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Effect of deposition methods on the properties of photocatalytic TiO_2 thin films prepared by spray pyrolysis and magnetron sputtering

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Abstract

Titanium dioxide thin films were deposited by DC reactive magnetron sputtering and spray pyrolysis methods onto glass and glass coated with fluorine doped tin oxide (FTO). The films were characterized by x-ray diffraction, scanning electron microscopy, atomic force microscopy and UV–visible spectroscopy. For films deposited by the sputtering technique we have studied the effect of the total pressure of an Ar–O_2 mixture on the substrate properties, on the deposition rate, phase composition, crystallinity, surface morphology and on the photocatalytic properties. Also transparent TiO_2 thin films have been prepared by spray pyrolysis using a low concentration of titanium precursor with different substrate temperatures. At higher substrate temperatures the films were polycrystalline in the anatase phase; at lower substrate temperatures the films presented an amorphous configuration. The photocatalytic properties of TiO_2 thin films were tested with the degradation methylene blue under UV light irradiation. The higher degradation rates were reached for films prepared by spray pyrolysis with a substrate temperature close to 400 °C, and for a high total pressure (16 mTorr) for films deposited by DC magnetron sputtering.

1. Introduction

Chemical wastes from manufacturing processes have too often been discharged into the environment with little or no treatment; this method of disposal causes potential environmental damage, but the use of titanium dioxide mediated photocatalysis is an alternative for remediation of contaminated water and air [1].

TiO_2 thin films can be prepared by a variety of methods. Among these, reactive sputtering [2] can be used to prepare good quality films, but they are quite expensive when

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large-scale production is needed. The spray pyrolysis method is a less expensive alternative [3] for large area film production.

In this work we compare the properties of pyrolytically sprayed and sputtered TiO_2 films deposited on glass and on glass covered surfaces. We study the effect of some of the deposition parameters such as substrate temperature on the structure and photocatalytic activity of the sprayed TiO_2 films. The effect of total pressure on the structure and photocatalytic properties of the TiO_2 films sputtered on an unheated substrate has also studied. The aim of this work is to compare the photocatalytic properties of TiO_2 thin films prepared by DC reactive magnetron sputtering and spray pyrolysis methods.

2. Experimental details

2.1. Sputtering deposition

TiO_2 thin films were prepared using the commercial system DC Magnetron Sputtering Hummer XII from Anatech Ltd. A 5 cm diameter titanium target of 99.995% purity was used, and a mixture of 99.5% pure oxygen and 99.997% pure argon, a substrate–target distance of 5 cm and a constant discharge power of 100 W. Before the deposition the chamber was evacuated to 10^{-5} Torr. We introduced in the chamber a gas mixture at different total pressures, 4, 8, 16 and 32 mTorr respectively. We made the gas mixture by a simple method: the argon and oxygen gas pressures were regulated by opening both tanks valves with the same flux values in order to obtain a 50/50 ratio.

2.2. Spray pyrolysis deposition

A solution of alcoholic titanium (IV) oxide acetyl acetonate $TiO[C_5H_7O_2]_2$ (ethanol, 100 cm^3; HCl, 5 cm^3) of 0.08 M concentration was prepared and sprayed onto the heated glass substrates (300, 350, 400 and 500 °C). A spraying period of 1 s was followed by an interruption of 30 s to avoid excessive cooling of the substrate during the spray. The spraying process was done with a glass nozzle using compressed air.

2.3. Characterization

An XRD analysis of TiO_2 thin films was carried out using a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation. The surface morphology of the films was studied by scanning electron microscopy (SEM) in a JEOL 5400 microscope and atomic force microscopy in a JSPM-4210 microscope. The film thickness was measured with a Sloan Dektak IIA profilometer. The optical transmission of the films was measured with an UV–visible Agilent 8453 spectrophotometer.

