

Rutherford backscattering spectrometry analysis of TiO₂ thin films

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Abstract

TiO₂ layers grown by microwave-activated chemical bath deposition (MW) and dip coating (DC), as well as by the combination of both techniques, were studied by Rutherford backscattering spectrometry (RBS), atomic force microscopy (AFM) and scanning electron microscopy (SEM). RBS analysis allows the determination of the stoichiometry and the thickness (in atoms/cm²) of the TiO₂ layers. TiO₂ layers grown by DC have higher growth rates on a TiO₂ film obtained by MW compared to deposition directly onto an indium–tin oxide (ITO) substrate. TiO₂ layers grown by MW on a film obtained by DC have higher growth rates when compared to layers deposited onto ITO substrates. In this case, AFM analysis shows that the surface is rough and RBS reveals the presence of holes in TiO₂ films.

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1. Introduction

One of the problems with dye-sensitized solar cells is the direct contact between the conducting support of the nanostructured and porous TiO₂ layer and the electrolyte. This may cause a short circuit with the counter electrode and the consequent reduction of photovoltage. One of the ways to overcome this problem is to use a sandwich-like structure of two TiO₂ layers because this structure could prevent short circuits. In this case, a thin, dense TiO₂ film is deposited on the conducting support before the depo-

sition of the thicker, porous TiO₂ structure, which holds most of the sensitize dye. The thin, dense TiO₂ film can be deposited by applying a novel microwave-based technique, the so-called “microwave-activated chemical bath deposition” (MW) [1,2], whereas the thicker layer can be deposited by the conventional dip-coating (DC) technique [3,4]. The layer obtained using the dipping technique is immersed in a precursor solution, which penetrates the porous structure. After microwave heating, the precursor solution (solution temperature <90 °C), nucleation inside the TiO₂ matrix should result in electrical contact between particles avoiding the annealing process for sintering at relatively high temperatures. This is one of the advantages of the present procedure because many substrates cannot tolerate high-temperature processing.

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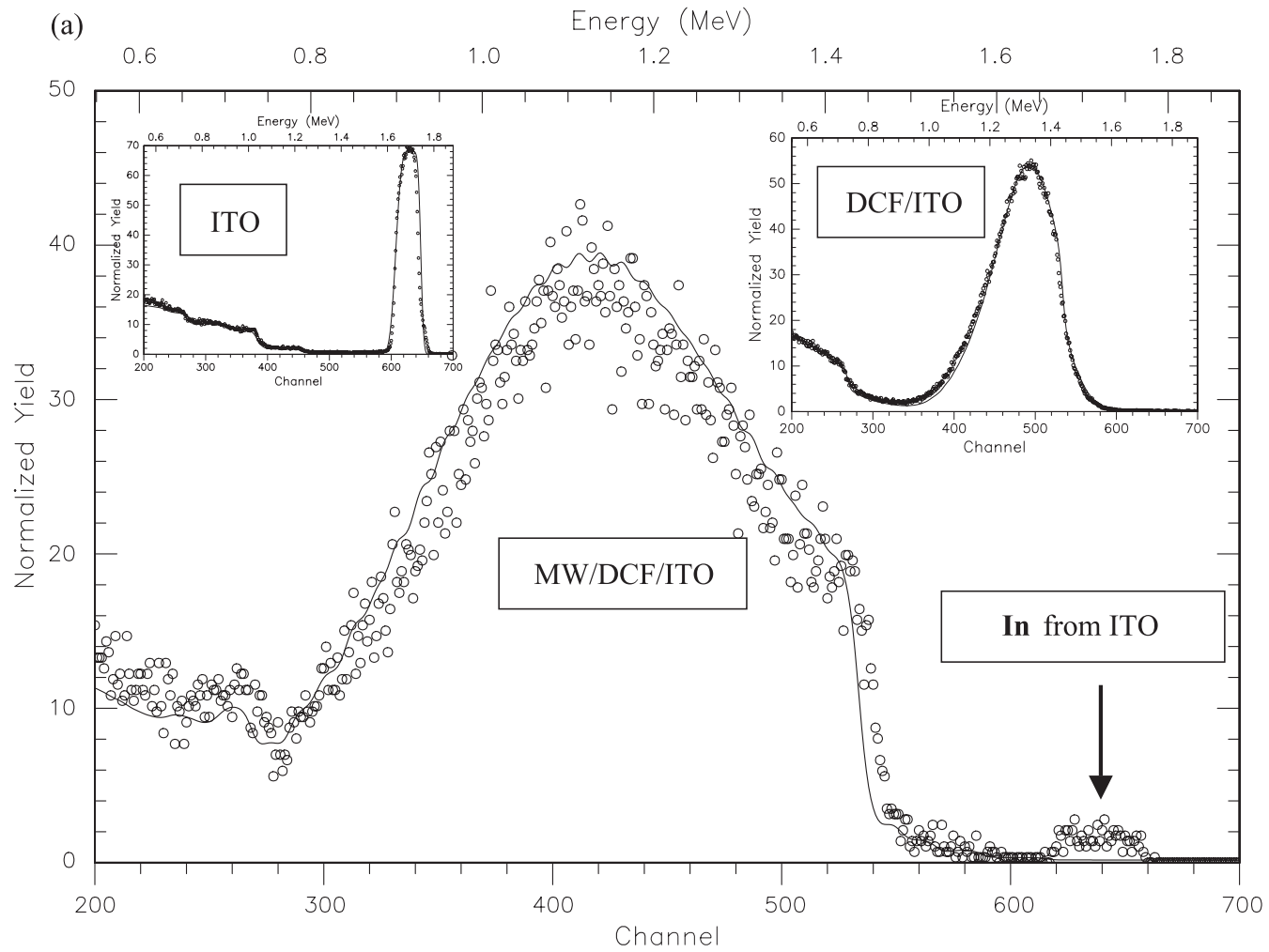


