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Water adsorption in porous TiO_2–SiO_2 sol–gel films analyzed by spectroscopic ellipsometry

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Abstract

High refractive index TiO_2–SiO_2 thin films were prepared by the sol–gel method and the optical properties were characterized by spectroscopic ellipsometry. The results of the optical analysis were related with the TiO_2–SiO_2 molar ratio of the porous films. It was obtained that the higher is the TiO_2 molar ratio, the higher is the refractive index and the lower is the thickness under the same deposition conditions. In fact, when the TiO_2–SiO_2 molar ratio varies from 70–30% to 100–0%, the refractive index and the thickness vary from ~1.85 to ~1.95 $\lambda = 500$ nm and from ~65 nm to ~40 nm, respectively. The water adsorption in the pores of the material produces a change in the refractive index of the film. The variation of the optical properties with the environmental relative humidity was also studied. In addition, information about the size and the shape of the pores was extracted from the water adsorption isotherms measured by ellipsometry.

Keywords: Spectroscopic ellipsometry; Water adsorption; TiO_2–SiO_2; Sol–gel

1. Introduction

The development of optical coatings processed by the sol–gel method have been widely investigated during the last years [1]. The sol–gel process is very suitable for optical applications due to the capability to control the optical properties, composition and nanostructure of the final material. In fact, the refractive index can be tailored depending on the specific application. In this sense, sol–gel processing has been successfully employed in the development of optical coatings and waveguides [2,3].

The size and shape of the pores of the material also can be modified. This feature has been exploited extensively using the sol–gel method to develop host matrixes containing active components (laser dyes, photochromic dyes, liquid crystals, photosensitive polymers, etc) [4,5].

It is well-know that the material porosity determines its behavior under different environment conditions [6]. Thus, the optical response will depend on the relative humidity for porous films. This feature should be taken into account during the design and manufacture phases of an optical coating as an anti-reflection coating or an interference filter. However, this characteristic can be utilized to develop optical humidity sensors.

In this work, TiO_2–SiO_2 films prepared by the sol–gel technique have been studied. The relationship between the TiO_2 molar ratio and the optical properties of the layer has been analyzed by spectroscopic ellipsometry. In addition, the optical behavior of the material under different humidity environmental conditions and the correlation with the pores size has been analyzed.

2. Experimental details

2.1. Samples preparation

TiO_2–SiO_2 films over glass substrates (microscope slides) were prepared using the sol–gel method. Three samples with different TiO_2–SiO_2 molar ratio were studied:

100% TiO_2

90% TiO_2/10% SiO_2

70% TiO_2/30% SiO_2

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In order to obtain these films reverse-micellar solutions in cyclohexane (CHX) were made by mixing 20 ml CHX, 3 g of igepal and 0.14 ml of distilled water (DWW) and overnight stirring. To 5 ml of this solution, 0.3 ml of titanium isopropoxide was added under vigorous stirring to the microemulsion for pure TiO_2 films. For TiO_2–SiO_2 thin films preparation, the sol–gel precursors were added to the microemulsion sequentially: first, titanium isopropoxide and second TEOS, always keeping the required molar ratio.

The resulting microemulsion was used at an early stage of gelation (10–20 min, depending of the composition) to dip coated glass substrates. The dipping was carried out under ambient conditions at a speed of 15 cm/min. The films were thermal treated at 450 °C for 20 min (heating ramp: 50 min) [7].

2.2. Optical characterization: spectroscopic ellipsometry

An rotating polarizer spectroscopic ellipsometer (ES-4G from SOPRA) was used to analyze the samples. The ellipsometer nominal repeatability is 0.005 for $\tan\Psi$ and $\cos\Delta$.

A climatic chamber specially design by us to be coupled to the ellipsometer was utilized to perform in situ measurements of the change of optical properties with the relative humidity (*RH*). Temperature and humidity inside the chamber were measured with a commercial sensor (PHM233 with the HMP46 probe from VAISALA). The accuracy was 0.2 °C and 1% *RH*, respectively.

Firstly, the samples were measured using an achromatic compensator at an incidence angle of 75.03°. This optical component was utilized in order to improve the ellipsometric measurements sensitivity when $\cos\Delta$ is close to 1.

