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Substrate temperature effects on the tin oxide films prepared by spray pyrolysis

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Indium-doped tin oxide films were prepared by the spray pyrolysis technique at different substrate temperatures ranging from 400–525 °C. Texture coefficients for (2 0 0) and (1 1 2) reflections of tetragonal SnO_2 were calculated. The surface morphology of the prepared films was revealed by using scanning electron microscopy. A dendrite structure was observed in the films deposited at a substrate temperature of 525 °C. The obtained specific resistances were correlated with those obtained from X-ray diffraction analysis and scanning electron microscopy. A study of the effect of film thickness on the plane of preferred orientation was carried out.

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.

It has been found that the spray technique is most suitable for obtaining tin oxide films in large-area substrate applications. The surface topography of undoped and indium-doped SnO_2 films have been studied by scanning electron microscopy [1–6] (SEM).

Tin oxide films not only have good adherence but also high chemical stability on a variety of substrates.

The structural and electrical properties of pure and doped SnO_2 with As, F and Sb have been investigated as a function of substrate temperature [7–17]. The aim of the present work is to study the effect of substrate temperature on the surface topography, structure and specific resistance of In-doped SnO_2 films prepared by spray pyrolysis. The present results will be compared with previous work, taking into consideration the effect of dopant type.

2. Experimental procedure

An inhouse spray pyrolysis set-up was used to prepare the thin films of indium-doped tin oxide. The structural details and schematic representation of the spray system are given elsewhere [15]. The spray solution is composed of 0.6 M Sn Cl_4 (Merck), dissolved in 98% ethyl alcohol. $InCl_3$ (Merck) (10 ml of 0.01 M) in distilled water was added to 100 ml of 0.6 M $SnCl_4$ in ethyl alcohol, in order to obtain indium-doped tin oxide films.

Chemically and ultrasonically cleaned glass substrates (2.2 × 1.1 × 0.1 cm) were used. The substrate was placed on the surface of a cylindrical stainless-steel block (diameter = 5 cm, height = 15 cm), electrically heated to attain the required substrate temperature. The temperature was measured by a Pt, Pt-Rh thermocouple with a temperature monitor Philips thermostat PT 2282A, which measures the temperatures from − 100 °C to 1000 °C. The furnace temperature was controlled by a Eurotherm proportional temperature controller to ± 2 °C. A fully automatic JESPEC model ST 3000 a.c. voltage regulator was used to stabilize the power, which supplies the spray system. Compressed air was used as a carrier gas, with a flow rate of 5 litres min^{-1}. The spray time was kept constant at 5 min for the whole substrate temperature range 400–525 °C. The effect of film thickness on the properties of the deposited films was previously studied. X-ray diffraction analysis was carried out using a Philips PW1710 X-ray diffractometer, with CuK_α radiation (λ = 0.1542 nm) and Ni filter at 40 kV and 30 mA. The specific resistance was measured by a conventional linear four-probe method using a 5-digit ammeter and voltmeter (G.L.A Electronica). (SEM) Siemens, was used to study the surface morphology of the deposited films.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction tracings of as-deposited indium-doped tin oxide films at different substrate temperatures ranging from 400–525 °C are presented in Fig. 1. Interplaner spacings and their relative peak intensities are calculated and compared with the

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Figure 1 X-ray diffraction traces of SnO_2 films at different substrate temperatures.

standard values given in the ASTM cards for SnO_2 powder. The *d*-values with their relative intensities together with the ASTM standard values are given in Table I.

The deposited tin oxide films have polycrystalline tetragonal rutile structure with preferential orientation along [2 0 0] for all substrate temperatures used. Traces of cubic SnO_2 are detected at substrate temperatures 425–525 °C, by the presence of (1 1 1) and (4 0 0) reflections. Also a reflection of $d = 0.205$ nm appeared, which may be due to the presence of SnO in the films.

Belanger *et al.* [3] have observed the reflections (1 1 0) and (2 0 0) for SnO_2: Sb films, prepared by the chemical vapour deposition (CVD) technique for a thickness of 0.3 μm, while for films of thickness 5 μm, the dominant plane was (2 1 1). They prepared SnO_2: F films and have observed that for films or thickness ~ 0.4 μm the dominant planes are (2 0 0), (4 0 0), (3 0 1) and (2 1 1). This means that fluorine enhanced the presence of (3 0 1) and (2 1 1) for films of large thickness. Chitra *et al.* [10] have prepared SnO_2: F films by spray pyrolyis. They found that for films of thickness 0.165 μm at substrate temperatures of 375–500 °C the films were preferentially oriented along the [2 0 0] direction, for undoped and F-doped SnO_2.

