# SOL-GEL TEMPLATE SYNTHESIS OF THE ORIENTED MESOPOROUS THIN OXIDE FILMS AND NANOSTRUCTURES

GERMAN M. TELBIZ*, VICTORIA GONCHARUK, PETRO MANORYK
*Institute of Physical Chemistry NASU, Pr. Nauky 31, Kyiv 03039, Ukraine*

OKSANA LYTVYN
*Institute of Semiconductor Physics NASU, Pr. Nauky 31, Kyiv 03039, Ukraine*

CHRISTOPHER DEFRANOUX, ANTONIO MORENO,
*SOPRA S.A., 26 rue Pierre Joigneaux, 92270 Bois Colombes, France*

**Abstract.** In this communication, a different approach to the preparation of mesoporous $SiO_2$ and $TiO_2$ thin films and nanocomposites has been adopted, aimed at preparation of oriented mesoporous thin films with highly stable roughness of the film surface and controlled pore dimension. We describe the preparation and compositional analysis of thin film coatings prepared using sol-gel techniques (thickness 50–500 nm, roughness ± 0.5 nm with pore distribution 2.4–8 nm for silica oxide and up to 300 nm for titanium oxide and porosity 30–50%). Analyses of these systems were based on XRD, AFM, FTIR, and elipsometry porosimetry data. The structural evolution of the film during thermal treatment was observed by FTIR spectroscopy and XRD.

**Keywords:** Mesopous oxide film, spin coating, silica oxide, Titanium oxide, AFM/elipsometry porosimetry, structural evolution, nanocomposites.

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* To whom correspondence should be addressed:. German Telbiz , Physic-Inorganic Chemistry Department Institute of Physical Chemistry, Nuke av., 31, 03028, Kyiv, Ukraine; e-mail: g_telbiz@yahoo.com

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## 1. Introduction

In the recent years, a substantial progress in the synthesis and performance characterization of $SiO_2$ and $TiO_2$ based materials has been achieved. First, there has been an interest in the development of mesoporous dioxide thin films. The preparation procedures usually combine the use of structure directing agents in non-aqueous or highly acidic solutions for organizing the network forming dioxide species and the dip-coating technique. Thin mesoporous films of silicon and titanium oxide have extensive applications in many fields such as photoelectric devices, optical components, materials for analytical sensing and separations of environmental contaminates and enhanced environmental measurements.[1,2] In this communication, a different approach to the preparation of mesoporous $SiO_2$ and $TiO_2$ thin films and nanocomposites has been adopted, namely the preparation of oriented mesoporous thin films with highly stable roughness of the film surface and controlled pore dimension is aimed at.[3] The latter property is of utmost importance for the above mentioned materials for separations of environmental contaminates and enhanced environmental measurements such as photo catalytic degradation of organic compounds highly diluted in water for titanium surface, which is, as mentioned above, unfortunately further enhanced due to the illumination, precludes efficient adsorption of organic compounds on the photo-catalyst surface and their effective degradation.[4]

## 2. Experimental

Silica and titania mesostructured films have been produced using evaporation induced self-assembling processing via spin-coating. Ionic and non-ionic surfactants as structure–directing agents such as cetyltrimethylammonium bromide (CTAB), block copolymer (Pluronic F-123) and 18-Crown-6 and have been removed from the films by calcinations (350–500°C). A source of silica and titania was tetraethylortosilicate (TEOS) and titanium tetraisopropoxide (TIP). The stock and templating solution was finally stirred at room temperature and subsequently aged with stirring before the films were spin-coated onto glass slides, cleaned by “piranha” solution, at various speed for silica and titania in the range of 2,000–5,000 $min^{-1}$. Then the films were aged overnight, calcined by heating at a rate of 5°C/min to 350–500°C (depending on the template) and held for 4 h to remove the organic species.

The templated films have been characterized as function of the temperature of calcination by FTIR (Fourier Transform Infrared Spectroscopy) to obtain compositional information and allow checked degree of structural evolution of the films during thermal treatment. Spectra had been recorded in the 4,000–400 $cm^{-1}$ range. Low angle X-Ray diffraction (XRD) was used to provide structural characterization. Texture parameters (Porosity and Pore Size Distribution) are calculated from the isotherm of adsorption using the Kelvin equation by Elipsometry Porosimetry method using water as the adsorptive. The parameters were measured and then modeled using a dispersion law in order to determine its exact refractive index.[5] Once determined, the optical parameters of the substrate were then implemented in the sample model. All starting values were determined for the first measurement which had been performed for a relative humidity (RH) of 0% before any adsorption took place. Morphological parameters of the films were obtained by combining several techniques. The surface relief of the films was revealed by atomic force microscopy (AFM) using NanoScope D 300 (Digital instrument) .The details of the surface texture were provided by transmission and scanning electron microscopy (TEM, SEM), using a Hitachi S-900 apparatus.

