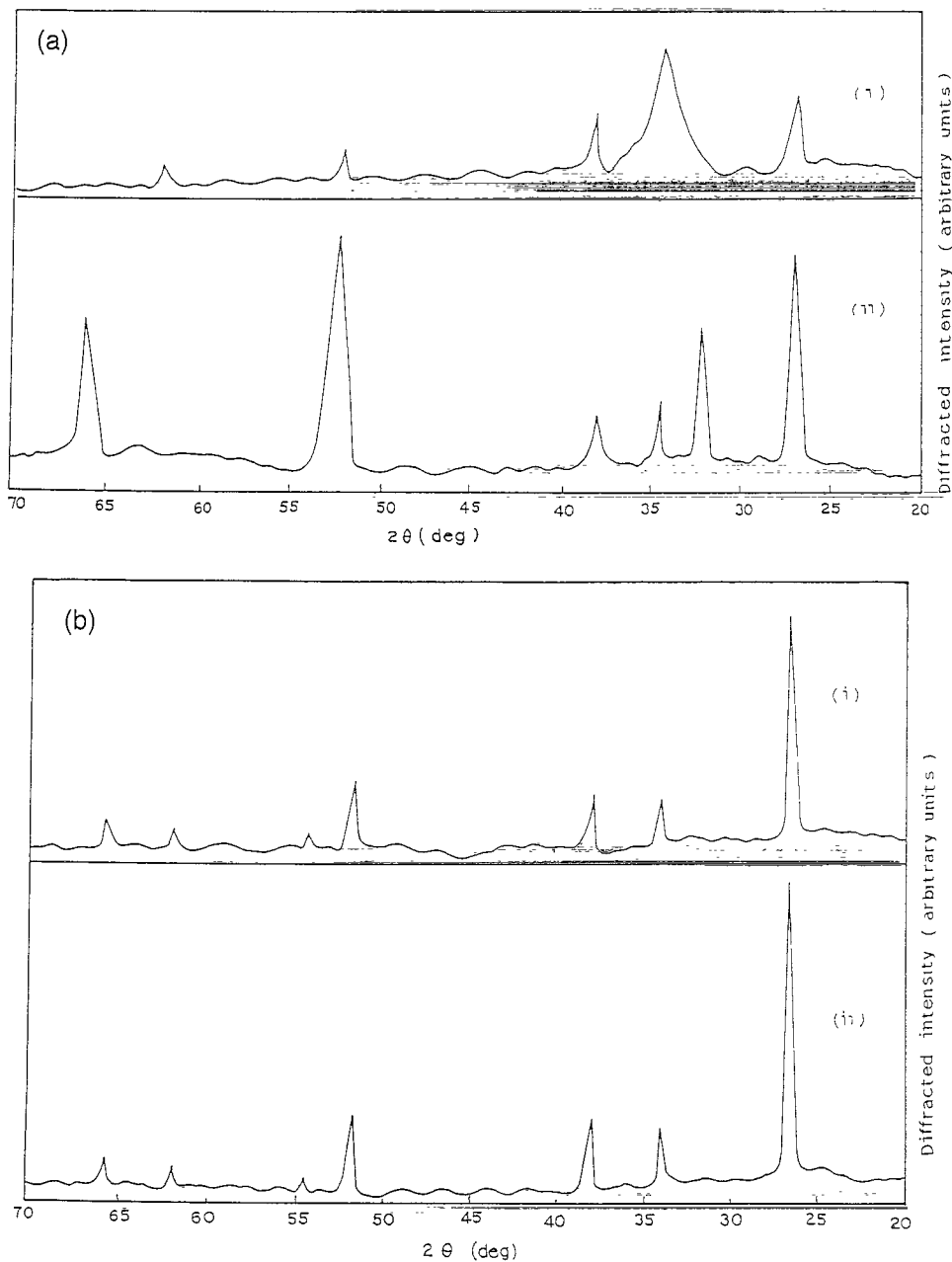


Fig. 2. (a) X-ray diffractogram of undoped  $\text{SnO}_2$  films of two different thicknesses ( $T_s = 400^\circ\text{C}$ ). (i)  $0.6\ \mu\text{m}$  (ii)  $2.5\ \mu\text{m}$ . (b) X-ray diffractogram of doped films ( $T_s = 400^\circ\text{C}$ ). (i) 1.5 at.% Sb-doped, (ii) 4.5 at.% F-doped.

