

INFLUENCE OF AN INTERMEDIATE ANNEALING AND SUBSTRATE NATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF SnO_2 THIN FILMS

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RESUMO

Filmes finos de dióxido de estanho dopados com Sb foram preparados pela técnica de molhamento via-sol-gel. O efeito de um tratamento térmico intermediário na sua preparação, é analisado através de medidas de reflexão especular de raios-X e microscopia eletrônica. Estes resultados mostram que a densidade para os filmes tratados a 400°C após cada imersão, é maior que aqueles produzidos com imersões múltiplas e um tratamento térmico no final. No entanto, apesar da condutividade elétrica ser baixa, os resultados das análises de transmitância no infravermelho mostraram que a transmissividade diminui com o aumento da concentração de Sb, em acordo com a teoria de Drude. Resultados comparando deposições em diferentes tipos de substratos são também mostrados.

ABSTRACT

Tin dioxide thin films doped with Sb have been prepared by sol-gel dip-coating technique. The effect of an intermediate annealing in its preparation is analyzed through X-ray reflectometry and electron microscopy. These results have shown that the density for films fired at 400°C after each dip is higher than that of multi-dipped films prepared with a single annealing. Although the electrical conductivity is rather low, results of infrared optical transmission have shown that transmission decreases with increase of Sb doping concentration, as predicted by Drude's theory. Results comparing depositions on different types of substrates are also shown.

1. INTRODUCTION

Tin dioxide (SnO_2) has a bandgap of about 3.5 eV and, due to oxygen vacancies and appropriate doping, it may become a highly conducting material. In the form of thin films, it may be characterized by high optical transmission (80-90%)^[1]. As undoped material, tin dioxide is an n-type semiconductor since oxygen vacancies and interstitial Sn^{4+} are donor sites. Then, conjunction of optical, electrical and structural properties make tin dioxide very attractive for many kind of applications in opto-electronic devices^[2], gas

sensors^[3,4] and solar collectors^[5]. SnO_2 properties are strongly influenced by preparation technique. Sol-gel process presents many advantages compared to other techniques, such as excellent homogeneity, thickness control and possibility of coating large and complex surfaces, due to its rather low-cost process. Conducting Sb-doped SnO_2 films exhibit increasing absorption coefficient in the infrared, where its spectra can be reasonably well described by Drude's free electron gas theory^[6,7]. Transmission coefficient decreases with increasing thickness and doping levels^[2], while reflection in the infrared region increases with increasing Sb concentration^[7,8].

In this work, we present sol-gel films prepared according to two distinct procedures, whose difference is basically a firing step at 400°C between each dip. This intermediate annealing yields thinner and less porous films. Besides, we discuss the effect of Sb doping to polycrystalline SnO_2 thin films deposited via sol-gel route with several concentrations of Sb (1.5%, 2%, 3% and 4%) on their electrical and optical properties. An influence of substrate nature is also investigated, comparing films deposited on regular borosilicate glass substrate to deposition on quartz substrate.

2. EXPERIMENTAL

Colloidal suspensions of Sb-doped SnO_2 nanoparticles have been prepared from Sn^{4+} aqueous solution (0.25 mol.l^{-1}), obtained by dissolution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbF_3 (Merck). Hydrolysis was promoted by addition of ammonium hydroxide (NH_4OH) under magnetic stirring until pH reaches 11. The precipitate obtained by this way was submitted to dialysis in order to eliminate as much as possible chloride, fluoride and ammonium ions. This procedure leads to stable $\text{SnO}_2\text{:Sb}$ colloidal suspensions for several doping concentrations. These suspensions, were used for film deposition on silicate glass substrates by dip-coating technique, with a withdrawing rate of 10 cm/min. Multi-dipped films were deposited basically according to two procedures, concerning firing between dips. Figure 1 shows a diagram of these two procedures, which can be described as follows:

Procedure I (PI) - After each dip, which takes place at room temperature, films are kept in air for 20 min and then dried

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in a oven at 50°C by 30 min. When the desired number of layers is obtained, films are annealed at 500°C for 1 hour under air or vacuum.

Procedure II (PII) – the only difference to procedure I is that between each dip, the deposited film is fired at 400°C for 10 min. In other words PII allows a significant increase on intermediate annealing temperature, which is carried out after each layer deposition.

