PS-PMMA Block Copolymer Lithography for Sub-25 nm Periodic Features

CNF Fellows Project

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Website: https://confluence.cornell.edu/display/CNFUserWiki/Block+Copolymer+Resist

Primary CNF Tools Used: ABM contact aligner, Oxford 80s, PT72, ULTRA/SUPRA scanning electron microscope (SEM), Hummer Au/Pd sputtering system, PMMA spinners, vacuum ovens, wet chemistry

Abstract:

Nanolithography is a fundamental requirement for the future of electronics patterning. Current trends indicate the end of Moore's Law for traditional lithography processes. Directed self-assembly (DSA) of block copolymers (BCPs) can generate ordered, periodic arrays of various structures down to single nanometer (nm) size scale. The heterogeneous nature of these structures acts intrinsically as their own mask, enabling nm scale resolution with a flood exposure and no traditional photo mask. BCP lithography offers low-cost processing of nm scale periodic structures typically only available by e-beam lithography and can act as a complementary technology to conventional photolithography. In this work, we develop a PS-*b*-PMMA BCP lithography process on SiO_2/silicon using CNF labs and tools, achieving ~ 20 nm pattern resolution.

Summary of Research:

BCP lithography relies on the microphase separation of the two comprising polymers to achieve a nanoscale pattern. Due to the reliance on self-assembly, the resulting photolithographic features are intrinsically periodic. As such, this process is useful for applications in areas where long range repeating structures are needed, such as nano-porous substrates, nanoparticle synthesis, or high-density information storage media.

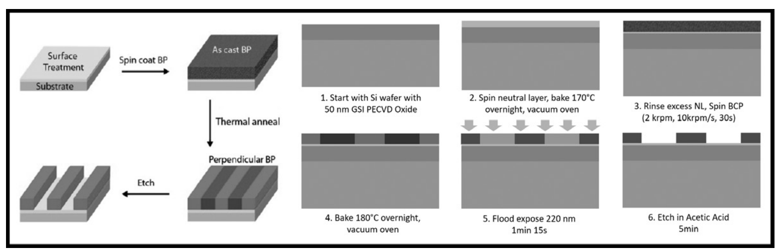

Figure 1: Left: Typical BCP lithography fabrication flow (adapted from [1]). Right: Fabrication flow for PS-b-PMMA BCP.

For the development of this method, we used a poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) *block* copolymer due to its popularity in literature, which stems from its excellent etch selectivity, low surface energy mismatch, and theoretical 12 nm feature size.

The typical fabrication flow for a BCP lithographic process is shown in Figure 1 (left) (adapted from [1]). First, a surface treatment is applied to create a neutral layer/brush. This prevents a surface parallel BCP domain orientation from occurring by making the substrate surface interfacial energy equal for both polymer phases. Next, the BCP is spin-coated and then thermally annealed allowing for phase separation and formation of the pattern. Finally, one phase is selectively removed, and subsequent substrate processing can occur from this point.

We used P9085-SMMAranOHT as our neutral layer and P8205-SMMA as our BCP (both obtained from Polymer Source). Our process flow follows that shown in Figure 1 (right), where the etch is accomplished using a 220 nm flood exposure followed by an acetic acid dip. Various polymer concentrations, film thickness, and anneal conditions were tested for their effect on pattern formation (morphology, uniformity, periodicity, etc.) and optimized. For detailed information and considerations, see the CNF User Wiki article [2]. Figure 2 shows SEM micrographs of the BCP at various points in fabrication for an approximately 25 nm thick film.

To quantify the effect of our parameter sweeps, it was necessary to develop an image processing technique that could quickly evaluate samples. We used ImageJ to develop two separate macros for; 1) measuring feature sizes and 2) evaluating inter-feature spacing. In our case, the BCP morphology is a hexagonal array of pores, so these methods were tuned to generate information on pore diameter and interpore spacing. The former was accomplished using built in ImageJ functions and the Particle Analysis tool. The latter is comprised of built in ImageJ functions along with an additional macro for K-Nearest Neighbor analysis that was expanded on from an existing implementation, as well as a custom Matlab script [3]. Again, the CNF Wiki Article has more detailed information and output examples of this image analysis.

