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Titanium dioxide thin films: the effect of the preparation method in their photocatalytic properties

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Abstract

Titanium dioxide thin films were deposited by DC reactive magnetron sputtering and spray pyrolysis methods on glass and glass coated with fluorine tin oxide (FTO). The films were characterized by X-ray diffraction, scanning and transmission electron microscopy, atomic force microscopy and UV–vis spectroscopy. The influence of a reactive atmosphere: a 50/50 Ar–O_2 mixture on TiO_2 thin films deposited by sputtering has been studied following the evolution of surface and structural properties and has been correlated, when possible, with photocatalytic properties under UV illumination. Also transparent TiO_2 thin films have been prepared by spray pyrolysis using a low concentration of titanium precursor and different substrates temperatures. At higher substrate temperatures the films were polycrystalline in anatase phase; at lower substrate temperatures the films presented amorphous configuration. The best photocatalytic activity was found for films deposited by spray pyrolysis at $T_s = 450\,^{\circ}C$ and for those deposited by magnetron sputtering those deposited at 16 mTorr gave the higher photodegradation rates.

Keywords: TiO_2; Thin films; Magnetron sputtering; Spray pyrolysis; Photocatalysis

1. Introduction

Chemical wastes from manufacturing processes have been too often discharged into environment with little or without treatment; this way of discarding have a potential environmental damage, the use of titanium dioxide mediated photocatalysis is an alternative for remediation of water and contaminated 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 large-scale production is needed. The spray pyrolysis method is a less expensive alternative [3,4] for large area films 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 studied the effect of some of the deposition parameters as substrate temperature on the structure and photocatalytic activity of the sprayed TiO_2 films. Also in this paper, the effect of total pressure on structure and photocatalytic properties of the TiO_2 films sputtered on unheated substrate was 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 for specific deposition parameters.

2. Experimental

2.1. Sputter deposition

TiO_2 thin films were prepared using a DC magnetron sputtering commercial system, Hummer XII from Anatech Ltd. A 5-cm diameter titanium target of 99.995% purity was used; a mixture of 99.5% pure oxygen and 99.997% pure argon, a substrate–target distance of 5 cm and for a constant

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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. The gas mixture was made by a simple method: the argon and oxygen gas pressures were regulated, opening both tanks valves with the same fluxes value in order to obtain a 50/50 ratio.

2.2. Tio_2 films by spray pyrolysis

A solution of alcoholic titanium (IV) oxide acetyl acetonate $TiO[C_5H_7O_2]_2$ (ethanol, 100 cc; HCl, 5 cc) 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 and purified air as transport gas.

2.3. Characterization

XRD analysis of TiO_2 thin films was carried out in a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation. The surface morphology of the films were studied by scanning electron microscopy (SEM) in a LV JEOL 5400 microscope and atomic force microscopy in a JSPM-4210 microscope. Conventional and high-resolution electron microscopy observations were carried out in a JEOL 100CX and JEOL 2010EF electron microscopes, respectively. The film thicknesses were measured with a Sloan Dektak IIA profilometer. The optical transmission of the films was measured with an UV–vis Agilent 8453 spectrophotometer.

We characterized photocatalytic properties of TiO_2 thin films with 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 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 comparison of optical transmitance of 650 nm radiation 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 photocatalytic activity of these films with decomposition of an aqueous methylene blue solution (MBS). The films of a size 7.5 cm^2 were dipped into a 10 ml of MBS 0.05 mmol/ml and irradiated with a sterilamp (10 W/m^2). The transmittance of the solution at 650 nm was measured at 2 h interval for a total irradiation time of 10 h.

Even when TiO_2 films investigated in this work were produced by both sputtering and spray techniques and we report the characterization of both kind of samples, particular attention is devoted to samples produced by the sputtering technique.

