

# Combining Advanced Lithographic Techniques and Self-Assembly of Thin Films of Diblock Copolymers to Produce Templates for Nanofabrication

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We are developing techniques to nanopattern substrates with regions of different wetting behavior using advanced lithography (proximity x-ray and extreme ultra violet) and to use these substrates to control the morphology of thin films of block copolymers over macroscopic dimensions. Block copolymers have tremendous potential for applications in nanofabrication because these systems generally microphase separate to form periodic structures (spheres, cylinders, or lamellae) with domains with length scales of 10 nm to 100 nm. For example, thin films of block copolymers may be used for optical devices, membranes, and templates for nanolithography.[1] One strategy to use thin films of block copolymers as nanolithographic templates involves inducing lamellae to form perpendicular to the substrate with controlled orientation in the plane of the film by nanopatterning substrates with alternating regions that are wet by the different blocks of the copolymer (Fig. 1).

Using a combination of Monte Carlo simulations and phenomenological models, we have quantitatively calculated phase diagrams (Fig. 2) of the morphology of thin films as a function of the boundary conditions. If the periodicity of the pattern on the substrate is commensurate with the bulk lamellar spacing of the polymer, and the top confining surface is neutral, then lamellae form perpendicular to the substrate, amplifying the pattern on the substrate throughout the film thickness and over macroscopic dimensions in the plane of the film.

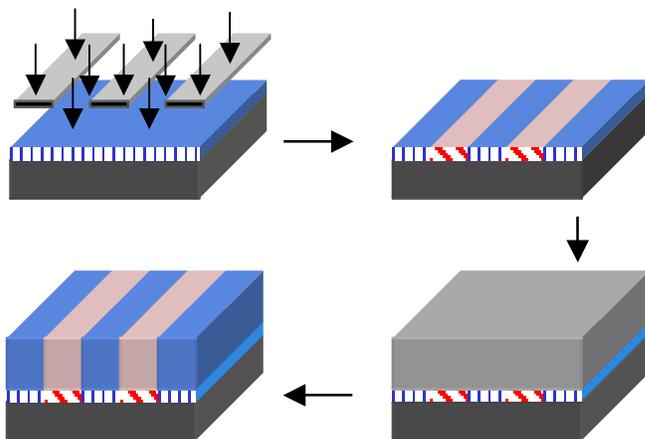
The phase diagram in Figure 2 requires chemically heterogeneous surfaces with periods commensurate with the bulk lamellar period of the diblock copolymer. To implement our strategy experimentally, x-ray and extreme ultra violet lithography are two possible candidates for nanopatterning surfaces at this scale. We developed an imaging layer for producing nanopatterned surfaces based on self-assembled monolayers (SAMs). The surface chemistry of SAMs of alkylsiloxanes on  $\text{SiO}_x$  was modified by exposure to proximity x-rays and extreme ultra violet radiation in the presence of air. The concentration of surface-grafted hydroxyl and aldehyde groups on exposed SAMs increased with increasing dose. The wetting behavior of thin films of poly(styrene-*b*-methylmethacrylate) (P(S-*b*-MMA)) on these chemically modified surfaces depended on the exposure dose. We tuned the surfaces such that dewetting, symmetric, neutral, and asymmetric wetting were observed with increasing dose (Fig. 3).

Chemically patterned surfaces were created by exposing the SAMs to proximity x-rays through a mask or to extreme ultra violet radiation using an interferometric mirror system. The behavior of thin films of P(S-*b*-MMA) on chemically patterned surfaces was investigated as a function of film thickness, surface energy (dose), and pattern dimensions (Fig. 4).

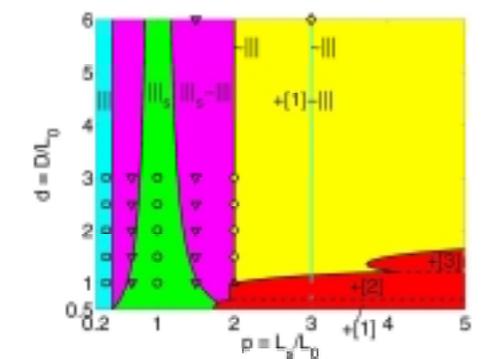
1. Park *et al.*, Science **276**, 1401 (1997).

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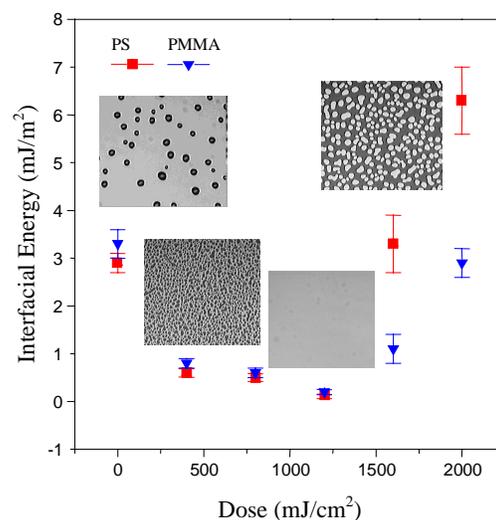
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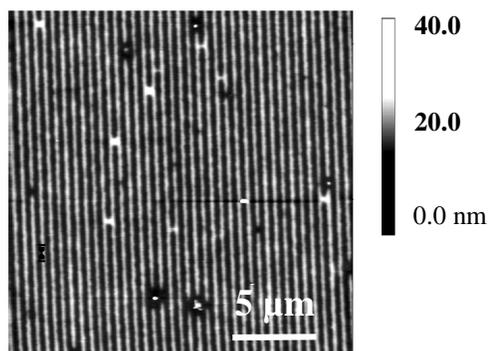
**Fig. 1.** Schematic of strategy to induce macroscopic orientation in thin films of symmetric diblock copolymers. (A) Expose imaging layer to radiation through a mask to create chemically heterogeneous substrate (B); (C) Deposit block copolymer film; (D) Macroscopically oriented lamellae after annealing.



**Fig. 2.** Phase diagram of block copolymer behavior on chemically heterogeneous substrates. X-axis is ratio of substrate pattern period to bulk lamellar period, and y-axis is reduced thickness. Perpendicular lamellae follow the substrate pattern for all thickness when  $L_s/L_0 = 1$  ( $|||_s$  region).



**Fig. 3.** Plot of interfacial energy vs. exposure dose for homopolymers of PS and PMMA on SAMs exposed to x-rays at 1 Torr of air pressure. The insets show the change in topography of the films on substrates with different surface energy that is characteristic of a change in the wetting behavior of the copolymer films.



**Fig. 4.** AFM image of film of P(S-*b*-MMA) deposited on chemically heterogeneous surface. The linewidth is 150 nm and the pitch is 600 nm. The step height is approximately 15 nm.