ESRF	**Experiment title: GISAXS in-situ monitoring of the self-assembly of block copolymer thin films by solvent annealing**	**Experiment number**: HC 1724
Beamline: BM2	**Date of experiment**: from: 19/11/2014 to: 24/11/2014	**Date of report**: 18/01/2016
Shifts:18	**Local contact(s)**: Nathalie Boudet	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Proposer

Name: Pr BUTTARD Denis

Address: C.E.A. - INAC/SP2M/SiNaPS, Bat. BCA Minatec 17 Rue des Martyrs, 38054 Genoble Cedex 9

Phone: 04 38 78 18 22 E-mail: denis.buttard@cea.fr

Co-proposers

Dr. Marc ZELSMANN CNRS Grenoble, Dr. Cécile M. P. GIRARDOT, Lab. des Technologies de la Microélectronique, Grenoble Cedex 9, Mrs. Sophie BÖHME, Lab. des Technologies de la Microélectronique Grenoble Cedex 9, Mr. Olivier MARCONOT Ecole Centrale de Lyon Ecully Cedex

Report:

Directed Self-Assembly (DSA) of Block CoPolymers (BCPs) is an effective approach to produce thin films with various nano-sized patterns. As a consequence, DSA was introduced in the International Technology Roadmap for Semiconductors (ITRS) as a potential solution in order to complement advanced optical lithography techniques by enhancing its resolution. Due to its ease of processing, a large majority of the lithographic BCP work reported so far concerned polystyrene-block-polymethylmethacrylate (PS-b-PMMA). Nevertheless, its Flory-Huggins parameter χ (measuring the incompatibility between the two blocks) is not very high (χ = 0.06 at 25 °C), limiting the resolution to about 15 nm. Researchers show now increased attention to BCPs with a higher Flory-Huggins parameter due to their improved resolution (possibility to fabricate sub-8 nm features). Among those, polydimethylsiloxane (PDMS) containing materials (polystyrene-block-polydimethylsiloxane (PS-b-PDMS) and Poly(D,L-lactic acid-b-dimethylsiloxane-b-D,L-lactic acid) (PLA-b-PDMS-b-PLA)) are particularly attractive. Their Flory–Huggins interaction parameter is relatively large and the PDMS block can readily form silicon oxide structures under an oxygen plasma whereas the PS block is degraded under the same treatment. This is leading to a SiO_2-like nanolithography mask that is well suited for pattern transfer in underlayers by plasma etching [1]. However, due to the high interaction parameter χ of this polymer, thermal diffusion is limited (i.e. the self-assembly process is extremely long) and non-standard processes have to be used. The most typical one is the so-called solvent annealing (SVA) process [2] where the sample is swelled by exposing it to solvent vapors, overcoming the diffusive energy barrier and allowing the self-assembly step to proceed at room-temperature. Nevertheless, to be easily introduced in a microelectronics fab, SVA and or harmful solvents generally associated with this treatment should be avoided if possible. This is the reason why thermal annealing alone should also be investigated on these materials. Then, to allow self-organization to take place in few minutes, dedicated BCP formulations presenting higher mobility (by including homopolymers, plasticizers or salts) are considered.

During these experiments, we measured ex-situ samples (organized before experiments) with different periodicities (from 18 to 35 nm), different PDMS block morphologies (cylinders and spheres), at different self-assembly stages and at different points in the etching process. An example concerning PDMS spheres is reported in Fig. 1.

Also, the evolution of the GISAXS pattern during the thermal self-assembly of a monolayer of horizontal PDMS cylinders and of a monolayer of PDMS spheres in a PS matrix on silicon substrates could be measured In Fig2, we report on the starting point of those samples, whereas in Fig. 3, the spectrum evolution during this

self-assembly process in the case of horizontal cylinders in a PS matrix (PS-b-PDMS) is shown. A clear transition around 80 °C is observed between a micellar state of the thin layer (17 nm periodicity) and the cylindrical state (21 nm period).

Additionaly, measurements were performed during the self-assembly of these thin layers during an exposure to a solvent environnement (solvent annealing). Nevertheless, due to experimental difficulties (evaporation of solvent under the X-ray beam in the used conditions), only limited exploitable data could be recorded during these experiments.

