



Ordered and disordered evolution of the pore mesostructure in hybrid silica anti-reflective films obtained by one-pot self-assembly method



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ABSTRACT

Hybrid mesoporous silica films were prepared in acid-catalysed medium using a one-pot self-assembly method. A gradual content of methyl groups was introduced into the inorganic framework by co-condensation of tetraethyl orthosilicate and methyltriethoxysilane. To better understand how the ordered and disordered transition occurs in mesoporous hybrid organosilica system as function of the MTES molar ratio in the starting solution, textural, chemical and optical properties of the films were studied by transmission electronic microscopy (TEM), grazing-incident small angle X-ray scattering (GISAXS), transmission Fourier transformed infrared (FTIR) and UV-visible spectroscopy. Increasing the loading of the incorporated organic groups (up to 40% in the starting solution) led simultaneously to a disorganization of the pore mesostructure and a reduction in the pore diameter. Concomitantly, a disordered domain of the silica rings in the walls was observed, which created bond strains in the silica wall contributing also to the disorganization of the pore mesostructure. Furthermore, an optimal MTES content was identified in order to obtain antireflection coatings, exhibiting low reflection in the visible range.

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1. Introduction

One-pot co-condensation of hybrid precursors in solution is a useful method to incorporate organic functional groups into a silica inorganic network, yielding specific pore surface properties such as hydrophobicity, optical, catalytic and electronic activities. Porous silica materials with well distributed mesophase can be obtained by the evaporation-induced self-assembly method (EISA) using a precursor solution containing a template [1,2]. Pyrolysis is usually used to destroy the template revealing a mesostructured void in the silica material. EISA have received great interest due to its simplicity to produce a wide range of mesoporous metal oxides [3,4]. Currently, this method also offers the best way to homogeneously disperse organic function within the silica oxide matrix or at its surface [5] and to control the stoichiometry of chemical pending groups [6]. Hybrid mesoporous material showed a wide range of potential applications in catalysis [7], sensing [8,9], energy [10] optics [11] etc. Mesostructured organosilica films obtained via the co-condensation of self-assembly hybrid precursors in solution of methyltriethoxysilane (MTES)-tetraethyl orthosilicate (TEOS) were

widely studied [12,13], mainly because of the relative stability of the methyl group during a calcination up to 400 °C [5].

Converting the inorganic framework to hybrid through the incorporation of an organic functional group can lower the dielectric constant of the film [14]. Although variable mesophases have been reported for hybrid systems [12,13,14], a systematic disordering of the mesostructure occurs when the molar ratio of the MTES in the starting solution increases. A threshold was often reported when pendant organic functionalities are incorporated and the ordering of the mesopore is generally completely lost above 20 mol% MTES in the starting solution [2]. Strong efforts have been made to produce highly ordered materials with the organic functionality required for device applications. The synthesis conditions were studied and designed to control the reactivity of the silica oligomer and to reduce the perturbation due to the modification of the surface energy at the organic-groups/template interface [12]. Electro-assisted deposition has been also applied as useful process to build hybrid system by co-condensation of alkoxysilane and organosilane [15]. Recently, electro-assisted method shows the ability to reach high functionalization level of (3-azidopropyl)trimethoxysilane up to 40 mol% of the starting solution [16].

While most of the research has been focused to make the mesostructure more stable, few studies were dedicated to better understand the disorganization of the mesostructure for such kind of hybrid systems. Several parameters are the potential causes of the loss of order. They are generally related to the synthesis conditions. Jung

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et al. [14] suggested that the disordering of the mesoporous organosilica films at high MTES/TEOS molar ratio is caused by a lengthy sol aging time. A longer organic side chain was also reported as detrimental to preserving the mesostructure [14].

In the present study, mesoporous methylated organosilicate thin films were synthesized by one-pot co-condensation of MTES and TEOS precursor with a rapid solvent evaporation *via* spin-coating. The films mesostructure as well as the hybrid wall chemical composition were investigated before and after calcination. The solvent evaporation and the kinetics of the condensation of the system which occurred simultaneously are discussed, in order to explain the disorganization mechanism of the mesostructure. Furthermore, optical properties of the films were evaluated by UV-visible spectroscopy as they are designed to be antireflective coating.

2. Experimental set up

Hybrid silica films were obtained by mixing TEOS with different proportions of MTES under acidic conditions. Sol synthesis and films elaboration were prepared by adapting the procedure described elsewhere [5]. Hybrid silica films were obtained using one-pot co-condensation of two precursors ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS, Aldrich and $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$, MTES, Aldrich) with different proportions in the presence of an adequate amount of water (Milli Q, 18 Ω), in ethanol (absolute grade). The pH was adjusted at <2 with hydrochloric acid (Aldrich, 37%). The molar ratio of MTES/(MTES + TEOS) was varied from 0 to 80 mol%. Final molar ratios after the template addition (triblock copolymer Pluronic P68; ~8.400; $\text{EO}_{80}\text{PO}_{30}\text{EO}_{80}$) were MTES/TEOS/ H_2O /EtOH/P68 = $x:y:10:20:0.01$. The coatings were obtained *via* spin-coating the so prepared hybrid solutions at 5000 rpm during 30 s on the substrates. The substrates were previously cleaned under sonication by detergent, acetone, ethanol and finally by MilliQ water (18 Ω). The films were submitted to a drying process during 6 h at 70 °C, and then the template was destroyed by heating the samples in air at 400 °C for 2 h using a heating ramp of 1 °C·min⁻¹.