## 3. Results and Discussion

Mesostructured films were obtained via evaporation-induced self-assembly, a deposition process, which is driven by the preferential evaporation of the solvent. Thin films of surfactant-templated mesoporous silica and titania have been prepared by a spin-coating method. In this method an oligomeric solution of silica or titanium was prepared prior to the addition of surfactant. Using the spin-coating method, the pore diameter could be controlled by surfactant chain-length as in bulk materials. In films with lamellar ordering, silica (titanium)/surfactant ratio value was found to control the wall thickness of the silica. Macroscopic cracks, which were observed in the films prepared by spin-coating, could be prevented by pre-treatment of the glass support with piranha solution: it was suggested that the pre-treatment invokes covalent bonds between the film and the substrate, and thus improves their adhesion.

The progress of mesostructure formation of the materials in the as-synthesized films was monitored by powder X-ray diffraction.[4] The as-synthesized and calcined silica films showed good optical quality, with thicknesses in the range of 30–700 nm. The XRD patterns of the films, in comparison with an as-deposited film, have shown decrease in *d*-spacing (equivalent to the increase in Bragg angle) suggesting that a contraction of the framework structure occurred in a direction perpendicular to the substrates, which resulted from the removal of the template as well as additional condensation of silanol (Si-OH) species.

The $TiO_2$ films calcined at temperature up to 300°C were amorphous by XRD. On the other side, diffraction peaks atlow $\Theta$ were found for the as dried film with template. Similarly these peaks disappeared after calcination at 300°C for Plutonic 123 film and 450°C for 18-Crown-6 template film. Diffraction peaks of crystalline $TiO_2$ (anatase) were found for samples calcined at 500°C. This result shows that surfactant was removed by heating in range 300–500°C. The XRD patterns hardly changed with the type and concentration of template. The relatively wide width of the peaks indicates small crystallite size, which was estimated to be approximately 9 nm using Scherrer's equation from the XRD peak broadening analysis at (101).[26] For the Crown templated $TiO_2$ film the crystallite size was more uniform and was estimate as 10 nm. It is worth to note that the crystallite size was in the range of 8–10 nm, which is known to be optimum for high catalytic activity. For the Crown templated $TiO_2$ film the crystallite size was more uniform and was estimated as 10 nm.

The microstructural evolution of the films during thermal treatment, up to a complete removal of the organic phase, was observed by FTIR Spectroscopy. Spectra had been recorded in the 4,000–400 $cm^{-1}$ range. The absorption band related to C-H mode vibration of the surfactant was detected in wave number range 2,700–3,000 $cm^{-1}$. For example, for the sample containing Pluronic as template, this band was complete absent after the 350°C thermal treatment. At 3,000–3,750 $cm^{-1}$, instead, there was the band of –OH groups, at 1,640 $cm^{-1}$ the absorption of molecular water and finally at 500–1300 $cm^{-1}$ the band related to the silica polymerization. In the 3,800–3,700 $cm^{-1}$ spectral region two overlapped regions of vibrational modes can clearly be distinguished. The first one in the lower wave number range, due to absorption of organic groups in Pluronic F127, can be taken as a signature of the presence of the block co-polymer within the material, and next one at higher wavenumber due to hydroxyl's absorption. This broad band appears as composed of several overlapping bands assigned to different types of O-H vibrational modes. In particular, at the low wave number side three overlapped vibrational modes at 3,743, 3,676 and 3,635 $cm^{-1}$ are appeared. According to literature data this bands are assigned as: free single silanol groups; pairs of silanols mutually hydrogen bonded where only one oxygen is participating in the hydrogen bonding and the same pairs of silanols where hydrogen atoms form H-bonds with an oxygen atom of an adjacent silanol respectively. These bands appear only after calcination at over 150°C.

Similar results can be obtained for samples synthesized using other surfacetant. After calcination at 350°C, the templating agents were removed (the block copolymer bands disappeared) whilst the –OH concentration increased in intensity in comparison with the non-mesoporous silica film (broad band in the 3,750–2,800 $cm^{-1}$ range). For a film synthesized with CTAB and 18-Crown-6 as templating agent the surfactant (bands at 2,950 and 2,860 $cm^{-1}$ was removed upon thermal calcination between 500°C and 550°C. FTIR study of short-range and local order in silica films was used for the crystallization analysis of the structure in situ. Correlation was found between shift maximum of Si-O-Si bands and the crystallization of the $SiO_2$ film structure. The finished spectra show that film is considered as a mixture of four- and six-fold rings of $SiO_4$ tetrahedra.

The Elipsometric Porosimetry investigations data are presented in Figure 1 by isotherms of water-adsorption-desorption for all prepared films. These isotherms are reported in terms of volume percent of water adsorbed at relative pressure of water applied at the film atmosphere. The first information is the porosity of each film that corresponds to the maximal volume of water adsorbed at high pressure. The maximal porosity is measured to be 47% at room temperature for calcined films. The second part of very useful information is a possibility to extract from isotherms the type of pore distribution and inter-connection between them. All plotted isotherms show stiff adsorption and desorption sloops at different relative pressures.

