Templated Self-Assembly of Block Copolymer Thin Films under Lithographic Confinement

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Physical or chemical templates can direct the self-assembly of block copolymers to achieve well-aligned nanoscale patterns. Complex patterns have been previously demonstrated using a sparse array of lithographically defined and chemically functionalized posts.[1,2] However, self-assembly of block copolymers confined inside a topographic template fabricated by electron-beam lithography has not been studied in detail. In this work, we describe how physical confinement affects the self-assembly of cylindrical morphology polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) block copolymer thin films. This work could lead to a new pattern generation technique that enables high-throughput pattern generation.

We used an array of square grid templates using electron-beam patterning of hydrogen silesquioxane (HSQ) resist. The patterned substrate was treated with a hydroxyl-terminated PS brush layer. 45.5 kg/mol PS-*b*-PDMS block copolymer was spin coated on the template and solvent annealed in a 5:1 mixture of toluene and heptane for 3 h at room temperature. The top PDMS layer and PS matrix were removed by CF_4 and O_2 reactive-ion etching, respectively. As shown in figure 1, PDMS microdomains formed a bar-shaped structure when confined inside a square grid. The bar-shaped structures were randomly aligned in horizontal and vertical direction because the size of the grid was equal in both directions. In figure 1(a), 18 structures were aligned horizontally and 18 structures were aligned vertically. As the size of the square was increased, some bar-shaped structures were not fully connected. In figure 1(b), such defects were observed. One additional bar was formed inside each square compared to the structures in figure 1(a).

To control the alignment direction of the bar-shaped structures, we fabricated a rectangular grid array. Bar-shaped PDMS structures similar to those shown in Figure 1(a-b) were produced, but with a horizontal alignment. Figure 2(a) and 2(b) show PDMS microdomains confined inside a rectangular grid array with an aspect ratio of 1.3 and 1.5, respectively. Because of high free energy penalty associated with forming T-junctions, the alignment direction of the bars was preferential to the direction resulting in less T-junctions.

[1] J. K. W. Yang, et al., Nat. Nanotechnol. **5,** 256 (2010).
[2] A. Tavakkoli K. G., et al., Science **336,** 1294 (2012).

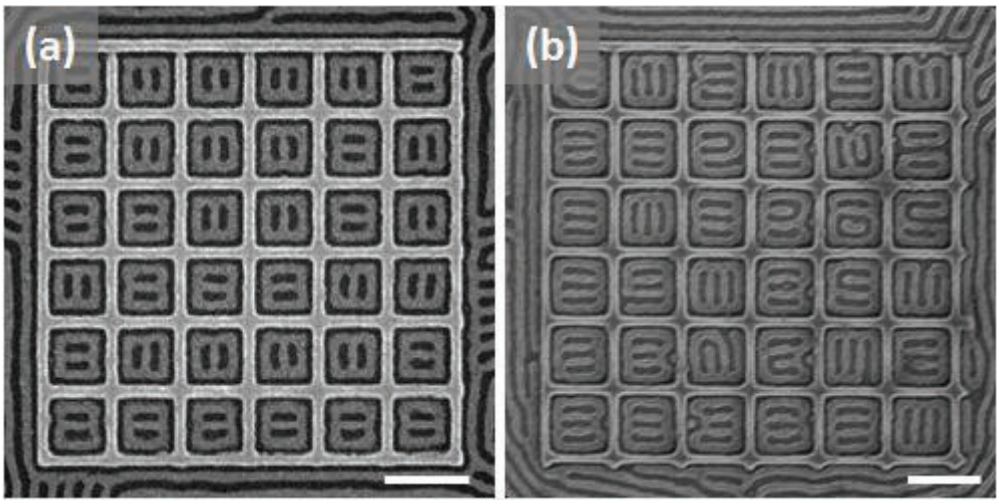

Figure 1: Scanning electron microscope (SEM) images of PDMS microdomains confined inside a square grid array. Size of the square grid was (a) 140 nm; and (b) 160 nm. All scale bars are 200 nm in length. (a) The PDMS microdomains formed bar-shaped structures with two T-junctions in each structure. Alignment direction of the structure was random. (b) The PDMS microdomains formed bar-shaped structures with four T-junctions in each structure. Several defects were observed. White lines are oxidized HSQ and gray lines are oxidized PDMS microdomains.

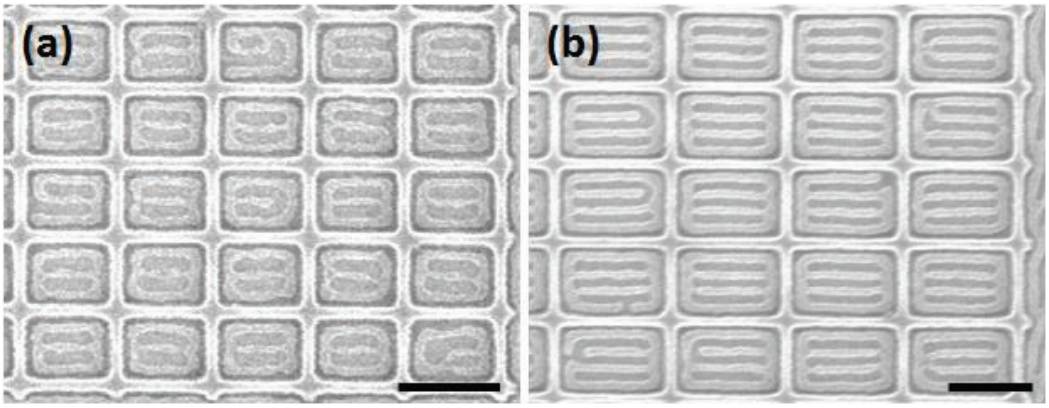

Figure 2: SEM images of PDMS microdomains confined inside a rectangular grid array. Width of the rectangular grid was (a) 160 nm; and (b) 250 nm. All scale bars are 200 nm in length. (a) The PDMS microdomains formed bar-shaped structures that were horizontally aligned. Two T-junctions were formed in each structure. (b) The bar-shaped structures were aligned horizontally and four T-junctions were formed in each structure. For both cases, the structures were aligned horizontally to reduce the number of T-junctions and therefore minimize free energy. Aspect ratio was (a) 1.3; and (b) 1.5.