Investigation of Templated Self-assembly of High-χ Diblock Copolymer

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Development of highly-ordered, defect-free, and tens-of-nanometers patterns through directed self-assembly (DSA) is an exciting approach for next-generation integrated chip production. DSA of block copolymers (BCP) with a higher Flory-Huggins Interaction Parameter (χ) allows for lower Degree of Polymerization (N) and therefore smaller natural BCP pitch (L_0)[1]. The use of hydrogen silsesquioxane (HSQ)-post templates for graphoepitaxy of BCPs has been previously reported[2,3]. An increased χ is expected to allow the development of small, ordered, and defect-free nanopatterns. We investigated a new BCP system with a high χ and the effects of HSQ-post templates on the DSA of this BCP system.

A lamellar-morphology BCP composed of surface-energy-dissimilar blocks was synthesized*. L_0 was determined to be 30 to 45 nm for a variety of molecular weights (or N). It exhibited a roughly $L_0 \propto N$ dependence, in contrast to $L_0 \propto N^{2/3}$, and requires more investigation[4]. A variety of thermal annealing conditions were tested. High-energy hydroxylated native silica was determined to be a neutral surface for perpendicular lamellar assembly[5]. The annealing temperature for the highest coherence length was determined to be 160°C. Example micrographs of annealed thin films for each MW are shown in Figure 1. HSQ-post templates were fabricated with electron-beam-lithography to direct the self-assembly of the BCPs. Square arrays of posts at pitches near or less than L_0 qualitatively directed the BCP self-assembly to higher linear order, as shown in Figure 2. Furthermore, templates with pitches constrained in a single orthogonal direction (and varied in the other) can direct the BCP as shown in Figure 3. We have preliminarily determined that both of the chemically-dissimilar blocks are nearly equally attracted to the templating posts, which contrasts previous graphoepitaxy results. These findings provide the opportunity to develop a novel and complex template scheme for the direction of high-χ BCPs.

*full chemical names withheld due to patent pending activity

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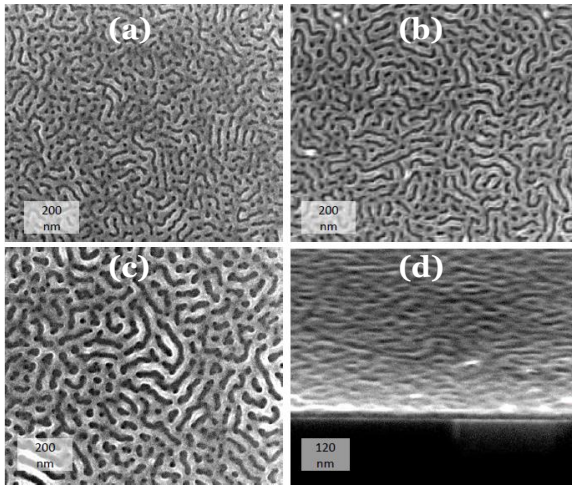

Figure 1: Thin Films of Disordered BCPs: (a-c) Scanning-electron-micrographs of different molecular weight BCPs, low to high from (a)to (c). Notice the associated increasing L_0. For imaging purposes, one of the polymer blocks has been removed and the images histogram contrast-stretched. (d) A side view of the BCP in (c) where the perpendicular phase is more obvious.

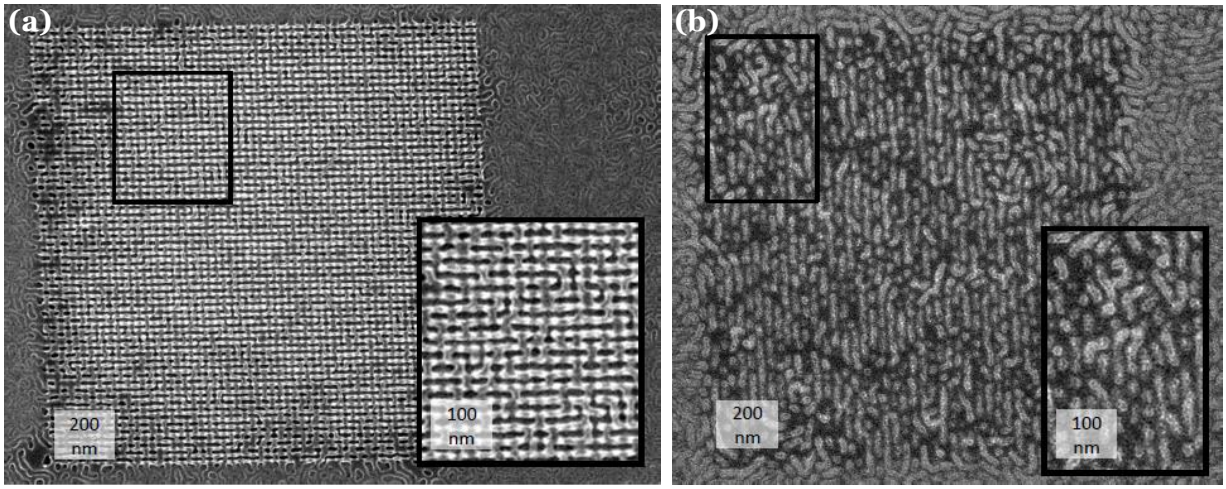

Figure 2: BCP TSA in Linear Direction: Scanning-electron-micrographs of the higher MW BCP directed in different directions through different templates and thicknesses. (a) HSQ posts in a 32-nm square array were used to template a 28-nm thick BCP thin film. Notice the orthogonality of the BCP whithin the template. (b) HSQ posts in a 40-nm square array were used to template a 24-nm thick BCP thin film. Notice the y-direction trend within the template. Inset is a zoom-in of template area.

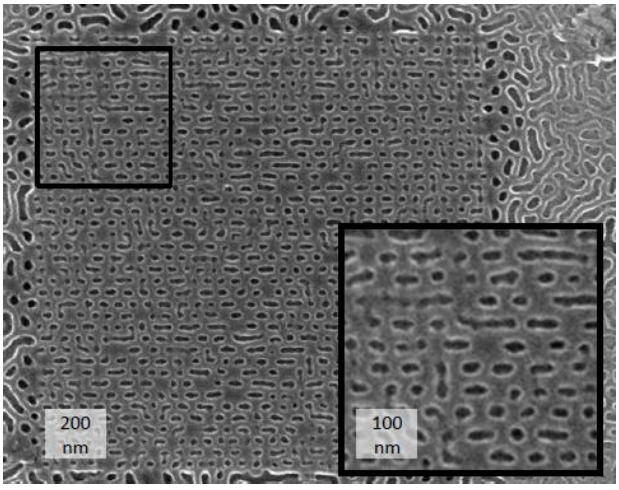

Figure 3: Voids Ordered in X-Direction: Scanning-electron-micrographs of directed self-assembly of the higher MW BCP. HSQ posts in a 30 x 36-nm pitch array were used to template a 28-nm thick BCP thin film. The smaller post pitch in the x-direction constrains the darker voids (lack of one of the polymer blocks) to align generally in the x-direction. The darker voids are not generally aligned in the y-direction. Inset is a zoom-in of template area.