

Highly Ordered Self-Assembled Mesostructured Hafnia Thin Films: An Example of Rewritable Mesostructure

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Self-assembly of supramolecular templates is a fascinating route that mimics natural processes to obtain porous organized materials. We have synthesized hafnia mesostructured films with a high degree of order, and the structure has been indexed as rhombohedral ($R\bar{3}m$ space group). The films have been revealed to be particularly interesting in their tunable state, immediately after solvent evaporation. We were able to modulate self-assembly under different conditions by changing the relative humidity in the deposition room and the intensity of the incident X-ray on the as-deposited film. The material has been shown to respond quickly and reversibly to changes in humidity in the deposition room, and the highly tunable state of hafnia films, before drying, has been used to “write” the structure through a high flux X-ray beam. The X-ray controlled reorganization path differs from those that have been traditionally observed because self-assembly can be achieved even in the absence of evaporation. Self-ordering, in this case, can be explained as an entropy-driven process, a general principle that is typical of biological systems.

Introduction

Mesostructured materials, prepared via self-assembly of supramolecular templates, are an important topic of nanoscience that has experienced a growing interest within the scientific community.¹ The formation of organized porous structures that maintain the shape and dimensions of the supramolecular templates has been revealed to be a very complex phenomenon. A combination of sol–gel and colloidal chemistry is used for self-assembly, which is a result of the cooperation between several factors during organization. The main phenomenology of the process seems, at present, quite well-understood, and the term “evaporation induced self-assembly” has been used to describe the synthesis of organized porous materials by supramolecular templates and sol–gel chemistry.² However, how organic micelles can organize themselves into a periodical array and why some ordered structures are obtained in preference of others are still puzzling questions. Ordering in colloidal and in biological systems is a process that governs the formation of complex structures and has several examples in nature.³ This phenomenon is known by different names: depletion

interaction in physics and chemistry⁴ and macromolecular crowding in biology.⁵ Self-assembly of block copolymers into supramolecular structures, such as spherical, lamellar, or cylindrical micelles, is observed when the polymers are mixed with a liquid that is a good solvent for one of its constituent blocks but not for the others.^{6–9} Under certain conditions this disordered ensemble of supramolecular structures may reach a higher degree of order by self-assembling into an ordered array. In an even more general scale, disorder–order transitions are reported for systems that can be modeled into a variety of hard and soft spheres (but even in mixtures of colloidal rodlike and spherelike particles) if enclosed in a low-dimensionality environment.¹⁰ In mesostructured materials the complexity of self-assembly is increased by the presence of “nanobricks” that condense on the micelle surface to form a solid network. Self-organization of the micelles can be achieved under these conditions only if the condensation rate of the building units (inorganic or hybrid organic–inorganic) is much slower than the kinetics of micelle formation and ordering.¹¹ To date, the strong

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tendency for condensation of non-siliceous systems has been considered as the main obstacle to obtain highly ordered self-assembled mesostructured thin films.¹² The high reactivity of transition metal oxide precursors toward hydrolysis and condensation increases the extent of uncontrolled phase separation between organic and inorganic components.¹² Livage et al. first demonstrated that in sol-gel systems the tendency for condensation is a function of the atomic number of elements with the same valence, for instance, silica < titania < zirconia < hafnia.¹³ In a recent paper by Brezesinski et al., the high reactivity of hafnia has been identified as the cause of the lack in mesostructural order.¹⁴ However, we have synthesized self-assembled HfO₂¹⁵ films showing an unexpected high degree of order. The material has been revealed to be particularly interesting in its tunable state,¹⁶ immediately after the solvent evaporation following dip-coating: we have modulated hafnia self-assembly by changing the relative humidity (RH) in the deposition room and the exposure time of the incident X-ray on the material by small-angle X-ray scattering (SAXS). The control of the mesophase organization, achieved by means of humidity changes, has been already well-described in several systems,¹⁷ and it is now an established part of the self-assembly theory. However, the possibility to use alternative sources, such as X-ray radiation, to drive some controlled changes into the film structure during the tunable state is an important new property for mesoporous films. On the grounds of the in situ experiments we propose a thermodynamic model, based on *entropy driven self-assembly*, to explain ordering and phase modulation of mesoporous films in their tunable state. These two in situ experiments on hafnia films also open new windows on the future exploitation of mesoporous materials.

Experimental Section

Film Synthesis. Pluronic F127, OH(CH₂-CH₂O)₁₀₆-(CH₂CH₂O)₇₀(CH₂CH₂O)₁₀₆H, hafnium tetrachloride (HfCl₄), and ethanol (EtOH) were purchased from Aldrich and used as received. The HfO₂ precursor sol was prepared by slow addition of HfCl₄ to an ethanol-surfactant mixture; water was then added to this sol under stirring. The molar ratios were HfCl₄/EtOH/Pluronic F127/H₂O = 1:40:0.005:20. The substrates, previously cleaned with hydrofluoric acid, water, EtOH, and acetone, were dip-coated in the fresh solution. The films were prepared by dip-coating using an electronically controlled homemade dip-coater that is able to minimize the vibrations during the preparation process. The deposition was performed in a specific chamber designed for in situ SAXS measurements with the possibility to control the RH.

