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Study of TiO_2 thin films growth on ITO substrate by electrodeposition using atomic force microscopy

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Abstract

The use of thin films for the development of high-performance solar panels has been widely studied. In this study, ITO substrate (glass coated with Indium Tin Oxide) was coated with TiO_2 nanoparticles by electrodeposition processes. AFM technique was used to study the morphology, thickness, and surface roughness. Five films were produced for different deposition times. The films' morphology was affected by the deposition time. The thickness increased as a function of the deposition time. The roughness decreased considerably when the deposition time increased. The coatings were considered uniform and homogeneous. These results were presented as an optimization of the TiO_2/ITO system that can enhance the application of these films in the technological field.

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Keywords: TiO_2, ITO, Roughness, Electrodeposition, Morphology

INTRODUCTION

Films of titanium dioxide TiO_2 are extensively studied because of their interesting chemical, optical [1], photocatalytic, antimicrobial properties, [2] and electrical properties, besides to be one of the most studied semiconductors to make photovoltaic devices [1-7]. These kinds of materials can be used as an anti-reflective and protective coating for optical elements [8,9]. The versatility of this semiconductor is associated with low toxicity, high photochemical stability, abundance, and the facility to obtain by conventional synthesis routes [10-13]. Additionally, TiO_2 has excellent enabling enhancement of these properties by chemical doping [14], heterojunction [15], or sensitization by dyes [16,17].

Photovoltaic devices based on titanium dioxide exhibit advantages in the conversion of solar light to electrical energy [16]. Among these, high stability to natural factors, low cost, easy to obtain, availability, and several methodologies of synthesis [16,18]. About the obtention of thin films, the electrodeposition [21, 22], spray pyrolysis [20], spin-coating [18], and sputtering [19] method was reported. In this context, Shriwastava and Singh [23] report the study of the growth of TiO_2 films using the pulsed laser on silicon substrates, obtaining the mixtures between the anatase, brookite and rutile polymorphs. While Granados et al. [24] obtained thin films (≈ 300 nm) of mesoporous TiO_2 (anatase) using the heat-treated spin-coating method at 300 to 600 ° C. Due to the strong relationship between the parameters relevant to each synthesis methodology and the textural properties, crystallite size and thickness of the obtained films, it is of interest to study the variables in the properties exhibited by the thin films. Therefore, in the study by Su et al. [4], thin films with high homogeneity were obtained using electrodeposition as a method for the growth of films, resulting in excellent photovoltaic properties.

The understanding of the growth mechanisms and the study of the morphology of the films are essential to prepare materials in a controlled way for the desired properties. Therefore, studies based on the films morphology when the thickness is variated give an idea

about the growth mechanism of these films [25,26]. Scanning probe microscopy techniques, such as atomic force microscopy (AFM), have been a technique widely reported in the morphological characterization in real space, determination of thickness, roughness, and particle size in thin films [10]. In the case of TiO_2, thin films were obtained by atomic layer deposition (ALD) and they were studied topographically by AFM using 2D and 3D analysis [27].

In the present work, we have focused our attention on the growth of nanostructured TiO_2 films on ITO substrates which were obtained using the electrodeposition technique under different times deposition. Morphology and roughness as a function of film thickness and time deposition of the films are discussed. A correlation is established between time deposition, surface roughness, and growth morphology of the TiO_2 films.

EXPERIMENTAL SECTION

TiO_2 deposition on ITO substrate

To prepare the electrolyte solution, previously, an ethanolic dispersion was prepared by mixing 2g of TiO_2 (21 nm, Sigma-Aldrich) in 80 mL of ethanol (Vetec) and 0.1 mL of acetylacetone (Vetec) and kept in magnetic stirring for 24 hours, and fowling the procedures, it was prepared by dissolving in the ultrasonic bath for 25 minutes 20 mg of iodine (Sigma-Aldrich) in 20 mL of ethanol (Vetec), 2 mL of deionized water and 2 mL of acetone (Synth). To make the deposition, conductive substrates of indium tin oxide (ITO) coated on glass (15 Ω/sq, Lumtech) were used. Afterward, the electrolyte solution was added to the TiO_2ethanolic dispersion and submitted to the ultrasonic bath for 25 minutes.

A specific holder with two connectors was used to place the ITO substrates of 2x1 cm, previously cleaned [10], in contact with 10 mL of the electrolyte solution containing TiO_2 dispersion. The exposed area to the dispersion was 1 cm^2 and the separation among the substrates of 2 mm. Positive and negative poles were connected to the respective output plug in the power supply (Agilent E3616A) and to the ITO substrate attached to the holder. The substrate attached to the negative pole was used in this study. The deposition process was carried out applying 10 V to the substrate immersed by 02, 04, 06, 08,

and 10 seconds in the solution of electrolyte and TiO_2 dispersion. After each deposition process, the solution and the substrate attached to the positive pole were renewed. Thereafter, the substrates were submitted at 300 ºC for 30 minutes after withdrawing the dispersion.