X-ray reflectometry measurements (RERX) have been done in a reflection chamber coupled to a conventional powder diffractometer Siemens D500. Structural parameters are obtained by fitting reflectivity curves to theoretical reflectivity function, using the Nevot-Croce model [9]. For X-ray diffraction measurements it was used a Rigaku diffractometer coupled with a Cu source of 40 kV and 20 mA of current. Detector rate is 3 degrees per minute with a 0.02 degree step. To verify the thickness of multi-dipped films, scanning electron microscopy (SEM) was carried out at CCDM-UFSCar, on samples with 50 dips, grown by both procedures. This is done with a Microscope Stereoscan 440-LEO. Infrared transmittance and reflection have been measured by a Nicolet spectrophotometer in the range 1.8-12 μm . For the range 200-900 nm it was used a Cary spectrophotometer.

To measure resistance of the film, electrical measurements were carried out in the range 25-350 K within 0.2 K of precision in an Air Products Cryostat. The pressure in the chamber is kept below 10^{-5} Torr.

3. RESULTS AND DISCUSSION

Figure 2 shows the experimental x-ray reflectivity and fitted curves for samples obtained by PI and PII. Figure 2(a) shows results for single dipped films obtained by PI. The critical angle (θ_c), corresponding to total reflection, is invariant if it is considered experimental error, indicating that samples have approximately the same density. Table I shows parameters obtained from RERX fitting. The average density for PI is figured out in $(3.6 \pm 0.2) \text{ g/cm}^3$. This low value indicates about 47% of pores when compared to SnO_2 single crystal. The periodicity of oscillation observed for $\theta > \theta_c$ indicates that films are continuous, presenting a uniform thickness. The film thickness shown in table I are deduced from period of oscillation. It varies with Sb concentration, even though no proportionality between thickness and Sb concentration is observed. Particularly for $\text{SnO}_2:1.5\%\text{Sb}$ films (composition used for MEV experiments - see next paragraph) the layer thickness is 15.7 nm. Figure 2(b) corresponds to X-ray reflectometry results and fitted curves for films obtained by PII. Films used in this case have 3 dips since 1 dip films obtained by this procedure turned out to be too thin and did not yield good simulation results. The density obtained from simulation parameters is shown in table I and the average value is $(4.7 \pm 0.1) \text{ g/cm}^3$, which indicates a porosity of about 33%. These films also present continuous increase in thickness of 17.6 nm to 23.0 nm as the Sb content increases from 0.0 to 4.0% (table I). Since these experimental curves correspond to films prepared with 3 dips, each layer of $\text{SnO}_2:1.5\%\text{Sb}$ film has 6.6 nm of average thickness.

