Control of the PS-b-PDMS directed self-assembly by silsesquioxane-based graphoepitaxial substrate engineering

M. Salaün, M. Zelsmann
Laboratoire des Technologies de la Microélectronique, LTM, CNRS-CEA/LETI-UJF, 17 rue des martyrs, F-38054 Grenoble, France
mathieu.salaun@cea.fr
O. Lorret, B. Dittert
Functional Surfaces and Nanostructures, Profactor GmbH, Steyr-Gleink, A-4407, Austria
D. Borah, B. Kosmala, M. Morris
University College Cork, Chemistry Department, Kane Building, College road, Cork, Ireland

Block CoPolymer (BCP) self assembly creates periodical pattern with feature size below 10 nm. However, ordering is only obtained in grains not larger than a few micrometers. Grain orientations are independent and randomly distributed which prevents the obtaining of a long range ordering. Segalman et al.[1] demonstrated that BCP self assembly in trenches of a pattern or above topography could create an order between the polymer micro-phases. Trench walls confine the polymer and guide the chains organization. More recently researchers have shown increased attention to PolyStyrene-block-PolyDiMethoxySiloxane (PS-b-PDMS) due to its natural tendency to create highly ordered patterns. Additionally, the PDMS block is very interesting in nanofabrication due to its high plasma etching resistance. Nevertheless, due to the difficulty to fabricate neutral surfaces for PS-b-PDMS and to the high affinity of PDMS with both silicon and air/vacuum (compared to PS), only very few results on PDMS vertical features (lamellas or cylinders perpendicular to the substrate) have been reported up to now in the literature.

In this work, we present results on directed self-assembly of PS-b-PDMS performed on pre-patterned SilSesQioxane (SSQ) based substrates. These templates are made by soft UV imprinting of different kinds of liquid SSQ-based resists using a hard-PDMS stamp. Surface properties of synthesized SSQ resists are tuned by grafting different kind of ligands to a same T8 SSQ cage (fluorinated, phenyl, acrylate, methacrylate, glycidyl and or epoxy ligands are used). The residual resist layer after the nanoimprint process is eventually removed by plasma etching at the bottom of the trenches, providing different surface chemistry geometries (SSQ walls with Si or SSQ bottom layer). Either vertical or horizontal orientations of the PDMS cylinders could be obtained in these templates by solvent annealing with a remarkable long-range order and registration (Figure 1). Tuning the configuration allows to get all 3 orientations. Investigations are now undergoing to understand more precisely the dependence of the self-organization process to the experimental conditions. For example, thickness changes in the BCP film allow thickness-dependence investigations (Figure 2).

[1] R. A. Segalman, H. Yokoyama, E. J. Kramer. Adv. Mater., 13 (2001), 1152.

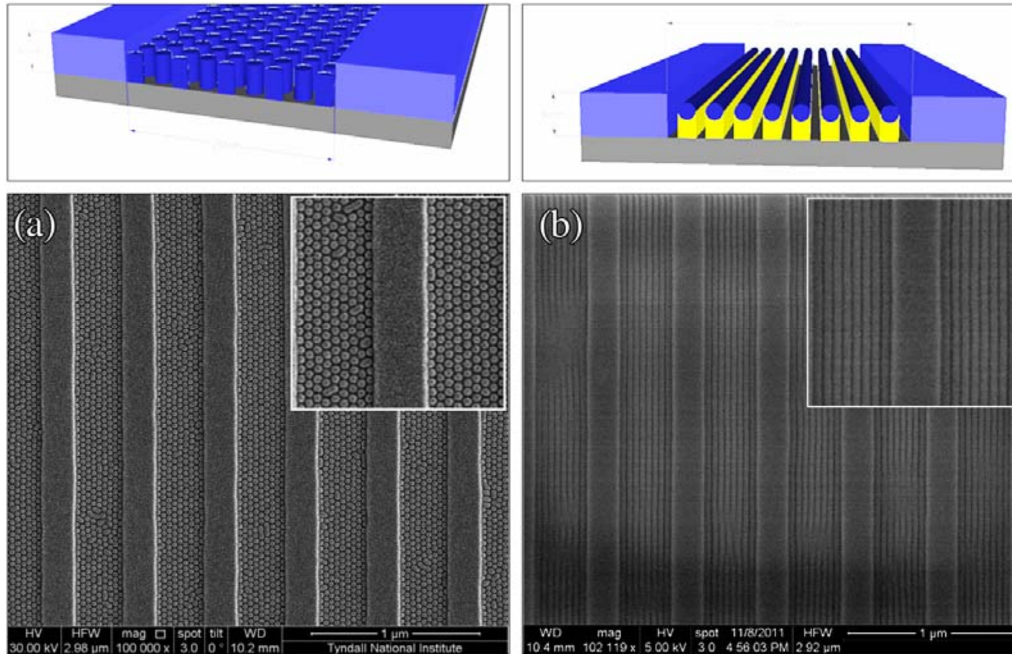

Figure 1: SEM images of directed self-assembled Poly(styrene-block-dimethoxysilane) features in a SSQ resist template (230 nm wide SSQ lines, 270 nm large trenches between the SSQ lines). Orientations perpendicular (a) or parallel (b) to the substrates plane are observed depending on the nature of the SSQ. Theoretical organization schemes are drawn above each picture.

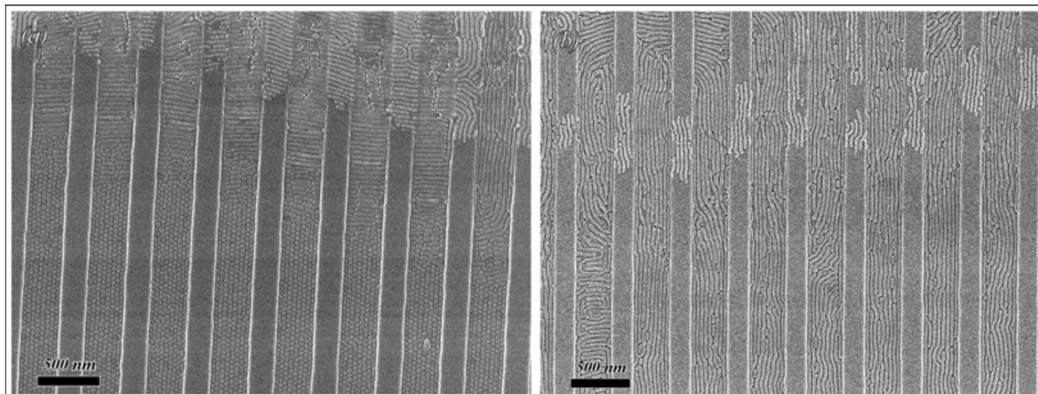

Figure 2: SEM images of directed self-assembled Poly(styrene-block-dimethoxysilane) features in a SSQ resist template (230 nm wide SSQ lines, 270 nm large trenches between the SSQ lines) at positions presenting BCP thickness differences (thicker on top, thinner at the bottom of the image). The polymer chains orientation changes with the thickness in case (a) but is kept horizontal in case (b) depending on the presence or not of a residual SSQ resist layer at the bottom of the trenches (below the BCP).