Influence of the growth parameters of TiO_2 thin films deposited by the MOCVD method
(Influência dos parâmetros de crescimento de filmes finos de TiO_2 depositados pelo método MOCVD)

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Abstract

The synthesis of TiO_2 thin films was carried out by the Organometallic Chemical Vapor Deposition (MOCVD) method. The influence of deposition parameters used during growth on the final structural characteristics was studied. A combination of the following experimental parameters was studied: temperature of the organometallic bath, deposition time, and temperature and substrate type. The high influence of those parameters on the final thin film microstructure was analyzed by scanning electron microscopy with electron dispersive X-ray spectroscopy, atomic force microscopy and X-ray diffraction.

Keywords: organometallic compounds, thin films.

Resumo

A síntese de filmes finos de TiO_2 foi feita pelo método de deposição química do vapor de organometálicos (MOCVD). Foi estudada a influência de parâmetros de deposição usados durante o crescimento, nas características estruturais finais. Foi feita uma combinação de vários parâmetros experimentais: temperatura do banho do organometálico, tempo de deposição, e temperatura e tipo do substrato. A forte influência destes parâmetros na microestrutura final do filme foi analisada por microscopia eletrônica de varredura com espectroscopia de raios X dispersiva de elétrons, microscopia de força atômica e difração de raios X.

Palavras-chave*: compostos organometálicos, filmes finos.*

INTRODUCTION

Titanium dioxide has several advantageous properties that make it a candidate for different applications. Reports of its high dielectric constant, chemical stability, high refraction index and semiconductor properties motivated research in the growth of high-quality thin films by a variety of techniques including MOCVD [1-3], pulsed laser deposition [4], sputtering [5-7], sol-gel [8] and filtered arc deposition (FAD)[9]. There are three types of TiO_2 crystalline structures: anatase, rutile, and brookite. Rutile presents the highest refractive index and is the most thermodynamically stable structure. It is also well-known that titanium dioxide presents two isomorphous crystal phases: the anatase and the rutile [10]. The anatase structure is obtained at temperatures of around 350 °C, which renders it more useful for industrial applications. At temperatures between 400 and 800 °C, the rutile phase is also present, while at higher temperatures, only the rutile structure is present.

The method known as Organometallic Chemical Vapor Deposition (MOCVD) consists of heating an organometallic solution, which evaporates and is deposited on a heated substrate. The films grown by this method usually requires expensive, sophisticated apparatus.

In this letter, we report on the sintering procedures for growing TiO_2 thin films using a simple, low-cost deposition apparatus especially built in our laboratory. The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

EXPERIMENTAL PROCEDURES

TiO_2 thin films were deposited on Si(100) and glass substrates using the organometallic chemical vapor deposition (MOCVD) system shown in Fig. 1. Titanium isopropoxide $[Ti\{OCH(CH_3)_2\}_4]$ which is liquid at room temperature (melting point 20 °C), was used as the organometallic (OM) precursor. The titanium isopropoxide was stored in a glass bubbler whose temperature was controlled by a hot plate. The vapor of the OM precursor was transported by high purity oxygen gas to the reactor. Pure oxygen was used as oxidant. Single-layer films were grown using Si (100) and glass substrates and different deposition times, substrate temperature and the organometallic temperature, while the other parameters remained fixed. Table I summarizes the deposition conditions.

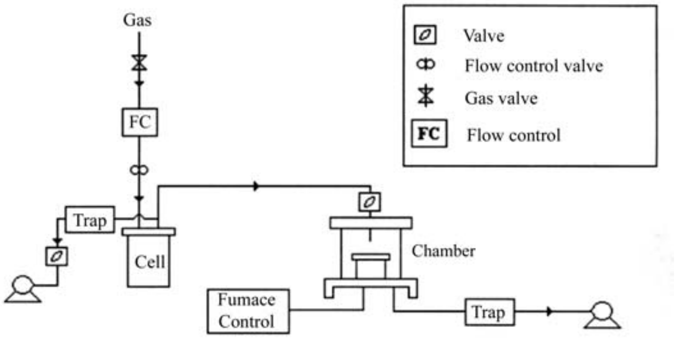


Figure 1: Schematic presentation of the MOCVD apparatus.

