

Post-Directed-Self-Assembly Membrane Fabrication for In-situ Analysis of Block Copolymer Structures

J. Ren, T. Segal-Peretz, P. Nealey

Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637
jxren@uchicago.edu

L. E. Ocola, R. Divan, D. A. Czaplewski

Center for Nanoscale Materials, Argonne National Lab, Lemont, IL 60439

Block polymers spontaneously form structures at the scale of 10 nm. Great efforts have been made to develop processes to direct the assembly of thin films of block polymers using lithographically defined pre-patterns to obtain levels of perfection in the structure that enable technological applications. Block copolymers are three dimensional in nature, and even in thin films the domain size and shape depend on the boundary conditions at the top surface and the patterned substrate. Surface characterization alone is inadequate to understand the complex assembly behaviors in block copolymer thin films and it is crucial to perform through-film analysis, such as resonant soft X-ray scattering and TEM tomography. Both require the polymer sample to be on thin membranes.

Conventional techniques for preparing polymer samples on membranes involve peeling off or floating off the block copolymer film from its original substrate and then transferring onto a membrane support. However, these processes inevitably damage the films and introduce undesirable artifacts. Alternative methods try to direct the assembly of block copolymer directly on pre-fabricated membranes, but the fragility and small size of membrane samples result in poor quality and reproducibility.

Here we developed a back etch process to prepare directed self-assembly of block copolymer thin films on silicon nitride membranes (Figure 1). Lithography and directed self-assembly is performed on 4" silicon wafers coated with silicon nitride on both sides. Front side nitride is pre-treated with oxygen plasma for polymer brush grafting, and the back side nitride is patterned to have 10 x 10 arrays of windows with cleave lines for separation. Only in the final step, the wafer, with the polymer side sealed-off by a holder, is immersed in KOH solution to back etch the silicon to get nitride membranes. The block copolymer is never subject to any additional processing beyond directed self-assembly and the structural details can be perfectly preserved. Working with a 4" wafer also allows us to systematically vary the pattern parameters on one sample but keep everything else the same. Membrane layout and substrate thickness can also be changed to cater to the specific requirement of TEM and X-ray scattering.

TEM tomography of directed self-assembly of PS-b-PMMA lamella with 3x density multiplication shows the evolution of defects through film thickness. Soft X-ray scattering of sphere-forming PS-b-PMMA shows the body-centered-cubic lattice formed by directed self-assembly of 3 layers of unit cells (Figure 2).

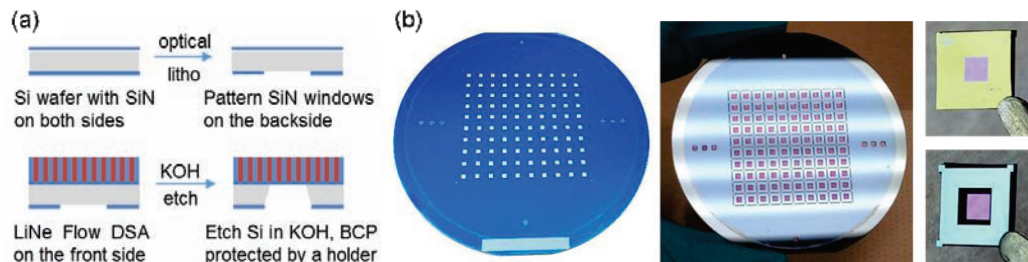


Figure 1: (a) Back etch process to prepare thin film of directed self-assembly of block copolymer on silicon nitride membrane. (b) 4" wafers and individual membranes after back etch

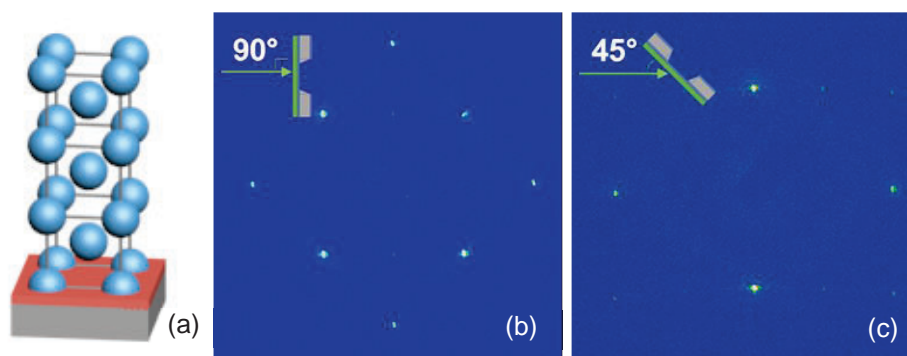


Figure 2: (a) Schematic showing directed self-assembly of sphere-forming PS-b-PMMA with 3 layers of unit cells in body-centered-cubic lattice. (b, c) Soft X-ray diffraction of the BCC assembly with incident angle of 90° (b) and 45° (c) respectively, perfectly matching crystallographic predictions.

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