

Structural Characterization of Electrodeposited Nanostructured Titanium Dioxide thin Films on Stainless Steel and on Indium Tin Oxide (ITO)

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Abstract: Nanostructured TiO₂ thin films are fabricated directly by an anodic electrodeposition using an aqueous TiCl₃ solution. TiO₂ thin films were deposited on stainless steel (SS) and indium tin oxide (ITO) substrates. As deposited, all TiO₂ films were amorphous. For TiO₂/stainless annealed at 350 °C, XRD patterns show both anatase and rutile phases. While, only anatase phase subsists for annealing temperature at 450 °C and 500 °C. The calculated grain sizes are around 20nm. By AFM analysis, surface root mean square (rms) roughness obtained for TiO₂ /Steel is around 56 nm and decrease with annealing to 30 nm. For TiO₂ thin films deposited on ITO and annealed at 350, 450, and 500 °C, only orthorhombic single phase is observed with grains size of about 25 nm. The rms of as-deposited TiO₂/ITO around 60 nm decrease with annealing to 40 nm confirming that annealing process improves the roughness of the as deposited samples. Copyright © 2014 IFSA Publishing, S. L.

Keywords: TiO₂, Nanostructured thin films, Electrodeposition.

1. Introduction

During the last decades, titanium oxide (TiO₂) is probably one of the most widely studied semiconducting metal oxides due to its non toxicity, a

high chemical stability and a great application potential in many fields, such as solar cells [1], gas sensors [2, 3], and lithium-ion batteries [4]. Anatase rutile and brookite are three well-known TiO₂ crystal phases [5-7]. Anatase is the most studied because it is

more stable compared to the two others. The most important factors for the properties are polymorphic form of TiO₂, the morphology of the oxide phase [8, 9], sizes of the crystallites [10], nanometer-sized particle thin films [11]. Many methods have been employed to control the properties of titanium oxide such sol-gel [12], template surfactant-directed [13], hydrothermal technique [14], chemical vapor deposition [15] and so on.

In this work electrodeposition process is used to prepare TiO₂ because it's low cost method and it's easy to control film thickness, morphology and composition through electrical parameters such as deposition current and applied potential, temperature, pH and deposit time. We describe the preparation of electrodeposited nanostructured titanium dioxide thin films on stainless steel and on indium tin oxide (ITO). X-ray diffraction, Scanning Electron Microscope (SEM) and Atomic Force Microscopic images (AFM) studies are reported.

2. Experimental

Titanium oxide films were deposited directly on two substrats: stainless steel (SS) foil (1 cm×2 cm) and on optical ITO coated glassplates by applying an anodic current density of 0.3 mAcm⁻² for 1 h. The electrodeposition bath was a 7 mM TiCl₃ solution prepared from a 20% solution of TiCl₃ in 3 % hydrochloric acid («Alfa Aesar»). The pH value of 2.5 was adjusted with 10 % Na₂CO₃ solution («PURKA»). Prior to electrochemical deposition, substrats were rinsed in acetone and de-ionized water, respectively. After deposition, the films were rinsed several times in de-ionized water and then annealed for 2 h in air at various temperatures. The electrochemical experiments were carried out in a three-compartment cell. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum foil was the counter electrode. Electrodeposition was carried out on a potentiostat/galvanostat (VoltaLab PGZ 301). The films were characterized by X-ray diffraction (XRD) using X'Pert Pro diffractometer with Cu K α radiation ($\lambda=1.54056$ Å). The surface morphology and chemical composition of TiO₂ layers were examined by scanning electron microscopy (SEM) (SEI Quanta 200) equipped with EDX analysis. Surface roughness was quantitatively measured by atomic force microscopy (AFM, VEECO Dimension 3100).

3. Results and Discussion

3.1. Structure and Morphology of Titanium Oxide Films Deposited on Stainless Steel.

Fig. 1 shows XRD patterns of the titanium oxide films as-deposited and after annealing at various temperatures.

