Diverse Patterns and Geometries in Self-Assembled Block Copolymer Thin Films Through Multilayer Mixing

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Materials

Abstract:

Lithography via the self-assembly of block copolymers is a promising tool for nanostructure fabrication on the order of 10 nm. Once assembled, one block of the copolymer can be selectively removed and metal can be deposited on the remaining pattern. This can be used to create structures such as metal nanodots and highly connected metal nanowire networks with varying periodicities. The morphology of the block copolymer self-assembly is dependent on the volume fraction of each block in the copolymer. A technique called multilayer mixing is presented, whereby we are able to change the morphology of block copolymer after the block copolymer has self-assembled, by increasing the volume fraction of one of the blocks. This is accomplished through spin casting a layer of homopolymer on top of it and solvent annealing the sample to let it reach the equilibrium morphology.

Figure 1: (a) All block copolymer is deposited on a silicon substrate (b), which is functionalized with a brush layer of PS-r-ePMMA. (c) Then, lamellar BCP is deposited on the brush via spin casting. (d) The block copolymer is then solvent annealed to form lamellae. (e) After annealing, PMMA homopolymer is deposited on top of the lamellae via spin casting and (f) the samples is solvent annealed once again, allowing the PMMA to mix with the lamellae ("multilayer mixing") to form cylinders.

Introduction:

Block copolymers (BCPs) are a class of macromolecules consisting of two chemically distinct, covalently bonded polymer chains. The BCP phase separates into regular patterns with structures on the order of 10 nm. These features have long range ordering, consistent across chips at least one square centimeter in size. The patterns formed through BCP self-assembly is dependent on the volume fraction of each block in BCP.

Materials and Methods:

A substrate with neutral preference for each block of the BCP was prepared by coating a silicon wafer with the random copolymer poly(styrene-r-methyl methacrylate-r-glycidyl methacrylate) $P(S_{0.58}\text{-r-}MMA_{0.41}\text{-r-}GMA_{0.01})$ brush layer, where the subscripts indicate the mole fraction of each monomer. Silicon wafers were purchased from Montco Silicon and rinsed with DI water, acetone, and toluene via spin casting prior to depositing the brush layer. The neutral substrate was then thermally annealed at 190°C for 60 min under vacuum, followed by sonication in toluene for 5 min and spin coating in toluene for 30 s at 5000 rpm.
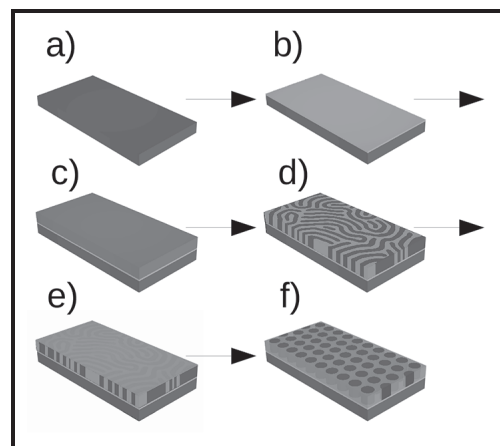
Lamellar forming poly(styrene-*b*-(methyl methacrylate-r-gylcidyl methacrylate), PS-*b*-(PMMA-r-GMA), was synthesized by sequential atom transfer radical polymerization of styrene (Sigma-Aldrich, 99%), methyl methacrylate (Acros, 99%), and glycidyl methacrylate (MP Biomedicals, 99%) as reported elsewhere [1]. All BCP samples were deposited via spin casting at 5000 rpm for 30 s. The BCPs were self-assembled through solvent vapor annealing in an even mixture of acetone and cyclohexane for 4 hr. The solvents were degassed in a 25 mTorr vacuum to remove any dissolved gases prior to solvent annealing.

Multilayer mixing was achieved by depositing a layer of PMMA homopolymer on the lamellar BCP after annealing. The PMMA homopolymer used for the multilayer mixing was purchased from Polymer Source (M.W. = 21.2 kg mol^{-1}, PDI = 1.07). Prior to deposition of this PMMA homopolymer, BCP samples were baked at 90°C for

30 min. The PMMA homopolymer was deposited via spin casting at 5000 rpm for 30 s. Samples were solvent annealed in the same conditions as the first solvent anneal. Samples were etched to improve image clarity (RIE, 160 mTorr oxygen plasma, 55W, 5 s).

Discussion:

Multilayer mixing was achieved as shown schematically in Figure 1. In essence, the method allowed the equilibrium morphology of the BCP to be changed, from lamellae to cylinders, through the addition of PMMA homopolymer. As shown in Figure 2, the addition of PMMA homopolymer increased the volume fraction of PMMA in the thin film, inducing a phase transition from the lamellar to the cylindrical morphology. A BCP that is 77% PMMA has an equilibrium morphology of hexagonally packed cylinders. This shows that multilayer mixing is capable of transitioning one equilibrium BCP morphology to a distinct equilibrium morphology.

