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Studies on tin oxide films prepared by electron beam evaporation and spray pyrolysis methods

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Abstract. Transparent conducting tin oxide thin films have been prepared by electron beam evaporation and spray pyrolysis methods. Structural, optical and electrical properties were studied under different preparation conditions like substrate temperature, solution flow rate and rate of deposition. Resistivity of undoped evaporated films varied from $2{\cdot}65 \times 10^{-2}$ Ω-cm to $3{\cdot}57 \times 10^{-3}$ Ω-cm in the temperature range 150–200°C. For undoped spray pyrolyzed films, the resistivity was observed to be in the range $1{\cdot}2 \times 10^{-1}$ to $1{\cdot}69 \times 10^{-2}$ Ω-cm in the temperature range 250–370°C. Hall effect measurements indicated that the mobility as well as carrier concentration of evaporated films were greater than that of spray deposited films. The lowest resistivity for antimony doped tin oxide film was found to be $7{\cdot}74 \times 10^{-4}$ Ω-cm, which was deposited at 350°C with 0·26 g of $SbCl_3$ and 4 g of $SnCl_4$ ($SbCl_3/SnCl_4$ = 0·065).

Evaporated films were found to be amorphous in the temperature range up to 200°C, whereas spray pyrolyzed films prepared at substrate temperature of 300–370°C were polycrystalline. The morphology of tin oxide films was studied using SEM.

Keywords. Spray pyrolysis; electron beam evaporated films; tin oxide films; transparent conducting coatings; optical and electrical properties.

1. Introduction

Tin oxide thin films are *n*-type semiconductors with high transparency and very good electrical conductivity. The films are chemically inert, mechanically hard and can resist high temperature. Owing to its low resistivity and high transmittance, tin oxide thin films are used as a window layer in solar cells (Frank *et al* 1983; Goetzberger and Hebling 2000), heat reflectors in solar cells (Colen 1981), various gas sensors (Nomura *et al* 1989; Brinzari *et al* 2001), liquid crystal displays etc. Doped or undoped tin oxide films can be prepared by many methods such as spray pyrolysis (Kulaszewicz 1980; Kulaszewicz *et al* 1983; Fantini 1986; Ansari *et al* 1997), electron beam evaporation (Das and Banerjee 1987; Lousa *et al* 1994), chemical vapour deposition (Lou *et al* 1983), magnetron sputtering (Minami *et al* 1988), Pechini method (Bernarti *et al* 2002).

Spray pyrolysis is one of the simplest methods of depositing transparent conducting oxide films such as ZnO (Van Heerden and Swanepoel 1997), CdO (Rao and Murthy 1999) etc. In this method the substrate temperature and flow rate controls the most desirable optical, structural and electrical properties of tin oxide films. Shanthi *et al* (1980) prepared tin oxide films by spray pyrolysis and reported an electrical resistivity of $2{\cdot}7 \times 10^{-2}$ Ω-cm at T_s = 500°C. The same film which was annealed in vacuum at 400°C showed a low resistivity of 1×10^{-2} Ω-cm and films annealed in air showed higher resistivity of about 10×10^{-2} Ω-cm. Antimony doped tin oxide films show a least resistivity value of $1{\cdot}9 \times 10^{-3}$ Ω-cm deposited with 1·4 mol% antimony.

Jagadish *et al* (1988) studied the optical and electrical properties of spray deposited films and reported that the sheet resistance of tin oxide films can be decreased by annealing them in hydrogen atmosphere below 350°C for 30 min. Thangaraju (2002) prepared antimony doped tin oxide films from $SnCl_2$ precursor and got a low sheet resistance of 8·1 Ω/□ for a doping concentration of ($SbCl_3$)/($SnCl_4$) = 0·6 wt%. Jarzebski (1982) reviewed physical properties of SnO_2 films prepared by various techniques.

Tin oxide films were also prepared by thermal beam evaporation where stoichiometry controls electrical and optical properties of the films. Highly transparent and conducting films can be developed by evaporating the metallic tin (99·99%) in the presence of oxygen. Das and Banerjee (1987) prepared tin oxide films by this method in presence of oxygen and obtained electrical conductivity of $4{\cdot}8 \times 10^2\ \Omega^{-1}\ cm^{-1}$ and an average transmission of 85%. Lousa *et al* (1994) prepared tin oxide films by reactive evaporation method and reported that the substrate tem-

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perature > 450°C and an oxygen partial pressure > 3×10^{-1} pascal can yield polycrystalline films. They have also reported the high electrical conductivity (s) of the order of $10^4\ \Omega^{-1}\ cm^{-1}$ for films deposited at about 490°C with an oxygen partial pressure of $3–4 \times 10^{-1}$ pascal.

