SELF-ASSEMBLED NANOSTRUCTURES IN BLOCK COPOLYMER THIN FILMS FOR
NANOFACTORICATION

by

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Self-assembled Nanostructures in Block Copolymer Thin Films for Nanofabrication

Thesis directed by Assistant Professor Mark P. Stoykovich

Abstract

Self-assembly of block copolymer in thin films provides an attractive approach to fabricating nanoscale dots and lines (5~100 nm) rapidly and in parallel over wafer-scale areas. This PhD dissertation mainly studies using the cross-linking reaction based on epoxide incorporated in copolymers to control the nanostructures of self-assembled block copolymer in thin films.

Although control over the domain orientation and long-range order of block copolymer nanostructures self-assembled in thin films has been achieved using various directed self-assembly techniques, more challenging but equally important for many lithographic applications is the ability to precisely control the shape of the interface between domains. This dissertation details a novel layer-by-layer approach for controlling the interface profile of block copolymer nanostructures, and demonstrates the application of an undercut sidewall profile for an enhanced metal lift-off process for pattern transfer. Bilayer films of lamellar-forming poly(styrene-block-methyl methacrylate) were assembled and thermally cross-linked on wafer substrates in a layer-by-layer process. Undercut or negative sidewall profiles in the PS nanostructures are proven, through electron microscopy and optical transmission measurements,
to provide better templates for the lift-off of Au nanowires by achieving complete and defect-free pattern transfer more than 3 times faster than comparable systems with vertical sidewall profiles.

Cross-linking and photopatterning of the self-assembled block copolymer morphologies provide further opportunities to structure self-assembled block copolymer materials for lithographic applications, and to also enhance the thermal, chemical or mechanical stability of such nanostructures to achieve robust templates for subsequent fabrication processes. We demonstrate that self-assembly and cross-linking of the reactive block copolymer materials in thin films can be decoupled into distinct, controlled process steps using solvent annealing and thermal treatment / ultraviolet exposure, respectively. Conventional optical lithography approaches can also be applied to the cross-linkable block copolymer materials in thin films and enables simultaneous structure formation across scales — micrometer scale patterns achieved by photolithography and lamellar nanostructures with different periods via sequential self-assembly of the smaller symmetric block copolymer on the photopatterned self-assembled symmetric block copolymer in thin film.
Dedication

Dedicated to family.
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Chapter 1 Introduction

Block copolymer self-assembly in bulk

Block copolymers are composed of different polymer chains linked by covalent bonds. According to the number of different blocks, their compositions, and the way they are connected together (linear, branched, or cyclic), in melt they can simultaneously form a variety of ordered structures with characteristic periods in the range of 5~100 nm.\[^1\] This distinct self-assembly into highly ordered structures or morphologies has been extensively studied by theoreticians and experimentalists all over the world during the last few decades.\[^2\text{–}^4\] Living anionic polymerization firstly enabled the controlled synthesis of block copolymers which allows a limited range of monomers.\[^5,^6\] The accessible monomers for block copolymer synthesis has expanded with the developments in various types of controlled polymerization.\[^5,^6\] This PhD thesis will mostly focus on the physics side and its role on nanofabrication of block copolymer self-assembly. The most well-characterized class of block copolymers is linear diblock copolymers (AB) composed of two immiscible blocks, A and B. Depending on the incompatibility degree $\chi_{AB}N$ and volume fraction $\phi_A$, they can form the following equilibrium morphologies, spheres (S), cylinders (C), double gyroid (G), lamellae (L), and the inverse structures as shown in Figure 1.1.\[^1\] Except the double gyroid, all other morphologies are characterized by a constant average curvature of the interface between the different domains in self-assembled nanostructure. For block copolymer with symmetric volume compositions the immiscible blocks form domains composed of alternating layers, i.e. lamellar phase (L). If the block copolymer has slightly asymmetric composition, the microphase separation results in the formation of a different layered structure known as perforated layers (PL) or catenoid phase. The
PL structure was first assigned as an equilibrium, but now it is known to be a long-lived metastable state that helps the transition from L to G phases.\textsuperscript{[7,8]} The PL structure is composed of alternating majority and minority component layers in which hexagonally packed channels of the majority component penetrate through the minority component. If the compositional asymmetry is increased even further, the block copolymer assembles in hexagonally packed cylinders (C) with the minority component in the matrix of the majority. If the asymmetry is pushed even further, a nanostructure of spheres mostly a body-centered cubic lattice arrangement will be obtained. Beyond that, finally a mixing on molecular level or disordered structure will be observed.

\textbf{Figure 1.1.} Phase diagram for linear AB diblock copolymers. a: Four basic equilibrium morphologies: spherical (S), cylindrical (C), gyroid (G) and lamellar (L) predicted by self-assembly mean-field theory. b: Experimental phase diagram for polyisoprene-\textit{b}-polystyrene diblock copolymers.\textsuperscript{[1]} Reproduced from Ref. 1. Copyright 1999 American Institute of Physics.
Block copolymer self-assembly in thin films

Block copolymer thin films are generally the cases that the polymer materials subjected to some levels of confinement when the film thicknesses are comparable to the block copolymer nanostructure periods. Block copolymers self-assemble into nanostructures that can relieve the stretching / compression or minimize the entropic penalty with favored enthalpic interactions at the substrate or free surface because stretching / compression of polymer chains under confinement is energetically unfavorable. Two major kinds of confinement are studied for substrate-supported block copolymer thin films: “hard” confinement means a film confined between two rigid interfaces; “soft” confinement describes a film where one interface (the “free surface”) is not confined to any rigid substrates. For soft confinement, chain energy penalty due to incommensurability between the film thickness ($t$) and polymer domain spacing ($L_0$) is minimized by the formation of islands or holes or by perpendicular orientation of the morphology (for cylinders and lamellae) depending on interfacial interactions. Substrate surfaces that are preferential for one block usually lead to island / hole formation, while non-preferential (or neutral) surfaces result in micordomain reorientation. Substrate surface chemistry and surface tension are important properties for manipulating block copolymer thin film self-assembly, both in terms of nanostructure stability and nanostructure orientation (especially for lamellae and cylinders). Preferential surfaces are mostly only wet by the preferred block, while neutral surfaces equally wets all blocks at the surface. The substrate surface chemistry / tension effect can be considered as a field that starts from the substrate surface and spread into the film. Obviously, the spreading distance depends on the strength of the field i.e. the strength of the interactions between substrate and block copolymer blocks, the competing interactions of the vacuum or air or solvent vapor with the free surface, and the energetics of the
equilibrium morphology. For neutral surface case, Han and his coworkers reported the substrate surface field orientation of perpendicular cylinders \(\sim 200 \text{ nm} (\sim L_0 \times 6)\) into the film evidenced by a cross-sectional transmission electron microscopy (TEM) image of a thick poly(styrene-\(b\)-methyl methacrylate) (PS-\(b\)-PMMA) film.\[^{13}\] For preferential case, Shin and his coworkers applied a strongly preferential surface to direct the alignment a thick lamellar poly(styrene-\(b\)-isoprene) (PS-\(b\)-PI) film parallel to the substrate surface over a thickness of \(40 \times L_0\).\[^{14}\]

Normally the substrate surface field spreads no more than \(6 \times L_0\) from the substrate interface while certainly the spreading distance is system-dependent because it involves the interactions between the polymer thin film with a specific substrate surface and free surface.\[^{13-18}\] The interaction between block copolymer thin films and free surface plays more important role or the film may adopt its bulk morphology with randomly oriented grain boundaries with enough distance away from the substrate surface which they confined to. Beside evidenced by cross-sectional imaging by TEM, the vertical orientations of lamellae and cylinders to a neutral substrate surface and parallel or mixed microdomains to the free surface has been also determined by neutron reflectivity,\[^{15,16,19}\] bottom layer imaging with scanning electron microscopy(SEM),\[^{13}\] reactive ion etching(REI) / subsequent SEM imaging,\[^{16}\] small angle neutron scattering (SANS)\[^{16,19}\], and grazing-incidence small angle X-ray scattering (GISAXS).\[^{17,20,21}\]

Chemical modification of the substrate surface by coating random copolymers or self-assembled monolayers (SAMs) and surface cleaning such as \(O_2\) RIE or piranha treatment are common approaches to produce neutral or preferential surfaces. The random copolymer methods is through varying the composition of the copolymer to tune the substrate surface chemistry / tension. The synthesized random copolymers (Scheme 1.1) can be end-grafted\[^{22}\] or side-grafted\[^{21,23}\] to substrate surface to form a brush layer or a cross-linked dense mat covering
Scheme 1.1. PS / PMMA random copolymers: (a) hydroxyl-terminated random copolymer (terminal-OH), (b) side-chain hydroxy-containing random copolymer (PH1), (c) side-chain epoxy-containing random copolymer (PG1). Reproduced from Ref 24. Copyright 2008 American Chemical Society.

the substrate. In the SAM coating methods for block copolymer thin film studies, they usually involve chlorosilane immobilize to silicon oxide surfaces. The methods have applied in partial monolayers on surfaces, oxidation of hydrophobic surface, and chemical materials that resembling the block copolymer behavior to control surface chemistry/tension. Cleaning processes such as O₂ RIE or piranha are used to remove the organics on substrate which normally creates a hydrophilic surface.

The use of block copolymer thin films in nanoscale templates has driven the interest in fabricating neutral surfaces to form perpendicular lamellae to produce line patterns perpendicular cylinders to create nanodot, nanomesh patterns or conducting channels. For the cases of lamellae and cylinders, the perpendicular orientation windows and the quality of the perpendicular self-assembled nanostructures rely not only on the surface neutrality of the
substrate, but also a lot on the film thickness, block copolymer compositions,\textsuperscript{[17,20,24,35]} methods

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{SEM images of self-assembled block copolymer films on a (a)terminal-OH, (b)PH1, and (c)PG1 modified surfaces containing different mole fractions of styrene in the random copolymer. PS-\textit{b}-PMMA (52kDa: 52kDa), 45 nm thick (first row); PS-\textit{b}-PMMA (50kDa:20kDa), 32 nm thick (second row); PS-\textit{b}-PMMA(20kDa: 50kDa), 22nm thick (third row). Black scale bars represent 200 nm. $F_{st}$ is the volume fraction of styrene.\textsuperscript{[24]} Reproduced from Ref 24. Copyright 2008 American Chemical Society.}
\end{figure}
of modification, and self-assembly conditions.\textsuperscript{[13,36]} Precise control of substrate surface neutrality has need researchers to take all of these variables in their considerations.\textsuperscript{[24]} The research on neutral surface have mostly been carried out using PS-\textit{b}-PMMA films because the PMMA block is easily degraded by UV exposure to remove by acetic rinsing to obtain a nanoscale template.\textsuperscript{[37]} Besides, a relative neutral free surface can be simultaneously created with suitable thermal annealing conditions.\textsuperscript{[13,38]} Film thicknesses close to the block copolymer periods ($L_0$) have been used most often due to the loss of perpendicular orientation or order in thicker films observed.\textsuperscript{[15–17,24]} On substrates modified with random copolymers (PS-\textit{r}-PMMA), the neutral surface compositions are determined by windows of perpendicular microdomain orientation. Not

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Perpendicular windows of terminal-OH, PH1, and PG1 for symmetric and asymmetric block copolymers. PS-\textit{b}-PMMA (52kDa: 52kDa), 45 nm thick (first row); PS-\textit{b}-PMMA (50kDa:20kDa), 32 nm thick (second row); PS-\textit{b}-PMMA(20kDa: 50kDa), 22nm thick (third row). Black scale bars represent 200 nm. $F_{st}$ is the volume fraction of styrene. \textsuperscript{[24]} Reproduced from Ref 24. Copyright 2008 American Chemical Society.}
\end{figure}
surprisingly, the higher PS concentration of the block copolymer has the perpendicular window at higher random copolymer PS fraction ($F_{st}$).\cite{17,24} However, the exact values and widths of the perpendicular windows also depend on the grafting methods for the used random copolymers in substrate modification (Figure 1.3).\cite{24} The perpendicular windows shifts to higher $F_{st}$ for substrate surfaces modified with cross-linked (PG1) and side-grafted (PH1) random copolymers compared with an end- grafted brush (Terminal-OH), resulting from the compensation for the polarity increase caused by the residual hydroxyl functional groups in the cases of cross-linked (PG1) and side-grafted (PH1) random copolymers. However, the perpendicular phase windows do not quantitatively match the trends of water contact angles on the modified substrates, possibly caused by the chain penetration of block copolymer into the underlying neutral layer. Further research that studies surface energetics in detail such as consideration of both surface polarity and surface topography may help explain the correlated trends. In addition, free energy studies suggest that the neutral condition for asymmetric block copolymers locate not in the middle of the perpendicular window and that the narrow range of the perpendicular window for the PS-cylinder-forming polymer may be explained by the influence from free-surface (Figure 1.3).