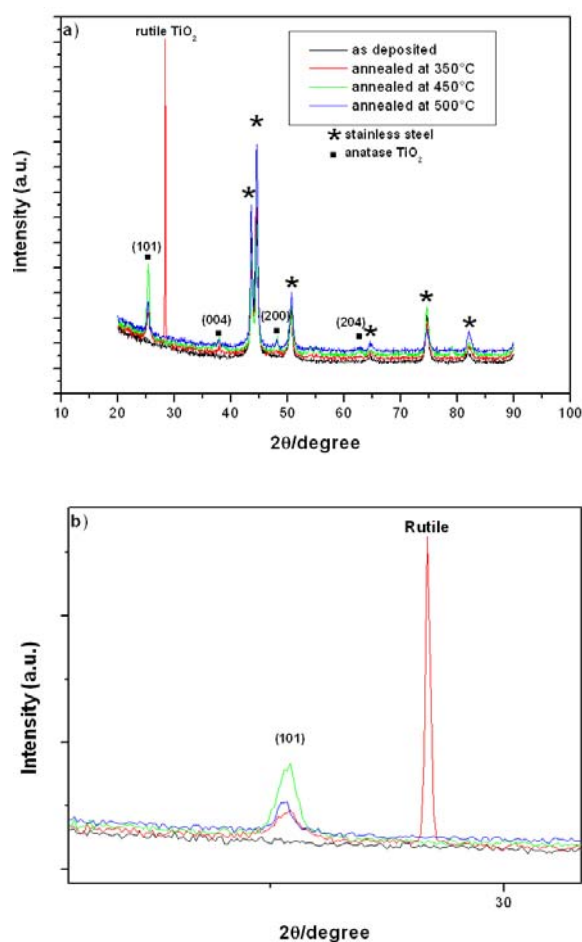


Fig. 1. a-b X-ray diffractograms of TiO₂ thin films as-deposited on SS and annealed at 350, 450 and 500 °C for 2 h in air.

The XRD pattern of the as-deposited film showed no peaks except peaks of the SS substrate ($2\theta = 44.5^\circ$), indicating an amorphous TiO_x. After annealing at 350 °C, XRD patterns show both anatase and rutile phases. While only anatase phase subsists after annealing temperature at 450 °C and 500 °C. The XRD peak (101) at about $2\theta = 25.2^\circ$ becomes finer as the annealing temperature increases from 350 to 500 °C which indicated a increase of the average grain size. The mean grain size D of the anatase TiO₂ for diffraction peak (101) at $2\theta = 25.2^\circ$ is calculated using Scherrer's equation: $D = 0.9\lambda / (\beta \cos\theta)$, where λ is the X-ray wavelength (1.54056 Å), β is the full width at half maximum (FWHM), and λ is the Bragg angle. D values at 350, 450, and 500 °C are 14, 18 and 23 nm, respectively.

Crevicees observed on SEM photographs of as-deposited TiO₂ thin films were enlarged by increasing the annealing temperature (Fig. 2). They were probably due to the removal of hydrated water during drying process and to stress variation resulting in crevicees induced by the phase transition from amorphous to anatase phase after annealing. These observations are in agreement with M. S. Wu et al. works [4].

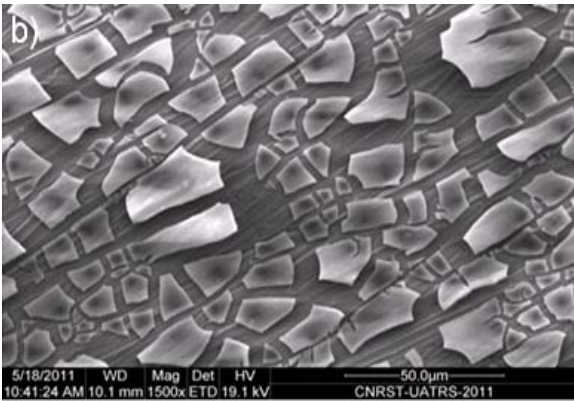
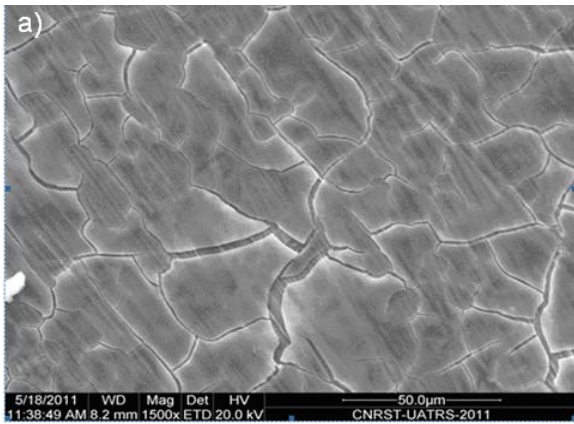


Fig. 2. SEM photographs of electrodeposited TiO₂ thin films: (a) as-deposited, (b) and after annealing at 450 °C.

By high magnification (50000 x), the surface morphology for as-deposited film reveals a structure composed of aggregates with sizes around 500–600 nm (Fig. 3).