We characterized the photocatalytic properties of TiO_2 thin films with a decomposition of methylene blue ($C_{16}H_{18}N_3S{\cdot}Cl{\cdot}3H_2O$). We used the same method reported by Zeman [2]. TiO_2 films were immersed in methylene blue solution 1 mM for 1 h and afterwards dried for 30 min in a dark room. The surface of TiO_2 covered with methylene blue was irradiated with UV light from a 20 W Sterilamp for 30 min. From a comparison of the optical transmittance of 650 nm light before (T_i) and after (T_f) the UV irradiation we obtained a quantitative evaluation of the degradation of the methylene blue ($\Delta ABS = \ln T_i/T_f$). We further characterized the photocatalytic activity of these films with a decomposition of an aqueous methylene blue solution (MBS). The films of size 7.5 cm^2 were dipped into 10 ml of MBS 0.05 mmol ml^{-1} and irradiated with a Sterilamp (10 W m^{-2}). The transmittance of the solution at 650 nm was measured at 2 h intervals for a total irradiation time of 10 h.

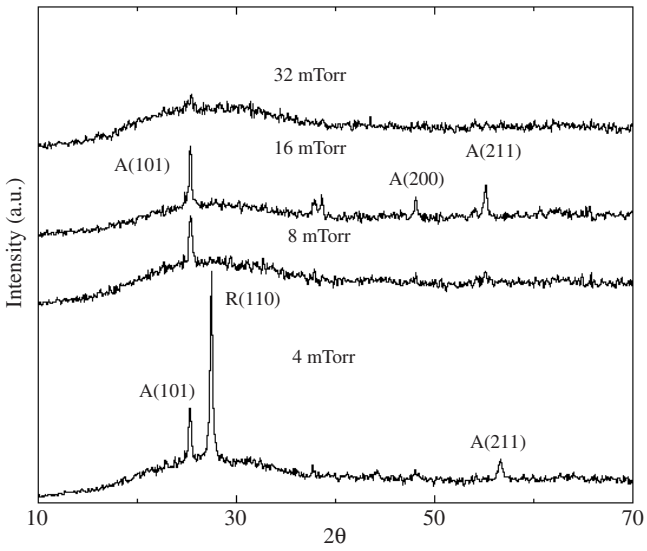

Figure 1. XRD patterns of TiO_2 thin films on glass prepared by DC reactive magnetron sputtering at different total pressures of a equimolar gas mixture Ar/O_2.

3. Results and discussion

3.1. TiO_2 film by magnetron sputtering

In figure 1 we present the evolution of TiO_2 film x-ray spectra for different total gas pressure values; it can be observed that crystallinity of our films increases for the lowest pressure values. Only the anatase phase was identified in these films and we only found a mixture of rutile and anatase phases for 4 mTorr.

In figure 2 we observe the behaviour of TiO_2 films with the same thickness when deposited on different substrates for a 16 mTorr gas pressure. It can be observed that TiO_2 thin films grown over a tetragonal substrate (FTO) present higher crystallinity than those deposited on an amorphous substrate (glass); the strongest peak corresponds to SnO_2 (on a FTO substrate). The effect of the substrate on the growth of anatase films is noticeable from the diffraction patterns in figure 2 and this behaviour might be due to the fact that the mobility of the ad-atoms on the amorphous substrate surface is different to that in the polycrystalline FTO film which in turn affects the type and rate of nucleation on the substrate.

The particle sizes were calculated from anatase (101) reflection and rutile (110) reflection, using the Scherrer equation [6]. The average particle size is around 30 nm for all films, see table 1. For a 4 mTorr pressure, we found a mixture of anatase and rutile phases in TO_2 films; it is possible to calculate the weight percentage of the anatase phase, W_A, using the equation [5]:

$$W_A = 1/[1 + 1.265 I_R/I_A] \tag{1}$$

where I_A denotes the intensity of the strongest anatase reflection and I_R is the intensity of the strongest rutile reflection. The films prepared at 4 mTorr have a percentage of the anatase phase equal to 25% as calculated with relation (1).