Similarly, surface preferentiality at the free surface can also be viewed as a field effect which starts from the free surface and spreading to the block copolymer thin film the and to substrate surface having preferential or neutral interactions influencing both microdomain orientation and stability. The free surface is a “soft” interface where surface preferentiality is partially controlled by the surface tension of the block copolymer domains, with the lower surface tension domain preferentially in contacting with the free surface. This surface behavior can be manipulated by the applications of different thermal annealing conditions. For example,
an fairly neutral free surface can be produced for the PS-\textit{b}-PMMA system by annealing block copolymer thin films during 170°C\textasciitilde230°C, where the block surface tensions are almost equal.\textsuperscript{[24,38]} However, many block copolymers contain blocks with very different surface tensions or blocks with sensitive functionalities that are vulnerable to thermal treatment (170°C\textasciitilde230°C) such as epoxide can start to polymerize on Silicon wafer substrate over 140°C. For block copolymers like these, solvent vapor annealing provides a promising alternative to thermal annealing. The solvent vapor environment during annealing achieves several purposes. First, the vapor sets surface preferentiality at the free surface of the block copolymer thin film.\textsuperscript{[39–43]} Second, the small vapor molecules swells the thin films and in effect lowers the glass transition temperatures ($T_g$) of the block copolymer domains, increasing polymer chain mobility.\textsuperscript{[41,43–46]} Third, the small solvent molecules in the thin films influences the interactions between blocks ($\chi_{\text{eff}}$) and possibly the relative volume fractions of domains, allowing interesting controls in morphologies.\textsuperscript{[39,41–44,46–50]} Fourth, solvent interactions with the substrate surface can result in the elimination of undesirable surface interactions\textsuperscript{[41,44,51,52]} or polymer thin film dewetting.\textsuperscript{[9,53]} Finally, solvent swelling and confinement of the film on substrate can lead to an actual $L_0$ that can be bigger\textsuperscript{[46,48,54]} or smaller\textsuperscript{[42,43,46,47,54]} than the bulk $L_0$. In a conventional solvent annealing setup, a reservoir of solvent is placed in a container with the block copolymer thin film samples for some period of time. The solvent is immediately removed after desired annealing time to lock the non-equilibrium but often nicely ordered structures.\textsuperscript{[43,44,48,50,53,55]} More recent setups with controlled solvent vapor flows have provided better control over the solvent atmosphere and the extent of film swelling.\textsuperscript{[43,45,51]}

Solvent annealing studies have investigated a number of variables to obtain desired morphologies such as solvent choice, annealing time, swollen film thickness, and solvent
removal rate. In some instances, the deposition conditions of the block copolymer thin films also plays roles in the final self-assembled nanostructure or the time needed to create well-ordered structures. In one instance, Xuan solvent annealed thin lamellar PS-b-PMMA films (<0.5$L_0$) with acetone (strongly PMMA selective), chloroform (slightly PMMA selective), toluene (slightly PS selective), and carbon disulfide (highly PS selective). The block copolymer thin film samples annealed with PMMA-selective solvents for 60 hours gave hexagonally packed microdomains, while films annealed with PS-selective solvents were mostly parallel with small bumps. The solvent preference for PMMA is required to overcome the free surface preference for the lower surface tension PS domain to form well-ordered structures. The need for a slightly selective solvent to produce an effectively neutral free surface also was reported. Although these cases are general, finding a single solvent to generate a neutral free surface for each block copolymer system is time-consuming and using solvent mixtures in deposition and annealing is a more promising alternative. Combined solvents were used by Ross to finely control phase transitions and microdomain sizes in a poly(styrene-b-dimethylsiloxane) (PS-b-PDMS) film with toluene (preferential for PS) and heptane(preferential for PDMS). The mixed solvent approach has also been applied in annealing and casting of poly(ethylene oxide) (PEO) containing block copolymers at different relative humidities. The mixed solvent approach has also been employed in annealing PS-b-PMMA to form perpendicular orientation on neutral surface by Stoykovich. Solvent annealing with selective solvents or under non-saturated solvent vapor conditions may be desirable to produce a specific morphology or avoid disorder. However, polymer chain mobility is not as high in these annealing conditions, so longer annealing times may help improve self-assembly. Longer annealing times has worked to form better order in some systems, but it has not had much success in generating long-range
ordering.\textsuperscript{[40,46,61]} One possible reason is that in a conventional solvent annealing process, continuous solvent absorbed from the vapor forces constant evolution of the nanostructure to adjusting interfacial interactions and commensurability conditions. Cavicchi controlled the extent of swelling in poly(isoprene-b-lactide) (PI-b-PLA) thin films annealed in chloroform solvent vapor and determined the relationship between the phase behavior and swollen film thickness.\textsuperscript{[51]} The author explained the relationship by that at high solvent concentration, the mild preference of chloroform for PLA compensates the free surface preference for the lower surface tension PI domain and reduce the substrate surface preference for PLA.\textsuperscript{[41]} In the proposed phase diagram, higher solvent concentrations favor perpendicular ordering which supports their conclusions. The research work by Zettl\textsuperscript{[45]} studied solvent uptake effects as a function of thin film thickness and annealing solvents vapor partial pressures. Their observations suggested that thinner films absorb more solvent than thicker films for the same annealing solvent partial pressure, indicating the importance of direct measurements of solvent uptake or understanding the how solvent vapor pressure influences solvent uptake.

Through manipulating solvent removal rates researchers have found another way to improve order and control microdomain orientation during deposition and solvent annealing. Since the study by Karim\textsuperscript{[62]} showing that cylinder orientation could be controlled by the rate of solvent evaporation upon spin-casting, attention has been drawn to understand morphology evolution during solvent evaporation in terms of $\chi_{\text{eff}}$, volume fractions, and commensurability conditions.\textsuperscript{[49,63]} Following Karim, Fukunaga found parallel orientations for slow solvent removal rates and perpendicular orientations for fast solvent evaporation in solvent-annealed lamellae-forming poly(styrene-$b$-2-vinylpyridine-$b$-$\text{tert}$-butyl methacrylate) (PS-$b$-P2VP-$b$-PrBMA) films.\textsuperscript{[64]} However, for solvent-annealed PS-$b$-P2VP-$b$-PrBMA thin
films with different block copolymer composition, Elbs observed a number of complex morphologies for different solvent removal rates.\textsuperscript{[65]} In addition, Zhang reported that removal of residual solvent in polymer thin films during thermal annealing produced unexpected perpendicular orientation of cylinders in PS-\textit{b}-PMMA thin films on preferential substrate surfaces.\textsuperscript{[66]} Due to the relatively limited number of research works in this area, the ability of the solvent removal rate to control copolymer self-assembly deserves deeper investigation.

The need for nanoscale functional materials has prompted developments in understanding the complicated interplay among surface / interfacial energetics, confinement, thermodynamic equilibrium, and kinetics on block copolymer self-assembly in thin film. A modified description of thin film free energy suggested by Han\textsuperscript{[24]} outlines a framework for the basic conceptual understanding of block copolymer self-assembly in thin film: 

\[ F = F_{\text{elastic}} + F_{\text{block}} + F_{\text{surface}} + F_{\text{interface}}, \]

where \( F_{\text{elastic}} \) expresses chain conformations including chain stretching at the substrate surface (favors chain ends and shorter blocks at the substrate); \( F_{\text{block}} \) describes block interactions which can be controlled by surface compatibilization using neutral substrate surfaces or the presence of solvent molecules, salts, or nanoparticles; \( F_{\text{surface}} \) refers to the free surface energy; and \( F_{\text{interface}} \) describes enthalpic interactions between substrate and copolymer. The practical applications of self-assembled block copolymer thin film require their near-perfect order and the desired layout controlled by external stimuli such as electric fields,\textsuperscript{[67]} shear alignment,\textsuperscript{[68]} zone-annealing,\textsuperscript{[69]} and substrate patterning,\textsuperscript{[70–73]} among others. Besides, block copolymer and homopolymer blending has been used to control block copolymer domain sizes and morphology, while salt-doping or nanoparticle addition has been applied to introduce functionality or change interfacial energetics.\textsuperscript{[74]}

Block copolymer thin film self-assembly on an unpatterned neutral substrate typically
results in local ordered nanostructures with numerous grain boundaries and defects,\textsuperscript{[75,76]} thus limiting block copolymer application in electronic devices that require precise control of the nanostructure layout.\textsuperscript{[70–73]} Graphoepitaxy (Figure 1.4a, topographic features on substrates) and chemoepitaxy are two common approaches to precisely direct the self-assembly of block copolymer in an attempt to promote the practical applications of block copolymer self-assembly in designed nanoscale layouts.\textsuperscript{[70,71,77–80]} Research efforts have demonstrated the creation of periodic nanopatterns of parallel lines (perpendicular lamellae, parallel cylinders)\textsuperscript{[81–83]} and dots arrays (perpendicular cylinders, spheres)\textsuperscript{[84–86]} using topographic guiding patterns. More complex structures such as concentric circles and bent lines also were fabricated through the careful

![Figure 1.4. Graphoepitaxy vs epitaxial self-assembly. (a) Graphoepitaxy utilizes topographic substrate pattern for directed block copolymer assembly. The substrate pattern remains in the finally formed nanopatterned morphology. (b) Epitaxial self-assembly utilizes nanoscale chemical pattern to register block copolymer assembly. Ultrafine chemical patterning requires](image-url)
design of prepatterned geometries or the induction of defects at the substrate walls.\textsuperscript{[88–90]} The guiding ordering mechanism is well understood in terms of commensurability and interactions of each block with substrates and walls.\textsuperscript{[92–95]} Two important downsides of graphoepitaxy are that valuable substrate area is lost due to prepatterning and precisely controlled lithographic patterning instruments are costly. For more details on graphoepitaxy, we refer the readers to published reviews.\textsuperscript{[78,79,87]} Compared with graphoepitaxy, chemical prepatterning (Figure 1.4b) does not lose substrate area and allows guidance of the block copolymer self-assembling and precise control over nanostructure shapes and dimensions.\textsuperscript{[78,96,97]} In many of prepatterning examples, circular, triangular, rectangular, and hexagonal patterns with varying dimensions usually were fabricated by extreme ultraviolet (EUV) lithography or e-beam lithography.\textsuperscript{[86,88,91]} Many of the essential features required for producing integrated circuits including dense and isolated bends, jogs, spots, and T-junctions have been achieved in block copolymer thin films through chemical prepatterning.\textsuperscript{[71,96]} However, this prepatterning method is also disadvantageous as it involves an expensive lithographic writing step, nominally at similar feature densities to those achieved by block copolymers.\textsuperscript{[70,98]} Even though block copolymer self-assembly permits quality nanopattern rectification with respect to the chemical prepatter, creating a prepatterned substrate in which every feature is written by e-beam lithography is prohibitive due to the long writing times required for nanopatterning large areas with high densities.