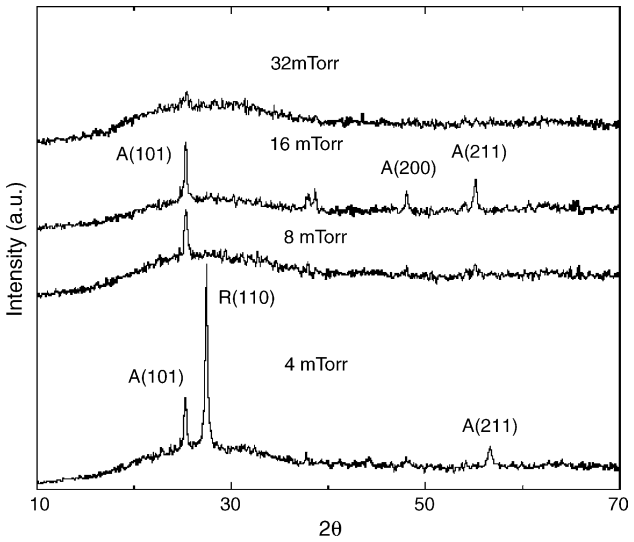

Fig. 1. XRD patterns of TiO_2 thin films on glass prepared by DC reactive magnetron sputtering at different total pressures of a equimolar gas mixture Ar/O_2.

3. Results and discussion

3.1. TiO_2 films by magnetron sputtering

In Fig. 1 we present the evolution of TiO_2 films X-ray spectra for different total gas pressure values; it can be observed that crystallinity of our films increases for the lowest pressure values. The anatase phase was detected in these films and only for a 4 mTorr pressure, we found the rutile phase.

The particle size was calculated from anatase (1 0 1) reflection and rutile (1 1 0) reflection, using the Scherrer equation [7]. 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 equation [5]:

$$W_A = \frac{1}{1 + 1.265\, I_R/I_A} \quad (1)$$

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

From optical transmittance measurements reported elsewhere [5] the optical band gap of our TiO_2 thin films was calculated according to the method described by Mardare et al. [6]. An optical band gap, E_g, around 3.2 eV has been observed by the films prepared at 8 and 16 mTorr due to the anatase phase, these values agree with the values reported in literature [8]. The band gap value is a very important parameter related to trigger a photocatalytic process when the organic material supported on TiO_2 to be degradated is irradiated with electromagnetic radiation of a specific energy.

Table 1
The correlation between deposition parameters and some physical properties of TiO_2 thin films deposited by magnetron sputtering is presented is this table

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

3.2. TiO_2 films by spray pyrolysis

Structural properties of titanium dioxide thin films deposited at substrate temperatures varying from 300 to 450 °C were studied using the X-ray diffraction analysis. Anatase structure with the (1 0 1) predominant plane of crystallization has been identified for the films deposited at 400 and 450 °C as shown in Fig. 2 the films deposited at substrates temperatures below 350 °C shows an amorphous nature. The peak intensity, i.e. the degree of crystallinity, increases when temperature is raised.

According to the method described by Mardare et al. [6], the optical band gap of the sprayed 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 spray pyrolysis method with different substrate temperatures, please see Table 2.

3.3. Surface and structural characterization

The evolution of film surfaces with the deposition conditions was followed by SEM and AFM, respectively. SEM micrographs allow us in most cases to follow at micrometer level the influence of different experimental pressures when magnetron sputtering is used or when the substrate temperatures are raised in spray pyrolysis deposition processes. In Fig. 3a and b we present SEM micrographs of samples that gave the best photodegradation activity. Fig. 3a is a micrograph from

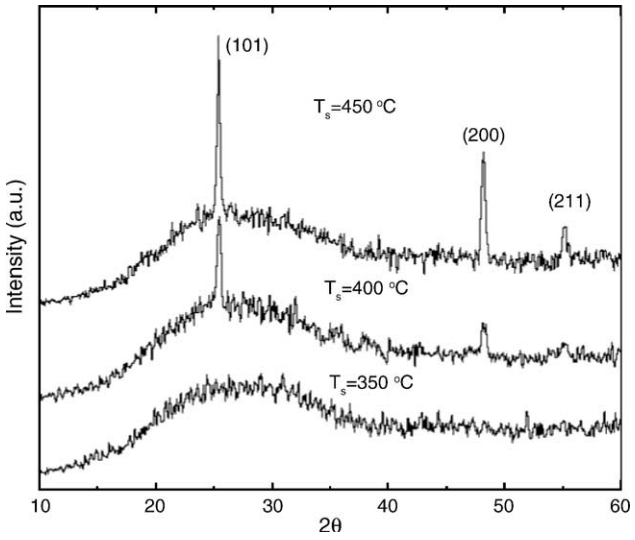

Fig. 2. XRD patterns of TiO_2 thin films on glass substrates prepared by the spray pyrolysis method at different substrate temperatures.