In figures 3(a) and (b) we present the optical transmittance spectra for TiO_2 films deposited by magnetron sputtering on glass and glass coated with FTO substrates; the highest values are obtained in both cases when a gas pressure of 32 mTorr was used. In the visible range the

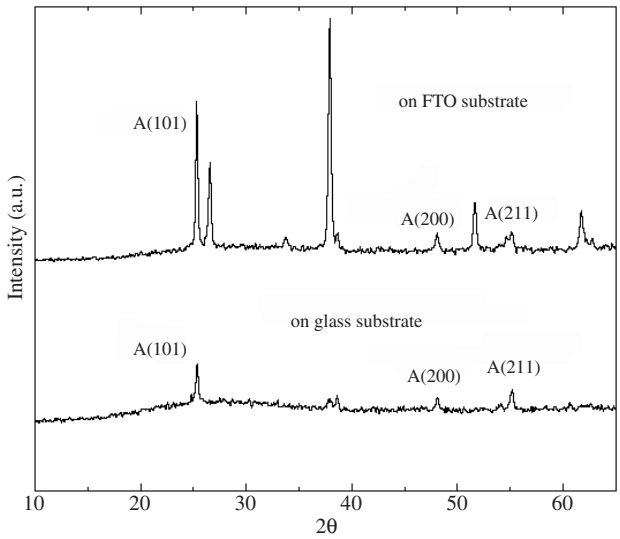

Figure 2. XRD patterns of TiO_2 thin films on different substrates by DC reactive magnetron sputtering at 16 mTorr.

Table 1. The correlation between deposition parameters and some physical properties of TiO_2 thin films deposited by magnetron sputtering.

Total pressure (mTorr)	Thickness (nm)	Phase	Grain size (nm)	E_g on glass (eV)	E_g on FTO (eV)
4	305	Rutile + anatase	28	3.12	3.14
8	280	Anatase	28	3.17	3.22
16	280	Anatase	30	3.18	3.22
32	240	Amorphous	30	3.29	3.30

Table 2. The correlation of physical parameters of the TiO_2 films deposited by spray pyrolysis for different substrate temperatures.

T_s (°C)	Phase	Thickness (nm)	Grain size (nm)	E_g (eV)
300	Amorphous	—	—	—
350	Amorphous	260	—	3.20
400	Anatase	270	32	3.25
450	Anatase	285	30	3.26

transmission of the films on glass is around 80%, whereas the TiO_2 films on FTO present a decrease in the transmission due to the absorption by FTO. The transmission decreased as the wavelength decreased due to the fundamental absorption of the light [5]. The optical band gap of our TiO_2 thin films was calculated according to the method described by Mardare *et al* [5]. An optical band gap, E_g, of about 3.2 eV has been observed by the films prepared at 8 and 16 mTorr due to the anatase phase; these values are agrees with the values reported in the literature [7].

