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Atomic force microscopy (AFM) and 3D confocal microscopy as alternative techniques for the morphological characterization of anodic TiO_2 nanoporous layers

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ABSTRACT

The morphologic characterization of self-organized TiO_2 nanostructures by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) was compared with results obtained by both atomic force microscopy (AFM) and 3D confocal microscopy, which were employed as alternative characterization methods. It is demonstrated that AFM with tuning fork configuration (intermittent mode) is also a powerful tool that allows obtaining conclusive information on the morphology of one-dimensional nanostructures. 3D confocal microscopy employed for the first time for obtaining thickness of nanoporous TiO_2 films, is a new and powerful method that provides definite information on thickness of the nanostructures. The results employed for the characterization are fairly reliable besides novel and interesting.

1. Introduction

Titanium oxide (TiO_2) obtained under a diversity of anodizing conditions [1] has been extensively investigated because of its versatile applications in several areas, e.g. dielectric mirrors, dye-sensitized solar cells (DSSCs) [2], biocompatible dental or bone implants [3].

Porous or tubular TiO_2 layers are some of the one-dimensional nanostructures (1D) most studied [4–6]. Due to their large specific surface area, ballistic charge transport and orthogonal carrier separation combined with TiO_2 semiconductivity, biocompatibility and low-cost, these nanostructures possess excellent properties that impart unique physicochemical properties to the material [7–9,5]. Therefore, the porous films are favorable for applications in various fields such as catalysis, medicine, energy, electronics, pharmacology [10–12], among others. The synthesis of TiO_2 nanostructures has been carried out using a variety of synthetic strategies [12,13], within which the electrochemical anodization of titanium in fluoride containing electrolytes has proven to be the most advantageous synthetic route [14]. Electrochemical anodization procedures allow obtaining precise dimensions of the nanostructures, i.e. length and diameter of the pores/tubes as well as thickness of the walls [15].

In order to characterize porous thin films, is necessary to employ reliable and accurate techniques for obtaining their morphological properties and thickness. Atomic force microscopy (AFM) ability to obtain images of various samples, along with its ease of operation and the relatively low cost of the instruments, means that AFM quickly gained acceptance in a wide range of fields such as physics, life sciences and industrial applications. As a result, it is difficult to think of a field of study involving solid surfaces, which has not been applied this technique. Nevertheless, as morphologic analysis is usually performed by field emission scanning electron microscopy (FESEM) and/or transmission electron microscopy (TEM), the AFM technique has not been usually used for the characterization of TiO_2 porous films [16]. Furthermore, 3D confocal microscopy is a powerful tool for the direct visualization of the 3D structure of materials that has been mainly used in biological samples and colloidal particles [17]. Nevertheless, to the author's knowledge, no studies have been published on the characterization of porous/tubular thickness of thin layers of semiconductor nanomaterials, employing 3D confocal microscopy.

This study aims at the analysis of the use of alternative

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microscopic techniques (AFM and 3D confocal microscopy) for the surface morphology characterization and thickness measurement of nanoporous TiO_2 layers obtained by electrochemical anodization of titanium in fluoride containing ethylene glycol solutions. In order to corroborate the results, the statistic analysis of the morphological features was compared to those obtained using the conventional microscopic characterization techniques for this type of materials (FESEM and TEM).

2. Material and methods

The anodization of titanium was performed as previously reported [15] by applying a step voltage $Ua = 60$ V in a 0.2% w/w ammonium fluoride, 3% v/v water and ethylene glycol electrolyte with continuous stirring at 20 °C. The surface morphology of the TiO_2 electrodes was characterized by FESEM using a Carl Zeiss Σigma model microscope, TEM using a LEO 1420 VP model and AFM using Nanonics MultiView MV1000 and MV2000 models. In AFM measurements, n-type silicon cantilevers ($f = 37.2$ kHz; $k = 0.01–0.60$ N/m; tip radius < 10 nm) for contact mode or optical fiber cantilevers (tip radius ≈ 10 nm; $f = 39.4$ kHz; $Q = 1576$) for intermittent mode were employed. For TEM measurements, an aqueous dispersion of TiO_2 nanotubes obtained by sonication of the anodized films in water during 15 min was employed. The thickness of the TiO_2 layers were obtained from lateral FESEM views as well as 3D reconstruction of the film surface using an Olympus LEXT 3D OLS4000 model confocal microscope (405 nm laser excitation). Prior to the thickness analysis, the samples were mechanically cracked in order to expose partially a free-oxide titanium surface. Statistical analysis of the obtained images was performed by implementing the image processing software Gwyddion 2.37.

