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TiO_2 Thin Film Growth Using the MOCVD Method

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Titanium oxide (TiO_2) thin films were obtained using the MOCVD method. In this report we discuss the properties of a film, produced using a ordinary deposition apparatus, as a function of the deposition time, with constant deposition temperature (90 °C), oxygen flow (7,0 L/min) and substrate temperature (400 °C). The films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and visible and ultra-violet region spectroscopy (UV-Vis). The films deposited on Si (100) substrates showed the anatase polycrystalline phase, while the films grown on glass substrates showed no crystallinity. Film thickness increased with deposition time as expected, while the transmittance varied from 72 to 91% and the refractive index remained close to 2.6.

Keywords: *thin films, TiO_2, MOCVD*

1. Introduction

Many theoretical and experimental investigations have been carried out on the electronic transport properties of semi-conducting oxides in thin films in the past few years.

Titanium dioxide (TiO_2) possesses a number of attractive properties, among which are its high refractiveness, high dielectric constant, semiconductor properties and chemical stability. Compact TiO_2 thin films deposited on conducting glass are used in new types of solar cells: liquid and solid dye-sensitized photoelectrochemical solar cells[1,2], as well as in solar cells with extremely thin organic or inorganic absorbers[3,4]. These thin films are also of interest for application in the photo-oxidation of water[5], photocatalysis[6], electrochromic devices[7], among other uses.

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. The anatase structure is obtained at low temperatures of around 350 °C, which is useful for industrial applications[8]. At temperatures between 400 and 800 °C, the rutile phase is also present while, at higher temperatures, only the rutile structure is present. Another possible phase present in the TiO_2 compounds are the brookite phase, but just present at high pressures and high temperatures.

Thin films have been prepared by many deposition techniques such as the Sol-Gel based process[9], metal-organic chemical vapor deposition (MOCVD)[10,11], atomic layer deposition[12], molecular beam epitaxy (MBE)[13], pulsed laser deposition[14] and various reactive sputtering techniques[15-17]. These deposition techniques control nucleation rates and, therefore, all the chemical and physical properties.

The method known as Metal-Organic 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, which generally requires expensive, sophisticated apparatus, are usually homogeneous, which is a crucial attribute for the study of optical properties.

In this article, we report the synthesis procedures to grow 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), atomic force microscopy (AFM) and visible and ultra-violet region spectroscopy (UV-Vis).

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The envelope method[18], which includes the consideration of loss of light intensity from the back surface of the substrate, has been shown to be a simple and convenient tool to calculate the optical properties of the film, using solely the transmission spectra in the regions of medium and weak absorption.

2. Experimental

TiO_2 thin films were deposited on Si(100) and glass substrates using the metal-organic 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 either Si(100) or glass substrates and different deposition times while the other parameters remained fixed. Table 1 summarizes the deposition conditions.

Each pair of thin film samples: (A1G, A1S), (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 2.

The structural properties of the deposited films were studied by X-ray diffraction (XRD), and the measurements were carried out with a Siemens D5000 diffractometer with Cu K radiation. The geometry of the diffractometer was the same for all the samples studied (grazing incidence diffraction - incidence angle = 2°, step time = 7 s, step scan = 0.007°, 2θ = 20-50°, U = 40 kV and I = 40 mA). Thickness of the TiO_2 thin films were determined analyzing the cross section images by scanning electron microscopy (SEM) using a Zeiss DSM940A microscope. The surface morphology of the TiO_2 thin films and roughness was obtained by atomic force microscopy (AFM) (Digital Instruments Multi-Mode Nanoscope III A).

The transmittance of the films was measured in the visible region by means of a Cary 5G UV-Vis-Nir double-beam spectrophotometer. Based on these analyses, the optical transmission behavior as a function of the wavelength was assessed by direct measurement. The transmittance spectra were analyzed using the modified envelope method, which allows for the optical coefficients, such as refraction index and absorption coefficient, to be determined.

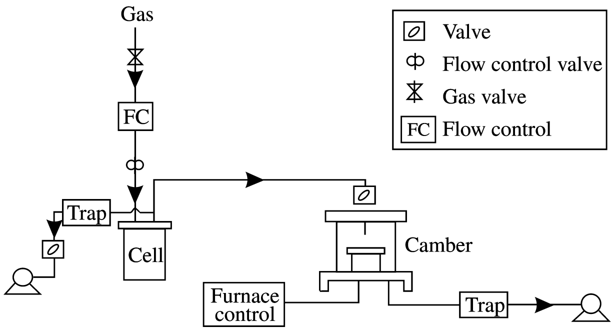


Figure 1. A schematic presentation of MOCVD apparatus.

