Time-resolved GISAXS investigation of the self-assembly of spin-coated PMO films

Periodic mesoporous organosilica (PMO) is a class of materials that possess periodically ordered pores with sizes between 2 and 50 nm and walls consisting of organically bridged polysilsesquioxanes. PMO thin films are considered for applications such as sensors, membranes, chromatography, insulating low-k in integrated circuits, etc. For each of these applications, the mesophase plays an important role determining the kinetics of molecular transport through the pores as well as the film mechanical properties. The mesostructuration is understood in terms of the evaporation-induced self-assembly mechanism which has been studied in dip-coated periodic mesoporous silica (PMS) films. Notably, the existence of a modulable steady state (MSS) has been shown when depending on the relative ambient humidity (RH) the final mesophase is determined. Another factor influencing the self-assembly is the degree of precursor polycondensation. While a few studies report spin-coated PMS films with designed pore organization, there is only a very limited number of publications about supported PMO films.

We report the time-resolved GISAXS investigation of the effect of ambient relative humidity (RH = 20, 40, and 70%) on the self-assembly of spin-coated PMO film. The lower RH values lead to mixed phases – 2D hexagonal and worm-like at 20% and lamellar and worm-like at 40%. In contrast, the initially observed lamellar mesophase transforms into a high quality 3-D hexagonal phase at RH=70% showing, for the first time, the existence of MSS in spin-coated PMO films. On the other hand, decreasing the RH from 70 to 20 % leads to a reduction of the domain size of the 3D mesophase but the associated SAXS pattern remains. A significant dependence of the mesostructuration on the solution aging was observed – 20 min aging leads to films with $P6_3/mmc$ symmetry while 70 min aging results in disordered films.