Table I - Summary of deposition parameters

Substrate materials	Si(100) and glass
Deposition time	60 and 14min
Growth temperature	400 ^{o}C and 550 ^{o}C
Reactor pressure	0.5 Torr
OM source	$Ti\{OCH(CH_3)_2\}_4$
OM source temperature	90 ^{o}C and 120 ^{o}C
OM source carrier gas (O_2) flow rate	7 sccm[a]

[a] *sccm: standard cubic centimeter per minute.*

Each pair of thin film samples (A1G-A1S and A2G-A2S) was obtained from the same deposition run (same conditions) but using different substrates; G stands for glass and S for silicon(100), as shown in Table II.

The structural properties of the deposited films were studied by X-ray diffraction, and the measurements were carried out with a Siemens D5000 diffractometer with CuK_α radiation. The geometry of the diffractometer was the same for all samples (grazing incidence diffraction - incidence angle = 2^{o}, step time = 7s, step scan = 0.007^{o}, $2\theta = 20 - 50^{o}$, U = 40 kV and I = 40 mA. The surface morphology of the TiO_2 thin films was analyzed by scanning electron microscopy using a Zeiss DSM940A microscope. Film thickness was determined by analyzing the cross section images. More detailed information on morphology and roughness was obtained by atomic force microscopy (AFM) (Digital Instruments Multi-Mode Nanoscope III A).

Table II - Growth conditions.

Film Labels	Substrate	Deposition Time (min)	Substrate Temperature (^{o}C)	Bath Temperature (^{o}C)
A1G	Glass	60	400	90
A1S	Si(100)	60	400	90
A2G	Glass	140	400	90
A2S	Si(100)	140	400	90
A3G	Glass	60	550	90
A3S	Si(100)	60	550	90
A4G	Glass	60	400	120
A4S	Si(100)	60	400	120

RESULTS AND DISCUSSION

The results show that the amorphous glass structure lead to titania in the amorphous phase. Otherwise, the crystalline silicon substrate, induced the anatase crystal structure for the film.

It was possible to observe that an obtained result, using the same deposition procedure, was always different depending on the used substrate. An exemple of this fact can be observed in Fig. 2 and Table II, for films grown in glass and Si (100) substrates following the same conditions. As can be seen from the XDR diffraction

Table III - Physical characterization results of TiO_2 thin films.

Film Labels	Thickness (nm)	Color of the film	Roughne ss (nm)	Lattice Parameters a(Å)	c (Å)	Crystallite Size (Å)	Cell Volume (Å^3)
A1G	130		3.4				
A1S	60	Light blue	4.8	3.7700	9.4548	325	134.38
A2G	230		0.9				
A2S	110	Green	2.0	3.7788	9.4970	723	135.62
A3G	varied		7.9				
A3S	varied	Colored*	10.4	3.7774	9.4970	643	135.51
A4G	varied		2.2				
A4S	varied	Colored*	-	3.7774	9.4916	420	135.44

(*) Colored means that the films have more than just one color.

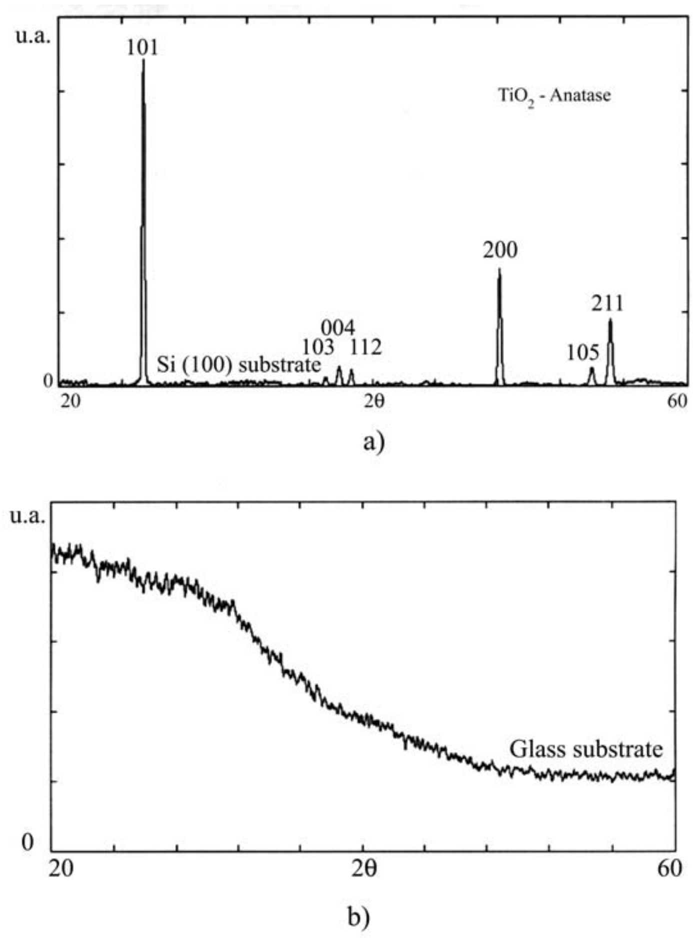


Figure 2: X-ray diffraction patterns of TiO_2 thin films deposited on glass and on Si (100) substrates, under the same conditions.

