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XRD and SEM studies of reactively deposited tin oxide thin films

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Abstract. Stoichiometric polycrystalline tin oxide thin films were deposited by the reactive evaporation of tin and the SnO_2 formation was found to be strongly dependent on the deposition parameters. The preferred orientation of the SnO_2 films deposited on different substrates was varying due to the dislocation defects arising during the thin film formation. The X-ray diffraction (XRD) studies identified a tetragonal structure while the scanning electron microscopic (SEM) studies revealed a polycrystalline surface for the SnO_2 films reactively deposited.

Keywords. Tin oxide; reactive evaporation; tetragonal; dislocation defects; recrystallization.

1. Introduction

Tin oxide thin films find applications in several technological areas, most notably as transparent conductors, spectrally selective coatings and gas-sensing elements (Chopra *et al* 1983). Thin films of SnO_2 have been obtained by several methods like reactive evaporation, chemical vapour deposition and sputtering (Leja *et al* 1979; Muranaka *et al* 1981; Cavicchi *et al* 1992; Zhu *et al* 1993). The chemical vapour deposition process of tin oxide, although inexpensive, is being substituted by physical vapour deposition process, which is more controllable, leading to thin films of better purity and properties. In the present study, the reactive evaporation technique was made use of in preparing SnO_2 thin films and the effect of deposition parameters is studied in detail.

2. Experimental

Thin films of tin oxides were prepared by the reactive evaporation of tin. The vacuum chamber was evacuated to about 10^{-5} torr before deposition and oxygen gas was admitted through a needle valve into the chamber until the required pressure was reached. Tin was evaporated by the resistive heating of tin granules with a constant deposition rate of about 0·3 nm/s, otherwise mentioned in the text. The deposition rate was monitored with a quartz crystal oscillator which was calibrated to measure the thickness of the film on the substrate. The substrate temperature was measured with a chromel-alumel thermocouple which was attached to one of the substrates. Thin films were deposited on glass and alumina substrates located about 18 cm from the source and the thickness ranged from 150 to 450 nm. Surface characterization studies were carried out using a Philips PW1701 X-ray diffractometer and a JEOL 35C scanning electron microscope.

3. Results and discussion

3.1 *XRD studies*

To study the influence of oxygen partial pressure in the formation of SnO_2, films were deposited at varying oxygen partial pressures. Table 1 gives the measured X-ray parameters and the identified surface phases of the films deposited at an oxygen partial pressure of 3×10^{-4} (S1), 3×10^{-3} (S2) and 10^{-2} torr (S3) at a substrate temperature of 823 K. It is clear from the table that pure SnO_2 was formed at an oxygen partial pressure of 3×10^{-3} torr. Polycrystalline SnO_2 films exhibited a tetragonal structure and a preferred orientation along the (101) plane. Other co-existing SnO_2 phases were of (110), (200) and (211) orientations. At an oxygen partial pressure of 3×10^{-4} torr, Sn and SnO phases were found to co-exist with the SnO_2 phases. This may be due to the lack of sufficient oxygen in the reacting zone. Again, at an oxygen partial pressure of 10^{-2} torr, where the percentage of oxygen was higher, we could not find any SnO_2 phases, instead β-Sn and β-SnO phases were present. At this partial pressure of oxygen torr, the mean free path of evaporated Sn atoms decreases due to the collision with the oxygen atoms. This reduces the energy of Sn atoms and the formation of SnO_2 molecules resulting in a Sn/SnO_x ($x < 2$) phase. The free energy of formation of the SnO and SnO_2 molecules are 61 and 122 kcal/mol, respectively.

Since an oxygen partial pressure of 3×10^{-3} torr was found to be favoured for the formation of SnO_2 films from the above results, SnO_2 films were deposited at varying substrate temperatures of 373 (S4), 573 (S5), 773 (S6) and 823 K (S7). Table 2 presents the measured X-ray parameters and the identified surface phases. The data shows that the thin films were amorphous at lower substrate temperatures and polycrystalline at higher temperatures. Amorphous film formation at low temperature may perhaps be due to the low surface mobility of the adsorbed particles so that the disordered state is

Table 1. XRD data and phase identification of reactively deposited thin films at different oxygen partial pressures.

