Neutral surface modification by e-beam exposure for PS-b-PMMA self assembly

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Block copolymers are very attractive materials for nanofabrication due to their ability to phase separate into ordered and chemically distinct domains of 10s nm size[1]. For lithography application, the domain (lamellae if the two blocks have similar volume) must be perpendicular to the substrate in order to facilitate pattern transfer into the substrate. Unfortunately, perpendicular lamella is not the natural arrangement, since normally the substrate wets better one of the two blocks, leading to a horizontal and layer by layer structure.

To obtain perpendicular lamellae, the substrate surface must be treated to be "neutral", without preferential wetting of either of the block. The most popular method to achieve a neutral surface for PS-b-PMMA (PS: polystyrene) is the grafting of a random PS-r-PMMA copolymer brush having the same PS/PMMA ratio as the block copolymer to be self assembled. Alternatively, a neutral surface can be obtained by a self-assembled mono-layer (SAM) of a surfactant; and previously we have demonstrated that vapor-phase deposited 3-MPTS (3-(p-methoxy phenyl) propyl trichloro silane, Gelest Inc.) can be employed to achieve perpendicular lamellae of symmetric PS-b-PMMA[2].

For some applications, it is desirable to have self assembled periodic structures on only part of the wafer surface with the rest area not patterned, or to have different types of structures (e.g. line/trench vs. dot/hole) on the same wafer. In this study, we will show that modification of the SAM by electron beam exposure can achieve this goal.

In the experiment, a small drop of 3-MPTS was placed in a wafer box (no vacuum) that had inside a piece of silicon wafer pre-cleaned by solvent and oxygen plasma. After two hours, the wafer was taken out, and the SAM of 3-MPTS was exposed with different e-beam doses. The block copolymer film was prepared by spin coating a toluene solution of PS-b-PMMA. Then the film was annealed at 180-190^{o}C for 5-20 min. In order to reveal the self-assembled pattern, the copolymer was exposed to 10 s oxygen plasma RIE. The etching rate of PMMA block is roughly 3× that of PS block, thus leading to fingerprint pattern if the perpendicular lamellae was formed.

As shown in Figure 1, for symmetric PMMA-b-PS without e-beam exposure of the SAM surfactant, clearly perpendicular lamellae was formed on the neutral surface prepared with 3-MPTS self assembled monolayer. Without this 3-MPTS surface treatment step, no feature was found (not shown), indicating an in-plane layer-by-layer self assembly. Upon exposure of the SAM by e-beam, the fingerprint pattern disappeared, indicating "damage" of the SAM layer and thus a layer-by-layer self assembly. For asymmetric PMMA-b-PS that gives cylindrical structure, the cylinder orientation can be tuned by e-beam exposure of the SAM layer, as shown in Figure 2.

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[1] R.D., Peters, X. M. Yang, Q. Wang, J. J. de Pablo, and P. F. Nealey, Journal of Vacuum Science & Technology B, 3530-3534 (2000).
[2] A. AlMutairi, B. Shokouhi, G. Yu and B. Cui, presented at EIPBN 2015.

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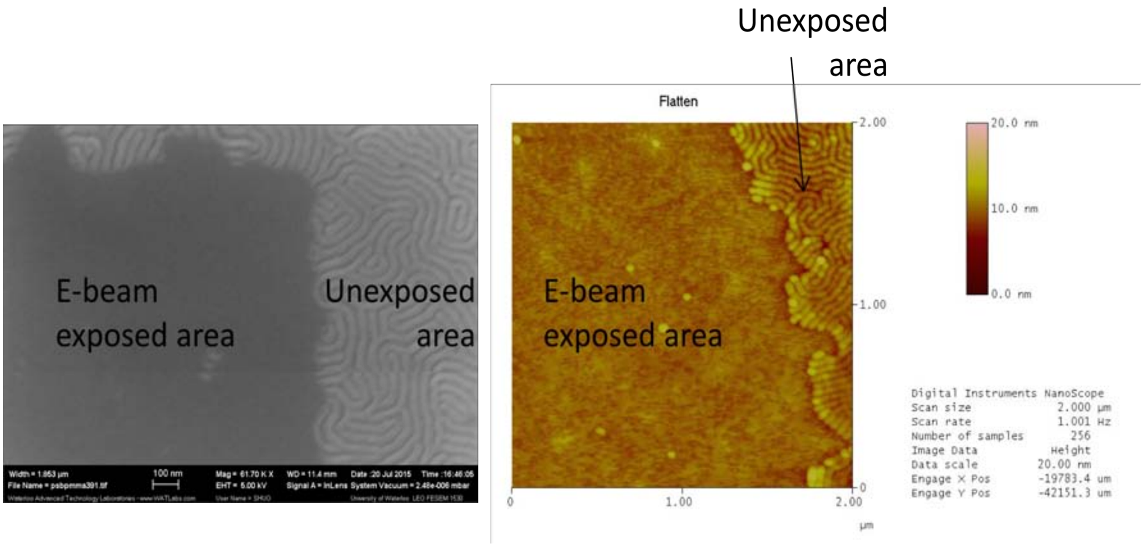

Figure 1 SEM and AFM images of self assembled symmetric (PS:PMMA 32.5:39.6 kg/mol) PMMA-b-PS structures, showing the effect of e-beam exposure of the 3-MPTS SAM layer on the BCP self assembly.

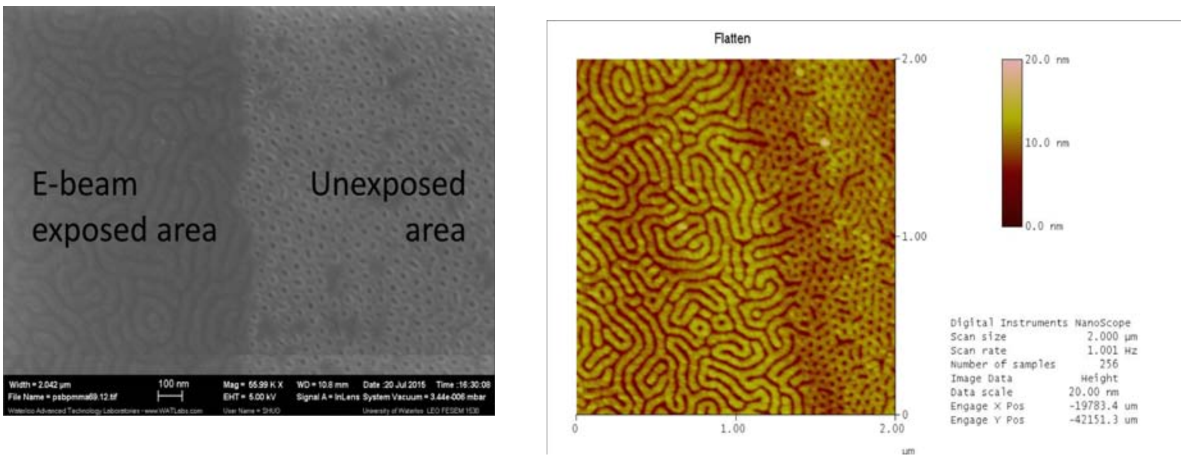

Figure 2 SEM and AFM images of self assembled asymmetric (PS:PMMA 69.1:33.0 kg/mol) PMMA-b-PS structures, showing that e-beam exposure of the surfactant changed the orientation of the cylindrical PMMA phase from perpendicular to horizontal (lateral).