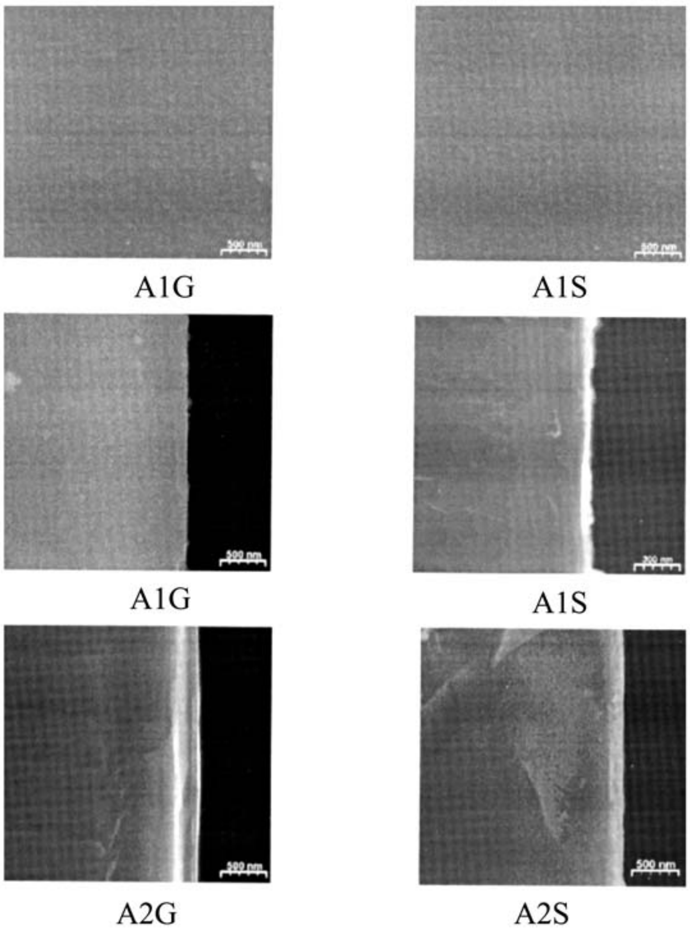


Figure 3: SEM micrographs of the cross section of TiO_2 thin films deposited on different substrates, under the same conditions: a) glass and b) Si(100).

patterns, the structures are different, showing the influence of the nature of the substrate in each case. Fig. 2 also shows that the films deposited on Si (100) present a polycrystalline structure with the anatase phase. The films grown on glass, on the other hand, do not show crystalline structure, preserving their amorphous character.

The nature of the substrate, crystalline or amorphous, provides different degrees of packing and, consequently, different stages of density and thickness in the morphological structure of the obtained films [11]. This may be attributed to the fact that the mobility of the atoms on the substrate surface, which is responsible for the degree and type of nucleation on the substrate, depends on its nature.

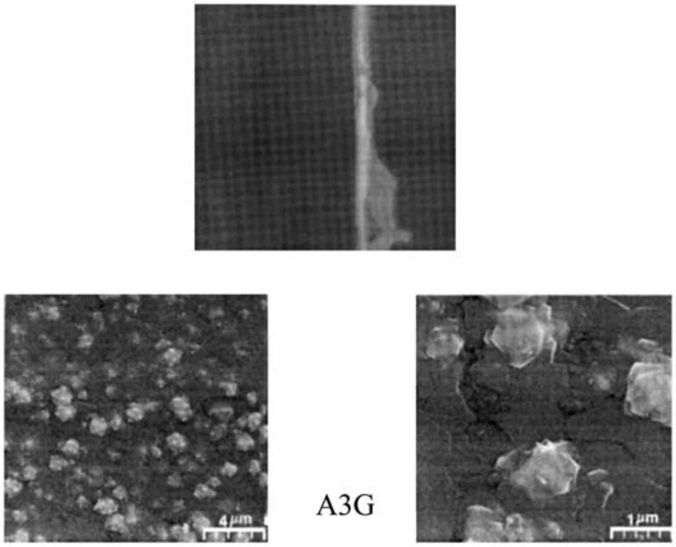
The morphological analyses were of key importance to choose the substrates and bath precursors temperature. The collection of SEM micrographs presented in Fig. 3 shows surface and cross section views for the obtained TiO_2 thin films. In Table II are listed the obtained films nomenclature.

