

DC sputtered Tin oxide films. Plasma parameters, composition and structure

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Tin oxide films were growth by DC sputtering in oxygen plasma in the constant current mode. Films were growth at different substrate temperatures, cathode currents and oxygen pressures, and they were characterized by x-ray diffraction and x-ray photoelectron spectroscopy. The cathode voltage was monitored during the growth. Uniform, transparent films were obtained, with composition ranging from SnO to SnO₂. At 40-60 mTorr a change in the crystallographic orientation of the films is observed. From the deconvolution of the x-ray diffractograms the texture parameter and the phase composition of the films were obtained.

Keywords: Reactive sputtering; Thin films; Tin oxide, X-ray diffraction

1. Introduction

Considerable attention has been devoted to the study of sputter deposited SnO₂ films, due to their wide range of applications [1,2]. On the other hand, despite its great advantages over compound targets, reactive sputter deposition from metallic targets often exhibit several troubles in the stoichiometry of the films, due to phenomena such as instabilities near the metal-to-compound transition region, the presence of more than one oxidation state of the metal and the “inert pair effect” [3,4]. In a previous study of the chemical and phase composition of DC sputtered SnO_{2-x}:F films grown under Ar-O₂-Freon plasmas [5,6], was found that Sn⁺⁴ is obtained only in the presence of Freon. There, a phase diagram and a model were proposed to show that the films are composed by a Sn⁺² and Sn⁺⁴ mixture, leading to a multiphase system where SnO, Sn₃O₄, Sn₂O₃ and SnO₂ are formed. In the present work, the structure of SnO_{2-x} films prepared by DC-reactive sputtering in O₂ plasma is studied by X-ray diffraction, looking for the best conditions where

stoichiometric, highly oriented SnO₂ films can be produced.

2. Experimental details

The experiments were carried out in the system described elsewhere [5], with a base pressure of 2 x 10⁻⁶ Torr, using the constant current mode of a DC source (Advanced Energy). Films were growth from a metallic tin target (Alfa Aesar, 99.9%) and an O₂ plasma (O₂ 99.999% Linde) and they were deposited onto temperature controlled Corning glass slides, fixed directly 35 mm below the target. Before the preparation of films, the discharge behavior was monitored at different oxygen pressures, i.e. at 1 mTorr, 10 mTorr and 100 mTorr, varying the current from 0 to 850 mTorr while scanning the cathode voltage. Films were deposited by 10 min, after a 5 min pre-sputtering cleaning. The growth conditions in the groups of prepared samples are shown in the Table 1 The groups of samples were planned to assess the effects of substrate temperature,

Table1. Growth conditions of the groups of prepared samples.

Parameter	Groups			
	G1	G2	G3	G4
Pressure (mTorr)	1, 10,100	100	100	10-100
Current (mA)	600	600	200-850	600
Temperature (°C)	500	200-500	500	500

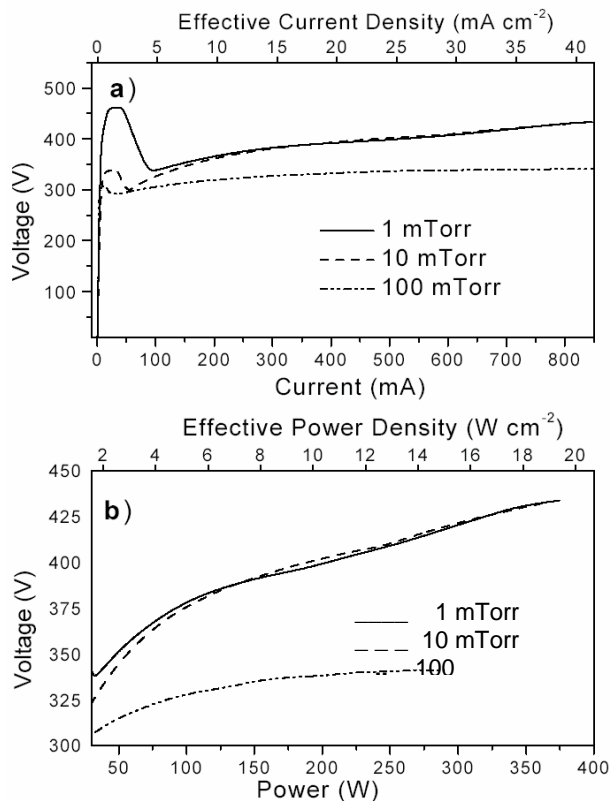


Figure 1. Electrical behavior of the oxygen plasma. a) Current-voltage curves. b) Power-voltage curves.

