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Variation of the structural and optical properties of sol–gel TiO_2 thin films with different treatment temperatures

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Abstract

Structural and optical properties of TiO_2 thin films prepared using a sol–gel process have been examined at different treatment temperatures and for different layer counts. XRD and Raman analyzes of our thin films of TiO_2 show that 3 layer films crystallize in anatase and brookite phases, starting from the temperature of annealing 350 °C. The grain size calculated from XRD patterns varies from 6.7 to 23.5 nm. Refractive index and porosity are found to vary with treatment temperature and number of dippings. Our films, irrespective of treatment temperature and number of dippings, are transparent in the visible range and opaque in the UV region. ***To cite this article: R. Mechiakh, R. Bensaha, C. R. Physique 7 (2006).***

Résumé

Variation des propriétés structurales et optiques des couches minces de TiO_2 obtenues par voie sol–gel à différentes températures de recuit. Les propriétés structurales et optiques de couches minces de TiO_2 obtenues par le procédé sol–gel ont été examinées à différentes températures de recuit ainsi qu'à différents trempages. Les analyses aux rayons X et spectroscopie Raman montrent que les couches minces de TiO_2 obtenues pour 3 trempages cristallisent, dans les phases anatase et brookite, à partir de la température de recuit 350 °C. La taille des grains calculée à partir des diagrammes de diffraction varie de 6,7 à 23,5 nm. L'indice de réfraction et la porosité varient en fonction de la température de recuit et du nombre de trempages. Nos couches sont transparentes dans le visible et opaques dans l'UV, et ceci quelles que soient la température et le nombre de trempages. ***Pour citer cet article : R. Mechiakh, R. Bensaha, C. R. Physique 7 (2006).***

Keywords: Thin layers; TiO_2; Sol–gel; Anatase; Brookite

Mots-clés : Couches minces ; TiO_2 ; Sol–gel ; Anatase ; Brookite

Version française abrégée

L'oxyde de titane est un matériau bon marché, largement utilisé dans différentes industries (traitements de diverses surfaces, ...) [1]. Le matériau est un semi-conducteur que l'on prépare en couches minces. Son insensibilité à la

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lumière visible, en raison de la large bande interdite (3,2 eV), ne lui permet d'absorber que dans le proche ultraviolet [2]. Il peut être sensibilisé par un grand nombre de colorants, dont certains permettent un taux de conversion photon incident–électron approchant l'unité. Ces différentes applications suscitent un intérêt certain, pour l'étude des couches minces d'oxyde de titane. Les utilisations les plus importantes de TiO_2 sous forme de couches minces sont les cellules solaires [3], les systèmes photocatalytiques [4], les systèmes électrochromes [5].

Nombre de méthodes ont été utilisées pour préparer des couches minces de TiO_2, parmi les quelles nous citerons l'évaporation par faisceau électrique [6], la pulvérisation [7], le dépôt de vapeur chimique [8] et la méthode sol–gel [9]. Cette dernière, qui est un procédé de dépôt par voie liquide utilisant la chimie douce. Elle permet d'obtenir des dépôts homogènes, exigeant moins d'équipement, est donc beaucoup moins coûteuse [10,11].

On sait que l'oxyde de titane se cristallise dans l'une des trois phases, le rutile (tétragonal), l'anatase (tétragonal) et le brookite (orthorombique). Dans la nature, le rutile est la phase cristalline la plus commune, tandis que la brookite est rare. La phase rutile est la plus stable à hautes températures (généralement dans le domaine 600–1855 °C). Par contre, l'anatase et la brookite sont des phases métastables ; et sont transformés en rutile par augmentation de la température [12].

Dans ce travail, les couches minces de TiO_2 ont été obtenues par le procédé sol–gel de dépôt. La solution de trempage a été préparées à partir du tetrabutyl–orthotitanate $(C_4H_9O)_4Ti$. Les couches minces ainsi préparées ont été étudiées par, diffraction des rayons X, spectroscopie Raman, macroscopie électronique à balayage (MEB) et spectroscopie dans les domaines visible et UV.

Les analyses par diffraction des rayons X de nos couches minces de TiO_2 montrent que l'oxyde de titane commence à cristalliser à partir de la température de recuit 350 °C. Les structures obtenues sont de types anatase et brookite. Les spectres de Raman de ces couches minces, nous confirment ainsi la présence de ces deux phases. La taille des grains calculée à partir des diagrammes de diffractions varie de 6,7 à 23,5 nm. Les couches sont transparentes dans le visible et opaques dans l'UV, et ceci quelles que soient la température et le nombre de trempages, L'indice de réfraction (n), et la porosité (p) sont calculés à partir des spectres de transmittance mesurés, obtenus à différentes températures de recuit et nombre de trempages. Nous remarquons d'une part que l'indice de réfraction des couches minces d'oxyde de titane augmente en fonction de l'élévation de la température de recuit et du nombre de trempages, et d'autre part nous constatons que la porosité diminue. Les valeurs calculées de ces paramètres varient entre (1,93–2,37) et (13,6–49,2)% respectivement pour l'indice (n) et la porosité (p).