They revealed that pores do grow in diameter 2.5–4 nm for STAB and from 5–7 nm for Pluronic 127 surfactant. In case of titanium oxide film we observes the pore do grow from 4 up to 100 nm in case of 18-Crown-6 as template.

Surface topographies of $SiO_2$ and $TiO_2$ mesoporous film have been revealed by AFM. Figure 2 compares the AFM images of typical mesoporous titania films obtained using of different template. Indeed a more regular topography is observed for the Pluronic-127 template derived films. Figure 2 shows that the

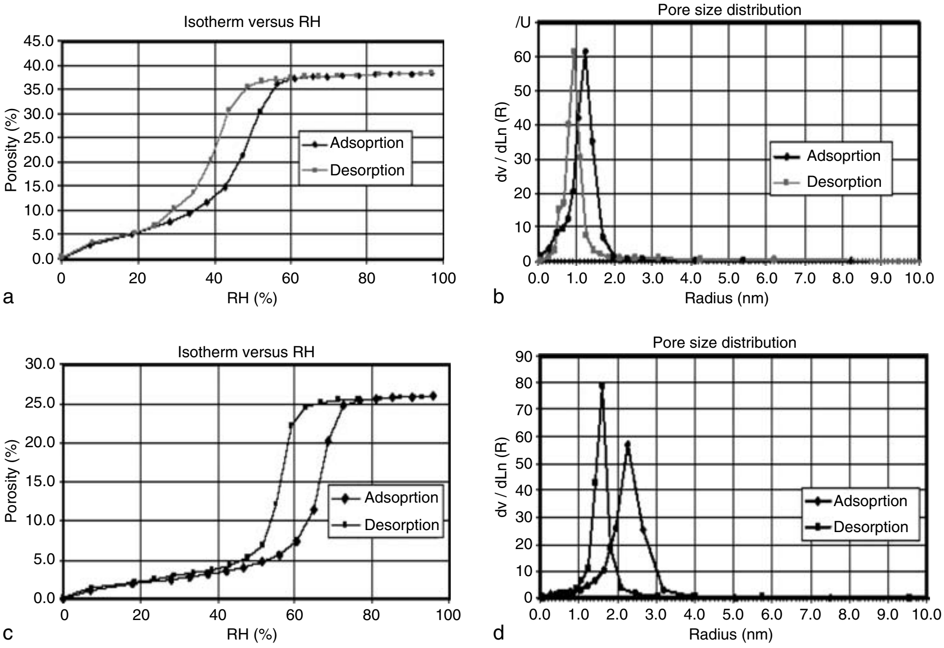

*Figure 1.* Adsorption-desorption isotherms (a, c) and pore size distribution from branches of isotherms (c, d) plotted for silica films templated by STAB (a, b) and triblock sopolimer (c, d).

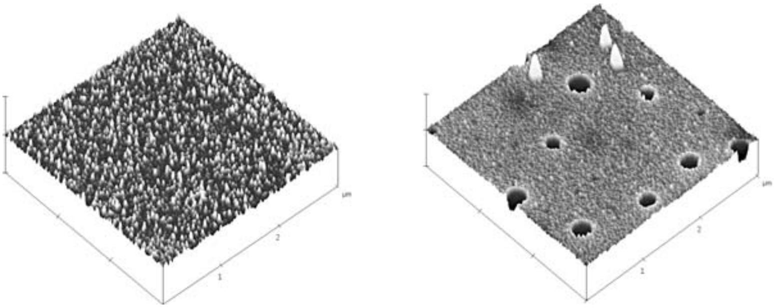

*Figure 2*. AFM image of calcined TiO2 films template by triblock copolimer (a) and 18-Crown-6 (b).

surface morphology of the 18-Crown-6 template film is rougher than that of the triblock copolymer films. The high roughness structure observed by AFM for 18-Crown-6 template attributed to the another mechanism of crystallisation of films when 18-Crown-6 template used. The STAB films presented morphologies with a surface roughness between 0.5 and 0.6 nm, Pluronic are 2–3 nm and for 18-Crown-6 up to 40 nm with quasi regular pores approximately 100 nm.

## 4. Conclusions

Macrostructure silica and titania films have been prepared by sol-gel method using different surfactants as template by a spin-coating method. We describe the preparation and compositional analysis of thin film coatings prepared using sol-gel techniques (thickness 50–500 nm, roughness ±0.5 nm with pore distribution 2.4–8 nm for silica oxide and up to 300 nm for titanium oxide and porosity 30–50%). Furthermore, the morphology and microstructure is strongly affected by organic template. Finally we have evaluated their possible applications as matrix for various nanostructures (semiconductor, dyes, and polymer) nanocasting such as sensing membranes for chemical sensor devices.

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