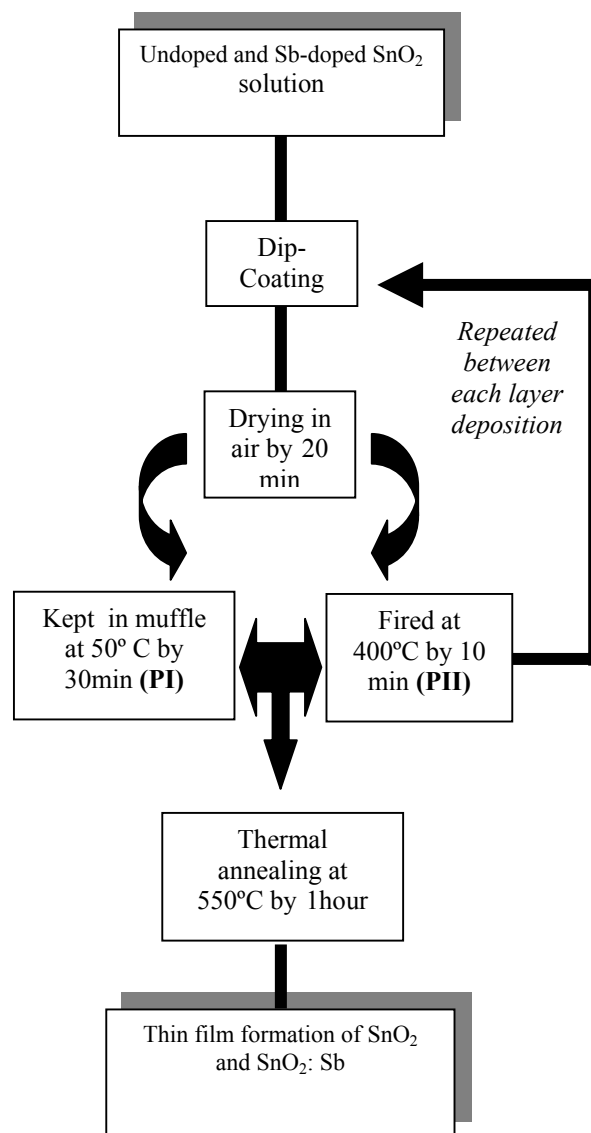


Figure 1 - Deposition diagram by dip-coating technique. Left and right side indicate PI and PII procedure respectively.

Scanning electron microscopy results (not included in this paper) for $\text{SnO}_2:1.5\%\text{Sb}$ films prepared by both procedures, with 50 dips, show that the film prepared by PI is about 400 nm thick, whereas film prepared by PII is about 300 nm thick. A qualitative analysis indicates that SEM results agree with X-ray reflectometry results, which means that temperature of 400°C for firing between dips (PII) decreases film thickness, since in both kinds of measurements PI yields thicker films than PII. The average thicknesses per dip calculated from these values are 8 nm and 6 nm for PI and PII, respectively. Then, a further comparison between results of SEM and X-ray reflectometry, yields that the agreement concerning film thickness obtained by these two procedures, is much better for PII than PI, since the monolayer thickness obtained by X-ray reflectometry is 15.7 nm and 6.6 nm for PI and PII respectively (see table I). This result suggests that using PII, the structural feature of single dipped layer is essentially preserved after multiple dip. On

the other hand, the thickness of each successive layer prepared by PI decreases as the number of dip application increases. This feature may be related to a higher porosity obtained from PI (47%), which suggests the existence of much more empty space, and a softer film which could either be more easily fulfilled by precursor solution or partially peeled during the upper layer application. As a consequence, it results in a non-homogeneous structure and a worse optical transmittance in the UV-visible wavelength range.

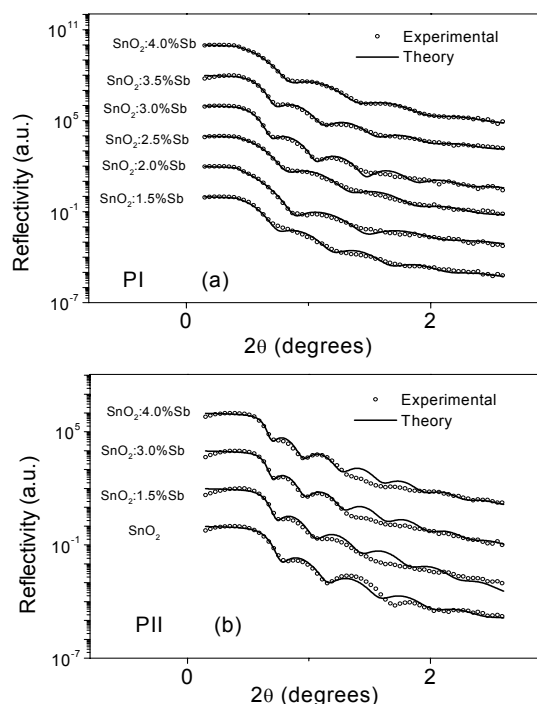


Figure 2 - Experimental X-ray reflectivity curves (points) and fitted curves (lines) for Sb - doped SnO₂ films. (a) films deposited by PI, single dip, (b) films deposited by PII with 3 dips.

