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Morphological characterization of N-doped TiO_2 thin films

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Abstract— Metallorganic chemical vapor deposition was used to grown TiO_2 and N-doped TiO_2 on borosilicate substrates at 400°C. Titanium isopropoxide IV was used as titanium and oxygen precursors and ammonia as nitrogen source. Analyses by atomic force microscopy showed that both films presented rounded well-defined grains. The results showed that nitrogen doping resulted in a decrease in the mean grain size and in the surface roughness.

Keywords— TiO_2, thin films, N-doped TiO_2.

I. INTRODUCTION

Titanium dioxide is a semiconductor that can be produced in the form of powders and films. It is friendly to the environment and exhibits good chemical stability, corrosion resistance, photostability and band gap energy compatible with sunlight[1-2]. TiO_2 presents allotropy in three crystalline phases: anatase, rutile and brookite. The rutile phase is the most stable thermodynamically, and anatase presents higher photocatalytic efficiency[3]. Due to its physical and chemical properties, TiO_2 has been used in many applications, from automotive sector to human health. In recent decades, it has been used as a photocatalyst in the photodegradation of organic pollutants and bacteria[2,4,5]. However, the high band gap values of 3.2 eV for anatase and 3.0 eV for rutile[6] limits its use as a photoactive material since it is activated only by UV light, which corresponds to about 3-4% of the solar spectrum[7]. Thus, an alternative that has been explored to allow its use under visible light is the doping of TiO_2 with metals or non-metals[6,8]. According to Reddy et al.[9], the doping with anions such as N, S and C alters the conductivity and the optical properties by introducing new surface states near the conduction or the valence band of the TiO_2. Asahi et al.[10] proposed that, in anatase nitrogen-doped TiO_2 the oxygen atoms are replaced by nitrogen atoms. The small difference between the ionic radii would facilitate this substitution and would not cause great distortion of the crystalline lattice. In this context, considering that the morphology, the roughness and the grain size influence the photocatalytic efficiency of TiO_2 films[11], the goal of this study was to grow films of TiO_2 and N-doped TiO_2 for use in photocatalysis, and to characterize the surface properties.

II. MATERIAL AND METHODS

Borosilicate substrates were cleaned in a 5% H_2SO_4 aqueous solution, rinsed in deionized water in abundance, dried in nitrogen and immediately inserted into the reactor chamber. Thin films of TiO_2 and N-doped TiO_2 were grown by metallorganic chemical vapor deposition (MOCVD) at 400° C for 40 minutes under a pressure of 50 mbar. Fig.1 shows schematically the MOCVD equipment. For the growth of TiO_2 films titanium isopropoxide IV was used as precursor of both titanium and oxygen. Nitrogen was used as vector and purge gas. To produce the N-doped TiO_2 films, ammonia was introduced into the system during the growth. The nitrogen and ammonia flows were set in 0.5 mL/min. The morphology, roughness and mean grain size were evaluated by atomic force microscopy (AFM) on a Bruker SPM equipment, model NanoScope IIIA.

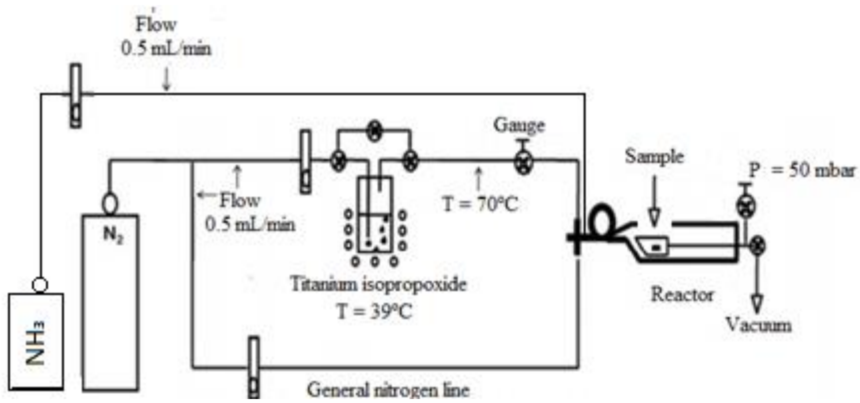

Figure 1: MOCVD equipment shown schematically (adapted from reference 12)