The water adsorption measurements were carried out at an incidence angle of 70.03° without the achromatic compensator in order to couple the climatic chamber properly.

3. Theory

Adsorption of water molecules and capillary condensation occurs in porous materials.

A change in the environment *RH* produces variations in the amount of water adsorbed in the pores of the film. It causes a variation in the effective refractive index of the porous material, and, therefore, a change in the ellipsometric parameters Ψ and Δ. The relationship between the amount of water adsorbed and the variation of the ellipsometric parameters is approximately linear [8,9].

The curves of the ellipsometric parameters variations (proportional to the amount of water adsorbed) against the *RH* at a controlled temperature are called adsorption isotherms. The adsorption isotherms provide information about the pore size distribution and the shape of the pores.

The Kelvin equation [6] establishes a relation between the environmental *RH* and the pore radius where the capillarity condensation occurs and, consequently, the amount of water adsorbed increases:

$$\ln RH = -\frac{2\gamma V_L}{RT}\frac{1}{r_m}, \tag{1}$$

where *RH*: relative humidity, r_m: pore radius minus the thickness of adsorbed films on the walls of the pores, γ: water surface tension, V_L: molar volume, R: perfect gases constant, T: temperature.

The pore size distribution of the material can be obtained applying the Kelvin equation to the adsorption isotherm following the Pierce method described in [6].

4. Results and discussion

4.1. Optical characterization of the films

The ellipsometric measurements of the samples (Fig. 1) were analyzed by fitting a theoretical model to the experimental data. The model utilized was a homogeneous film with a Sellmeier law dispersion and two Lorentz peaks:

Sellmeier law

$$\varepsilon_r = 1 + \frac{(A^2-1)\lambda^2}{\lambda^2 - B}$$

$$\varepsilon_i = \frac{C}{\lambda} + \frac{D}{\lambda^3} + \frac{E}{\lambda^5}, \tag{2}$$

Lorentz peak

$$\varepsilon_r = \frac{A\cdot\lambda^2(\lambda^2 - L_0^2)}{(\lambda^2 - L_0^2)^2 + \gamma^2\lambda^2}$$

$$\varepsilon_i = \frac{A\cdot\lambda^3\gamma}{(\lambda^2 - L_0^2)^2 + \gamma^2\lambda^2}, \tag{3}$$

The glass substrate was previously measured and the optical constants obtained were introduced in the model. The regressions were performed on the ellipsometric parameters α and β. Low standard deviations were obtained ($\sigma < 0.0003$) and the experimental data were properly fitted along all the spectrum.

The results of the regression (Table 1) are in agreement with the analysis carried out by the inversion