2. Experimental

2.1 *Electron beam evaporation*

Tin oxide films were prepared in a conventional evaporation system by electron beam evaporation of the metallic tin (99·99%) in the presence of both neutral and ionized oxygen at a pressure of 2×10^{-4} m bar and a discharge current of 200 milli amps was used. Homemade discharge tube was used to get the ionized oxygen. The substrates were heated and the temperature was measured using a thermocouple, which was in contact with the substrate holder and was varied between 50 and 200°C. The film thickness and the rate of deposition were controlled using a quartz crystal monitor. The rate of deposition of the films was varied between 1 and 3 Å/s. The thickness of the films was measured using a spectrophotometer from the interference peaks and it was in the range 100–300 nm.

2.2 *Spray pyrolysis*

Spray pyrolysis set up used in the present work is explained elsewhere (Rao and Murthy 1999). It is a chemical deposition technique where the endothermic thermal decomposition takes place at the hot surface of the substrate to give the final product. The substrate temperature plays an important role in the film formation. When the substrate temperature is below 250°C, the spray falling on the substrate will undergo incomplete thermal decomposition (oxidation) giving rise to a foggy film whose transparency as well as electrical conductivity will be very poor. If the substrate temperature is too high (> 500°C) the spray gets vaporized before reaching the substrate and the film becomes almost powdery. Whereas at optimum substrate temperature in the range of 250–450°C the spray reaches the substrate surface in the semi vapour state and complete oxidation will take place to give clear SnO_2 film as a final product as observed in our experiments. It is a simple and low cost method of preparing transparent and conducting oxide films of uniform thickness and with electrical and optical properties that can be comparable with vacuum deposited films. One more speciality of this method is, by the optimization of the solution flow rate through carrier gas pressure it is possible to improve optical and electrical properties of the films. Undoped tin oxide films were deposited on glass and quartz substrates at different temperatures (250–370°C) using a resultant solution of tin tetra chloride ($SnCl_4$) dissolved in ethanol of known concentration (0·1 M and 0·2 M). In order to prepare the antimony doped tin oxide films, known weight of $SbCl_3$ (0·10–0·65 g) was added to 4 g of $SnCl_4$ with a few drops of concentrated HCl and the mixture was dissolved in 100 ml of ethanol. The solution flow rate (5 ml/min) was controlled by carrier gas pressure (0·5 kg/cm^2).

Optical transmission studies of all the films prepared by both the methods were made using a Hitachi UV, visible and near IR double beam spectrophotometer (Model No. 330). The structure of the films was studied by X-ray diffraction (XRD) using CuK_a radiation. Scanning electron microscope (SEM) and EDAX were used for morphology and chemical analysis of the films. The electrical properties were studied by Van der Pauw resistivity method and Hall coefficient method (Schroder 1990).

3. Results and discussion

3.1 *Optical properties*

Evaporated tin oxide films deposited at 100°C with neutral oxygen were found to be less transparent in the visible region. However, the films deposited with ionized oxygen at T_s = 100–200°C were highly transparent (90%). Figures 1 (a)–(b) show the transmission spectra of evaporated tin oxide films deposited at different substrate temperatures with ionized oxygen. From the transmission spectra, optical parameters like absorption coefficient (a), refractive index (n) and optical band gap, Eg have been evaluated. The absorption coefficient at shorter wavelengths was determined from the spectrophotometer readings using the relation:

$$(a) = (2{\cdot}303/d) \log_{10} (1–R)/T,$$

where d is the thickness of the film in cm, T and R are the transmittance and reflectance of the film. For a typical evaporated film deposited at a substrate temperature of 200°C, $(a)^2$ vs energy graph is plotted (figure 2a) and by extrapolating the straight line, it is made to cut the energy axis at $a = 0$ and the corresponding optical energy band gap is found to be around 3·68 eV using the Swanepoel (1983) technique. The refractive index of this film was calculated from transmission data and it was found to be around 1·88 at a wavelength of 500 nm (figure 3 (a)). These values are in good agreement with the reported values (Das and Banerjee 1987).

Figures 1 (c)–(d) give the transmission spectra of the spray deposited tin oxide films at a substrate temperature of 300 and 370°C, respectively. It was found that the average transmittance of undoped films is around 85%. Figures 4 (a)–(b) give the plot of $(a)^2$ vs energy for spray deposited films prepared at a substrate temperature of 250°C and 300°C, respectively. The optical band gap was estimated in the lower wavelength region and it was found to be 3·56 eV and 3·62 eV, respectively. Refractive

index was estimated from transmission data and it was found to be around 2·03 at 500 nm (figure 3 (b)) for a typical spray deposited film of thickness 250 nm, deposited at 370°C.

Figures 5 a–c give the transmittance spectra of antimony doped tin oxide films with an average transmittance of about 80%. It was observed from figures 3 (a)–(b) that the refractive index of both the films decreases with the wavelength and then attains almost constant value towards higher wavelengths. The refractive index for spray deposited films is higher compared to the evaporated films.

