Directed assembly of cylinder-forming ternary blend of block copolymer and their respective homopolymers on chemical patterns with density multiplication of features

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The underlying motives for pursuing directed assembly of block copolymers for patterning are resolution enhancement and precise control over the shapes and dimensions of patterned features. Chemically nanopatterned substrates may be prepared by advanced lithographic tools and utilized to create useful, well-defined nanostructures, with both registration and a high degree of order in block copolymer films upon equilibration. In comparing the lithographically defined pre-patterns to the assembled structures in the overlying block copolymer film, the resolution may be enhanced by factors of four or more, and the dimensional uniformity and control of features size and shape may be significantly improved. Previously we have also shown that blending homopolymer with a block copolymer can facilitate the assembly of non-regular, device-oriented patterns. We anticipate that for some applications in which patterns of regular and non-regular features are required, it may be advantageous to assemble blended materials. Here we investigate directed assembly of a cylinder-forming ternary blend of block copolymer and their respective homopolymers on lithographically defined chemical patterns with density multiplication. Specifically, we extend the implications of using blended material in lieu of pure block copolymer on the desirable patterning attributes of directed assembly in terms of improved critical dimension control and enhanced resolution.

Figure 1 shows schematics of our experimental approach. We deposit polystyrene-*random*-poly(methyl methacrylate) (PS-*ran*-PMMA) brush on silicon wafer as an imaging layer. The brush is non-preferentially wet by the blocks of the copolymer. Resist on the top of the imaging layer is patterned using e-beam lithography to create hexagonal and rectangular spot arrays. Areas unprotected by the resist are exposed to O_2 plasma. Residual resist is removed by rinsing with chlorobenzene. The exposure intensity during e-beam lithography was varied from 1000 to 6000 $\mu C/cm^2$ to vary the diameters (d_{spot}) of the patterned regions. The periodicity of the pattern (L_S) is 55nm. Spots are preferentially wet by the PMMA in neutral background. The ternary blend is coated on the patterns and assembled at 230°C for 12 hrs in vacuum. Cylinder-to-cylinder periodicity (L_0) and the cylinder diameter of the blend in a bulk state are ~55 nm and ~31nm, respectively. A hexagonal spot pattern was used to direct the blend with 1:1, assembled domains:patterned spots. A rectangular spot pattern was used to multiply the density as 2:1.

The assembled nanostructures on hexagonal spot patterns are well registered and have uniform size and shape at the top-surface of the films as in Figure 2. The dimensions of the assembled domains, as imaged top-down, remain constant (~ 31nm) on patterns with varying d_{spot} (data not shown).

The rectangular spot pattern has different periodicities in the *x*- and *y*-directions (L_{Sx}, L_{Sy}) as $L_{Sy} = \sqrt{3}L_{Sx}$ and $L_{Sx} = L_0$. The assembled structures (domains) in the blend film multiply the density of the features compared with the chemical pattern by a factor of two as shown in Figure 3A. The SEM images were taken from the edge of the patterns and we can easily distinguish the domains over the patterned and unpatterned areas. The diameters of the domains (d_{cyl}) at the top-surface of the films are different than the d_{spot} on the imaging layer. On the pattern with smaller d_{spot}, the d_{cyl} over the patterned spots is larger than d_{cyl} over the background area. In contrast, on the pattern with larger d_{spot}, the d_{cyl} over the patterned spots is smaller than d_{cyl} over the background area as in Figure 3B. From these results, we expect the shape of the domains to be truncated cones as indicated in the schematics. For the chemically patterned surfaces with intermediate size of d_{spot}, the d_{cyl} is close to the cylinder diameter of the blend in a bulk state over the patterned spots and over the background areas alike. Here we expect the domain diameter to remain relatively constant through out the thickness of the film.

As a conclusion, it has been shown that sizes and three-dimensional shapes of the nanostructures of block copolymer ternary blends through registration and density multiplication are regulated by the size of the patterned area, which is controlled by exposure intensity in the lithographic process. It should be noted that assembly of ternary blends, at least with high volume homopolymer fraction, does not have as large of a process window as assembly of pure block copolymer with respect to achieving uniform feature dimensions and shapes for assembly with density multiplication.