1. Introduction

Titanium oxide is a cheap non toxic, non biodegradable material, widely used in various industries (treatments of various surfaces, ...) [1]. Moreover, it is a semiconductor under the form of thin films. Its insensitivity to visible light, because of its broad gap (3.2 eV), which enables it to absorb only in the near ultraviolet region [2]. It can be sensitized by a great number of dyes, some of which allow a conversion rate incident photon–electron approaching unity. These various applications arouse great interest in the study of titanium oxide thin films. The most important uses of TiO_2 in the form of thin films are in solar cells [3], photo-catalytic [4], and electrochromic systems [5].

A number of methods have been employed to prepare TiO_2 films, including e-beam evaporation [6], sputtering [7], chemical vapor deposition [8], and the sol–gel process [9]. The sol–gel process, a liquid-deposit process using soft chemistry, giving homogeneous deposits, is less demanding in terms of equipment, and is thus less costly, and gives the opportunity to deposit films with large surface areas [10,11].

It is known that titanium dioxide has three crystalline modifications rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). In nature, rutile is the most common crystal phase while brookite is scarce. Rutile is the stable high temperature phase (generally in the 600–1855 °C), whereas anatase and brookite are metastable and are readily transformed to rutile when heated [12].

Therefore, it is necessary to study systematically the structural and optical properties of sol–gel TiO_2 thin films as a function of the preparation conditions. In this Note, TiO_2 thin films were prepared by a sol–gel dip-coating process using titanium alkoxide. We used several experimental techniques to characterize the structural evolution and the optical properties resulting from different annealing treatments and different dipping iterations: X-ray diffraction, Raman spectroscopy, Scanning Electron Microscopy (SEM) and UV spectroscopy.

2. Experiments

The thin films of TiO_2 were prepared by sol–gel dip coating on an ITO substrate. The use of ITO substrate has great advantages in solar cells applications. These are 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 butanol (C_4H_9OH) as a solvent and four moles of acetic acid ($C_2H_4O_2$); one mole of distilled water is added as well as one mole of tetrabutyl–orthotitanate $(C_4H_9O)_4Ti$; this solution is transparent, of yellowish color and is ready for the deposit. The substrates of carefully washed ITO coated glass are dipped in the solution of deposit and are withdrawn from it with a constant speed. After each dipping, these thin films are dried for 30 minutes at 100 °C. The TiO_2 thin films were annealed in the temperature range of 350–500 °C with increasing temperature rate of 5 °C min^{-1} for 2 h in furnace. Fig. 1 shows the chart of the process of making a TiO_2 thin film. The thickness of the thin films obtained varies between 89 (3 layers) and 285 nm (8 layers) depending on the temperature of annealing and the number of dippings.

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 X-rays diffraction patterns were recorded with a copper anticathode ($I = 20$ mA and $V =$ 40 kV), using step-scanning, between 10° and 70° at 0.1°/s. Raman spectra were taken at room temperature with a Jobin-Yvon T64000 company, with excitation laser of $\lambda = 514.5$ nm and liquid nitrogen cooled CCD detector with a resolution of 2 R cm^{-1}. The UV–visible spectra from our samples are obtained using a SHIMADZU (UV3101PC) double-beam spectrophotometer, controlled by computer. Its useful range is between 190–3200 nm. The treatment of the spectra is carried out using the UVPC software.

3. Results and discussion

3.1. Structural properties

The TiO_2 thin films obtained after 3 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