Fig. 1. (a) 2.0-MeV $^4\text{He}^+$ RBS spectra and simulation of the MW/DCF/ITO and DCF/ITO films and ITO substrate and (b) 2.0-MeV $^4\text{He}^+$ RBS spectra and simulation of the DCS/MW/ITO and MW/ITO films and ITO substrate.

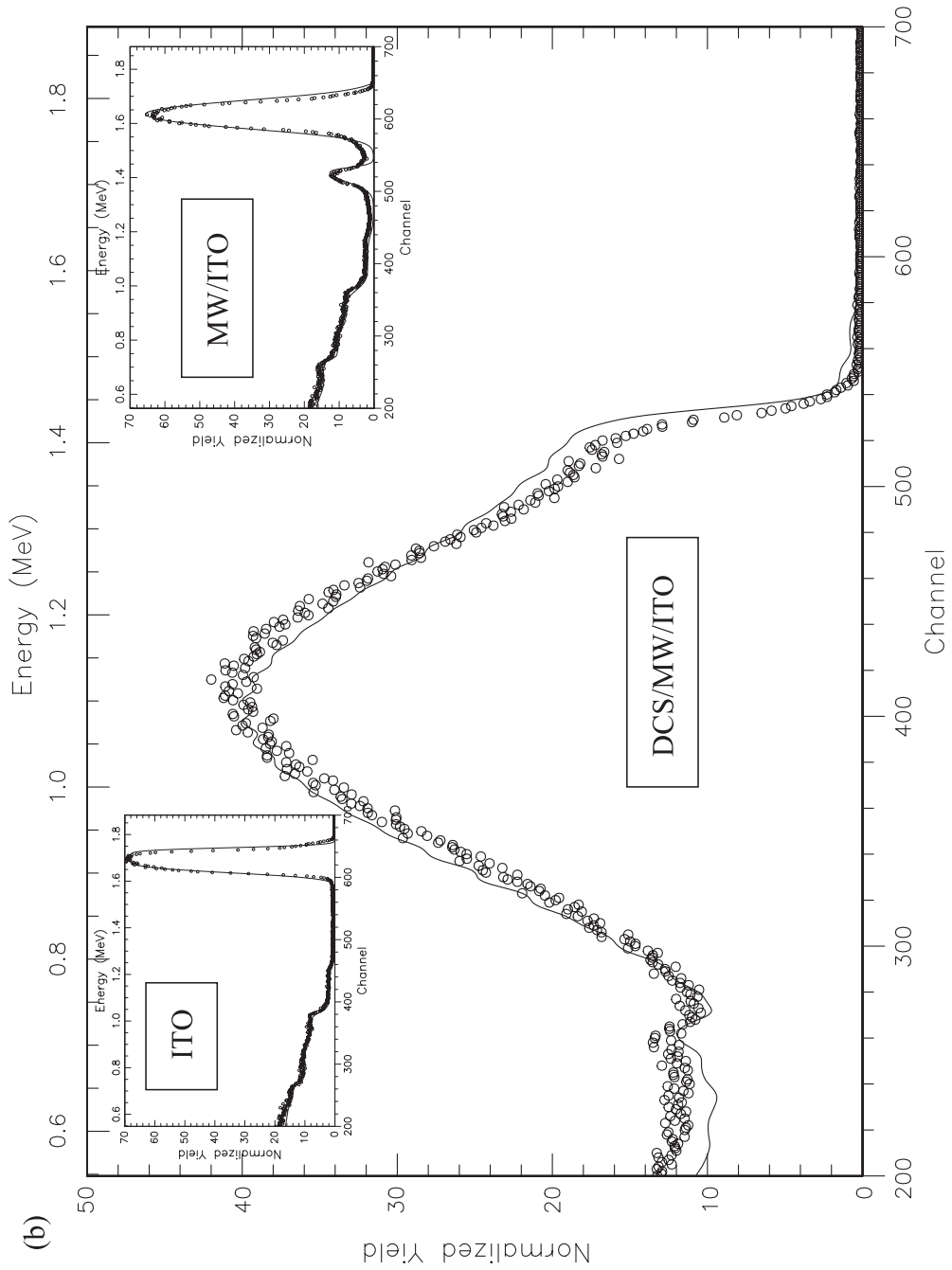


Fig. 1 (continued).

In the present work, we describe the influence and the characteristics of the combination of MW and DC techniques by using Rutherford backscattering spectrometry (RBS) for the analysis of thickness, stoichiometry, composition and surface coverage of the grown TiO_2 layers. In addition, for a better morphological characterization, the topography and the roughness of the TiO_2 films have been characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Two different suspensions were used to investigate the influence of TiO_2 particle aggregation on thickness, substrate coverage and roughness of the TiO_2 layers obtained by DC technique. It was expected that as the size of particle aggregates decreases, better substrate coverage and smoother film surfaces (decreased roughness) could be achieved. An investigation of the effects of the sequence of TiO_2 layer deposition was also performed.

2. Experimental details

The TiO_2 samples were prepared onto indium–tin oxide (ITO)/glass substrates (resistivity of $15 \Omega/\square$ and ITO thickness of 100 nm) at the Physics Faculty-IMRE, University of Havana, Cuba, by MW and the DC techniques. Details of both techniques were published elsewhere [1–3]. A homogenous aqueous precursor solution of