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Structural analysis of TiO_2 films grown using microwave-activated chemical bath deposition

F. Fernández-Lima[a], D.L. Baptista[b], I. Zumeta[c], E. Pedrero[d], R. Prioli[e], E. Vigil[d], F.C. Zawislak[b,*]

[a]*Institute of Nuclear Sciences and Technologies, Havana, Cuba*
[b]*Instituto de Física, Universidade Federal do Rio Grande do Sul, C.P. 15051, 91501-970 Porto Alegre, Brazil*
[c]*Institute of Materials and Reagents, University of Havana, Havana, Cuba*
[d]*Institute of Materials and Reagents – Faculty of Physics, University of Havana, Havana, Cuba*
[e]*Van de Graaff Laboratory, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil*

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Abstract

TiO_2 layer films were grown using the microwave (MW)-activated chemical bath deposition technique on two different indium tin oxide substrates. The TiO_2 films are studied to determine their structural response when changing the MW heating power. Thickness (areal density), oxygen concentration profile, composition and surface homogeneity were determined using Rutherford backscattering spectrometry, nuclear reaction analysis and atomic force microscopy. The analysis showed that the composition, thickness and surface structure of the films are highly influenced by MW heating power. The substrate, acting as seed for nucleation, influences the layer thickness, indicating that a thinner layer of TiO_2 is obtained for the more conducting substrates. The oxygen concentration profile is constant in the TiO_2 layer at low MW heating, power ($\approx 20\%$). The rugosity of the samples and the non-homogeneity increase with the MW heating power. If the MW heating power is high enough pinholes in the TiO_2 layer of the order of the sample thickness are produced.

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1. Introduction

Interest in some very perspective applications of nanostructured TiO_2 has given rise to a considerable number of reports concerning different techniques for obtaining nanostructured thin films of this semiconductor [1–14].

The use of microwave (MW) heating has recently been reported for TiO_2 thin films growth, showing an advantage over the traditional techniques due to (a) the characteristics of the grown layers (good adherence and transparency), (b) the simplicity of the technique, (c) the possibility of controlling the layer thickness with MW heating time, (d) the low temperature needed, and (e) the possibility of reusing the precursor solutions.

In this paper we describe for the first time the influence of the substrate (ITO/glass) and the MW heating power, using the Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) techniques for the analysis of thickness, stoichiometry and oxygen concentration profile of the grown TiO_2 layers. In addition the topography and the rugosity of the TiO_2 films have been characterized by atomic force microscopy (AFM).

2. Experimental description

The TiO_2 layers were grown using chemical bath deposition activated with MWs and titanyl sulphate precursor solution prepared as described in Refs. [13,15].

The TiO_2 films were grown on two different ITO/glass (In_2O_3(Sn)/glass) substrates. The first substrate (called A) has a resistivity of 15 $\Omega/\square$ and ITO layer

*Corresponding author. Tel.: +55-51-331-66427; fax: +55-51-331-66510.
E-mail address: zawislak@if.ufrgs.br (F.C. Zawislak).

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Table 1
Growth regimes and areal densities of the TiO_2 films

Sample	Substrate	% of MW heating power intensity	Areal densities 10^{15} atoms/cm^2	Number of processes
3	A	100	500 ± 50	10
4	A	30	310 ± 15	10
5	A	20	270 ± 15	5
6	B	20	230 ± 15	5

thickness of 100 nm. The second substrate (called B) has a resistivity of 10 Ω/□ and ITO layer thickness of 155 nm. Growth regimes also differed in the intensity of MW heating power and the number of growth processes, one on top of the other, in order to obtain greater TiO_2 layer thickness (Table 1).

The ion-beam analyses were made using the 3 MV TANDETRON accelerator of the Institute of Physics, Federal University of Rio Grande do Sul, Brazil. The Rutherford backscattering analysis of the samples were made with ^{4}He ions of 2.0 MeV. A surface barrier detector with 12 keV FWHM at an angle of 165° was used. The RBS spectra were processed with the program RUMP [16]. The oxygen profile was determined by NRA, using the narrow resonance of the $^{16}O(\alpha,\alpha)^{16}O$ reaction at 3045 keV in the same experimental setup.

The AFM was made using Multi Mode atomic force microscope from Digital Instruments.

3. Results and discussion

The areal density and composition of the TiO_2 thin films were determined from the analysis of the RBS spectra. The results of the areal density determination are shown in Table 1.

Fig. 1 shows the RBS spectra of sample 3 taken in two geometries. The first one with the incident α beam normal to the sample ($\theta_1=0°$) and the second with $\theta_1=45°$. The spectra clearly show that the sample has In at the surface (and also Ti). This means that the TiO_2 does not cover completely the ITO substrate layer. Nevertheless the comparison of samples 3 and 4 (Table 1) shows that the sample 3, produced with the highest MW power, presents the largest values of areal density, corresponding to the thicker film. However this is an average areal density, because the TiO_2 film is not homogeneous. The non-homogeneity of the TiO_2 film of sample 3 will be discussed later on, correlated to the AFM data.

