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EFFECT OF SUBSTRATE TEMPERATURE ON ELECTRICAL AND OPTICAL PROPERTIES OF SPRAY DEPOSITED SnO_2:Sb THIN FILMS

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Thin films of ~ 1.2 µm thick antimony doped tin oxide (SnO_2:Sb) have been prepared using an economic spray pyrolysis technique from $SnCl_2$ precursor at two different substrate temperatures (T_s), namely 350 °C and 400 °C. The effect of substrate temperature on the electrical and optical properties is studied and presented in this article. A minimum sheet resistance of 2.17 Ω/□ was obtained for the film prepared at 400 °C. This minimum sheet resistance observed in the present study is the lowest among the reported values for SnO_2:Sb films prepared from $SnCl_2$ precursor. Irrespective of the substrate temperature, the transmittance was found to decrease with the increase in Sb doping concentration. The highest optical transmittance obtained for the films prepared at lower T_s (350 °C) is found to decrease from 63 % to a value of 54 % (at 800 nm) for the films prepared at higher T_s (400 °C). The calculated IR reflectivity was found to be in the range of 93 -97 % and 94 - 98 % for the films prepared with lower and higher substrate temperatures, respectively. The estimated high IR reflectance of these films suggests that the films are useful in flat plate collectors and in different electrode processes.

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Keywords: Spray pyrolysis, Tin oxide thin films, $SnCl_2$ precursor, Antimony doping

1. Introduction

Economical and stable transparent conductive SnO_2 films are of considerable interest, due to their application in solar cells, optoelectronic devices, thin film resistors, antireflection coatings, photochemical devices and electrically conductive glass [1]. An attempt has been made in the present study to prepare SnO_2 films by employing economic spray pyrolysis technique. It has been reported already that the spray pyrolysis technique is most suitable for obtaining tin oxide films in large-area substrate applications [2-4]. Tin oxide films doped with antimony have interesting electrochemical properties in different electrode processes, such as low temperature electrochemical combustion of organic pollutants, ozone production, and organic electro-synthesis [5,6]. Hence in the present study, the antimony doped SnO_2 films were prepared by spray pyrolysis technique and their electrical and optical properties are explored.

2. Experimental details

Thin films of antimony doped tin oxide thin films (SnO_2:Sb) were prepared by homemade spray pyrolysis setup from $SnCl_2$ precursor. The details on the experimental setup can be found elsewhere [7]. The films were prepared at two different substrate temperatures of 350 °C and 400 °C. The substrate temperature (T_s) of 400 °C was optimized as the best suitable temperature for the preparation SnO_2:F thin films from our previous study [7]. The same temperature was applied for the preparation of SnO_2:Sb thin films in the present study. For comparison the films were also prepared at

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substrate temperature of 350 °C. For both temperatures the Sb doping was varied from 0.5 to 4.0 wt. %. An economic stannous chloride ($SnCl_2 \cdot 2H_2O$) was used as the source of tin whereas antimony III chloride ($SbCl_3$) for Sb doping. 11g of $SnCl_2 \cdot 2H_2O$ was dissolved in 5 ml of concentrated hydrochloric acid by heating at 90 °C for 10 minutes. The solution subsequently diluted with methanol formed the starting solution. For Sb doping $SbCl_3$ dissolved in isopropyl alcohol was added to the starting solution on requirement of doping concentration. In each case, the spray solution prepared was 50 ml and the predetermined amount of solution was sprayed so as to achieve approximate uniformity in the film thickness. The films are highly reproducible which was confirmed from the repeated experiments of each concentration.

The as-deposited films were characterized for their physical properties and the electrical and optical properties are compared in this paper. The electrical studies were made by the combination of Hall coefficient and van der Pauw resistivity measurements. The negative sign of the Hall voltage confirmed that the films are n-type conducting. The temperature dependence of resistivity measurements showed that the films are degenerate. Further the film degeneracy was confirmed by evaluating Fermi energy. The optical studies were made with the use of Hitachi U-3400 UV-VIS-NIR spectrophotometer by recording transmittance and reflectance spectra.