TiOSO_4 (5 mM) and H_2SO_4 (2.5 mM) was used for the microwave deposition. The MW samples were prepared by a 10-step process with 630 W of microwave heating during each 15-s step. The DC samples were grown using an aqueous solution of TiO_2 and subsequently baked for 1 h at 450 °C. In order to study the influence of the segregation state in DC process, two series of films were grown:

- (i) DCS/ITO using a decanted 10% suspension and
- (ii) DCF/ITO using an undecanted 10% suspension.

Different sequences of MW and DC processes were performed, and three structures were obtained:

- (i) MW/ITO by 10 steps of microwave film processing,

- (ii) DCS/MW/ITO by 10 steps of MW processing followed by 10 baths in a decanted 10% suspension,
- (iii) MW/DCF/ITO where a TiO_2 layer was grown by the 10-step microwave processing onto a layer grown by 10 baths in an undecanted 10% solution.

RBS was carried out using the 4-MV Van de Graaff accelerator of the Physics Department of the Pontifical Catholic University of Rio do Janeiro, Brazil. The RBS analysis of the samples was performed with 2.0 MeV of ^4He ions. A surface barrier detector with 18 keV of FWHM-energy resolution was positioned at an angle of 165°. The RBS spectra were analyzed using the RUMP code [5]. Because of the complexity of the RBS spectrum of these multilayer structures, the overall spectra simulation took into account the RBS analyses results of the ITO substrate and of specially prepared samples, each one corresponding to one step of the multilayer growth process.