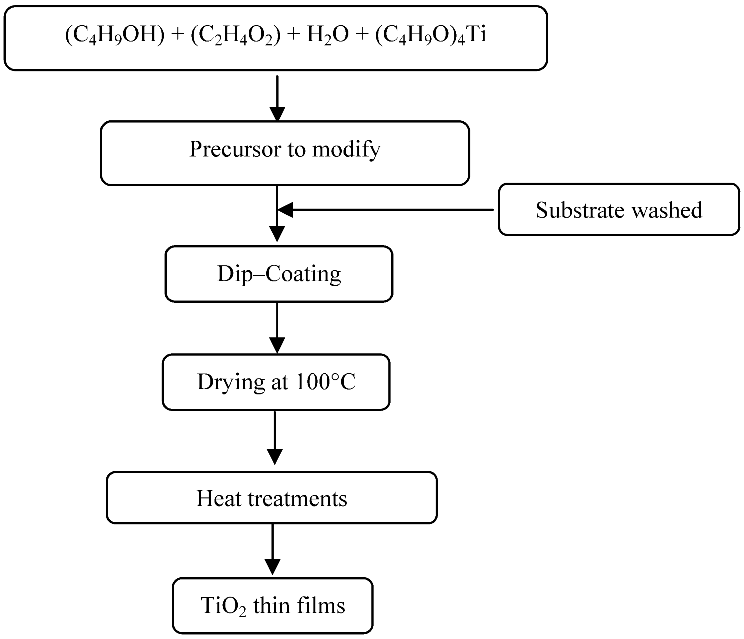

Fig. 1. The process of fabrication of TiO_2 thin films.

Fig. 1. Le processus de la fabrication des couches minces TiO_2.

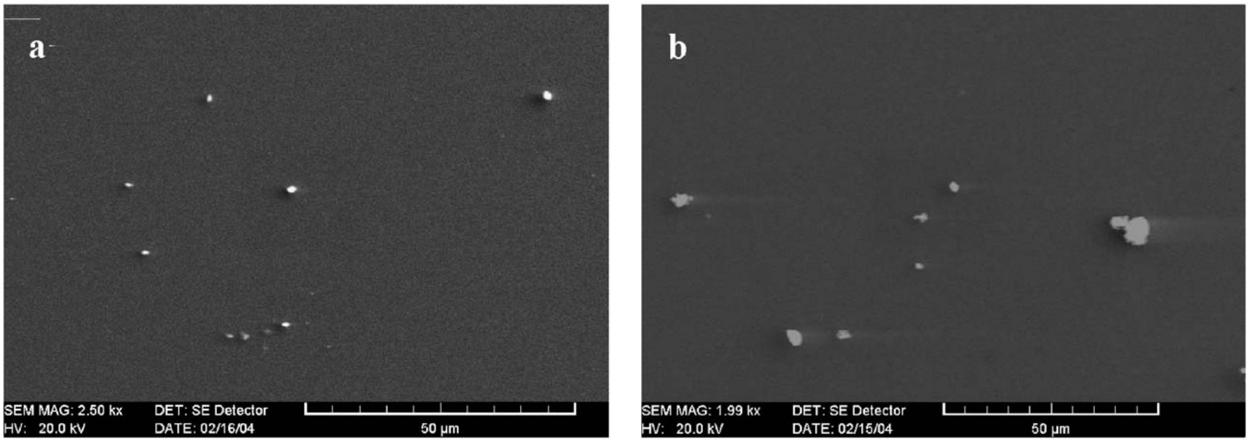

Fig. 2. SEM micrographs of the TiO_2 thin films obtained after 3 dippings and various annealings: 400 °C (a) and 500 °C (b).

Fig. 2. Image MEB des couches minces de TiO_2 obtenues pour 3 trempages et différentes températures du recuits : 400 °C (a) et 500 °C (b).

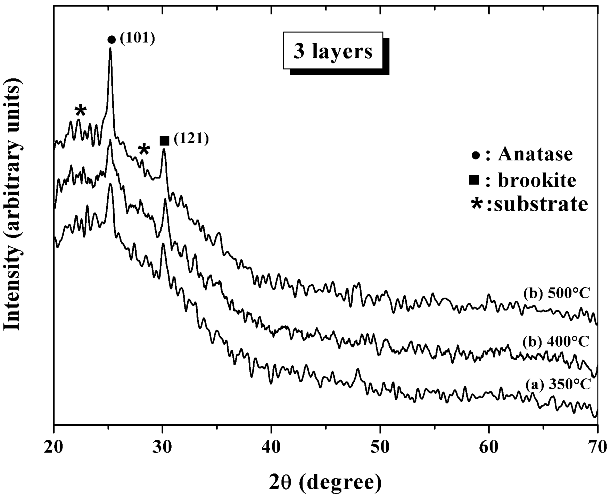

Fig. 3. The evolution of diffraction patterns of the thin films of oxide obtained after 3 dippings and various annealings at 350 °C (a), 400 °C (b) and 500 °C (c).

Fig. 3. Diagramme de diffraction de rayons X des couches minces de TiO_2 obtenues pour un nombre de 3 trempages et différentes températures de recuit 350 °C (a), 400 °C (b) et 500 °C (c).

