High throughput sub-10-nm fabrication based on templated self-assembly of block copolymer

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Templated self-assembly of block copolymers using topographical templates to produce dense nanoscale patterns is attractive because of its scalability and high throughput. The pitch of a block copolymer can be scaled down by decreasing its molecular weight and the throughput can be increased by decreasing the density of the topographical templates. In our previous work, high throughput sub-20-nm patterns were achieved based on sparse templates using 45.5kg/mol polystyrene polydimethylsiloxane (PS-PDMS) block copolymer¹.

Here, we demonstrate high throughput sub-10-nm feature sizes by applying the same approach to a cylindrical morphology 16kg/mol PS-PDMS block copolymer. The half-pitch of the PDMS cylinders of this block copolymer film is 9 nm, so sub-10-nm structures can be fabricated (figure 1a).

We first demonstrated that the orientation of the PDMS cylinders can be controlled by topographical templates. To control the orientation of 9 nm halfpitch PDMS cylinders, a rectangular lattice of posts with height of 19 nm and diameter of 8 nm and period L_x and L_y was fabricated on silicon substrate by electron-beam exposure of hydrogen silsesquioxane (HSQ) resist (figure 1b). The surface of the template and substrate were coated by short-chain hydroxylterminated 0.9kg/mol PDMS homopolymer. PS-PDMS block copolymer solution was spin-coated onto the substrate and annealed in acetone vapor. After that the PS microdomains were selectively removed by oxygen reactive ion etching (RIE) leaving oxidized PDMS features. The block copolymer film annealed on an unpatterned substrate resulted in 18-nm-pitch (L₀) PDMS cylinders without longrange order (figure 1a). When the same block copolymer film was annealed on templates satisfying the commensurate condition $(1/L_o^2 = \alpha^2/L_x^2 + \beta^2/L_y^2)$, where α and β are integers), PDMS cylinders formed a long-range ordered region in which the angle between the PDMS cylinders and the x-axis was given by $atan(\alpha L_v/\beta L_x)$. By varying the two lattice parameters L_x and L_y , a broad range of block copolymer lattice orientation angles was achieved (figure 2).

On a lattice with L_x larger than 72 nm, PDMS cylinders lost long-range order (figure 3a) because the energy barrier between two cylinder orientations is smaller than 0.01kT and can be easily overcome by thermal fluctuations (figure 3b). To further decrease the density of the templates and therefore increase the throughput without losing long-range order, a sparse lattice of triple-posts was tested. As a result, a region of well-aligned PDMS cylinders with width of 750nm was achieved (figure 3c). The template posts occupy only 1/70 of the final PDMS line pattern. This result suggests that if instead of writing the complete pattern, electron-beam lithography is used to create post arrays and the pattern is then completed by a block copolymer, the throughput of electron beam lithography could be increased dramatically.

¹ J. K. W. Yang, et al., Nature Nanotech., **5**, 256 (2010).



Figure 1. Scanning electron microscope (SEM) images (a) untemplated 16kg/mol PS-PDMS block copolymer film after PS matrix is removed by RIE (b) a template consisting of single posts with height of 19 nm and diameter of 8 nm.



Figure 2. (a)~(l) SEM images of PS-PDMS block copolymer films templated by rectangular lattices of single-posts. Gray lines are PDMS cylinders after the PS matrix is removed by RIE and white dots are the HSQ posts. Arrows indicate the direction of the PDMS cylinders. Each figure is annotated L_x , L_y ($\alpha \beta$). Scale bar = 100 nm.



Figure 3. (a) SEM image of PDMS cylinders templated by a rectangular lattice with L_x of 81 nm. The lattice satisfies the commensurate condition different orientations coexist. (b) Free energy per polymer chain for each orientation ($\alpha \beta$) as a function of L_x . L_y changes depending on L_x with $L_x/L_y=1.5$. Each color represents a different orientation. At L_x of 81 nm, the free energy barrier between (0 3) and (1 3) is 0.002kT. This is much smaller than the energy barrier at L_x of 72 nm (0.013kT). (c) SEM image of 750-nm-width region with a single orientation templated by a lattice of triple-posts.