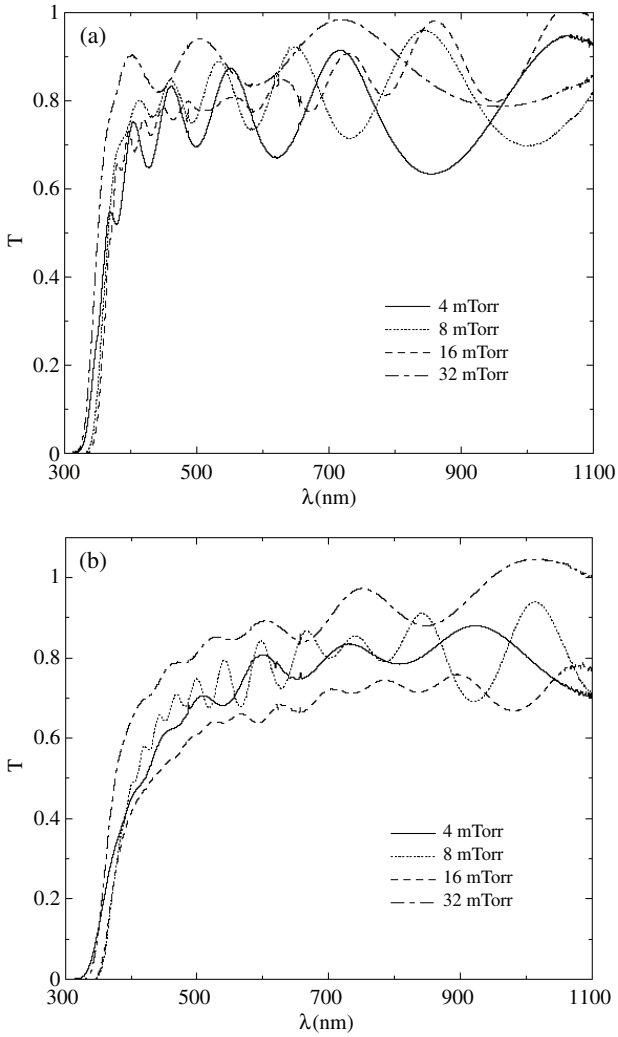

Figure 3. UV–visible transmission spectra of TiO_2 thin films prepared by DC reactive magnetron sputtering at different total pressures of a equimolar gas mixture Ar/O_2. On different substrates: (a) on glass and (b) on glass coated with FTO.

3.2. Spray pyrolysis deposition

The structure properties of titanium dioxide thin films at substrate temperatures varying from 300 to 450 °C were studied using x-ray diffraction analysis. The anatase structure with the (101) predominant plane of crystallization has been identified for the films deposited at 400 and 450 °C as shown in figure 6 the films deposited at substrate temperatures below 350 °C shows an amorphous nature. The peak intensity, i.e. the degree of crystallinity, increases when substrate temperature is raised.

Figure 7 shows the measured transmission curves for sprayed TiO_2 coatings at different substrate temperature. The transmission in the visible region increases with the substrate temperature. The increase in transmission value could be attributed to the well adherence and to the crystallized nature of the film, which is due to the evaporation of the undesired