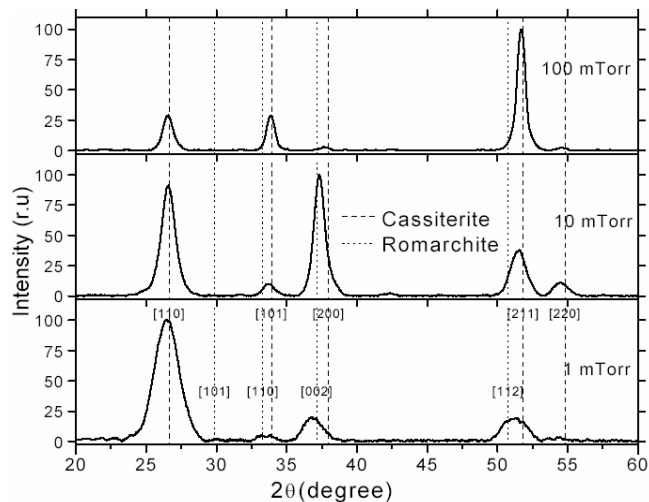


Figure 2. Normalized x-ray diffractograms of the G1 group samples: I = 600 mA, T = 500°C.

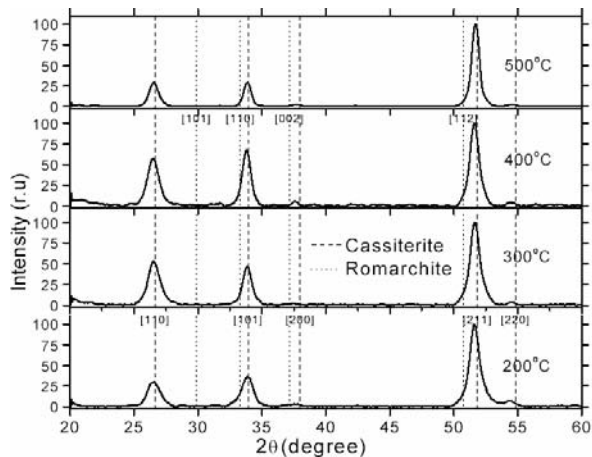


Figure 3. Normalized x-ray diffractograms of the Group 2 samples. I = 600 mA, 100 mTorr O₂

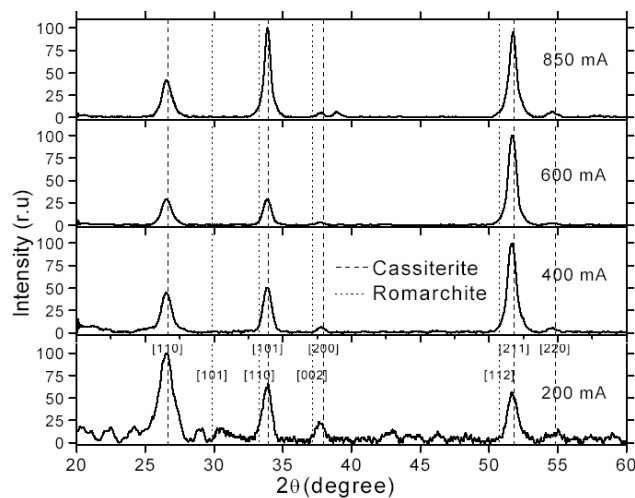


Figure 4. Normalized x-ray diffractograms of the Group 3 samples, 100 mTorr O₂, 500°C.