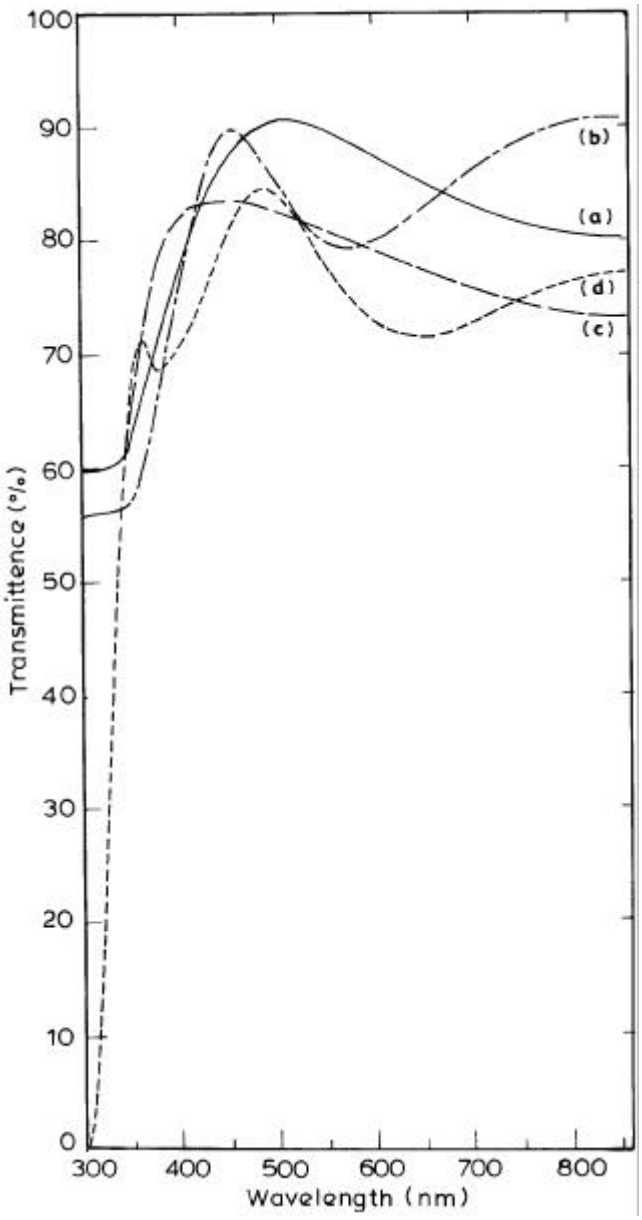

Figure 1. Transmission spectra of undoped, evaporated and spray deposited SnO_2 films. (**a**) Evaporated film deposited at 150°C, (**b**) evaporated film deposited at 200°C, (**c**) spray deposited film prepared at 300°C and (**d**) spray deposited film prepared at 370°C.

This may be mainly due to high substrate temperature in the case of spray deposition. High substrate temperature favours the denser films as well as higher refractive index. In the case of electron beam evaporated films there is a difficulty in increasing the substrate temperature beyond 200°C as it heats up the whole chamber and thereby has a deleterious effect on the vacuum.

3.2 *Structural properties*

Structure of the films was studied by taking X-ray diffraction patterns. XRD data for evaporated films showed that both as-deposited (even at elevated substrate temperature) and air annealed films were amorphous in nature. Scanning electron micrograph also confirms the amor-

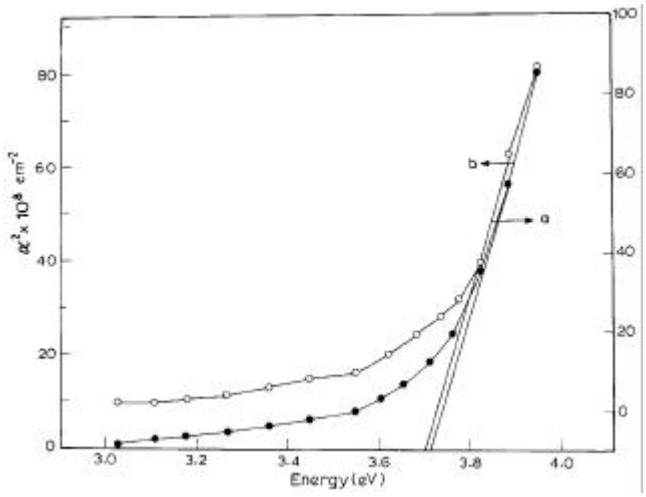

Figure 2. $(a)^2$ vs energy plots for evaporated tin oxide films deposited at **a**. 150°C and **b**. 200°C.