3. Thin film characterization

Transmission electron microscopy (TEM) images were obtained with JEOL 2000FX instruments, working under an acceleration voltage of 200 kV. The samples were scratched off from the substrate and dispersed in ethanol. A droplet of the suspension was deposited on the copper grid and dried before analysis.

The mesostructure of the mesoporous hybrid silica films before and after calcination was carefully checked by small-angle X-ray scattering at grazing incidence of 0.2°. The GISAXS-Rigaku S-max 3000 facility was equipped with a microfocus source $\lambda = 0.154$ nm and a 2D Gabriel type detector. The distance between samples and the detector was fixed at 1494 mm. The transmitted and specular reflected beams were masked by a vertical beam-stop.

Fourier transform infrared (FTIR) spectra (200 scans were averaged with a resolution of 4 cm⁻¹) were recorded using Bruker EQUINOX 55 spectrometer in static air in the range of 4000 cm⁻¹ – 400 cm⁻¹. The spectra of the hybrid silica thin films were obtained by coating the KBr pellets by 0.1 ml of precursor solutions, which enables specific recording of the IR region meanwhile the soda lime slide was not transparent to it. Maintaining the same amount deposited in KBr pellets enables to have a quite-quantitative comparison of the infrared spectra. The spectrum of a non-coated KBr pellet was used as the background. Measurements were performed for the thermally-treated samples at different temperatures (70 °C in air for 6 h and 400 °C in air for 2 h) and following identical successive and variable condensation–consolidation temperatures as described above for the films.

Static water contact angles (θ) were measured at ambient temperature and humidity using the sessile drop method and image analysis of the drop profile. The instrument, consisting of a CCD

camera and an image analysis processor, was purchased from Electronisch Ontwerpbureau De Boer (The Netherlands). The water (Milli-Q, Millipore, Molsheim, France) droplet volume was 3 μl and the contact angle was measured 5 s after the drop deposit onto the sample. For each sample, the reported value consisted of the average of the results obtained using at least 5 droplets.

Transmittance measurements in the range of 300–800 nm were carried out using a UV-Visible spectrophotometer (Cary5E) at a normal angle of incidence.

The thickness of the film is measured using atmospheric ellipsometric porosimetry (A-EP) performed with equipment from Sopra (Model GES-5E, A-EP, Sopra, Paris, France) using the software package “WinElli2”. More details concerning the procedure used can be found elsewhere [9].

4. Results and discussion

4.1. TEM analysis

The ordered and disordered evolution of the mesostructured for hybrid silica films obtained by self-assembly method and after calcination at 400 °C was first analyzed as function of the molar ratio of MTES by TEM (Fig. 1). The mesoporous silica thin film prepared using solely TEOS precursor (Fig. 1.a) shows a well-organized and defect-free mesostructure. From the TEM images, it is challenging to unambiguously distinguish whether the bright circular features were attributable to cylindrical or spherical pores. In the image taken in plane view, the spheres appear overlapped such as forming cylinders. This confusion results from the observation angle, which was previously observed for Body-centered cubic mesostructure [17,18]. Thus, the identification of the mesophase structure is not straightforward. GI-SAXS technique was, therefore, effectively applied to achieve a better identification of the organized mesophases (see below). The hybrid silica film with a 10% of MTES molar ratio in the starting sol shows the same organization of the pore over a large area (Fig. 1.b). However, the periodicity of the mesopore was destroyed at MTES molar ratios higher than 10%. Wormlike structure appeared as a result of randomly distributed micelles for molar ratio of MTES ranging between 25% (Fig. 1.c) and 40% in starting sol (Fig. 1.d). Besides a disorganization of the mesostructure, an increase in loading of the incorporated organic groups leads to a reduction in the pore diameter. A non-porous hybrid silica film was obtained when the MTES molar ratio exceeded 60% in the starting sol (Fig. 1.e and .f).

4.2. GISAXS analysis

GISAXS patterns of the films before and after calcination are presented in Fig. 2. Both patterns exhibit two kinds of repartition for the X-ray diffuse scattering.

Firstly, for MTES contents of 0 and 10 mol%, the Bragg diffraction spots are clearly observed. This confirms that the pores are highly organized and structured, and drying steps did not affect the organization. This pattern can be indexed as the Body-Centered Cubic (BCC) $\text{Im}\bar{3}\text{m}$ unit cell in, showing only reflections [011] perpendicular to the plane. Cell parameter “ a ” is of 8.53 nm and 8.36 nm for non-calcined 0 and 10% of MTES molar ratio, respectively. The films retain their ordered mesostructure up to 400 °C. However, the unit cell parameter a contracts to 8.3 nm and 8.1 nm after the calcination, as indicated from GISAXS patterns. The intensity of the Bragg diffraction spots before calcination is lower compared to that obtained after calcination, which is due to the lower contrast of electron density between the pores filled by the template and the silica matrix. The films are influenced by a deformation which occurred in a direction perpendicular to the substrate. Indeed, the spots position of q_z are localized at a higher position after the heating, whereas they are at the same position in q_y -position. This confirms that the thermal treatment has no effect on the periodic structure in the film plane parallel to the substrate. However, a contraction along

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