3. Results and discussion

In the study of geometrical parameters of TiO_2 nanostructures (*e.g.* pore diameter or thickness), obtaining representative values corresponding to the overall sample is of paramount interest in order to correlate these values with the formation conditions such as applied voltage, time of anodization and temperature, among others.

Fig. 1 shows FESEM top and lateral (inset) views (Fig. 1a) and TEM (Fig. 1b) images obtained for nanoporous TiO_2 films. A highly ordered self-assembled nanopores array was obtained. The diameter of the pores, obtained from both techniques ranges from 110 to 130 nm, while the average pore length estimated from the lateral FESEM images, is in the 10–11 μm range.

Fig. 2 shows AFM images for anodic TiO_2 obtained in contact mode, using the beam bounce (2a) and intermittent tuning fork (2b) configurations. In Fig. 2a, despite of the noticeable high definition of the tubular structures in the film (see Fig. 1), pores are not clearly detected. However, darker hues in the image can be seen, which would be attributed to the presence of pores. The 3D image would evidence tubular structures, even though they are not completely defined. These results show that the measurements performed with this type of microscope using the contact mode is not good enough in order to characterize these highly organized nanostructures with 120 nm of pore diameter.

Whereas the AFM beam bounce configuration does not provide the expected results, the characterization using the tuning fork configuration was performed. After several attempts changing gain values, it was possible to observe clearly the pores of the TiO_2 samples. High quality images compared to those reported previously using AFM [16,18,19], were obtained. These results are probably due to several advantages of the intermittent tuning fork over contact mode in beam ounce configurations, i.e. high sensitivity in amplitude and phase, high mechanical quality factor and a large spring constant, which allow acquisition of real images with high resolution of the nanostructures (Fig. 2b). In order to analyze statistically the images obtained, a mask to measure the average pore radius was applied and the radii obtained were fitted to a Gaussian curve. The mean radius values obtained from the AFM images (57 ± 19 nm) are very similar to those obtained from FESEM experiments (60 ± 15 nm). The fact that low values of χ^2 were estimated, reflects that the morphological information obtained by atomic force microscopy for TiO_2 nanotubes is reliable and representative. In addition, the results presented show that the intermittent tuning fork AFM mode, is also a powerful tool for the characterization of highly ordered porous structures as providing conclusive information about the morphology of such 1D nanostructures. It should be keep in mind that the finite size of the surface feature and the tip radius are intrinsically responsible for the loss of true dimensions in any mode of AFM measurements due to convolution of tip and sample. Therefore, there is a resolution limit that not only affects the lateral resolution, but also affects height measurements of nanoscale sample features. Thus, using standard cantilevers (tip radius of around 10 nm), only TiO_2 pores wider than or separated by a distance larger than 2-fold the tip radius may be differentiated.

Because of the scanning area covered in SEM experiments is very small and unrepresentative of total electrode surface, the measure of thickness of nanoporous oxide layers is difficult and imprecise. As an attractive alternative, thickness measurements of nanoporous TiO_2 films can be performed by means of 3D Confocal Microscopy (Fig. 3a and b). The scanned area corresponds to 0.044 mm^2, which represents a significant portion of the electrode surface. This makes measurements more reliable than the approximate estimations that can be performed with scanning