Table 2
The correlation of physical párameters of the TiO_2 films deposited by spray pyrolysis for different substrate temperature is observed in this table

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

a sample deposited at $T_s = 400$ °C and Fig. 3b comes from the sample deposited by sputtering at 16 mTorr. Slight differences in surface roughness can be observed in these images. In Fig. 4a and b and also for comparison purposes, we present

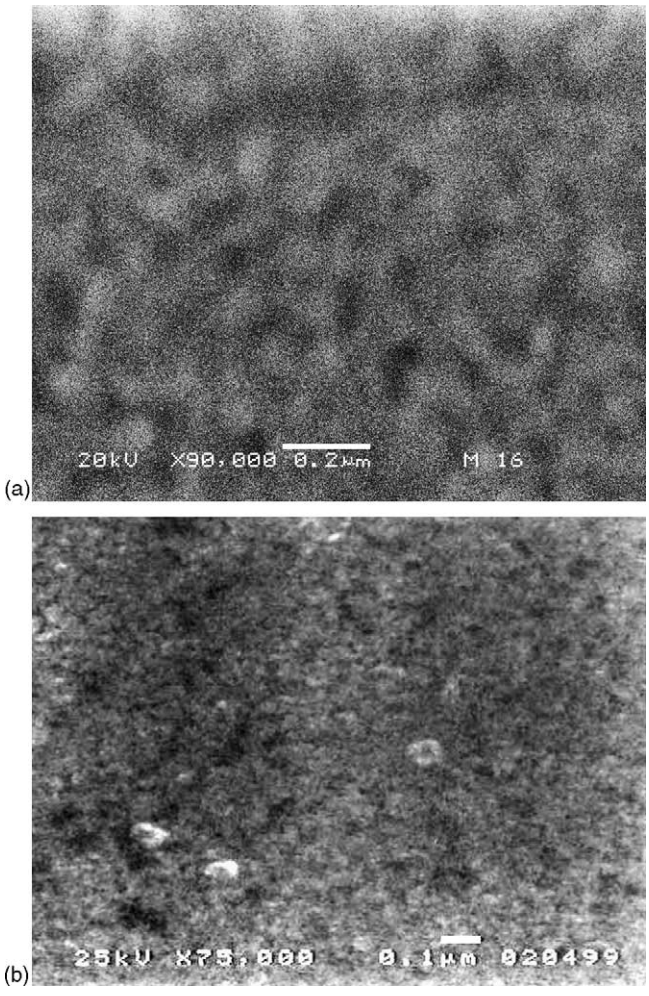

Fig. 3. (a) SEM micrograph come from sample deposited by spray pyrolysis at $T_s = 400$ °C. (b) SEM micrograph from a TiO_2 thin film deposited at 16 mTorr by DC magnetron sputtering.

