

Report on the experiment HE-2077 ‘Grazing incidence Small Angle X-ray Scattering study of the mesostructure formation in dip-coated silica and hybrid films’

Introduction

The interest in ordered mesoporous films is justified by their potential use as functional materials in advanced applications, for example in microelectronics and optics, due to their interesting properties such as high surface area, well-ordered and well-defined porosity and possibility of grafting functional moieties. These films are obtained by dip-coating of a precursor solution containing an alkoxyde or a metal salt as the inorganic precursor and a block copolymer as the structure-directing agent. The copolymer self-assembles into an ordered periodic structure, which constitutes a supramolecular scaffold for inorganic polycondensation. The organic ordered mesophase is then removed by thermal decomposition and leaves an ordered array of well-defined pores.

In the last 15 years research work has allowed to unveil the formation mechanism of mesoporous films and the main parameters which influence the final structure of the film. At present it is possible to synthesize mesoporous films with an accurate control on the physical (pore dimension, symmetry of mesophase, crystallization of inorganic walls) and chemical (composition, presence of chemical functionalities) properties. This is especially true for silica and transition metal oxide films.¹

Transition metal oxide (TMO) and mixed-TMO mesoporous films are of particular interest due to their electronic, optical and magnetic properties. In particular, in mixed-TMO systems the final chemical composition is easily adjustable by selecting the quantity and type of inorganic precursors in the dip-coating solution. The inorganic framework of the as-deposited films is amorphous and must undergo a suitable thermal treatment in order to form a crystalline phase. This is a critical step because the structural rearrangements associated with phase transitions may disrupt the ordered porous architecture and cause the collapse of the mesostructure. Therefore, it is important to study carefully the formation of the mesostructure in the as-deposited films and track its evolution with the thermal treatment.²

The presence of an ordered porous structure that can be tailored by the control of the synthesis parameters suggests the employment of mesoporous films as nanoreactors for the controlled synthesis of nanostructured materials. Basically, the mesopores can be filled with suitable liquid or gaseous precursors which subsequently form nucleation seeds, for example by precipitation or oxidation reactions. The growth of the solid phase is controlled by the chemical and the physical properties of the mesostructure (pore size, hydrophobicity, etc.). With spherical mesopores of the order of few nm, one can obtain quantum dots or metal nanoparticles with controlled size and composition.³

The main structural characterization in mesoporous films is generally performed with Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). In situ studies are carried out by SAXS analysis using synchrotron light, as the monochromaticity, high brilliance and high coherence of synchrotron radiation allow for a time-resolved study of the structural evolution of the mesophase. Therefore, SAXS with synchrotron radiation has become the principal tool for the study of ordered mesoporous films, especially if coupled with analytical techniques providing complementary information such as TEM, and aided by computer simulations.⁴ Our research group has contributed to the development of SAXS as a characterization tool for mesoporous films.^{5, 6} Recently, the combination of SAXS with FTIR performed in situ enabled us to time-resolve some important chemical aspects associated with mesostructure formation.⁷

Experimental and preliminary results

Mesoporous mixed oxides

We have synthesized two-oxide mesoporous films based on silica-germania, titania-ceria and hafnia-ceria, with different compositions. The precursor solutions contained anhydrous metal chlorides as the inorganic precursors and a triblock copolymer, Pluronic F127 [poly(ethylene oxide)₁₀₆-poly(propylene oxide)₇₀-poly(ethylene oxide)₁₀₆], as the templating agent. The molar ratio of the two metals was varied between 0:1 to 1:0 with steps of 0.1 for each of the three systems. The films were dip-coated on (100) Si substrates at the extraction speed of 14 cm/min. Therefore we prepared a total of 30 samples (that is, SiO₂-GeO₂, TiO₂-CeO₂, HfO₂-CeO₂, each repeated for 10 inorganic molar ratios). The films have been thermally treated at 100°C for 2 hours. This mild thermal treatment does not remove the organic template and does not induce inorganic crystallization, while it promotes inorganic polycondensation so that undesired changes in the order of the mesostructure that could be induced by external conditions (such as change in RH) are inhibited.

