

On the Wavy Behaviour of Grain Growth in Sprayed Thin Films

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Abstract: Tin oxide films were prepared by spray pyrolysis technique with different deposition times (60 - 240 s) while the substrate temperature (773 K), the deposition rate (0.22 ml/s) and the concentration (0.2 M) of tin chloride (hydrous) solution were kept constant. Variation of grain size with film thickness (deposition time) is found useful to model a mechanism for film growth. Depending on the mode of layer growth followed by 3D crystallite growth (Stranski and Krastaniv, SK) as well as on the variation of the standard deviation of pole densities, a proposed model of growth mechanism of thin film was suggested. Consider the fact that "what you see depends on how you look", a wavy nature was suggested for the variation of the mean grain size with the film thickness using XRD analysis and SEM/AFM images. The discrepancy between the present result and others was understood on the basis of either the definition of the grain size measured by the different techniques (XRD or SEM) or the proposed wavy behaviour of the grain growth with the film thickness. Interpretation of the results of the grain size variation that extracted from the combined use of XRD and SEM/AFM can provide useful information about the growth mechanism.

Keywords: Crystallite size, Growth mechanism, XRD/SEM/AFM, Thin film, Spray pyrolysis, SnO₂

I. Introduction

The wavy behaviour seems to be a character of the nature. Concerning the variation of specific property with certain parameter, plenty of the observed data in literatures show either a wavy nature or they may exhibit maximum (dome shape) or minimum (well shape). The wavy nature of property change of many oxides and of plastic deformation of solids has been encountered before [1, 2]. The degree of deformation upon mechanical activation was expected to change the characteristics of solids according to a continuous function, e.g., lattice distortion and grain growth after heat treatment. However, when increasing the treatment, activation is followed by passivation, lattice distortion by recovery and increase of internal energy by release of energy. Neutron irradiation of solids showed radiation damage followed by saturation and further annihilation [3]. On the other hand, although the total contribution of the defects and the microstructure features (grain size and internal strain) show normal monotonic variation with film thickness [4], the mobility, conductivity and transverse magneto-resistance of bismuth films exhibit an oscillatory behaviour in the same range of thickness [5].

Considering the interpretation of the mechanism of film growth, ambiguities are not uncommon. Depending on thermodynamic criteria (surface energy criteria), the growth mechanism can be classified to three principal modes [6], which were named after their original investigators: 1- layer-by-layer (Frank-van der Merwe, FM), 2- three dimensions (3D) crystallite growth (Volmer and Weber, VW) and 3- layer growth (up to one or a few layers) followed by 3D crystallite growth (Stranski and Krastanov, SK). However, evidences were found for additional two modes [7]:

1-simultaneous multilayer growth (SM) and 3-monolayer plus simultaneous multilayer growth (MSM). Between the different modes, one can envisage many possibilities depending on the degree of surface mobility and how the mobility varies with coverage. There is a difference between the mobility of the condensate on the substrate and that on itself. The mobility on the bare substrate is considered to be rapid enough to produce continuous growth of the first layer as in FM mode [6]. Thereafter, the mobility drops and the growth mode changes subsequently. This difference would lead to expect more than one mode during film growth from the first layer on the bare substrate to the subsequent layers.

The present work aims to probe the growth mechanism of SnO₂ thin films. Variation of the crystallite size with film thickness (deposition time) will be investigated in particular. The different values of grain size that are measured by different techniques (XRD or SEM/AFM) will be considered.

II. Experimental and Computation

SnO₂ thin films were prepared by spray pyrolysis technique onto glass substrate using tin chloride (hydrous) solution of concentration (molarity) $M = 0.2$ mol and substrate temperature = 773 K. These two preparative parameters were kept constant with continuous spraying regime while the spraying time was varied from 1 to 4 min. The film thickness was measured by stylus instrument [8] calibrated by a standard sample with known thickness measured by optical interferometry method [9, 10]. The film thickness increases with spraying time and a continuous grow with the deposition time was observed.

The X-ray diffractograms of the prepared films were obtained by Diano $\theta/2\theta$ diffractometer (type XRD 8000). Fe-filtered Co-K α radiation at 50 kV and 30 mA was used. A 2θ -range from 20 to 80 $^\circ$, which covers the main diffraction peaks of SnO₂, was scanned with step of 0.1 $^\circ$ (2θ) and counting time of 3 s per step. Diffraction patterns of sufficient resolution were obtained with no peak overlap and high peak-to-noise (background) ratio that are promising conditions for line profile analysis.