The AFM measurements were performed with a commercial microscope (Nanoscope III, Digital Instruments) operated in tapping mode for the analysis of the topography. All the experiments were performed at room temperature and the relative air humidity was kept constant at 40%. The root mean square roughness was measured in several areas ranging from 2×2 to $10 \times 10 \mu\text{m}^2$ with a scan speed of 2 $\mu\text{m}/\text{s}$. A Carl-Zeiss DSM 960 SEM was used for surface topography characterization. Both microscopy techniques were performed at the Pontifical Catholic University of Rio do Janeiro, Brazil.

3. Results and discussion

The thickness values and the composition of the grown layers were obtained from the analysis of the RBS spectra and the RBS simulations. The composition analysis showed a constant stoichiometry of two oxygen atoms per titanium atom in all grown layers. This result agrees with previous X-ray diffraction analysis: an anatase-type tetragonal crystal structure in the layers grown by DC and the combination with MW [1,2].

The RBS spectrum obtained from a MW/DCF/ITO sample is shown in Fig. 1a. The presence of In at the

Table 1
Sample thickness as determined by RBS

Sample	TiO ₂ total thickness (10 ¹⁵ atoms/cm ²)
MW/ITO	600 ± 10
DCS/ITO	3000 ± 20
DCF/ITO	3700 ± 20
DCS/MW/ITO	6050 ± 20
MW/DCF/ITO	5700 ± 50

sample surface is a clear indication of pinholes in the TiO₂ multilayer structure, because the surface of the ITO surface was directly exposed to the particle beam. These pores or holes appear after the microwave processing; they are not present in the spectrum obtained from a DCF/ITO sample, as shown in the figure inset. The holes could be produced by the enhanced nucleation of TiO₂ due to the microwave power heating during the microwave processing. This effect was only observed in this layer; the obtained TiO₂ layers completely covered the ITO surface in all other samples.

Fig. 1b contains the RBS spectrum obtained from a DCS/MW/ITO sample. From the tail shape of the

signal in the RBS spectrum (insert at the upper right of Fig. 1b) [6,7] it appears that this sample is rougher than the one shown in the insert at the upper right side of Fig. 1a. This is a characteristic of the DC technique; the films exhibit greater roughness values compared with the MW samples [8].

The values of the TiO₂ layers thickness (in atoms/cm²) are shown in Table 1. It is important to note that RBS, as well as all other ion beam techniques, provided quantitative results for the amount of atoms in each layer. A film thickness measurement can be obtained only if the actual atomic density of the layers is known. It is clear from the RBS analysis presented in Table 1 that there is no significant difference between the thickness of TiO₂ layers grown by DC using both undecanted and decanted 10% suspension. In Fig. 2, SEM images of the MW/ITO, DCS/ITO and DCF/ITO samples are shown. These micrographs show varying degrees of surface roughness. The SEM images show that the DC film grown in a 10% undecanted solution, which slightly promotes the film growth as shown in Table 1, appears to have increased surface roughness. The DCF film is the thicker of the two films, approximately 18% greater than the DCS

