

Analysis of Optical and Structural Properties of Sol–Gel TiO₂ Thin Films

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Titanium dioxide (TiO₂) is widely used in various industries (cosmetics; painting; solar cells; used-water reprocessing; electrochromatic systems; etc.). It exists under different crystalline forms: rutile, anatase, and brookite. We have prepared our samples using an alcoholic solution of Tetra-buthylorthotitanate, hydrolysed in a water/alcohol/acid mixture. The solution thus prepared was deposited by a sol–gel method on an ITO substrate. The layers undergo a heat treatment at temperatures varying from 300 with 500°C, and various dippings. DRX analysis of our thin films of TiO₂ shows that the titanium oxide starts to crystallize starts from the temperature of annealing 350°C. The structure obtained is anatase. At higher temperatures (400 and 450°C), and for a number of layers (dipping iterations) increasing from 4 to 9, we observe in addition to anatase, the formation of brookite. The intensities corresponding to the lines characteristic of anatase (101) and brookite (111) increase with temperature. This increase in the intensities of the peaks is interpreted as due to an increase in size of the grains (nanocrystals) of titanium oxide with the increase in the annealing temperature. The Raman spectra confirm the presence of titanium oxide starting from the temperature 350°C, the peaks characteristic of anatase (tetragonal) appear near bands centred around 153 and around 193cm⁻¹. For the higher temperatures (400 and 450°C) we note also the formation of brookite which corresponds to the wavelength 650 cm⁻¹. The calculated size of the grains varies from 11.9 to 17.1nm for anatase and from 25 to 10.2nm for brookite. The index of refraction (*n*), and porosity (*p*) are calculated starting from the measured transmission spectra, and vary between 1.63 and 2.59 for *n*, and from 3.5 to 68.7% for porosity.

Keywords: Sol-Gel; titanium dioxide; thin films; anatase; brookite.

1. INTRODUCTION

Titanium dioxide (TiO₂) thin films are extensively studied because of their interesting chemical, electrical and optical properties (high bandgap, transparent to visible light, high refractive index and high dielectric constant) which are considered for various optical applications such as high refractive index component of multilayer optical filter, gas sensors, antireflective coating, photocatalysts, planar waveguides, integrated optical amplifiers.[1,2].

Crystalline TiO₂ film exist in three phases: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [3], rutile being the most stable of the three, and the formation of its phase depending on the starting material, deposition method and temperature treatment. In particular, TiO₂ thin films can transform from amorphous phase into crystalline anatase and from anatase into rutile by changing temperature. A number of methods have been employed to prepare TiO₂ films, including e–beam evaporation [4], sputtering [5], chemical vapor deposition [6], and sol–gel process [7]. Sol-gel method has emerged as one of the most promising process as it is particularly efficient in producing thin, transparent, homogenous layers on various substrats at low cost and it allows the choice of refractive index and thickness of the layer by changing elaboration conditions. In general, the preparation conditions of TiO₂ films in sol-gel process can strongly affect physical properties of the film [8]. Therefore, it is necessary to study systematically the structural and optical properties of sol-gel TiO₂ thin film as a function of the preparation conditions.

In this paper, we report the investigation of TiO₂ thin films prepared by sol-gel process using titanium alkoxide. Structural and optical characterizations are investigated for different annealing temperatures and different dipping iterations using suitable techniques including: Scanning Calorimetry (DSC), X-Ray

Diffraction, Raman Spectroscopy, Scanning electron microscopy (MEB) and UV Spectroscopy.