The films were deposited at the withdrawal rate of 150 mm·min⁻¹ and at a temperature of 25 °C.

SAXS. The mesostructure of the films was investigated using the SAXS¹⁸⁻²¹ apparatus at the Austrian high-flux beamline of the electron storage ring ELETTRA (Trieste, Italy).²² The energy of the X-ray radiation was set at 8 keV (wavelength 1.54 Å). The instrumental glancing angle between the incident radiation and the sample was set to either 90° (transmission mode) or <3° (grazing incidence mode). With a two-dimensional charge-coupled device (CCD) detector (1024 × 1024 pixels, Photonic Science) the *out-of-plane* diffraction maxima (in transmission mode) and the *in-plane* diffraction maxima (in grazing incidence mode) were acquired. The software used for data processing was FIT2D.²³ The distance between the sample and the detector was calculated using the diffraction pattern of a salt having a known lattice constant (silver behenate, H(CH₂)₂₁COOAg). The beam center position was set as the center of the circle calculated with the least-squares fit of 40 coordinates, corresponding to 40 positions in the silver behenate powder diffraction ring. To identify the peaks, a radial integration of the intensity of each recorded image was performed, starting from the beam center (000). Typically, the whole image was masked leaving out the peak of interest, and successive intensity integrations were made. This procedure minimized peak position errors caused by the overlap of information in diffraction patterns. Knowing the distance between the sample and the detector, it was possible to calculate 2θ and *d*_{hkl} for each spot and the lattice constants of the observed mesophase. The calculation of the cell parameters was performed using an algorithm implemented in Mathematica 5.1, which minimizes an error function calculated using the experimental and the calculated *d* spacing values for each spot. An error function *s*(*a*,*α*) is defined for each spot, as the difference between the measured and the calculated *d* spacing values ("single error function"). This is a function of two variables, *a* and *α*, which are the parameters of the rhombohedral unit cell. The error functions are averaged, calculating the norm as *f*(*a*,*α*) = [∑*s*(*a*,*α*)²]^{1/2}. This "total error function" *f*(*a*,*α*) has a minimum because it is coercive and continuous; therefore, the minimum point can be found by setting the partial derivatives ∂*f*/∂*a* and ∂*f*/∂*α* equal to zero. The corresponding values (*a*,*α*) for which ∂*f*/∂*a* = ∂*f*/∂*α* = 0 are the calculated cell parameters.

In situ SAXS measurements in transmission mode were performed during dip-coating using a thin silicon substrate (20 μm, double side polished, Virginia Semiconductors). Multiple images were recorded every second, with an exposure time of 1 s (no delay between acquisitions). Grazing incidence measures (GI-SAXS) were conducted on films deposited on the (100) surface of thick silicon wafers (440 μm, p-type boron doped, one side polished, Jocom). For an optimal determination of the mesophase, SAXS and GI-SAXS single images were obtained, taking for each image the average of 20 single acquisitions with 2 s exposure time.

Atomic Force Microscopy (AFM). The surface morphology of irradiated and stabilized samples (40 min at 60 °C) has been investigated by means of an atomic force microscope (NT-MDT

