

STRUCTURAL PROPERTIES OF $\text{SnO}_2:\text{F}$ FILMS DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE*

CHITRA AGASHE, B. R. MARATHE, M. G. TAKWALE AND V. G. BHIDE

School of Energy Studies, University of Poona, Pune 411007 (India)

Thin films of SnO_2 and $\text{SnO}_2:\text{F}$ were deposited by a spray pyrolysis technique. The effect of substrate temperature on the structural and electrical transport properties of these films was investigated.

The standard deviation of these films from ASTM data explains the growth mechanism with other process parameters at optimum values.

1. INTRODUCTION

Transparent conductive coatings are good optical filters and also have good electrical conductivity. Hence they are used in thin film solar cells as a window material and as an electrode to collect the charge. Several materials, especially metal oxides and also their composites, have been investigated from this aspect by various researchers¹. Amongst these oxides, tin oxide (SnO_2) is known as the most chemically stable in atmospheric ambients and so was selected for development as a transparent conductive coating for $\text{CdS}/\text{Cu}_2\text{S}$ and amorphous silicon solar cells. The deposition technique used was spray pyrolysis which is very sensitive to the process parameters. The undoped and fluorine-doped tin oxide films were deposited at different substrate temperatures and the structural and electrical transport properties were investigated at room temperature and an attempt has been made to correlate them.

2. EXPERIMENTAL DETAILS

Various process parameters affecting the film properties have been optimized as given in our previous paper². The results reported are concerned with undoped and fluorine-doped tin oxide films of thickness about $0.165\text{ }\mu\text{m}$ deposited with optimum deposition conditions. The substrate temperature was varied from 375 to $500\text{ }^\circ\text{C}$ ($\pm 5\text{ }^\circ\text{C}$). These films were characterized for electrical properties by sheet resistance measurements and Seebeck measurements. The structural properties were investigated by an X-ray diffraction technique using both $\text{Fe K}\alpha$ ($\lambda = 1.937\text{ }\text{\AA}$)

* Paper presented at the 7th International Conference on Thin Films, New Delhi, India, December 7–11, 1987.

and Cu K α ($\lambda = 1.542 \text{ \AA}$) radiations with a Philips PW 1840 diffractometer. Other conditions were kept constant while the diffractograms were taken.

The texture coefficient of the films defined by Barret and Massalski³ was used to describe the preferred orientation. The texture coefficient $TC(hkl)$ is given by

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \bigg/ \frac{1}{N} \sum_N \frac{I(hkl)}{I_0(hkl)} \quad (1)$$

where $TC(hkl)$ is the texture coefficient of the (hkl) plane, I_{hkl} is the measured intensity, I_{0hkl} is the intensity of the corresponding plane when the sample is in the form of a powder (these intensities were taken from the ASTM data file⁴) and N is the reflection number.

Also, to explain the growth mechanism the standard deviation σ from the powder diffraction condition was calculated by using the following expression⁵:

$$\sigma = \left\{ \frac{\sum I_{hkl}^2 - (\sum I_{hkl})^2 / N}{N} \right\}^{1/2} \quad (2)$$

where I denotes the relative intensity of the (hkl) plane.

3. RESULTS AND DISCUSSION

In the case of thin films, the substrate temperature governs the film properties through structural and stoichiometric changes. As a result of this the sheet resistance of these films varies as shown in Fig. 1. The doping with fluorine has substantially decreased the sheet resistance.

With reference to Figs. 2–4, the variation in charge carrier concentration n , mobility μ and specific conductivity σ_s could be explained for undoped and doped SnO_2 films as follows. In the case of undoped SnO_2 the electrical properties of the

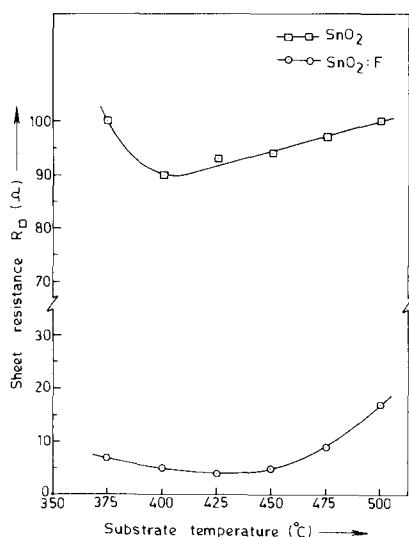


Fig. 1. Variation in sheet resistance with substrate temperature.

