In-Situ Characterization of Block Copolymer Density Multiplication on Chemically Patterned Surfaces by Coherent Small Angle X-ray Scattering

Guoliang Liu, Sean Delcambre, Karl Stuen, Gordon S. W. Craig, Juan J. de Pablo, and Paul F. Nealey*

Department of Chemical and Biological Engineering, University of Wisconsin, Madison, Wisconsin 53706

K. Nygård, D. K. Satapathy, O. Bunk, H. H. Solak, and J. F. van der Veen

Department of Synchrotron Radiation and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Directed assembly of block copolymers and block copolymers blends is shown to be an attractive means of fabricating patterned template with dimensions of 5-50 nm for a variety of applications including microelectronics and magnetic data storage media. Block copolymer patterns from directed assembly has many advantageous features, such as the registration to the underlying substrate, high degree of perfection, and improved line edge roughness (LER) and critical dimension (CD) control. [1-6] Additionally, device-oriented geometries, including bends, jogs, terminations, and junctions, can be formed via the directed assembly process.[7-10] Recent developments of the density multiplication of block copolymers on chemically patterned surfaces have shown that the resolution of patterned template can be enhanced and the feature dimensions can be shrunk to sub-30 nm.[4, 11-14] Yet the mechanism and the principles that determine the quality of density multiplication of block copolymers on patterned substrates are still unknown.

In this work, we used *in situ* coherent small angle x-ray scattering to monitor and characterize the assembly of block copolymers domains on chemically patterned surfaces designed specifically for pattern density multiplication. A 50-nm-thick film of polystyrene-*block*-poly(methyl methacrylate) (natural period L_o=50 nm) on a striped chemical pattern (pattern period L_s= 100 nm) was annealed at 240 ^{o}C. Small angle x-ray scattering in transmission mode was used to monitor the annealing process in real time. As shown in Figure 1, the directed assembly of block copolymers on chemical patterns with $L_s = 2\ L_o$ occurred in three distinct stages: (I) microphase separation of block copolymer domains on the patterned stripes into its natural period (without a scattering peak at L_s), (II) registration of block copolymers on patterned stripes to the pattern period (with a scattering peak at L_s), and (III) assembly of block copolymer to its natural period, resulting in pattern density multiplication, and registration with the chemical pattern (without a scattering peak at L_s). The appearance and disappearance of the scattering peak at L_s showed that the behavior of the block copolymer on chemical patterns designed for density multiplication was different from that of block copolymers directed to assemble one-to-one chemical patterns (L_s=L_o).

The morphology of the block copolymer with longer annealing times is shown in the scanning electron microscope images in Figure 2. After 1 h of annealing, the block copolymer formed microphase separated small domains on the free surface at the beginning. These domains gradually grew together to form longer, disordered lamellae. With increasing time, these small lamellar domains grew larger and eventually formed defect-free lamellae over large areas. The growth and ordering of the lamellae domain was compared with molecular simulations, with good agreement. These interesting phenomena of block copolymer density multiplication could offer better understanding of block copolymer behavior on chemically patterned surfaces and give insight for applications of directed assembly of block copolymers.

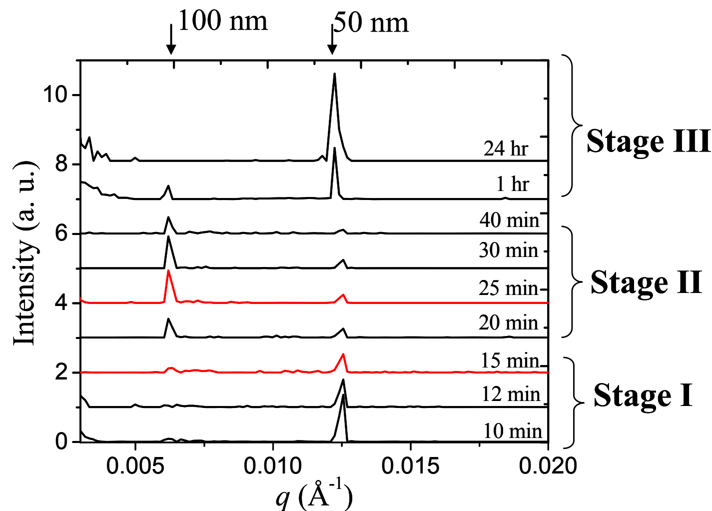

Figure 1. Coherent small angle x-ray scattering (cSAXS) spectra of PS-*b*-PMMA density multiplication on chemically patterned surfaces with various annealing time. The spectra are offset for clarity. The annealing time is shown on the corresponding spectrum. The density multiplication can be delineated into three stages according to the existence of the scattering peak at 100 nm.

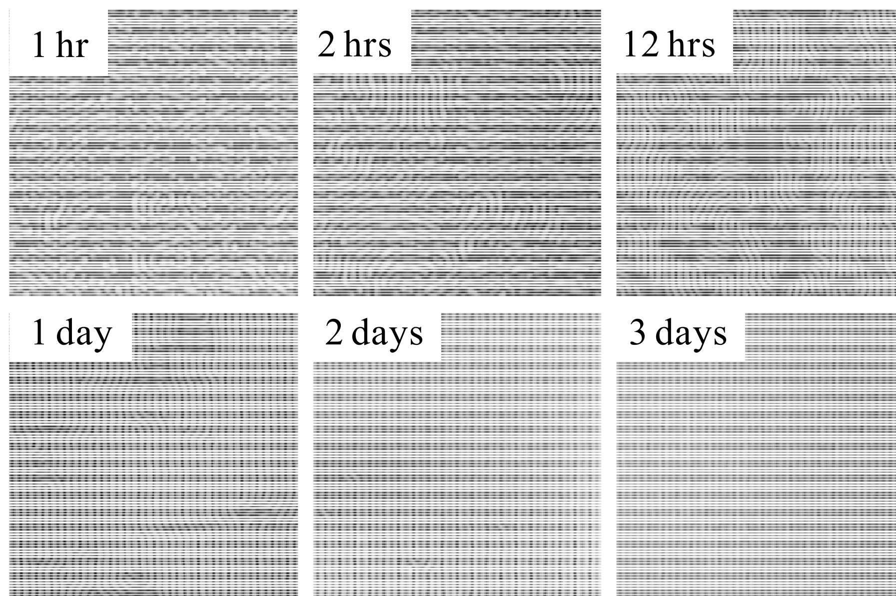

Figure 2. Plan-view scanning electron microscopy images of PS-*b*-PMMA density multiplication on chemically patterned surfaces for various times. The chemically patterned stripes on PS brushes run vertically from top to bottom in the images. The natural period of block copolymer, L_o=48.4 nm, and the pattern period, L_s=100 nm≈2L_o. Polystyrene appears light and PMMA appears dark. Each image represents an area of 2μm by 2μm.

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