2. EXPERIMENTAL

The thin films of TiO₂ were prepared by the sol–gel method. The latter is based on the hydrolysis of alkoxydes in alcoholic solutions in the presence of an acid catalyst. The procedure of preparation includes the dissolution of one mole of tetrabutyl–orthotitanate (C₄H₉O)₄Ti and four moles of acetic acid (C₂H₄O₂), one mole of distilled water is added as well as one mole of butanol (C₄H₉OH) as solvent; this solution is transparent, of yellowish color and is ready for the deposit. The substrates of carefully washed ITO are dipped in the solution of deposit and are withdrawn from it with a speed of 0.625 mm/s. After each dipping, these thin films are dried for 30 minutes at a distance of 40cm from a 500W-light source. The thickness of the thin films obtained varies between 20 and 285nm depending on the temperature of annealing and the number of dippings. DSC tests were carried out using a SETARAM DSC–92 analyzer equipped with a processor and a measuring cell to determine the characteristics of the phase shifts. The thermal cycle applied consists of heating from room temperature to the temperature 520°C, holding for 5min at this temperature and finally cooling back to room temperature with the same rate (5°C/min). Scanning electron microscopy (SEM) observations were obtained by using Leica Cambridge S360. To follow the variations of the lattice parameter and of the crystalline structure, an automated powder diffractometer was used (Siemens D5005). The spectra of diffraction of x-rays were recorded with a copper anticathode (I=20mA and V=40kV), using step-scanning, between 10° and 70° at 0,1°/s. The UV–visible spectra from our samples are obtained using a SHIMADZU (UV3101PC) double–beam spectrophotometer controlled by computer. Its useful range is between 190–3200nm.

The treatment of the spectra is carried out using the UVPC software.

3. RESULTS AND DISCUSSION

3.1. Structural properties

The thermal curve shows two singularities (figure 1):

An endothermic peak spreading from 50 to 250°C, which corresponds to the evaporation of water, the thermal decomposition of butanol as well as the carbonization or the combustion of the acetic acid and certain elements which constitute our alkoxyde. An exothermic peak spreading from 290 to 410°C, which corresponds to the crystallization of titanium oxide, is also observed.

This analysis shows that an annealing at a temperature equal or higher than 400°C would be largely sufficient to form titanium oxide completely.

The TiO₂ thin films obtained after 4 dippings and various annealings at 400, and 500°C (Fig. 2) were gold coated and examined in a scanning electron microscope (SEM) to investigate their structure and surface characteristics. It was observed that the coating was transparent and homogeneous without any visual cracking over a wide area. The increase in the treatment temperature, did not affect the uniformity of the film.

Figure 3 shows the evolution of diffraction spectra of the xerogel as well as of the thin films of oxide obtained after 4 dippings and various annealings at 350, 400 and 450°C

We observe that the titanium oxide starts to crystallize starting from the annealing at 350°C. These spectra (fig. 3), shows a peak corresponding to the (101) plane, which is attributed to the presence of anatase regardless of the temperature of annealing. Then, at higher temperatures (400 and 450°C), and for a number of layers (dipping iterations) increasing from 4 to 9 (Figs. 3(c) and (d), Figs. 4) we observe in addition to anatase, the formation of brookite which crystallizes with the (121) plane parallel to the surface. These thin films deposited on ITO substrates, annealed at 350, 400 and 450°C, are stoichiometric. We also observe that the intensities corresponding to the lines characteristic of anatase (101) and brookite (121) increase as the annealing temperature increases. This increase in the intensity of the peaks, leads us to deduce the amount of titanium oxide as a function of the annealing temperature.

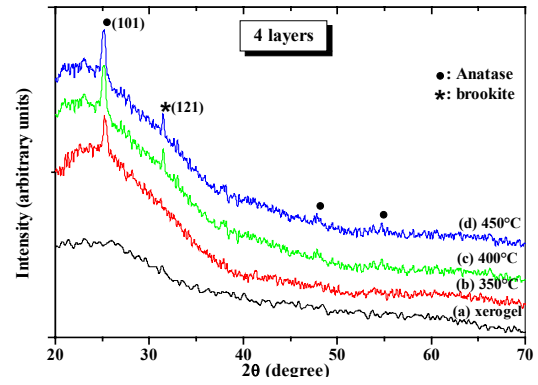


FIG. 3. The evolution of diffraction spectra of the xerogel, as well as of the thin films of oxide obtained after 4 dippings and various annealings.

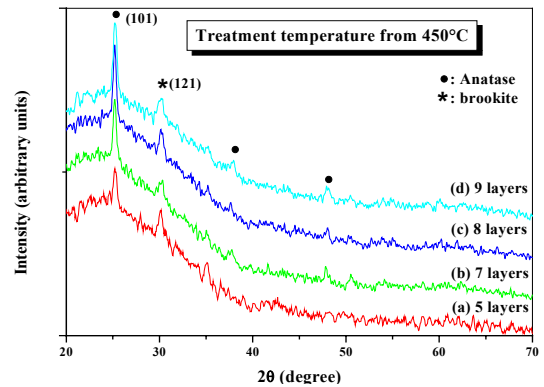


FIG. 4. The evolution of diffraction spectra of the thin films of oxide obtained after the temperature 450°C and various of the number of dippings.