Sanon *et al.* [7] have prepared SnO_2 by CVD on glass substrates and found that the dominant plane was (1 0 1) for films of thickness 0.4–1.31 μm, while for films of thickness 2.3 μm the dominant plane was (2 0 0) together with the plane (2 1 1) and (1 0 1). For films prepared by Afify *et al.* [15] of SnO_2: F by spray pyrolysis in the thickness range 0.08–0.35 μm, the planes (2 0 0), (1 0 0) and (3 0 1) appeared, with (2 0 0) the preferred orientation at a substrate temperature of 450 °C.

SnO_2 films have been prepared [17] by spray pyrolysis at substrate temperatures of 450–600 °C and for film thicknesses 3–15 μm. The dominant plane was (2 1 1) for a film deposited at 450 °C, while at 500 °C it was the (1 1 0) plane. At 550 °C the (2 0 0), (1 1 0) and (1 0 1) planes have been observed. Yagi *et al.* [16] have prepared SnO_2 films by spray pyrolysis at a substrate temperature of 480 °C and found that the dominant plane was (1 1 0) while the (2 1 1) plane had a weak peak intensity, for a film thickness of 1.0 μm.

Comparing the X-ray diffraction results with previous ones, it can be concluded that for SnO_2 films of thickness 3 μm the dominant plane is (2 1 1) for those prepared by spray pyrolysis for substrate temperatures of 450 °C. On the other hand, for films of small thickness prepared either by CVD or by the spray technique, the dominant plane is (2 0 0). Also, the plane (3 0 1) of weak intensity can be obtained at substrate temperature 400 °C of SnO_2: F and SnO_2: In films. This agrees with the results of the present work for SnO_2: In of thickness 0.3 μm by spray pyrolysis except for the absence of the (3 0 1) plane.

The plane (1 1 2) was not previously observed. This plane is perpendicular to the (2 1 1) plane, which was observed previously for thicker films. This means that at the first stage of deposition the crystallites orient themselves along the [1 1 2] direction. As the film

TABLE I

ASTM Cards					Substrate temperature (°C)											
Material	System	d (nm)	I_0	$h k l$	400 °C		425 °C		450 °C		475 °C		500 °C		525 °C	
					d (nm)	I	d (nm)	I	d (nm)	I	d (nm)	I	d (nm)	I	d (nm)	I
SnO_2	Cubic	0.2842	100	1 1 1	–	–	0.2831	32	0.2831	6	0.2849	4	0.2831	5	0.2831	8.6
SnO_2	Tetragonal	0.2369	24	2 0 0	0.2368	100	0.2368	100	0.2368	100	0.2368	100	0.2368	100	0.2356	100
SnO	–	0.208	–	–	0.2058	21	0.20535	22	0.2050	23	0.2058	22	0.2058	20	0.2049	24
SnO_2	Tetragonal	0.1439	17	1 1 2	0.1455	80	0.1451	50	0.1451	50	0.1451	64	0.1449	75	0.1443	62
SnO_2	Cubic	0.1226	5	4 0 0	0.1236	17	0.1233	14	0.1230	15	0.1233	18	0.1236	16	0.1230	17
SnO_2	Tetragonal	0.11840	3	4 0 0	0.1185	6	0.1182	6	0.1180	6	0.1182	6	0.1180	6	0.1177	6

thickness approaches a few microns, the perpendicular [2 1 1] direction is preferred.

The appearance of the cubic SnO_2 phase leads to a slight effect, compared with the major part of the tetragonal phase. This can be observed from the intensity of the planes (4 0 0) and (1 1 1) of the cubic SnO_2.

The texture coefficient $TC\ (h k l)$ is calculated from the X-ray diffraction results as follows [9, 10]:

$$TC\,(h k l) = \frac{I\ (h k l)/I_0\ (h k l)}{I/N \Sigma_N I\ (h k l)/I_0\ (h k l)}$$

where I is the measured X-ray diffraction peak intensity, I_0 is the corresponding intensity given in the ASTM cards for the powder, and N is the number of reflections.