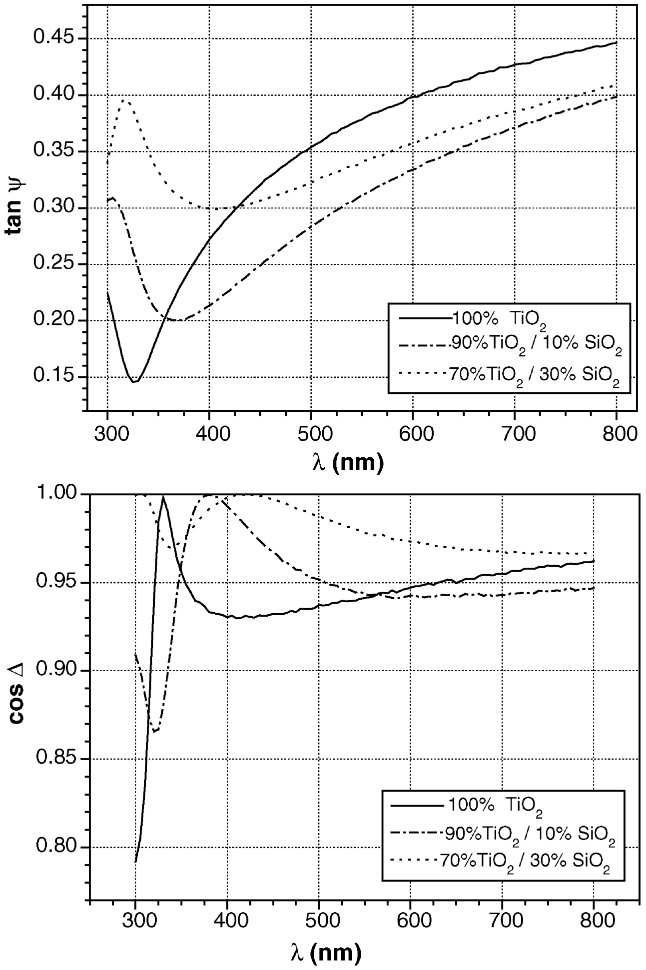

Fig. 1. Ellipsometric measurements of the TiO_2–SiO_2 samples vs. the molar ratio.

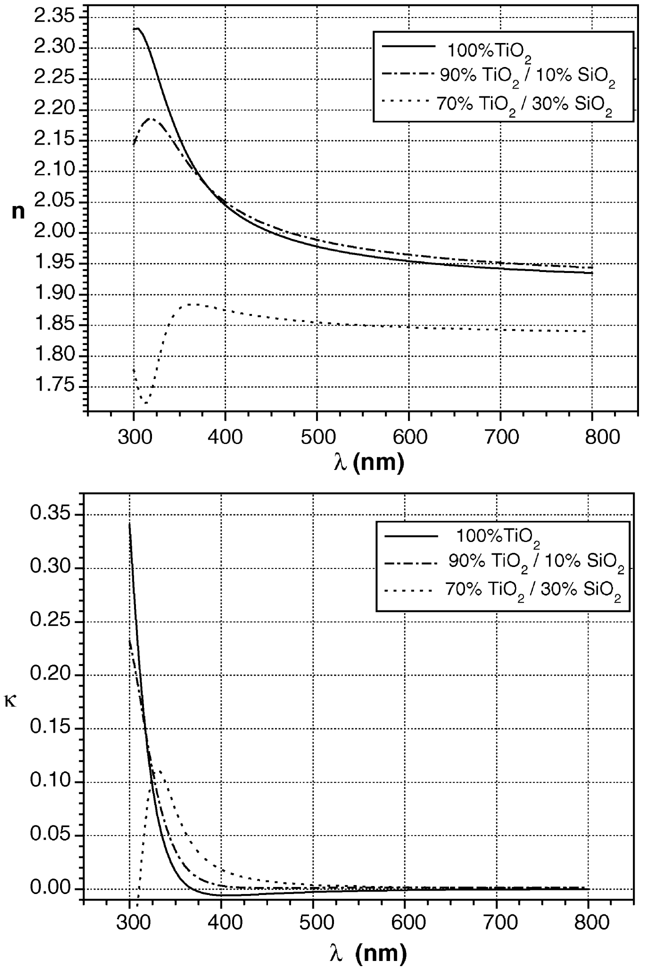

Fig. 2. Complex refractive index of the TiO_2–SiO_2 samples vs. the molar ratio.

method. Firstly, $\kappa = 0$ was assumed from $\lambda = 500$ nm to $\lambda = 800$ nm in order to obtain the film thickness. The resulting thickness was utilized to extract the n and κ values of the film from $\lambda = 300$ nm to $\lambda = 800$ nm.

Table 1 shows that the higher is the TiO_2 molar ratio, the lower is the thickness of the film. As it can be observed in Fig. 2, the complex refractive index decreases for the sample with 70% TiO_2 molar ratio. In the case of the 90% TiO_2 film, this downward trend can be appreciated (see UV range), but the small difference with the 100% TiO_2 sample is lower than the experimental errors.