Various techniques have been developed to fabricate functional nanostructures, and the use of patternable block copolymers (Figure 1.5) has proved to be one of the most exciting areas
because of its simplicity, elegance, and high productivity.\textsuperscript{[98]} The nanoscale structures generated from the self-assembly of disordered molecular building block copolymer are often referred to as “bottom-up”. Alternatively, nanometer-sized structures can also be generated using lithographic methods. The techniques like these are often referred to as “top-down” techniques that the final patterns are formed from large structures to small structures. Both top-down and bottom-up patterning approaches have been used in various nanofabrication processes to generate nanoscale structures that can be transferred to other materials. High-resolution nanopatterned substrates, patterned nanoparticles, nanoporous materials, as well as nanoreplicated materials have been fabricated from block copolymer templates. A combination of these two patterning approaches provides hierarchical control of block copolymer structures such that self-assembled nanoscale patterns with long-range ordering and tunable orientation can be created within lithographically defined submicron patterns. Because most practical applications require block copolymer thin films with large area of ordered patterns, special attention is paid to the improvement of bottom-up structures in block copolymer thin films and the combination of these self-assembled structures with top-down approaches to achieve multilevel control of the resulting nanostructure.

\textbf{Figure 1.5.} Schematics of the photopatterning process in a) positive- and b) negative-tones using the cross-linkable block copolymer materials.
Block copolymer self-assembly in 3D Nanofabrication

The 3D devices can be constructed layer by layer by using a sequence of steps, each of which forms a 2D block copolymer pattern which is then transferred into a functional material using subtractive or additive processes. Sequential processing of 2D block copolymer patterns can build multiple layers of nanostructures composed of the same or different morphologies, with various orientations or registration between the layers. This strategy can create 3D microdomain arrays with non-periodic structure along the vertical direction, compared with the 3D structures formed by deposition and self-assembly of thick block copolymer films\cite{99,100} in which the structure contains microdomains with the same morphology and usually same orientation. However, stacking or layer-by-layer methods can be categorized into two types: self-alignment stacking approach of an upper layer of microdomains with a lower layer and an independent stacking approach. Registration between upper and lower layers requires direct contact between two block copolymer thin film layers so that the morphology of the underlying nanostructure can guide the orientation and location of the upper nanostructure. An example is the self-assembly of high aspect ratio out-of-plane lamellae on a lower layer consisting of in-plane parallel half-cylinders of the same period,\cite{101,102} or layer-by-layer stacking of perpendicularly oriented cylinders of a cross-linkable block copolymer into high aspect multilayer structures.\cite{103} Sequential stacking self-assembly of block copolymers\cite{103,104} was also demonstrated in which higher density patterns in the upper layer were guided by topographical features formed by etching or pattern transfer of the lower layer. The resulting pattern density was increased by 2 or more, and unusual hierarchical structures were generated such as spheres in perforated lamellae\cite{104} or nanodot / nanowire layouts in Figure 1.6a, b.\cite{105} Independent stacking processes do not depend on chemical or topographical epitaxy of the lower layers of
block copolymers. Figures 1.6c, d illustrate an iterative method to fabricate mesoporous structures composed of several block copolymer layers with independent orientations for different layers. After the spin-coating and self-assembly of PS-b-PMMA block copolymers, a thin Si film was coated to form a permeable membrane structure which allows the removal of the underlying PMMA microdomains by UV exposure and acetic acid rinsing. The subsequent

Figure 1.6. Sequential fabrication 3D structures. a,b) Sequential assembly, c,d) Separation layer, e,f) Graphene separation layer, g,h) Nanotransfer printing of BCP. Reproduced from Ref 106. Copyright 2013 John Wiley & Sons, Inc.
deposition of a thicker Si film acted as a new substrate to form an another block copolymer layer. Another stacking process involving directed self-assembly used graphene as a separation layer, achieving the formation of multilayered metallic nanowires\textsuperscript{[108]} shown in Figure 1.6 e, f. Transfer-printing of ordered block copolymer thin films, Figure 1.6 g, h, generates 3D structures such as crossed silica nanowire patterns without the use of separation layers, manipulating the in-plane orientation of the microdomains in each layer.\textsuperscript{[109]} The block copolymer thin film in the followed layer were self-assembled under a mold by solvent annealing before transfer printing. Combinations of these sequential stacking or layer-by-layer methods can produce diverse multilayer nanostructures with tunable dimensions, spacings, and orientations. The key challenges of sequential layer-by-layer fabrication are the time-consuming nature of the approach and the difficulty in ensuring precise registration of the layers.

References


Chapter 2 Profile Control in Block Copolymer Nanostructures in Thin Films

This chapter was published in Advanced Functional Materials in September 2014.

ToC Figure

Figure 2.S1. Table of Content Figure

Bilayer thin films of lamellar-forming poly(styrene-block-methyl methacrylate) were self-assembled and thermally cross-linked on wafer substrates in a layer-by-layer process. This layer-by-layer approach can provide novel control over the interface profile of block copolymer nanostructures and enables an undercut sidewall profile that enhances metal lift-off processes for pattern transfer.

Keywords: block copolymers, self-assembly, hierarchical structures, thin films, lift-off
Abstract

Although control over the domain orientation and long-range order of block copolymer nanostructures self-assembled in thin films has been achieved using various directed self-assembly techniques, more challenging but equally important for many lithographic applications is the ability to precisely control the shape of the interface between domains. This manuscript details a novel layer-by-layer approach for controlling the interface profile of block copolymer nanostructures, and demonstrates the application of an undercut sidewall profile for an enhanced metal lift-off process for pattern transfer. Bilayer films of lamellar-forming poly(styrene-block-methyl methacrylate) were assembled and thermally cross-linked on wafer substrates in a layer-by-layer process. The top layer, while being directed to self-assemble on the lamellae of the underlying layer, had a tunable composition and polystyrene domain width independent of that of the bottom layer. Undercut or negative sidewall profiles in the PS nanostructures are proven, through electron microscopy and optical transmission measurements, to provide better templates for the lift-off of Au nanowires by achieving complete and defect-free pattern transfer more than 3 times faster than comparable systems with vertical sidewall profiles. More broadly, the layer-by-layer approach presented here provides a pathway to achieving sophisticated interface profiles and user-defined three-dimensional block copolymer nanostructures in thin films.

Introduction

Block copolymer self-assembly in thin films spontaneously generates nanostructured patterns, however, for many lithographic applications the pattern must be transferred to a functional electronic,[1] optical,[2] or magnetic material.[3] Thus the block copolymer
nanostructures often mimic a patterned photoresist film, serving as a template for the deposition of the functional materials or as a mask for substrate etching. Pattern transfer processes using block copolymer nanostructures have been challenging, due in part to the thin films that are used (e.g., usually <100 nm as required to maintain low feature aspect ratios\[4\]), the less than ideal polymeric constituents (e.g., common block copolymer systems provide poor etch resistance\[4-5\]), and a lack of structural and interfacial control. Lift-off processes for the additive vapor-phase deposition of materials using conventional lithographic techniques, for example, benefit from photoresist patterns with an undercut or negative sidewall profile as illustrated in Figure 2.1.\[6\]

**Figure 2.1.** Common sidewall profiles of photoresist structures after lithographic patterning.

Selective removal of the deposited material from the photoresist protected regions is facilitated during lift-off by the undercut profile preventing continuous coverage over the substrate and photoresist features. Photoresist structures with an undercut profile therefore serve two purposes – first they allow solvent to directly access and dissolve the photoresist, and second they let the unconnected material freely float away and be removed. Lift-off using photoresist structures with vertical or positive sidewall profiles (see Figure 2.1) may be slow, may be troubled by retention or inhomogeneous pattern transfer across the substrate,\[7\] and can lead to rough edges or ‘ears’ on the patterned material.\[8\] In conventional photoresists, undercut profiles are achieved through careful design of the molecular composition of the photoresist (e.g.,
negative versus positive tone)\textsuperscript{[9]} or the development of special processing conditions (\textit{e.g.}, via the exposure dose or presoaking the photoresist film in solvent to create a gradient in relative solubility).\textsuperscript{[6]} Alternatively, bilayer photoresist films\textsuperscript{[10]} are often used to achieve T-top shaped structures (see Figure 2.1), with the top layer being less soluble than the underlying layer at the given exposure and development conditions.

The control of sidewall profiles in block copolymer nanostructures is inherently more difficult. Block copolymer structures oriented perpendicular to the substrate have interfacial shapes dictated by the thermodynamics of the system and preferentially adopt vertical sidewall profiles.\textsuperscript{[11]} In many cases this is an attractive feature of self-assembly, such that block copolymer structures have been shown to provide critical dimension control,\textsuperscript{[12]} to self-heal defects,\textsuperscript{[13]} and to reduce line edge roughness.\textsuperscript{[14]} Here we have developed an approach, analogous to that in bilayer photoresist films, to achieve tunable interface shapes and sidewall profiles in block copolymer nanostructures in thin films. It is demonstrated that such interfacial control provides the unique opportunity to design block copolymer nanostructures specially tuned for pattern transfer, including in lift-off processes.

**Results and Discussion**

The step-by-step schematic in Figure 2.2 illustrates our approach to control the sidewall profiles of block copolymer nanostructures through the use of bilayer self-assembled thin films. Briefly, block copolymer thin films were deposited on a neutral brush treated surface and solvent annealed under a mixed solvent vapor leading to the self-assembly of lamellae oriented perpendicular to the substrate.\textsuperscript{[15]} A cross-linking reaction was subsequently performed within the self-assembled domains by heating the sample to 190 °C for 1 hr. The resulting
cross-linked nanostructures were thus fixed and became relatively insoluble. A second layer of block copolymer could then be deposited and processed under identical conditions (i.e., self-assembly via solvent annealing followed by cross-linking upon thermal treatment). In this manner, the underlying first layer served as a chemically patterned substrate that directed the self-assembly of the block copolymer structures in the second layer. Individual block copolymer layers were ~25 nm thick, thereby generating a nanostructured film with a total thickness of 50 nm. The system used here consisted of polystyrene (PS) and poly(methyl methacrylate) (PMMA) components, which is advantageous because it is a well-characterized, model block copolymer system and the PMMA domain can be selectively removed through standard processes. This approach can be generalized to most block copolymers systems, but other such materials may exhibit subtle differences in the structures self-assembled in thin films from those presented here due to more disparate domain surface tensions than in the PS / PMMA system (e.g., it may be more difficult to achieve perpendicular interfaces and nanostructures even on a neutral surface).

![Figure 2.2](image)

**Figure 2.2.** Step-by-step process flow to achieve a bilayer undercut profile in self-assembled block copolymer nanostructures.