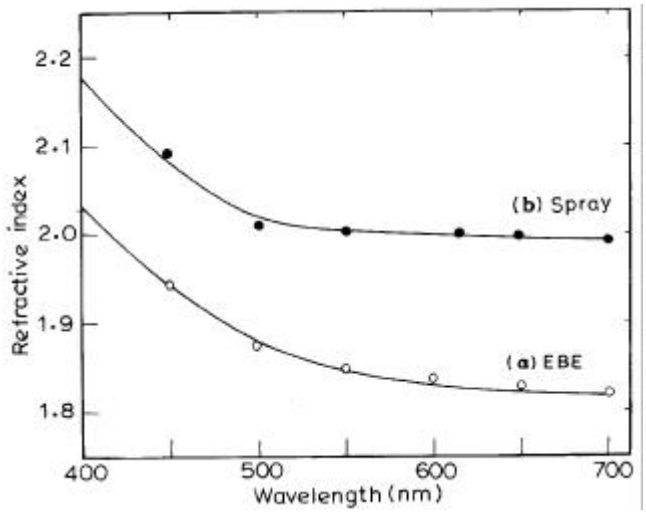

Figure 3. Refractive index vs wavelength of tin oxide films: (**a**) evaporated film deposited at 200°C and (**b**) spray deposited film deposited at 370°C.

phous nature of the film. The films deposited at a substrate temperature of 65°C were annealed in air at different temperatures such as 100, 150, 200 and 250°C for 3 h and XRD patterns were studied. It was found that the films were still amorphous and the resistivity was found to increase. Figure 6 shows the XRD pattern of spray deposited tin oxide films of both undoped (a, b) and antimony doped (c, d) and it was found that the undoped tin oxide films were crystalline in nature with well defined peaks which are characteristic of SnO_2 thin films and the ASTM (*hkl*) (see table 1) values were compared with the reported values (Melsheimer and Tesche 1986). Film deposited at 370°C was more crystalline and more conducting than the film prepared at 250°C. This shows that the conductivity and polycrystalline nature depends directly on the substrate temperature. Figures 7 (a)–(b) show the scanning electron micrographs of the films deposited at 250°C and 370°C, respectively and it is found that the film deposited at 370°C is more crystalline compared to the film deposited at 250°C. Similar results have been observed by Fantini (1986).

In the case of antimony doped films, high intensity peak of (200) is observed at $2q = 37{\cdot}95°$ irrespective of the substrate temperature and percentage of antimony. But there is an extra peak corresponding to (211) plane which was observed for a film doped with ($SbCl_3/SnCl_4 = 0{\cdot}09$) prepared at a substrate temperature of 300°C (figure 6c). When the undoped film deposited at 300°C was annealed in air at 400°C, it was observed that the number of peaks

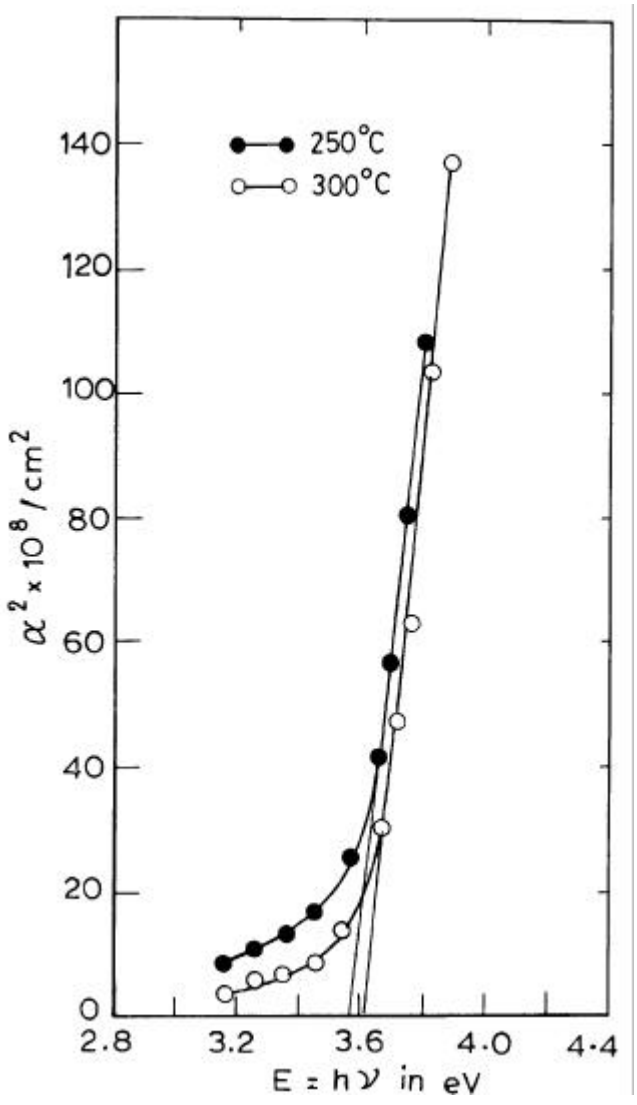

Figure 4. $(a)^2$ vs energy plots for spray deposited films of same thickness: (**a**) film deposited at 250°C and (**b**) film deposited at 300°C.

