Neutral surface prepared by vapor phase coating for PS-b-PMMA self assembly

Babak B. Shokouhi, Wadha Alyalak, Mustafa Yavuz and Bo Cui
Waterloo Institute for Nanotechnology (WIN), University of Waterloo
200 University Ave West, Waterloo, ON, N2L 3G1, Canada
E-mail: bbaradar@uwaterloo.ca

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 3-MPTS (3-(p-methoxy phenyl) propyl trichloro silane, Gelest Inc.) has been successfully employed to achieve perpendicular lamellae of symmetric PS-b-PMMA[2]. However, 3-MPTS was coated onto the substrate from liquid phase for as long as 48 hours.

In this study, we will show that 3-MPTS can also be coated from vapor phase. Compared to liquid phase surface treatment and random copolymer brush grafting, vapor phase uses far less material (a tiny drop of μL volume is often enough), is of much higher throughput (many wafers can be stacked inside the container), and is free from contaminant that can be a serious issue for liquid phase treatment when the silane surfactant reacts with dissolved water and forms particles inside the liquid.

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. The block copolymer film was prepared by spin coating a toluene solution of 7.5 wt/vol % PS-b-PMMA (symmetric, total molecular weight 130 kg/mol). After coating on the 3-MPTS treated wafer, the film was annealed at 190^{o}C for 20 min. In order to reveal the self-assembled pattern, the copolymer was exposed to 10 s oxygen plasma RIE with RF power 20 W, O2 flow 20 sccm, and 1 mTorr pressure. 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(b-c), clearly perpendicular lamellae were formed on the neutral surface prepared with 3-MPTS self assembled monolayer. The characteristic periodicity of the fingerprint pattern was 67 nm. Without this 3-MPTS surface treatment step, no feature was found (Figure 1(a)), indicating an in-plane layer-by-layer self assembly.

---

[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] B. H. Sohn and S. H. Yun, Polymer, 43(8), 2507-2512 (2002).

Neutral surface prepared by vapor phase coating for PS-b-PMMA self assembly

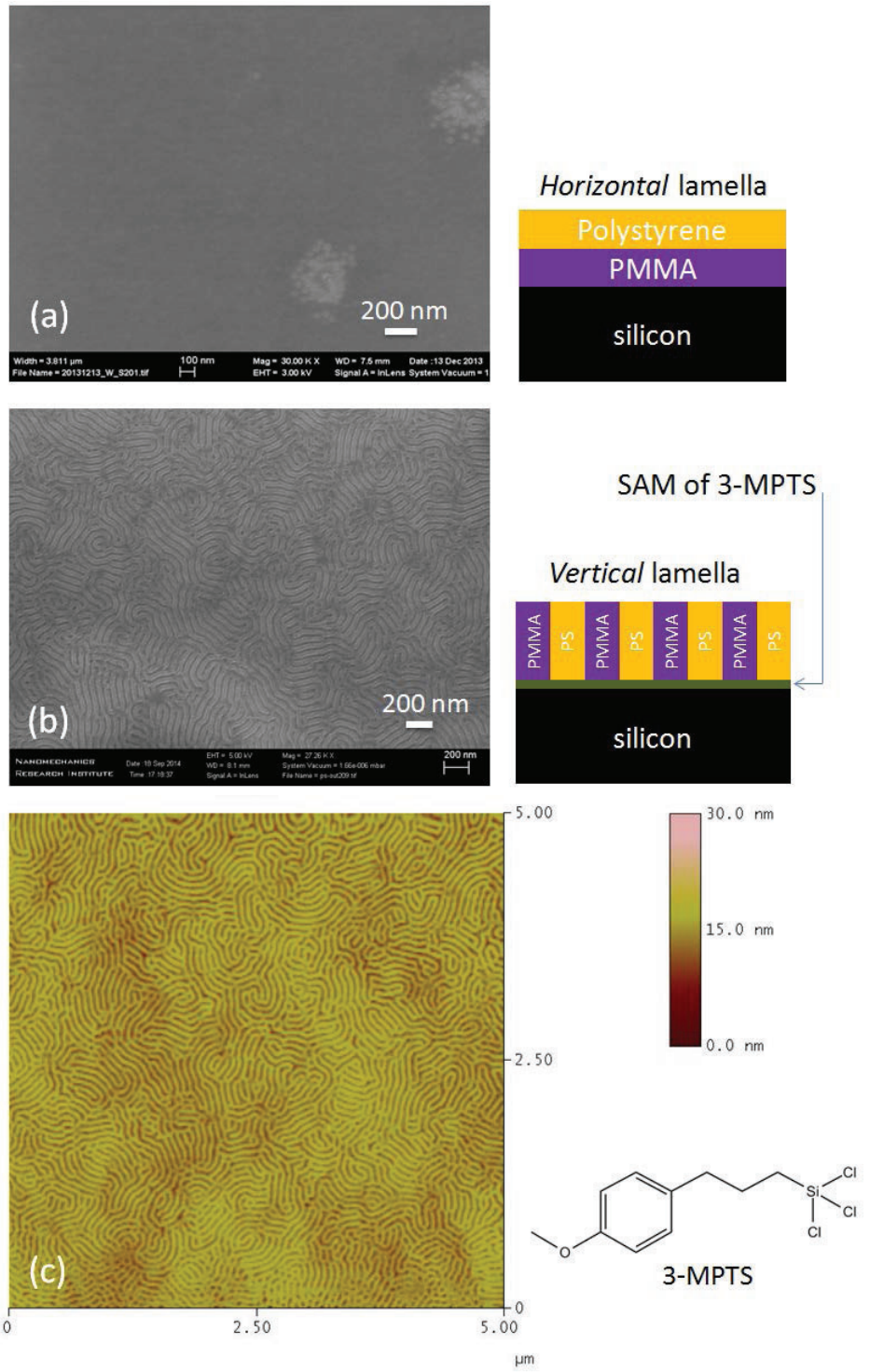

Figure 1. SEM and AFM images of self-assembled diblock copolymer PS-b-PMMA, coated on bare silicon substrate (a), and on silicon substrate that was vapor phase treated with 3-MPTS surfactant (b-c). Characteristic fingerprint pattern was clearly seen for the surfactant-treated substrate, but not for the un-treated substrate.