Table 1
Regression results for the sol–gel TiO_2–SiO_2 films

Sample		100% TiO_2	90% TiO_2–10% SiO_2	70% TiO_2–30% SiO_2
Thickness		40 ± 2 nm	54 ± 3 nm	64.4 ± 0.7 nm
Sellmeier law	A	1.806 ± 0.009	1.87 ± 0.02	1.828 ± 0.003
	B	0.009 ± 0.002	0.017 ± 0.003	0.0051 ± 0.0009
Lorentz peak 1	A	1 (fixed)	1 (fixed)	1 (fixed)
	L_0	0.278 ± 0.003	0.295 ± 0.009	0.3149 ± 0.0008
	γ	0.071 ± 0.005	0.101 ± 0.008	0.063 ± 0.003
Lorentz peak 2	A	-0.60 ± 0.08	-0.8 ± 0.1	-0.98 ± 0.01
	L_0	0.299 ± 0.008	0.31 ± 0.01	0.3118 ± 0.0008
	γ	0.116 ± 0.004	0.1 ± 0.01	0.063 ± 0.003
S.D.		0.00014	0.0002	0.00013

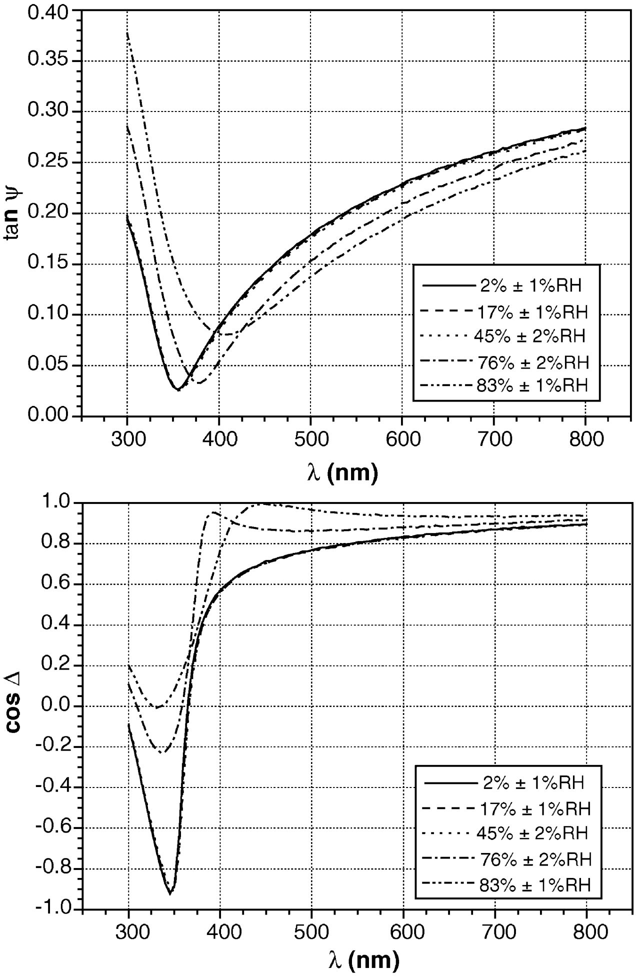

Fig. 3. Changes of the ellipsometric parameters tanΨ and cosΔ with environmental relative humidity (100% TiO_2 sample, $T = 22.0 \pm 0.3$ °C).

4.2. Water adsorption

The behavior of the 100% TiO_2 sample was studied under different relative humidity environmental conditions ($T = 22.0 \pm 0.3$ °C). Fig. 3 shows that the ellipsometric parameters change strongly for relative humidity higher than 45%.

A new ellipsometric model has been developed to explain this optical response. This model considers a H_2O layer of a few nanometers of thickness over the TiO_2 film and an interface layer. This model fit to the experimental data measured at 76% *RH*. The thickness of the H_2O and the interface layers obtained from the regression increase for the measurement at 83% *RH*. Hence, it can be concluded that a H_2O layer is adsorbed over the film external surface for high relative humidity ($\geq 75\%$ *RH*). Also, the water is adsorbed inside the pores of the film, but the effect of the adsorption over the external surface is higher due to the low thickness of the TiO_2 films. Note that the thickness of the TiO_2 film has the same order of magnitude than the thickness of the external adsorbed water film.