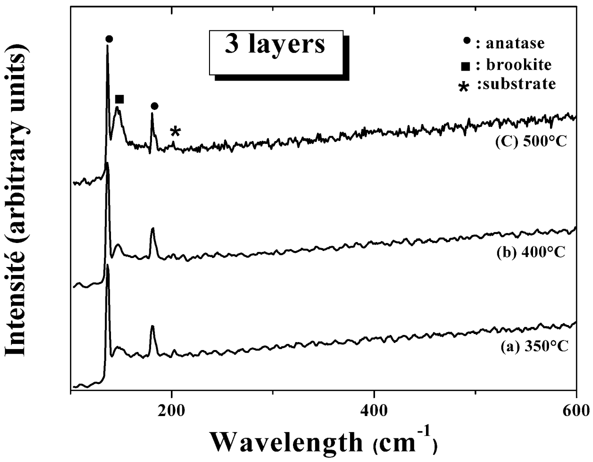

Fig. 4. The Raman spectra of the thin films of oxide obtained after 3 dippings and various annealings at 350 °C (a), 400 °C (b) and 500 °C (c).

Fig. 4. Spectres Raman des couches minces de TiO_2 obtenues pour un nombre de 3 trempages et différentes températures de recuit 350 °C(a), 400 °C (b) et 500 °C (c).

was observed that the coating was homogeneous without any visual cracking over a wide area. The increase in the treatment temperature, did not affect the uniformity of the film.

Fig. 3 illustrates the XRD patterns of the TiO_2 thin films obtained after 3 dippings (3 layers) and various annealings at 350, 400 and 500 °C. We observe that the titanium oxide starts to crystallize starting from the annealing at 350 °C (Fig. 3(a)), the structures obtained are the anatase type tetragonal symmetry and brookite of orthorhombic symmetry appears near peaks centred around 25.24° and 30.28° respectively. As we raise the temperature of annealing, from 350 to 500 °C (Fig. 3 (a), (b) and (c)), we observe the intensities corresponding to the lines characteristic of anatase and brookite increase with temperature. This increase in the intensities of the peaks is interpreted as due to an increase in proportion of titanium oxide with the increase in the annealing temperature and an improvement of the crystalline quality.

Table 1
Crystallite size L (nm) of the TiO_2 thin films for different annealing temperatures

Tableau 1
Taille des cristallites L (nm) des couches minces de TiO_2 obtenue pour différentes températures

Samples	Phases	L (nm)	(hkl)
3 layers at 350 °C	Anatase	6.7	(101)
	Brookite	18.8	(121)
3 layers at 400 °C	Anatase	9.9	(101)
	Brookite	19.2	(121)
3 layers at 500 °C	Anatase	15.4	(101)
	Brookite	23.5	(121)

The size of the crystallite can be deduced from XRD lines broadening for the Scherrer relation, angle units have to be given [13].

$$L = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where L is the crystallite size of TiO_2 thin films, K is a constant (= 0.94), λ is the wavelength of X-ray ($CuK_\alpha = 1.5406$ Å), β is the true half-peak width, and θ is the half diffraction angle of the centroid of the peak in degree.

The values deduced are given in Table 1.

Table 1 shows the variation of the size of the grains of the oxide layer with the annealing temperature. As temperature increases, TiO_2 crystallites continue to develop. The crystallite size of anatase and brookite increases with the increase in the annealing temperature from 6.7 to 15.4 nm for anatase, and from 18.8 to 23.5 nm for brookite.

Fig. 4 shows the evolution of the Raman spectra of the thin films of oxide obtained after 3 dippings and various annealings: 350, 400 and 500 °C.

The Raman spectra (Fig. 4) confirm the presence of crystalline titanium oxide starting from the temperature 350 °C, the peaks characteristic of anatase (tetragonal) appear near bands centred around 137 and around 181 cm^{-1} while brookite (orthorhombic) peak occurs around 147 cm^{-1} [14–16]. The Raman data are in good agreement with the XRD results.

3.2. Optical properties

Figs. 5 and 6 show the UV–VIS spectra TiO_2 thin films for different annealing temperatures and the number of dippings in wavelength range 300–1000 nm. 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 [17]. The bands due to the interference color of the film appeared in the wavelength range 350–800 nm. The amplitude of interferences spectra increased with increasing treatment temperature and the number of dippings.

The refractive index of the prepared TiO_2 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 [18]. The refractive index $n(\lambda)$ over the spectral range is calculated by using the envelopes that are fitted to the measured extreme:

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

$$S = \frac{1}{2}\big(n_0^2(\lambda) + n_S^2(\lambda)\big) + 2n_0 n_S \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda) \times T_{\min}(\lambda)} \tag{3}$$

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.