Table I – Parameters obtained from fitting of experimental results of X-ray reflectivity curves (1 layer for PI films and 3 layers for PII)

SnO ₂ %Sb	Thickness (nm)		Density (g.cm ⁻³)	
	PI	PII	PI	PII
0.0	-	17.58	-	4.74
1.5	15.66	19.87	3.49	4.69
2.0	12.06	-	3.56	-
2.5	14.02	-	3.81	-
3.0	18.99	22.60	3.59	4.62
3.5	17.63	-	3.81	-
4.0	13.35	23.09	3.78	4.54

Figure 3 shows optical transmittance in the near infrared of films prepared by procedure PII. The transmittance

decreases as Sb concentration increases. A quite similar result is observed by optical transmission of films grown by procedure PI. Optical reflection results (not included here) points to a increase in film reflection with Sb concentration, in good agreement with transmission data. Regions of lower transmittance are coincident with reflection maximum, meaning that the reflected fraction of the incident beam is probably more significant than absorption fraction in the infrared range. In near infrared region the classical Drude theory applies, whenever the carrier concentration is high enough to allow plasma resonance phenomena. Then, reflection in infrared region increases with increasing Sb concentration [8]. This result suggests that films may have indeed a high free carrier concentration in the neutral bulk region, but there is also a very high electron scattering at boundary layer. Sol-gel films used in our measurements have small grain size (3-10 nm) and their resistivity is rather large. Then there is a large amount of crystallites concomitant with potential barrier at grain boundary which is related to large grain boundary depletion layer [10]. It leads to a strong electron scattering at grain boundary. Besides, the presence of pores must be taken into account since it decreases the electron free path. Typical conductivity as function of temperature, in the range 25-350 K, is shown in figure 4. These values are evaluated from resistance x temperature data, measured with a pressure of about 8×10^{-6} Torr, and taken into account the film conduction channel (distance between contacts, film thickness, and contact width). This result concerns an undoped SnO₂ film obtained by procedure PII. Room temperature resistivity is rather high (about 300 Ω .cm) and the conductance decreases with temperature, a typical semiconductor behavior. It is clearly seen in the figure 4 that the slope changes as the inverse of temperature varies, which means that more than one impurity level is being excited. The n-type conductivity also increases with Sb-doping, which are not shown here, since it is not the scope of this paper. However, more data on SnO₂ conductivity have been published elsewhere [11-13]. It is interesting to mention that annealing to 550°C under vacuum increases the film conductivity. However this is not a permanent effect. Exposure to atmospheric air recovers the low conductivity. As already mentioned, this behavior is related to high grain boundary scattering [11].

Figure 5 shows absorption spectra for sol-gel SnO₂ thin films deposited on different kinds of substrates and different thicknesses, grown by procedure PII. As it can be seen, the number of deposited layers influences the absorption of SnO₂ deposited on quartz substrates, whereas the number of layers does not affect the absorption of samples grown on borosilicate glass substrate as shown in the inset of figure 5. This result indicates that absorption from glass substrate may influence the behavior of photoinduced transport when film is excited by ultraviolet sources [12] and, besides, this substrate absorption must be taken into account to explain characterization results of sol-gel deposited thin films, since in most published papers tin dioxide thin films are deposited on glass.

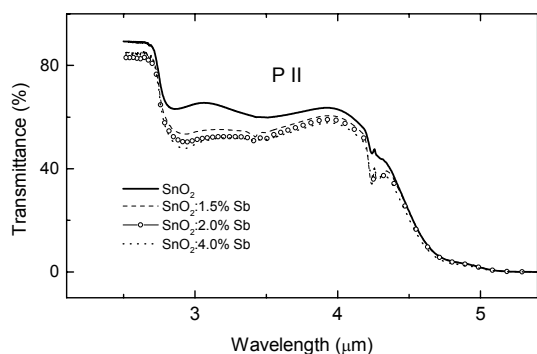


Figure 3 - Near infrared transmittance spectra of SnO₂ thin films deposited by PII with several Sb doping composition. Inset - near infrared transmittance spectra of films deposited by PI.

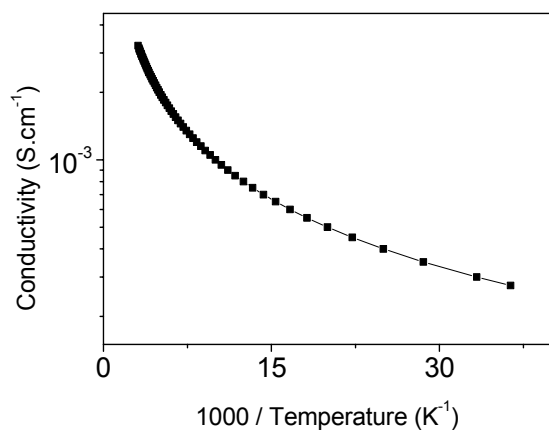


Figure 4 – Typical conductivity as function of temperature for an undoped SnO₂ film, obtained by PII