The texture coefficients are calculated for the reflections (2 0 0), (4 0 0) and (1 1 2) of the tetragonal tin oxide (SnO_2) doped with indium at the covered substrate temperature range. Variations of the texture coefficients of (2 0 0) and (1 1 2) reflections with the substrate temperature are shown in Fig. 2. TC (4 0 0) has the same behaviour as TC (2 0 0), but with a smaller peak intensity.

The growth mechanism could be explained from the standard deviation, σ, calculated from TC:

$$\sigma = \left[\frac{\Sigma I^2}{N} - \left(\frac{\Sigma I}{N}\right)^2\right]$$

where I is the relative intensity of the $(h k l)$ plane.

The dependence of the standard deviation, σ, on the substrate temperature is shown in Fig. 2. The results are in good agreement with those reported by Chitra *et al.* [9, 10]. The decrease of σ at lower substrate temperatures followed by stability at higher ones, may be due to the homogeneous nucleation and preferential SnO_2 growth for the deposited films. At a substrate temperature of 400 °C, the comparatively larger values of σ may be caused by non-homogeneous but preferential SnO_2 growth, which is confirmed by the d-values.

From the texture coefficient in Fig. 2 it appears that at the substrate temperature range 400–450 °C, the preferential [2 0 0] orientation is enhanced, while the [1 1 2] orientation is suppressed. However, at the substrate temperature range 450–500 °C the preferential [2 0 0] orientation is suppressed while the [1 1 2] orientation is enhanced. At 525 °C the [2 0 0] preferential orientation is comparatively larger than the [1 1 2] orientation.

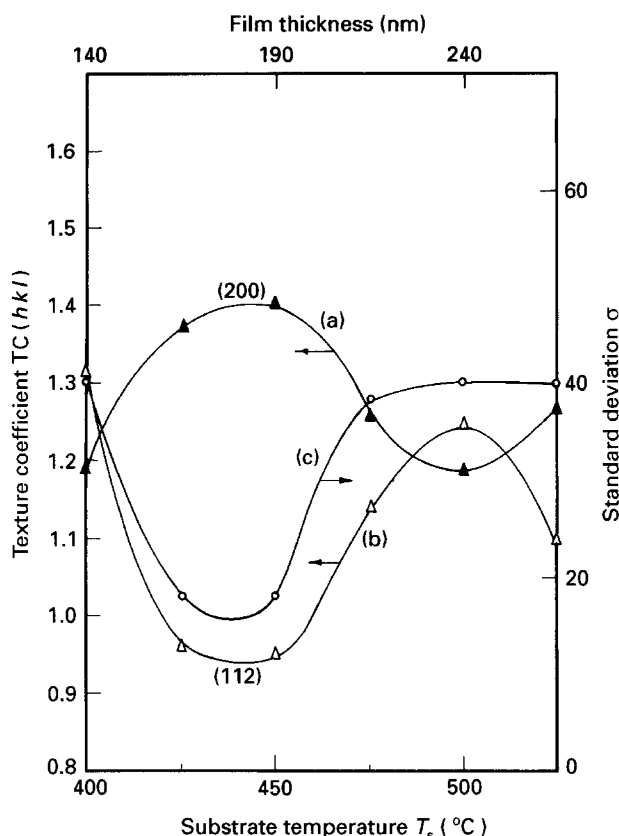

Figure 2 Effect of substrate temperatures on (a) TC (2 0 0) (b) TC (1 1 2) and (c) standard deviation, σ.

3.2. Scanning Electron Microscopy (SEM)

Details of the surface morphology of as-deposited indium-doped tin oxide films for the substrate temperature range 400–525 °C, were studied by SEM. The SEM micrographs are presented in Fig. 3a–f.