Table 1

Prominent peak positions ( $2\theta$  values) of the X-ray diffraction peaks, corresponding  $d$ -values, relative intensities ( $I/I_0$ ) and their identification for F-doped  $\text{SnO}_2$  films

Observed values			Comparable values from ASTM data file			
$2\theta$	$d$ -value [ $\text{\AA}$ ]	$(I/I_0)$	$2\theta$	$d$ -values [ $\text{\AA}$ ]	$(I/I_0)$	$hkl$
26.60	3.347	100	26.57	3.351	100	110
33.90	2.641	21	33.86	2.644	80	101
37.95	2.368	32	37.94	2.369	25	200
51.75	1.764	34	51.73	1.765	65	211
54.85	1.671	12	54.74	1.675	18	220
61.95	1.496	12	61.86	1.498	14	310
65.90	1.415	13	65.94	1.415	16	301

posited at a substrate temperature of  $400^\circ\text{C}$  are shown in Fig. 3. It is observed that in all cases except that of Mo-doped films large size grains of  $\sim 1.7 \mu\text{m}$  are spread throughout the film over a background of grain size  $\sim 0.6 \mu\text{m}$ . These large grains are observed to disappear when doped with Mo. The average grain size for Sb- and F-doped films is found to be larger, while that for Mo-doped films is smaller compared to the undoped ones.

Films were also deposited on different substrates to investigate the substrate effect. Fig. 4 shows the SEM micrographs of undoped  $\text{SnO}_2$  films deposited on mica and aluminium sheet at a substrate temperature of  $400^\circ\text{C}$ . It is also evident from Fig. 4 that the grain size of the undoped  $\text{SnO}_2$  films deposited on crystalline mica and aluminium substrate is larger than that deposited on glass substrates. Table 2 shows the grain size variation of the films deposited.

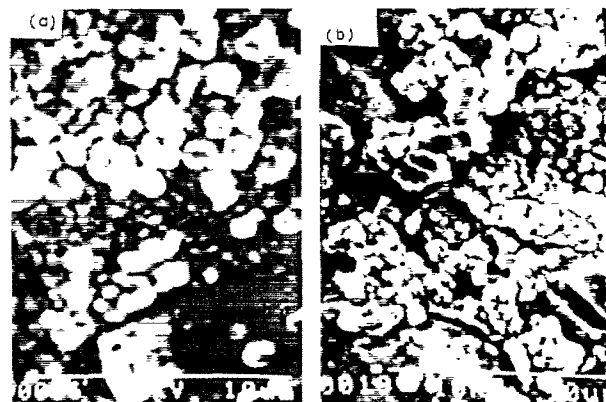


Fig. 4. Scanning electron micrographs of  $\text{SnO}_2$  thin films on different substrates ( $T_s = 400^\circ\text{C}$ ). (a) On mica, (b) on aluminium sheet.

### 3.3. Electrical properties

Results of detailed measurements of the sheet resistance of the films as a function of thickness, temperature and dopant concentration are shown in Figs. 5 and 6.

Fig. 5 shows the variation of sheet resistance with thickness of undoped films deposited at three substrate temperatures. It is evident from the curves that the room temperature resistivity of the undoped films decreases to its minimum value when deposited at a substrate temperature of  $400^\circ\text{C}$  but increases again when deposited at a higher substrate temperature of  $450^\circ\text{C}$ . This is due to the fact that, on increasing the substrate temperature from  $350^\circ\text{C}$  to  $400^\circ\text{C}$ , a better degree of crystallinity is achieved, leading to improved electronic, optical and structural properties [8,26]. It is also known that [5] both the carrier