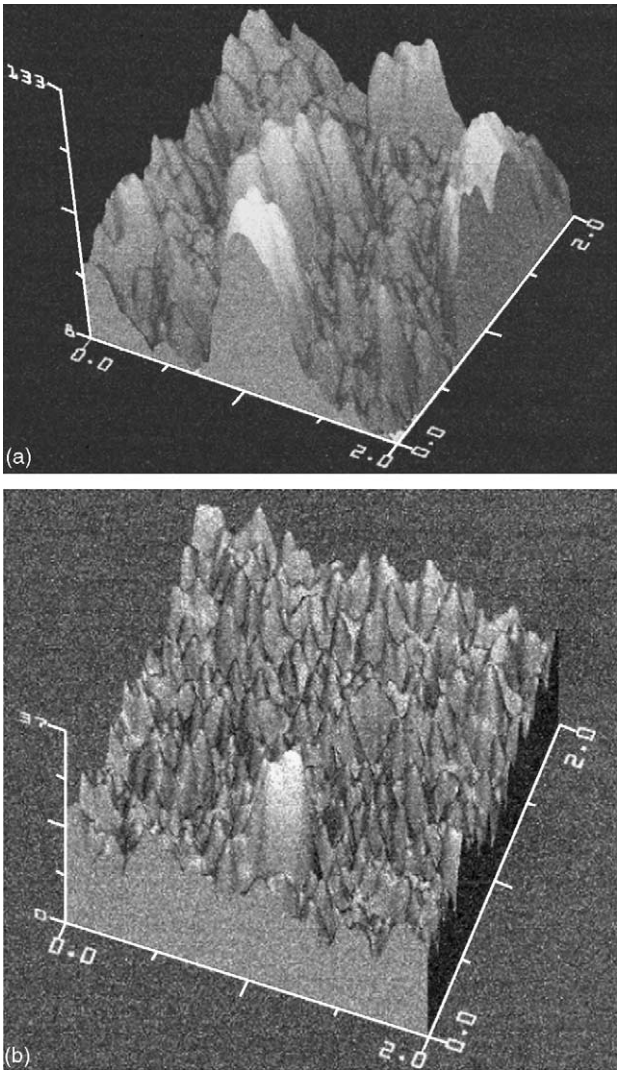

Fig. 4. 3-D AFM micrographs of TiO_2 films (a) prepared by spray pyrolysis at 400 °C. (b) Prepared by DC magnetron sputtering at 16 mTorr. The surface roughness details can be observed in both micrographs.

Table 3
Interplanar distances derived from selected area electron diffraction (SAED) patterns from samples deposited by magnetron sputtering at several gas pressures

TiO_2	*h k l*	4 mTorr	8 mTorr	16 mTorr	32 mTorr
3.520	1 0 1	3.536	3.536	3.541	3.522
2.431	1 0 3	–	–	2.536	2.528
2.378	0 0 4	–	2.363	–	–
1.892	2 0 0	1.925	1.904	1.933	1.940
1.667	2 1 1	–	1.677	1.677	1.676
1.481	2 0 4	–	1.470	1.485	1.485
1.338	2 2 0	1.354	1.347	–	–
1.265	2 1 5	1.267	–	1.244	1.250
1.161	3 1 2		–	1.155	1.160
2.188*	1 1 1*	2.193			
1.687*	2 1 1*	1.687			
1.624*	2 2 0*	1.629			
1.480*	0 0 2*	1.494			

The asterisks correspond to the rutile phase.

3-D AFM micrographs from the surface of the TiO_2 films for which the best photodegradation activity was detected. Fig. 3a comes from a sample spray deposited at $T_s = 400\,^{\circ}C$ and Fig. 4b comes from sample deposited by sputtering with a work pressure of $P_w = 16$ mTorr. The film thickness is close 420 nm for both cases. The differences in roughness and texture are noticeable from these two images and it is expected that these influence the difference in photodegradation activity presented in Fig. 8 and 9, respectively. The type of surface roughness might have to do with trapping of the compounds to be degradated on the TiO_2 surface under UV irradiation and has to do with variation of specific surface area for catalytic activity from one sample to another. Electron

