Block Copolymer Self-Assembly Using Sacrificial Template

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Previous results have shown that a physical template can direct block copolymer (BCP) self-assembly. For these methods, templates were coated with a brush of the etch-resistant-block of the BCP (Figure 1-a), which results in patterns with a well-defined geometry at high-throughput[1], but suffers from the incorporation of the templating features into the final functional patterns. This approach can also lead to nonuniformity in the final pattern geometry, for example, in the fabrication of gratings, localized fluctuations in line-width are present (Figure 1-a, step 3). Furthermore, the dissimilar etch rates between the BCP and the template pattern causes nonuniform pattern transfer (Figure 1-a, step 4). In this study we solved these problems by used a sacrificial template, which was coated with a brush of the etchable-block of the BCP. This gives better linewidth control of the templated microdomains of the etch-resistant block. In addition, the sacrificial template was removed along with the etchable-block during the etching process; so it does not form part of the final pattern and differences in etch rates are therefore not an issue.

The major steps of the process are shown and described in Figure 1-b. In the first step, arrays of poly(methylmethacrylate) (PMMA) posts were fabricated using electron beam lithography (EBL) on a silicon substrate. To fabricate the post array template, high dot doses were delivered to the PMMA resist and results similar to a negative-tone resist[2] were achieved. After development, ultrasonication in acetone was used to remove the unexposed PMMA resist. We then coated the patterns with hydroxyl-terminated polystyrene (PS) brush (1 kg mol^{-1}). In the second step, a polystyrene-b-polydimethylsiloxane (PS-b-PDMS) BCP (MW=45.5 kg mol^{-1} and f_PDMS=0.32) was spin-coated onto the substrates. Afterwards, we used a mixture of heptane and toluene to solvent-anneal the BCP. Reactive ion etch (RIE) was used to remove both the PS matrix and the PMMA template and leave the oxidized-PDMS (ox-PDMS) patterns on the substrate. Then, the ox-PDMS pattern could be transferred into the substrate.

Figures 2 and 3 show scanning electron microscopy (SEM) images of the results of the process, in which the template patterns were removed during RIE. In Figure 2 uniform cylinder gratings were self-assembled with different orientation. The orientation of the gratings depends on the post periodicity compared to the BCP equilibrium period as was shown in previous work[1]. Figure 3 shows the results of using an incommensurate post spacing, leading to a morphology change of the PDMS microdomains from cylinders to a perforated lamella consisting of a close-packed array of holes.

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[1] Yang, J. K. W. et al. Nature Nanotechnology **5,** 256-260 (2010).
[2] Duan H. et al. Journal of Vacuum Science and Technology B 28 C6C58-C6C62 (2010)

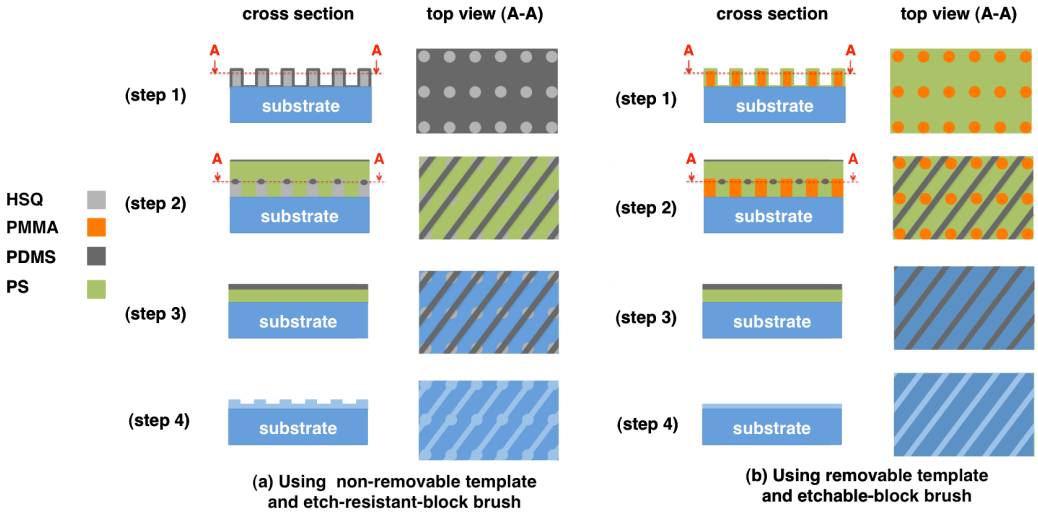

Figure 1: Schematic of the major steps of the method for the directed self-assembly using (a) a non-removable template with an etch-resistant-block brush and (b) a removable template with an etchable-block brush, (step 1) fabrication of the templates using EBL of a HSQ or PMMA resist and functionalizing the templates with a PDMS or PS brush, (step 2) spin coating and annealing of the BCP, (step 3) removing the PS matrix and the PMMA template using oxygen RIE, (step 4) transferring the pattern into a desired substrate through directional etching.

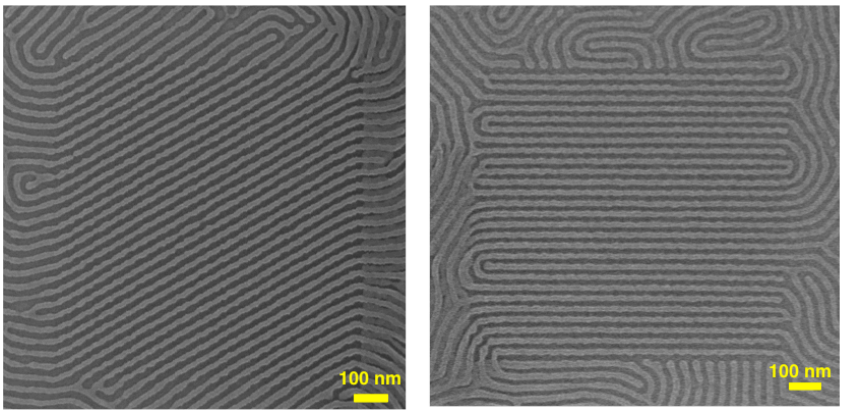

Figure 2: SEM image of the ox-PDMS gratings guided by a sacrificial template. Different directions of gratings can be achieved depending on the periodicity of the template posts. The bright grey color represents ox-PDMS gratings remaining after RIE.

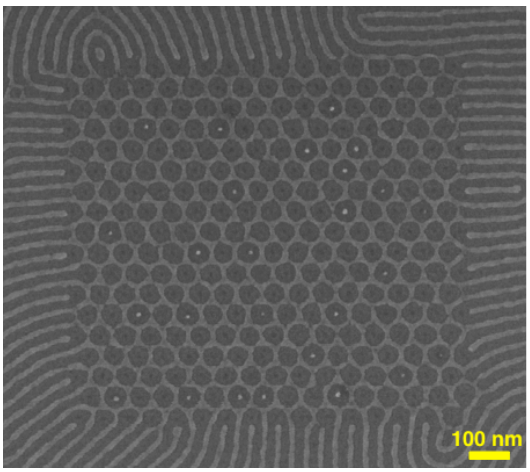

Figure 3: SEM image of the ox-PDMS microdomains formed by changing the morphology of the BCP from cylinder to perforated lamella and using a sacrificial template. A hexagonal lattice of nanoholes formed inside the template whereas cylindrical PDMS microdomains formed outside the template. The bright grey color represents ox-PDMS gratings remaining after RIE. A few white dots represent incompletely removed PMMA posts.