However, for the samples with less than 77% PMMA, notice in Figure 2 that the cylinders tended to follow the lamellae rather than have hexagonal packing. This suggests that the mechanism of multilayer mixing involves lamellae breaking up into cylinders. This was further substantiated by annealing BCP with 77% PMMA for less than 4 hr, as shown in Figure 3. With less annealing time, the samples did not have enough time to reach their equilibrium morphology of hexagonally packed cylinders. These images then show how the process of solvent annealing evolved over time. Figure 3 suggests that, in this process, cylinders first formed following the previously existing lamellae and then reorganized to achieve hexagonal packing. If so, the spacing of cylinders can be controlled by first directing the assembly of lamellae before the multilayer mixing.

Conclusions:

It has been shown that it is possible to control the self-assembled patterns of block copolymers via the technique of multilayer mixing. This has applications, for instance, to computer memory devices, allowing the creation of smaller nanodots and nanowires for computer chips. Future research could include directing the assembly of lamellae to guide cylinder formation.

Acknowledgements:

References:

[1] He, C. et al., Small, 2015 DOI: 10.1002/smll.201403364.
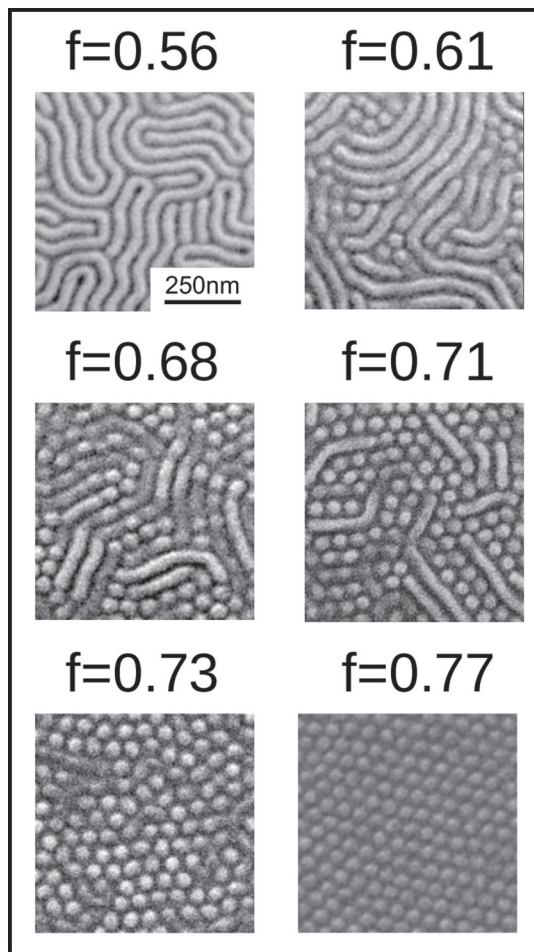

Figure 2: SEM images of BCP morphology after multilayer mixing with varying volume fraction of PMMA. A second layer of varying concentration of PMMA (M.W. = 21.2 kg mol^{-1}) was spin cast and allowed to mix with the BCP layer under solvent vapor for 4 hours to create samples with varying volume fraction of PMMA (f).
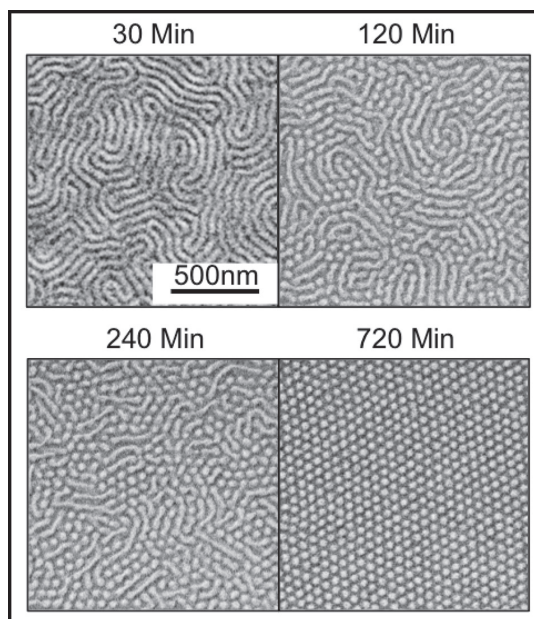

Figure 3: SEMs of cylinders created from multilayer mixing with PMMA annealed at varying times. Each image is a snapshot of the annealing process as a function of time.