The films were characterized by grazing incidence SAXS (GISAXS). The sample, in air, was rotated so that the angle of incidence was slightly higher than the critical angle ($\approx 0.22^\circ$). The incident wavelength was set to 0.154 nm, corresponding to an energy of 8 keV. Diffraction patterns were acquired using a two-dimensional CCD detector. For each sample, different patterns were collected varying the incident angle. This was done in order to identify dynamical effects due to multiple interactions of the incident radiation with the sample: refractions in the film and reflections at the film-substrate and film-air interface.⁴ We also acquired a diffraction pattern of a silver behenate reference standard in order to perform quantitative measurements (identification of group symmetry of the mesostructure and calculation of its cell parameters).

Each film was then thermally treated in the preparation lab in order to study the influence of the temperature on the order of the mesostructure. The temperatures chosen were 250, 350, 450, 550°C. Therefore, GISAXS patterns were acquired for each film at temperatures up to 550°C. We observed at least two effects. (1) Even at 550°C there is a clear diffraction pattern suggesting that the mesostructure is not disrupted by the thermal treatment. This is a very important result because we can conclude that the films synthesized meet the essential requirement that the mesostructure be stable at high temperatures without being disrupted by the inorganic crystallization.¹ (2) The d-spacings associated to the crystallographic planes parallel to the substrate decrease markedly: this is consistent with a uniaxial thermal shrinkage, which is common to all mesoporous films. The mesostructure seems to be consisted with a tetragonal symmetry, *I4/mmm* in the space group, which was previously observed in hybrid silica films.⁵

Growth of Au nanoparticles

Mesoporous hafnia films treated at 350°C were chosen to be used as templates for the growth of Au nanoparticles. Hafnia was chosen because it has a well-ordered mesostructure.⁸ The films were treated in three impregnation steps by an electroless deposition procedure, reported in detail elsewhere⁹: (1) impregnation with a solution containing Sn²⁺ ions, which are adsorbed on the pore surface; (2) activation with Ag⁺ ions; (3) ion exchange with Au ions, which are then reduced to metallic gold by formaldehyde. We could obtain a controlled and reproducible growth of Au nanoparticles, as confirmed visually by the bright purple coloration of the films within one minute from the beginning of the third impregnation step, and by UV-Vis spectra on the final products, which confirm the presence of the gold resonance plasmon at 520 nm. The dimension of the gold aggregates depend critically on the time of impregnation in the third step: when the reaction is not

¹ At the time of writing no XRD characterization has been carried out yet. However, we can reasonably postulate the presence of a crystalline inorganic phase, at least for T=450°C and T=550°C, as the typical crystallization temperatures for titania and hafnia are around 400°C.

stopped before a critical time, further uncontrolled growth of Au takes place and a layer of bulk gold forms on top of the film.

We have acquired GISAXS patterns of hafnia films which were treated at different times in the third impregnation step. This sequence of GISAXS patterns gives information about the structural evolution of the mesostructure during the nucleation and growth of Au nanoparticles. After 10 seconds of impregnation, the GISAXS pattern doesn't differ from the pattern of a reference (non-treated) sample. The patterns taken at 20 and 30 seconds show less intense spot and the disappearance of the signal associated with the mesostructure. Data acquired at times greater than 30 seconds are somewhat similar to that taken at 10 seconds, which indicates the absence of further relevant structural modification of the mesostructure. This results suggests that, while for short impregnation time the Au clusters fill the pores preserving the ordered structure of the matrix, at the end of the process the Au nanoparticles (at least) partially destroy the mesostructure. Further investigation are needed to estimate the Au cluster size and the degree of self-assembly. We have also made a test to evidence if in our samples the anomalous scattering from Au nanoclusters is strong enough to give information on the degree of order of the Au clusters with respect to that one of the mesoporous matrix: for one of our best ordered Au-doped system, different GISAXS patterns were recorded at fixed incidence angle and by varying the incoming beam energy (5eV step) in the Au L₃ region, whose edge energy is 11919 eV; the incoming x-ray flux was also measured to provide a correct signal normalization. The quantitative analysis is still in progress.