Microstructural characteristics (crystallographic texture and crystallite size) were determined from the profile fitting of experimental X-ray diffraction patterns by WinFit program [11]. The fitted data gives ideal peaks for profile analysis, which are completely noise-free and background-corrected. Thus, the peak parameters (integrated intensity, peak position as well as FWHM and integral breadth) were determined analytically from the function's equation rather than by step-wise integration of the original curve [12]. The crystallite size was determined using Delhez et al., [11,13].

The pole density, P_{hkl} , was defined according the Harris texture index [14] given as:

$$P_{hkl} = \frac{I_{hkl}}{I_{r,hkl}} / \frac{1}{n} \sum \frac{I_{hkl}}{I_{r,hkl}}$$

where: n is the number of reflections,

I_{hkl} is the observed integrated intensity of (hkl) diffraction peak and

$I_{r,hkl}$ is the intensity of (hkl) diffraction peak of randomly oriented sample.

The standard deviation (σ_P) [15, 16] of the pole density was calculated from P_{hkl} values and their average \bar{P} using the following formulae:

$$\sigma_p = \sqrt{\frac{1}{n} \sum_{i=1}^n (P_{hkl} - \bar{P})^2}$$

A computer program was written in FORTRAN code to calculate the pole density and the standard deviation depending on the above formulae.

III. Result and Discussion.

The X-ray diffractograms of the deposited SnO₂ films as a function of spraying time are shown in Figure 1 with high peak-to-noise ratio and good resolution without peak overlap. The simulated diffraction patterns of SnO₂ are also given for comparison as a standard sample. All films are polycrystalline and the main peaks of SnO₂ with the tetragonal Rutile structure are observed. The crystallographic preferred orientation was identified using the values of pole density, P_{hkl} , that are given in Table (1). It was found that P_{200} is larger than unity within the investigated deposition time but the value decreases as the deposition time increases. On the other hand, P_{211} is less than unity at deposition time ≤ 2 min but becomes higher than P_{200} at deposition time ≥ 3 min. In any case the angle between the two plans $\approx 35^\circ$, which is less than between the other plans. Thus, it can be considered that the (200) plan is mainly parallel to the film surface.

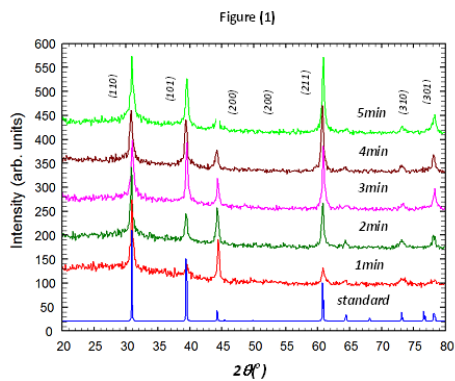


Figure 1: X-ray diffraction pattern of SnO₂ films prepared with different spray time simulated and diffraction patterns of the standard sample.

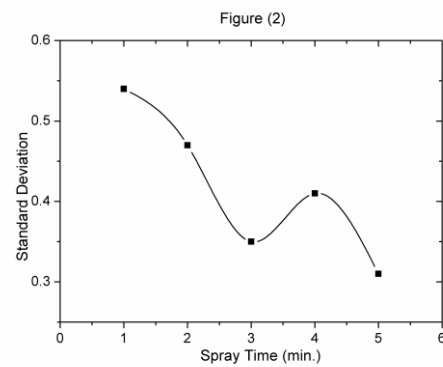


Figure 2: Variation of standard deviation with spray time.

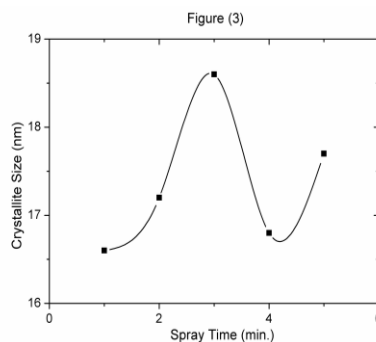


Figure 3: Variation of crystallite size with spray time.

Table 1: The pole density, Phkl, at different deposition times.