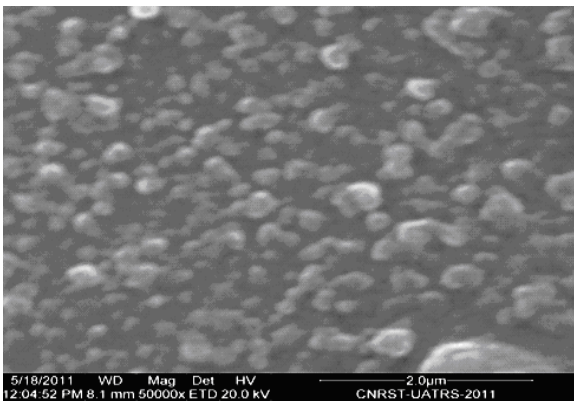


Fig. 3. High magnification images of SEM photographs of as-deposited TiO₂ thin films.

For annealed film at 450 °C the surface morphology becomes more compact aspect (Fig. 4).

Chemical composition of TiO₂ was analyzed using the EDX in order to confirm the presence of titanium and oxygen. Peaks of Fe Ni and Cr are originated from stainless substrate (Fig. 5).

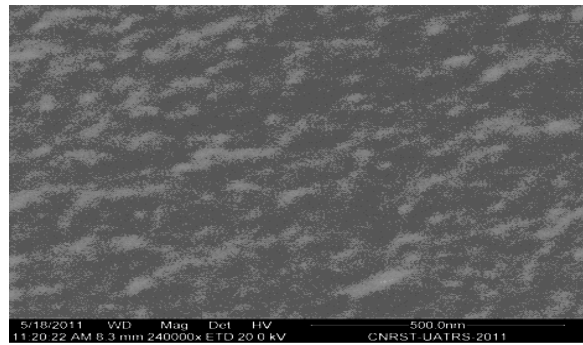


Fig. 4. High magnification images of SEM photographs of TiO₂ thin films annealing at 450 °C.

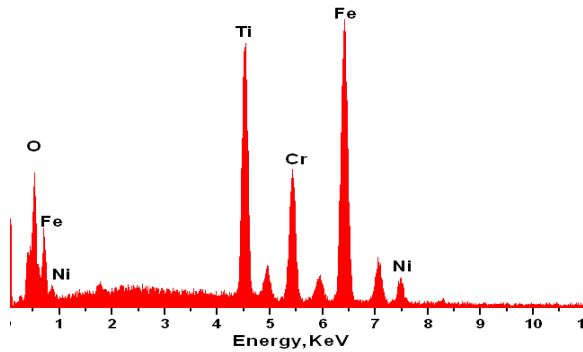


Fig. 5. EDX spectrum of as-deposited TiO₂ thin films.

By AFM analysis, we have confirmed the change in surface topography after heat treatment since the rms decrease from 56 nm for as-deposited to 30 nm after annealing at 450 °C (Fig. 6).

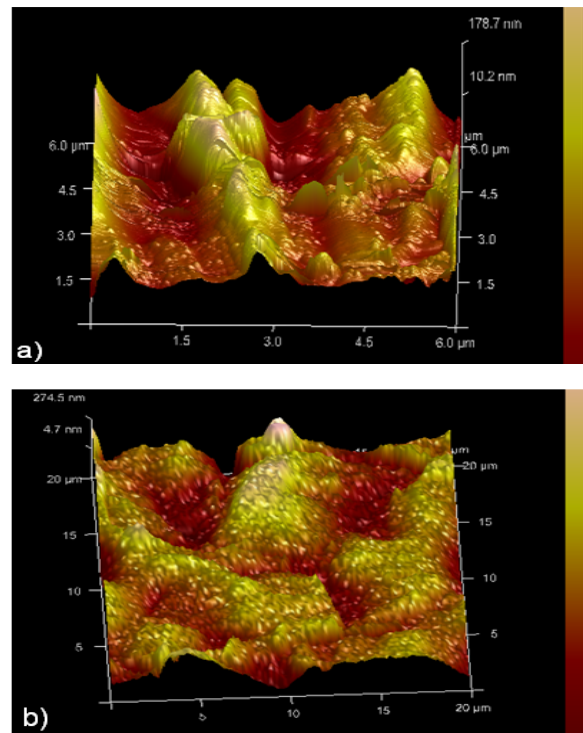


Fig. 6. AFM topography of electrodeposited TiO₂ thin films on Stainless steel: (a) after annealing at 450°C (b) as-deposited.

3.2. Structure and Morphology of Titanium Oxide Films Deposited on ITO

Fig. 7 shows XRD patterns of titanium oxide films as-deposited on ITO and after annealing at various temperatures. One can note that only orthorhombic single phase is observed.