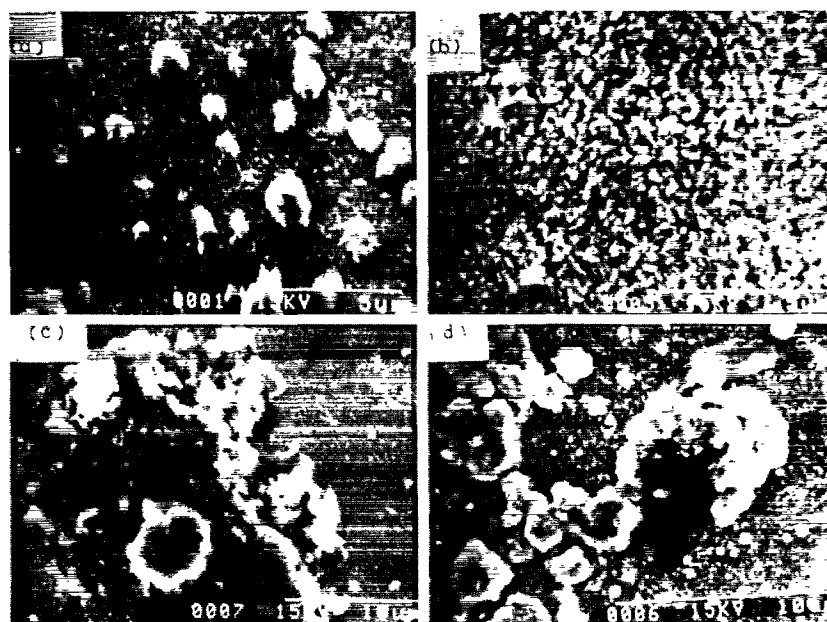


Fig. 3. Scanning electron micrographs of  $\text{SnO}_2$  thin films on glass substrates ( $T_s = 400^\circ\text{C}$ ). (a) Undoped  $\text{SnO}_2$ ; (b)  $\text{SnO}_2:\text{Mo}$  (6 at.%); (c)  $\text{SnO}_2:\text{Sb}$  (1.5 at.%); (d)  $\text{SnO}_2:\text{F}$  (4.5 at.%).

Table 2

Grain size variation of doped (on glass) and undoped (on different substrates)  $\text{SnO}_2$  films (deposition temperature  $T_s = 400^\circ\text{C}$ )

Films	Substrate	Average grain size [ $\mu\text{m}$ ]
$\text{SnO}_2$ undoped	glass	1.20
$\text{SnO}_2:\text{Sb}$	glass	4.00
$\text{SnO}_2:\text{Mo}$	glass	0.60
$\text{SnO}_2:\text{F}$	glass	4.75
$\text{SnO}_2$ undoped	mica	2.00
$\text{SnO}_2$ undoped	aluminium	1.50

concentration and mobility increase with the increase of substrate temperature where mobility variation is larger than that of the carrier concentration. A further increase in substrate temperature produces films of increased resistivity. This is due to the fact that in undoped  $\text{SnO}_2$ , conduction electrons arise from oxygen vacancies, and a higher substrate temperature causes an increased oxygen evolution from the substrate, leading to more nearly stoichiometric films [8,27]. The resistivity of the undoped films prepared at a substrate temperature of  $400^\circ\text{C}$  is estimated to be  $4 \times 10^{-3} \Omega \text{ cm}$ , which agrees well with the values reported earlier in the literature [8].

The effect of dopants (Mo, Sb, and F) at various concentrations on the resistivity was studied. It is found that for every dopant, there is an optimum concentration at which the resistivity is a minimum. These values are listed in Table 3.

Thus it is observed that the introduction of Mo reduces the resistivity by a maximum factor of 2 whereas Sb and F reduce it by factors of 5 and 10, respectively. Similar results are reported by Gordillo et al. [7]. The relatively

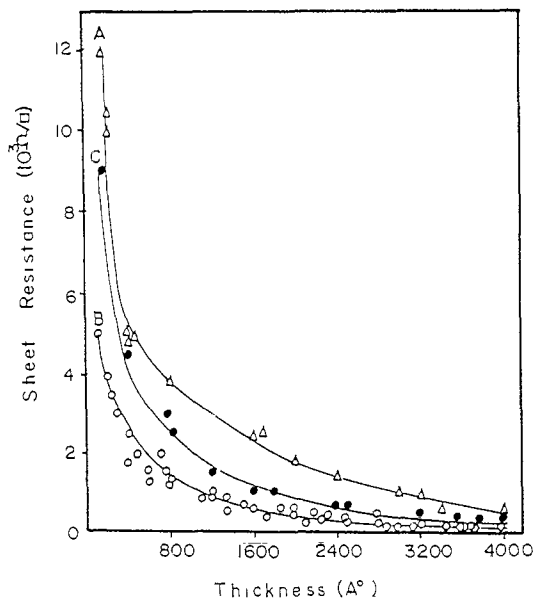


Fig. 5. Variation of sheet resistance with thickness of undoped  $\text{SnO}_2$  films deposited at various substrate temperatures. A,  $350^\circ\text{C}$ ; B,  $400^\circ\text{C}$ ; C,  $450^\circ\text{C}$ .