A multilayer approach to controlling the interface profiles of block copolymer nanostructures allows the composition, and thus dimension, of each self-assembled layer to be adjusted independently. In this study, negative or undercut sidewall profiles in the PS domain
were targeted in order to enhance the success of such self-assembled nanostructures to serve as a mask for lift-off processes for pattern transfer. This type of profile in a block copolymer nanostructure requires that each layer have the same periodicity but differing domain widths. Such an undercut profile was fabricated from a bilayer thin film, with the bottom layer having a PS volume fraction \( \phi_{PS} \) of 50.0 vol\% and the top layer having \( \phi_{PS} = 60.0 \) vol\%, as indicated by the notation ‘Bilayer 50-60PS’ used in this manuscript. Each layer consisted of a block copolymer / homopolymer blend with 80.0 vol\% lamellar-forming PS-\( b \)-PMMA and 20.0 vol\% cross-linkable homopolymers x-PS and x-PMMA (note that these are not truly homopolymers but rather random copolymers with 1 mol\% concentrations of a reactive epoxy functionality, but, for clarity, they are labeled as such throughout). The relative amount of x-PS and x-PMMA added was carefully tuned to control the final volume fractions of PS and PMMA in the block copolymer blends. Three different block copolymer compositions \( \phi_{PS} = 40, 50, \) or 60 vol\%) were considered for the layers, but each self-assembled into lamellar structures with similar periodicities \( L_0 = 56-58 \) nm) (see Figure 2.S2). It is important to comment, however, that for the materials presented here, the block copolymer and homopolymers are not cross-linked together and, given sufficient time, the block copolymer could be mixed within the layers or completely extracted. Future implementation of these systems may benefit from cross-linkable block copolymers that can be directly reacted into the molecular network to fully inhibit mixing between layers and make the structures insoluble (although in some cases this might be undesirable, for example in the PS nanostructures used for lift-off as detailed below).
Figure 2.3 shows top-down SEM images of 50-40PS and 50-60PS bilayer films after removal of the PMMA domain, as well as a single layer 50PS film of equivalent total thickness. The light regions in the SEM images correspond to the PS nanostructures. The formation of lamellar structures was observed throughout indicating that the block copolymer self-assembled in the top layer matched and was registered with the pattern in the underlying layer, which for these systems had an identical composition. The top-down SEM images from the 50-40PS to
50-60PS bilayers also exhibit the visual trend that the PS domains become wider while the PMMA domains become narrower, which is consistent with the profiles targeted in these bilayer thin films. On the right side of Figure 2.3, an analysis of the grayscale top-down SEM images confirms this trend. Histograms of the grayscale color of each pixel in the images were determined and have two clear peaks corresponding to the PMMA (dark, low grayscale color) and PS (light, high grayscale color) domains. In order to quantify the relative composition of each domain at the top surface of the bilayer film, a threshold was applied corresponding to the

![Figure 2.3. Top-down SEM images (left) and the corresponding histograms of grayscale color (right) for bilayer block copolymer films with top layer polystyrene compositions of a) 40, b) 50 and c) 60 vol%. The blue and red shaded areas indicate the pixels assigned to belong to the PMMA and PS domains in the SEM image, respectively. Note that, in this case, the PMMA domains were removed prior to SEM imaging.](image-url)
minimum probability between the two peaks in the distribution. Table 2.1 summarizes the measured PS and PMMA compositions at the top surface of the films, which ranged from 44 to 70 vol% PS and closely matched the targeted surface compositions of 40 to 60 vol% PS (for 50-40PS to 50-60PS, respectively).

**Table 2.1** The areal fraction of PS and PMMA at the free surface of the block copolymer bilayer films as determined by top-down SEM imaging.

<table>
<thead>
<tr>
<th>3D Structure Design (as denoted by composition)(^a)</th>
<th>Measured PS composition at the film surface [vol%]</th>
<th>Measured PMMA composition at the film surface [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayer 50-40PS</td>
<td>46% ± 2%</td>
<td>54% ± 2%</td>
</tr>
<tr>
<td>Monolayer 50PS</td>
<td>54% ± 1%</td>
<td>46% ± 1%</td>
</tr>
<tr>
<td>Bilayer 50-60PS</td>
<td>70% ± 1%</td>
<td>30% ± 1%</td>
</tr>
</tbody>
</table>

\(a\) Notation of “50-40PS” means the multilayer structure was built with a bottom layer consisting of 50 vol% PS and 50 vol% PMMA and a top layer of 40 vol% PS and 60 vol% PMMA.

One domain of the block copolymer nanostructures must be selectively removed to fabricate masks or templates suitable for pattern transfer processes such as lift-off. Here the PMMA domain of the lamellar nanostructures in the bilayer film was selectively removed by exposure to UV light (254 nm, 1 J/cm\(^2\)) and development in acetic acid (a non-solvent for the PS domain).\(^{18b}\) The remaining PS template was then descummed by a short oxygen plasma treatment. Subsequently an adhesion layer of 1.0 nm of Cr and 5.0 nm of Au was deposited by thermal evaporation.

The undercut profile achieved by the bilayer 50-60PS film is evidenced in the cross-sectional SEM images of **Figure 2.4**. Figure 2.4a shows the cross-sectional SEM image of bilayer 50-60PS after descumming by oxygen plasma treatment, while Figure 2.4b shows the same structures after metal deposition. The designed undercut structure is evident in both images, although cross-sectional imaging of the polymer nanostructures alone is difficult and subject to
charging and changes in shape due to surface melting. The metal coated structures in Figure 2.4b provide a better indication of the T-topped shaped structures achieved by this 50-60PS bilayer system and the flat topped surfaces of the nanostructures. The sidewall angle of the undercut profile was measured to be $7 \pm 3^\circ$ from the substrate normal for the 50-60PS bilayer system (by linear fitting of the line edges in Figure 2.4b), which is close to that predicted through strictly volumetric arguments for this bilayer composition ($\sim 11^\circ$) and substantially different from the perpendicular interfaces achieved in the monolayer block copolymer system. Notably such features of the bilayer nanostructures are able to withstand the descumming process, which uses an isotropic O$_2$ plasma that likely etches such corners and surfaces more rapidly.$^{[19]}$ Most importantly for lift-off processes, the undercut profile leads to breaks in the continuity of the deposited metal film, such that minimal metal on the photoresist sidewalls and gaps at the bottom.

![Cross-sectional SEM images of bilayer 50-60PS films with undercut profiles: a) the PS mask remaining after the PMMA domain is removed and b) the Cr and Au metal film deposited on the PS mask, with two breaks or gaps in the film continuity highlighted with the red arrows.](image)

**Figure 2.4.** Cross-sectional SEM images of bilayer 50-60PS films with undercut profiles: a) the PS mask remaining after the PMMA domain is removed and b) the Cr and Au metal film deposited on the PS mask, with two breaks or gaps in the film continuity highlighted with the red arrows.
of the photoresist layer are clearly observed (in Figure 2.4b as indicated with red arrows). These discontinuities in the deposited metal layer allows solvent (in this case toluene) to penetrate and dissolve the sacrificial PS template, as well as to enable the unconnected metal to freely lift-off the surface.

Characterization of the metal lift-off process using the bilayer block copolymer nanostructures with controlled sidewall profiles was performed as shown in Figures 2.5 and 2.6. Metal films were deposited on the PS templates on Si wafer or glass slide substrates, and lift-off was performed by sonicating the samples in a toluene bath at 55 °C. Improvements in the lift-off process achieved using the undercut profile self-assembled by the 50-60PS bilayer system were compared to systems with vertical (50PS monolayer) and positive (50-40PS bilayer) sidewall profiles. Figure 2.5a shows defect-free metal nanowires (25 nm wide, 6 nm thick) fabricated by lift-off for 600 min using the undercut 50-60PS bilayer structures. In contrast, under identical lift-off conditions, the PS templates with vertical (Figure 2.5b) or positive (not shown) sidewall profiles exhibited retention and did not allow for complete lift-off, as indicated by substantial portions of the substrate remaining blanketed with metal coating the PS template.
Figure 2.5. Top-down SEM images of metal nanowires after a) successful and b) incomplete lift-off. Under identical lift-off conditions (sonication at 55 °C for 10 hrs), a) a block copolymer template with an undercut profile (bilayer 50-60PS film) achieves complete lift-off and defect-free pattern transfer, whereas b) a block copolymer template without an undercut profile (monolayer 50PS film) does not allow for successful lift-off (the dark regions on the bottom left and right show the desired outcome, while the remaining brighter areas have not been successfully lifted-off and have metal blanketing the PS template).

The progress of the lift-off process over large areas can be characterized optically as shown in Figure 2.6 for the three bilayer block copolymer structures with distinct sidewall profiles. The extent of lift-off was studied by monitoring the UV-vis transmittance (as reported at a wavelength of 495 nm) as a function of the lift-off time (measured every 15 min). As indicated in the transmittance spectra across the UV-vis range, the wavelength of 495 nm
corresponds to the maximum transmittance, whereas ~580 nm corresponds to a minimum in transmittance that results from the localized surface plasmon resonance (LSPR) for such Au nanostructures. While either wavelength could be used to monitor the extent of metal liftoff as a function of time, transmittance at 495 nm has been reported to decouple the extent of liftoff from the LSPR response that depends on structure size and spacing which varies throughout the liftoff process.

Figure 2.6. a) Transmittance at 495 nm of the Au coated block copolymer nanostructures during the course of the lift-off process as a function of sonication time. The error bars represent 1σ variation of three measurements taken across the sample. b) Transmittance spectra for the 50-60PS system before and after completion of the metal lift-off process.

The optical data in Figure 2.6 has a number of interesting features. First, lift-off was completed in ~450 min when using the PS masks with an undercut profile (Bi-layer 50-60PS), which is approximately an order of magnitude faster than the masks with a positive sidewall profile (~4000 min). Furthermore no significant lift-off was observed until ~600 min for the
templates with a vertical or positive sidewall profile. The significantly faster rates of lift-off achieved with sidewall control are important for potential pattern transfer processes and nanomanufacturing using block copolymers in thin films. Second, there is a period for all samples before which there is no change in transmittance as a function of lift-off time. This induction period likely corresponds, in part, to the time necessary for the solvent to access the PS template and solubilize it. Finally, the transmittance remains constant after lift-off is complete and has very low variation across the sample surface. From this observation, it can be concluded that the metal nanowires are homogeneous across the substrate (in terms of the extent of lift-off and the film thickness) and that adhesion of the metal nanowires to the substrate is strong.

Conclusions

In summary, we have presented a simple approach to control the sidewall profile of block copolymer nanostructures self-assembled in thin films and demonstrated the ability of such profile control to enhance lift-off pattern transfer processes. The approach utilizes bilayer block copolymer films, with each layer having a well-defined composition and characteristic dimension, and is analogous to profile control techniques developed for commercial photoresists and lithographic processes. The improved liftoff process detailed in this manuscript will simplify the transfer of such block copolymer patterns into functional metallic or semiconducting materials, or even into other sacrificial layers. For example, we have used this lift-off process to deposit thin Cr or alumina hard masks for anisotropic reactive ion etching and achieved high aspect ratio (>5) features etched into Si substrates. The proof-of-concept demonstration presented here can easily be scaled to smaller dimensions, implemented in cylinder-forming
systems, or adapted to other block copolymer materials. The processes and materials used here are also compatible with conventional nanofabrication tools, including those being developed specifically for block copolymer lithography (e.g., tools for solvent vapor annealing) and directed self-assembly such as with chemically patterned substrates. Experiments and mean-field simulations on the directed self-assembly of PS-\(b\)-PMMA lamellae on chemically patterned surfaces indicate that the domain interface depends strongly on the film thickness and the mismatch in periodicity between the block copolymer and the surface pattern. Thus, optimization of the sidewall profile of block copolymer nanostructures may be expanded to other applications, in the future, by controlling the thickness of each layer or the use of multilayer (3 or more layers) films to create complex, three-dimensional profiles.

**Experimental Section**

*Processing of bilayer block copolymer thin films:*

A neutral substrate for the self-assembly of lamellar-forming PS-\(b\)-PMMA block copolymers with perpendicular orientations was prepared by coating a P(S-r-MMA-r-GMA) random copolymer brush onto Si substrates. Si wafers were purchased from Montco Silicon and piranha treated with a mixture of 30% \(\text{H}_2\text{O}_2\) / 70% \(\text{H}_2\text{SO}_4\) (v/v) at 70 °C for 20 min. The cleaned substrates were rinsed extensively with distilled water, and then further rinsed with acetone and toluene. The random copolymer was synthesized by free-radical polymerization from styrene, methyl methacrylate, and glycidyl methacrylate monomers to achieve a final molar composition of 58% styrene, 31% methyl methacrylate, and 1% glycidyl methacrylate as confirmed by \(^1\text{H}-\text{NMR}\). A 0.3 wt% solution of the random copolymer in anhydrous toluene (EMD Chemicals, 99.8 wt%) was prepared and spincast to a film thickness of 10 nm onto the
clean silicon wafers. Annealing at 170 °C for 4 hrs cross-linked the random copolymer into a dense mat, and subsequent sonication in a toluene bath removed unreacted polymer.