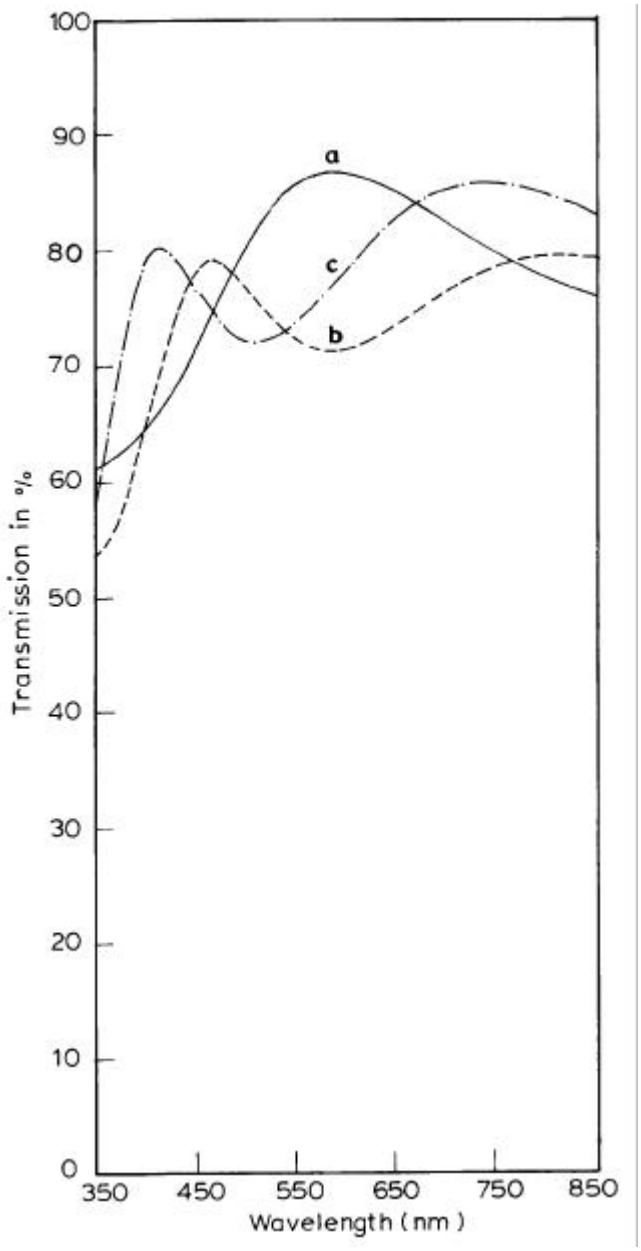

Figure 5. Transmittance spectra of antimony doped tin oxide films: (**a**) film deposited with $SbCl_3/SnCl_4 = 0{\cdot}065$ at T_s = 300°C, (**b**) film deposited with $SbCl_3/SnCl_4 = 0{\cdot}09$ at $T_s = 300°C$ and (**c**) film deposited with $SbCl_3/SnCl_4 = 0{\cdot}065$ at $T_s = 350°C$.

have been increased but at the same time there was a sharp increase in resistance which may be due to further oxidation.

3.3 *Electrical properties*

Electrical parameters like sheet resistance (R_s), resistivity (r), carrier concentration (n) and mobility (m) of tin oxide films were measured at room temperature using Van der Pauw resistivity technique and Hall effect measurement by applying a magnetic field of 3 to 4 K gauss (1 K gauss = 0·1 Tesla). Table 2 shows the electrical properties of evaporated films. Sheet resistance of films prepared at ambient temperature with neutral oxygen was found to be high of the order of 10^5 Ω/□ whereas deposited films with ionized oxygen at T_s ranging from 50–200°C were found to be highly conducting and transparent. It was also observed that the films prepared at higher substrate temperature > 200°C and with higher rate of deposition (2 Å/s) show lower resistance. A typical film deposited at 200°C with a rate of (2 Å/s) has a sheet resistance of 453 Ω/□. Antimony doped (5 wt%) tin oxide films prepared by evaporation method at a substrate temperature of 100°C showed a sharp increase in the sheet resistance and it was found to be around 15 k Ω/□. Whereas the film deposited at higher substrate temperature of 200°C with same percentage of antimony has a low sheet resistance value of 7·5 kΩ/□ which indicates that substrate temperature plays an important role in enhancing electrical properties of the films. It can be seen from the above results that the antimony doped (5 wt%) tin oxide films prepared at 200°C exhibited higher resistance (7·5 kΩ/□) compared to undoped films (453 Ω/□) at the same temperature. Kulaszewicz (1980) has studied the effect of antimony dopant in tin oxide films on the electrical conductivity and achieved the best conductivity when the dopant is in the range of 0·01–0·02 (g Sb) (g Sn)$^{-1}$. Hence it is possible to improve the conductivity of the films by doping an optimum percentage of antimony and the work is in progress.