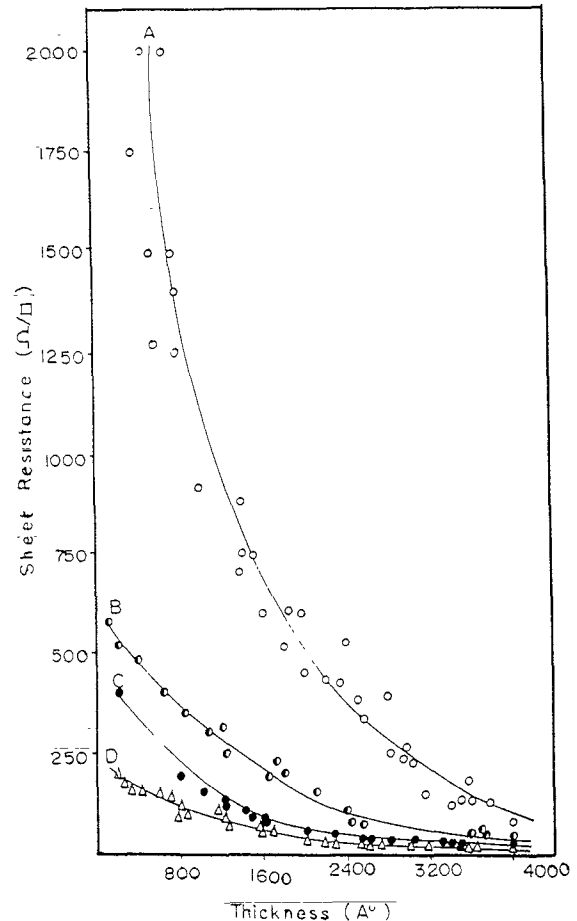


Fig. 6. Sheet resistance–thickness relationship for undoped (curve A) and doped (curve B,  $\text{SnO}_2:\text{Mo}$  (6 at.%); curve C,  $\text{SnO}_2:\text{Sb}$  (1.5 at.%); curve D,  $\text{SnO}_2:\text{F}$  (4.5 at.%))  $\text{SnO}_2$  films prepared at a substrate temperature of  $400^\circ\text{C}$ .

higher resistivity and lower optical transmission of the Mo-doped  $\text{SnO}_2$  films compared to the Sb-doped and F-doped films may be due to their small grain size as observed from the SEM micrograph. It is known that with the decrease in grain size the grain boundary potential increases, leading to an increased grain boundary scattering and a corresponding increase in resistivity [5]. In the case of Sb-doped and F-doped  $\text{SnO}_2$  films, the resistivity decreases up to 1.5 at.% Sb-doping and 4.5 at.% F-doping, respectively, which may be due to (i) increased carrier concentration, (ii) larger grain size and (iii) preferred orientation. Beyond the above concentration the observed

Table 3

Minimum resistivity values of undoped and doped  $\text{SnO}_2$  films on glass substrate ( $T_s = 400^\circ\text{C}$ )

Films	Resistivity [ $\Omega \text{ cm}$ ]
$\text{SnO}_2$ (undoped)	$4 \times 10^{-3}$
$\text{SnO}_2:\text{Mo}$ (6 at.%)	$2 \times 10^{-3}$
$\text{SnO}_2:\text{Sb}$ (1.5 at.%)	$8 \times 10^{-4}$
$\text{SnO}_2:\text{F}$ (4.5 at.%)	$4 \times 10^{-4}$

increases in resistivity may be due to the increase in the contribution from ionised impurity scattering [5].

The variation of sheet resistance with thickness for optimum concentrations of the dopants is shown in Fig. 6.

### 3.4. Optical properties

The variation of the average optical transmission over the range 400–800 nm as a function of sheet resistance for undoped and doped films is shown in Fig. 7. The optical transmission is observed to decrease with decreasing sheet resistance in the case of both undoped and doped films. It is seen for all the films that the optical transmission drops off more rapidly at lower values of the sheet resistance. This is due to an increase in surface roughness of films having a low sheet resistance which have a proportionately higher thickness [1,26]. However, F-doped films are found to have a high optical transmission even at a low sheet resistance of 100  $\Omega/\square$ .

The films are found to compare quite favourably in terms of electrical and optical properties with those prepared by other methods as shown in Table 4. The figure of merit  $\phi_{TC}$  for the films has been calculated according to Haacke's [28] relation  $\phi_{TC} = T^{10}/R_s$  for transparent conducting films, where  $T$  is the transmission and  $R_s$  the sheet resistance.