The crystallite size of TiO₂ thin films can be deduced from XRD line broadening using the Scherrer equation [9]. The computed values of the size of the grains are given in table 1.

Samples	Phases	$L(nm)$	(hkl)
Xerogel	–	Amorphous	–
4 layers at 350°C	Anatase	11.9	(101)
4 layers at 400°C	Anatase	12.3	(101)
	Brookite	24.2	(121)
4 layers at 450°C	Anatase	13.3	(101)
	Brookite	25	(121)
7 layers at 450°C	Anatase	19.5	(101)
	Brookite	6.3	(121)
8 layers at 450°C	Anatase	18.6	(101)
	Brookite	8.7	(121)
9 layers at 400°C	Anatase	14.8	(110)
	Brookite	7.3	(121)

The Raman spectra (Fig. 5 and 6) show the presence of titanium oxide. The Raman spectra (Fig. 5(a)) confirm the presence of titanium oxide starting from the temperature 350°C, the peaks characteristic of anatase (tetragonal) appear near bands centered around 153 and around 193 cm^{-1} [10]. For the higher temperatures (Fig. 6(a), (b) and (c)), and for a number of layers (dipping iterations) increasing from 5 to 7, we observe in addition to anatase, the formation of brookite; we note also the formation of brookite (orthorhombic) which corresponds to the wavelength 650 cm^{-1} .

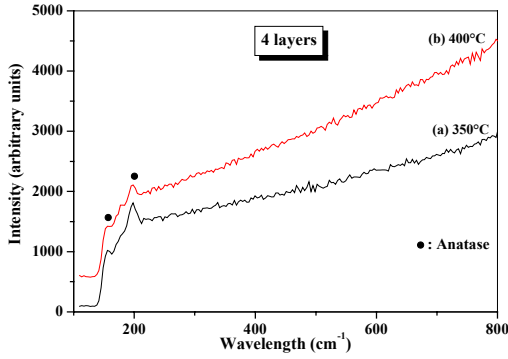


FIG. 5: The Raman spectra of the thin films of oxide obtained after 4 dippings and various annealings

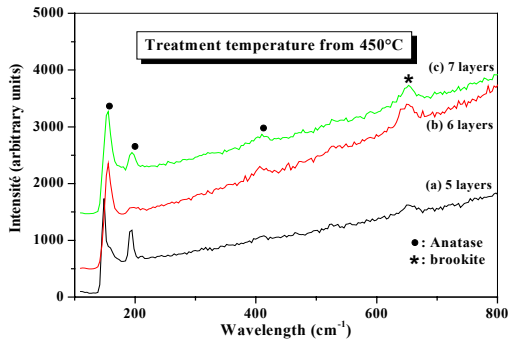


FIG. 6: The Raman spectra of the thin films of oxide obtained after the 450°C and various of the number of dippings.

3.2. Optical properties

Figures 7 and 8 show the UV–VIS spectra TiO₂ thin films for different annealing temperatures and the number of dippings in wavelength range 300–1000nm. The transmission of the thin films of titanium oxide decreases with the increase in annealing temperature and in the number of dippings. This can be linked with the formation stage of anatase and with the increase in the grain size [11]. The bands due to the interference color of the film appeared in the wavelength range 350–800nm. The amplitude of interferences spectra increased with increasing treatment temperature and the number of dippings.

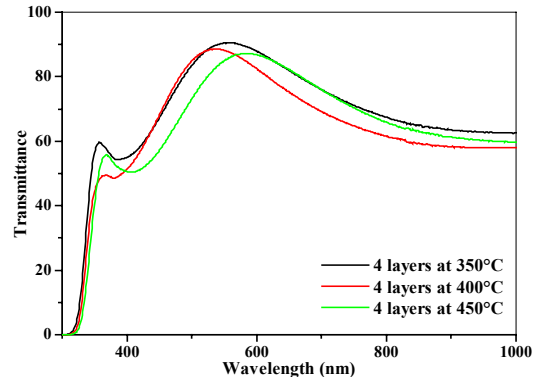


FIG. 7. UV–VIS spectra of the TiO₂ thin film, for 4 layers at various temperatures.