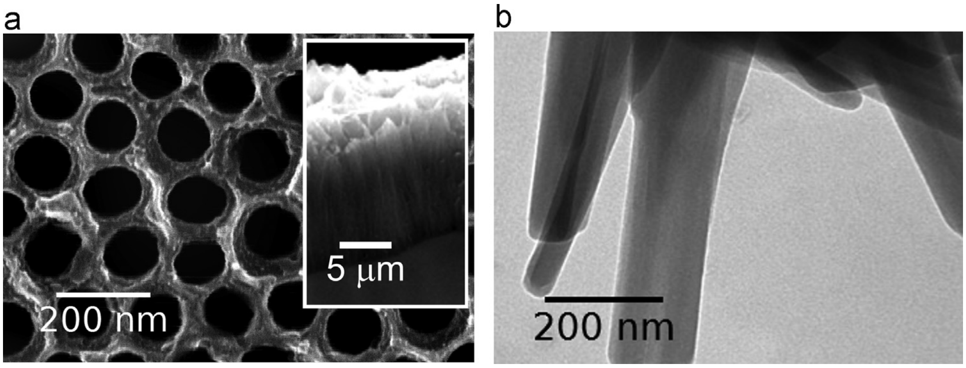

Fig. 1. (a) FESEM top and lateral (inset) views and (b) TEM images, for anodic TiO_2 nanoporous films.

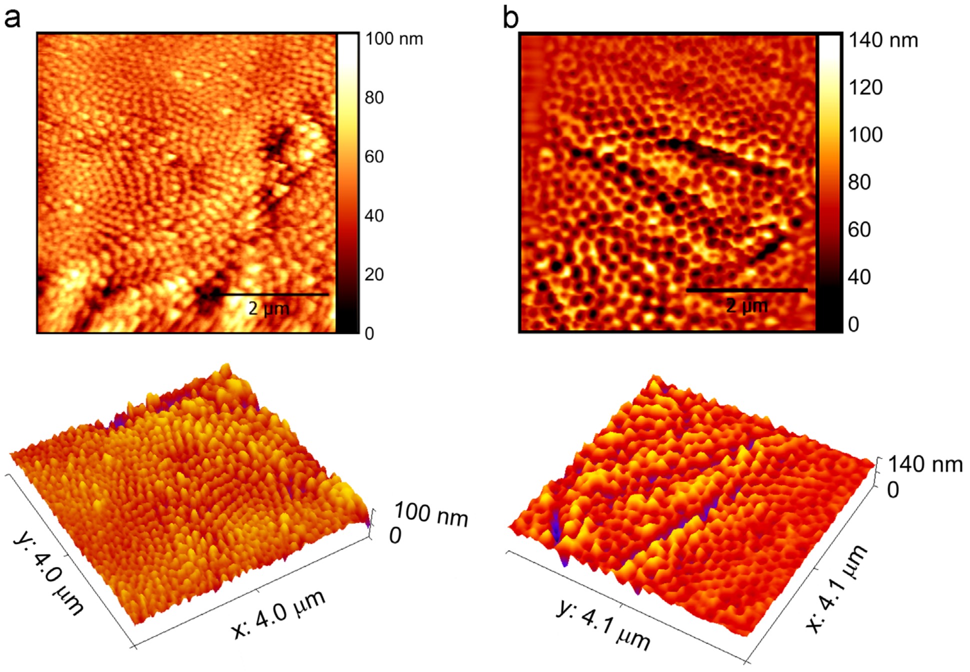

Fig. 2. 2D and 3D AFM images using contact mode beam bounce configuration (a) and intermittent tuning fork configuration (b) for nanoporous TiO_2 films.

electron microscopy, which gives a local value of thickness. A limitation of the 3D confocal microscopy is that only rigid materials (i.e. semiconductor-based materials, dielectrics, metal or oxide films, and resists) can be explored, while viscoelastic-type materials are not adequate.

In order to obtain the average thickness of the porous layer of TiO_2, four height profiles were taken at different zones on the sample (see lines 1, 2, 3 and 4 in Fig. 3a and the corresponding height profiles in Fig. 3c). A height step of around 8.7 µm is measured from the selected profiles. Additionally, the statistical height analysis of the complete image was performed (Fig. 3d) showing two well-differentiated average heights. The lowest height found at 2.70 ± 0.01 µm, corresponds to the rough surface of the titanium substrate while the highest one at 11.44 ± 0.03 µm, to the region covered by the titanium oxide film. Then, the average film thickness is determined by the difference (8.74 ± 0.04 µm). In comparison with the less accurate thickness values obtained from FESEM lateral images, this statistic value is a reliable measure of the total average thickness of the whole oxide layer.