Time (min)	(hkl)				
	(110)	(101)	(200)	(211)	(220)
1	0.81	0.31	1.91	0.52	0.46
2	0.63	0.41	1.74	0.88	0.58
3	0.85	0.67	1.06	1.16	1.22
4	0.64	0.81	1.03	1.47	0.59
5	0.78	0.71	1.04	1.48	0.54

The change of the standard deviation of the pole density, σ_P , is depicted in Figure 2. Values of σ_P started at high value then decrease with the deposition time up to 3 min followed by an increase. This variation will be considered below in the discussion of the proposed mechanism.

In any case, the measured crystallite size by XRD analysis is in the normal direction to the reflecting plan, i.e., perpendicular to the substrate surface. In the present case, it was considered above from the quantitative results (Phkl) of crystallographic preferred orientation that mainly the [100] direction is normal to the film, So, it was found better to measure the crystallite size from XRD line profile analysis of the (200) diffraction peak.

The size variation with deposition time is depicted in Figure (3). The crystallite size increases up to deposition time of 3 min followed by a decrease, thus, a wavy behaviour of the variation is observed. Surface (top view) SEM/AFM and cross-section (side view) SEM images are also given in Figure (4). At long deposition time (4 min), it is clear that small grins are deposited on large ones. On the other hand, from the cross-section images, the columnar structure of the films is verified. The observed variation of crystallite size is in contrast with the results given by Jadsadapattarakul et al. [17]; that the mean grain size increases as the deposition time increases. However, they [17] found an increase in the mean grain size up to certain deposition time then no further increase was observed at longer time. For the first glance, it seems that this is contradiction with the present results, but it is not if there results are considered as the first half of the wave-nature observed in Fig. (3). This will be described based on the proposed behaviour of growth mechanism given below and the corresponding variation of grain size with deposition time (film thickness).

In fact, what you get depends on how you see and what you see depends on how you look. So, one has to ask, what do the different investigated techniques see? It is worth mentioning that the measured crystallite size from XRD profile analysis using Bragg-Brentano focusing geometry is, by definition, the average value in the normal direction to the reflection plane, i.e., in the direction perpendicular to the substrate (z-direction). However, surface SEM/AFM images depict the two dimensions (x- and y-direction) parallel to the substrate. Thus, XRD recognizes the variation of the grain size in z-direction (Figure 5a) but not the changes in x- and y-direction (Figure 5b) and vice versa in case of surface SEM/AFM images. Therefore, one should carefully interpret and discuss the extracted information; one technique (XRD) shows increase in the values of grain size in certain period of time (film thickness) or under certain deposition conditions while the other (SEM/AFM) does not detect this variation. Therefore, contradictions in the proposed mechanisms are not impossible. However, there are attempts to determine the thin film growth mechanisms by a combined use of spectroscopic techniques [18]. Thus, a combined use of XRD on one hand and SEM/AFM on the other hand can give useful information about the growth mechanism under specific deposition conditions.

There are different growth models for SnO₂ thin film formed by spray pyrolysis method [17, 18], which are proposed depending on the variable parameter and the type of the substrate as well as the measured technique. Murakami et al. [18] has describe his proposed model and growth mechanism according to the relation between surface roughness and film thickness considering a continuous increase of the grain size with the film growth. The question is to which extend this increase in size will continue?