The observed rounded grains could be attributed to the non-uniformity of the deposited Sn oxide layer caused by the broad droplet size that forms 'island structures' of different sizes. The difference in island size leads to a competitive growth process and thereafter columns with domed tops are developed. At substrate temperatures > 500 °C, the solvent vaporizes as the droplet approaches the substrate, then the

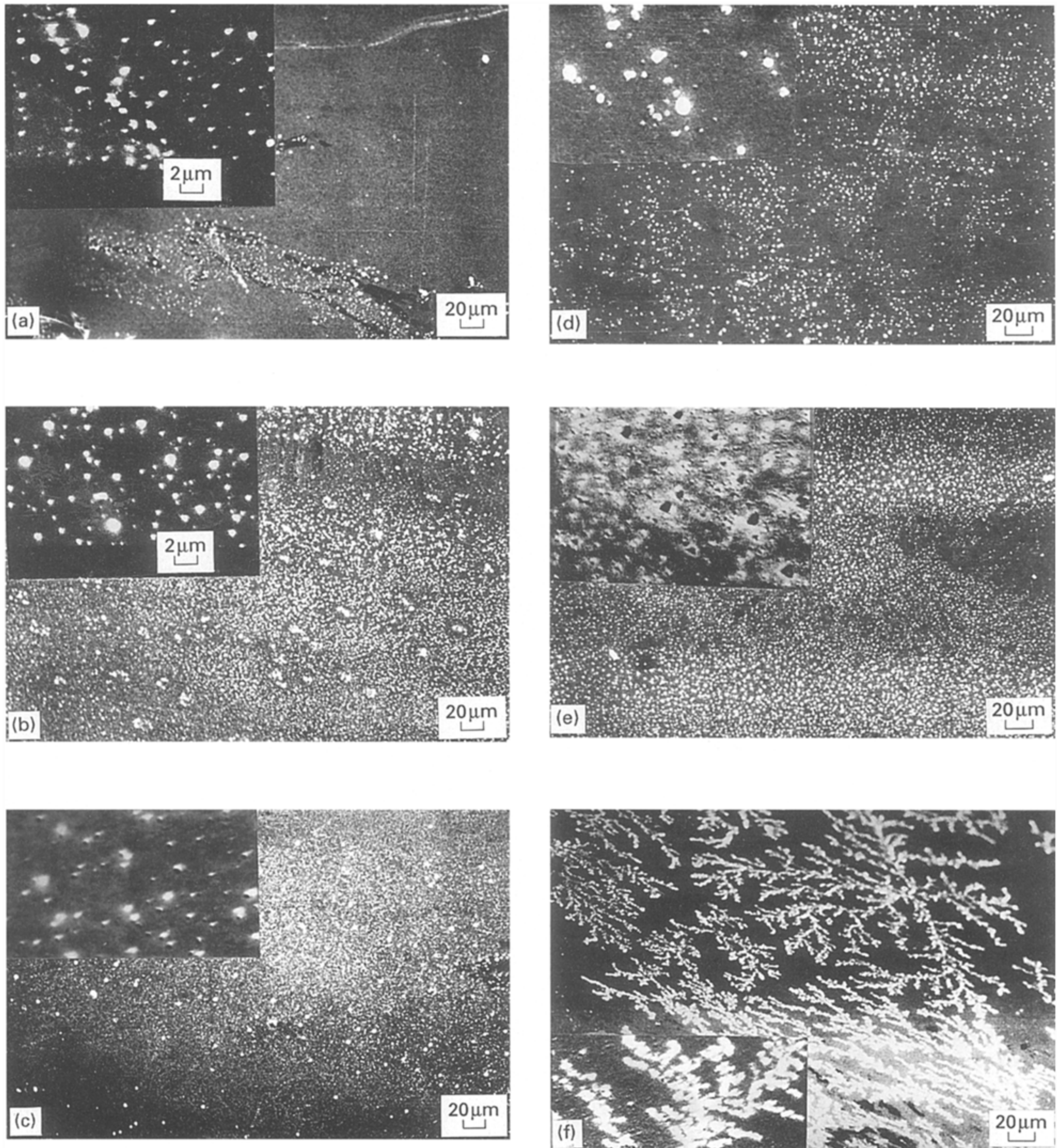

Figure 3 SEM micrographs at substrate temperatures of 400, 425, 450 475, 500 and 525 °C, as illustrated in (a), (b), (c), (d), (e) and (f), respectively.

solid melts and vaporizes. The vapour diffuses to the substrate to undergo a heterogeneous reaction [18]. Consequently, the growing islands will have approximately the same size. In this case the boundary of the island extends and no growth-competition occurs. This leads to a columnar structure of the film, in which the columns grow perpendicular to the substrate plane. This was the assumption reported by Fan *et al.* [19].

