ESRF	**Experiment title:** GISAXS study of periodic mesoporous organosilicas	**Experiment number**: SL-2105
Beamline: BM02	**Date of experiment**: from: Dec. 6th, 2010 to: Dec. 10th, 2010	**Date of report**: July 22nd, 2014
Shifts: 6	**Local contact(s)**: Jean Paul Simon*, Mireille Maret*	*Received at ESRF:*

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Report:

Framework of the Project :

In the most advanced integrated circuits, porous dielectrics were introduced in order to decrease parasitic capacitance between metallic lines. In order to optimize these porous dielectrics; one idea is to structure the porosity, both to achieve the best mechanical properties and to have closed pores. In this frame, a contract with the "Agence Nationale de la Recherche" entitled “Structuration de la porosité des matériaux à faibles permittivités (ULK) en vue de leur intégration dans les inter-connexions microélectroniques” has been obtained in partnership between four laboratories, LETI, IEM, SOPRA and SIMAP.
First, mesoporous silica with well-known pore patterns (2D hexagonal arrangement of cylindrical pores, mono-dispersed spheres in a regular pattern) were studied to obtain the mechanical constitutive laws model systems. In parallel, first ULK layers were prepared from methyltriethoxysilane (MTES), tetraorthosilicate (TEOS) and 1,2 bistriethoxysilyl(ethane) (BTSE) as matrix precursors and commercial amphiphilic copolymers (Brij56) as porogen and were studied by GISAXS in the MA687 experiment (2008).
In 2010, new mesoporous hybrid silica based thin films with reproducible hydrophobic properties were developed by spin-coating. Pure MTES was used as skeleton precursor and mixed with new amphiphilic copolymers made of Polystyrene block polyethylene oxide (PS-PEO) as structuring agent. The pore volume fraction, the pore size and the pore size ordering were tuned by controlling different synthesis parameters, i.e. the PS-PEO/MTES ratio, the molecular weight and Hydrophilic Lipophilic Balance of the PS-PEO block copolymers. Moreover, different calcination processes were investigated (thermal annealing vs. UV assisted thermal annealing).

Experimental method and strategy :

Grazing Incidence Small Angle X-Ray Scattering (GISAXS) using a 2D detector allow multiplying the signal by ~200 compared to conventional SAXS. In this experiment, GISAXS was performed at 9.8 keV with a distance of 715 mm: it appears that images look like GIRD at small angles, with sharp Bragg peaks: Since there is an epitaxial texture, the beam selects several domains of the layer in Bragg conditions, i.e. with different cuts of the zone axis. Indeed, the GIRD 2d images are independent from a rotation normal to the layer.

Results

From GISAXS analysis, information on the size, shape and roughness of the pores (through the form factor) and also information on the spatial distribution of these pores (through the structure factor and radial distribution function) were obtained. For instance, copolymers PS(1600)-b-PEO(2500)-14 and PS(2300)-b-PEO(3100)-14 show well-ordered centred cubic phase as shown in Fig. 1. The mean pore size can be estimated and is close to 5-7 nm. These experiments show also that different structures can be obtained depending of the film composition. For instance, PS(1600)-b-PEO(1800)-18 presents an hexagonal structure (Fig. 2). Finally, the calcination using a UV assisted thermal curing (only few minutes long in comparison to few hours by thermal curing) allows keeping the structure (see Fig.3 for PS(2300)-b-PEO(3100)-14) and only slightly modify the porous material (due to a higher film shrinkage).

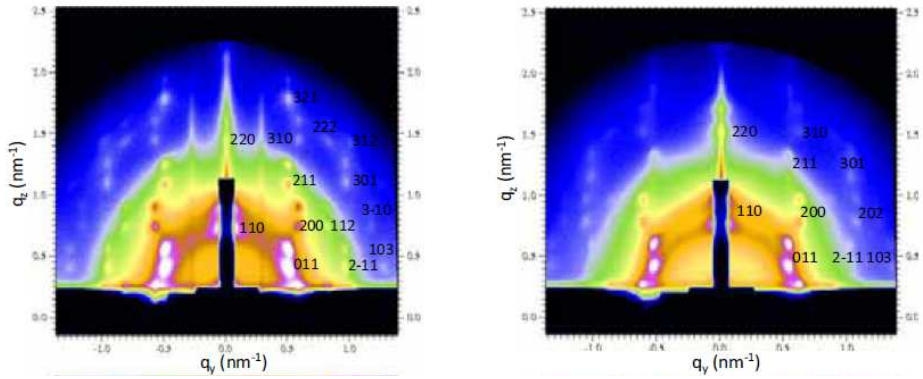

Fig 1. GISAXS patterns obtained on (a) PS(1600)-b-PEO(2500)-14 and PS(2300)-b-PEO(3100)-14 after calcination. The numbers under bracket corresponds to polymer mass in g.mol^{-1} and the last number corresponds to the PS-b-PEO/MTES ratio.

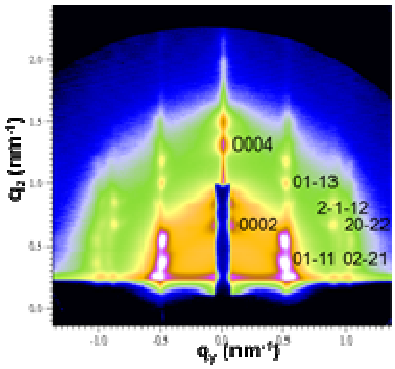

Fig 2. GISAXS pattern obtained on PS(1600)-b-PEO(1800)-18 and showing an hexagonal 3D meso-structure after calcination.

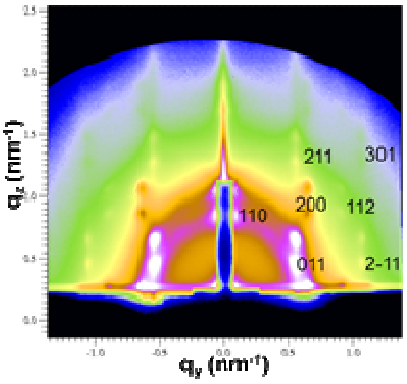

Fig 3. GISAXS pattern obtained on PS(2300)-b-PEO(3100)-14 after UV curing.