AFM Imaging

An Innova AFM from Bruker (Santa Barbara, CA, USA), operated on a taping mode, with a scan rate of 0.5 Hz, was used to make the surface characterization. The samples were scanned in air, and 40±1% relative humidity, over scanning areas of 5 x 5 μm^2, with a resolution of 256 x 256 pixels using a silicon cantilever (k=40 N/m). The feedback control to obtain the best possible images was adapted to each surface and for all the applied scans. The analysis of the images was completed with the WSXM software, version 5.0, development 9.1 [28] and, through the images, it is possible to obtain the surface roughness.

RESULTS AND DISCUSSION

AFM Measurements Analysis

The obtained films were analyzed by Atomic Force Microscopy to determine the morphological parameters of the surface and to interpret the growth according to the deposition time. The change in morphology of the TiO_2 film as a function of its thickness has been followed by AFM and, to measure these thicknesses, topographical images of the film edges were performed. Two regions were scanned spanning the edge of a wear track as shown in figure 1, where a typical measure of thickness, together with a graphic profile of a line, is presented. In such an image, ten different thickness measurements were done, and the average thickness of the film was obtained.

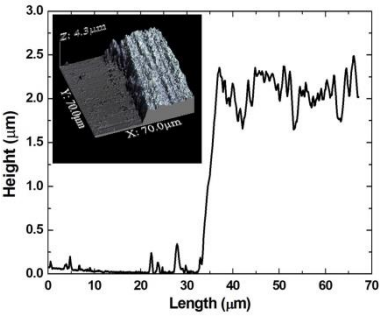

Figure 1. An AFM image and one respectively line profile used to measure the films thickness.

To correct distortions on topographical data, images were processed using a plane fit in the plane region, which corresponds the ITO surface. To produce the step between TiO_2 film and the substrate, a small piece of adhesive tape was glued over ITO. As shown in figure 1, a line profile which was taken in the direction perpendicular to the step, it has an abrupt increase during the transition ITO/TiO_2. From figure 2, it can be noted that the thickness has an increasing behavior without any evidence of saturation, varying from 1054,40 ± 101,23 nm to 2561,82 ± 87,97 nm.

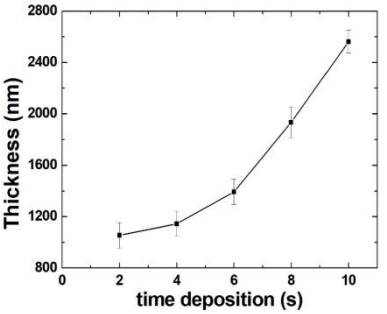

Figure 2. An AFM image and one, respectively line profile used to measure the films thickness.

The influence of the deposition time on the microstructure and morphology surface of TiO_2 deposited on the ITO substrate via electrodeposition can be observed through figure 3. The most relevant images of the 2D and 3D topography are shown in figure 2 a-e. Previously to any surface analysis, the originally acquired height data were processed using a plane fit, to first order, in both x and y

directions to correct any tilt between the tip and the sample plane, and the average height of the lines was adjusted by a zero order flatten procedure using WSXM software. No other processing was done after to avoid an overestimation of thickness or roughness calculations when examining the film surface by AFM.

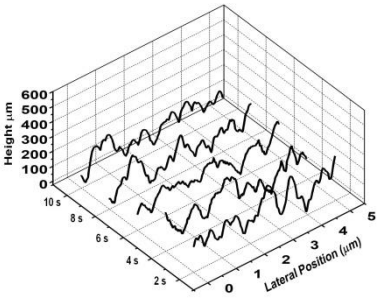

Figure 3. Typical three-dimensional 5 x 5 □m² AFM images of TiO_2 films with deposition times of: (a) 2, (b) 4, (c) 6, (d) 8, and (e)10 s.

It can be clearly seen in figure 2 the evolution of surface features with deposition since the films surface morphology varies considerably with the increase in their thickness. This trend can be followed through figure 4, in which the profile of a single line of the image is presented according to the thickness of the film. It can be noted that the height, that is, the width of the interface, of the film profiles, does not change severely with increasing deposition time and, consequently, with the film thickness. It is also possible to note that the distribution of peaks and valleys has become more homogeneous as the deposition time increased.