Table 1. Summary of deposition parameters.

Substrate materials	Si(100) and glass
Growth temperature	400 °C
Reactor pressure	0.5 Torr
OM source	$Ti\{OCH(CH_3)_2\}_4$
OM source temperature	90 °C
OM source carrier gas (O_2) flow rate	7 sccm[a]

[a]sccm: standard cubic centimeter per minute.

3. Results and Discussion

3.1. Film structure and morphology

It is well known that the temperature and partial oxygen pressure are the most important parameters in the optimization of the crystal structure of TiO_2 thin films deposited by MOCVD[19].

In order to obtain crystalline structures (anatase), the temperature of the substrate was fixed at 400 °C during deposition. Figure 2 shows the XRD data for films grown on Si (100) and glass substrate. As can be seen from the XDR diffraction patterns, the structures were different, illustrating the influence of the substrate in each case. This figure also shows that the films deposited on Si(100) presented a polycrystalline structure with the anatase phase. Otherwise, the films grown on glass presented no crystalline structure, preserving their amorphous character.

Concluding, the structure of the films was influenced by the nature of the substrate. This may be attributed to the

Table 2. Growth conditions.

Film codes	Substrate	Deposition time (min)
A1G	Glass	30
A1S	Si(100)	30
A2G	Glass	60
A2S	Si(100)	60
A3G	Glass	75
A3S	Si(100)	75
A4G	Glass	120
A4S	Si(100)	120
A5G	Glass	140
A5S	Si(100)	140

fact that the mobility of the atoms on the substrate surface, which is responsible for the degree and type of nucleation on the substrate. It is also well know that the crystalline substrate favors a better packing, leading to a minor density and consequently, a smaller thickness[20].

Figure 3 presents a SEM micrograph obtained from the TiO_2 thin films under study. As can be observed, the films deposited on the glass substrates were thicker than those grown on the Si (100) under the same conditions. It is also possible to observe that the thickness increases with the deposition time, result shown in Table 3. As expected by the interference color theory[21], the films with different thicknesses presented different colors.

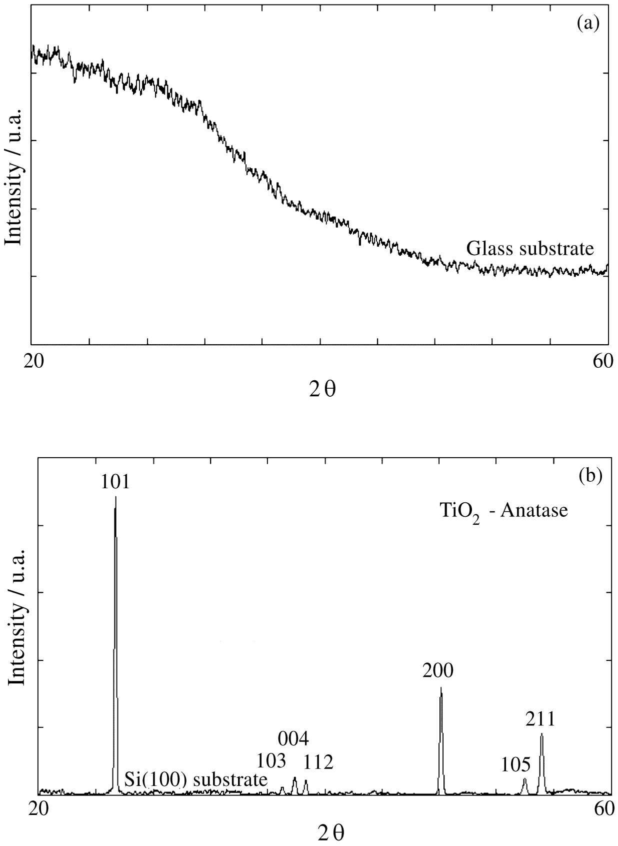
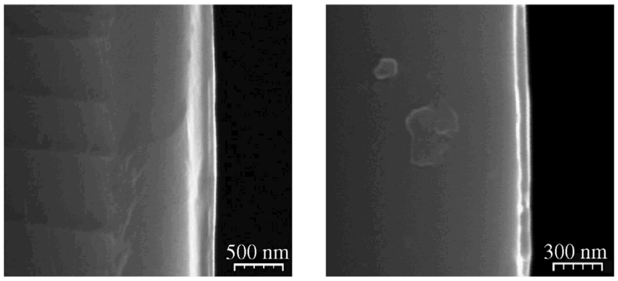


Figure 2. a) X-ray diffraction patterns of TiO_2 thin films deposited on glass, b) X-ray diffraction patterns of TiO_2 thin films deposited on glass on Si (100) substrates, under the same conditions.

