476d Gisaxs and Fesem as Tools to Investigate the Order and Orientation of Self-Assembled Mesoporous Silica Thin Films on Gold Substrates

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The field of surfactant templated mesoporous materials has grown rapidly since its inception a little over a decade ago with the development of many types of mesoporous materials. Of particular interest are mesoporous silica thin films which have applications ranging from low-k dielectrics1 to templates for nanowires in nanostructured thermoelectric cooling devices.2 However, these applications remain elusive; due in large part to the lack of reproducibility, uniformity, and long-range order of the films. To overcome these challenges and thus make possible the transition from materials discovery to application, the tools of scale-up must be in widely available and understood. For mesostructured thin films, these tools remain largely underdeveloped. Two characterization methods that have the potential to propel mesostructured thin films to the application stage are grazing-incidence small angle x-ray scattering (GISAXS) and high-resolution field-emission scanning electron microscopy (FESEM).

We recently used this combination of GISAXS and FESEM to establish the order and orientation of self-assembled mesoporous silica thin films templated with Pluronic P123 in order to determine regions where direct surface to substrate mesopore accessibility may exist.3 These reproducible films were dip coated and then evaporation-induced self-assembled4-10 onto silica and conducting gold substrates. The symmetry, order, and orientation of the films were studied as a function of the silica-to-ethylene oxide block ratio (Si/EO) under tightly controlled relative humidity (RH). The long-range order and oriented R-3m symmetry mesostructure was observed at an Si/EO ratio of 4.24 and 60% RH, while a medium-range order and oriented c2mm mesostructure was observed at 3.62 Si/EO ratio and 10% RH. The FESEM confirmed the GISAXS data that the transition from R-3m symmetry to c2mm symmetry matches the transition from spherical micelles to cylindrical rods. These changes in mesostructure are in good agreement with the shape factor model, which predicts the template structure based on the ratio of the area of the head group to volume ratio. In addition to the changes in symmetry of the mesophase, changes in the orientation of the thin films were observed. These changes in orientation are not predicted by the geometric shape factor model. Films with Si/EO ratio 3.62 or greater were well ordered, while films less than 3.29 were not oriented. This trend is observed true for all RH tested and regardless of the mesostructure symmetry. Finally, two other distinct regions were observed. At low Si/EO ratios and high RH a disordered mixture of spherical micelles and cylindrical rods were observed. This mixture region is intriguing because there is likely direct mesopore access from the surface to the substrate in this region. At very high RH for all Si/EO ratios tested, streaking of the Bragg peaks in the GISAXS patterns occurs. This streaking is attributed to faulting of the mesophase in the direction perpendicular to the substrate which is likely caused by a disruption of the smooth continuous drying line at very high RH.

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