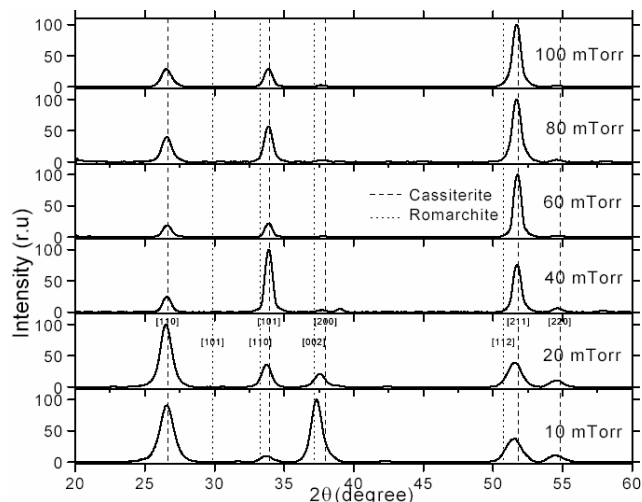


Figure 5. Normalized diffractograms of the Group 4 samples. I: 600 mA, temperature 500°C.

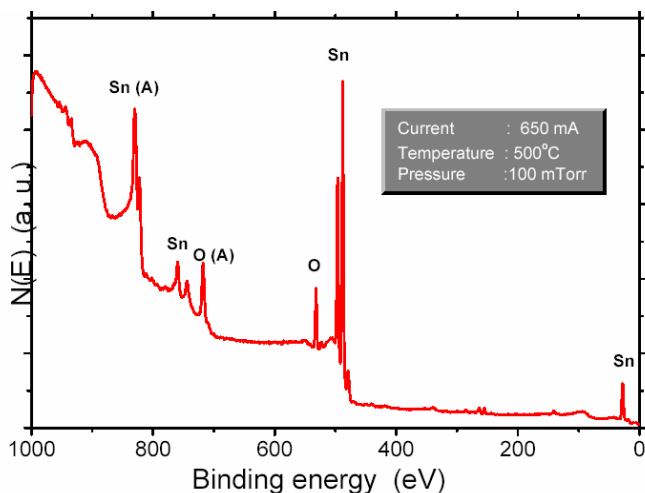


Figure 6. Typical XPS general scan of a sample prepared at 650 mA, substrate temperature 500°C, pressure 100 mTorr.

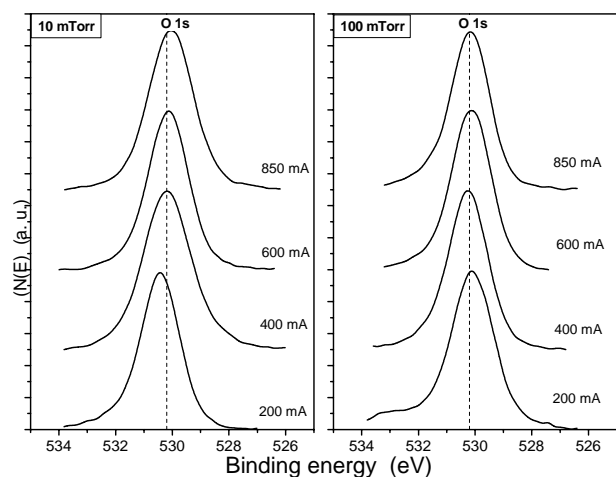


Figure 7. High resolution scan at O 1s window. Current 200-850 mA, temperature 500°C, pressure 10 and 100 mTorr.

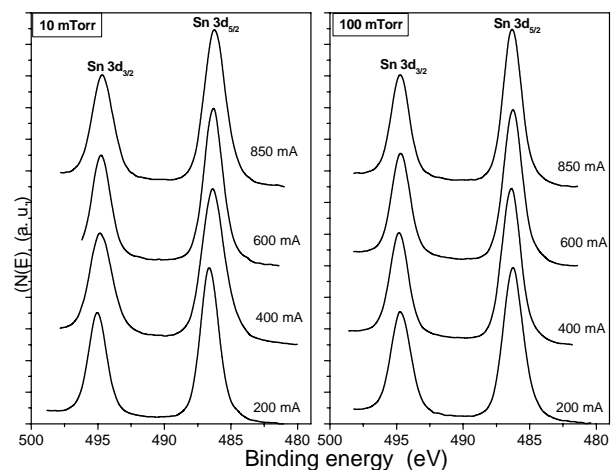


Figure 8. High resolution scan at Sn 3d_{5/2} window. Current 200-850 mA, temperature 500°C, pressure 10 and 100 mTorr.

plasma current and oxygen pressure in the composition and crystalline orientation of the films.

