



## TRANSPARENT AND CONDUCTING TIN OXIDE THIN FILMS DEPOSITED BY SPRAY PYROLYSIS

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### ABSTRACT

*The chemical spray pyrolysis technique has been one of the major techniques to deposit a wide variety of materials in thin film form, for different applications. The most important control parameters for obtaining good quality thin film are the nature and temperature of the substrate, the composition of the precursor solution, the gas and solution flow rates and the deposition time.*

*The paper presents the morphology, the electrical and optical properties of tin oxide (SnO<sub>2</sub>) thin films deposited by spray pyrolysis technique onto glass substrates at 400<sup>o</sup>C using SnCl<sub>2</sub> as precursor and methanol as solvent. The change in the grain shapes and orientation is presented based on SEM data. The minimum sheet resistance of 21.4 Ω/sq was obtained, being the lowest value reported in the literature for these materials. Optical transmittance in the range of 58-85 % has been obtained for the prepared films.*

Keywords: spray pyrolysis, tin oxide thin films, transparent conductive oxide

### 1. Introduction

Thin films of tin oxide (SnO<sub>2</sub>) that belong to the category of transparent and conducting oxides have been successfully used in various applications such as optical windows in solar cells [1], flat panel displays (FPD), low-emissivity (low-e) windows, electromagnetic shielding of CRTs in video display terminals, as electro-chromic (EC) materials in rear-view mirrors of automobiles, EC-windows for privacy (smart windows), oven windows, touch-sensitive control panels [2], light emitting diodes (LEDs) [3], and electrochromic displays (ECDs) [4], due to their outstanding properties. The versatility of SnO<sub>2</sub> thin films in the before mentioned various applications motivated us to deposit these films by the economical spray pyrolysis deposition technique.

### 2. Experimental details

#### 2.1. Thin films preparation

An economic stannous chloride (SnCl<sub>2</sub>) was used as precursor of tin oxide films. The amount of tin precursor was varied for achieving films with different thickness. Microscopic glass slides were used as substrates. The substrates were cleaned using

distilled water and organic solvents such as acetone and isopropyl alcohol. Cleanliness of the substrate plays a vital role in deciding the quality of the deposited film. In the present work, the following substrate cleaning procedure was adopted. The microscopic glass slide substrates were cleaned initially with soap (to remove greasy material) and then with distilled water. The substrates were then kept in acetone and finally washed with isopropyl alcohol to remove any traces of dust particles or other contaminants.

The substrate was placed in contact with a hot plate and its temperature (T<sub>s</sub>) was monitored by a temperature controller using a standard thermocouple system. The substrates were pre-heated to the required temperature. After deposition, the coated substrates were kept in the spray chamber itself and allowed to cool down naturally at room temperature.

The tin precursor (SnCl<sub>2</sub>) was dissolved in hydrochloric acid and methanol to form the starting solution. The repeated experiments of each deposition showed that the films could be reproduced easily. An extensive care was taken in giving sufficient spray interval between successive sprays for the substrates to get back to deposition temperature after undergoing thermal decomposition. The substrate temperature (T<sub>s</sub>) was between 350-400<sup>o</sup>C. For each concentration

of the precursor solution, several sets of films were prepared and found to be reproducible.

## 2.2 Thin films characterization

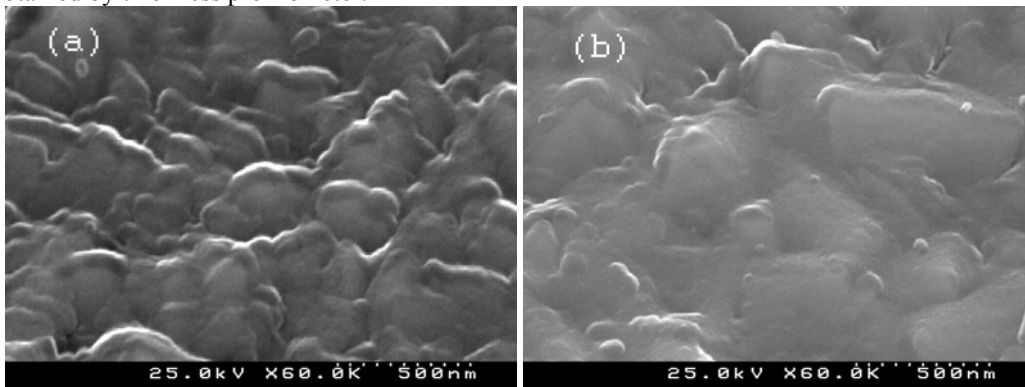
The thickness of the films was measured using a surface profilometer (Dektak<sup>3</sup>), with an accuracy of  $\pm 20$  nm. Optical transmittance was measured using a double-beam spectrophotometer (Shimadzu UV-3100) with a bare substrate in the reference path of the beam. The surface morphology was analyzed using Scanning Electron Microscopy (Hitachi, SU-70).