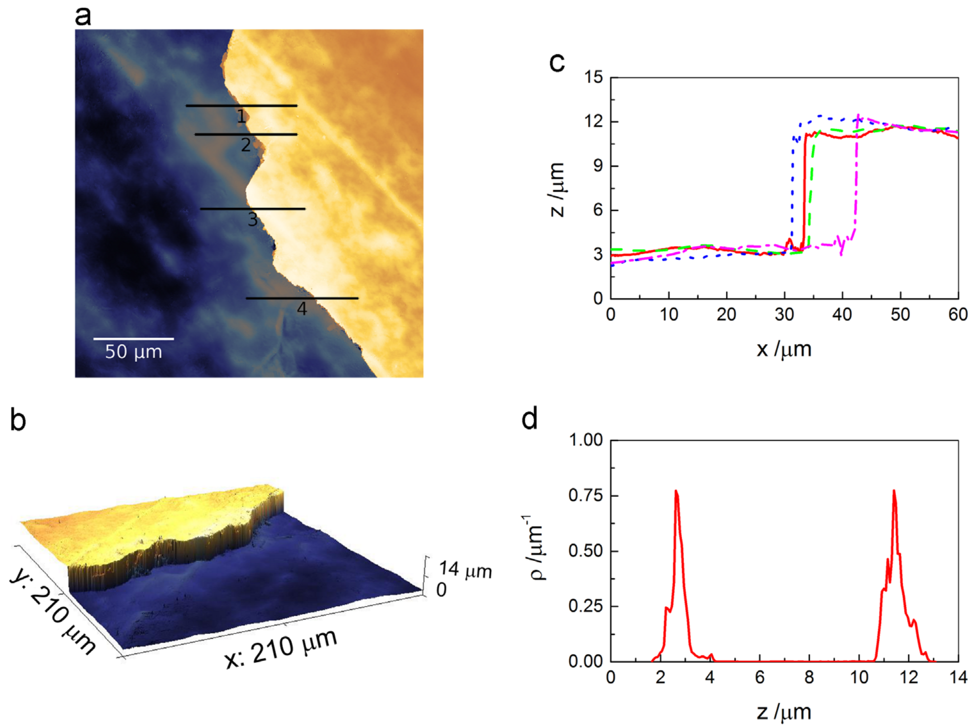

Fig. 3. Surface (a) and 3D (b) confocal images of TiO_2 nanoporous films. Lines correspond to height profiles taken at four different zones and shown in (c): 1 (——); 2 (— —); 3 (⋯⋯) and 4 (— · —). (d) Statistical distribution of heights.

4. Conclusions

The characterization of the surface morphology by FESEM and TEM was compared with the results obtained by both AFM and 3D confocal microscopy. Characterization of porous oxide layers by AFM shows that the microscope with tuning fork configuration (intermittent mode) presents advantages over the beam bounce configuration (contact mode) namely high sensitivity in amplitude and phase, as well as high mechanical quality factor. This, in turn, allows the acquisition of real images of high resolution of the organized nanostructures. Additionally, the average radius values obtained from the AFM experiments are very similar to those obtained from FESEM images, which reflects that the morphological information obtained by atomic force microscopy for TiO_2 nanotubes is reliable and representative of the properties of the system. In brief, the intermittent AFM mode using tuning fork configuration is a powerful tool for characterizing highly ordered porous nanostructures as it provides conclusive information about the morphology of this one-dimensional nanostructures. On the other hand, 3D confocal microscopy was employed for the first time for obtaining the true thickness of porous TiO_2 layers. The method provides reliable measurements of thickness of nanoporous TiO_2 layers because a large area of the surface of the film is covered, compared with approximate or local results that are obtained by FESEM. Thus, 3D confocal microscopy is a new and powerful tool for the characterization of highly ordered porous structures as it provides conclusive information about the thickness for such one-dimensional nanostructures.

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