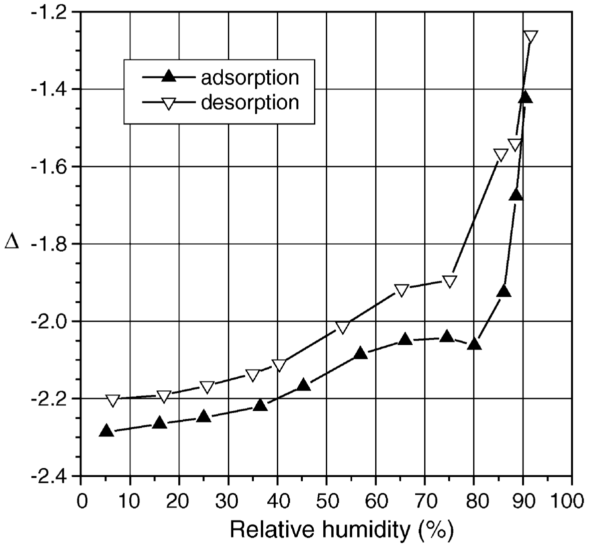

Fig. 4. Water adsorption isotherm of 100% TiO_2 sample measured by ellipsometry ($T = 24.5 \pm 0.2$ °C, $\lambda = 340$ nm).

Simulations assuming films with identical complex refractive index but different thickness support the following statement: the effect on the ellipsometric measurements of the adsorption over the external surface is higher for thin films (approx. 40 nm) and the effect of adsorption inside the films is higher for thick layers (approx. 1 μm).

Nevertheless, an estimation of the size of the pores can be extracted from the variations of the ellipsometric parameters with *RH* at $\lambda = 340$ nm and $T = 24.5 \pm 0.2$

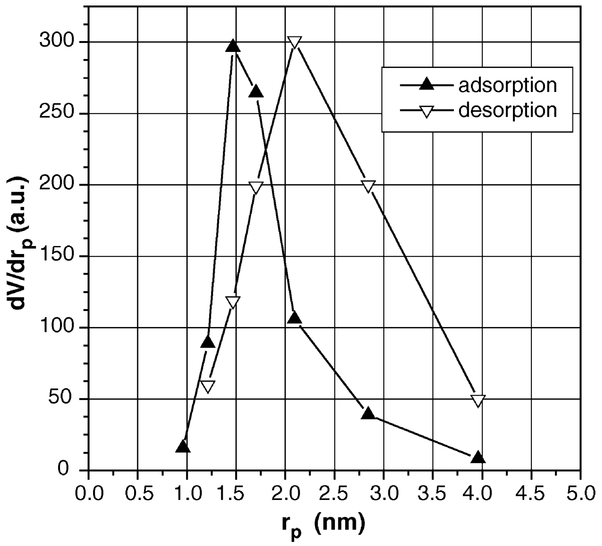

Fig. 5. Pore size distribution calculated with the Pierce method applying the Kelvin equation to the water adsorption isotherm corresponding to the 100% TiO_2 sample.

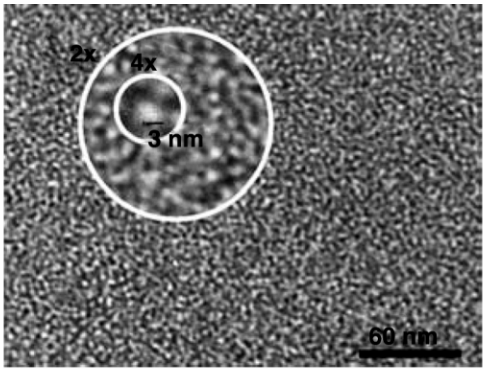

Fig. 6. TEM micrograph of the 100% TiO_2 sample.

°C (Fig. 4). The Kelvin equation has been applied to the relative humidity range (20–80% *RH*) where the capillary condensation inside the film mainly occurs. The resulting pore size distribution (Fig. 5) is in concordance with the TEM micrograph obtained from the sample (Fig. 6): the most probably pore radius of the TiO_2 is ~1.5–2.0 nm.

5. Conclusions

The refractive index of sol–gel TiO_2 films can be tailored selecting the TiO_2 molar ratio. The thickness of the layer will depend on the TiO_2 concentration as well. The higher is the TiO_2 molar ratio, the higher is the refractive index and the lower is the film thickness.

A layer of water is adsorbed on the external surface of the film and capillary condensation occurs in the pores of the film. The radius of the pores (approx. 1.5–2.0 nm) can be extracted from the adsorption isotherms measured by ellipsometry. These results are in concordance with the TEM micrograph obtained.

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