Thin films of PS-\(b\)-PMMA block copolymer and block copolymer / homopolymer blends were spincast onto the prepared neutral surfaces. The lamellar-forming block copolymer (PS-\(b\)-PMMA, 47k:53k, PDI = 1.12) was purchased from Polymer Source, Inc. Homopolymers with a low concentration of thermally cross-linkable functionality were synthesized through atom transfer radical polymerization.[21] These cross-linkable homopolymers included x-PS (17.4 kDa, PDI = 1.28) and x-PMMA (25.2 kDa, PDI = 1.47) each with 1 mol% of glycidyl methacrylate functionality randomly incorporated. Solutions of block copolymer and homopolymer were prepared at a concentration of 1.5 wt% by weighing out dry polymer and adding toluene dropwise. Three blend solutions of block copolymer and cross-linkable homopolymer were prepared by blending the solutions of block copolymer and homopolymer as indicated in Table 2.2, targeting different total volume fractions of styrene and methyl methacrylate in each solution, but identical volume fractions of homopolymer. The ~50 nm monolayer block copolymer thin film was produced by spincasting (5000 rpm for 30 s) a 1.5 wt% solution. Each ~25 nm thick layer in the bilayer block copolymer thin films was achieved using block copolymer blend solutions diluted to 0.75 wt% concentrations and spincasting (4000 rpm for 45 s).

**Table 2.2.** Block copolymer blends with controlled volume fractions of PS.

<table>
<thead>
<tr>
<th></th>
<th>40PS</th>
<th>50PS</th>
<th>60PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 wt% PS-(b)-PMMA [mL]</td>
<td>2.000</td>
<td>2.000</td>
<td>2.000</td>
</tr>
<tr>
<td>1.5 wt% x-PS [mL]</td>
<td>0</td>
<td>0.237</td>
<td>0.471</td>
</tr>
<tr>
<td>1.5 wt% x-PMMA [mL]</td>
<td>0.529</td>
<td>0.263</td>
<td>0</td>
</tr>
<tr>
<td>Total volume fraction of PS</td>
<td>40.0%</td>
<td>50.0%</td>
<td>60.0%</td>
</tr>
<tr>
<td>Volume fraction of homopolymer</td>
<td>20.0%</td>
<td>20.0%</td>
<td>20.0%</td>
</tr>
</tbody>
</table>
Solvent vapor annealing was performed by exposing the block copolymer thin films to a saturated vapor of mixed solvents. Acetone (30 mL, Fisher, 99%) and cyclohexane (30 mL, Fisher, 99%) were added to the bottom of a glass desiccator (1.5 L volume). The solvents were degassed under house vacuum (25 Torr) to remove any dissolved gases prior to solvent annealing. The thin film samples were suspended on a metal frame above the solvent mixture. The system pressure was then lowered to 20 Torr, the desiccator was sealed, and the polymer thin films were swollen in the mixed solvent environment for 2 hrs. The solvent vapor annealing process was quenched by opening the chamber to vacuum to remove solvent vapor and followed by opening the entire chamber to air to allow the swollen block copolymer thin films to dry. Subsequently, the solvent vapor annealed samples were thermally treated (190°C for 1 hr under ~10 Torr vacuum) to remove residual solvent, improve microphase separation of the self-assembled structures, and to complete the thermally-activated cross-linking reaction. This process for deposition and self-assembly was then repeated for a second layer (~25 nm film) of block copolymer, in some cases using block copolymer systems of identical composition and in other cases with block copolymer systems of differing composition.

**Pattern transfer to metal nanostructures via a lift-off process:**

The block copolymer thin film samples were exposed to UV light (UVP CL-1000 Ultraviolet Cross-linker at \(\lambda = 254\) nm and an exposure dose of 1 J/cm\(^2\)) and rinsed in acetic acid to remove the PMMA domain.\[^{18b}\] The remaining PS template was descummed by an oxygen plasma treatment (gas: O\(_2\), flow rate: 5 SCCM, pressure: 150 mTorr, power: 40W) to remove residual PMMA and the brush layer used for surface treatment. Metal thin films consisting of 1 nm Cr and 5 nm Au were evaporated sequentially using a CVC 3-boat thermal evaporator. The lift-off process was carried out by sonicating (Fisher Scientific FS30H ultrasonic cleaner) the
metal deposited samples in toluene at 55°C. The samples were dried in a stream of N₂ prior to SEM imaging.

**Nanostructure characterization:**

The block copolymer morphology in thin films and the metal nanostructures were imaged by scanning electron microscopy (SEM) using a JEOL JSM-7401F. Top-down SEM images were collected using gentle beam mode operating at an accelerating voltage of 1 kV and a gun emission current of ~10 mA. Samples for cross-sectional SEM imaging were cleaved in liquid nitrogen. Cross-sectional SEM images were collected with the sample tilted at 80° from the sample normal using an accelerating voltage of 5 kV.

**Optical characterization of extent of lift-off:**

The extent of lift-off was determined by transmission measurements (light source: Mikropack HL-2000-FHSA, detector: Ocean Optics USB4000) using metal films deposited on glass slides. Note that the block copolymer processing was identical on the glass substrates (pre-cleaned Fisher Scientific plain microscope slides) as it was on the Si substrates. A glass slide with a 10 nm layer of neutral brush was used as bright reference spectrum for the transmission measurements, i.e., corresponds to 100% transmission. Transmission measurements (beam spot with a diameter of ~3.0 mm) were collected at three distinct locations across the substrate, thus allowing for the extent of lift-off to be quantified across large areas.

**References**


Chapter 3 Multilayer Thin Films Nanostructures of Cross-linkable Block Copolymer / Homopolymer Blends

This chapter was submitted for publication in December 2014.

Abstract

Thin films of block copolymers are widely recognized as promising candidates for nanoscale fabrication of semiconductor devices, membranes, and other structures because of microphase separation to simultaneous form well-organized nanostructures with periods of a few nm and above. However, the three-dimensional structure of block copolymer microdomains could enable them to make 3D devices and structures directly, which could lead to efficient fabrication of complex heterogeneous structures. This chapter details the nanofabrication processes and their characterizations of 3D multilayer based on epoxide functionalized cross-linkable block copolymer and homopolymer blends. The cross-linkable block copolymer and homopolymer were both synthesized by atom transfer radical polymerization. Multilayer films of poly(styrene-block-methyl methacrylate) were assembled and thermally cross-linked on wafer substrates in a layer-by-layer process. The followed layer, while being directed to self-assemble on the lamellae of the underlying layer, had a tunable composition and polystyrene domain width. The 3D multilayer structure was verified by film thickness measurements, top-down SEM images and the registration of corresponding block copolymer domains between layers were confirmed by cross-sectional SEM.
Introduction

Nanoscale patterns achieved from the self-assembly of block copolymers have been extensively studied from a fundamental chemistry and physics perspective\(^{[1-4]}\) as well as in various applications such as nanolithography, electronic and magnetic devices, nanoreactors, and separation membranes.\(^{[5-11]}\) Based on the volume fraction of each block, the segmental interaction between two components \(\chi\), and the degree of polymerization (N), block copolymer exhibit well-organized arrays of lamellar, cylindrical, gyroid, and spherical microdomains that are tens of nanometres in size.\(^{[2]}\) By directed self-assembly a simple route is applied to nanoscaled arrays in the fabrication of multi-level thin film devices, since the balanced interfacial interactions between the chemical modified surfaces and the domains of block copolymer allows the block copolymer to perpendicularly self-assemble to the surface.\(^{[12-17]}\) The use of oriented microdomains of block copolymers for lithography improves traditional photolithography for applications, including nanolithographic templates,\(^{[18,19]}\) etching masks,\(^{[20-22]}\) nanowire fabrication,\(^{[23]}\) nanoparticle deposition,\(^{[24]}\) nanoporous membranes,\(^{[25]}\) and nano-textured surfaces.\(^{[26]}\) For such applications, control over the microdomain interfaces is of crucial importance for many of the desired practical uses.

In the last three decades, significant effort has been devoted to controlling two-dimensional (2D) nanostructures of block copolymer films by chemical and topographical modification to substrate surface\(^{[27-32]}\) as well as fabricating nanostructures with patternable block copolymer.\(^{[33,34]}\) However, the controlled formation of more complex, three-dimensional (3D) scaffolds presents more unique opportunities in block copolymer nanofabrication.\(^{[35]}\) The 3D mesoporous structures were fabricated by an iterative method \(i.e.\) independently stacking multiple self-assembled block copolymer films supported by Si membranes.\(^{[36]}\) Profile control in
block copolymer nanostructures using bilayer thin films has been proved to significantly improve the lift-off process in pattern transfer.\textsuperscript{[37]} Multilayer nanostructures with different morphologies between layers were obtained by the directed self-assembly of lamellar forming block copolymer thin film with the guidance of underlying cross-linked self-assembled cylindrical forming cross-linkable block copolymer with reactive azido (-N\textsubscript{3}) incorporated in one block. formation of multilayer block copolymer thin films.\textsuperscript{[38]} Multilayer thin films prepared from cross-linkable block copolymers with benzocyclobutene functionality in one block allows size controllability and the registration between layers.\textsuperscript{[39]}

In this study, a layer-by-layer approach to fabricating multilayer nanostructure of block copolymer thin films with controlled microdomain interfaces in polystyrene-\textit{block}-polymethyl methacrylate (PS-\textit{b}-PMMA) by varying the volume fractions of block copolymer domains is presented. Block copolymer PS-\textit{b}-PMMA with reactive epoxide functionality in the MMA block, denoted PS-\textit{b}-P(MMA-\textit{r}-GMA) (or PS-\textit{b}-\textit{ePMMA}), homopolymer P(S-\textit{r}-GMA) (\textit{x}-PS) and P(MMA-\textit{r}-GMA) (\textit{x}-PMMA) were synthesized by atom transfer radical polymerization.\textsuperscript{[40-42]} The PS-\textit{b}-\textit{ePMMA} copolymers were designed to form lamellar microdomains, with a total number-average molecular weights of 93.7 kg mol\textsuperscript{-1}, PS volume fraction of 0.53, and MMA containing epoxide (GMA: 4.5 mol\%). The layer-by-layer fabrication was carried out by thermally cross-linking self-assembled block copolymer / homopolymer thin film on neutral surface and using the cross-linked layer to guide the self-assembly of the followed layer. The volume fractions of layers were carefully tuned by blending different amounts of homopolymers \textit{x}-PS and \textit{x}-PMMA. Here we present that the epoxide functionalized PS-\textit{b}-PMMA / \textit{x}-PS / \textit{x}-PMMA system can 1) readily form insoluble and thermally stable cross-linked, self-assembled multilayer nanostructures, 2) realize registration between layers through a layer-by-layer
approach using the underlying layer to guide the self-assembly of the top layer, 3) control the overall profile through carefully tuning the volume fractions of the blocks each layer of block copolymer thin film.

**Results and discussion**

The schematic in Figure 3.1 illustrates a layer-by-layer approach to fabricating multilayer self-assembled block copolymer nanostructures through the use of self-assembled block copolymer / homopolymer blends in thin films. Block copolymer thin films were spin-cast on a silicon substrate with a neutral brush surface and solvent annealed under a mixed solvent vapor leading to the self-assembly of lamellae oriented perpendicular to the substrate. By heating the sample to 190°C for 1 hr under vacuum, a cross-linking reaction was then allowed to happen within the self-assembled domains. The resulting cross-linked nanostructures were thus locked and became relatively insoluble. The followed layers of block copolymer could then be deposited and processed using the same conditions (i.e., self-assembly via solvent annealing followed by cross-linking upon thermal treatment). The underlying layer acted as a chemically patterned substrate that guided the self-assembly of the block copolymer structures in the followed layer. Each block copolymer layers were ~50 nm thick, thereby generating a nanostructured film with a total thickness increasing with the number of layers. The materials polystyrene-block-poly(methyl methacrylate-random-glycidyl methacrylate) (PS-b-P(MMA-r-GMA) or PS-b-ePMMA), polystyrene-random-(polyglycidyl) (P(S-r-GMA) or x-PS), and poly(methyl methacrylate)-random-poly(glycidyl methacrylate) used here were synthesized by atom transfer radical polymerization (ATRP). The diblock copolymer system of PS and PMMA is advantageous because it is a well-characterized, model block
copolymersystem\[49\] and the PMMA domain can be selectively degraded by exposing in UV (254 nm) and removed by rinsing in acetic acid\[50\] This approach can be generalized to most block copolymers systems, but other such materials may exhibit subtle differences in the structures self-assembled in thin films from those presented here due to more disparate domain surface tensions than in the PS / PMMA system (e.g., it may be more difficult to achieve perpendicular interfaces and nanostructures even on a neutral surface).

