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TiO_2 mesoporous thin films studied by Atmospheric Ellipsometric Porosimetry: A case of contamination

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ABSTRACT

Anatase mesoporous TiO_2 thin films are frequently prepared by surfactant templating to control porosity development and Atmospheric Ellipsometric Porosimetry is a reliable and fast technique allowing the determination of the porosity of such films. After prolonged exposition to high-vacuum (6.4×10^{-6} mbar), the films porosity exhibits a degraded behavior during porosimetric measurements, indicating a vacuum-induced modification. The main effect resulting from such exposition to high-vacuum is a wettability modification of the films, resulting in an increase of the hydrophobic character of the TiO_2 surface. This evolution induces non-correct results in porosimetric measurements due to the fact that the contact angle parameter needed to calculate the pore size distribution is highly different from the reference films. A surface contamination explains such modifications and a restoration of the films is obtained by using ultraviolet treatment.

1. Introduction

Due to its semiconductor metal oxide properties, titanium dioxide is widely used in the form of thin films for applications such as gas sensor [1–3], anti-reflective and self-cleaning surfaces conditioning [4,5], catalyst for the photodegradation of organic molecules (pollutants [6] or industrial dye [7]) or inorganic [8] and as photoelectrode for low-cost photovoltaic applications [9–11]. Particularly, Dye Sensitized Solar Cells (DSSC) were first based on porous TiO_2 films and it became a very promising material for photo-electric production [12]. The sensitization of such films is obtained by adsorption of a dye as a monolayer at the surface of the TiO_2 [12,13]. In order to maximize the surface of TiO_2 reachable to the dye without modifying film thickness, a mesoporous structure is required and can be obtained by using a sol–gel deposition method as previously reported [14–17].

As a simple, rapid, non-destructive and reliable technique, the spectrometric Ellipsometric Porosimetry (EP) is used for industrial production controls and laboratory investigations [18–22,17]. The Atmospheric Ellipsometric Porosimetry (AEP) technique, a particular EP technique using water as adsorbate, allows the characterization of the mesoporous structure of films [21,23]. This technique consists of plotting an adsorption–desorption isotherm measured during variations of film refractive index induced by the change of partial pressure of the solvent above the film. The thickness variations are also monitored during the measurement and a pore size distribution (PSD) in the mesoporous domain (defined by a pore range of 2–50 nm according to the IUPAC recommendations [24]) is obtained from the isotherm curves.

Traditional nitrogen adsorption porosimetry is based on the adsorption and desorption of N_2 vapor near the boiling point by gas adsorption manometry of the adsorptive adsorbed and condensed in the pores [25]. In contrary, AEP takes place at room pressure and temperature, with a simple controlled mixing of dry and humid air flows in a chamber [21]. What is more, in the case of thin films with less than 1 μm thick, the main limitation of the N_2 technique comes from the detection unit requesting large samples in order to compensate the relative low sensitivity [18]. Again, AEP appears as an efficient tool for the characterization of porous thin films even with very low content of porous matter.

We used a α-2 MeV Rutherford back-scattering (RBS) technique to verify the stoichiometry of the deposited TiO_2 and to demonstrate the possibility to obtain complementary informations about the mesoporosity of the films. Nevertheless, after being submitted to RBS analysis, we observed that the samples gave a different response during AEP measurements. The mesoporosity was highly degraded and the pore size distribution (PSD) exhibited sub-populations with an increase of the mean pore radius. The exposition to the high vacuum of the RBS analysis chamber was then identified as the origin of this TiO_2 properties evolution. Two hypothesis were proposed to explain this behavior. First, the exposition to

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high vacuum (typically 10^{-5} to 10^{-6} mbar) induced modifications of the mesostructure, by breaking sidewalls resulting in the observed displacement of the PSD. Such an increase of the pore size range could make the AEP technique inoperative. In this case, Environmental Ellipsometric Porosimetry (EEP) with large molecular solvent, such as toluene, should be used. Alternatively, TiO_2 surface properties could have been modified, impacting the AEP measurements. In this case, the water used as a adsorbate remains sufficient but the calculation of PSD has to be corrected according to a traditionally negligible parameter, the contact angle between the adsorbate (water) and the material (TiO_2) in the air.

2. Experimental

The TiO_2 films are deposed on a (001)-oriented silicon substrates from MEMC (Electronic Materials, It) previously passivated in nitric acid (1 mol L^{-1}). The SiO_2 film at the substrate surface was determined by ellipsometric measurements and was found about 4 nm thick. The precursor solution is prepared by mixing 1-butanol (Acros Organics), Pluronic P123 surfactant added as a porogen template (Sigma–Aldrich), titanium tetraisopropoxide (Acros Organics) and concentrated hydrochloric acid (Merck, 36 wt.%) [26–28]. The films are then deposited by dip-coating of the substrate in the precursor solution. The withdrawal rate is set at 0.8 mm s^{-1} and the relative humidity (RH) in the dip-coating chamber is controlled at 25% during a few minutes at a temperature of 25 °C. Relative humidity conditions control the solvent and hydrochloric acid evaporation and thus the inorganic network condensation as well as the spatial organization of pores [29,30].