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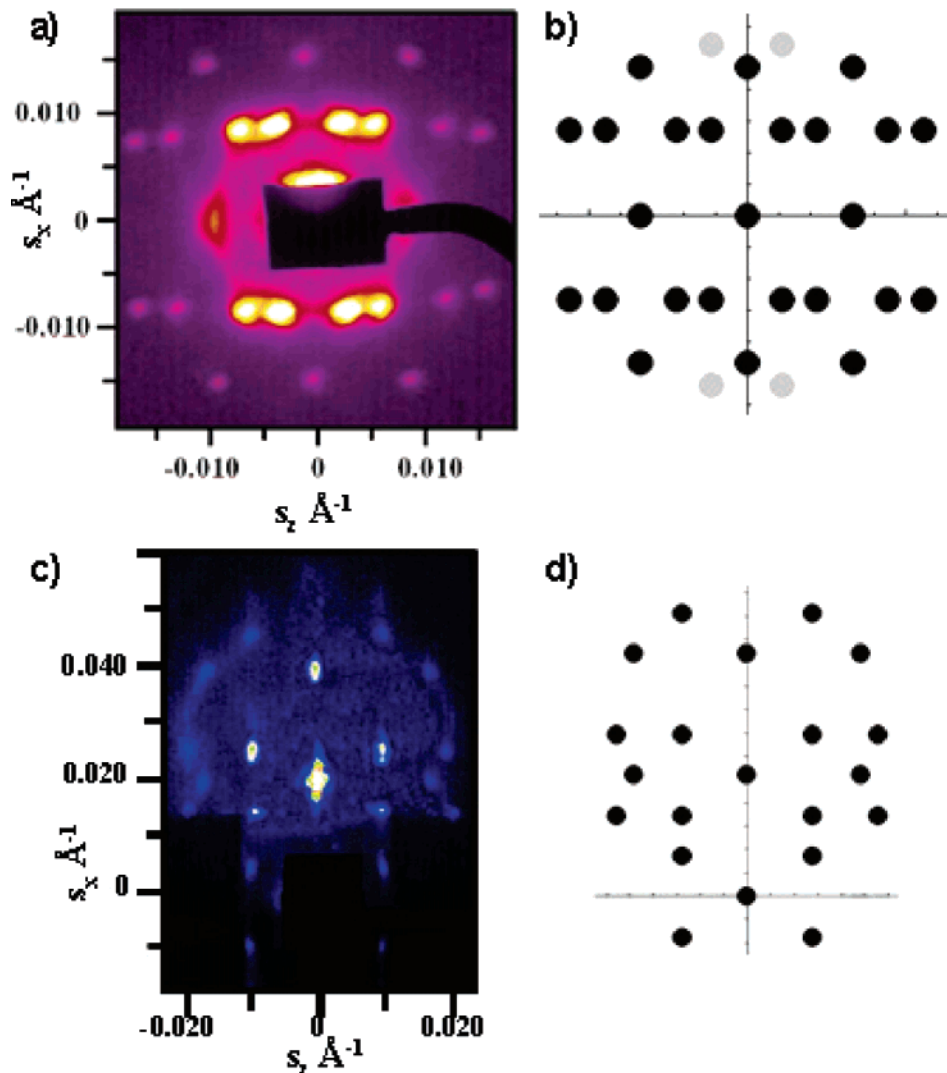


Figure 1. Transmission mode SAXS pattern of an as-deposited hafnia film (a) and results of a Nanocell simulation using a $R\bar{3}m$ rhombohedral unit cell (b); the gray spots are barely visible on the SAXS measurement (a). Grazing incidence SAXS pattern of a hafnia film treated at 150 °C (c) and its Nanocell simulation for the same unit cell.

Ntegra) in contact mode. The typical curvature radius of the tip used is 10 nm, and the elastic constant of the cantilever was 0.2 N·m⁻¹. We have acquired both large area (50 μm × 50 μm) and small area (1 μm × 1 μm) scans to verify the roughness on different length scales.

Results and Discussion

Determination of the Hafnia Mesoporous Structure. The transmission mode SAXS diffraction pattern of an as-deposited mesoporous hafnia film is shown in Figure 1a. Several spots, up to the third order, are observed: this is evidence for a highly ordered mesophase. In particular, it is important to stress that the spots belonging to the second and third order appear separated, and no ring is observed. To our knowledge, this is the first time that such a high order of diffraction spots is clearly detected in transition metal oxide mesoporous films. The presence of clear spots and no ring in transmission configuration denotes a periodic arrangement of pores not only *in-plane*, as it is usually the case in mesoporous films,²⁴ but also *out-of-plane* like a three-dimensional quasi-crystal structure.^{25,26} To identify the symmetry of this phase, we have performed structure simulations

using the Nanocell code developed by the Hillhouse research group.^{27,28} On the grounds of these simulations, we observed that at least two space groups are compatible with the pattern shown in Figure 1a, that is, $Fm\bar{3}m$ and $R\bar{3}m$ oriented with the [111] direction perpendicular to the substrate.

The GI-SAXS pattern of a sample treated at 150 °C for 15 min is presented in Figure 1c: the two-dimensional pattern shows enough spots to allow an accurate determination of the mesophase symmetry and the calculation of the cell parameters. Simulations show that the best fit of the GI-SAXS pattern corresponds to a rhombohedral symmetry,

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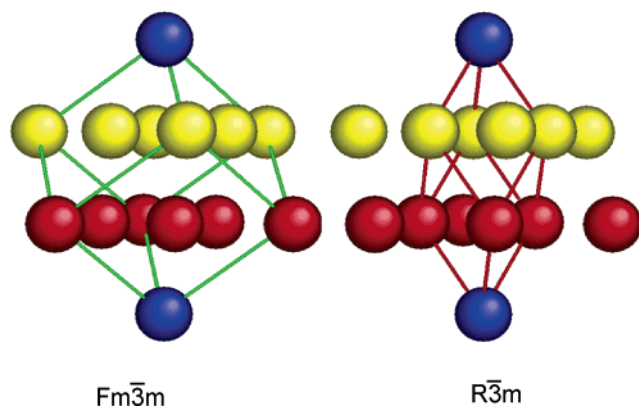