3. Results and discussion

3.1. Electrical properties

The film thickness has been estimated from the cross-sectional SEM studies and found to be ~ 1.2 μm. The values of sheet resistance (R_{sh}) and resistivity (ρ) are shown as a function of Sb doping concentration in Fig. 1a & 1b respectively for the films prepared at both temperatures. Irrespective of the substrate temperature both the sheet resistance and resistivity of the deposited films were found to decrease with increasing Sb doping concentration to reach a minimum value at a certain level of doping but then increased with the further increase in Sb doping. The corresponding valley of R_{sh} and ρ has been occurred at 2 wt. % of Sb doping for both the temperatures. The effect of substrate temperature was found to vary only on the values of the R_{sh} and ρ and not the trend they follow.

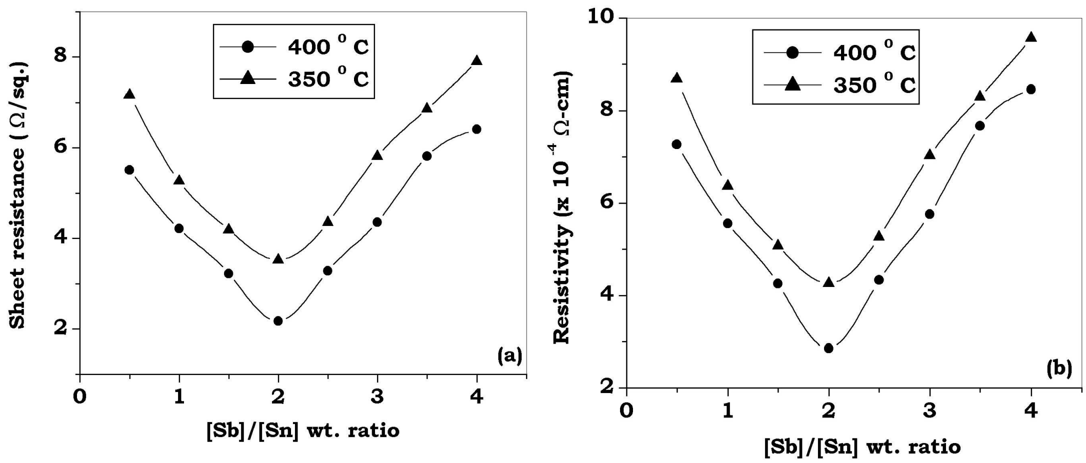

Fig. 1. Variation of sheet resistance (a) and resistivity (b) of SnO_2:Sb thin films as a function of Sb doping concentration prepared at different temperatures.

The minimum R_{sh} and ρ values obtained for the films prepared at 400 °C were found to be lower than those obtained at 350 °C. The minimum R_{sh} values of 2.17 Ω/□ and 3.52 Ω/□ & ρ values of 2.86 Ω-cm and 4.65 Ω-cm were obtained for the films prepared at higher and lower T_s respectively. The sheet resistance value of 2.17 Ω/□ is the lowest among the reported values for these materials prepared from $SnCl_2$ precursor. The comparison of sheet resistance with the prior reports has been made in our earlier report [8]. From this study, it can be stated that 400 °C is the best suitable temperature for achieving better electrical properties.