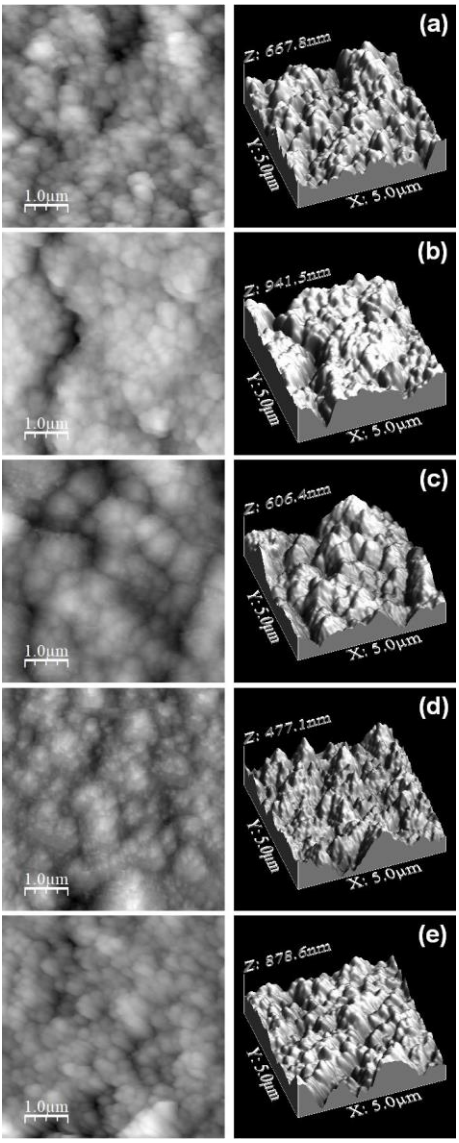

Figure 4. Evolution of surface profile of TiO_2 films as a function of deposition time.

The mean square roughness R_{RMS} is the standard deviation of the surface height distribution and is used to describe the surface roughness using statistical methods, being calculated by the equation [29]:

$$R_{RMS} = \sqrt{\frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y}\left(z(i,j) - \frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y} z_{ij}\right)^3} \quad (1)$$

The arithmetic mean roughness of the surface (R_A) is one of the most universally used parameters and is defined as the absolute mean deviation of irregularities in the roughness of the midline over a length of the surface. R_A is defined as [29]:

$$R_A = \frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y}\left|z(i,j) - \frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y} z_{ij}\right| \quad (2)$$

where N_x and N_y represent the number of points on the x and y axes, respectively. It is important to note that, comparatively R_{RMS} is more sensitive to large deviations from the midline of the surface.

For each TiO_2 film, the RMS and RA roughness was obtained by evaluating at five AFM images measured in different regions of each sample. Figure 5 presents a graph of the Roughness as a function of the number of deposition cycles. It can be observed that both RMS and RA have the same behavior. RMS varies from 69,19 ± 6,83 nm to 122,75 ± 24,05 nm and RA varies from 54,24 ± 5,25 to 96,14 ± 19,6 per 5 μm^2 area.

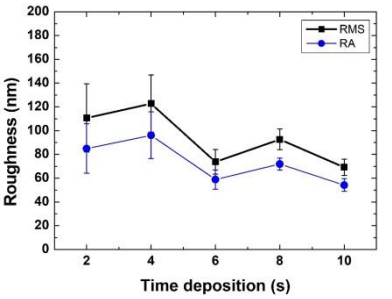

Figure 5: Graphic representation of RMS and RA roughness as a function of deposition time.

The surface of a thin film is highly reactive. It is necessary to control the superficial parameters to produce useful films without structural

failures [30]. In general, the morphology of the films was like those found in recent works (e.g., [31, 32]). In addition, grain size does not appear to be affected by deposition time. In fact, it was possible to observe uniform grains without variation in shape and size, of course, because the electrodeposition was carried out without changing the temperature. In contrast, Sertel *et al*. [33] deposited TiO_2 on silicon plates and observed changes in grain size because they studied the effect of temperature.

However, the thickness of the films increased exponentially (Fig. 2), simultaneously promoting the formation of less rough films (Fig. 5). For applications in solar systems, uniform energy absorption by the films is required. Therefore, it is necessary that the film has an appropriate thickness, so as not to create fragile films [34]. Very rough coatings promote diffuse reflection and, consequently, non-uniform absorption of energy by the films. The formation of flatter and thinner coatings was a positive point for these films.

It is known that the smaller thickness of the film, the greater the mechanical resistance is generally observed, because for greater thickness the minimum of stress can cause failure of the material [35]. The film produced with the longest deposition time was less thick than that developed by Chang *et al*. [36] (~2.5 against 10-12 μm). Therefore, the development of thin films using electrodeposition promoted the formation of uniform coatings and with a characteristic morphology of the TiO_2 / ITO system. Moreover, we have achieved excellent results for films that are thinner than those found in the literature.

CONCLUSIONS

In this paper, thin TiO_2 films were deposited on ITO substrates. Morphologies characteristic of the TiO_2/ITO system were observed for all deposition times, but with a change in the profile from 2 to 10s. Furthermore, the distribution of peaks and valleys has become more homogeneous. The thickness of the film increased with the deposition time, but the values found were lower than those reported in the literature. The grains showed no variation in shape and size when the deposition time increased. Finally, the lower roughness achieved for higher thicknesses promoted the formation of flatter films. The

optimization of the TiO2 / ITO system can provide more effective coatings for capturing solar energy by solar panels based on this system.

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