Figure 2. Schematic drawing showing the equivalence between a face-centered cubic cell ($Fm\bar{3}m$) and a rhombohedral ($R\bar{3}m$) unit cell.

space group $R\bar{3}m$, where the unit cell is [111] oriented (Figure 2). Because only the rhombohedral space group can retain its characteristic operation symmetries after the uniaxial shrinkage caused by thermal treatment,²⁹ we conclude that the mesostructure can be unambiguously attributed to a rhombohedral cell. As a matter of fact, the nonprimitive face-centered cubic cell contains a primitive rhombohedral cell having an angle $\alpha = 60^\circ$,³⁰ and this is why the structure we observe in the as-deposited film can be assigned either to a rhombohedral or to a slightly distorted face-centered cubic cell, both of them having direction [111] normal to the substrate.²⁹ The observed symmetry of the as-deposited film is justified if we admit a thermodynamic driving force by which the micelles stack with a close-packed structure: spheres of equal size occupy the maximum amount of space when they are in a face-centered cubic cell arrangement with a packing factor $f = 0.74$. The cell parameters for the as-deposited film are $a = 20.8 \pm 2.0$ nm and $\alpha = 62.0 \pm 6.2^\circ$. The constants for the film treated at 150 °C are $a = 14.3 \pm 1.4$ nm and $\alpha = 83.2 \pm 8.3^\circ$. This confirms that a uniaxial shrinkage occurs during annealing along the [111] direction, which does not reduce the symmetry operations of this type of structure. Considering the reported error bar, the angle $\alpha = 62^\circ$ calculated for the rhombohedral cell of the as-deposited film is close to that of the undistorted $Fm\bar{3}m$ cell, $\alpha = 60^\circ$. This suggests that the rhombohedral structure of the as-deposited film originates from an $Fm\bar{3}m$ cell that slightly shrinks along [111] during the drying process in the first seconds after deposition.

SAXS analysis performed in samples after thermal treatments at temperatures from 50 up to 550 °C showed (not reported in figures) that the films maintained organization until 450 °C, even if it was with some order loss. The films did not show any crack after the thermal treatments, and the thickness was around 250 nm, measured by spectroscopic ellipsometry. Fourier transform infrared (FTIR) analysis performed on the films (see Supporting Information) showed also that at 150 °C extended formation of Hf–OH is observed and that at 450 °C the film is fully condensed. The surfactant was removed after thermal treatment at 250 °C.

Disorder-to-Order Transition Induced by Humidity Changes. Mesostructured hafnium oxide films have been revealed to be particularly interesting in their tunable phase. The tunable steady state is a typical feature in mesostructured films:¹⁶ it can be described as a physical state of the film where the viscosity of the film still allows a rearrangement of micelles and takes place immediately after the solvent evaporation that follows the dip-coating, until the viscosity becomes too great to allow further rearrangements of the mesophase. The material has been shown to respond quickly and reversibly to changes in humidity in the deposition room when the film was in its tunable state: an increase in humidity, that is, in the amount of water absorbed by the film, causes the structure to organize into an ordered mesophase. In situ SAXS measurements performed during dip-coating have revealed that the mesostructure undergoes a disorder-to-order transition within a few minutes of deposition upon exposure to an external RH around 80%. Figure 3 shows the sequence of SAXS images taken in transmission mode at different stages of the process. Snapshot a shows a diffuse ring indicating poorly ordered monodisperse micelles. The increase in humidity in the deposition chamber (from 40% to 80% RH) produced a micelle swelling, as shown by the decrease in the diffraction ring diameter, due to water absorption in the hydrophilic crown of the block copolymer (snapshot b). After a few minutes the appearance of defined diffraction spots indicates a highly organized self-assembled mesophase (c and d). In these conditions it was possible to obtain various reversible disorder–order and order–disorder transitions simply by varying the RH. The experimental results also show unambiguously that micelle swelling is directly linked with organization and rearrangement of the mesophase. The overall process is shown in Figure 4: the precursor solution is an isotropic sol whose concentration, c , is lower than the critical micelle concentration, cmc . With the beginning of solvent evaporation $c = cmc$, and micelles are formed. At this stage, when a weakly condensed film is formed, a disordered array of micelles can be self-ordered by increasing the external humidity. The water absorption by the micelles causes their swelling, and this effect pushes the system to reorganize (vide infra). This experiment shows that hafnia mesostructured films exhibit, after the deposition, a tunable state that can be “gently” driven toward order, because the flexibility of the oxide network still allows a rearrangement of the templating micelles when their dimensions are increased. At this stage the material is compliant enough, and reversibility of the disorder-to-order transition is still allowed.