The intensity of the grains is very low at 400 °C, while at substrate temperatures 425–500 °C the intensity of the grains increased to give values of 50–125 grains cm^{-2} as the substrate temperatures increased. The grain sizes at this temperature range were distributed at each substrate temperature in the range of 0.1–3.0 μm. At 525 °C dendrites are grown with grain size 0.3–4 μm. The dendritic structure indicates that crystallization of the film at 525 °C occurred but the crystallites are not well oriented yet, since at this substrate temperature both (2 0 0) and (1 1 2) are present.

The variation of the specific resistance of the prepared as-deposited indium-doped tin oxide film with substrate temperature is shown in Fig. 4. The specific resistance decreases with substrate temperature, giving a minimum value at 450 °C, then it increases again. This agrees with the results given previously [9, 10].

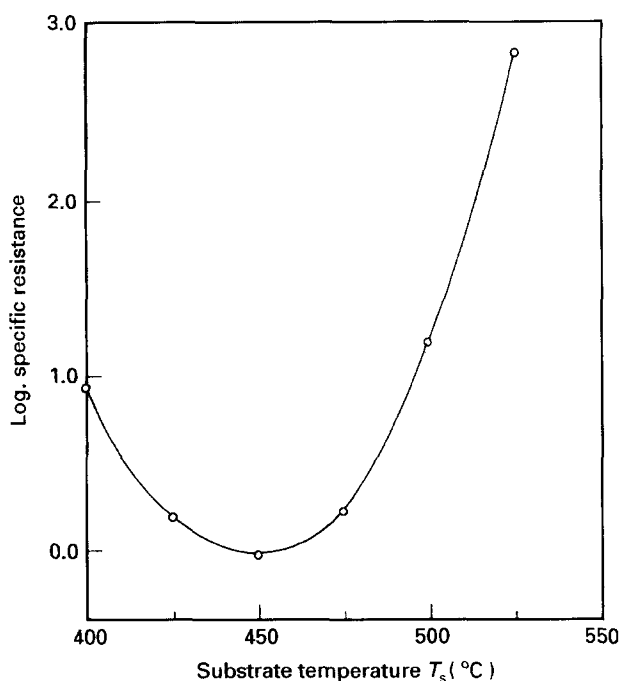

Figure 4 Effect of substrate temperatures on the specific resistance.

Correlating the results of the specific resistance and the texture coefficient, one can observe that at a substrate temperatures range of 450–500 °C the specific resistance decreases due to the enhancement of the [2 0 0] preferential orientation of the grown film, while the increase in the specific resistance from substrate temperature 450 °C to 500 °C is referred to the suppressed preferential [2 0 0] orientation and the increase in [1 1 2] orientation. At a substrate temperature of 525 °C the [2 0 0] and [1 1 2] orientations are present to nearly the same degree. In conclusion, comparing this result with the SEM result, the dendrite structure leads to an increase in the sheet resistance. From the standard deviation σ, irrespective of the change in sheet resistance with substrate temperature, preferential SnO_2 formation is confirmed to be present at the covered substrate temperature range in the present work.

The number of grains per unit area (intensity of the grains) plays an important role in the specific resistance for the studied films of thicknesses 0.1–0.3 μm. As the thickness increases more than 0.3 μm, the growth process is enhanced, yielding films of large size and high grain intensity. For thick films it would be expected that the dominant plane will be (2 1 1) or (1 1 0).

Conclusion

(1) SnO_2 films of 0.3 μm thickness have the dominant plane (2 0 0) when the films are prepared by either chemical vapour deposition or spray pyrolysis at substrate temperatures 400–600 °C for any of the dopants In, F or Sb. On the other hand, as the film thickness increases to ≥ 3 μm the dominant planes will be (2 1 1) and (3 0 1).

(2) Cubic SnO_2 phase but with a small ratio appeared in the present work. A slight effect of the cubic SnO_2 is expected on the specific resistance. The intensity of grains in the prepared films plays a considerable role in the specific resistance, while the grain size is slightly affected by the substrate temperature.

(3) A dendritic shape is observed for films prepared at a substrate temperature of 525 °C, indicating an initial step of crystallization, although the dendrites led to an increase in the specific resistance.

(4) The presence of (2 0 0) as the dominant plane and for film thickness ≤ 0.3 μm shows that the specific resistance is relatively high for the whole investigated substrate temperature range.

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