Afterwards, two successive thermal treatments are applied. The first is applied near after dip-coating: the layer is stabilized at 300 °C during 15 min on a thermalized plate. This stabilization step is necessary to achieve a complete evaporation of the solvent and improve the condensation of the inorganic network. What is more, this prevents the redissolution of the film during a subsequent dip-coating step in case of stacked multilayer films.

The second thermal treatment is a calcination in a furnace at 350 °C during 2 h and with a ramp of temperature set at 1 °C/min. This step allows the combustion of the surfactant and the crystallization of the anatase phase of the TiO_2.

A substrate size of 3×4 cm^2 is used and 12 samples are prepared by cleaving. This method allows better results in terms of thickness homogeneity across the samples and reduces possible border effects during deposition. The final thickness obtained, determined by spectroscopic ellipsometry (SE), is 318 ± 4 nm at the top of the substrate, decreasing to 284 ± 4 nm at the bottom.

The vacuum setup is made of a cluster containing a primary and a turbo pump (from Pfeiffer vacuum) and a vacuum gauge mounted on a chamber, located near the samples. Fig. 1 shows the measure of the vacuum level in the chamber during the pumping process. A repeated measure with a sample inside the chamber does not show noticeable difference, indicating that possible degas from the as-prepared samples do not modify the velocity of the pumping. The letters on the curve refer to the samples exposition conditions. The vacuum obtained with only the primary group pumping is early stabilized at 3 mbar. A first batch of films is exposed to this vacuum level for 16 h (batch A). The best vacuum achievable with the complete system pumping is 6.4×10^{-6} mbar after more than 2 h. A second batch of samples is submitted to this vacuum level (batch B) during 16 h. In order to achieve a stable modification of the porous films, some samples from each batch were submitted to a second pumping cycle after a return to atmospheric pressure. Vacuum breaking is done by stopping the turbo pump first and 10 min are required to return to the ambient atmosphere.

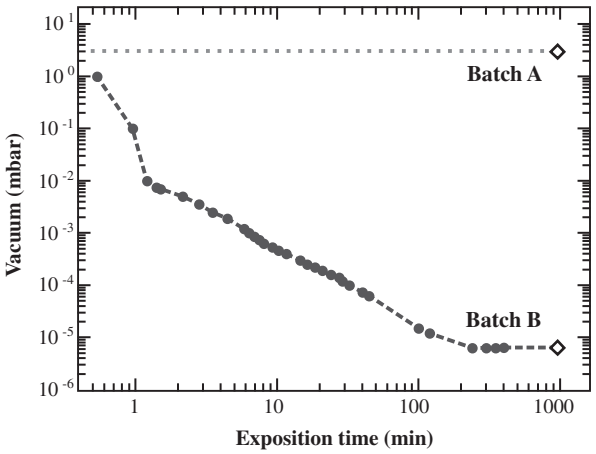

Fig. 1. Measured vacuum inside the chamber versus time while pumping. Letters refers to sample batches as described in the text.

X-ray diffraction analyses were performed on a Philips D8 diffractometer in a θ—2θ configuration with an incident angle of 2° and Cu Kα radiation. A complete [10–70°] scan is first realized for the identification of the Titania phases and the (101) peak at 25.3° is then used for anatase detection [14].

TEM micrographs were taken at an acceleration voltage of 200 kV (Tecnai G2 Twin, FEI) on the films scratched off the substrate and dispersed in ethanol under ultra-sounds, then deposited on a formvar-coated grid.

Thickness and mesoporosity of the TiO_2 films are determined with a GES-5E ellipso-porosimeter from SOPRALAB using demineralized water as solvent. A UV–visible high resolution scanning spectrometer analyzes the signal reflected by the sample. The light source is a 40 W Xenon lamp and measurements are performed on the spectral range of 1.23–4.00 eV. Data treatments are performed with the associated WinElli II software. The use of a micro-spot ($\varnothing$ 400 nm) is required in this case due to the chamber geometry allowing controlled air-flow extraction through holes on the sides of the chamber [21].

Rutherford back-scattered (RBS) spectroscopy has been performed at the IPNAS-CEA Laboratory of Liège on a beam line of a 2.5 MV Van de Graaff accelerator. Samples were placed in the beam path in a vacuum chamber (10^{-6} mbar) and the impact of the beam was visualized with a CCD camera. Classic particle detection equipment and geometry were implemented with use of a 100 μm thick PIPS particle-detector (Canberra PD-50-10-100) exhibiting a 10 keV energy resolution and sustaining a diffusion angle of 165°. The vacuum chamber is electrically isolated, so that the measure of the dose hitting the sample is controlled by a current integrator (ORTEC 439).

Then, the SIMNRA codes [31] was used for deconvolution and interpretation of diffused particle spectra.

3. Results and discussion

3.1. Morphological characterization

A first wide angle XRD diagram (10–70°, not shown here) was acquired in order to identify the TiO_2 phases formed during the furnace anneal. As expected according to the relatively low temperature used in the furnace (350 °C) [32,33], only the anatase phase is observed. In Fig. 2, the presented XRD diffraction pattern (inset) is centered on the (101) anatase peak at 25.3°. The measures were taken before vacuum exposition and on the 2×16 h exposed film, from sample batch B after two times 16 h of vacuum exposition. No shift or intensity variation are observed between the peaks,