X-ray Lithographic Writing. In principle, different external sources, other than water, should be able to influence the organization of the mesophase when the film is still in the tunable state. This state, considered as a “metastable phase”, can be used not only to modulate the order of the mesophase but also to “write” through external sources the film structure. Because in the tunable state of the film it is possible to modify the mesophase (for instance, changing the phase or disarraying the mesostructure), performing this operation locally is equivalent to storing information on the film (i.e., “write”). The reversibility of this transition should

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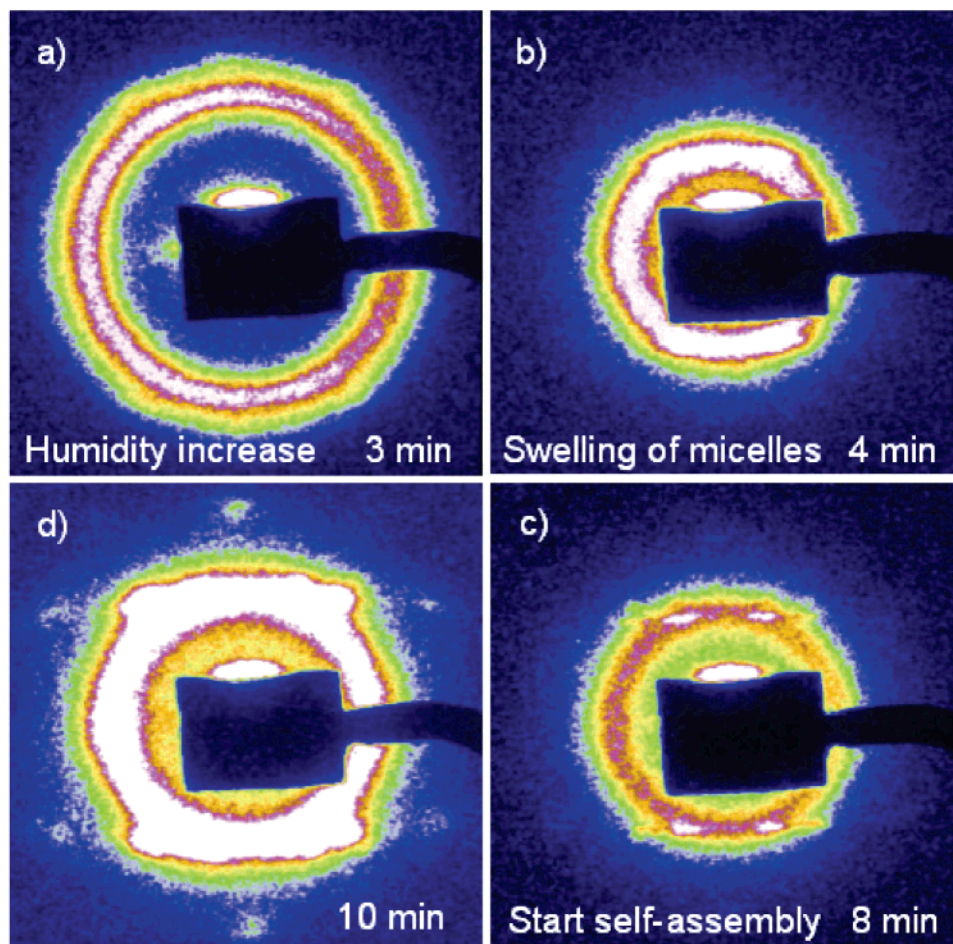


Figure 3. Self-assembly induced by water absorption and micelle swelling. The SAXS patterns are recorded at different times after dip-coating. The increase in humidity (a) causes a micelle swelling (b) that after 8 min (c) produces self-assembly of the HfO_2 films (d). The conditions of instrumental acquisition were maintained constant during self-assembly of the film. For this reason, in snapshot d the first order of the diffraction spots is totally saturated and appears as a bright ring.

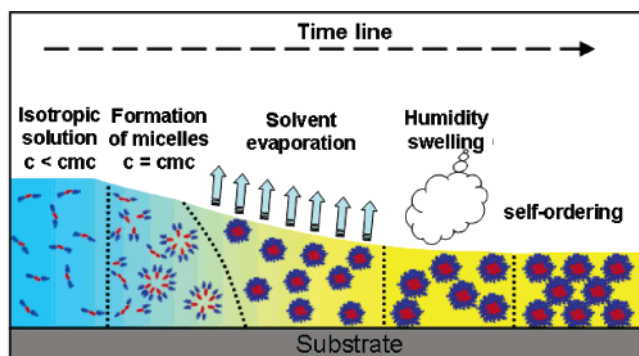


Figure 4. Schematic drawing of the self-assembly taking place during the experiments on a mesostructured hafnia film, which is caused by humidity swelling of the micelles.