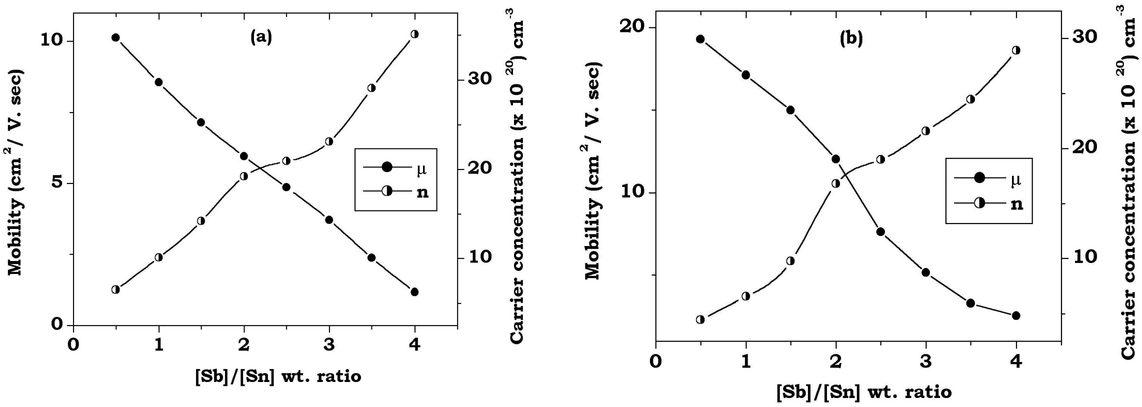

Fig. 2. Variation of Hall mobility and carrier concentration of SnO_2:Sb films with antimony doping (a: T_s = 350 °C; b: T_s = 400 °C).

The negative sign of Hall voltage confirmed that the films are n-type conducting. The variation of Hall mobility and carrier concentration of SnO_2:Sb thin films is shown for the films prepared at different temperatures in Fig. 2a & 2b respectively. It is apparent from the figure that irrespective of T_s the mobility of the films shows a consistent decrease and the carrier concentration shows a consistent increase with increase in Sb doping concentration. For a given Sb doping concentration, the mobility of the films obtained at lower T_s is lower than those prepared with higher T_s, whereas the carrier concentration obtained for the films prepared at lower T_s show slightly higher value than those prepared at higher T_s. For example, the mobility of 10.13 cm^2/V. sec obtained for the films doped with 0.5 wt. % of Sb at lower T_s has been increased to a value of 19.28 cm^2/V. sec for those prepared at higher T_s. The carrier concentration of 6.5×10^{20} cm^{-3} obtained for the films doped with 0.5 % Sb at lower T_s has been decreased to a value of 4.5×10^{20} cm^{-3} for those prepared at higher T_s.

The temperature dependence of sheet resistance in the range 30-200 °C indicated that the antimony doped films are degenerate semiconductors. The film degeneracy was further confirmed by evaluating its Fermi energy (E_F). The mean value of 0.27 m_e is used as effective mass for the calculations. The calculated E_F values (~ 1.5 eV) are very high compared to room temperature *kT*. Further, the E_F values are proportional to $n^{2/3}$ that is the characteristic for degeneracy of materials.

3.2. Optical properties

The obtained transmittance and reflectance spectra from the optical studies are shown in Figs. 3 & 4 respectively. It was found that the transmittance decreased with increasing Sb doping concentration irrespective of the deposition temperature. Further it was found that for a given doping concentration the transmittance shows higher value for the films deposited at low temperature (350 °C). For example, the transmittance value of 63 % observed for the film with 0.5 wt. % of Sb prepared at 350 °C was found decreased to a value of 54 % (at 800 nm) for the film prepared with the same doping concentration at 400 °C. This is in contradiction to the electrical behaviour where the higher deposition temperature (400 °C) leads to better electrical properties.