### 3.5. Conclusions

Undoped and Mo-, Sb-, and F-doped  $\text{SnO}_2$  films deposited by the Open Air Chemical Vapour Deposition (OACVD) technique have been investigated in detail. The films show a high degree of crystallinity along with the largest values of electrical conductivity and optical transmission when deposited at a substrate temperature of 400°C. X-ray diffractometric study suggests that Sb- and F-doped  $\text{SnO}_2$  films show a preferred orientation along the (110) plane. The surface morphology study by scanning

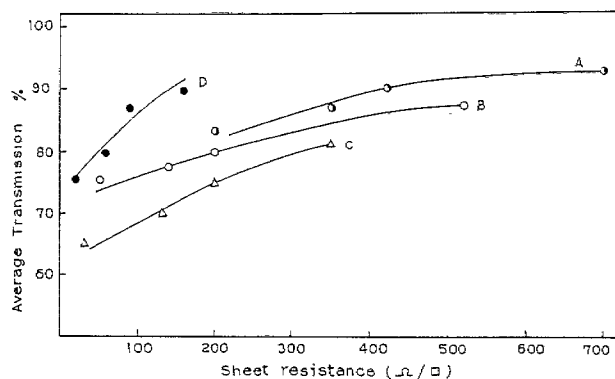


Fig. 7. The average optical transmission over 400–800 nm versus sheet resistance for undoped (curve A) and doped (curve B,  $\text{SnO}_2\text{:Mo}$  (6 at.%); curve C,  $\text{SnO}_2\text{:Sb}$  (1.5 at.%); curve D,  $\text{SnO}_2\text{:F}$  (4.5 at.%))  $\text{SnO}_2$  films prepared at a substrate temperature of 400°C.

Table 4

Comparison of the electrical and optical properties of tin dioxide films prepared by various workers

Material	Deposition technique	$\rho$	$R_s$	$T_a(\Delta\lambda)$	$\phi_{TC}$
$\text{SnO}_2$	SP [27]	$5 \times 10^{-3}$	84	85 (0.5–2)	2.40
	CVD [29]	$7 \times 10^{-2}$	1200	93 (0.3–0.7)	0.41
	present work	$4 \times 10^{-3}$	100	90 (0.4–0.8)	3.48
$\text{SnO}_2\text{:Sb}$	SP [1]	$4.2 \times 10^{-3}$	28	87 (0.3–1)	9.40
	CVD [30]	$2 \times 10^{-3}$	55	88 (0.4–0.7)	5.06
	present work	$8 \times 10^{-4}$	20	75 (0.4–0.8)	2.82
$\text{SnO}_2\text{:F}$	SP [1]	$4.6 \times 10^{-4}$	10	85 (0.4–1)	19.68
	CVD [13]	$5 \times 10^{-4}$	20	90 (0.4–0.8)	17.43
	present work	$4 \times 10^{-4}$	10	85 (0.4–0.8)	19.68
$\text{SnO}_2\text{:Mo}$	present work	$2 \times 10^{-3}$	50	80 (0.4–0.8)	2.15

$\rho$  – resistivity [ $\Omega \text{ cm}$ ],  $R_s$  – sheet resistance [ $\Omega/\square$ ],  $T_a(\Delta\lambda)$  – average optical transmission (wavelength range [%] ( $\mu\text{m}$ )),  $\phi_{TC}$  – figure of merit [ $\times 10^{-3} \Omega^{-1}$ ], CVD – chemical vapour deposition, SP – spray pyrolysis.

electron microscope suggests that for films deposited on glass substrates, the grain size increases in the case of Sb-doped and F-doped  $\text{SnO}_2$  films but decreases for Mo-doped  $\text{SnO}_2$  films. The grain size for undoped films on mica and aluminium sheet substrate is also larger than that for films deposited on glass substrates.

The lowest values of sheet resistance at a particular thickness are obtained for 6 at.% Mo-doped, 1.5 at.% Sb-doped and 4.5 at.% F-doped  $\text{SnO}_2$  films on glass substrate. A typical value of resistivity of 4.5 at.% F-doped  $\text{SnO}_2$  films is  $4 \times 10^{-4} \Omega \text{ cm}$  and that for 1.5 at.% Sb-doped  $\text{SnO}_2$  is  $\sim 8 \times 10^{-4} \Omega \text{ cm}$ .

The films compare quite well in terms of electrical conductivity and optical transmission with those obtained by other methods. The average optical transmission over the range of 400 to 800 nm is found to decrease as the sheet resistance decreases for Mo- and Sb-doped films. But for F-doped films, a negligible increase in transmission loss with decreasing sheet resistance is found to occur.

