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Characterization and Photocatalytic Behavior of TiO_2 Thin Films Grown by MOCVD Process

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Abstract **—** This research aims to evaluate the influence of the thickness on the photocatalytic behavior of TiO_2 thin films grown at 400ºC by metalorganic chemical vapor deposition. Titanium dioxide films with 280 and 468 nm of thickness were grown on borosilicate substrates. The photocatalytic behavior was evaluated by monitoring the degradation of methyl orange dye under UV light for 2h. The results show that both films presented anatase crystalline phase and that increasing the thickness the grain size and the roughness were also increased. The best photocatalytic performance was attributed to the film of 468 nm of thickness that exhibited 40% of dye degradation after 2h under UV light.

Keywords — TiO_2, thin films, MOCVD, photocatalysis.

I. INTRODUCTION

Advanced Oxidation Processes (AOP) are methods used to degrade recalcitrant substances present in water and is based on the utilization of highly oxidizing species[1]. AOPs are employed to improve the efficiency in the treatment of wastewater[1]. Heterogeneous photocatalysis is an oxidative process that uses the radiant energy (visible or ultraviolet) absorbed by a photocatalyst to mineralize organic compounds[2]. Titanium dioxide (TiO_2) is a crystalline ceramic that acts as a photocatalyst due to its semiconductor properties, producing hydroxyl radicals to degrade pollutants released into the waters and effluents[3]. The goal of this work is to grow TiO_2 thin films at 400ºC by metalorganic chemical vapor deposition (MOCVD), characterize the structural and morphological properties of the films, and to study the influence of the thickness on the photocatalytic efficiency to degradate methyl orange dye under UV light.

II. MATERIAL AND METHODS

The growth of TiO_2 thin films was performed in a conventional horizontal MOCVD reactor at 400ºC. Titanium Tetraisopropoxide (TTiP) was used as precursor of titanium and oxygen. Nitrogen was employed both as purge and vector gas. The borosilicate substrates (25x76x1 mm) were previously cleaned in a 5% H_2SO_4 aqueous solution, rinsed in deionized water, dried in nitrogen, and immediately inserted into the reactor. For the morphological characterization of the films, scanning electron microscopy (FEG-SEM) was used, through a *JSM6701F* equipment, and atomic force microscopy (AFM) Tapping Mode, by means of *SPM Bruker* equipment, model *NanoScope IIIA*, employing a silicon tip with a curvature radius of 15 nm. X-ray diffraction (XRD) was used to identify the phases formed and to determine the crystallite size. The photocatalytic properties of the TiO_2 films were analyzed by spectrophotometry (*Global Trade Technology* equipment) by measuring the degradation of methyl orange dye under UV light radiation. For this purpose, the films were placed in a reactor containing 40 mL of the dye solution and were illuminated by two tubular UV lamps (λ = 352 nm) for 2 hours.

III. RESULTS AND DISCUSSION

Fig. 1 exhibits the results of TiO_2 thin film grown with thickness of 280 nm. FEG-SEM image (Fig. 1b) reveal the formation of a dense film. By means of AFM image (Fig. 1a), it is noted that the film presents a homogeneous morphology, rounded grains with mean size of 96.5 nm and RMS roughness value of 19.1 nm. Fig. 2 shows the results of TiO_2 thin film grown with thickness of 468 nm. According to AFM image (Fig. 2a), the film has higher mean grain size – 213.8 nm – and values of roughness in the same order of magnitude. It is possible to observe the formation of a dense film with columnar structure (Fig. 2b).

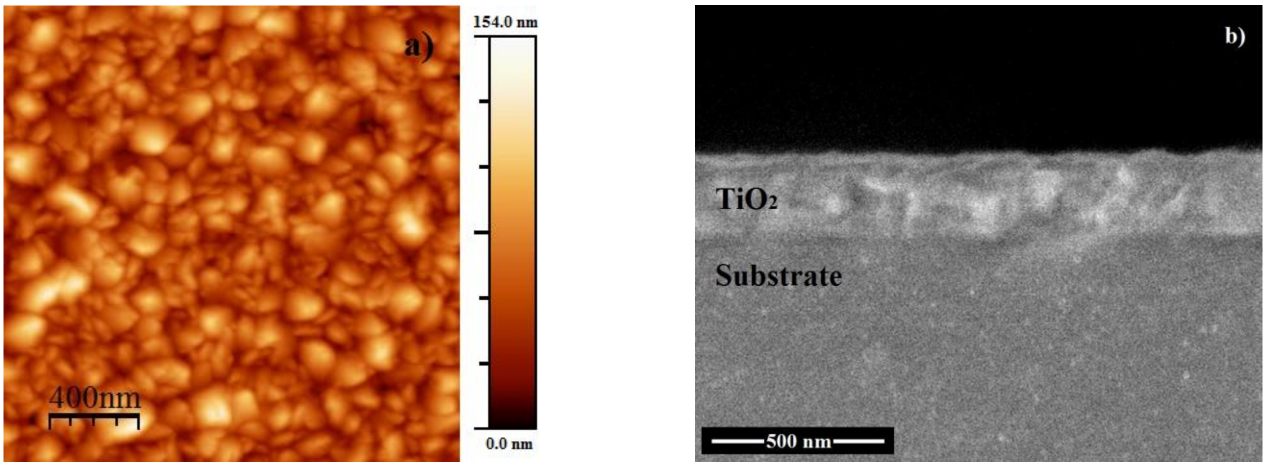

Fig. 1. Micrographs of TiO_2 film grown on borosilicate at 400ºC with thickness of 280 nm; a) AFM topography; b) FEG-SEM cross section.