Through this system of evaluation, we were able to achieve BCP films of 30 nm thickness with long range order. Pore sizes of ~ 23.12 nm with 1.78 nm standard deviation and interpore spacing of ~ 54.26 nm with 7.33 nm standard deviation and a circularity of ~ 0.92 were obtained. Figure 3 shows example SEM images of a typical sample. Using these films, pattern transfer through 50 to 100 nm of oxide has been achieved, as well as a subsequent Si etch (Figure 4).

In the future, we are working on various path forwards for BCP lithography implementation at the CNF. One path is further process tuning to reduce defects in the film and improve uniformity and periodicity. Beyond this, we are also looking into additional processing steps required to alter the BCP film morphology. We are working on a graphoepitaxy process that will result in parallelly aligned domains, rather than pores. Finally, we are also investigating other BCP systems for smaller features sizes (< 10 nm), such as PS-*b*-PDMS.

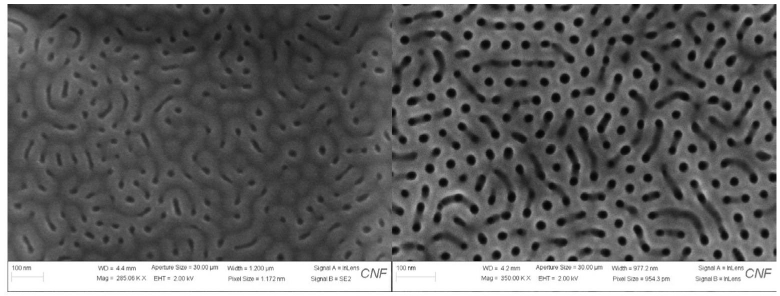

Figure 2: SEM micrographs of BCP film. Left: after annealing. Right: after etching. The increase in contrast comes from the removal of the PMMA phase in the pore regions after the etch.

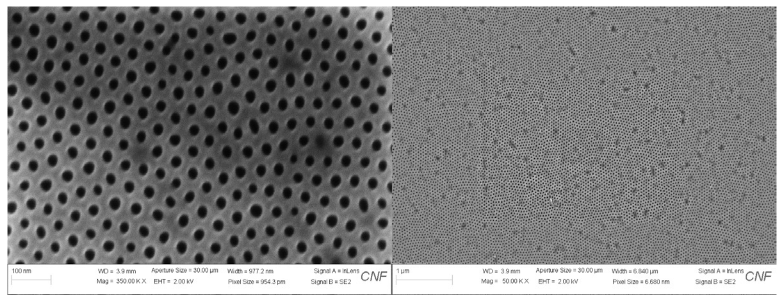

Figure 3: SEM micrographs of optimized BCP film. Left: 350kx magnification showing pore diameter and interpore spacing uniformity. Right: 50kx magnification showing long range order.

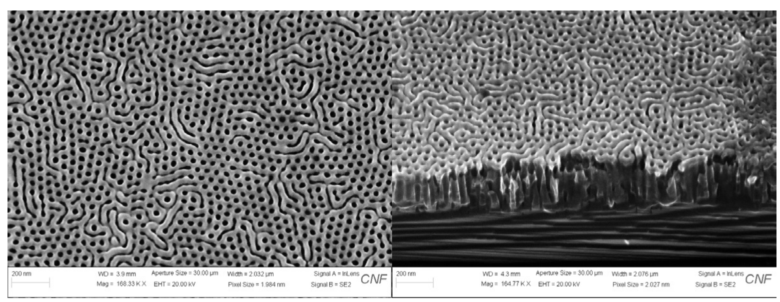

Figure 4: SEM micrograph of BCP on 50 nm of SiO_2 on Si after CH_2F_2/He and HBr/Ar etch. Left: Top down. Right: Cleaved, 45 degrees.

References:

[1] C.M. Bates, et al., Block Copolymer Lithography, Macromolecules, 2014, 47 (1), pp 1-12.

[2] Block Copolymer Resists, CNF User Wiki, Alexander Ruyack, https://confluence.cornell.edu/display/CNFUserWiki/Block+Copolymer+Resists.

[3] Burri, Olivier, 2D K Nearest Neighbors Python script, GitHub repository, https://gist.github.com/lacan/2643f2ce7e33d1bb07adafde9ff94101 (2017).