Sample No.	2Θ (degree)	d (nm)	I/I_0 (%)	Identification
	26·7	0·3338	7	SnO_2(110)
	30·7	0·2912	100	β-Sn (200)
	32·1	0·2788	76	β-SnO (004)
S1	33·9	0·2644	4	SnO_2(101)
(3×10^{-4} torr)	43·9	0·2061	20	β-Sn (220)
	44·9	0·2018	39	β-Sn (211)
	55·4	0·1658	6	β-Sn (301)
	26·7	0·3338	59	SnO_2(110)
S2	33·9	0·2644	100	SnO_2(101)
(3×10^{-3} torr)	37·9	0·2373	27	SnO_2(200)
	51·9	0·1761	65	SnO_2(211)
	30·6	0·2921	100	β-SnO (—)
	32·1	0·2788	52	β-SnO (004)
S3	43·9	0·2061	12	β-Sn (220)
(10^{-2} torr)	44·9	0·2018	24	β-Sn (211)
	55·4	0·1658	4	β-Sn (301)

Table 2. XRD data and phase identification of reactively deposited thin films at different substrate temperatures.

Sample No.	2Θ (degree)	d (nm)	I/I_0 (%)	Identification
S4 (373 K)	—	—	—	Amorphous
S5 (573 K)	—	—	—	Amorphous
	30·0	0·2978	54	α-SnO(101)
	30·8	0·2902	100	β-SnO(101)
	32·2	0·2779	42	Sn_3O_4(112)
	33·0	0·2714	9	Sn_2O_3(200)
S6	33·9	0·2636	4	SnO_2(101)
(773 K)	37·4	0·2404	8	α-SnO(002)
	44·1	0·2053	14	α-SnO(102)
	45·1	0·2010	20	Sn_2O_3(131)
	50·9	0·1793	9	α-SnO(112)
	26·7	0·3338	59	SnO_2(110)
S7	33·9	0·2644	100	SnO_2(101)
(823 K)	37·9	0·2373	27	SnO_2(200)
	51·9	0·1761	65	SnO_2(211)

frozen before the particles are able to reach the most preferred energetic sites corresponding to their respective crystallographic structures.

Further, the data in table 2 shows that though SnO_2 has formed at a substrate temperature of 773 K, other phases of tin were also found to co-exist. By increasing the substrate temperature to 823 K, the formation of SnO_2 was found to be complete.

To study the influence of substrate surface on the deposited film structure, SnO_2 films were also deposited on a polycrystalline alumina surface at a substrate temperature of 823 K and an oxygen partial pressure of 3×10^{-3} torr. Table 3 gives the calculated X-ray parameters corresponding to the identified SnO_2 and Al_2O_3 phases. From the data it can be seen that though polycrystalline SnO_2 was formed, the preferred orientation of the SnO_2 films deposited on alumina shows a tendency to orient in the (110) plane with increasing thickness.

As per the thin film formation mechanism (Volmer and Weber 1925), film growth usually takes place first by nucleation, followed by the growth of nuclei and later by their coalescence. The nuclei growing on a substrate may have various crystallographic orientations for various growth conditions. It has been established that when two islands which are of different sizes and crystallographic orientations, coalesce, the resultant crystallite assumes, as a rule, the orientation of the larger one.

Electron-optical examinations of fcc metals by the moire technique (Eckertova 1986) have revealed that there are almost no defects in separate nuclei and that they arise only after the coalescence process begins. The most frequent defects are dislocations, which arise at the boundary of two crystal regions that are somewhat angularly displaced with respect to each other. Dislocations are also formed at the boundary between the thin film and substrate surface owing to the difference in their crystal lattice. And to eliminate the difference in orientation, the islands can move or rotate somewhat to eliminate the difference in orientation. Moreover, as per the concepts of thin film

Table 3. XRD data and phase identification of tin oxide thin films reactively deposited on alumina substrate.