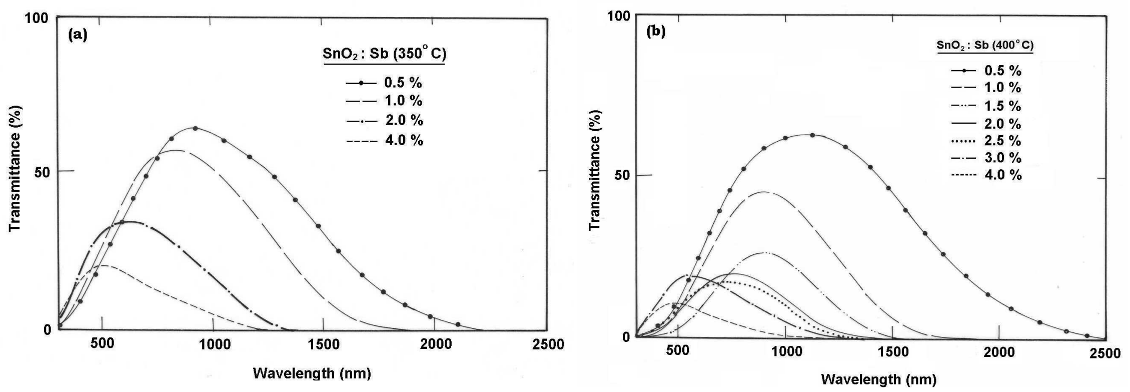

Fig. 3. Transmittance spectra as a function of wavelength for SnO_2:Sb thin films prepared at T_s of (a) 350 °C and (b) 400 °C respectively.

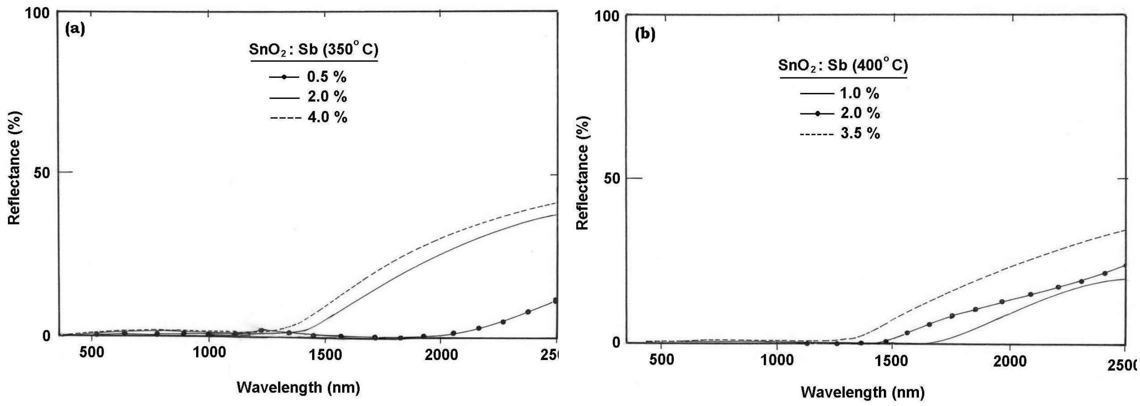

Fig. 4. Reflectance spectra as a function of wavelength for SnO_2:Sb thin films prepared at T_s of (a) 350 °C and (b) 400 °C respectively.

From the plot of reflectance spectra, it is under stood that the reflectance of all the films is almost zero till the wavelength of around 1500 nm for both substrate temperature. For the film prepared with 0.5 wt. % of Sb at 350 °C, the reflection starts only after 2000 nm. For both substrate temperatures, the films show increase in reflectance (above 1500 nm) with the increase in Sb doping. The films prepared at lower substrate temperature have slightly higher reflectance values than those prepared at higher substrate temperature above the wavelength of ~1500 nm.

The transmittance for the selected wavelengths of 600, 700, 800, and 900 nm are plotted against the function of Sb doping in Fig. 5 for the films prepared at lower and higher substrate temperatures respectively. It is clear from the figure that for the films prepared at lower temperatures the transmittance value at each selected wavelength decreases with increasing Sb doping concentration. It was understood that as the doping increases, the rate of decrease of transmittance of the higher wavelengths (800 and 900 nm) is higher than that of lower wavelengths (600 and 700 nm). As a consequence, the transmittance that showed increment with increasing wavelength at lower doping levels (< 2 wt. %) found to show decrement in transmittance with increasing wavelength at higher doping levels (> 2 wt. %). For the films prepared with higher substrate temperature, as the doping concentration increase, the transmittance shows a consistent decrement for the higher wavelengths. Whereas the transmittance for the lower wavelengths shows a decrement till the Sb doping of 1.5 wt. % but then shows a slight increase.