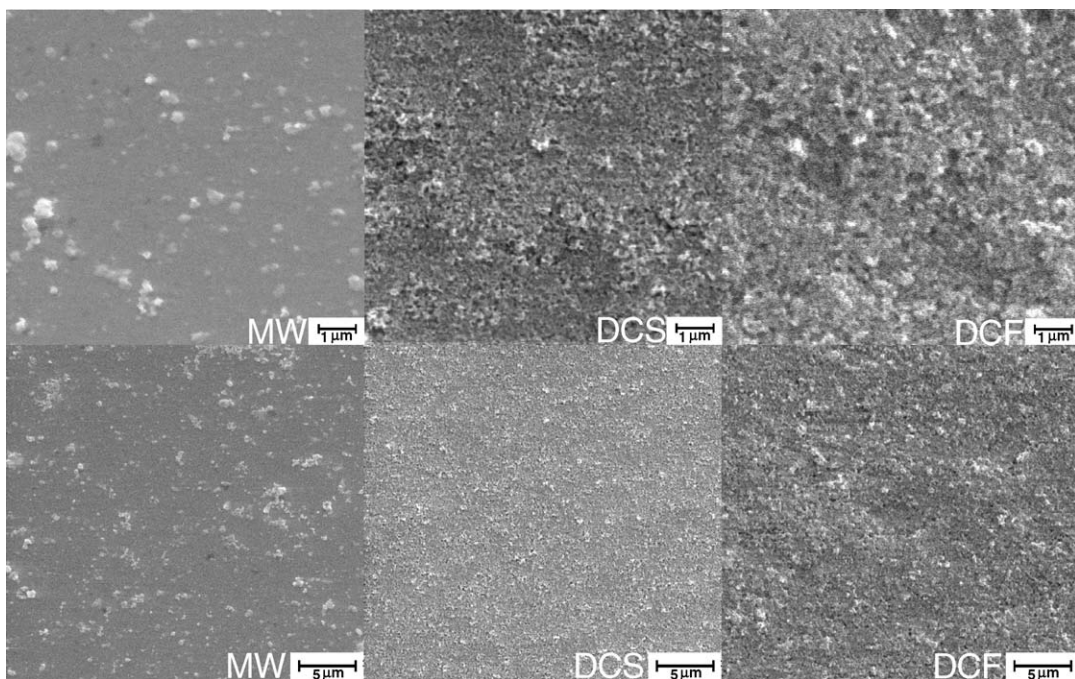


Fig. 2. SEM images of the MW/ITO (left), DCS/ITO (center) and DCF/ITO (right) samples.

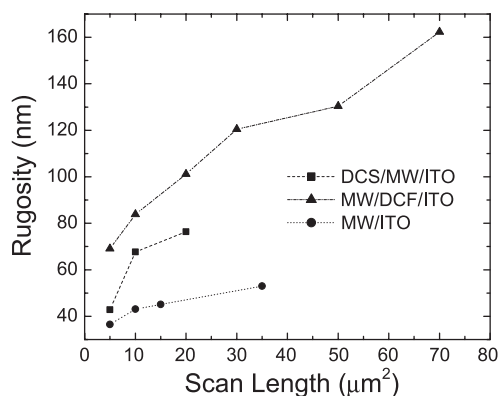


Fig. 3. Roughness as a function of the scan length for the MW/ITO, DCS/MW/ITO and MW/DCF/ITO samples.

film. It is also clear from Fig. 2 that layers grown by MW onto the ITO substrate have a smoother surface, consistent with the RBS spectra.

By comparing the DCF (DCS)/ITO layers and MW/ITO layers, it appears that microwave processing is less efficient for one-step processing. In contrast, comparing the results for the DCS/MW/ITO (MW/DCF/ITO) samples and the DCS/ITO (MW/ITO) samples, it is clear that the films grown by the combination of two techniques are much thicker. The comparison of the thicknesses of the DCS/MW/ITO layers and DCS/ITO layers indicate that the suspension adheres much better to the thin TiO₂ layer grown by MW than to the ITO substrate.

To obtain a better morphological characterization of the films, the samples were analyzed by AFM. AFM images were processed with the Scion program, and the roughness values were calculated and presented in Fig. 3 for different scan lengths. The MW/ITO sample exhibits the lowest roughness values. From the values shown in Fig. 3, one can observe the difference between the combinations of DC and MW. The presence of pores or holes previously detected by the RBS analysis of the sample MW/DCF/ITO is consistent with its much higher roughness values.

4. Conclusions

The analysis of the thickness (atoms/cm²) showed that in the DC/MW sample, the film growth is favored on TiO₂ film as compared to the layer growth directly

onto an ITO film substrate. This may be because of better wetting of the suspension over the TiO₂ film obtained with MW, resulting in a thicker layer. In the case of MW/DC sample, the growth is also favored by the presence of the initial TiO₂ layer. In this case, it is speculated that the increased growth is favored by the larger real surface area of the DC TiO₂ layer compared to the ITO layer, because the roughness of DC TiO₂ layer is greater than that of the ITO surface. However, AFM analysis shows that the DC TiO₂ sample is considerably rougher, and RBS indicates the presence of pinholes in the TiO₂ films grown by the sequence MW after DC, probably associated with the heating that occurs during the microwave processing.

Acknowledgements

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