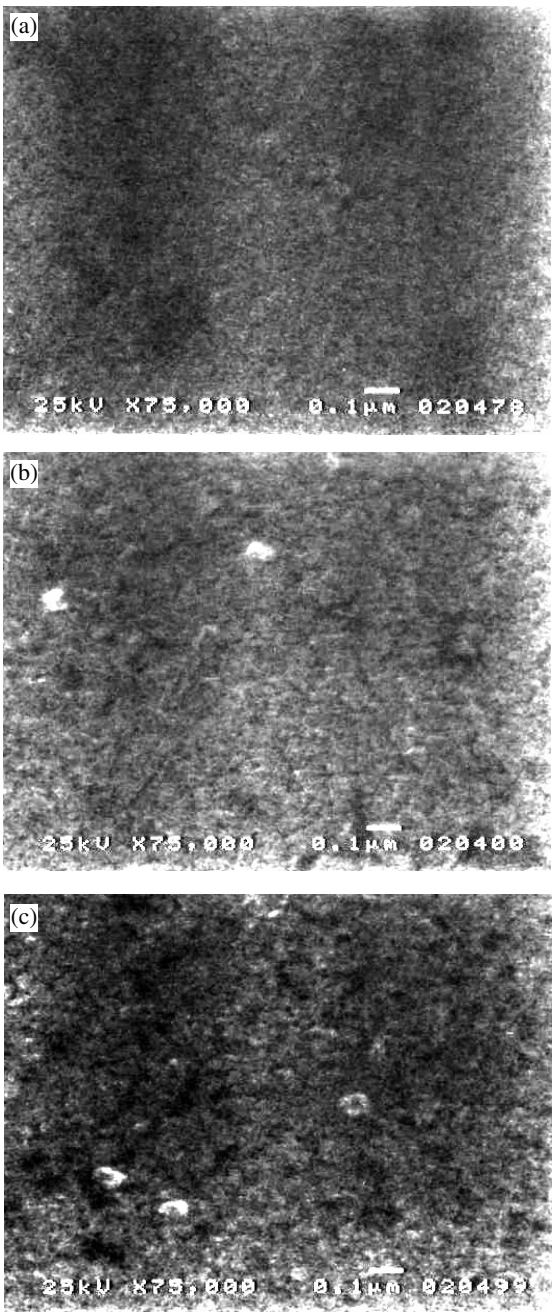

Figure 4. SEM micrographs of TiO_2 thin films prepared by DC reactive magnetron sputtering technique for different total work pressures: (a) 4 mTorr, (b) 8 mTorr and (c) 16 mTorr.

by-products and improvement in the crystallinity [3]. In the visible range the transmission of the films is around 70% and the spectra show waveforms that are characteristic of the interference light [4]. The transmission decreased as the wavelength decrease due to the

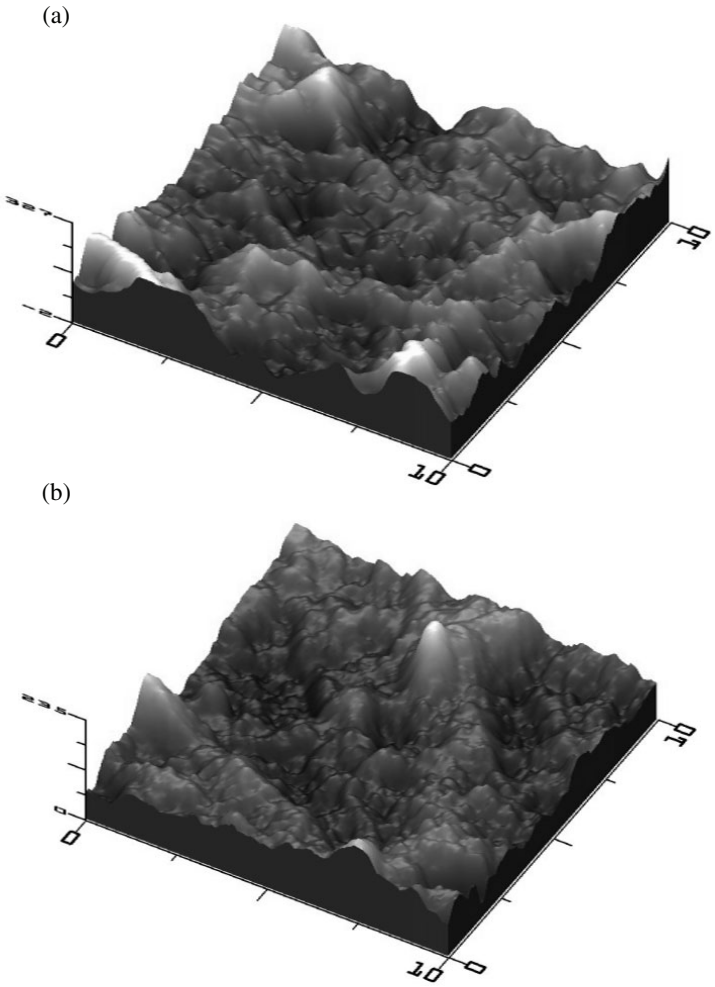

Figure 5. AFM micrographs of TiO_2 films with two different thickness: (a) 270 nm and (b) 400 nm, deposited by spray pyrolysis at $T_s = 400\,^{\circ}C$. The scale runs from 0 to 10 μm.

fundamental absorption of the light [5]. According to the method described by Mardare *et al* [5], the optical band gap of TiO_2 thin films was calculated. An optical band gap, E_g, of about 3.2 eV has been observed for the films prepared by the spray pyrolysis method with different substrate temperatures, see table 2.

