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Fractal Perception of Change

AUSTRIAN SAXS BEAMLINE AT elettra

Austrian Small Angle X-ray Scattering (SAXS) Beamline at ELETTRA

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SUBSTRATE AND DRYING INDUCED CHANGE IN THE SHAPE OF MICELLES INSIDE CTAB-SILICA MESOSTRUCTURED FILMS

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Surfactant-templated mesostructured silica materials, discovered by Mobil researchers in 1992 [1], are the subject of intense research due to their potential applications as membranes, low dielectric-constant insulators (so-called low κ-materials), sensors, optoelectronic devices, etc. [2-4] In many applications, such materials often are required in the form of thin films, which can be grown by a procedure called evaporation-induced self-assembly (EISA) [2]. In the thin film form, film-substrate interaction and the subsequent drying with time can play an important role in controlling the structure of the film. The adsorption of surfactant molecules on solid surfaces in aqueous solutions suggests the strong role of the substrate surface condition, apart from concentration of the surfactant, in structure formation through different attachments [5]. The substrate surface condition can be modified through termination of the surface with OH or H groups, which essentially modifies the surface free energy or polar-nonpolar (hydrophilic-hydrophobic) or electrostatic nature of the surface [6-8]. However, not much work has been carried out to understand the role of such substrate surface conditions on the initial attachment of silica coated surfactant molecules, which can not only control the initial mesostructure [9] but also the final mesostructure of the film through subsequent drying. Moreover, understanding the role of alcohol on those structures and their control is very important, as it is known that alcohol can act as cosolvent or cosurfactant and can modify the mesostructure, accordingly [10].

In order to understand those issues, mesostructured films (by selecting fixed ratio of surfactant and silica) were prepared after adding different amounts of alcohol before spin coating on OH- and H-terminated Si substrates and were then characterized using complementary the x-ray reflectivity (XR) [8,11,12] and grazing incidence small angle x-ray scattering (GISAXS) [13,14] techniques. XR measurements were performed on a versatile x-ray diffractometer setup (D8 Discover, Bruker AXS at Saha Institute) [8] as a function of time (the first measurement of each sample was carried out 15 hours after the preparation) to see the effect of drying in the structure of the film. GISAXS measurements of the dried films were performed using a synchrotron source (SAXS beam line at Elettra) at an energy of 8 keV [15]. The scattered beam was detected using a 30 cm diameter (2000×2000 pixels) image plate detector (mar300, Marresearch GmbH), by placing it at about 90 cm downstream of the sample. For data collection, α was kept slightly greater (0.5-0.6°) than the critical angle α_c of the sample. The direct beam was stopped and the specular reflected beam was attenuated to avoid saturation of the detector.

A centered rectangular (*c*2*mm* space group) structure (Figure 1) is observed in dried films on both the substrates showing a clear deviation from a perfect 2D-hexagonal (*p*6*m*) structure. Such deviation (Figure 2) is directly related to the change in the shape of the micelles with or without silica coating layer inside the film. With time the silica materials try to squeeze due to drying, which can be expressed exponentially with a critical drying time of about 1 day. However, such squeezing is only allowed along the out-of-plane direction and not along the in-plane direction due to the attachment of the film on the substrate. Asymmetric squeezing makes the structure compressed and also creates stress. The latter deteriorates the ordering of the film. The compression depends on the silica wall thickness; the larger the thickness the larger is the compression. The silica wall thickness again depends on the amount of excess

alcohol. More we add the excess alcohol less is the thickness and hence the compression, which is clearly observed in the structure of the film. Excess alcohol not only acts as cosolvent as mentioned before, but also acts as cosurfactant. According to the latter, the size of the micelles increases exponentially in the measurement domain with a critical amount of excess alcohol of 15 cc. The analysis of the XR data measured in different time intervals and the GISAXS data measured on the dried films suggest that during deposition, cylindrically shaped micelles are circular on hydrophilic OH-Si substrates to form a perfect 2D-hexagonal structure (with $r_l/r_s \approx 1$), while elliptically on hydrophobic H-Si substrates to form compressed 2D-hexagonal structure (with $r_l/r_s \approx 1.1$). Such difference in shape is related to the different attachment of the film on the substrate, namely silica on OH-Si substrate and hemicylindrical micelles on H-Si substrate. For the dried films, maximum and minimum deformed structures (i.e. $r_l/r_s \approx 1.62$ and 1.35) are observed for the thick film on OH-Si substrate and for the thin film on H-Si substrate, respectively. However, considering the shape of the micelles, the maximum and minimum deformed shapes are predicted for the thick film on H-Si substrate and for the thin film on OH-Si substrate, respectively. Combining the initial shape and the effect of compression with time, which are related to the nature of the substrate and the amount of excess alcohol, respectively, final structures of the dried films along with the shape of the micelles are formed, which are of immense importance for their proper use as template and other applications.

