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Microstructural study of SnO_2-based nanoparticles by X-ray diffractometry

Hossein Mahmoudi Chenari [a,*], Florentino Sánchez-Bajo [b]

[a] Department of Physics, Faculty of Science, University of Guilan, Namjoo Ave. P.O. Box 41335-1914, Rasht, Iran
[b] Departamento de Física Aplicada, Escuela de Ingenierías Industriales, Universidad de Extremadura, Avda de Elvas s/n. 06006, Badajoz, Spain

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ABSTRACT

Two tin dioxide samples undergone to different thermal treatments have been studied by X-ray diffraction profile analysis, using the modified Williamson-Hall and Warren-Averbach methods. Assuming $<10\text{-}1>\{101\}$ slip system and screw dislocations, the area and volume-weighted average particle sizes have been evaluated for both samples. The assumed log-normal particle size distribution has been calculated from these values. This distribution is in good agreement with the derived from SEM micrographs for the sample with lower particle size. Values of the dislocation densities were estimated around 10^{14} m^{-2} for the sample with lower grain size and around 10^{12} m^{-2} for the sample with greater grain size. The difference in the results for the analyzed samples could be explained from the difference between the treatments after synthesis.

1. Introduction

Nanostructured materials are of great interest in numerous applications due to their unique properties. In this way, tin dioxide (SnO_2), an *n*-type semiconductor oxide with a wide band gap (3.7 eV), has been extensively studied because of its very attractive properties and applications such as gas sensor [1–3], in optoelectronics [4,5], in electrochemical applications [6], etc. These properties are highly dependent on the microstructural features of the material such as the dislocation density and the dislocation slip system involved in the plastic deformation. Therefore, it is very important to understand the deformation mechanism in terms of microstructural parameters in order to predict the behavior of the nanomaterial. In regard to this, X-ray powder diffractometry (hereafter, XRD) is a powerful technique to perform the microstructural characterization of the materials that it has been widely used [7–9]. It is well known that XRD patterns are broadened due to the smallness of crystallites and the presence of strains (lattice distortion). Different methods based on the study of the shape and width of the diffraction peaks, measured by means of the full width at half maximum, the integral breadth and the Fourier coefficients of the profile, allow the separation of the above effects [10]. Note that, in many cases, XRD analyses provides only mean values of the crystallite size (or diffraction domain size) and microstrains –usually, by means of the root-mean squared strain, or r.m.s. strain-. Although the mean crystallite size and r.m.s. strain are important microstructural parameters, sometimes a more detailed microstructural information such as the measurement of the crystallite size distribution is needed in order to explain the behavior of the material. Note that, although microscopy techniques (as TEM or SEM), also can provide particle size distributions, these have a local character and an exhaustive global analysis is time-consuming as compared with the determination of crystallite size distributions by XRD. On the other hand, with respect to the lattice distortion, it has been shown that the strain anisotropy in XRD peaks can be well accounted using dislocation models for the root-mean square strain that depend on the contrast factors of dislocations, related to the nature and slip system of dislocations present in the crystal [11]. In regard to this, recently, two classical procedures extensively employed in XRD analysis, the Williamson–Hall plot [12] and the so-called Warren-Averbach method [13] have been modified in order to include the effects of dislocations in the strain term of the model. The results of these modified methods can be used altogether with the aim to determine the particle size distribution – considered *hkl* independent- and the dislocation density.

The aim of the present study is the characterization of the microstructure properties of nanoparticle SnO_2 samples by means of both the modified Williamson-Hall and Warren-Averbach procedures, assuming a dislocation model of the root-mean square strain for the modeling of the strain-broadened profiles. In the next sections we present, firstly, the experimental procedure and

* Corresponding author.
E-mail addresses: mahmoudi_hossein@guilan.ac.ir, h.mahmoudiph@gmail.com (H.M. Chenari).

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then, the results of the XRD analysis. Finally, these results are discussed and the conclusions presented.

2. Experimental procedure

SnO_2 nanoparticles were synthesized by a simple sol-gel method; the details of the procedure are described elsewhere [14]. Briefly, the synthesis of SnO_2 was performed from $SnCl_4 \cdot 4H_2O$: n-propanol : i-propanol : H_2O with different molar ratios, but using a ratio of n-propanol/i-propanol of 2/1. All reagents were of analytical grade without further purification. The SnO_2 powders thus obtained were processed in different ways. In regard to this, the sample named Sn-1 in that paper, was calcined at 600 °C during one hour period, whereas a second sol, named Sn-2, was prepared at a calcination temperature of 1200 °C for two hours. Subsequently, the obtained specimens were characterized at room temperature by XRD with a Philips X'Pert diffractometer using CuKα radiation (λ=1.5418 Å) in step-scanning mode. Measurements were taken under beam-acceleration conditions of 40 kV/35 mA. The samples were scanned between 15.015° and 74.985°(2θ) with a step of 0.03° and a counting time of 68.955 s

The above two samples described in the paper of [14] -hereafter, A, for Sn-1, and B, for Sn-2-, were selected in order to characterize them microstructurally. These samples have been also analyzed from the point of view of their electrical properties [15] and by means of X-ray photoelectron spectroscopy [16], in this case using only the sample A.