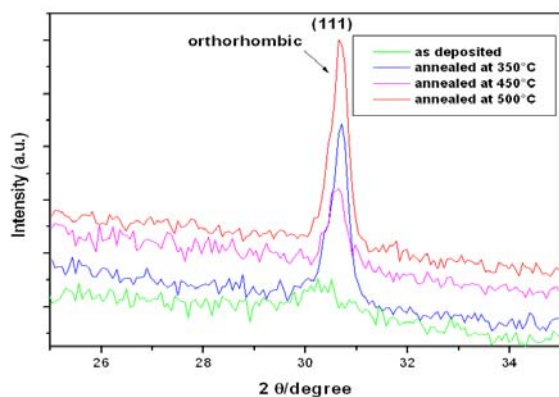


Fig. 7. X-ray diffractograms of TiO₂ thin films as-deposited on ITO and sintered (annealed) at 350, 450 and 500 °C for 2 h in air.

The XRD peak at about $2\theta = 30.9^\circ$ becomes finer as the annealing temperature increases from 350 to 500 °C indicated an increase of the average grain size.

From (111) diffraction peak, the calculated grain sizes at 350, 450, and 500 °C were 20, 25, and 31 nm, respectively. EDX spectroscopy confirms the presence of titanium and oxygen in TiO₂ deposited on ITO. Peaks of In, Sn and Si are originated from ITO/glass substrate (Fig. 8).

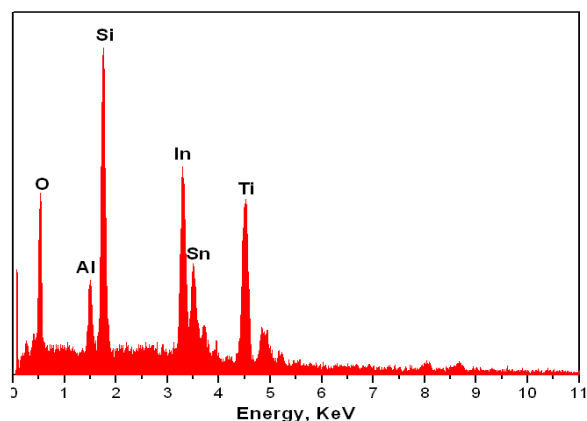


Fig. 8. EDX spectra of as-deposited TiO₂ thin films.

By AFM topography, it can be seen that the samples deposited on ITO are less dense than samples obtained on SS substrate (Fig. 9). The rms of TiO₂/ITO around 60 nm for non annealing samples decreases after annealing to 40 nm confirming the change in surface topography after heat treatment

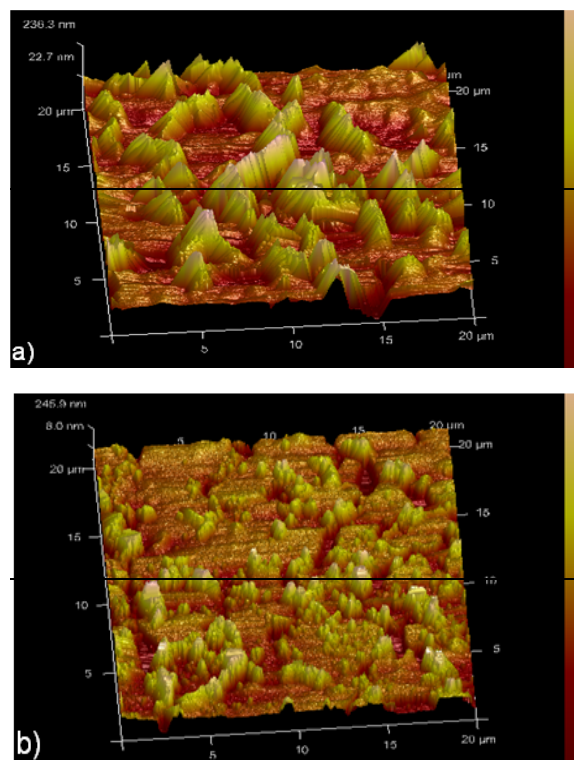


Fig. 9. AFM topography of electrodeposited TiO₂ thin films on ITO: (a) after annealing at 450 °C; (b) as-deposited.

4. Conclusions

Nanostructured titanium oxide films were successfully electrodeposited onto the Stainless steel and ITO substrates from aqueous titanium chloride. The as-deposited film on Stainless steel converts from amorphous into two phases (anatase and rutile) at 350 °C annealing temperature. For temperature exceeding 450 °C only anatase phase subsists. For TiO₂ film deposited on ITO, XRD results showed that the as-deposited film converts from poorly crystalline into only orthorhombic single phase after annealing at various temperatures.

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