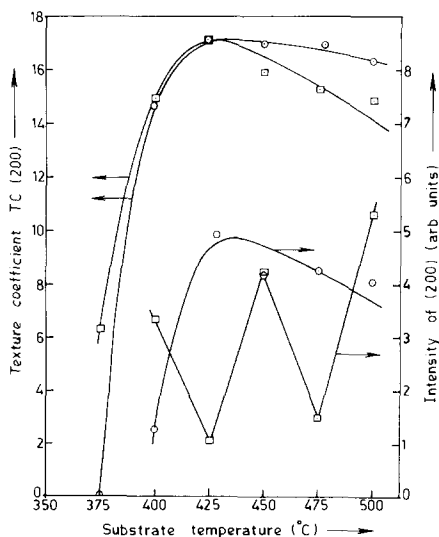
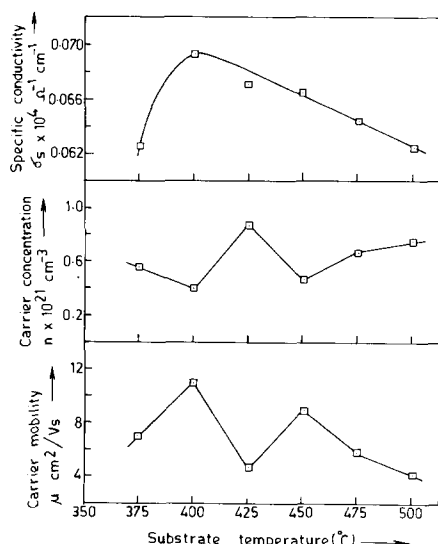
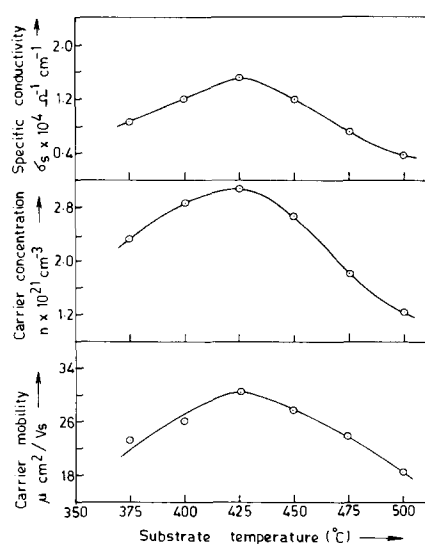


Fig. 2. Variation in texture coefficient $TC(200)$ and intensity of the (200) reflection with substrate temperature.

Fig. 3. Variation in electrical transport parameters with substrate temperature for SnO_2 films.Fig. 4. Variation in electrical transport parameters with substrate temperature for $\text{SnO}_2\text{:F}$ films.

films would depend on the quality of the film, stoichiometry and structural properties.

At lower temperatures than the optimum (425°C) the quality of the film would be poor, the film would be less stoichiometric and the structural properties would also be poor. This would result in lower values of n , μ and σ_s at lower temperatures.

At higher temperatures than the optimum the quality appears to change little, the stoichiometry improves and the structural properties deteriorate slightly. This results in lower n , lower μ and consequently lower σ_s . The mobility seems to have a dependence on the extent of orientation and the texture coefficient of the film.

The results are similar for fluorine-doped films. In addition, one would expect a reduction in μ due to the increase in n . However, the observed increase in μ is due to an improvement in the structure (Fig. 2) and an improvement of about 27% in the grain size (estimated from X-ray data).

The growth mechanism of SnO_2 films is clear from the standard deviation σ which compares the results with ASTM data (Fig. 5). The value of σ decreases as the substrate temperature is increased from 375 to 425°C and then saturates at higher substrate temperatures.

The higher σ value at lower temperature is evidence of the adsorption-desorption phenomenon⁶ (preferential SnO growth) whereas the saturation of σ values at higher temperature is a consequence of homogeneous nucleation and a diffusion-controlled process (preferential SnO_2 growth).

To summarize, the films were preferentially oriented along $[101]$ at 375°C and along $[200]$ for higher temperatures irrespective of doping. Doping improved the intensity as well as the texture coefficient of the (200) plane. However, the effect of temperature was much more pronounced than that of doping. Other phases of tin oxide were not observed in the X-ray diffraction pattern, these results being similar to those of Sundaram and Bhagavat⁷ and Maudes and Rodriguez⁸. Other planes such as (110) , (101) , (310) , (301) and (211) were also observed, with variation in their

intensities. The relative intensities of the planes were different from the corresponding ASTM intensities, probably as a result of the different effective thickness of the samples while investigating the powder samples and thin films. The less densely populated (200) plane is observed to be preferentially oriented in most of the cases, probably because of its lower surface energy of interaction.

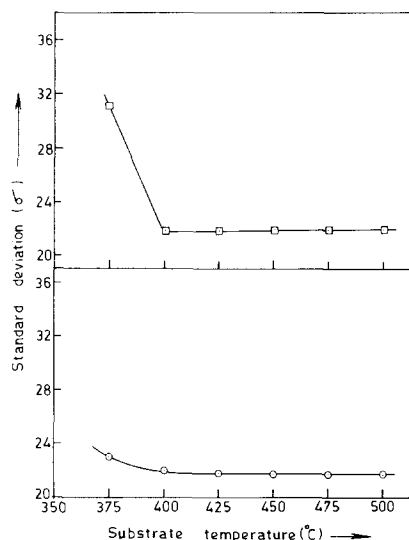


Fig. 5. Variation in standard deviation with substrate temperature; —□—□— SnO₂, —○—○— SnO₂:F.

ACKNOWLEDGMENT

This work was supported by the Council of Scientific and Industrial Research, New Delhi, India.

REFERENCES

- 1 K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films*, 102 (1983) 1.
- 2 C. Agashe, M. G. Takwale, B. R. Marathe and V. G. Bhide, *Sol. Energy Mater.*, 17 (1988) 99.
- 3 C. Barret and T. B. Massalski, *Structure of Metals*, Pergamon, Oxford, 1980, p. 204.
- 4 Joint Committee on Powder Diffraction Standards, *ASTM Powder Diffraction File*, Card No. 5-0467.
- 5 J. R. Holland, in E. F. Kaelble (ed.), *Handbook of X-rays*, McGraw-Hill, New York, 1967, pp. 18–38.
- 6 J. P. Hirth and K. L. Moazed, in G. Hass and R. E. Thun (eds.), *Physics of Thin Films*, Vol. 4, Academic Press, New York, 1967, Chap. 2, p. 98.
- 7 K. B. Sundaram and G. K. Bhagavat, *Thin Solid Films*, 78 (1981) 35.
- 8 J. S. Maudes and T. Rodriguez, *Thin Solid Films*, 69 (1980) 183.