In conclusion, tin dioxide films having a sheet resistance of 10–1000  $\Omega/\square$  and an average optical transmission of 75–90% could routinely be obtained by this method. The merit of the present method is its extreme simplicity by which one can deposit useful tin dioxide films for device applications either on one side or both sides of a planar substrate or inside of a tube quite easily in any laboratory.

### References

- [1] K.L. Chopra, S. Major, D.K. Pandya, Thin Solid Films 102 (1983) 1–46.
- [2] C.S. Rastomjee, R.S. Dale, R.J. Schaffer, F.H. Jones, R.G. Egdell, G.C. Georgiadis, M.J. Lee, T.J. Tate, L.L. Cao, Thin Solid Films 279 (1996) 98–105.
- [3] I. Kocemba, T. Paryjczak, Thin Solid Films 272 (1996) 15–17.
- [4] B.J. Hwang, K.L. Lee, Thin Solid Films 279 (1996) 236–241.

- [5] E. Shanthi, V. Dutta, A. Banerjee, K.L. Chopra, *J. Appl. Phys.* 51 (12) (1980) 6243–6251.
- [6] E. Shanthi, A. Banerjee, K.L. Chopra, *Thin Solid Films* 88 (1982) 93.
- [7] G. Gordillo, L.C. Moreno, W. de la Cruz, P. Teheran, *Thin Solid Films* 252 (1994) 61–66.
- [8] A.L. Unaogu, C.E. Okeke, *Solar Energy Mater.* 20 (1990) 29–36.
- [9] H. Kim, H.A. Laitinen, *J. Am. Ceram. Soc.* 58 (1975) 23.
- [10] E. Shanthi, A. Banerjee, V. Dutta, K.L. Chopra, *Appl. Phys.* 53 (1982) 1615.
- [11] G. Maurodien, M. Gajardziska, Novkovski, *Thin Solid Films* 113 (1984) 93.
- [12] J. Bruneaux, H. Cachet, M. Froment, A. Messad, *Thin Solid Films* 198 (1991) 129–142.
- [13] J. Proscia, R.G. Gordon, *Thin Solid Films* 214 (1992) 175–187.
- [14] Yan Dawei, Ma Xiaocui, Wang Zongchang, *Wu Jiam. Thin Solid Films* 224 (1993) 257–262.
- [15] A. Fujisawa, T. Nishino, Y. Hamakawa, *Jpn. J. Appl. Phys.* 27 (4) (1988) 552–555.
- [16] M.R. Kadam, N. Vittal, R.N. Karekar, R.C. Aiyar, *Thin Solid Films* 187 (1990) 199.
- [17] B.J. Baliga, S.K. Ggandi, *J. Electrochem. Soc.* 123 (1976) 941.
- [18] J.P. Chatelon, C. Terrier, E. Bernstein, R. Berjoan, J.A. Roger, *Thin Solid Films* 247 (1994) 162–168.
- [19] C.J. Brinker, A.J. Hurd, P.R. Schunk, G.C. Frye, C.S. Ashley, *J. Non-Cryst. Solids* 147&148 (1992) 424–436.
- [20] Y. Takahashi, Y. Wada, *J. Electrochem. Soc.* 137 (1990) 267.
- [21] H. Demiryont, N. Tezey, *Thin Solid Films* 101 (1983) 345.
- [22] A. Czapla, E. Kusior, M. Bucko, *Thin Solid Films* 182 (1989) 15.
- [23] M.K. Karanjai, D. Dasgupta, *J. Phys. D* 21 (1988) 356–358.
- [24] H. Dislich, E. Hvssmann, *Thin solid films* 77 (1980) 129–142.
- [25] J.L. Vossen, in: G. Hass, M.H. Francombe, R.W. Hoffmann (Eds.), *Physics of Thin Films*, Vol. 9, Academic Press, New York, 1977, pp. 1–71.
- [26] A. De, S. Ray, *J. Phys. D* 24 (1991) 719–726.
- [27] J.C. Manificier, L. Szepessy, I.F. Bresse, M. Perotin, R. Stuck, *Mater. Res. Bull.* 14 (1979) 163.
- [28] G. Haacke, *J. Appl. Phys.* 47 (9) (1976) 4086–4089.
- [29] J. Kane, H.P. Schweizer, W. Kern, *J. Electrochem. Soc.* 122 (1975) 1144.
- [30] J. Kane, H.P. Schweizer, W. Kern, *J. Electrochem. Soc.* 123 (1976) 270.