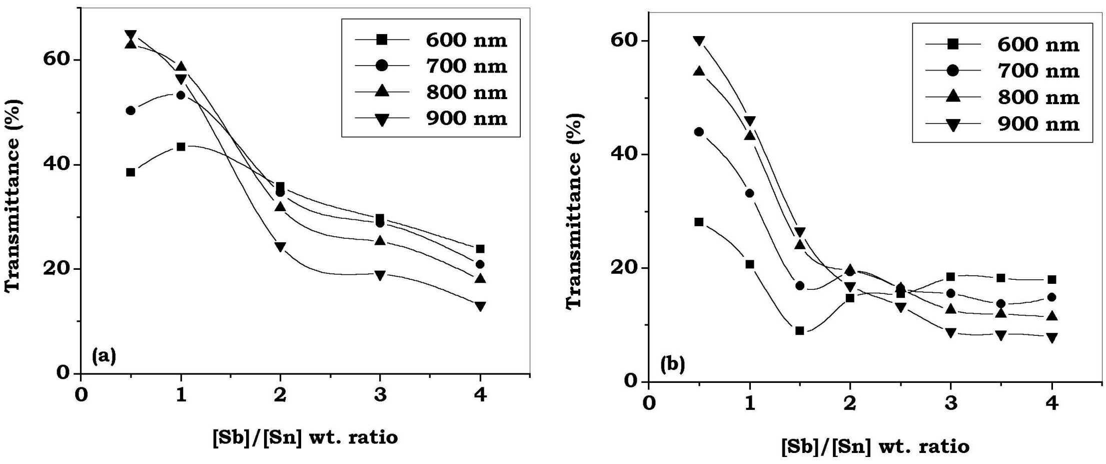

Fig. 5. Transmittance spectra of selected wavelengths for SnO_2:Sb thin films prepared at T_s of (a) 350 °C and (b) 400 °C, respectively.

The IR reflectivity of the films was calculated using the relation [9]

$$R = (1 + 2\varepsilon_0 c_0 R_{sh})^{-2} \tag{1}$$

with ε_0 c_0 = 1/376 Ω^{-1}. This is equation is valid over a wide range in the IR region. The calculated IR reflectivity was found to be in the range of 93-97 % and 94-98 % for the films prepared with lower and higher substrate temperature. Since the above equation is inversely proportion to sheet resistance, it is expected that the films prepared with higher substrate temperature to have higher IR reflectance because of their low sheet resistance. The estimated high IR reflectance of these films suggests that the films are useful in flat plate collectors and in different electrode processes.

4. Conclusions

Thin films of antimony doped tin oxide thin films were prepared by spray pyrolysis technique from $SnCl_2$ precursor at two different substrate temperatures. The films prepared at higher substrate temperature showed minimum sheet resistance. The minimum sheet resistance achieved in the present study is the lowest among the reported values for these materials prepared from $SnCl_2$ precursor. Irrespective of the substrate temperature, the transmittance of the films decreases continuously with increase in Sb doping concentration. The films prepared at lower substrate temperature showed the maximum transmittance. The estimated IR reflectance suggests that these films can be useful in flat plate collectors and in different electrode processes.

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References

[1] H. H. Afify, F. S. Terra, R. S. Momtaz, J. Mater. Sci.: Materials in Electronics **7**, 149 (1996).
[2] B. Thangaraju, Thin Solid Films **402**, 71 (2002).
[3] A. Malik, A. Seco, E. Fortunato, R. Martins, J. Non Cryst. Solids **227-230**, 1092 (1998).
[4] J. Bruneaux, H. Cachet, M. Froment, A. Messad, Thin Solid Films **197**, 129 (1991).
[5] B. C. Lozano, Ch. Comninellis, A. De Battisti, J. Electrochem. Soc. **143**, 203 (1996).
[6] S. Stucki, R. Kotz, W. Suter, B. Carcer, J. Appl. Electrochem. **21**, 99 (1991).
[7] E. Elangovan, K. Ramamurthi, J. Optoelectron. Adv. Mater. **5**, 45 (2003).
[8] E. Elangovan, K. Ramamurthi, Submitted in revised form to Cryst. Res. Technol., (2003)
[9] G. Frank, E. Kauer, H. Kostlin, Thin Solid Films **77**, 107 (1981).