The electrical parameters were estimated using a Hall measurements setup (Bio Rad HC5500 Hall system) with a permanent magnet of 5 KG in van der Pauw configuration).

## 3. Results and Discussion

### 3.1 Thin films thickness and morphology

The initial estimation of film thickness was obtained through the conventional weight-gain (gravimetric) method. This method is earlier applied to calculate the thickness of the films deposited by spray pyrolysis technique [5-8]. The standard density value of tin oxide ( $6.99 \text{ g/cm}^3$ ) was used for the calculations [9]. This preliminary estimation of thickness was found in good agreement with the values obtained by thickness profilometer.



**Fig.1.** SEM morphology on the surface of the films deposited on glass substrate using precursor solution of 0.3 mol/l (a) and 0.75 mol/l (b).

### 3.2 Electrical properties

The electrical measurements were carried out using Hall measurement in van der Pauw configuration.

The negative sign of Hall coefficient confirmed that the films are n-type conducting.

A maximum sheet resistance ( $R_{sh}$ ) of  $\sim 486 \Omega/\text{sqr}$  was obtained for the films with a thickness of 144 nm. The  $R_{sh}$  is found to decrease with the increase in the thickness of the film until  $\sim 23 \Omega/\text{sqr}$  for the films of 850 nm thick.

It is known that the step required by the thickness profilometer measurement cannot be made on the spray deposited samples during film deposition, due to diffusion effect below the mask. Hence, the step was formed after deposition by selective etching on different place of sample surface. The solution used for the etching is ETCH-Cr (A). With the step formed by this etching procedure, the film thickness was estimated at 4 corners of the sample with dimension of  $50 \text{ mm} \times 50 \text{ mm}$ .

The estimated values suggested that the film is uniform through the entire substrate area.

Average value is taken for the calculations such as resistivity and absorption coefficient. The films thickness ranges from about 144 nm to about 850 nm, depending on the concentration of the  $\text{SnCl}_2$  precursor solution. It increased with the increasing amount of precursor to reach a maximum of  $\sim 850 \text{ nm}$ . The Fig. 1 shows the SEM images on the films surface.

This data indicates that the grain growth follows the increase in the concentration of the precursor solution.

The grains seem to be agglomerated together to appear as big as  $\sim 350 \text{ nm}$  in size (Fig 1a). Apart from this agglomeration, grains with size as small as  $\sim 70 \text{ nm}$  are observed.

The agglomerated grains transform in bigger grain size with the increasing film thickness, following the increase in amount of precursor, as seen in Fig. 1b.

The electrical parameters obtained from the Hall measurements are presented in Table 1. It can be noticed that the resistivity ( $\rho$ ) decreases when the film thickness increases. Minimum value of  $\sim 1.4 \times 10^{-3} \Omega\text{cm}$  was obtained for the film of about 720 nm thick. On the other hand, the carrier mobility ( $\mu$ ) is found to increase with the increasing of the film thickness. The minimum value of  $\sim 2.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  increased at  $18.5 \text{ V}^{-1} \text{ s}^{-1}$  when the film thickness decreases from 850 nm to 144 nm. The variation trend of  $\rho$  and  $\mu$  is also comparative, as shown in Table 1.

**Table 1.** Electrical properties of the films, obtained from the Hall measurements

Film thickness	Sheet resistance	Resistivity	Mobility	Carrier concentration
[nm]	[ $\Omega/\text{sqr}$ ]	[ $\Omega \text{ cm}$ ]	[ $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ]	[ $\text{cm}^3$ ]
144	486	$7.0 \times 10^{-3}$	2.2	$4.0 \times 10^{20}$
565	46	$2.6 \times 10^{-3}$	14.9	$1.6 \times 10^{20}$
850	21	$1.4 \times 10^{-3}$	18.5	$2.5 \times 10^{20}$

In Table 2 are presented the sheet resistance and resistivity values reported in literature up-to-now, comparing with our best result.