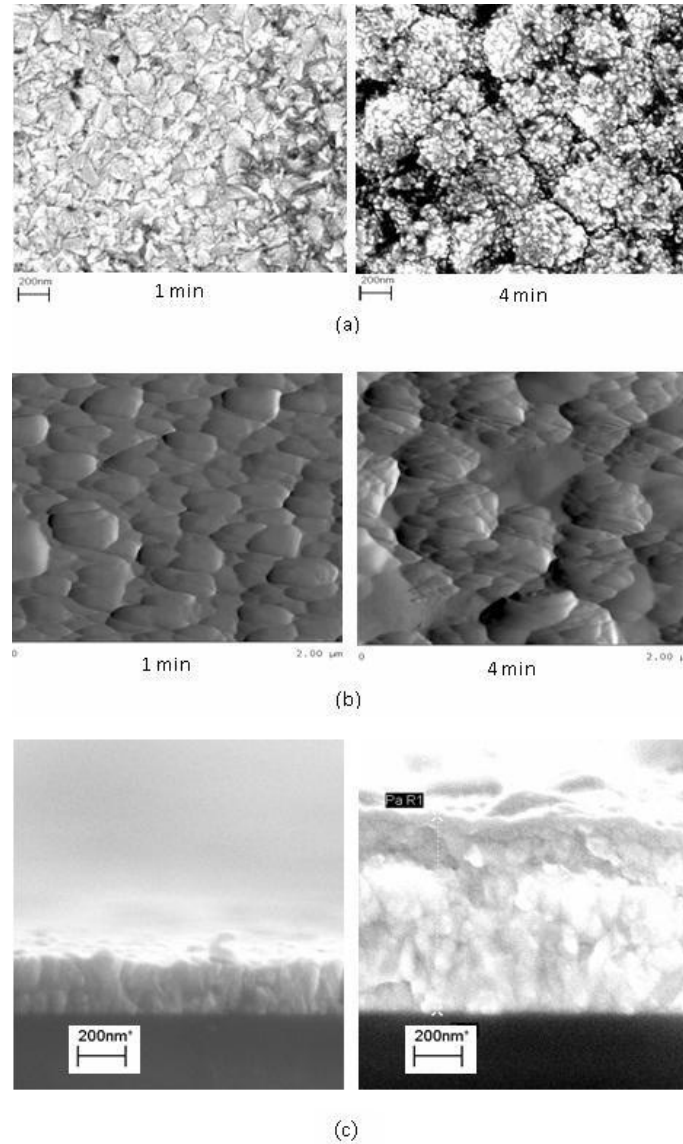


Figure 4

Figure 4: a) Top view SEM, b) Top view AFM and c) Side view SEM images at spray time of 1 and 4 min.

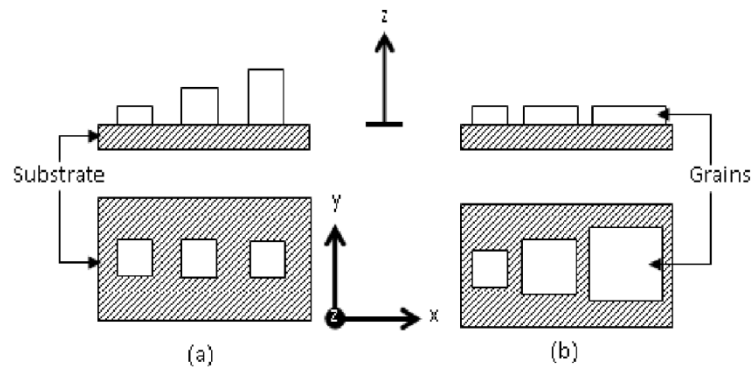


Figure (5)

Figure 5: Two schematic projections of the deposited grains on the substrate surface: a) Growth normal to substrate in the z -direction and b) Growth parallel to substrate in x - y plan.

On the other hand, Jadsadapattarakul et al. [17] suggested their growth mechanism on the basis of the relation between the grain size and spray time (film thickness). It was concluded that the film grows on the substrate surface seems to be derived from a rapid nucleation of new crystallite on the existing one, rather than grain growth of the primary nuclei. Therefore, at a critical time, when a new crystallite is nucleated, the mean value of the crystallite size determined by XRD profile analysis has to show an abrupt decrease in the mean value of grain size. Then with further increase in the spray time the average crystallite size increase again up to the time at which a new crystallite is nucleated and so on. This film growth mechanism does not result in continuous increase in the observed grain size. This can be realized by considering the wave behaviour of grain growth with the spray time (film thickness) as given by the proposed model; sketched in Figure 6.