X-ray diffraction was performed in a Siemens D5000 diffractometer with Cu K_α radiation. The grazing incidence geometry was used, with the detector pivoting around the goniometer circle, with a beam incidence angle over the sample of 3°. Diffraction scans at 0.025° steps were acquired with a step time of 10 s in 2θ interval from 20 to 60 degree. The diffractograms were smoothed, K_{α2} and background stripped using the diffractometer software and they were normalized to their maximum intensity values to be deconvoluted into their respective SnO₂ and SnO contributions as described in a previous work [6] by using the 2θ positions from the powder patterns of cassiterite for SnO₂ (PDF 41-1445) and romarchite for SnO (PDF 06-0395).

The degree of preferred orientation in the films was calculated from the SnO₂ peak intensities using the method of Harris [7] for polycrystalline fiber texture analysis:

$$p[abc] = N \left(\frac{I[abc]}{I_o[abc]} \right) \left(\sum \frac{I[hkl]}{I_o[hkl]} \right)^{-1}$$

where N is the number of peaks in the region considered, I[a b c] is the measured intensity of the peak [a,b,c] and I_o[a,b,c] is the relative intensity from a powder reference.

XPS analysis was performed in a Perkin-Elmer PHI 560/ESCA-SAM system, equipped with a double-pass cylindrical mirror analyzer, with a base pressure of 2×10⁻⁹ Torr. Argon ion sputtering for cleaning was performed with 4 keV energy ions and 0.36 μA/cm² current beam. For the XPS analyses, samples were excited with 1253.6 eV energy MgK_α x-rays. The spectrometer was calibrated using the Cu 2p_{3/2} (932.4 eV) and Cu 3p_{3/2} (74.9 eV) lines. Binding energy calibration was based on C 1s at 284.6 eV.

3. Results and discussions

3.1 Discharge diagnosis

The electrical behavior of the oxygen plasma at different pressures is shown in Figure 1. The I-V curves presented in the Figure 1a) have the typical glow discharge behaviour of the I-V curves obtained when the DC source is used in the constant current mode and the plasma current is increased. The corresponding Power-Voltage curves are shown in Figure 1b). As can be observed, the cathode voltage increases monotonically as power does, without abrupt voltage transitions characteristic of metal-to-compound transitions in the target, as observed in a previous work [5]. It is important to point out that the eroded cathode ring zone always visually looked clean and brilliant in these conditions, indicating that no target poisoning and therefore no metal-to-compound transitions in the plasma voltage would take place. However the inner

Table 2. Cassiterite orientation parameter and relative SnO₂ concentration as function of the substrate temperature.

Temperature °C	Texture parameter			Relative Cassiterite Concentration (%)	
	[110]	[101]	[211]	[101]	[211]
200	0.46	0.38	2.55	43	100
300	0.77	0.92	2.57	100	100
400	0.56	0.89	1.71	100	100
500	0.44	0.61	2.58	100	100

I = 600 mA P = 100 mTorr

and outer ring zones were covered by tin oxides, as confirmed by powder x-ray diffraction of a target fragment. As observed from the Figure 1b), when using oxygen pressures of 1 and 10 mTorr, the cathode voltages increases continuously from about 325 to 450 V, while when using 100 mTorr the cathode voltage increases, but tends to stabilize about 325-350 V. In previous work it has been shown that Sn⁺⁴ is obtained when the cathode voltage is below 350 V [5,6]; up to 350 V a mixture of Sn²⁺ and Sn⁴⁺ is expected. In the following experiments an O₂ pressure of 100 mTorr was used as top value. Higher O₂ pressures were not used as the discharge needs higher currents to ignite and arcing was observed.

3.2 Structural characterization

The x-ray diffractograms of the G1 group, prepared at O₂ pressures of 1, 10 and 100 mTorr and at substrate temperature of 500 °C are shown in Figure 2. The first peak, centered at around 26.6°, corresponds to the [110] cassiterite reflection [8]. The second peak, at around 33.6-33.8° lies between the cassiterite [101] and the [110] romarchite reflections [8]. The third peak at around 37° contains the romarchite [002] and the [200] cassiterite reflections. The fourth peak centered near 51° corresponds to the romarchite [112] and the cassiterite [211] reflections respectively. The last peak centered near 54° corresponds to the [220] cassiterite reflection.