Sample No.	2Θ (degree)	d (nm)	I/I_0 (%)	Identification
	26·7	0·3338	14	$SnO_2(110)$
	33·9	0·2644	13	$SnO_2(101)$
	35·2	0·2549	95	$Al_2O_3(103)$
S8	37·7	0·2386	27	$Al_2O_3(200)$
(200 nm)	43·4	0·2084	100	$Al_2O_3(202)$
	51·9	0·1758	7	$SnO_2(211)$
	52·7	0·1736	23	$Al_2O_3(403)$
	57·7	0·1597	98	$Al_2O_3(203)$
	26·6	0·3351	31	$SnO_2(110)$
	33·9	0·2644	17	$SnO_2(101)$
	35·2	0·2549	84	$Al_2O_3(103)$
S9	37·7	0·2386	27	$Al_2O_3(200)$
(360 nm)	43·4	0·2084	100	$Al_2O_3(202)$
	51·8	0·1764	10	$SnO_2(211)$
	52·7	0·1736	43	$Al_2O_3(403)$
	57·7	0·1597	98	$Al_2O_3(203)$

formation (Maissel and Glang 1970; Eckertova 1986), an increase in substrate temperature can stimulate oriented overgrowth facilitating recrystallization. Any of the above mentioned lattice misfits must have taken place in the case of SnO_2 films deposited on the alumina substrate at greater thickness. So, the SnO_2 islands might have rotated or moved to eliminate this dislocation. And, in this process, the islands with (110) texture might have grown in prominence compared to the (101) texture.

In our further studies, it was found that the preferred orientation of the SnO_2 films deposited on the polycrystalline quartz substrates was also along the (110) plane as in the case of alumina substrates, while it was only along the (101) plane even for a 400 nm thick SnO_2 films deposited on glass substrates.

The influence of rate of evaporation on the SnO_2 film formation was also studied. Under the optimum conditions for the SnO_2 film formation, SnO_2 films were reactively deposited at a rate of 1 nm/s. Though the XRD analysis identified a well defined polycrystalline SnO_2 film, trace amounts of β–Sn, α–SnO and β–SnO were also found. Such a mixed state of Sn, SnO and SnO_2 was found when the source-substrate distance was reduced to 9 cm. So, a very short distance or a faster rate of deposition results in an incomplete reaction in which the unreacted species are incorporated into the films.

3.2 *SEM studies*

The scanning electron micrographs of the reactively deposited SnO_2 films are shown in figure 1. Figure 1(a and b) depicts the morphology of film deposited on glass at a substrate temperature of 373 K at an oxygen partial pressure of 3×10^{-3} torr. The surface morphology of the SnO_2 films deposited at a substrate temperature of 823 K and an oxygen partial pressure of 3×10^{-3} torr on glass and alumina substrates for thickness 200 and 360 nm, are shown in figure 1(c and d) and figure 1 (e and f),