One can notice that the resistivity of film reported in this paper is lower than the one mentioned in the literature.

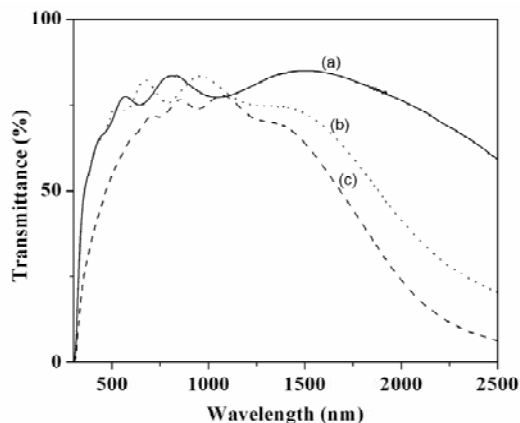
**Table 2.** Comparison of sheet resistance of  $\text{SnO}_2$  films in previous reports and this paper

Substrate temperature	Film thickness	Sheet resistance	Resistivity	Reference
[ $^{\circ}\text{C}$ ]	[nm]	[ $\Omega/\text{sqr}$ ]	[ $\times 10^{-3} \Omega \text{ cm}$ ]	
400	638	23	1.4	This work
400	$480 \pm 50$	$66 \pm 19$	$3.2 \pm 1.2$	[10]
400	720	51	1.5	[11]
400	441	1320	58.2	[12]
350	300	12.4	20.3	[13]
400	850	21.4	1.4	[This paper]

### 3.3 Optical properties

Fig. 2 shows the transmittance spectra obtained at the wavelength between 300-2500 nm. The optical transmission depends on the film thickness. The increase of the film thickness leads to higher absorption and thus reducing the transmittance. The average visible transmittance (AVT) calculated in the wavelength ranging 400-700 nm varied between ~58 and 85 %.

A maximum AVT of 85 % obtained for 144 nm thick films is decreased to a minimum of ~58 % when the thickness of the film increased to 850 nm.



**Fig. 2.** Variation in the optical transmittance of  $\text{SnO}_2$  films as a function of the film thickness: 144 nm (a), 565 nm (b) and 850 nm (c).

The fundamental absorption refers to band-to-band transitions, i.e. to the excitation of an electron

from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the band gap of materials.

The absorption coefficient ( $\alpha$ ) can be calculated from the transmittance values at the absorption edge in the transmittance spectra. The variation of absorption coefficient against photon energy ( $h\nu$ ) for direct band-to-band transition has the form of  $\alpha = A (h\nu E_g)^x$ .

Where  $h\nu$  is the photon energy,  $E_g$  the band gap and  $A$  the edge parameter. The  $\text{SnO}_2$  films are proven to possess direct allowed transition and thus the value of  $x$  is  $1/2$ . Hence plots have been made by taking  $h\nu$  along x-axis and  $(\alpha h\nu)^2$  along y-axis.

The values of direct band gap were estimated from the extrapolation of the linear portion of the curve to zero absorption and found to be in the range 3.88 - 3.90 eV for  $\text{SnO}_2$  films with different thickness. Theoretically, a gap of at least 3.5 eV is needed for a TCO in most anticipated applications [10] and the obtained values confirm that the produced films meet this requirement.

## 4. Conclusions

Thin films of tin oxide ( $\text{SnO}_2$ ) was successfully prepared by spray pyrolysis technique. The experimental results showed that the growth rate and subsequently the films thickness can be controlled by solution concentration, substrate temperature and the deposition time. SEM images showed that the



agglomerated grains transform in bigger grain size with the increasing film thickness.

The minimum value of  $\sim 2.2 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$  increased at  $18.5 \text{ V}^{-1}\text{s}^{-1}$  when the film thickness decreases from 850 nm to 144 nm.

The variation trend of  $\rho$  and  $\mu$  is also comparative.

A maximum *AVT* of 85 % for 144 nm thick films decreases to a minimum value of  $\sim 58$  % when the thickness of the film increases to 850 nm.

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