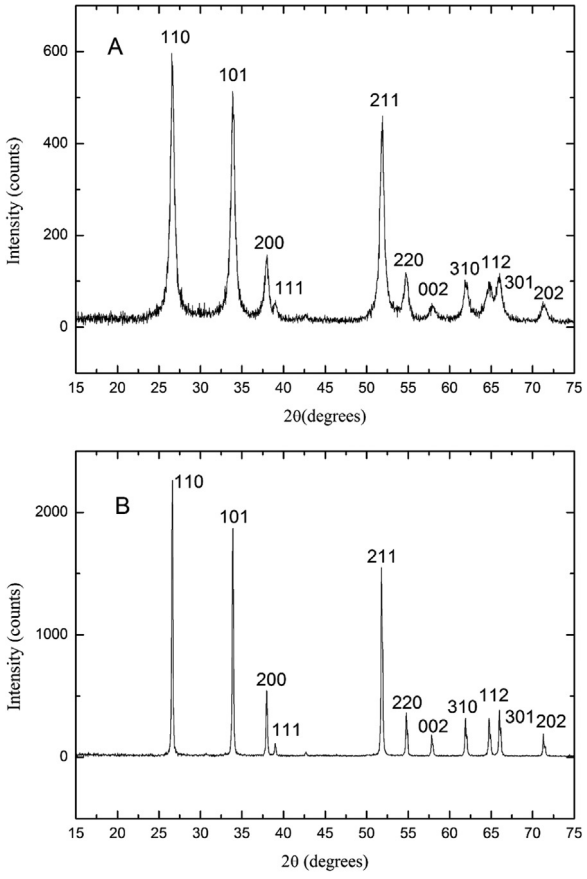

Fig. 1. XRD patterns of the SnO_2 samples with different grain sizes: A and B. The Miller indices of the main reflections are indicated.

3. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of the A and B SnO_2 specimens, where the peaks were indexed according to the tetragonal rutile-type structure (space group $P4_2/mnm$).Differences in the widths between the peaks of the two samples are related to the differences in the microstructure, especially with respect to the crystallite size. In order to get information about the microstructure, the XRD patterns of the samples were analyzed by using the modified Williamson-Hall plot [11], [17–19]. With this goal, the FWHM ("Full Width at Half Maximum") and integral breadths of the SnO_2 peaks were determined, correcting them from instrumental broadening using a sample of Si.

Assuming that dislocations are the main source of strain in crystallites, the FWHM can be expressed as

$$\Delta K = \frac{\gamma}{D} + \alpha K \bar{C}^{1/2} \tag{1}$$

γ being 0.9, and the integral breadth as

$$\Delta K' = \frac{1}{d} + \alpha K \bar{C}^{1/2} \tag{2}$$

where $K=\frac{2\sin\theta_0}{\lambda}$, D is a size parameter related to the column length of the crystallites, d is the volume-weighted average column length, α is a parameter related with the Burgers vector, the effective outer cut-off radius and the density of dislocations and C is the average contrast factor of the dislocations, depending on the relative positions of the diffraction vector and the Burgers and line vectors of the dislocations and on the character of dislocations. In this context, the modified Warren-Averbach equation is expressed as

$$\ln A(L) = \ln A^S(L) - \frac{\pi\rho b^2}{2} L^2 \ln\left(\frac{R_e}{L}\right) K^2 \bar{C} \tag{3}$$

where $A(L)$ is the real part of the Fourier transform of the diffraction profile, $A^S(L)$ the size Fourier transform, b the modulus of the Burgers vector, R_e the effective outer cut-off radius of dislocations and ρ the density of dislocations.

Different dislocation slip systems have been described for SnO_2, although the most usual are the systems based on the $<10\text{-}1>$ Burgers vector. For the point group symmetry of SnO_2 (4/mmm), the averaged contrast factor is described by equation [20]:

$$\bar{C} = \frac{E_1(h^4+k^4) + E_2 l^4 + 2E_3 h^2 k^2 + 2E_4 l^2(h^2+k^2)}{(h^2+k^2+\frac{a^2}{c^2}l^2)^2} \tag{4}$$

Where h, k and l are the Miller indices of the reflection, a and c the cell parameters of SnO_2 and E_i, the coefficients of the fourth-order strain invariant that define the dependence of strain on the Miller indices [21].

In order to determine D and d, linear fits of ΔK and $\Delta K''$against $K\,C^{1/2}$ were performed. In this way, the values of the E_i's for the different slip systems of SnO_2, for edge or screw dislocations [20], where used to determine the averaged contrast factor for each reflection. The best linear fitting was obtained for $<10\text{-}1>\{101\}$ slip system, assuming screw dislocations, for both samples. As example, in Fig. 2 is shown the integral breadths of the peaks of both samples versus $K\,C^{1/2}$.

The modified Warren-Averbach equation has been used to determine the area-weighted average column length in both samples. In this way, the Fourier transform of the diffraction profile was calculated for different values of L for each reflection (that is, for the K^2C value corresponding to the reflection). According to Eq. (3), the linear fit of $A(L)$ against K^2C for a particular value of L provides as intercept the size Fourier transform for that