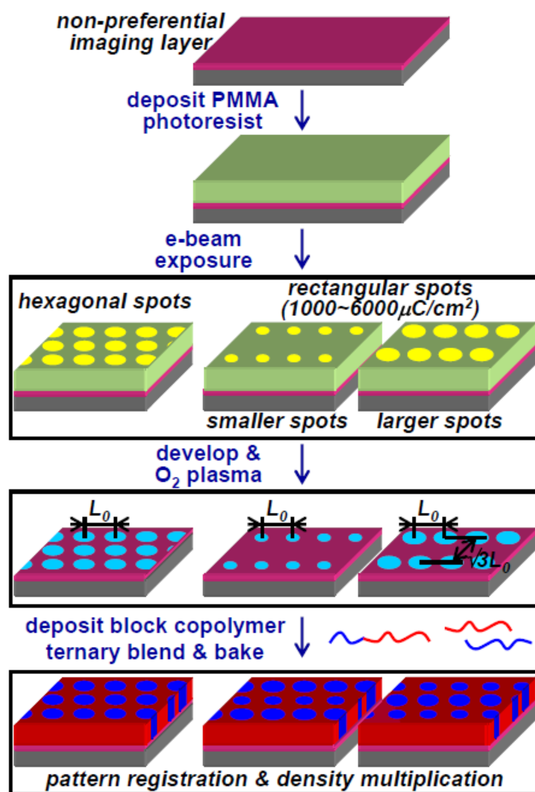

Figure 1. Schematics of hexagonal and rectangular chemical spot patterns and directed block copolymer ternary blend films with pattern registration and density multiplication.

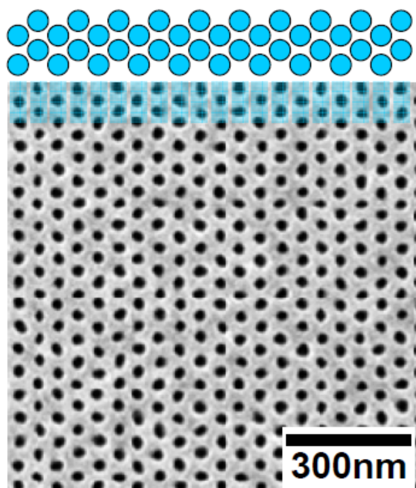

Figure 2. Top-down SEM image of the directed ternary blends on hexagonal chemical spot patterns after selective etching process for removing PMMA domains. The blue spots and blue area are the geometry and locations of the actual patterned spots.

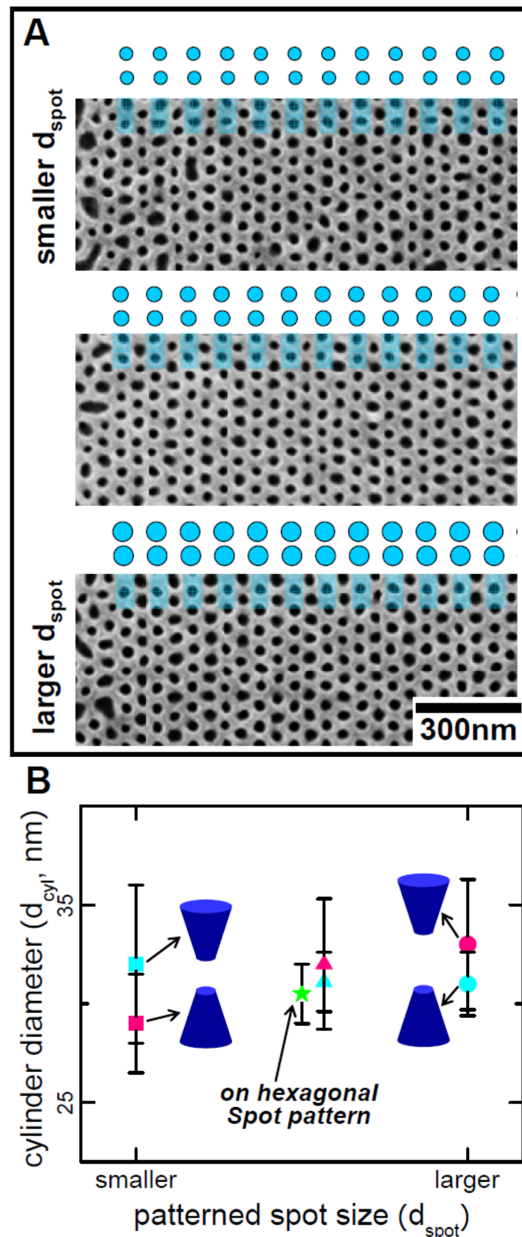

Figure 3. Top-down SEM images (A) and measured cylinder diameters at top-surface of the films (B) of the directed ternary blends on rectangular hexagonal chemical spot patterns. Blue symbols denote the size of the registered domains on the patterned area with different d_{spot} and pinks are on the imaging layer. Green star is for the assembled domains on hexagonal spot pattern for comparison.