**Figure 3.1.** Layer-by-layer approach to fabricate multilayer self-assembled block copolymer nanostructures.

The self-assembly of block copolymer / homopolymer blend thin films on neutral surfaces is shown in the SEM images in **Figure 3.2.** In thin films the blends undergo morphological transitions with increasing $\phi_{PS}$ (volume fraction of PS) from disorder to spherical / cylindrical with PMMA (dark gray regions) as matrix to lamellar to spherical / cylindrical with PS (light gray regions) as matrix and to disorder which matches excellently with the microphase separated morphologies in bulk.\[2\] The SEM images of $\phi_{PS}$ at 30% and 70% which is supposed to be cylindrical but both showed a mix of cylindrical and lamellar-like mophologies. The lamellar-like nanostructures are the cylindrical morphology applied a parallel orientation to the substrate. This can be explained by that the neutral surface used is a lamellar forming neutral surface for symmetric block copolymer to adopt a perpendicular orientation.\[12–17\] Spherical / cylindrical morphologies are found in the cases of of $\phi_{PS}$ at 20% and 80% while for the $\phi_{PS} = 80\%$ case some adjacent spheres merged to form short PMMA domains. In the scenario of $\phi_{PS} = 10\%$ and 90%, no nanostructure were found because the volume fractions of one domain fell in the region of disorder which means PS and PMMA mixed on molecular level.
Figure 3.2. Top-down SEM images of lamellae self-assembled in single layer films on neutral brushes by PS-\textit{b}-PMMA blends with homopolymers and 10, 20, 30, 40, 50, 60, 70, 80, 90 vol% of PS.

Multilayer approach to controlling the interface profiles of block copolymer nanostructures allows the composition, and thus dimension, of each self-assembled layer to be adjusted independently. One important advantage of using cross-linkable block copolymer and cross-linkable homopolymer is that the formed nanostructure will is much more stable in the mechanical and chemical processing. In this work, three-dimensional multilayered nanostructures trilayer of cross-linkable block copolymer / homopolymer were achieved with controlled composition of the two copolymer domains in each layer. Four of such multilayered nanostructures were fabricated two from bilayer with the bottom layer having a PS volume fraction ($\phi_{PS}$) of 50.0 vol% and the top layer having $\phi_{PS} = 60.0$ vol% (or 40.0 vol%), as indicated by the notation and two from trilayer thin films with the bottom layer having a PS volume fraction ($\phi_{PS}$) of 50.0 vol%, middle layer having $\phi_{PS} = 60.0$ vol% (or 40.0 vol%), and the top layer having $\phi_{PS} = 70.0$ vol% (or 30%), as indicated by the notation ‘Trilayer 50-60-70PS or 50-40-30PS’ used in this manuscript. Each layer consisted of a block copolymer / homopolymer blend with lamellar-forming PS-\textit{b}-ePMMA and cross-linkable homopolymers x-PS and x-PMMA (note that these are not truly homopolymers but rather random copolymers with 1 mol% concentrations of a reactive epoxy functionality, but, for clarity, they are labeled as such throughout). The relative amount of x-PS and x-PMMA added was carefully tuned to
control the volume fractions of PS and PMMA in the block copolymer blends. Three different block copolymer compositions ($\phi_{PS} = 30, 40, 50, 60, \text{or } 70 \text{ vol\%}$) were considered for the layers.

**Figure 3.3.** Top-down SEM images (top) and the corresponding histograms of grayscale color (bottom, x-axis: Pixel Gray) for block copolymer films with top layer polystyrene compositions of 30, 40, 50, 60, and 70 vol\%. The blue and red shaded areas indicate the pixels assigned to belong to the PMMA and PS domains in the SEM image, respectively. Note that, in this case, the PMMA domains were removed prior to SEM imaging.

**Figure 3.3** shows top-down SEM images of 50-40-30PS, 50-40PS, 50-60PS, and 50-60-70PS multilayer films after removal of the PMMA domain, as well as a single layer 50PS film of equivalent thickness for each layer. The light regions in the SEM images correspond to the PS nanostructures. The top-down SEM images from the 50-40-30PS to 50-40PS to 50PS to 50-60PS and to 50-60-70PS also exhibit the visual trend that the PS domains become wider while the PMMA domains become narrower, which is consistent with the profiles targeted in these bilayer thin films. An comparison between the top-down SEM images of $\phi_{PS} = 70\%$ in Figure 3.2 with 50-60-70PS shows that the top layer $\phi_{PS} = 70\%$ formed lamellar nanostructure even though the width of the PS domain is much bigger than that of the PMMA domain. The copolymer blend $\phi_{PS} = 70\%$ which is supposed to form cylindrical nanostructure adopted lamellar morphology because the gradual domain composition change from the bottom to the top and thus the whole system has less energy penalty to form defects like disclination or dislocations.\textsuperscript{[51–53]} On the bottom side of Figure 3.3, an analysis of the grayscale top-down SEM
images confirms this trend. Histograms of the grayscale color of each pixel in the images were determined and have two clear peaks corresponding to the PMMA (dark, low grayscale color) and PS (light, high grayscale color) domains. In order to quantify the relative composition of each domain at the top surface of the bilayer film, a threshold was applied corresponding to the probability change slope closest to 0 between the two peaks in the distribution. interesting Table 3.1 summarizes the measured PS and PMMA compositions at the top surface of the films, which ranged from 35 to 74 vol% PS and closely matched the targeted surface compositions of 40 to 60 vol% PS (for 50-40PS to 50-60PS, respectively). One domain of the block copolymer nanostructures was selectively removed by exposure to UV light (254 nm, 1 J/cm²) and development in acetic acid (a non-solvent for the PS domain).[15]

Table 3.1. The areal fraction of PS and PMMA at the free surface of the block copolymer bilayer films as determined by top-down SEM imaging.

<table>
<thead>
<tr>
<th>3D Structure Design (as denoted by PS composition) a</th>
<th>Measured PS composition at the film surface [vol%]</th>
<th>Measured PMMA composition at the film surface [vol%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>trilayer (50-40-30 PS)</td>
<td>35%±1%</td>
<td>65%±1%</td>
</tr>
<tr>
<td>bilayer (50-40 PS)</td>
<td>43%±3%</td>
<td>57%±3%</td>
</tr>
<tr>
<td>monolayer (50 PS)</td>
<td>52%±2%</td>
<td>48%±2%</td>
</tr>
<tr>
<td>bilayer (50-60 PS)</td>
<td>66%±1%</td>
<td>34%±1%</td>
</tr>
<tr>
<td>trilayer (50-60-70 PS)</td>
<td>74%±2%</td>
<td>26%±2%</td>
</tr>
</tbody>
</table>

a Notation of “50-40-30PS” means the multilayer structure was built with a bottom layer consisting of 50 vol% PS and 50 vol% PMMA, a second layer of, and a third layer of 30 vol% PS and 70 vol% PMMA.

A remarkable advantage of the cross-linkable PS-b-PMMA thin films is their insolubility when the samples are cross-linked after thermal annealing (190°C for 1 hour), which allows their subsequent use in further processes, such as the fabrication of 3-dimensional
multi-layered arrays, that exploit directed self-assembly for adjacent layers. Once the cross-linked thin films are prepared, the resulting thin films of PS-b-PMMA are insoluble and hence the next layer can be fabricated on underlying cross-linked thin films via a layer-by-layer fashion as described in Figure 3.1. The multilayer nanostructure 50-60-70PS in cross-linkable block copolymer / homopolymer blend is evidenced in the cross-sectional SEM images of Figure 3.4. Figure 3.4a shows the SEM images taken at a tilt angle of 65 to probe a crosssection of the multi-layered thin films of PS-b-PMMA with 4.5 mol% epoxide. From Figure 3.4a, it can be clearly seen that the lamellar microdomains persisted throughout the entire thickness at 3 layers (110 nm as shown in the thickness dependent on the number of layers of cross-linked copolymers), suggesting that the microdomains of two consecutive layers were in register. The ability to prepare multi-layered cross-linked thin films with accurate registration on the nanometre scale demonstrates the power of using functionalized block copolymers and may be further utilized as a new route to fabricate 3-dimensional arrays via directed self-assembly.

**Figure 3.4.** a) Cross-sectional SEM images of multilayer 50-60-70PS films showing the registration between layers, b) Thicknesses of cross-linked film on silicon substrate with brush with increasing layers of block copolymer films.

The thermal cross-linking reaction of PS-\textit{b}-ePMMA in the self-assembled (via solvent
annealing) block copolymer thin films was studied by thermally annealing the block copolymer thin films on substrate with different brushes as shown in Figure 3.5. The cross-linking reaction extent was quantified by measuring the residual film thickness after cross-linking and sonication in toluene. The measured thin film thicknesses were normalized using the as-spun film thickness as control. Neutral brushes PS$_{57}$-MMA$_{41}$-HEMA$_4$, PS$_{58}$-MMA$_{41}$-GMA$_1$, and PS$_{61}$-MMA$_{35}$-GMA$_4$ with increasing amount of epoxide molar fraction were coated on silicon wafers by thermal annealing at 190°C from 15 minutes to 120 minutes. The cross-linking of PS-\(b\)-ePMMA reached its full extent ~90% on brush PS$_{61}$-MMA$_{35}$-GMA$_4$ within 15 minutes which has the highest concentration of epoxide while on PS$_{61}$-MMA$_{35}$-HEMA$_1$ or PS$_{57}$-MMA$_{41}$-HEMA$_4$ more than 30 minutes is needed. Note that the normalized film thickness upon thermal treatment plateaus at ~90%, with this 10% reduction in film thickness being attributed to the densification of the film upon heating$^{[54]}$ and contractile film stresses upon cross-linking$^{[55]}$. The highest normalized film thickness of PS-\(b\)-ePMMA on brush PS$_{57}$-MMA$_{41}$-HEMA$_4$ is lower than 60%. Therefore, brush with higher concentration of epoxide enables the cross-linking to happen faster and to reach higher extent.
Figure 3.5. The extent of cross-linking as reported by the normalized residual film thickness (relative to the initial, as-deposited film thickness) as a function of the thermal annealing time and substrate brushes.

A proposed surface acid-catalyzed cross-linking mechanism illustrated in electron pushing process is shown in Scheme 3.1. The process starts from the proton transfer from the acetic surface of silicon substrate with brush to protonate the oxygen in the epoxide. The hydroxyl group on the surface acts as a nucleophile and attached to the ternary carbon of the epoxide. The epoxide undergoes ring opening and a hydroxyl group produced. Thus, the
Scheme 3.1. Proposed mechanism of cross-linking of block copolymer on silicon substrate with brush.

polymer linked to the surface. The cross-linking between PS-\(b\)-ePMMA can also be explained by this process which is already shown in the scheme. When the cross-linking reaction reach the surface, the cross-linking process is terminated because the complete consumption of epoxides and hydroxyl groups will be the end cap. The low extent of cross-linking on brush PS\(_{57}\)-MMA\(_{41}\)-HEMA\(_{4}\) can be explained by the proposed cross-linking surface acid-catalyzed cross-linking mechanism. On the substrate with polymer brushes, there will be some hydroxyl group after the brush cross-linked to the piranha treated silicon wafer. The major difference between brush PS\(_{57}\)-MMA\(_{41}\)-HEMA\(_{4}\) and the other two epoxide included brush is that the hydroxyl group of HEMA attach to the silicon surface and the amount of hydroxyl group will decreased by the reaction. However, in the epoxide case once a hydroxyl group on the substrate consumed, a new hydroxyl group will be produced because the ring opening reaction happened on the epoxide group. Thus, the total hydroxyl group will be dependent on the concentration of
epoxide groups. This also explains that the cross-linking reaction on PS$_{61}$-MMA$_{35}$-GMA$_{4}$ happened more than twice faster than that on PS$_{58}$-MMA$_{41}$-GMA$_{1}$.

