In Situ Characterization of Block Copolymer Ordering on Chemically Nanopatterned Surfaces by Time-Resolved SAXS

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Improving the lithographic process for microelectronic manufacturing is a considerable challenge, since the techniques to fabricate low-cost sub-30 nm features with low line-edge roughness and good critical dimension (CD) control remain elusive. One alternative to conventional lithography is the directed assembly of block copolymers on chemically patterned surfaces,[1,2] in which the thermodynamics of a block copolymer film governs the dimensions and uniformity of the pattern. The block copolymer annealing process has not been fully characterized or optimized. Previous kinetic investigations have been limited to time-point experiments and metrology such as SEM that only images the top surface of the film.[3] Here we characterize the ordering process in real-time and throughout the thickness of the film using small-angle x-ray scattering (SAXS).

A PS brush was patterned using x-ray interference lithography, as previously reported,[4] to fabricate stripes of alternating surface chemistry with 100 nm pitch (Figure 1). A ternary block copolymer blend (PS-b-PMMA + PS + PMMA) with a natural period of ~ 100 nm was spincoated onto the patterned PS brush. The film was then annealed on a heating stage while x-ray scattering data was collected. Our experimental setup had a number of characteristics that made the experiment possible (Figure 2). The cSAXS line at the Swiss Light Source provided a bright x-ray beam and a state-of-the-art, fast, single-photon counting PILATUS x-ray detector to give us a sufficient signal-to-noise ratio.

The intensity of scattered light varied dramatically as a function of annealing time and temperature, following the annealing process of the block copolymer film[3] (Figure 3). The scattered intensity first decreased, then increased to a maximum and finally decayed slightly. The sample initially produced a small scattering intensity due to the thin layer of block copolymer that wets the chemical pattern after spincoating (Fig. 4(A)). The decrease in intensity up to 150 s can be attributed to the formation of a transient morphology, where the blocks at the free surface and at the substrate at a given point are opposite, attenuating the signal (Fig. 4(B)). At 300 s the intensity reached a maximum, indicating the formation of assembled lamellae (Fig. 4(C)). For times greater than 600 s, the signal decayed, possibly due to x-ray damage and oxidation of the film. The scattering signal could only be observed on the striped chemical pattern over which vertically oriented lamellae formed grating structures and not from unordered vertically oriented lamellae. These results provided insight into the mechanism of ordering and highlight a new technique that may inspire new annealing protocols to improve processing and reduce pattern defects.

[1] S. O. Kim et. al., Nature **424**, 411 (2003).
[2] Stoykovich et. al., ACS Nano **1**, 168 (2007).
[3] Edwards et. al., J Poly Sci B **43**, 3444 (2005).
[4] Edwards et. al., Adv Mat **16**, 1315 (2004).

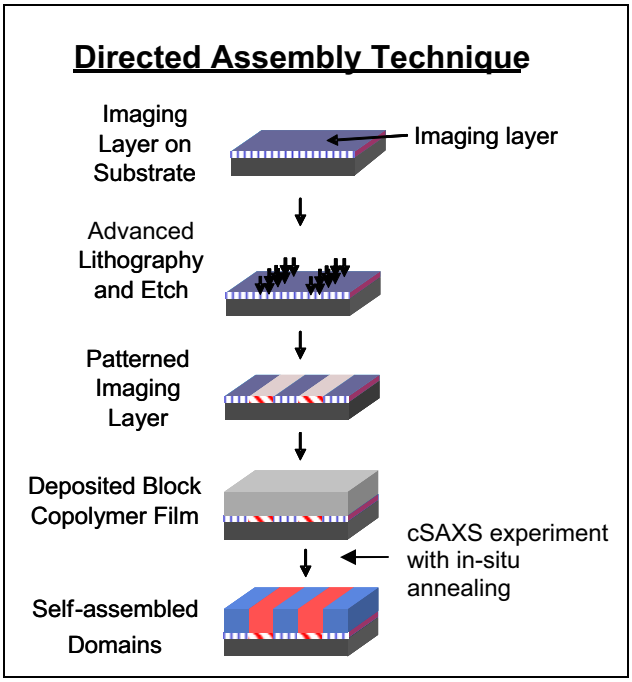

Figure 1. The directed assembly of a block copolymer film on a chemically patterned surface. For this experiment the block copolymer was annealed in the cSAXS beamline.