The comparison of samples 5 and 6 shows the role of the substrate (Table 1), acting as seed for nucleation. On the more conducting substrate layer (sample 6), a thinner TiO_2 film grows. This seems to contradict the hypothesis of Ref. [15] regarding a preferential heating of the ITO layer due to scattering of free electrons by the lattice, which favors nucleation. Nonetheless, more

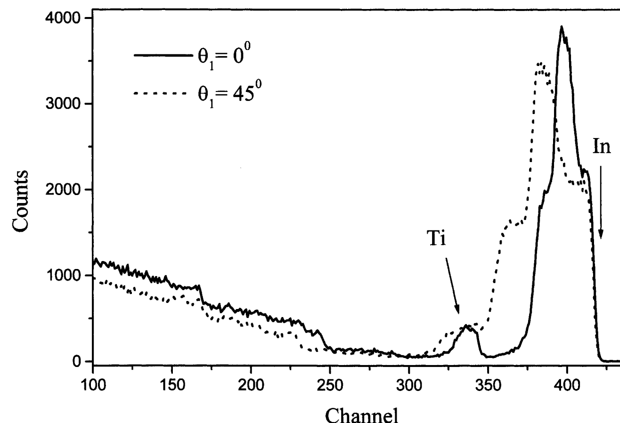

Fig. 1. RBS spectra of sample 3 obtained at normal and 45° incident α beam.

detailed experimentation is needed regarding the crystal structure and the texture of the ITO layers in order to explain this result.

The analyses of the RBS spectra of samples 4, 5 and 6 indicate that the TiO_2 films are stoichiometric. Nevertheless a precise investigation of the oxygen stoichiometry was made in sample 5 by analysis of the oxygen concentration profile using the resonant reaction $^{16}O(\alpha,\alpha)^{16}O$ by varying the beam energy. The oxygen contribution in the two layers and in the glass substrate can be seen in Fig. 2. The TiO_2 film is thinner than the ITO layer. When the resonant peak of the reaction is in the thin TiO_2 film the oxygen contribution is constant. When the energy is increased the resonant peak penetrates into the ITO layer and at larger energies also into the glass substrate.

From Fig. 2 it is seen that the oxygen contribution fraction of the TiO_2 layer with respect to the ITO layer is ≈ 1.33. This contribution corresponds to a relation of 2 oxygen atoms per titanium atom in the TiO_2 layer,

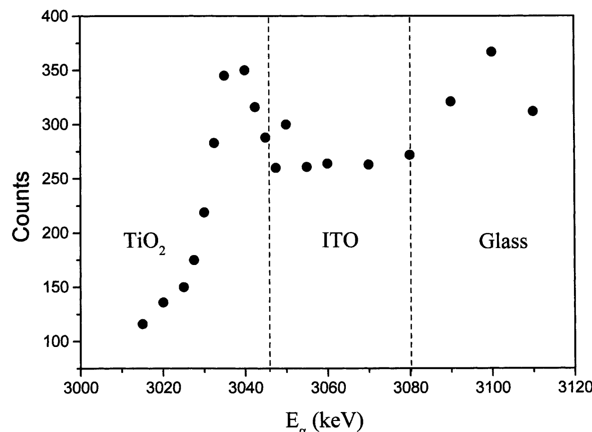

Fig. 2. Oxygen concentration profile for sample 5 obtained via the $^{16}O(\alpha,\alpha)^{16}O$ reaction.

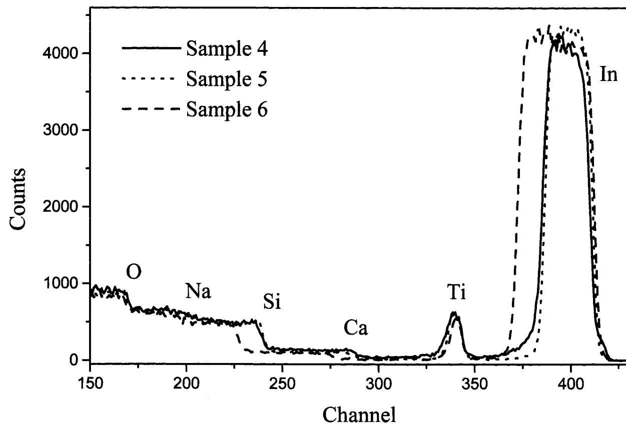

Fig. 3. 2 MeV α RBS spectra of samples 4, 5 and 6.

and 1.5 oxygen atoms per In atom in the ITO layer. The relation is further corroborated in the glass substrate, which is mainly SiO_2, and as shown in Fig. 2 the oxygen concentration is the same as in the TiO_2 layer. A possible excess of oxygen at the surface of the thin TiO_2 film, linked to adsorption of water molecules was not observed in our measurement. The oxygen concentration was measured via the $^{16}O(\alpha,\alpha)^{16}O$ nuclear reaction with a depth resolution not sufficient to distinguish a narrow peak of adsorbed oxygen. In fact we measured the average concentration of oxygen in the layers, and as the oxygen relation is correct in the three layers, we conclude that an eventual presence of additional oxygen at the TiO_2 surface must be very small. The RBS spectra of samples 4, 5 and 6 (Fig. 3), show well-defined Ti and In(Sn) layers, indicating that the TiO_2 film was grown homogeneously. This shows a remarkable difference from sample 3, which was grown with maximum MW heating power. Probably in this case, the layer growth is very sudden giving rise to much greater non-homogeneity. The Ca, Na and Si edges shown in Fig. 3 correspond to the glass substrate.