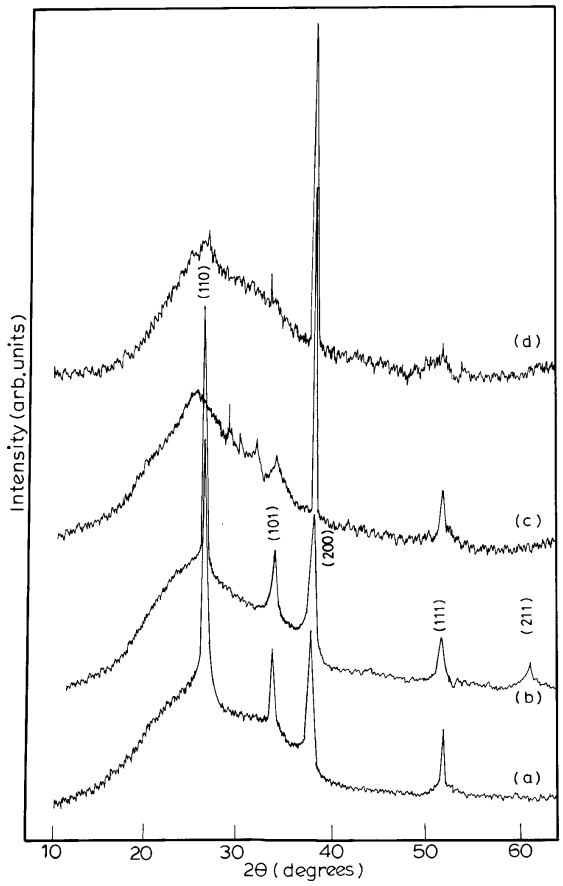

Figure 6. XRD spectra of undoped and antimony doped spray deposited tin oxide films: (**a**) undoped film deposited at 300°C, (**b**) undoped film deposited at 370°C, (**c**) antimony doped film with 0·09 wt% of Sb at 300°C and (**d**) antimony doped film with 0·065 wt% of Sb at 350°C.

In case of spray deposited tin oxide films substrate temperature, solution flow rate and molarity of the solution play an important role in depositing transparent conducting oxide films. It was observed that increase in substrate temperature from 250–370°C has resulted in sharp fall in sheet resistance from 8·16 kΩ/□ to 1·3 kΩ/□. Flow rate of the solution can be controlled by carrier gas pressure to improve conductivity of the films. A typical film deposited at 250°C with a flow rate of 5 ml/min has less sheet resistance than a film deposited with slightly higher flow rate of 6 ml/min. This may be due to the fact that at lower flow rates the spray will get sufficient time to react endothermically at the heated substrate surface to give the final film in the near stoichiometric phase of SnO_2.

When antimony is added to SnO_2, Sb atoms are incorporated into the Sn^{4+} sites of the SnO_2 lattices substitutionally. In antimony doped SnO_2 films, Sb can be present in two different oxidation states, Sb^{5+} and Sb^{3+}. During the initial addition of Sb in the film, the Sb^{5+} substituted on Sn^{4+} sites act as donors and creates excess electrons. Thus the carrier concentration (n) increases and sheet resistance decreases with the addition of Sb up to a certain level. In our work a typical film prepared at 300°C by spraying a solution containing 0·26 g of $SbCl_3$

Table 1. XRD details of spray deposited tin oxide films.

	(*hkl*) values	
d values (Å)	T_s = 300° C	T_s = 370° C
3·360	(110)	(110)
2·642	(101)	(101)
2·373	–	(200)
2·255	(111)	(111)
1·764	(211)	(211)
1·495	–	(310)

with 4 g of $SnCl_4$ ($SbCl_3/SnCl_4 = 0{\cdot}065$) showed a minimum sheet resistance of 66·4 Ω/□. Further addition of Sb, i.e. ($SbCl_3/SnCl_4$) = 0·09, will introduce Sb^{3+} sites, which act as acceptors. The Sb^{3+} species would compensate the donor levels which were created by the Sb^{5+} sites leading to an increase in the sheet resistance to a value of 308 Ω/□. By keeping the same concentration of antimony ($SbCl_3/SnCl_4 = 0{\cdot}065$), it was found that the sheet resistance decreased from 66·4 Ω/□ to 38·7 Ω/□ (resistivity = $7{\cdot}74 \times 10^{-4}$ Ω-cm), when the substrate temperature was increased from 300°C to 350°C. The mobility and carrier concentration of this typical film was found to be 7 cm^2/V-s and $10 \times 10^{20}/cm^3$, respectively.