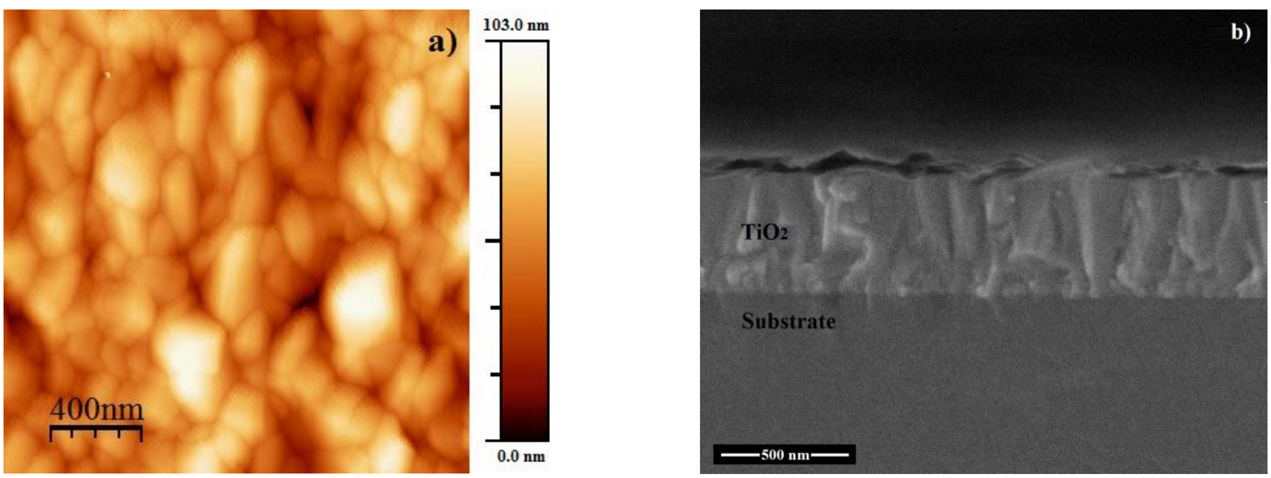

Fig. 2. Micrographs of TiO_2 film grown on borosilicate at 400ºC with thickness of 468 nm; a) AFM topography; b) FEG-SEM cross section.

In Fig.3 it can be seen the diffraction spectra of TiO_2 films grown at 400°C. It suggests the formation of anatase crystalline phase (JCPDS 21-1272 file). The mean crystallite size values were determined from the X-ray diffraction spectra (XRD) shown in Fig. 3, applying the Scherrer Equation[4]. The films with 280 nm and 468 nm presented mean crystallite size of 28.1 nm and 31.7 nm, respectively.

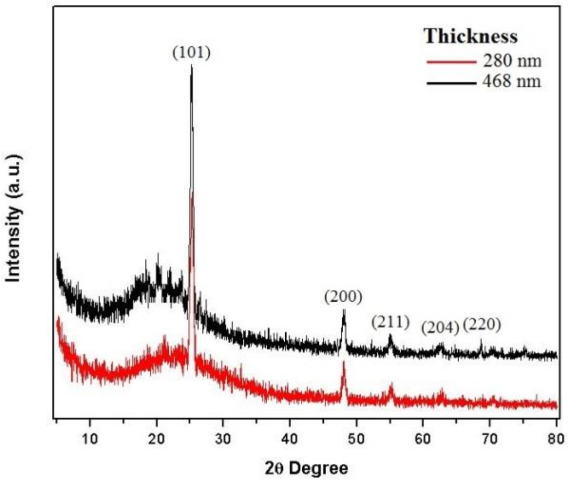

Fig. 3. X-ray diffraction patterns of the TiO_2 films grown on borosilicate at 400ºC.

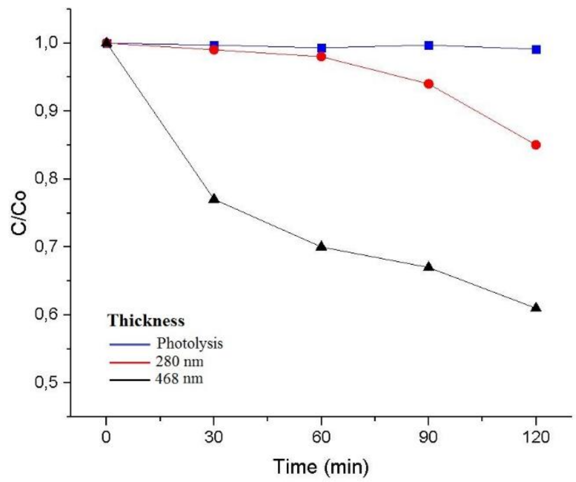

Fig. 4. Dye concentration as a function of the time of exposure to UV radiation and to TiO_2 films grown at 400ºC.

Fig. 4 exhibits the C/C_0 graphs as a function of the time of exposure to UV radiation, where C represents the dye concentration at each time interval; and C_0 is the initial concentration. The photolysis curve demonstrates that, without the presence of the catalyst, there was no degradation of the dye. It is observed that the best result occurred for the TiO_2 film with 468 nm of thickness, showing 40% of dye degradation for a total test time of 2 hours. The increase in thickness is favorable for photocatalytic efficiency of the TiO_2 films, since less thick films have a higher electron recombination rate than thicker films[5].

IV. Conclusions

The results allow concluding that the TiO_2 films grown by MOCVD at 400ºC are effective in the photodegradation process of the methyl orange dye. The films presented the formation of anatase phase, and surface morphology composed of rounded grains. The best photocatalytic result occurred for the TiO_2 film with thickness of 468 nm, that exhibited 40% of dye degradation.

V. References

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