ensure a number of write–erase cycles, until the condensation of the inorganic phase hinders the local structural change. We have performed five write–erase cycles within an interval of time of ~ 3 h. X-ray radiation was used as a lithographic pen to direct controlled changes into the film structure during the tunable state.^{24,31} At the radiation fluxes that are normally used for analytical purposes, no observations about damages or effects on the mesophase organization have been reported on siliceous and non-siliceous systems studied, to date. The results of the radiation effects on the

HfO_2 films are shown in Figure 5. In snapshot a, which corresponds to time $t = 0$ of radiation exposure, the transmission SAXS image shows that the film is highly organized in the rhombohedral mesophase; the diffraction spots show an intensity that decreases as a function of time (snapshot b, taken after 4 min) until they totally disappear after around 20 min of exposure to the radiation flux. During the whole experiment the film was maintained in stationary conditions in the deposition room with controlled and stable levels of humidity and at constant temperature. The observed disarray is, therefore, induced only by the incident radiation. A confirmation is obtained by moving the samples in different positions not previously affected by the incident radiation beam: here intense diffraction spots are detected in all the areas of the film, which confirms that the disassembly effect is induced only by the X-rays, locally. Thirty minutes after the radiation was turned off, during which the film is left in the deposition room at 80% RH (Figure 5, snapshot d), the appearance of new intense diffraction spots indicates the reorganization of the structure in the rhombohedral phase previously observed (Figure 1). Because the micelles can reorganize even after the beam irradiation, we conclude that the X-rays do not induce a massive condensa-

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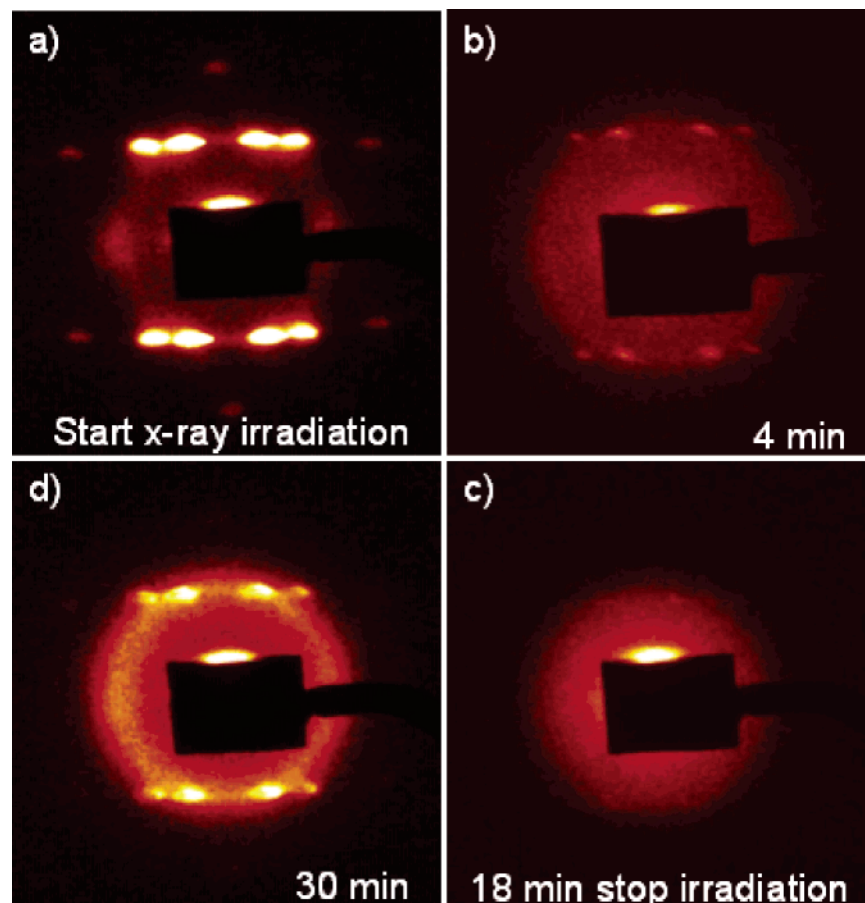


Figure 5. Organization disarray induced by intense X-ray radiation and disorder-to-order transition. In situ SAXS patterns recorded at different irradiation times. A high flux radiation causes on a highly organized film (a) the disarray of the rhombohedral mesophase (b). After 18 min of irradiation the organization is completely disrupted. Self-assembly is again observed after switching off the X-ray flux and maintaining the film in stationary conditions of humidity and temperature.