The films were visible to the naked eye once the color changes, being observed by reflection. TiO_2 layers on Si (100) showed different colors (see Table 3). These colored films presented a good adhesion to the substrate. The homogeneity of the layer was also visible owing to the interference phenomenon, which has been reported on in the literature[22]. It was also possible to note from the data presented in Table 3 that the film roughness on glass substrates was always lower than those presented for the Si (100). This is a remarkable characteristic since the roughness the glass substrate (0.92 nm) is higher than the Si (100) one (0.20 nm).

Surface morphology and roughness were evaluated using an atomic force microscope (AFM), as shown in Fig. 4. An analysis of these data permitted us to confirm that the films on glass presented an poorly-crystalline structure, since only amorphous pattern was detected in the XRD experiments. Otherwise, the Si (100) films showed well-defined grain formations, corroborating the XRD data.

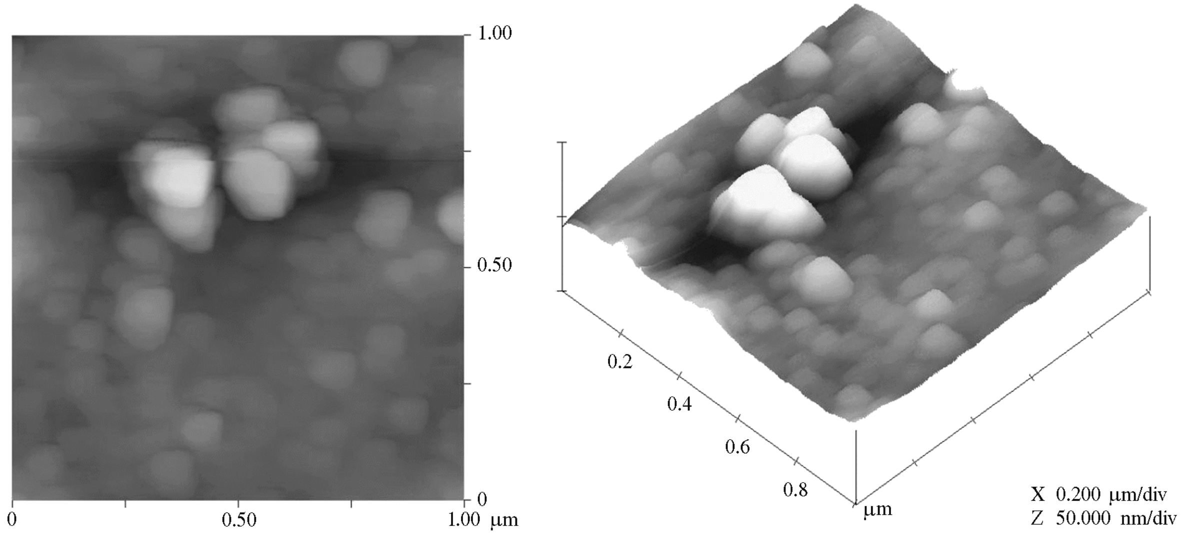


a) A3G b) A3S

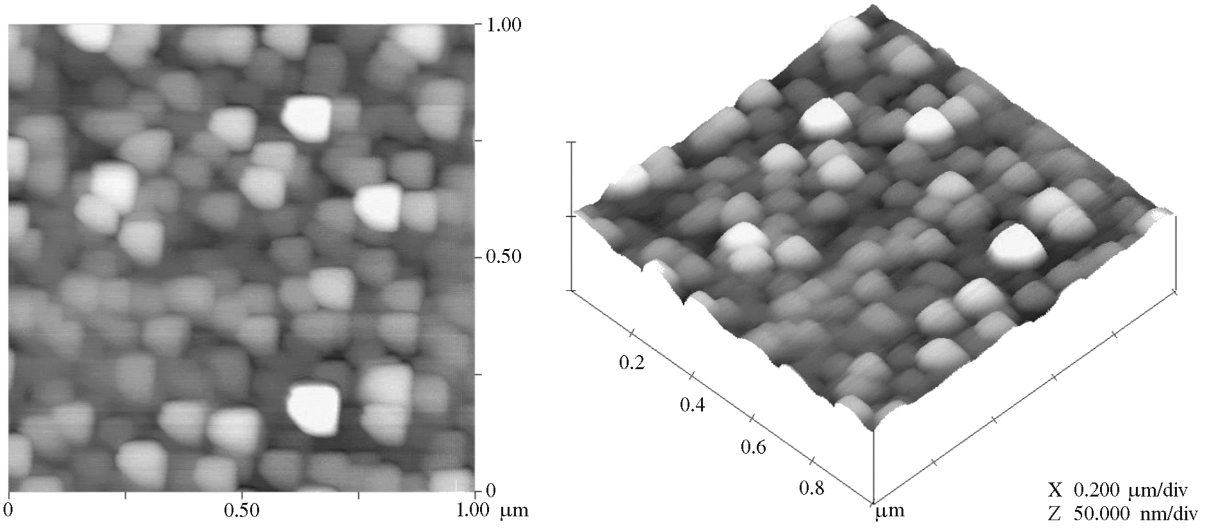
Figure 3. SEM micrographs of the cross section of TiO_2 thin films deposited on different substrates, under the same conditions: a) glass and b) Si(100).