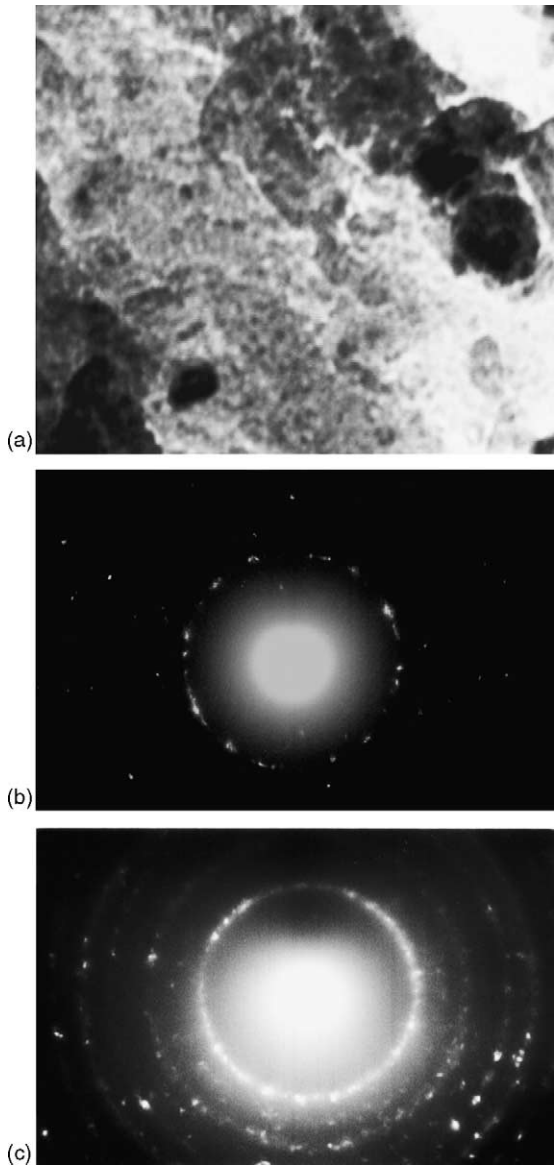

Fig. 5. (a) In this bright field transmission electron microscopy the typical configuration of our sputtered thin film can be observed in the arrowed zone. (b) This is a SAED pattern coming from sample deposited at 8 mTorr. (c) The polycrystalline nature of the sample deposited at 16 mTorr can be observed in this SAED pattern.

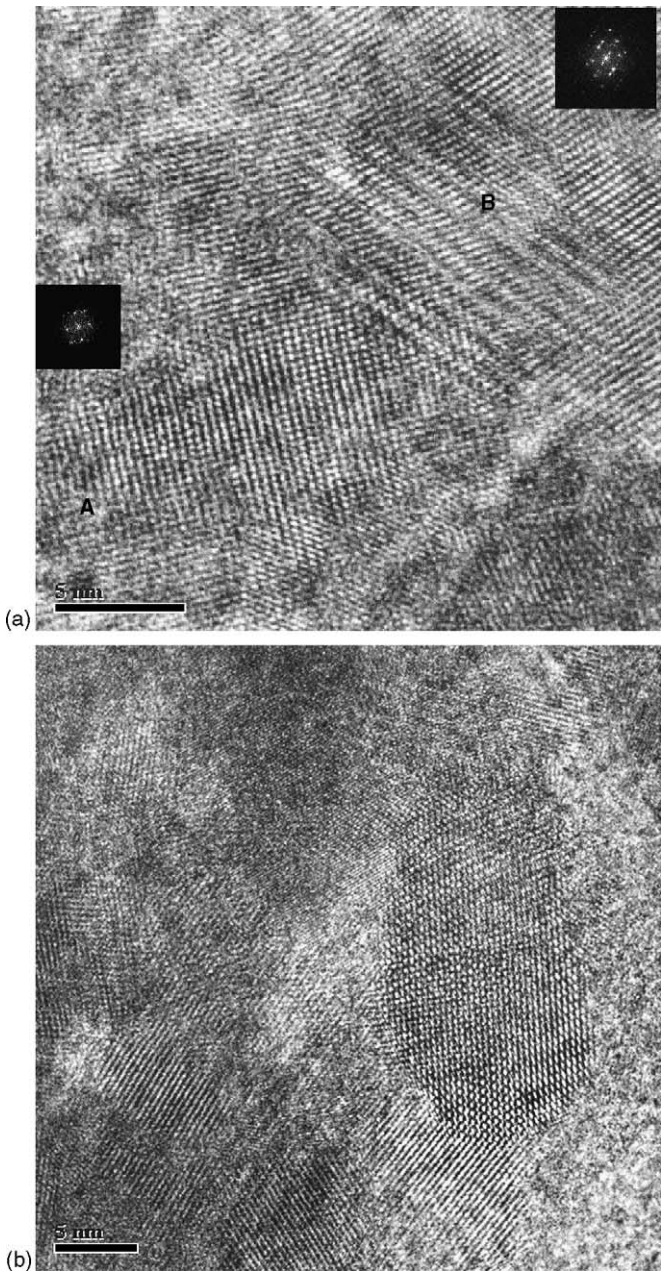

Fig. 6. (a) In this HREM micrograph from sample deposited at 8 mTorr, can be observed aggregated phases configuring a nanostructural architecture of the TiO_2 thin films. (b) This is a HREM micrograph from sample deposited at 16 mTorr. In upper right side (B), a structural defect with its corresponding diffraction pattern can be observed. In the left side (A) the tetragonal anatase configuration together with its diffraction pattern is presented.