tion in the oxide backbone, and the film, even after the micellar organization is disarrayed, is still in a tunable state. To explain this behavior we suppose that the local increase of temperature³² induced by the incident X-ray beam decreases the micellization driving force. We suppose that the absorbed energy was released by thermal nonradiative pathways or by a photoelectric effect with consequent damage of the mesostructure. Because the critical micelle concentration, cmc, is a function of temperature, upon exposure to the X-ray the micelles will be, at least partially, disrupted, causing the observed loss of an organized mesophase within the film. At this stage, however, the film is still in its tunable state: after turning off the X-ray beam the sample cools, and the surfactant molecules can recombine into new micelles. It is important to point out that, after micelle formation, self-ordering is observed without solvent evaporation: the thermodynamics of the system plays the main role in mesostructure ordering process. To check if the radiation affects the surface roughness or the total thickness of the film, we have compared the morphology of both the irradiated and the nonirradiated areas, finding that the roughness increases after X-ray exposure (sampled on 10 different points on the surface). We associate such a difference with a loss of micelle organization, without, however, causing any

cracking or damage. The thickness is also not affected by the radiation: an AFM image has been taken close to the borderline between the irradiated and nonirradiated regions (Figure 6) showing no difference on the average height of the surface. These observations are very important for a practical development of lithographic techniques based on the present finding. When the X-ray beam is used as a lithographic pen, the self-induced order can be locally corrupted enabling information to be recorded in the film. A post-writing thermal processing can “freeze” the ordered–disordered regions in the material. The overall process is illustrated in Figure 7. We also plan in the future to perform similar experiments with different sources, such as high power laser radiation.

Entropy-Driven Ordering in Self-Assembly. We discuss here the experiments on the basis of a preliminary thermodynamic model. The experiments suggest, in fact, a possible thermodynamic interpretation of self-assembly in the final step of the process, as a self-ordering stage. Self-assembly in films is driven by solvent evaporation until the formation of the oxide network. The film, before full condensation, is in a temporal window which is defined as the intermediate stage or tunable state. At this stage, however, randomly distributed micelles (Figure 3c) can still be reorganized in an ordered disposition (Figure 3d) even in the absence of solvent evaporation, and the interpretation needs to be founded on

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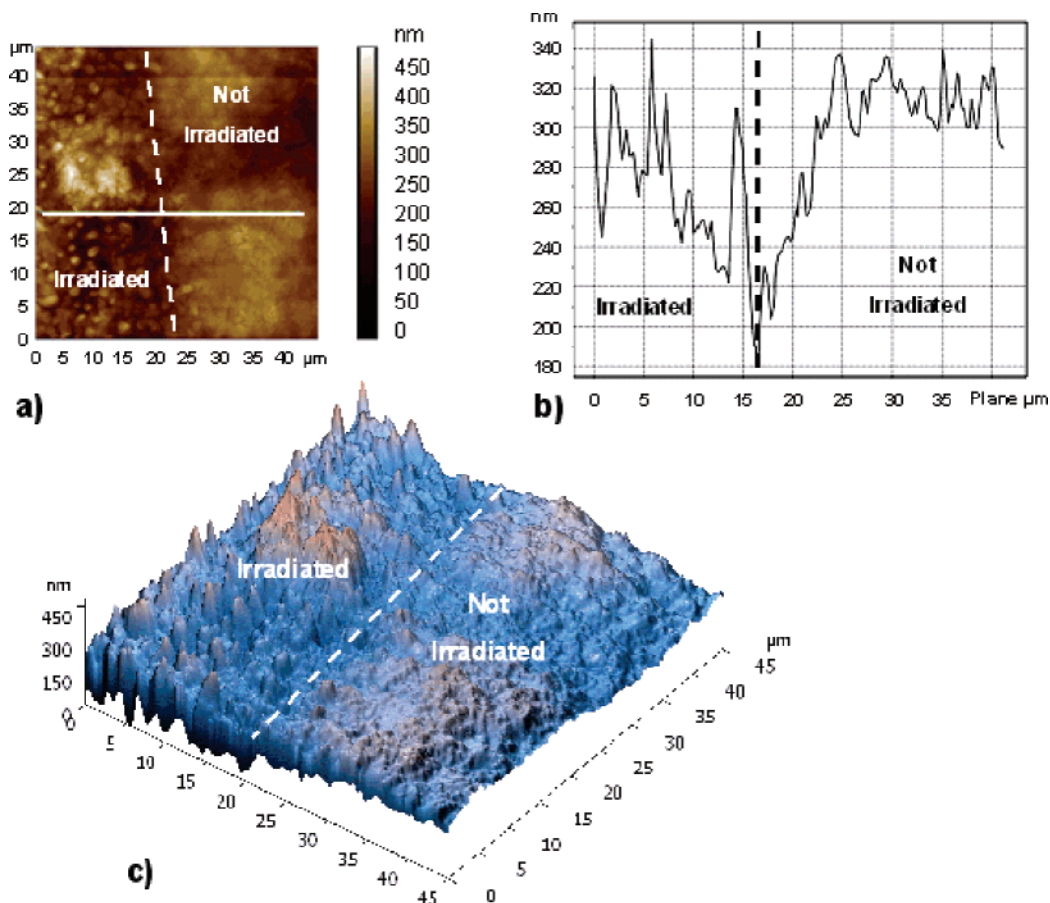


Figure 6. AFM image of a mesostructured hafnia film after X-ray exposure taken in contact mode on a stabilized film (40 min at 60 °C). Plane (a) and perspective (c) views of the boundary region between irradiated and nonirradiated areas. In part b, the depth profile of the hafnia film across the irradiation boundary is shown.