Table 3. Physical characterization results performed in TiO_2 thin films.

Film codes	Thickness (nm)	Color of the films	Roughness (nm)	Transmission (%)	Optical energy gap (eV)
A1G	100		3.6	91	3.7
A1S	50	Yellow	5.4		
A2G	130		3.4	88	3.8
A2S	60	Light blue	4.8		
A3G	170		2.2	87	3.7
A3S	80	Dark blue	3.1		
A4G	210		1.3	80	3.7
A4S	100	Light green	2.5		
A5G	230		0.9	79	3.6
A5S	110	Green	2.0		



a) A3G



b) A3S

Figure 4. AFM surface morphology of TiO_2 thin films deposited on different substrates, under the same conditions: a) glass (amorphous) and b) Si(100) (crystalline).

The low roughness values also confirm the good homogeneity of these films. Roughness was also found to decrease with deposition time.

3.2. Optical properties

The transmittance of TiO_2 films on glass was measured using air as a reference. We modified the structure of TiO_2 thin films by two means: deposition on different substrates and different deposition times.

Figure 5 shows a high TiO_2 transmittance spectrum for a film grown on glass. The film is totally transparent, allowing the use of the modified envelope method to obtain its refraction index. A refractive index value of 2.6 was obtained at a wavelength of 638.2 nm, corresponding to the

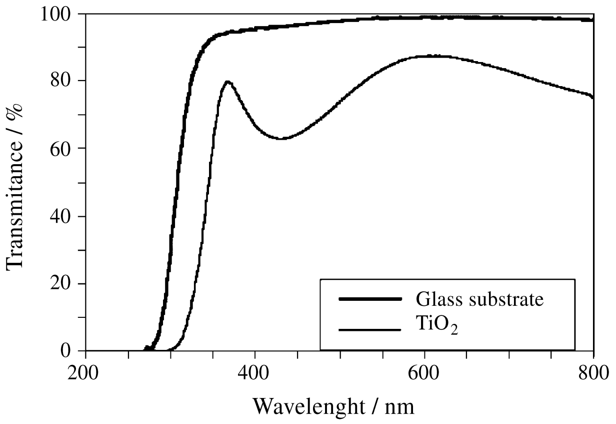


Figure 5. Utraviolet-visible transmission spectra for a TiO_2 thin film comparing with a glass substrate.

He-Ne laser. The structural differences explain why TiO_2 amorphous films exhibit lower refractive indexes than crystalline TiO_2 films ($n_m = 2.55$).

The spectral values were processed in order to obtain the energy band gap, using Eq. (1), which corresponds to indirect gap for semiconductors.

$$\alpha\,(h\nu) = A\,(h\nu - Eg)^2 \tag{1}$$

where α stands for absorbance, h is Planck's constant, ν the frequency, Eg the optical band gap energy and A is a dimensional constant.

Although the films show a high specular reflectivity, this can be disregarded when compared to the absorbance in the high absorption region since, in this region, the absorbance is directly proportional to the absorption coefficient. The gap energy values obtained are shown in Table 3.

4. Conclusions

Good quality (homogeneous, adherent, specular and fairly smooth) TiO_2 thin films were obtained using a simple, homemade device and the MOCVD method. The nature of the substrate showed a strong dependence on the structural properties of the films, whose optical properties it thus altered. The final thickness of the films increased with longer deposition times; however, this increase was more strongly evident on the glass than on the Si(100) substrate. At 400 °C, crystalline films were deposited on Si (100), whereas amorphous films were deposited on glass. The films with different thicknesses presented different colors.

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