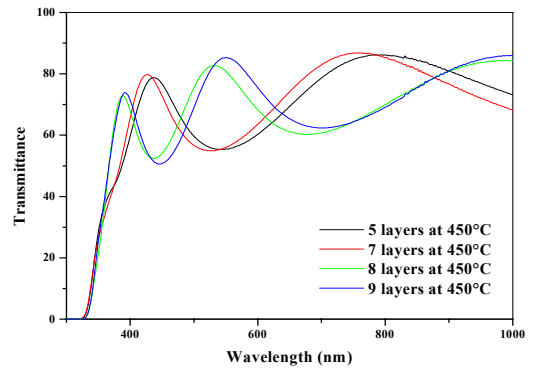


FIG. 8. UV–VIS spectra of the TiO₂ thin film, for the temperature 450°C at various layers.

The refractive index of the prepared TiO₂ thin films was calculated from the measured transmittance spectrum. The evaluation method used in this work is based on the analysis of the transmittance spectrum of a weakly absorbing film deposited on a non-absorbing substrate [12]. The refractive index $n(\lambda)$ over the spectral range is calculated by using the envelopes that are fitted to the measured extreme:

$$n(\lambda) = \sqrt{S + \sqrt{S^2 - n_0^2(\lambda)n_s^2(\lambda)}}$$

$$S = \frac{1}{2}(n_0^2(\lambda) + n_s^2(\lambda)) + 2n_0n_s \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda) \times T_{\min}(\lambda)}$$

Where n_0 is the refractive index of air, n_s is the refractive index of film, T_{\max} is the maximum envelope, and T_{\min} is the minimum envelope. The thickness of the films was adjusted to provide the best fits to the measured spectra. In this study, all the deposited films are assumed to be homogeneous.

The porosity of the thin films is calculated using the following equation [13].

$$Porosity = \left(1 - \frac{n^2 - 1}{n_d^2 - 1}\right) \times 100(\%)$$

Where n_d is the refractive index of pore-free anatase ($n_d = 2.52$ [14]), and n is the refractive index of the porous thin films.

Fig 9 shows the results of the calculation of the refractive index (n) and porosity (p) of the TiO₂ thin films for different annealing temperatures. It is noted that of the refraction index of the thin films of titanium oxide increases with the increase in the treatment temperature (from 1.82 to 2.37). In addition porosity decreases. (from 57.1 to 13.6). This can be connected with the change in the crystalline structure (anatase, anatase-brookite, and rutile), the increase in the size of the grains and/or the density of the layers.

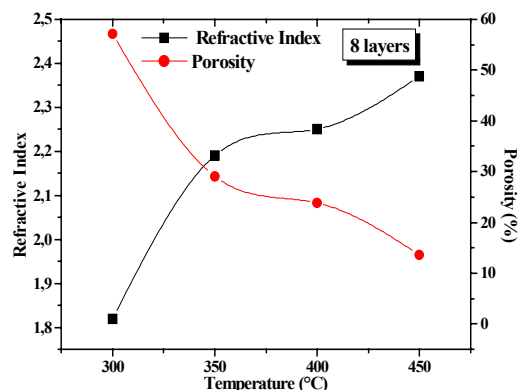


FIG. 9. Refractive index and porosity of the thin film, at different temperatures (from 300 to 450°C).

4. CONCLUSION

X-ray and Raman analyses show that the thin films obtained crystallize into tetragonal titanium oxide anatase starting from the annealing at 350°C. At higher temperatures (400–450) °C, we note also the formation of the orthorhombic brookite phase. On the other hand, for the deposit with ten layers annealed at 400°C, only tetragonal rutile is obtained. The calculation of the grain size by Scherrer's formula, gives us sizes varying from 5 to 25nm for brookite. The analysis of the transmission spectra shows that TiO₂ thin films are transparent in the visible range and opaque in the UV region, irrespective of the treatment temperature and the number of dippings.

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