**Conclusions**

In summary, polymer thin films from cross-linkable PS-\textit{b}-PMMA copolymers containing the reactive epoxide functionality were prepared by solvent annealing and subsequent cross-linking at elevated temperatures, leading to robust thermoset, nano-structured thin films. By controlling the extent of cross-linking, either by varying the concentration of epoxide or by limiting the extent of cross-linking, a simple route to fabricate multilayer cross-linked block copolymer nanostructure has been shown where the microphase separations of adjacent layers were in registry, leading to a propagation of the orientation and ordering of the thin film over large distances. The mechanism of the cross-linking reaction was discussed to explain the cross-linking reaction processes including epoxide functionality. This work demonstrates a promising route to fabricate 3-dimensional structure with controlled placement of elements.

**Experimental Section**

*Synthesis of cross-linkable block copolymer.*

Atom transfer radical polymerization (ATRP) was applied to synthesize the PS-\textit{b}-P(MMA-\textit{r}-GMA) or PS-\textit{b}-ePMMA block copolymer. The monomers styrene (Sigma-Aldrich, stabilized, 99%) and methyl methacrylate (Acros, stabilized, 99%) were purified by distillation with the presence of calcium hydride under reduced pressure. The catalysts copper (I) bromide and copper (I) chloride was purified by heating to reflux in acetic acid for 10 hours, filtered, washed with degased methanol and acetone, and dried under vacuum. All other
chemicals and solvents were used as received. The polymerization started with synthesizing polystyrene (PS) to obtain narrow distributed macroinitiator with bromine at one end. The purified styrene monomer, (1-bromoethyl)benzene (Sigma-Aldrich, 97%) as the initiator, and 

\[ \text{N,N',N''-pentamethyldiethylenetriamine} \]

as the stabilizing ligand were loaded to a Schlenk flask. The mixture was run three cycles of freeze-pump-thaw and copper (I) bromide as the catalyst was added to the frozen mixture. The flask was sealed and heated to 100°C in the absence of solvent. The reaction was terminated after about 48 hours when most of the monomer solidified meaning no more homogeneous mixing. The reaction mixture was then cooled to room temperature. DOWEX Marathon MSC (H) ion-exchange resin (Sigma-Aldrich) and dichloride methylene was added and stirred for 24 hours to absorb the catalyst copper (I) bromide or copper (II) bromide. The ion-exchange resin was removed by filtration with a layer of neutral alumina. The filtrate was precipitated out in 10 times methanol and the obtained polymer white powder was dried under vacuum at room temperature. The PS macroinitiator (M.W. = 47.3 kg mol\(^{-1}\), PDI = 1.04) was used as the initiator to extend the second block. The PS macroinitiator, the purified methyl methacrylate glycidyl methacrylate (MP Biomedicals, 99%) monomers, and 

\[ \text{N,N',N''-pentamethyldiethylenetriamine} \]

were dissolved in anhydrous THF (Sigma-Aldrich) and loaded to a Schlenk flask. The mixture was run three times of freeze-pump-thaw cycle. The catalyst copper (I) chloride was added to the frozen mixture. The Schlenk flask was then sealed and the mixture was heated to 50°C for 48 hours. The purification of the block copolymer was the same as the macroinitiator. The symmetric block copolymers PS-\(b\)-PMMA (99.5 kg mol\(^{-1}\), PDI = 1.14, volume fraction of PS \(\phi_{PS} = 50.4\%) \) and PS-\(b\)-ePMMA (93.7 kg mol\(^{-1}\), PDI = 1.11, \(\phi_{PS} = 53.4\%, \text{GMA: 4.5 mol}\% \)) The composition of the block copolymers and the PS macroinitiator were characterized by \(^1\text{H NMR.} \) Homopolymers with a
low concentration of thermally cross-linkable functionality were synthesized through ATRP. These cross-linkable homopolymers included x-PS (17.4 kDa, PDI = 1.28) and x-PMMA (25.2 kDa, PDI = 1.47) each with 1 mol% of glycidyl methacrylate functionality randomly incorporated.

Neutral brush preparation and self-assembly by solvent annealing:

The neutral substrate for the self-assembly of lamellar-forming PS-\(b\)-PMMA block copolymers with perpendicular orientations was prepared by thermally cross-linking a P(S-r-MMA-r-GMA) random copolymer brush onto Si substrates. Si wafers were purchased from Montco Silicon and were treated with piranha solution a mixture of 30% H\(2\)O\(2\)/70% H\(2\)SO\(4\) (v/v) at 70°C for 20 minutes. The cleaned substrates were rinsed extensively with distilled water, and then further rinsed with acetone and toluene. The random copolymers [P(S\(_{0.58}\)-r-MMA\(_{0.31}\)-r-GMA\(_{0.01}\)), P(S\(_{0.61}\)-MMA\(_{0.35}\)-GMA\(_{0.04}\)), P(S\(_{0.57}\)-MMA\(_{0.41}\)-HEMA\(_{0.04}\))] were synthesized by free-radical polymerization by heating up a mixture of styrene, methyl methacrylate, glycidyl methacrylate and azobisisobutyronitrile (AIBN) in toluene to 80°C for 8 hours and purified by precipitating in methanol and filtration. A 0.3 wt% solution of the random copolymer in anhydrous toluene (EMD Chemicals, 99.8 wt%) was prepared and spin-cast onto a film thickness of 10 nm onto the clean silicon wafers. Thermally annealing at 190 °C for 1 hour allowed the random copolymer cross-link into a dense mat and be sonicated in a toluene bath removed unreacted random copolymer.

Thin films of PS-\(b\)-ePMMA block copolymer and block copolymer / homopolymer blends were spin-cast onto the prepared neutral surfaces. Solutions of block copolymer and homopolymer were prepared at a concentration of 1.5 wt% by weighing out dry polymer and
adding toluene dropwise. Nine blend solutions of block copolymer and cross-linkable homopolymer were prepared by blending the solutions of block copolymer and homopolymer as indicated in Table 3.2, targeting different total volume fractions of styrene and methyl methacrylate in each solution. The ~50 nm monolayer block copolymer thin film was produced by spincasting (5000 rpm for 30 s) a 1.5 wt% solution.

**Table 3.2.** Block copolymer blends with controlled volume fractions of PS.

<table>
<thead>
<tr>
<th></th>
<th>10PS</th>
<th>20PS</th>
<th>30PS</th>
<th>40PS</th>
<th>50PS</th>
<th>60PS</th>
<th>70PS</th>
<th>80PS</th>
<th>90PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 wt% PS-b-ePMMA [mL]</td>
<td>0.5</td>
<td>0.7</td>
<td>1</td>
<td>1.375</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>1.5 wt% x-PS [mL]</td>
<td>0.0</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>0.412</td>
<td>1.02</td>
<td>1.24</td>
<td>1.7</td>
</tr>
<tr>
<td>1.5 wt% x-PMMA [mL]</td>
<td>2.35</td>
<td>1.27</td>
<td>0.85</td>
<td>0.37</td>
<td>0.35</td>
<td>0.09</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total volume fraction of PS [%]</td>
<td>10.0</td>
<td>20.0</td>
<td>30.0</td>
<td>40.0</td>
<td>50.0</td>
<td>60.0</td>
<td>70.0</td>
<td>80.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Volume fraction of homopolymer [%]</td>
<td>81.6</td>
<td>63.1</td>
<td>44.4</td>
<td>20.2</td>
<td>19.9</td>
<td>20.6</td>
<td>35</td>
<td>56.7</td>
<td>78.2</td>
</tr>
</tbody>
</table>

Solvent vapor annealing was carried out by exposing the block copolymer thin films to a saturated vapor of mixed solvents. Acetone (30 mL, Fisher, 99%) and cyclohexane (30 mL, Fisher, 99%) were added to the bottom of a glass desiccator (1.5 L volume). The solvents were degassed under house vacuum (25 Torr) to remove any dissolved gases prior to solvent annealing. The thin film samples were suspended on a metal frame above the solvent mixture. The system pressure was then lowered to 20 Torr, the desiccator was sealed, and the polymer thin films were swollen in the mixed solvent vapor environment for 4 hours. The solvent vapor annealing process was quenched by opening the chamber to vacuum to remove solvent vapor and followed by opening the entire chamber to air to allow the swollen block copolymer thin films to dry.

*Processing of multilayer block copolymer thin films:*
The multilayer fabrication started with spincasting the blend 50PS onto a neutral substrate and then solvent annealed in the saturated vapor of acetone and cyclohexane for 4 hours. The solvent vapor annealed samples were thermally treated (190°C for 1 hour under ~10 Torr vacuum) to remove residual solvent, improve microphase separation of the self-assembled structures, and to complete the thermally-activated cross-linking reaction. This process for deposition and self-assembly was then repeated for followed layers (~50 nm film) of block copolymer, in some cases using block copolymer systems of identical composition and in other cases with block copolymer systems of differing composition. The thermal-activated cross-linking conditions (190°C for 15, 30, 60, or 120 minutes) on brush PS\textsubscript{57}-MMA\textsubscript{41}-HEMA\textsubscript{4}, PS\textsubscript{58}-MMA\textsubscript{41}-GMA\textsubscript{1}, and PS\textsubscript{61}-MMA\textsubscript{35}-GMA\textsubscript{4} were studied by annealing block copolymer nanostructures self-assembled by solvent annealing. The thermally treated samples were sonicated in a toluene bath at 22°C for 3 minutes and thermally annealed at 190°C for 1 hour. The residual film thickness was measured by ellipsometry and reported relative to the thickness of an as-deposited block copolymer thin film. The multilayer cross-linked block copolymer followed the same procedure for the deposition for each layer.

Nanostructure characterization:

The block copolymer morphology in thin films and the metal nanostructures were imaged by scanning electron microscopy (SEM) using a JEOL JSM-7401F. Top-down SEM images were collected using gentle beam mode operating at an accelerating voltage of 1 kV and a gun emission current of ~10 mA. Samples for cross-sectional SEM imaging were cleaved in liquid nitrogen. Cross-sectional SEM images were collected with the sample tilted at 60° from the sample normal using an accelerating voltage of 5 kV.
References


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Chapter 4 Block Copolymer Nanostructures across Scales in Thin films

This chapter was submitted for publication in August 2014.

Figure 4.S1. ToC figure

An epoxide functionalized PS-PMMA block copolymer system is developed capable of self-assembling into nanostructures and subsequently cross-linking in response to heat or light. The cross-linking process in thin films is characterized in response to thermal-activation or photoinitiation. Positive- and negative-tone optical photopatterning using a dual-tone nanostructure development process is achieved in a single cross-linkable block copolymer system, thus enabling such cross-linkable materials to be applied for lithographic applications across multiple scales.

Keywords: block copolymer, self-assembly, lithography, hierarchical structures, thin film, polymerization
Abstract

The self-assembly of block copolymers in thin films provides an attractive approach to patterning 5~100 nm structures. Cross-linking and photopatterning of the self-assembled block copolymer morphologies provide further opportunities to structure such materials for lithographic applications, and to also enhance the thermal, chemical or mechanical stability of such nanostructures to achieve robust templates for subsequent fabrication processes. Atom transfer radical polymerization was used to synthesize model lamellar-forming diblock copolymers of polystyrene and poly(methyl methacrylate) with an epoxide functionality. We demonstrate that self-assembly and cross-linking of the reactive block copolymer materials in thin films can be decoupled into distinct, controlled process steps using solvent annealing and thermal treatment / ultraviolet exposure. Conventional optical lithography approaches can also be applied to the cross-linkable block copolymer materials in thin films and enables simultaneous structure formation across scales — micrometer scale patterns achieved by photolithography and lamellar nanostructures with different periods via sequential self-assembly of smaller symmetric block copolymer on the photopatterned self-assembled symmetric block copolymer in thin film.