From the figure can be observed that the films grown at the lowest O₂ pressure are oriented in the [110] cassiterite reflection. The peaks are wide, indicating low crystallinity and a mixture of SnO and SnO₂ is present as expected from the mentioned above. Similar structures had been obtained when using a 50/50-Ar/O₂ discharge [5]. When the O₂ pressure is increased, an increase of relative intensity of the third and the fourth peaks and a corresponding reduction of their width is observed, indicating a change in the film crystalline orientation, as well as a enhancing in the crystalline quality of the films. It

can also be noticed that the position of the fourth peak moves towards the [211] cassiterite position with the O₂ pressure increment, and at 100 mTorr the peak position is completely outside the [112] romarchite reflection, indicating the romarchite concentration falls.

In the Figure 3 are presented the x-ray diffractograms from the G2 group, where the substrate temperature was varied from 200 °C to 500 °C, the plasma current was 600 mA and the O₂ pressure was set at 100 mTorr. It can be observed that the peak structure is very similar for all the temperatures used, all the samples have the preferred [211] orientation and not significant influence of the substrate temperature can be appreciated, except for small changes in the relative peak intensities. In the Table 2 are summarized the structural features, and can be mentioned that the cassiterite orientation parameter is slightly different from sample to sample, presumably because the presence of SnO, and that the 200°C sample appears to be oxygen deficient, probably because at this substrate temperature the films does not oxidize completely at the substrate. From these results, the better choice to get stoichiometric SnO₂ is 500°C, so this temperature was taken for the following experiments.

The x-ray diffractograms of the samples prepared at different plasma currents, when the O₂ pressure and substrate temperature were fixed are shown at the Figure 4. A noisy scan can be seen at 200 mA with the most intense peak at the [110] cassiterite reflection position. When the current is incremented, the intensity of this peak decreases, while the [211] cassiterite reflection increases. The peak widths look very similar, indicating that samples of similar crystalline quality are obtained. Table 3 resumes the cassiterite orientation parameter and the relative concentration as function of current of the G3 group. In the Table 3 can be appreciated that the [211] texture is maximum at 600 mA. At 850 mA the [101] and [211]

textures are similar, suggesting that a new change in films orientation would take place at higher currents. However, it was not possible to grow at higher currents

Table 3. Cassiterite orientation parameter and relative SnO₂ concentration as function of the cathode current.

Current mA	Texture Parameter			Relative Cassiterite Concentration (%)	
	[110]	[101]	[211]	[101]	[211]
200	0.55	0.42	0.54	62	96.
400	0.50	0.76	1.93	96	95
600	0.44	0.61	2.58	100	100
850	0.41	1.30	1.60	100	100

T = 500 °C P = 100 mTorr

because the presence of arcs. On the other hand, from the Table 3 can be seen that stoichiometric films were achieved at 600 mA. Then, to avoid the arcing problems, 600 mA was chosen as plasma current for the following experiments.

In the Figure 5 are presented the x-ray diffractograms of the samples prepared when the oxygen pressure was varied (G4 group). The diffractogram of the film growth at 10 mTorr presents wide peaks, very similar to those obtained in a previous work [5]. The texture appears to be [200], but it can be doubtful because the presence of the [002] reflection of the SnO. The film prepared at 20 mTorr exhibit [110] texture, and as the oxygen pressure increases, the texture shifts towards to the [211] plane. The texture evolution is better appreciated in the Table 4, where the cassiterite orientation parameter and the relative SnO₂ concentration as function of the oxygen pressure are presented. From this table, the highest [211] orientation occurs at 60 mTorr. On the other side, the SnO₂ concentration increases with the O₂ pressure, as expected from the literature [9]. The highest concentration of SnO₂ is then obtained at 100 mTorr.

3.3 XPS Analysis.

General XPS analysis was performed until 1000 eV in the films prepared at 10 mTorr and 100 mTorr, at substrate temperatures of 500°C and plasma current of 600 mA. A typical scan is shown in Figure 6, where tin and oxygen XPS and Auger peaks can be observed. A small tip corresponding to the Cu at 932 eV was observed in some spectra and can be attributed to cathode holder contamination. To judge the nature of the chemical bonding, high resolution scans at the O 1s and Sn 3d windows energy were carried out. Typical scans for the samples prepared at 10 mTorr and 100 mTorr respectively are shown in Figures 7-8. For all the cases, as observed in

the figures, the position (486.2 ± 0.2 eV) and shape of the Sn 3d_{5/2} peak indicates that SnO₂ compound is formed. This is also confirmed by the position and shape of the O1s peak, at 530.2 ± 0.2 eV. The Sn²⁺ and the Sn⁴⁺ contributions can not be separated with the available XPS resolution.