Comparing the micrograph studies for A1 (S and G) with the A3 (S and G), growth using substrate temperature T_S = 400 °C and T_S = 500 °C, respectively, it was observed that the A6G thin film presents a distinct structure than other films. This special feature has already been observed in thin films obtained by the microwave growth technique [12]. For the A3S film, on the other hand, it was observed that the growth occurred in order to form plane plates with low adherence. Analyzing both A1S and A1G films, one can observe that these films present a homogeneous surface, with no denditric or plate-form arrangements and uniform thickness. On the contrary, for the growth of A3 films, the determination of the thickness was not possible due to morphology irregularities. These results indicate that T_S, the optimum temperature of the substrate for deposition of TiO_2 films using the built apparatus is 400 °C.

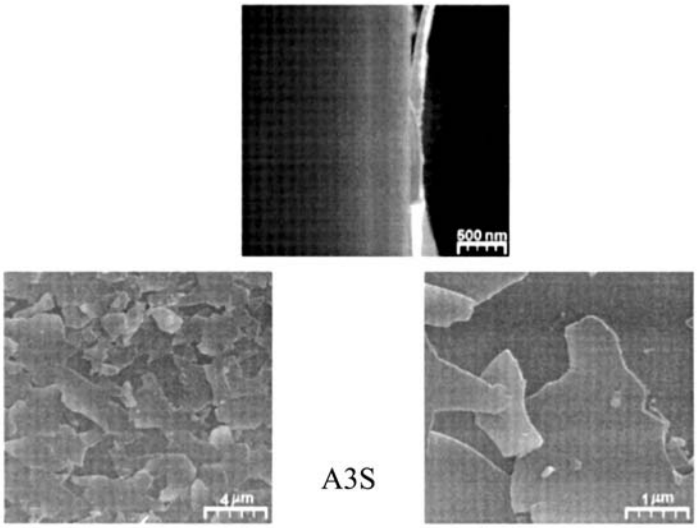
A comparison of the results of A1(S and G) with the A4(S and G) growth in the bath temperature (T_B) of 90 °C and 120 °C, respectively, was done. These temperatures are thoroughly related to the partial pressure of the organomettalic compound, and the higher is the temperature, the vapor partial pressure is so high that the deposition is inadequate, leading to a non-homogeneous film. Hence, it is possible to conclude that the temperature of 90 °C favors the growth of clean and more homogeneous films, since for films grown at 120 °C, A4 films, agglomerates are formed in the film surface.

In order to establish the chemical composition of the observed agglomerates, a chemical element mapping for the A4G film was also performed using the energy dispersive X-ray electron spectroscopy (EDS), as can be observed in Fig. 9. The elements found in such agglomerates are Au, from the recovering, Si, Na and Ca.These elements are present in the composition of the substrate and the occurrence of Na indicates a possible migration from the substrate surface to the film at this temperature.

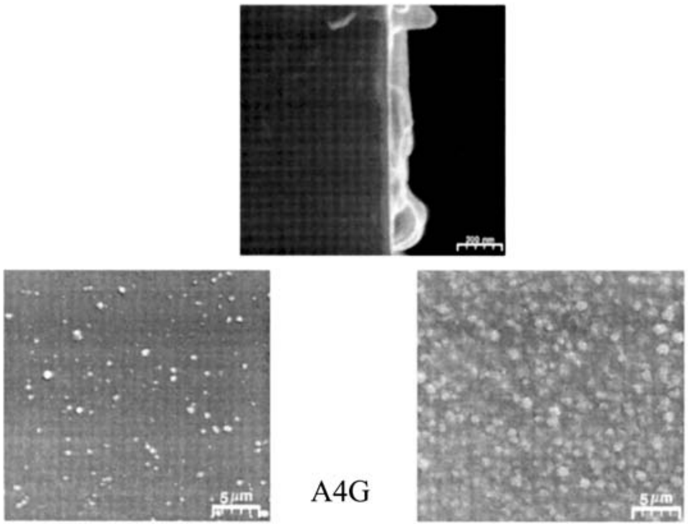
After these analyses, it was established that the best temperature conditions were substrate temperature T_S=400 °C and bath temperature T_B=90 °C. Using these parameters, it was possible to