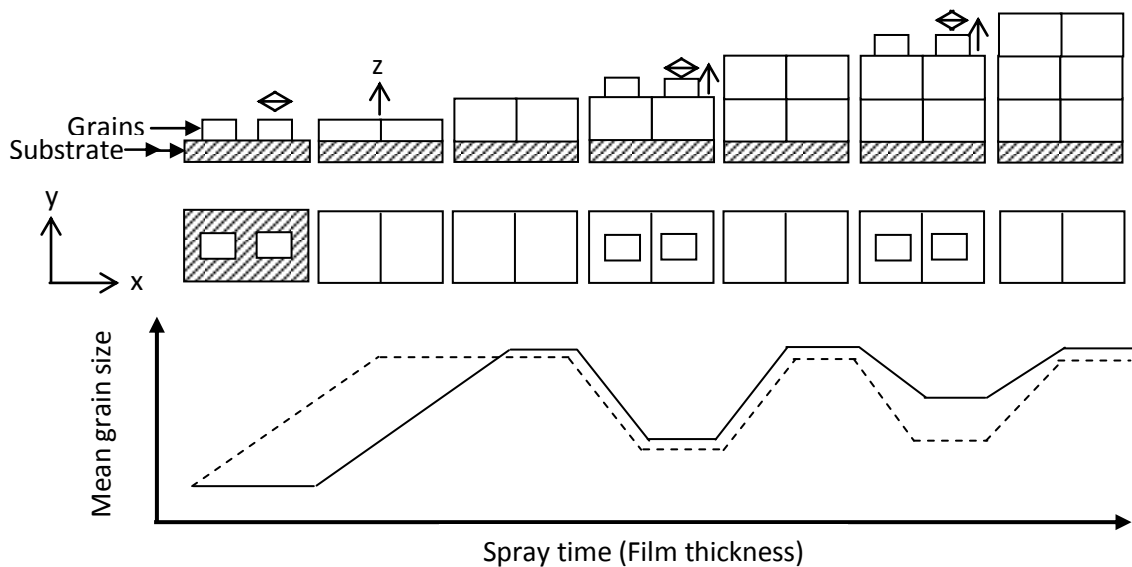


Figure 6: Proposed model of film growth: a) Sketch and b) Corresponding variation of grain size with film thickness (dotted line: mean size parallel to the substrate from SEM/AFM and solid line: mean size perpendicular to the substrate from XRD).

Based on the above suggestions and the columnar structure of the films as well as depending on the mode of layer growth followed by 3D crystallite growth (SK) [6] and the variation of the standard deviation [15, 16], a proposed model for thin film growth mechanism based on wavy behaviour of grain size variation with thickness (Figure 6a) is given as:

- 1- Nucleation of isolated nuclei of oriented crystallites are formed on the bar substrate with adsorption-desorption and lateral growth of nuclei by surface diffusion of the impinging flux (this results in high σ_P value).
- 2- Nucleation (random orientation) and grow of the nucleated crystallites in two dimensions parallel to the substrate (x- and y-directions) until the deposited layer is completely formed (continuous film) through the coalescence among the neighboring grains (decrease of σ_P value).
- 3- The crystallites start to grow in the third dimension normal to the substrate (z-direction) up to a limited size before the next layer starts to grow.
- 4- Oriented overgrowth by preferred nucleation of new crystallite on the existing growing surface, rather than the continuous growth of the existing crystallite. This results in an abrupt decrease in the mean value of the grain size and an increase in the number of grains along the preferred direction (increase of σ_P value).
- 5- Growth of few monolayers according to steps 2, 3 and 4.
- 6- 3D crystallite growth.

Thus, the first layer of the deposited materials is completely formed and grows to certain thickness before the subsequent layer starts to grow. A change in the observed mean grain size would occur at the completion of each monolayer. The SEM may see an increase in the grain size before XRD see. However, it has to be reminded that, in case of XRD, as the film thickness increases the amplitude of oscillation decreases. On the other hand, in case of SEM/AFM the observed values of the mean size may alternate about a constant value. This wave behaviour is illustrated in the graph given in Figure 6b.

The proposed model for thin film growth mechanism of wavy behaviour for variation of grain size with thickness can explain what it looks as contradiction between the results of crystallite size versus film thickness (spray time) in different literatures, e.g., Jadsadapattarakul et al. [17]. Inspection of Figure 6 shows two possibilities:

- A) Using different techniques for crystallite size investigation in the same film thickness range: in (t1 - t2) range, no variation in the measured values of grain size in case of XRD while increase in case of SEM and vice versa in (t2 - t3) range.
- B) Using the same technique but in different film thickness ranges: XRD; increase of size in (t2-t3) range while decrease in (t3-t4) range and SEM/AFM; increase of size in (t1- t2) range while decrease in (t3 - t4) range.

Finally, one can decide that, as the attempts to determine the thin film growth mechanisms by a combined use of spectroscopic techniques [18], a combined use of XRD on one hand and SEM/AFM on the other hand can give useful information about the growth mechanism under specific deposition conditions.

IV. Conclusions

The definition of grain size measured from different techniques should be considered when correlated with any preparation condition. Different thin film growth mechanism can be proposed depending on the criteria of morphology and structure characterization. Depending on the mode of layer growth (one or few layers) followed by 3D crystallite growth (SK) as well as on the variation of the standard deviation of pole densities, a proposed model of growth mechanism of thin film was proposed. The corresponding variation of the mean grain size by XRD and SEM/AFM led to suggest a wavy nature for the variation mean grain

size with the film thickness. Combined use of XRD and SEM/AFM is promising to identify the film growth mechanism.

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