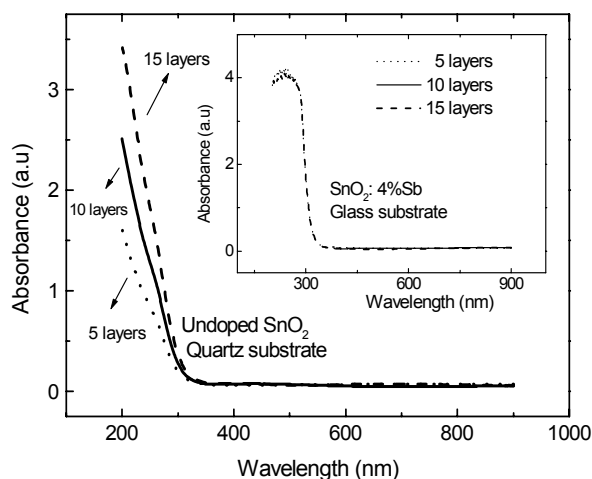


Figure 5 - UV-visible absorption of undoped SnO₂ thin film deposited on quartz substrate. Inset - UV-visible absorption of undoped SnO₂ thin film deposited on glass substrate.

Figure 6 shows X-ray diffraction results for SnO₂ thin films deposited on different kinds of substrates, grown by procedure PII. Both films have 30 deposited layers. It can be seen that the film grown on quartz substrate presents a preferential crystal growth direction at (110), whereas the film deposited on glass substrate grows preferentially on (101) direction. It leads to believe that films deposited on quartz substrate are better defined structurally, since in cassiterite structure as well as in the SnO₂ crystal^[14] the (110) direction is the dominant. Results on nanocrystalline powders^[15] also confirm that (110) direction as the predominant, as well as results of X-ray diffraction in thin films deposited by plasma-enhanced chemical vapor deposition on corning glass substrates^[16].

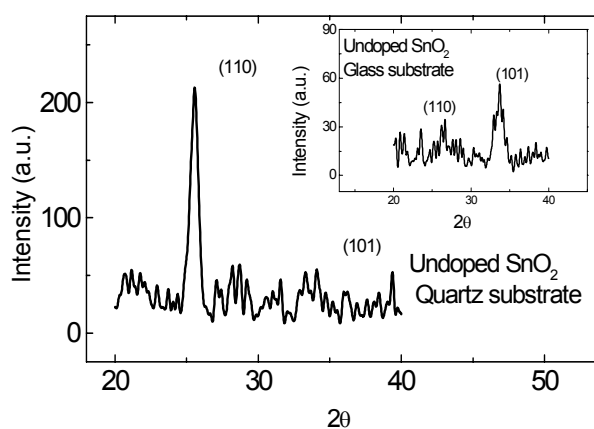


Figure 6 – X-ray diffraction for undoped SnO₂ deposited on quartz substrate. Inset - X-ray diffraction for undoped SnO₂ deposited on borosilicate glass substrate.

4. CONCLUSION

The firing process between each dip during deposition of SnO₂ thin films turned out to be responsible for a more compact arrangement of layers leading to more dense and thinner films concomitant with less pores. Besides this firing at 400°C between dips promotes better agreement between X-ray reflectometry and SEM results, which means that as the number of dips increase films submitted to intermediate annealing keep their thickness proportional to the number of deposited layers, whereas films with no firing between dips are subject to a shrinking as the deposition goes on. X-rays diffraction results on films grown by PII indicate that the utilization of quartz substrates may improve the crystalline organization. Besides this kind of substrate contribute to a better understanding of electro-optical properties.

Infrared optical transmission of SnO₂ thin films, deposited by dip-coating via sol-gel, decreases with

increasing Sb doping. This behavior can be explained based on Drude's free electron gas theory, which can be also applied to our films. The intermediate firing process leads to films with improved morphology and optical transmission in the visible range, however the conductivity is still low and probably can be increased by elimination of excess of oxygen from grain boundary layer and other defects.

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