A3G

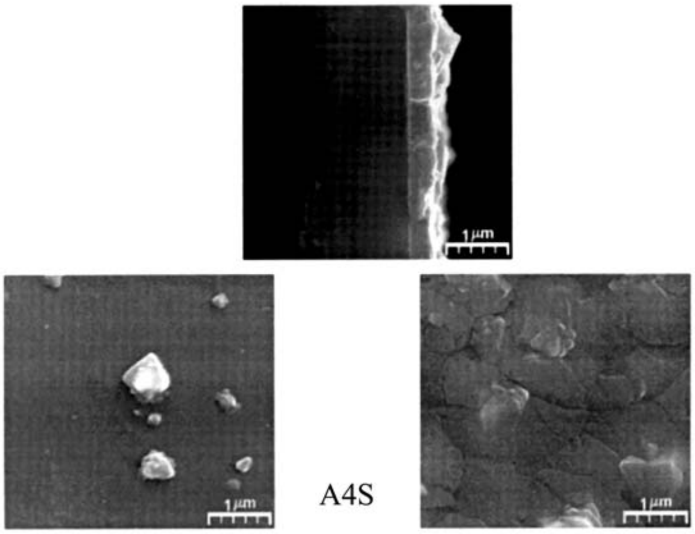


A3S



A4G

Figure 4: Sample A4S surface EDX analyses, exhibiting TiO_2 precipitation.



A4S

Figure 5: AFM surface morphology of TiO_2 thin films deposited on different substrates, under the same conditions: A1G and A2G, glass (amorphous) and A1S and A2S, Si(100) (crystalline).

study the influence of the deposition time. The results, shown in Fig. 3, present just an increase in the thickness of the film. One can observe that the films deposited on the glass substrates are thicker than those grown on the Si (100) under the same conditions. It is also possible to observe a variation of color patterns with the increase of thickness, as shown in Table III. This effect of color variation is more evident for TiO_2 films grown on Si (100) substrates; it could also be observed on the glass ones, fact already reported elsewhere [12].

The films were visible at naked eye, once their color change, observed by reflection. TiO_2 layers on glass showed different colors (see Table III). These colored films were well red. The layer homogeneity was also visible, due to the interference phenomenon, also previously reported [13].

Studies of Atomic Force Microscopy were also performed to investigate the morphology of the films. In Fig. 5 it is possible to inspect an exemple of the surface structure and roughness listed in Table III. The data shows different crystallization patterns for both Si (100) and glass substrates. While the films grown on glass were composed by poorly defined grains, the films on Si (100) presented grain formations, in agreement with XRD data. It is necessary to point out that XRD experiments yields long and medium range order analysis, and on the contrary, the AFM is able to detect short range order. In our opinion, the AFM images of thin films on glass substrates here reported are just exhibiting the initial stage of crystallization, not detectable by X-ray diffraction analysis. Besides, observing the data presented in Table III, one can notice that the film roughness on glass substrates was always lower than those presented for the Si (100). This seems to confirm our results, since the roughness of the glass substrate (0,92 nm) is higher than that of Si (100), 0.20 nm.

The roughness values indicate the good quality and homogeneity of the films, showing that the increase of the deposition time leads to a decrease in the roughness, as reported for SnO_2 films obtained using the Pechini method [14].

A first explanation is certainty related to the fact that the titania vapor is deposited over an organized structure resulting in a crystalline phase, or oppositely, the deposition over a random structure of those products leads to an amorphous specimen. Not just the crystal structure of the substrate, but also its chemical bonding affects the growth of the film, conditioned to the energy competition between the volume and the interface, and furthermore, to the growth kinetics, that is dependent on substrate temperature (ST) and deposition rate (DR).

CONCLUSIONS

It was possible to obtain good quality thin films of TiO_2 with acceptable homogeneity, adherent, speculating and with minor roughness using a simple and non-expensive equipment.

The films showed a strong dependence of the kind of substrate on the structural characteristics, and consequently to a variation of optical properties. The results suggested that the obtained film thickness is directly related to the deposition time.

Through the analysis of the films grown under different conditions, it was chosen the temperature of 90 °C for the organometallic bath and 400 °C for the substrate temperature. Using these conditions, it was possible to obtain crystalline thin films using Si (100) substrates and amorphous thin films using glass substrates.

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