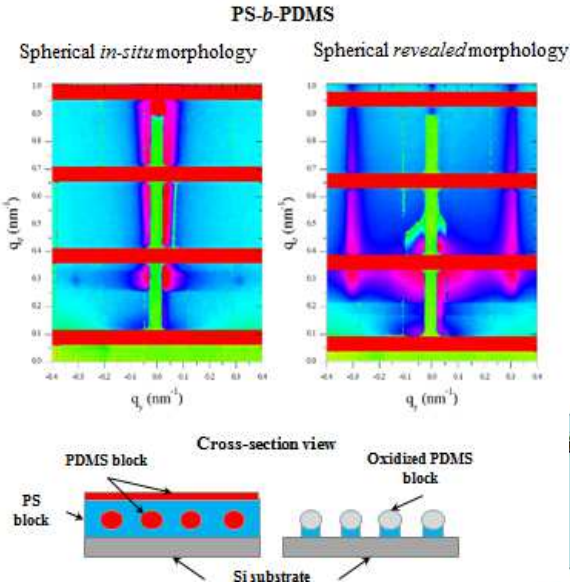

Figure 2. Ex-situ GISAXS measurements of PDMS spheres at two different steps of the etching process (before and after the spheres revelation)

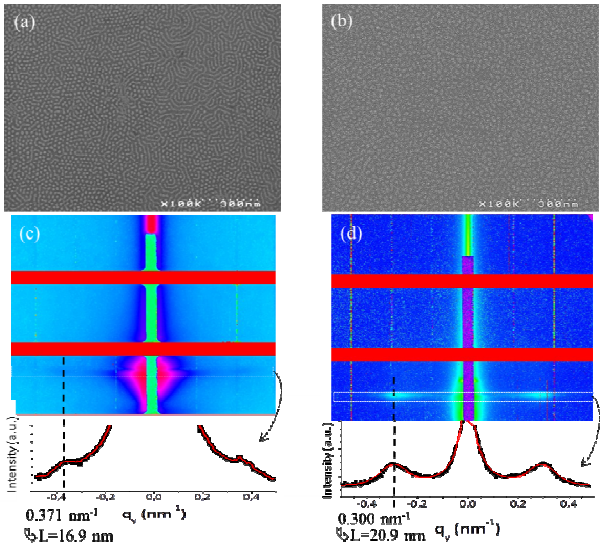

Figure 1. SEM images of as spun films from PGMEA solution and in situ GISAXS patterns with the corresponding line profile integrated from a 20 pixels band along qz as a function of qy of (a)(c) PS-PDMS films with a mixture of cylinders and dots morphologies confirm by diffuse GISAXS signals suggesting no homogeneous pattern; (b)(d) PLA-PDMS-PLA micellar structures with a majority of dots present a more intense and define GISAXS signal suggesting a most homogeneous morphology on all the surface

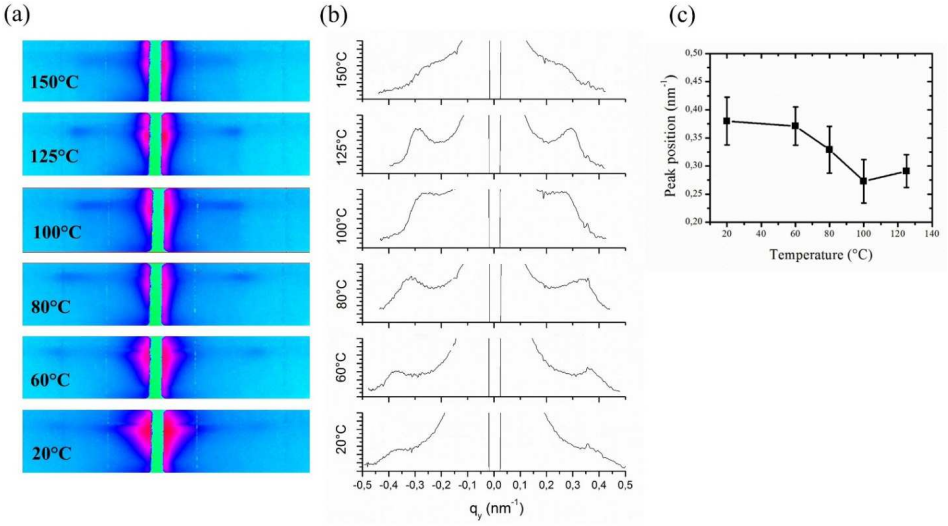

Figure 3. (a) Evolution of the GISAXS pattern of a thin layer (22 nm thick) of 21-nm pitch PS-PDMS during a thermal ramp evidencing a transition between a micellar and a horizontal cylindrical morphology around 80 °C, (b) intensity profiles along qy and (c) peak positions and standard deviations

Reference:

[1] C. Girardot et al., ACS Appl. Mat. Inter. 18, 16276 (2014)
[2] C. Sinturel et al. Macromolecules 46, 5399 (2013)