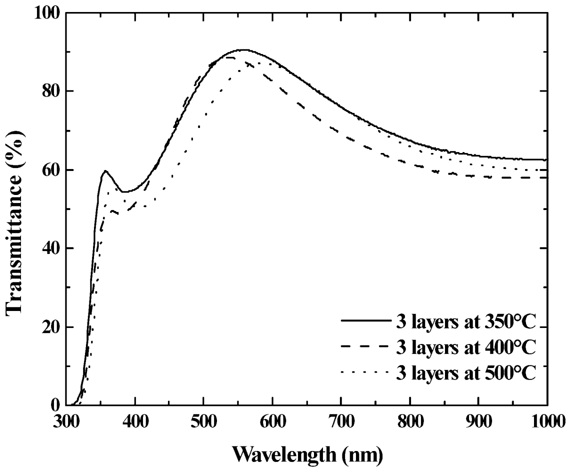

Fig. 5. UV–VIS spectra of the TiO_2 thin film, for 3 layers at various temperatures 350, 400 and 500 °C.

Fig. 5. Spectres de transmissions de couches minces de TiO_2 obtenues pour un nombre de 3 trempages et différentes températures de recuit 350, 400 et 500 °C.

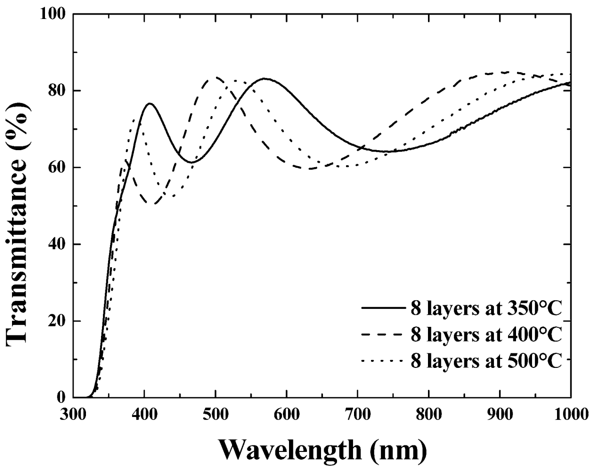

Fig. 6. UV–VIS spectra of the TiO_2 thin film, for 8 layers at various temperatures 350, 400 and 500 °C.

Fig. 6. Spectres de transmissions de couches minces de TiO_2 obtenues pour un nombre de 8 trempages et différentes températures de recuit 350, 400 et 500 °C.

Table 2
The variation of the refractive index (n) and porosity (p) for different annealing temperatures and the number of dippings

Tableau 2
Variations de l'indice de réfraction (n) et de la porosité (p) des couches minces de TiO_2 obtenues pour différentes températures et différents nombre de couches

T	3 layers		8 layers	
	n	*Porosity*	*n*	*Porosity*
350 °C	1.93	49.2%	2.19	29%
400 °C	1.95	47%	2.25	23.9%
500 °C	1.98	45.7%	2.37	13.6%

The porosity of the thin films is calculated using the following equation [19].

$$Porosity = \left(1 - \frac{n^2 - 1}{n_d^2 - 1}\right) \times 100(\%) \tag{4}$$

where n_d is the refractive index of pore-free anatase ($n_d = 2.52$ [20]), and n is the refractive index of the porous thin films.

The resultant refractive index (n) and porosity (p) of the TiO_2 thin films for different annealing temperatures and number of dippings at 550 nm wavelength are listed in Table 2.

It is noted that of the refraction index of the thin films of titanium oxide increases with the increase in the treatment temperature and the number of dippings. In addition porosity decreases. This is due to film densification and pore destruction in films during different treatment temperatures.

4. Conclusion

TiO_2 thin films were prepared by a sol–gel dip-coating process using titanium alkoxide. XRD and Raman analysis of our thin films of TiO_2 shows that 3 layer films crystallize in the phases anatase and brookite, starting from the temperature of annealing 350 °C, the crystallite size of anatase and brookite increases with the increase in the annealing temperature. The analysis of the transmission spectra shows that TiO_2 thin films are transparent in the visible range and opaque in the UV region, irrespective of the treatment temperature and the number of dippings. The refractive index of the thin films of titanium oxide increases with the increase in the treatment temperature and the number of dippings, in addition porosity decreases. From this study, we successfully fabricated optical materials in thin films, having desired structural and optical properties by sol–gel dip coating using the titanium alkoxide as a starting material.

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