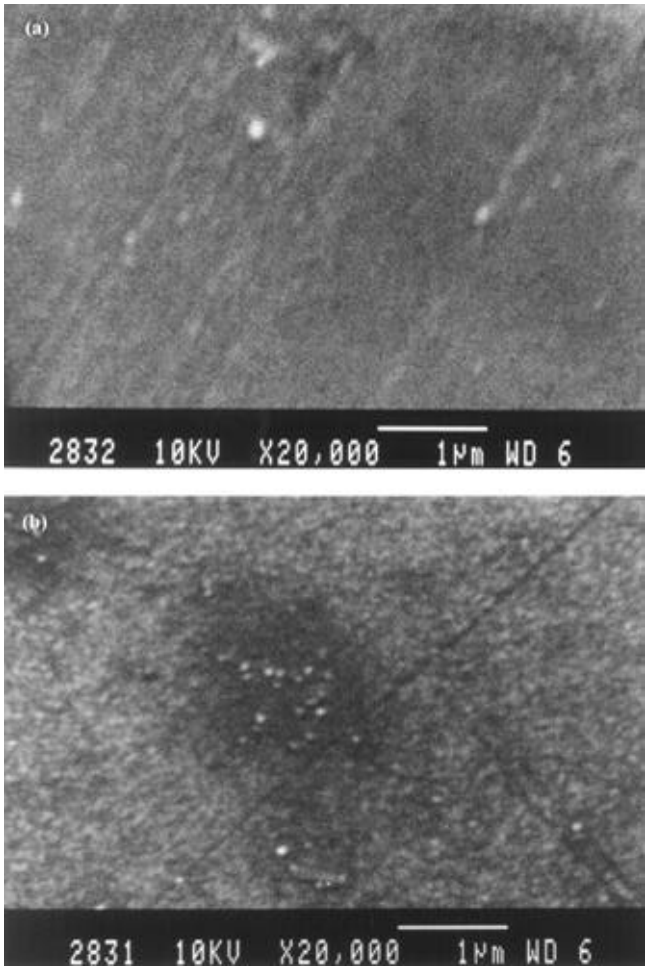

Figure 7. SEM photographs of spray deposited film at a substrate temperature of (**a**) 250°C and (**b**) 370°C.

Table 3 gives the details of the electrical properties of the spray deposited films of both undoped and antimony doped tin oxide films under various preparation conditions. The resistivity of undoped tin oxide film prepared at 300°C with 0·1 M solution of $SnCl_4$ is more than that of the film prepared at the same temperature but with 0·2 M solution. It was also found from the XRD that the crystallinity is more pronounced in case of the film prepared at higher substrate temperature (370°C) as shown in figure 6 (b).

4. Conclusions

Transparent and conducting tin oxide films were prepared by electron beam evaporation and spray pyrolysis methods. Optical, structural and electrical properties of these films were studied as a function of substrate temperature, deposition rate, molarity of the solution and doping percentage of antimony. The optical band gap of evaporated film was in the range 3·70–3·71 eV and that of spray deposited films was in the range 3·56–3·62 eV. Refractive indices were 1·88 and 2·03 at a wavelength of 500 nm for evaporated and spray deposited films, respectively. Resistivities of undoped evaporated tin oxide films were less than that of the spray deposited films. Antimony doped spray deposited films show a sharp decrease in the resistivity. The optimum doping concentration of antimony in tin oxide films was found to be ($SbCl_3/SnCl_4$) = 0·065 which gives the lowest resistivity of $7{\cdot}74 \times 10^{-4}$ Ω-cm

Table 2. Electrical properties of evaporated tin oxide films.

Method of preparation	Rate (Å/s)	Thickness (nm)	R_s (Ω/□)	r (Ω-cm)	N (cm^3)	m (cm^2/V·s)	T_s
Electron beam evaporation	3·0	100	200 K	2	–	–	100°C
	1·0	140	1·9 K	$2{\cdot}67 \times 10^{-2}$	$4{\cdot}46 \times 10^{18}$	5·21	150°C
	3·0	150	1·63 K	$2{\cdot}44 \times 10^{-2}$	$4{\cdot}47 \times 10^{19}$	5·73	150°C
	1·5	150	453	$7{\cdot}3 \times 10^{-3}$	$1{\cdot}46 \times 10^{20}$	6·30	200°C
5 wt% antimony	2·0	250	15 K	$3{\cdot}75 \times 10^{-1}$	$7{\cdot}6 \times 10^{18}$	2·00	Sn : Sb 100°C
	1·5	250	7·5 K	$1{\cdot}8 \times 10^{-1}$	$3{\cdot}4 \times 10^{18}$	10·20	Sn : Sb 200°C

Table 3. Electrical properties of undoped and antimony doped spray deposited tin oxide films.