3.3. Surface characterization

The evolution of surface with deposition condition was followed by SEM and AFM techniques respectively. SEM micrographs show the influence of different work pressures in the sputtering deposition chamber as can be observed in figures 4(a)–(c). As the work pressure is increased from 4 to 16 mTorr the surface roughness increases together with porosity. This kind of surface favours the trapping of the compounds to be degraded on the TiO_2 surface under UV irradiation and also is related with a higher specific surface area. Atomic force micrographs presented in figures 5(a) and (b) come from TiO_2 thin films deposited by spray pyrolysis at a substrate

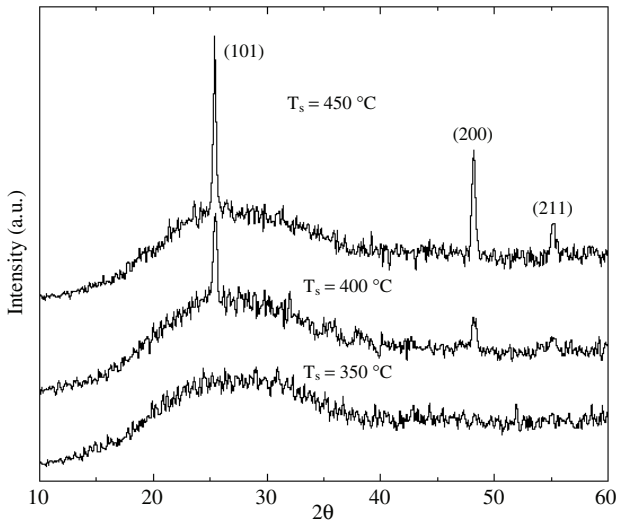

Figure 6. XRD patterns of TiO_2 thin films on glass prepared by spray pyrolysis at different substrate temperatures.

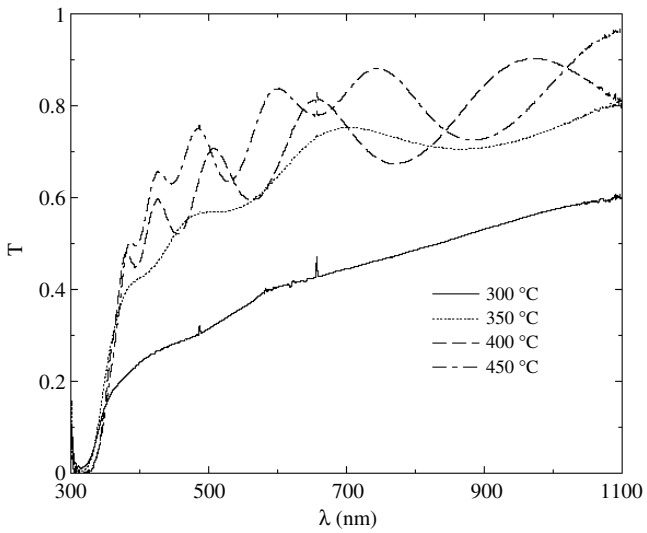

Figure 7. Optical transmission spectra of TiO_2 thin films prepared by spray pyrolysis at different substrate temperatures.

temperature of 280 °C. The films thicknesses are 270 and 400 nm respectively, and from both micrographs high roughness at nanometre level can be observed.

3.4. Photocatalytic activity

The photocatalytic process is initiated by the absorption of a photon with energy equal to or greater than the band gap of TiO_2 (∼3.2 eV in anatase phase), producing an electron–hole pair. The resultant electron–hole pair has a lifetime in the space charge region that enables its