III. RESULTS AND DISCUSSION

Fig.2 and 3 show the AFM topography of TiO_2 and N-doped TiO_2 thin films. Rounded and well defined grains can be observed in these surfaces. From Tab.1 it can be seen that the undoped film presented mean grain size of 96 nm and roughness of 19 nm, and the N-doped TiO_2 film presented 67 nm and 4 nm for mean grain size and roughness, respectively. According to our results it was found that the surface roughness and the mean grain size decrease in N-doped TiO_2 films.

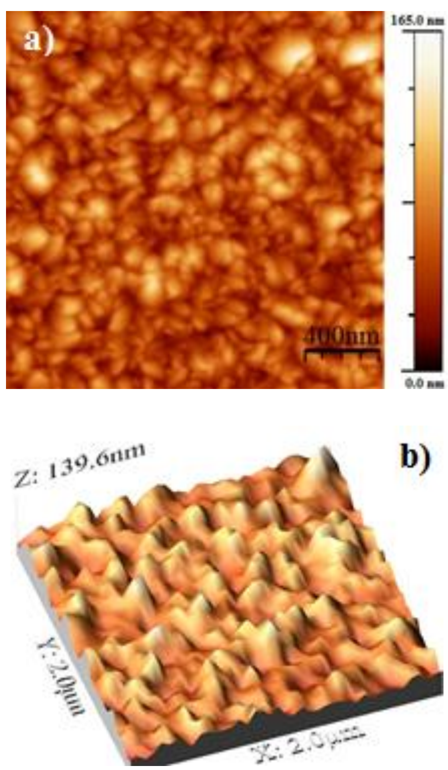

Fig.2 AFM image of the TiO_2 film grown at 400ºC (a) topography; (b) 3D image.

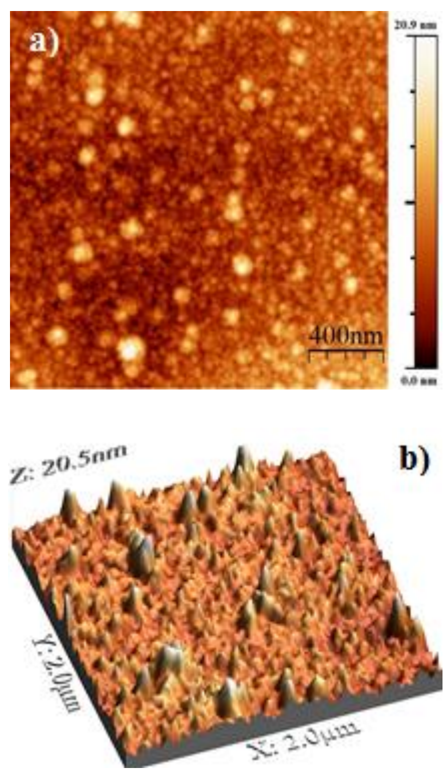

Fig.3 AFM image of the N-doped TiO_2 film grown at 400ºC (a) topography; (b) 3D image

Table 1 - Mean grain size and RMS (Root Mean Square) roughness for N-doped and undoped TiO_2 thin films

	Mean Grain Size	RMS roughness
undoped TiO_2	96 nm	19 nm
N-doped TiO_2	67 nm	4 nm

IV. Conclusions

The MOCVD process allows to grow undoped and N-doped TiO_2 films. Nitrogen doping decreased the grain size and the surface roughness of TiO_2 films. In fact, the TiO_2 film presented a mean grain size of 96 nm and roughness of 19 nm, whereas the N-doped TiO_2 film showed a mean grain size of 67 nm and roughness of 4 nm.

V.References

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