diffraction studies were done from selected-area electron diffraction (SAED) patterns like the ones presented in Fig. 5b and c, respectively, that were obtained for samples deposited by magnetron sputtteirng at work pressures of 4,8,16 and 32 mTorr, respectively; for all the cases the samples presented polycrystalline configurations and the results are summarized in Table 3. Noticed that only for the samples deposited at 4 mTorr, both rutile and anatase were detected; for the rest of the samples the reflections measured correspond to more

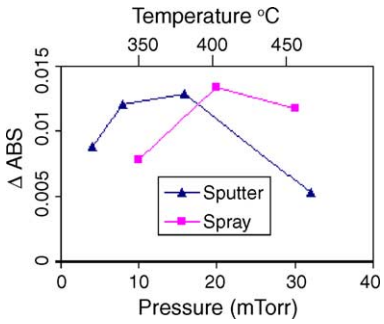

Fig. 7. The change of absorbance ΔABS of methylene blue film formed on TiO_2 surface as a function of different deposition parameters, e.g. temperature for spray and pressure for sputtered deposited films.

than 95% of the anatase phase being present. High-resolution electron microscopy micrographs like the ones presented in Fig. 6a and b, reveal that our films have nanostructural configuration, this detail can be clearly observed like in Fig. 6a. This characteristic was found in all the samples. For the samples obtained at 16 and 32 mTorr, besides the nanostructural details, a higher number of structural defects were detected in HREM micrographs. This is less evident in sample obtained at 32 mTorr. The presence of structural defects like dislocations, twins, polytypes etc. is a point that must be considered related to degradation processes given that these defect can be a source of donor or acceptor centers [10], which in turn influence the oxidation or reduction processes of organic compounds in contact with the TiO_2 material.

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 the anatase phase), producing an electron–hole pair. The resultant electron–hole pair has a lifetime in the space charge region that enables its participation

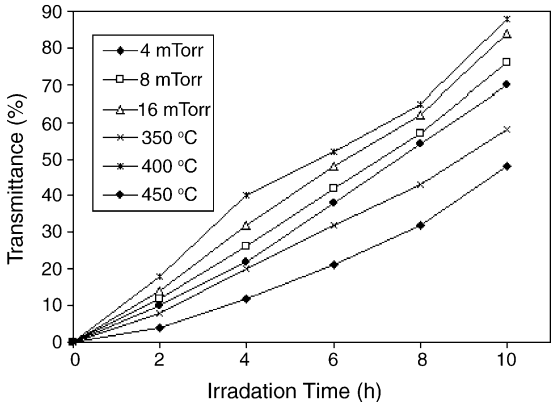

Fig. 8. Transmittance at 650 nm of an aqueous methylene blue solution as a function of irradiation time when the TiO_2 films are inmersed in the test cell.

in chemical reactions. The postulated reactions are [9]:

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

$$O_{2ad} + e^- \rightarrow O_2{}^-{}_{ad} \quad (3)$$

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. Fig. 7 shows the degradation of methylene blue film formed on the TiO_2 surface. The change of the absorbance (ΔABS) characterizing the decomposition of methylene blue is presented in Fig. 8.

From these figures, it can be seen that the highest photocatalytic activity is achieved for the TiO_2 thin films deposited by the spray pyrolysis method at 400 °C and that deposited by DC reactive magnetron sputtering at 16 mTorr total pressure. Both films present an open-structure, anatase phase oriented along (1 0 1), (2 0 0) and (2 1 1) planes.

4. Conclusions

In this work we have investigated the effect of different deposition parameters on the photocatalytic activity of the TiO_2 thin films prepared by DC reactive magnetron sputtering and spray pyrolysis methods, respectively. Similar band gap energy values, a key parameter for photocatalysis using TiO_2 + UV light, for the different deposition methods were obtained from optical parameters. The highest photodegradation rate was found for TiO_2 thin films deposited by spray pyrolysis with a substrate temperature T_s = 400 °C. The variation in surface characteristics for each kind of films (both sputtered and sprayed) are presented in Figs. 7 and 8, respectively, and seem to be principally responsible for the behavior observed in the photodegradation of methylene blue in the presence of TiO_2 thin films.

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