Experimental

Pluronic F127 $(OH(CH_2\text{-}CH_2O)_{106}(CHCH_3CH_2O)_{70}(CH_2CH_2O)_{106}H)$, tetraethylorthosilicate (TEOS), methyltriethoxysilane (MTES) and ethanol (EtOH) were purchased from Aldrich and used as received. (100) oriented, P-type / Boron doped silicon wafers were employed as the substrates.

A stock solution was prepared, with molar ratios of TEOS : MTES : EtOH : HCl: $H_2O = 1 : 0.56 : 4.17 : 0.11 : 1.55$. The solution was stirred for one hour to allow the hydrolysis of the silane units. A template solution was prepared, containing 1.3 g Pluronic F127, 15 ml EtOH and 1.5 ml HCl $5 \cdot 10^{-3}$ M. Next, 7.7 ml were taken from the stock solution and added to the template solution. The resulting solution was then aged for one week. The final molar ratios were TEOS : MTES : EtOH : H_2O : HCl: F127 = 1 : 0.56 : 24.48 : 14.70 : 0.11 : $7.6 \cdot 10^{-3}$.

The substrates, previously cleaned with hydrofluoric acid, water, EtOH, and acetone, were dip-coated in the aged solution. The dip-coating system was a home-built model, specifically designed for *in situ* measurements. The substrate was mounted on a fixed rod, while the beaker containing the solution was moved up and down by a moveable stage connected to an electrical engine: in this way, the sample remained fixed and the solution was raised and lowered during the dip-coating procedure. The relative humidity (RH) in the deposition chamber was set at 40%, the withdrawal speed was set at 15 cm·min^{-1}. Finally, the samples were thermally treated in air at different temperatures.

A spectroscopic study of the films was performed using a Nicolet Nexus Fourier transform infrared (FTIR) spectrophotometer: the spectra were obtained in transmission, using silicon wafers as substrates, in the range 400-5000 cm^{-1} averaging 256 scans with 4 cm^{-1} of resolution. A silicon wafer was used, in transmission mode, to measure the background. A Gaussian peak fitting procedure has been applied to the FTIR spectra (Microcal Origin Software), the quality of the fitting was evaluated on the basis of the χ^2-values (in the order of 10^{-6}) and correlation coefficient values ≥ 0.998.

In situ infrared (IR) study to investigate the kinetics of polycondensation reactions during EISA was performed at synchrotron infrared beamline (SINBAD) in the Laboratori Nazionali (Frascati, Italy) of the Istituto Nazionale di Fisica Nucleare (INFN). The IR radiation is extracted from a bending magnet of the electron ring and

transmitted to an interferometer at the distance of about 25 m. The beam line is kept under ultra-high vacuum up to the diamond window placed at the entrance of the interferometer which is a Bruker equinox 55 modified to work down to 10^{-2} mbar and equipped to operate in far-IR region. The measure was done in air via transmission mode with a Bruker IR microscope that is installed laterally with respect to the interferometer. Mid-IR measurement were performed using the interferometer working in vacuum, in the range 500-6000 cm^{-1} and with a resolution of 4 cm^{-1}. A MCT detector (1 mm^2 size) cooled to the nitrogen temperature and a KBr beam splitter were used. The IR spectra were recorded with an interval of 3 seconds, which was a good compromise between a signal-noise ratio and the possibility to follow the reactions during film formation. A 2 µl drop was cast on a diamond disk and the measure was immediately started after the deposition. Diamond was selected as substrate because of the excellent transmission in the 700-2000 cm^{-1} region[i]. We have carefully selected the volume of solution to be cast with a series of systematic experiments performed with increasing amounts of solutions, up to 50 µl per drop. Larger volumes of solution cast on the diamond disk gave, in fact, saturation of the spectra, or the kinetics was too slow to simulate a film formation.

The mesostructure of the films were investigated using the high-flux grazing incidence small angle X-ray scattering (GI-SAXS) apparatus at the Austrian high-flux beamline of the electron storage ring ELETTRA (Trieste, Italy)[ii], taking for each image the average of 10 single acquisitions and 3 seconds of exposure time. The instrumental grazing angle was set maintaining an incident X-ray beam (wavelength 1.54 Å) smaller than 3°. From the recording of the CCD detector (1024 × 1024 pixels, Photonic Science) the *out of plane* diffraction maxima were observed. The distance between sample and detector was calculated from the diffraction pattern of a salt having a known lattice constant (silver behenate, $H(CH_2)_{21}COOAg$): it was possible to obtain this distance (991 mm) with a good precision (±1 mm). The beam centre position was set from the least squares fit of a circle of 40 entered coordinates, corresponding to 40 positions in the silver behenate powder diffraction ring. For picks identification, a radial integration of the intensity of each recorded image was performed, starting from the beam centre (000). Typically, the whole image was masked leaving out the peak of interest and successive integrations were made. This procedure minimized peak position

errors caused by the overlap of information in diffraction patterns. Knowing the distance between sample and detector, it was possible to calculate 2θ and d_{hkl} for each spot and the lattice constants of the observed mesophase. Supposing that the radially integrated spot intensities fit a Gaussian curve, the error on the *x*, *y* position of the spot on the GI-SAXS image was estimated to be ± 6% by the FWHM of the curve.

To study the kinetics of self-assembly during EISA, in situ SAXS measures were performed during dip-coating in transmission using a thin silicon substrate (8 mm). Multiple images were recorded every second, with an exposition time of 1 second (no delay between acquisitions). A home-made dip-coater was used for the deposition of the film.

Transmission electron microscopy (TEM) structural and compositional characterization was performed with a field-emission gun FEI TECNAI F20 SuperTwin FEG-(S)TEM microscope operating at 200 kV equipped with an EDAX energy-dispersive x-ray spectrometer (EDS). The samples were prepared as cross-sections cutting the mesoporous films along two perpendicular directions with respect to the Si substrate in order to have access to different crystallographic projections of the mesostructures. The ordered sample phase was investigated in two ways: (i) by conventional selected area electron diffraction (SAED) using a nominal microscope camera length of about 2 m to increase the separation among the spots arising from the mesostructures; (ii) by acquiring TEM images in scanning mode (STEM) in which a small electron probe (about 1 nm FWHM) is rastered over the sample. The electrons which were incoherently scattered from the sample are collected by a high-angle annular detector to form dark-field STEM images of the samples, in which the image contrast is proportional to the local atomic number. In this way the contrast between pores and the matrix is greatly enhanced with respect to conventional bright-field (BFTEM) mode. Then, the crystallographic analysis on the mesophase is performed by fast-Fourier transforming (FFT) the STEM images.

[i] Wetzel, D. L., *Vibrat. Spectroscopy* **2002,** *29*, 291.

[ii] Amenitsch, H.; Rappolt, M.; Kriechbaum, M.; Mio, H.; Laggner, P.; Bernstorff, S. *J. Synchrotron Radiation* **1998**, *5*, 506.