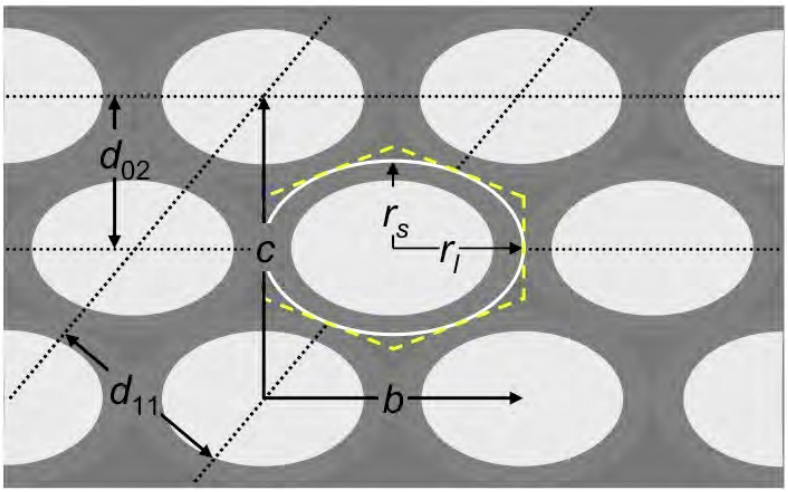

Figure 1. Schematic of a compressed 2D-hexagonal i.e. centered rectangular (*c*2*mm*) mesostructure with unit cell parameters (*b* and *c*), lattice spacing (d_{02} and d_{11}), Wigner-Seitz cell (yellow dashed lines) and corresponding ellipse (white curve) with semi-major (r_l) and semi-minor (r_s) axis.

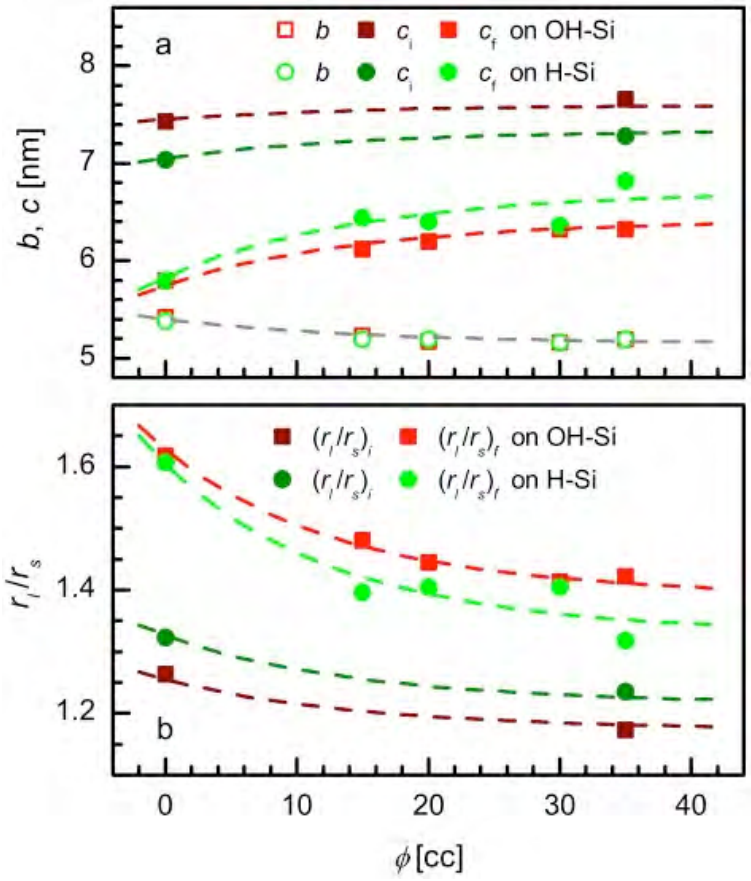

Figure 2. Influence of excess alcohol (ϕ) on (a) the in-plane (b) and out-of-plane (c) unit cell parameters of the compressed 2D-hexagonal structure and (b) the ratio of semi-major and semi-minor axis (r_l/r_s) of elliptical shaped micelles including silica coating layer for the films of different thickness on hydrophilic and hydrophobic Si substrates. Subscripts i and f represent parameters corresponding to the initial and final time of the measurements, respectively.

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