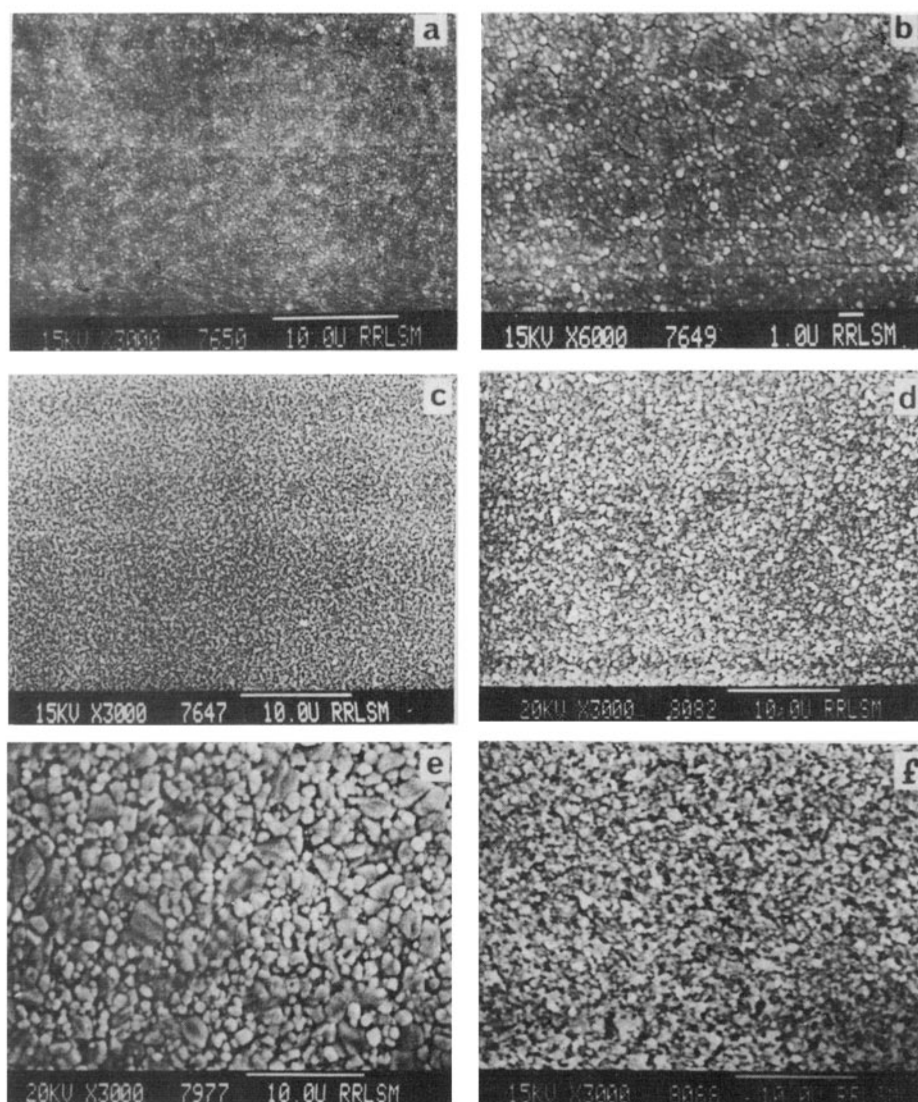

Figure 1. SEM of tin oxide thin films (**a, b**) of thickness 200 nm deposited on glass at a substrate temperature of 373 K; (**c, d**) of thickness 200 and 360 nm, respectively, deposited on glass at a substrate temperature of 823 K; and (**e, f**) of thickness 200 and 360 nm, respectively, deposited on alumina at a substrate temperature of 823 K.

respectively. Films deposited at low substrate temperatures reveal an amorphous surface texture with microcracks throughout the entire surface of the film (figure 1(a and b)). Small and bright spots can also be seen distributed almost uniformly over the surface. These spots may be the nucleation centres. Figure 1(c) exhibits an ultrafine polycrystalline structure for the films deposited on glass, whereas, figure 1(e) displays almost uniform spreading of a lot of islands on the background of a polycrystalline alumina surface. These islands may be due to the preferred nucleation of the SnO_2 molecules in the cavities between the grain boundaries of the alumina

surface. When these films grow in thickness, a more textured polycrystalline surface could be seen with an increased grain size (figure 1(d and f)). In the case of films deposited on alumina substrates, figure 1(e and f), with the increase in thickness the SnO_2 film covers the entire substrate surface as is evidenced by the disappearance of the polycrystalline background of alumina substrate surface and the film growth also seems to be more coagulated. Moreover, figure 1 (d and f) exhibit a coarse and smooth surface, respectively, which may be due to the preferred orientation of the polycrystalline surface in the (101) and (110) planes, respectively.

4. Conclusions

The structure of the SnO_2 films was found to strongly depend on the deposition parameters. Tin oxide films were formed at an oxygen partial pressure of 3×10^{-3} torr, substrate temperature of 823 K, a source-substrate distance of 18 cm and at an evaporation rate of 0·3 nm/s. The as-deposited films were polycrystalline and exhibited a tetragonal structure. The preferred orientation of the SnO_2 films deposited on glass substrate was along the (101) direction, while it was along the (110) direction for films deposited on alumina substrate. And, the variation in the orientation of the films was due to the recrystallization that had occurred in the case of films deposited on alumina substrate, so as to minimize the dislocation defects arising during the formation of the thin films.

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