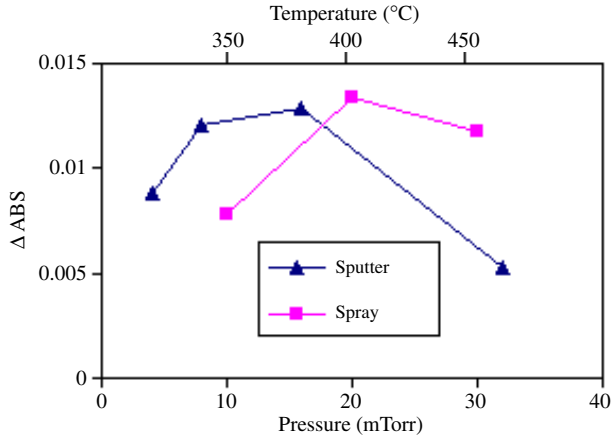

Figure 8. The change of absorbance ΔABS of methylene blue film formed on the TiO_2 surface as a function of different deposition parameters, e.g. temperature for spray and pressure for sputtered deposited films.

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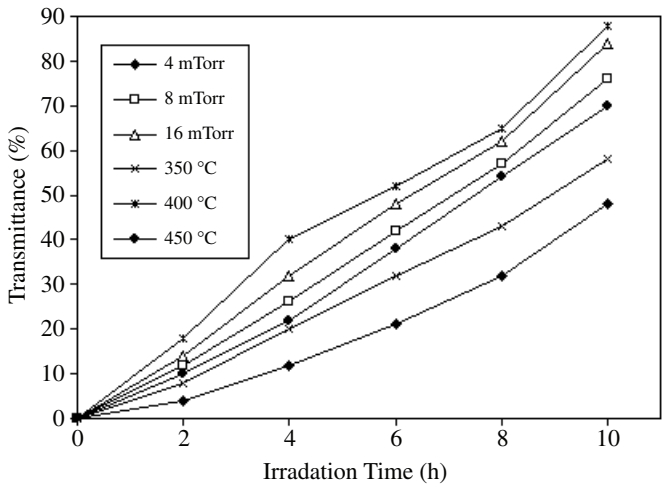

Figure 9. Transmittance at 650 nm of an aqueous methylene blue solution as a function of irradiation time when the TiO_2 films are immersed in the test cell.

participation in chemical reactions. The postulated reactions are [8]:

$$OH^-_{ad} + h^+ \rightarrow {}^\bullet OH_{ad} \quad (2)$$

$$O_{2ad} + e^- \rightarrow O^-_{2ad}. \quad (3)$$

Hydroxyl radicals ($^\bullet$OH) and super-oxide ions (O^-_2) are highly reactive species that will oxidize the organic compounds adsorbed on the semiconductor surface. Many kinds of organic pollutants can be oxidized by TiO_2. Figure 8 shows the degradation of methylene blue film formed on the TiO_2 surface for both kind of deposited thin films. The change of the absorbance (ΔABS) characterizing the decomposition of methylene blue is presented in figure 9. From these figures we can see that the highest photocatalytic activity is achieved for the TiO_2

thin films deposited by the spray pyrolysis method at 400 °C and for the one deposited by DC reactive magnetron sputtering at 16 mTorr total pressure. Both films present a open structure, anatase phase oriented along (101), (200) and (211) planes.

4. Conclusions

The deposition methods used and the corresponding parameters involved, have noticeable effects on the structure and on the photocatalytic activity of the TiO_2 thin films prepared by DC reactive magnetron sputtering and spray pyrolysis respectively. Similar band gap energy values were found for films deposited with the two techniques reported in this work and this makes our film suitable for photodegradation processes given that band gap energy together with preferential crystallinity are key parameters for the photocatalytic degradation of pollutants. From x ray diffraction results the higher degradation rates can be associated with the anatase TiO_2 phase in our films. From our results, the spray pyrolysis technique provides the best perspective for the preparation of a TiO_2 photocatalyst to be used in photodegradation for remediation of organic contaminated waters. In addition, the fact that it is a less expensive technique would all it to be introduced easily, doping atoms from the starting solutions in the TiO_2 films in order to improve the catalytic photoconversion of pollutants.

Acknowledgments

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