The influence of the MW heating power on the samples 4, 5 and 6 can be studied from the tail shape of the Ti peak in Fig. 3. The tail shape of Ti peak in sample 4 is more pronounced, showing that the surface film of this sample is less homogenous that the other two samples. The non-homogeneity produces different ion paths which results in energy fluctuations and consequently larger tail in the Ti RBS spectrum [17,18].

In order to further study rugosity vs the used MW heating power, the samples were analyzed in an AFM. The rugosity of the samples was calculated from AFM images. Samples were scanned increasing scanning area successively from 0.5×0.5 up to 10×10 μm^2. Fig. 4 displays two typical AFM images of samples 3 and 5 showing a much smaller rugosity in sample 5. The calculated rugosities are shown in Fig. 5.

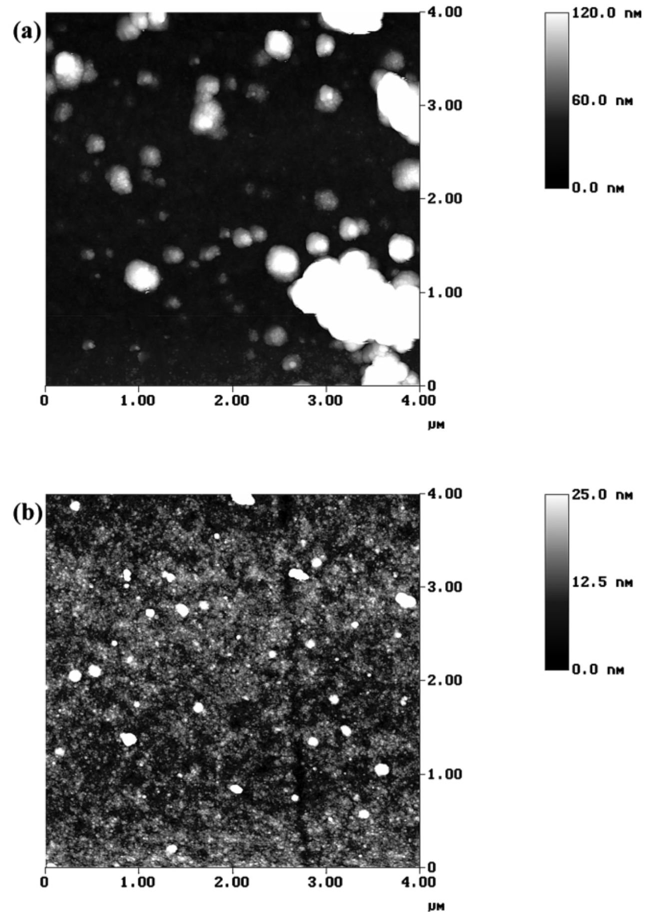

Fig. 4. (a) AFM image of sample 3 and (b) of sample 5.

Sample 3 has the highest value of rugosity and it can be attributed to the fast and disordered nucleation of the TiO_2 at the substrate surface. From the analysis of samples 5 and 6, it is seen that the substrate has not great influence on the rugosity and both samples are quite homogenous. The values of rugosity in Fig. 4 are related to the values of MW heating power intensity. As

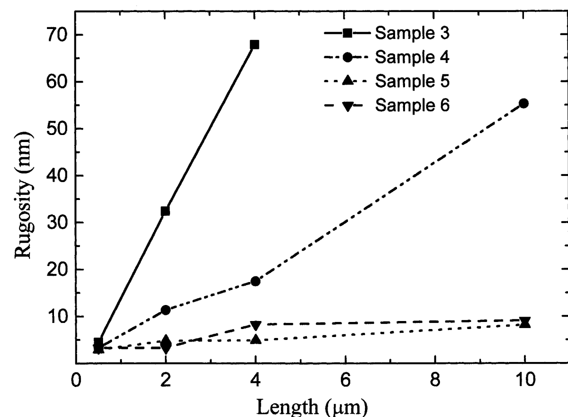

Fig. 5. Rugosity values as function of the scan length.

can be seen, the rugosity of the samples is mainly determined by the nucleation dependence on the MW heating power.

4. Conclusions

The composition, thickness and surface structure of TiO_2 films grown on ITO substrates are studied as function of the MW heating power. Our results indicate that the substrate, acting as seed for nucleation, influences the thickness of the layers, resulting thinner layers on the more conducting substrates. The layers at low MW heating powers (Pot. $\leqslant$30%) present stoichiometric TiO_2 films. The oxygen concentration profile is constant in the TiO_2 layer at low MW heating powers ($\approx$20%). The rugosity of the samples and the non-homogeneity increase with the MW heating power. If the MW heating power is high enough, pinholes in the TiO_2 layer of the order of the sample thickness are produced.

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