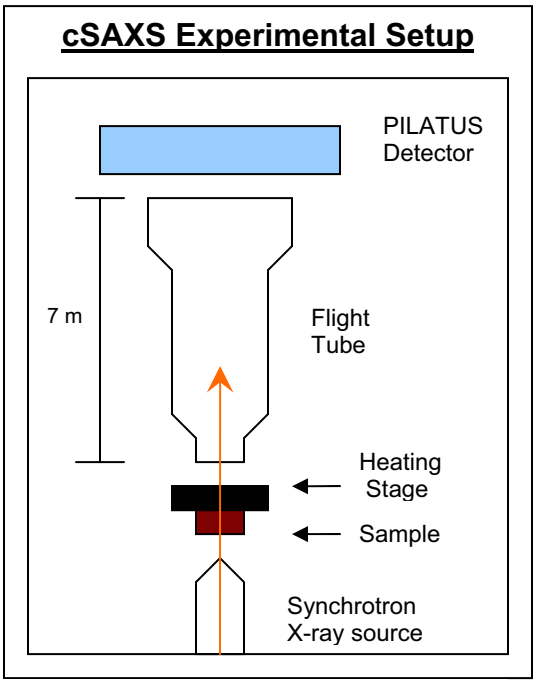

Figure 2. The cSAXS beamline at the SLS Synchrotron has a number of unique features that make this experiment possible: a bright, stable x-ray source, a 7 m flight tube and a 2M pixel PILATUS detector.

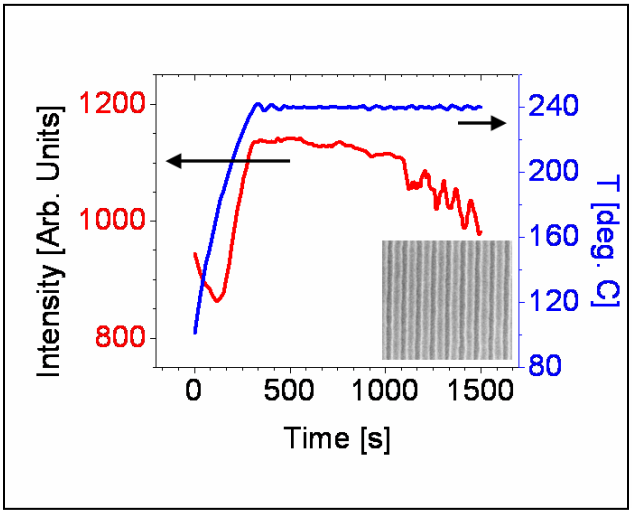

Figure 3. SAXS signal intensity over time for 100 nm pitch block copolymer pattern. Red line is intensity and blue line is stage temperature. Inset micrograph shows top-down SEM image of block copolymer after 1500 s.

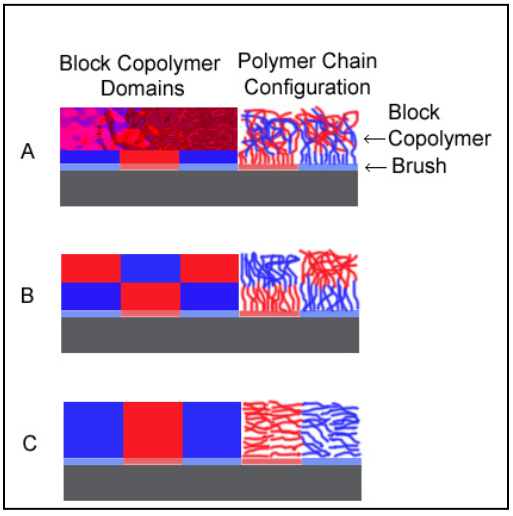

Figure 4. Schematic of block copolymer film cross section.[3] (A) Initially, a thin layer of block copolymer wets the pattern. (B) After a short time the opposite block goes to the free surface. (C) Final annealed structure.