Conclusions

SnO_{2-x} films were obtained by DC reactive sputtering from a metallic target in a O₂ plasma using the constant current mode. The analysis of the discharge indicates that no abrupt transitions related with metal-to-compound mode switching are present, enabling a better deposition control. Films prepared with increasing O₂ pressure increase their SnO₂ fraction, being stoichiometric at 100 mTorr and change their preferential orientation from [110] to [211], having the maximum [211] texture at 60 mTorr O₂. When the substrate temperature is increased from 200°C to 500°C the texture is almost unchanged, but at 200°C the films are oxygen-deficient. When the plasma current is varied from 200 mA to 600 mA the texture changes from [110] to [211], having the maximum [211] texture at 600 mA, where stoichiometric SnO₂ films are obtained. Beyond this current the [101] direction increases, suggesting a new texture change, but higher plasma currents can not be used because arcing. The results suggest that the [110] texture is characteristic of oxygen deficient films prepared at soft deposition conditions i.e. low plasma currents and low substrate temperature, while [211] textured and stoichiometric SnO₂ films are obtained only at relatively hard conditions, such as high plasma current, high substrate temperature and high O₂ pressures. This difficulty to prepare stoichiometric SnO₂ films has been previously demonstrated in our previous work and attributed to the reluctance of the Sn to get into its Sn⁴⁺ form. Further work

Table 4. Cassiterite orientation parameter and relative SnO₂ concentration as function of the oxygen pressure.

Oxygen Pressure		Texture Parameter			Relative Cassiterite Concentration (%)	
mTorr	[110]	[101]	[211]	[101]	[211]	
10	0.91	0.05	0.52	52	45	
20	1.03	0.34	0.38	36	58	
40	0.26	1.46	1.45	97	100	
60	0.30	1.24	2.88	96	98	
80	0.55	1.06	2.40	97	100	
100	0.44	0.61	2.58	100	100	

T = 500 °C I = 600 mA

on the optical and structural properties of these films is actually on run.

Acknowledgements

The authors would acknowledge to V. Rejón, O. Gómez, W. Cauich and R. Sánchez for the technical support and to L. Pinelo for secretarial assistance. A. Martel and F. Caballero-Briones acknowledge New Materials Group at CINVESTAV-IPN Unidad Mérida for the research facilities. This work was partially supported by CONACYT under projects number 38667-E and 38493-U, and by CGPI-IPN and COFAA-IPN under EDI and SIBE grants.

References

- [1] M. Di Giulio, D. Manno, G. Micocci, R. Rella, P. Siciliano and A. Tepore, *Sol. Energy Mat. Sol. Cells* **31**, 235 (1993).
- [2] D. Bonnet & M. Harr, *Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*. 6-10 July, Vienna, Austria, (1998). Edited by J. Schmid; H.A. Ossenbrink; P. Helm; E.D. Dunlop. Report EUR 18656 Energy Joint Research Center European Commission. p. 397.
- [3] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, (1984)
- [4] B.E. McCandless, L.V. Moulton and R.W. Birkmire *Progress in photovoltaics: Research and Applications*, **5**, 249 (1997).
- [5] A. Martel, F. Caballero-Briones, J. Fandiño, R. Castro-Rodríguez, P. Bartolo-Pérez, A. Zapata-Navarro, M. Zapata-Torres and J. L. Peña. *Surface Coatings Technology*. **122**,. 136 (1999).
- [6] A. Martel, F. Caballero-Briones, A. Iribarren, R. Castro-Rodríguez, P. Bartolo-Pérez and J. L. Peña *Surface Coatings Technology*, **148**,103 (2001).
- [7] G. B. Harris, *Philos. Mag.*, **43**, 133 (1952).
- [8] ICCD, JCPDS-International Center for Diffraction Data. PDF 41-1445 (SnO₂) and PDF 06-0395 (SnO).
- [9] R. Snyders, M. Wautelet, R. Gouttebaron, J.P. Dauchot, M.Hecq, *Thin Solid Films* **423**, 125 (2003).