Method of preparation	Flow rate (ml/min)	Thickness (nm)	R_s (Ω/□)	r (Ω-cm)	N (cm^3)	m (cm^2/Vs)	T_s
	6 (0·2 M)	150	15·48	$2{\cdot}3 \times 10^{-1}$	–	–	250°C
	5 (0·2 M)	150	8·16 k	$1{\cdot}22 \times 10^{-1}$	$1{\cdot}2 \times 10^{19}$	4·1	250°C
	5 (0·2 M)	135	2·03 k	$2{\cdot}7 \times 10^{-2}$	$1{\cdot}44 \times 10^{20}$	2·9	300°C
	5 (0·2 M)	130	1·30 k	$1{\cdot}69 \times 10^{-2}$	$1{\cdot}2 \times 10^{20}$	3·0	370°C
	5 (0·1 M)	252	1·85 k	$4{\cdot}66 \times 10^{-2}$	$1{\cdot}1 \times 10^{19}$	11·9	370°C
	5	230	1·30 k	3×10^{-2}	–	–	300°C 0·1 g $SbCl_3$
Spray pyrolysis	5	93	308	$2{\cdot}86 \times 10^{-3}$	1×10^{21}	2·04	300°C 0·36 g $SbCl_3$
	5	280	294	$8{\cdot}2 \times 10^{-3}$	5×10^{20}	1·7	300°C 0·36 g $SbCl_3$
	5	297	144·3	$4{\cdot}28 \times 10^{-3}$	$6{\cdot}6 \times 10^{20}$	2·2	300°C 0·36 g $SbCl_3$
	5	201	66·4	$1{\cdot}3 \times 10^{-3}$	5×10^{20}	9·8	300°C 0·26 g $SbCl_3$
	5	200	38·7	$7{\cdot}74 \times 10^{-4}$	10×10^{20}	7·0	350°C 0·26 g $SbCl_3$
	5	400	4·3 k	3×10^{-2}	–	–	300°C 0·06 g $SbCl_3$

at a substrate temperature of 350°C. It was found that the conductivity of the films directly depends on the substrate temperature and structure of the films.

References

Ansari S G, Gosavi S W, Gangal S A, Karekar R N and Aiyer R C 1997 *J. Mater. Sci. Mater. Electron.* **8** 23

Bernarti M I B, Soledade L E, Santos E R, Leite I A, Longo E and Valela J A 2002 *Thin Solid Films* **405** 228

Brinzari V, Korotcenkov G and Golovanov V 2001 *Thin Solid Films* **391** 167

Colen S 1981 *Thin Solid Films* **77** 127

Das Debajyoti and Banerjee Ratnabali 1987 *Thin Solid Films* **147** 321

Fantini M 1986 *J. Cryst. Growth* **74** 439

Frank G, Kaur E and Kostlin H 1983 *Solar Energy Matter* **8** 387

Goetzberger A and Hebling C 2000 *Sol. Energy Mater. and Solar Cells* **62** 1

Jarzebski Z M 1982 *Phys. Status Solidi* **(a)71** 13

Jagadish C, Dawar A L, Sangay Sharma, Shishodia P K, Tripathi K N and Mathur P C 1988 *Mater. Lett.* **6** 149

Kulaszewicz S 1980 *Thin Solid Films* **74** 211

Kulaszewicz S, Lasocka I and Michalski C Z 1983 *Thin Solid Films* **55** 283

Lousa A, Gimeno S and Marti J 1994 *Vacuum* **45** 1143

Lou J C, Lin M S, Chyi J I and Shieh J H 1983 *Thin Solid Films* **106** 163

Melsheimer J and Tesche B 1986 *Thin Solid Films* **138** 71

Minami Tadatsugu, Hidehito, Hidechito Nanto and Takata Shinzo 1988 *Jap. J. Appl. Phys.* **27** L-28

Nomura K, Ujihira Y and Sharma S S 1989 *J. Mater. Sci.* **24** 937

Rao K S R K and Murthy L C S 1999 *Bull. Mater. Sci.* **22** 953

Schroder Dieterk 1990 *Superconducting material and device characterization* (New York: John Wiley and Sons Inc)

Shanthi E, Banerjee A, Dutta V and Chopra K L 1980 *Thin Solid Films* **71** 237

Swanepoel R 1983 *J. Phys.* **E16** 1214

Thangaraju B 2002 *Thin Solid Films* **402** 71

Van Heerden J L and Swanepoel R 1997 *Thin Solid Films* **299** 72