Conclusions and perspectives

We were able to synthesize mesoporous films based on three binary (AB) oxide systems, that is SiO₂-GeO₂, TiO₂-CeO₂, HfO₂-CeO₂, with the presence of an ordered porosity starting from A:B=1:0 up to A:B=0.5:0.5 molar ratios. The mesostructure is stable up to the temperature of (at least) 550°C, with a thermal shrinkage in the direction perpendicular to the substrate. Further studies on these samples include XRD in order to determine the crystallization of the oxides and TEM as information supporting the identification of the symmetry group and the calculation of the lattice constants using GISAXS.

GISAXS patterns of Au nanoparticles grown in hafnia mesoporous films confirm that we could successfully obtain the growth of matter inside the mesopores without causing the complete disruption of the mesostructure. Besides, this gives information on the time scale of the process. The anomalous scattering analysis will help in quantify the degree of order of the Au clusters with respect to that one of the mesoporous matrix

Further studies include XRD and TEM in order to estimate the dimension of the Au aggregates in the mesopores.

References

1. Grosso, D.; Cagnol, F.; J. de A A Soler-Illia, G.; Crepaldi, E. L.; Amenitsch, H.; Brunet-Bruneau, A.; Bourgeois, A.; Sanchez, C., Fundamentals of mesostructuring through evaporation-induced self-assembly. *Adv. Funct. Mater.* **2004**, 14, 309-322.
2. Crepaldi, E. L.; J. de A A Soler-Illia, G.; Grosso, D.; Cagnol, F.; Ribot, F.; Sanchez, C., Controlled formation of highly organized mesoporous titania thin films: from mesostructured hybrids to mesoporous anatase TiO₂. *J. Am. Chem. Soc.* **2003**, 125, 9770-9786.
3. Della Savia, V.; Marchi, M. C.; Otal, E. H.; Bozzano, B.; J. de A A Soler-Illia, G., Tuned photoluminescence emission of CdS dots embedded in mesoporous silica, EMRS Spring Meeting. **2005**.
4. Tate, M. P.; Urade, C. N.; Kowalski, J. D.; Wei, T.-C.; Hamilton, B. D.; Eggiman, B. W.; Hillhouse, H. W., Simulation and interpretation of 2D diffraction patterns from self-assembled

nanostructured films at arbitrary angles of incidence: From grazing incidence (above the critical angle) to transmission perpendicular to the substrate. *J. Phys. Chem. B* **2006**, 110, 9882-9892.

5. Falcaro, P.; Costacurta, S.; Mattei, G.; Amenitsch, H.; Marcelli, A.; Cestelli Guidi, M.; Piccinini, M.; Nucara, A.; Malfatti, L.; Kidchob, T.; Innocenzi, P., Highly ordered "defect-free" self-assembled hybrid films with a tetragonal mesostructure. *J. Am. Chem. Soc.* **2005**, 127, 3838-3846.

6. Innocenzi, P.; Malfatti, L.; Kidchob, T.; Falcaro, P.; Costacurta, S.; Guglielmi, M.; Mattei, G.; Bello, V.; Amenitsch, H., Thermal-induced phase transitions in self-assembled mesostructured films studied by small-angle X-ray scattering. *J. Synchrotron Rad.* **2005**, 12, 734-738.

7. Innocenzi, P.; Malfatti, L.; Kidchob, T.; Falcaro, P.; Costacurta, S.; Piccinini, M.; Marcelli, A.; Morini, P.; Sali, D.; Amenitsch, H., Simultaneous in-situ and time resolved infrared and small angle X-ray scattering analysis, submitted.

8. Malfatti, L.; Kidchob, T.; Costacurta, S.; Falcaro, P.; Schiavuta, P.; Amenitsch, H.; Innocenzi, P., Highly ordered self-assembled mesostructured hafnia thin films: An example of rewritable mesostructure. *Chem. Mater.* **2006**, Published on web 08/24/2006.

9. Menon, V. P.; Martin, C. R., Fabrication and evaluation of nanoelectrode ensembles. *Anal. Chem.* **1995**, 67, 1920-1928.