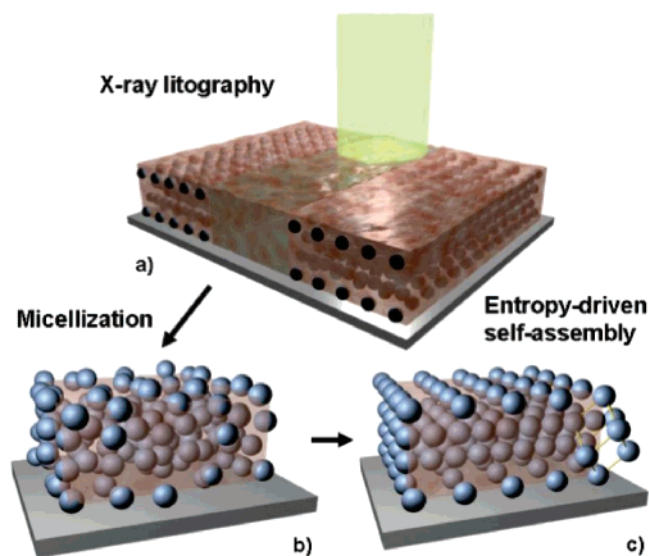


Figure 7. Representative picture of the reversible X-ray lithography process. After the disassembly induced by X-ray exposure (a), the entropic driving force pushes the system toward micellization (b) and self-ordering (c).

thermodynamic bases. If we model the micelles as spheres in which interpenetration is forbidden and the interaction energy is zero,³⁴ the enthalpy variation of the system during self-assembly can be neglected. This is a good assumption because the spheres are not in contact because of the presence of the inorganic walls.³⁵ It is important to stress that even if

enthalpy plays an important role during solvent evaporation, once the micelles and the solid inorganic network are formed, we assume that it does not have any other significant change. As a consequence, only the entropic term in $\Delta G = \Delta H - T\Delta S$ should be responsible for the decrease in ΔG that pushes the system to self-organization. The counter-intuitive idea that entropy is the source of order can, therefore, be used to explain the experimental findings in the tunable state of self-assembly. In fact, the loss in entropy with ordering is more than compensated for by the gain in entropy due to the increase in free volume³⁶ of the ordered films.^{37,38} In the first part of the experiment, swelling and increase in volume of the micelles by water absorption is an entropy-driven ordering process. The swelling of the micelles increases the volumetric fraction of the organic mesophase within the film, so that the micelles have lower translational entropy. In these conditions, the only way to maximize the entropy of the whole system is to increase the free volume by packing the micelles in an ordered structure. Organization is allowed with the only external condition that

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the oxide framework is compliant enough to allow micelle reorganization.

The organization achieved in the second part of the experiment when the micelles, after their disruption, self-order to maximize the entropy is also an entropy-driven process. This example is of particular importance because the self-ordering process is never pushed by solvent evaporation but only driven by the entropy of the system. Self-assembly in mesostructured films appears, therefore, as a highly tunable process: evaporation induced self-assembly drives the organization toward a first intermediate stage. The highly compliant nature of the porous network, which is only partially condensed, can still allow modulation of organization. A direct application of this phenomenon is the possibility to induce disordered regions into the mesostructured film with the aim, for example, to produce films with a very sharp gap in the refractive index. It is possible to perform several X-ray write–erase cycles as long as the viscosity of the film allows a certain mobility of the micelles. As a matter of fact, the entropy-driven self-assembly process is reversible and can, therefore, enable reversible writing on mesostructured films as long as they are in their metastable state. The patterned structure becomes permanent once the films are thermally stabilized.

Conclusions

Hafnia films with a highly ordered rhombohedral mesostructure can be synthesized despite the high reactivity of

the precursor that should reduce the possibility to achieve very ordered mesostructures. The hafnia films show, after deposition, a highly tunable state, and during this stage ordering can be controlled by different sources from the external environment. We used synchrotron X-rays and air humidity to control reversible disorder–order transitions in the mesophase. X-rays are also able to “write” the mesophase, and several write–erase cycles can be performed, which opens the route to a new lithographic process for mesostructured films. This process produces sharp interfaces between dense and porous organized regions of the films, with no differences in film thickness induced by X-ray lithography. Reorganization of mesostructured films represents a case of self-ordering without solvent evaporation, and in this case, self-assembly can be modeled as an entropy-driven process.

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Supporting Information Available: FTIR absorption spectra for films treated at different temperatures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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