Directed Assembly of Asymmetric Ternary Block Copolymer-Homopolymer Blends Thin Films into Checkerboard Trimming Chemical Pattern

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Block copolymers are of interest for lithographic applications due to their ability to self-assemble into spherical, cylindrical and lamellar morphologies with the characteristic length of less than 20nm.[1] Moreover, the self assembling materials can be directed to create well-defined nanostructures with perfection and registration by the minimization of interfacial energy between the components of material and a topographically or chemically patterned surface. [2,3,4] However, typical 2-dimensional projections of ordered block copolymer morphologies after assembly in thin films include periodic lines or hexagonal arrays of spots, and therefore may not be suitable for patterning even strictly periodic device-oriented arrays consisting, for example, of lines and spots, such as a checkerboard trimming pattern (dashed lines and, alternating lines and dashed lines) used in the fabrication of dynamic random access memory (DRAM).[5]

Here we show the asymmetric ternary polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA)/homopolymer PS/homopolymer PMMA blends can be directed to assembly on checkerboard trimming chemical patterns. The checkerboard trimming patterns was fabricated by e-beam lithography with control of the periodicity (L_S), length (D) and spacing (S) of the exposed lines or dashed lines, as defined in Fig. 1.

The degree of perfection and domain uniformity of the assembled block copolymer thin films was quantified as a function of overall composition of PS (φ_S) or PMMA (φ_M) and total homopolymer fraction (φ_H) in the blends, and the pattern area fractions (a_S is the area fraction of the pattern preferentially wet by PS) of chemical pattern surface. Fig. 1 shows the best results and SEM images that we obtained using an asymmetric blend with φ_S=0.43 and φ_H=0.29 on various chemical patterns. In contrast in Fig. 2, the blends have similar φ_S, but the assembled morphologies were not registered because the φ_H is too low (φ_H=0.19) or too high (φ_H=0.40). Moreover, Fig. 3 shows that a_S should be commensurate with φ_S. The chemical pattern in Fig. 2 and 3 is same as the pattern of Fig. 1A. By matching polymer volume fractions (φ_S or φ_M, and φ_H) and a_S, blends composed of lamellae-forming block copolymer and substantially asymmetric fractions of the two homopolymers could be assembled into the desired equilibrated line and dash morphologies.

[1] F. S. Bates, and G. H. Fredrickson, Annual Review of Physical Chemistry **41**, 525 (1990).
[2] S. O. Kim *et al.*, Nature **424**, 411 (2003).
[3] M. P. Stoykovich *et al.*, Science **308**, 1442 (2005).
[4] M. P. Stoykovich *et al.*, ACS Nano **1**, 168 (2007).
[5] M. Fritze *et al.*, Journal of Vacuum Science & Technology B **23**, 2743 (2005).

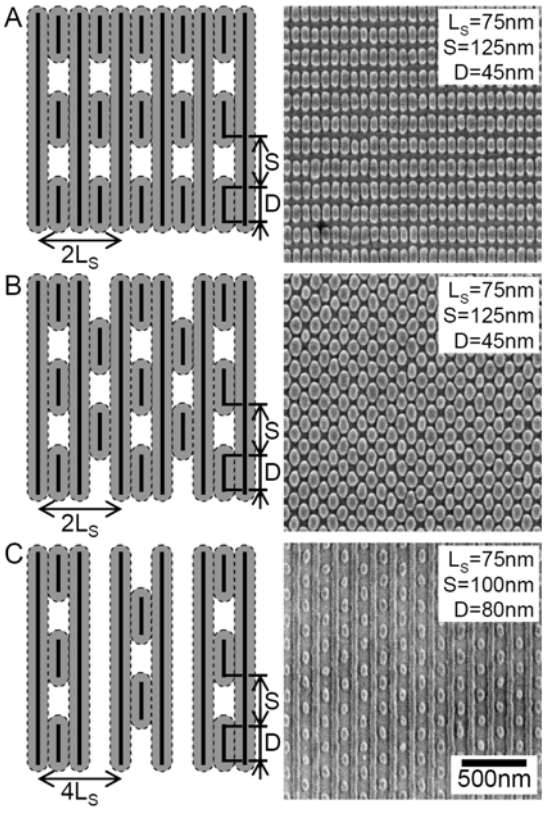

Figure 1.
Schematics of checkerboard trimming pattern and top-down SEM images of directly assembled asymmetric PS-b-PMMA/PS/PMMA blend thin films of 0.70/0.05/0.25 (φ_S=*0.43,* φ_H=*0.29*) as a *volume fraction* on dashed lines (A), zigzag dashed lines (B) and, alternating lines and dashed lines (C). On schematics, the solid lines are actual e-beam writing and gray region represents exposed region by proximity effect with electron transport on the substrate, and the exposed regions are preferentially wetted by PMMA. The bright region on SEM is PS domains and the dark is PMMA.

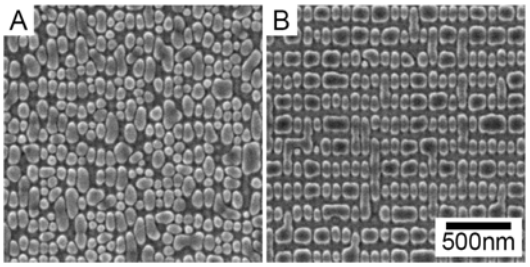

Figure 2.
Top-down SEM images of directly assembled asymmetric PS-b-PMMA/PS/PMMA blend thin films of 0.80/0.00/0.20 (φ_S=*0.42,* φ_H=*0.19* and A) and 0.60/0.10/0.30 (φ_S=*0.44,* φ_H=*0.40* and B) on dashed line pattern (Fig. 1A).

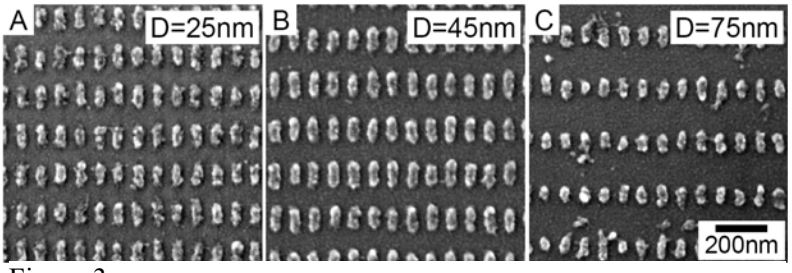

Figure 3.
Top-down SEM images of PMMA removed directly assembled asymmetric PS-b-PMMA/PS/PMMA blend thin films of 0.70/0.05/0.25 on dashed line pattern with controlled D length as 25 nm (a_S=*0.47* and A), 45 nm (a_S=*0.41* and B) and 75 nm (a_S=*0.36* and C).