1. Introduction

The self-assembly of block copolymers in thin films has been extensively pursued as a promising candidate for the lithographic patterning of 5~100 nm densely-packed, ordered nanostructures with high-throughput.[1–4] Techniques for directed self-assembly, often involving the use of external fields[5–7] or guiding chemical[8,9] and topographic[10–18] templates, have achieved success in controlling the long-range perfection, orientation, geometry and dimension,
and spatial registration of block copolymer nanostructures, although challenges still remain\textsuperscript{[4,19,20]}. Reactions within these nanostructured systems after self-assembly can provide additional unique opportunities\textsuperscript{[21,22]}. For example, selective degradation of one copolymer domain can generate topographic templates for pattern transfer processes\textsuperscript{[23–28]} or the block copolymer domains may be functionalized with spatial control with external inorganic components or small molecules\textsuperscript{[29–37]}. Furthermore, Ober\textsuperscript{[38]}, Ross\textsuperscript{[39]}, and co-workers have used cross-linkable block copolymers [poly(\(\alpha\)-methylstylene)-block-4-hydroxystyrene) and poly(styrene-block-dimethylsiloxane), respectively] in combination with electron beam lithography and solvent vapor annealing to yield co-existing line and dot patterns in thin films. In both of these cases, the exposed regions become cross-linked which stabilizes the pre-formed block copolymer nanostructures, such that subsequent solvent annealing allows the unexposed regions to evolve structurally.

Cross-linking reactions also allow for control over the thermophysical, solubility, mechanical, and structural properties of block copolymer nanostructures, such as in phenol-formaldehyde or epoxy resin thermosets at industrial-scales. Recently, benzocyclobutene (BCB) and azido functionalities have been included in block copolymer systems to fabricate cross-linked nanoporous polystyrene templates\textsuperscript{[40]}, control the size of nanoscale domains\textsuperscript{[41]}, or achieve insoluble multilayer or three-dimensional assemblies\textsuperscript{[41–43]}. These thermally- and ultraviolet-activated cross-linking chemistries are also analogous to those employed in random copolymers designed to covalently functionalize substrates with tuned wettability and provide control over block copolymer domain orientations in thin films (\textit{e.g.}, to generate the so-called ‘neutral’ surfaces need to perpendicularly orient block copolymer nanostructures in thin films)\textsuperscript{[44–46]}. Cross-linking in the BCB or azido functionalized block copolymers was achieved by thermal treatment at a temperature (\(T_{\text{cross-linking}}\) typically is 250\textdegree{}C) significantly higher than the
self-assembly temperature \( (T_{\text{self-assembly}}) \). Thus, processing conditions could be selected such that self-assembly was performed first and then subsequently, in a distinct step, cross-linking could be achieved at elevated temperatures. The BCB and azido functionalities, while enabling decoupled self-assembly and cross-linking processes, may limit the choice of block copolymer chemistries as the elevated temperatures that are required may cause the self-assembled nanostructures to further evolve prior to cross-linking. This morphology evolution may result from inducing order-order transitions\[^{[47]}\] between microphase separated morphologies, exceeding the order-disorder transition temperature \( T_{\text{ODT}} \) (i.e., \( T_{\text{cross-linking}} > T_{\text{ODT}} \) causing the material to revert to the disordered state and become unstructured), or thermal degradation.

In this article, we present the implementation of epoxide functionalized poly(styrene-block-methyl methacrylate) (PS-\( b \)-PMMA) block copolymers and characterize their self-assembly and thermal cross-linking behavior in thin films. The thermal cross-linking of the epoxide is found to occur at temperatures \( T_{\text{cross-linking}} > 140^\circ \text{C} \), which is slightly below the thermal self-assembly conditions of \( T_{\text{self-assembly}} \approx 170 - 210^\circ \text{C} \). Solvent vapor annealing enables self-assembly at reduced temperatures (often room temperature)\[^{[48-51]}\] and was used here as a processing route to enhance the rate of self-assembly such that lamellar morphologies could be achieved prior to cross-linking. Alternatively, unlike the BCB and azido systems, \( T_{\text{cross-linking}} < T_{\text{self-assembly}} \) allows the block copolymer thin films to be cross-linked prior to self-assembly thereby inhibiting nanostructure formation. The epoxide functionalized block copolymers used here are also compatible with conventional optical lithography techniques. Epoxide chemistries are the basis for common negative-tone photoresists such as SU-8, in which the materials become insoluble upon exposure to ultraviolet (UV) or electron radiation. Similarly, when combined with a cationic photoinitiator, UV curing of an epoxide functionalized
poly(isoprene-\textit{block}-ethylene oxide) system has been shown to permanently trap cylinder and gyroid morphologies\cite{52}. Here we demonstrate that the epoxide functionalized PS-\textit{b}-PMMA system can 1) readily form insoluble and thermally stable cross-linked, self-assembled nanostructures, 2) decouple self-assembly from cross-linking in thin films by both thermal treatment and UV photoinitiation, 3) pattern self-assembled films in both ‘positive’- and ‘negative’-tones using 365 nm optical lithography to achieve ~50 nm period lamellar nanostructures in the exposed and unexposed regions, respectively, and 4) fabricate lamellar nanostructures with different periods (~50 nm and ~25 nm periods) on the same substrate in block copolymer thin films rapidly over wafer-scale areas.

![Scheme 4.S1. Synthesis of PS-\textit{b}-P(MMA-\textit{r}-GMA)](image)

2. Results and Discussion

The results presented here were enabled by the preparation of epoxide functionalized block copolymers in the model and previously well-characterized polymer pair of polystyrene / poly(methyl methacrylate)\cite{53}. Lamellar-forming symmetric block copolymers were synthesized through atom transfer radical polymerization using the reaction scheme in Scheme 3.S1\cite{54,55}.
Specifically, an uncross-linkable block copolymer poly(styrene-block-methyl methacrylate) (PS-b-PMMA, $M_n = 99.5$ kg mol$^{-1}$, PDI = 1.14, volume fraction of PS $\phi_{PS} = 50.4\%$) and an epoxide functionalized, cross-linkable block copolymer poly(styrene-block-(methyl methacrylate-random-glycidyl methacrylate)) (PS-b-P(MMA-r-GMA) or PS-b-ePMMA, $M_n = 93.7$ kg mol$^{-1}$, PDI = 1.11, $\phi_{PS} = 53.4\%$) were prepared. The epoxide functionality in the PS-b-ePMMA system (at a loading of 4.5 mol%) may be acid or base catalyzed to react and polymerize upon thermal treatment$^{[20]}$ $^{[56]}$ or in the presence of a photogenerated acid$^{[52]}$.

The self-assembly and cross-linking behavior of the epoxide functionalized PS-b-ePMMA block copolymer in thin films is presented in Figure 4.1 and compared to the reference, uncross-linkable PS-b-PMMA system. When solvent vapor annealing in a mixed system of non-preferentially swelling solvent (acetone and cyclohexane) is performed at room temperature ($22^\circ$C) for 4 hrs, the self-assembly of characteristic lamellar morphologies in thin films (i.e., the ‘fingerprint’ structures) are observed in both materials (Figure 4.1a). The lamellar domains are oriented perpendicular to the substrate, for all thin films considered in this manuscript, due to pretreatment of the substrate with a random polystyrene / poly(methyl methacrylate) copolymer mat with $\phi_{PS} = 58\%$ that is non-preferentially wetted by either domain of the block copolymer (often called the ‘neutral’ surface treatment). The lamellar morphologies self-assembled by the PS-b-ePMMA and PS-b-PMMA materials are well-developed and similar structurally, and the minor difference in domain periodicity (52 nm versus 48 nm) is the result of the small disparity in polymer molecular weight$^{[57]}$. 
Figure 4.1. Top-down scanning electron micrographs of 49 nm thick films of symmetric PS-\textit{b}-PMMA copolymer systems on neutral surfaces processed by a) solvent annealing at 22°C for 4 hrs and b) thermal annealing at 190°C for 24 hrs. Standard uncross-linkable PS-\textit{b}-PMMA (left) and cross-linkable PS-\textit{b}-P(MMA-\textit{r}-GMA) (right) materials are shown for each processing condition.

On the other hand, as shown in Figure 4.1b, the microphase separated morphologies differ drastically for the PS-\textit{b}-ePMMA and PS-\textit{b}-PMMA materials when thermally annealed. The as-deposited block copolymer films were thermally annealed with standard processing conditions (190°C for 24 hrs) on the same neutral-wetting substrates. The uncross-linkable block copolymer self-assembled into a standard lamellar morphology (Figure 4.1b, left), whereas the cross-linkable PS-\textit{b}-ePMMA exhibited poor self-assembly (Figure 4.1b, right). Thus it is suggested that the microphase separation in the cross-linkable epoxide functionalized PS-\textit{b}-ePMMA material was rapidly arrested due to the kinetics of the cross-linking reaction being faster than that of self-assembly, \textit{i.e.}, $T_{\text{cross-linking}} < T_{\text{self-assembly}}$. Although some small nanostructures are observed upon cross-linking, the morphology is not lamellar and the resulting microphase separated structures are more similar to those often observed upon spin casting of
block copolymer films from solution\textsuperscript{[58–60]}. As detailed below, at 190°C cross-linking is nearly completed within 15 min, suggesting the block copolymer does not have an opportunity to significantly microphase separate or evolve significantly from the as-deposited state (Figure 4.S1). During thermal treatment of the epoxide functionalized block copolymer thin films, the cross-linking reaction is thought to be initiated by acidic groups on the substrate and thus propagates from the substrate to the top surface of the film. This is supported, in part, by prior observations that similar epoxide functionalized polymers in the bulk are thermally stable at significantly higher temperatures\textsuperscript{[52]} (277°C). The ability to either self-assemble the PS-\textit{b}-ePMMA material by solvent annealing, or to cross-link it to prohibit nanostructure formation, indicates that the competing self-assembly and cross-linking processes may be decoupled.

\textbf{Figure 4.2}. Self-assembly and self-healing of lamellar nanostructures using the cross-linkable PS-\textit{b}-PMMA system in 49 nm thin films on neutral surfaces. Top-down SEM images after a) self-assembly by solvent annealing at 22°C for 4 hrs, b) cross-linking by thermal treatment at 190°C for 4 hrs, c) sonication in a toluene bath for 3 min to test the insolubility of the cross-linked structure, and d) regeneration of the microphase separated lamellar structures upon thermal annealing at 190°C for as short as 30 s.

\textbf{Figure 4.2} qualitatively demonstrates the effect of cross-linking on the solubility of block copolymer nanostructures self-assembled in thin films. After self-assembly by solvent annealing (Figure 4.2a), lamellar nanostructures formed by PS-\textit{b}-ePMMA in thin films were cross-linked...
by thermal treatment (190°C for 4 hrs). The lamellar morphology and domain periodicity ($L_0 = 48$ nm) of the cross-linkable block copolymer were maintained (Figure 4.2b). To test the extent of cross-linking and the solubility of the resulting nanostructures, the thin films were immersed in a toluene bath and sonicated for 3 min at 22°C. Figure 4.2c shows that the cross-linked PS-$b$-ePMMA nanostructures are stable and not dissolved, unlike uncross-linked PS-$b$-PMMA, PS or PMMA thin films, under these harsh conditions. Toluene can effectively solubilize both PS and PMMA (e.g., it is used as the spin casting solvent used to deposit the block copolymer films), and sonication is often used as means for providing physical energy at the surface for the purposes of cleaning. Instead of being solubilized, the cross-linked lamellae underwent surface reconstruction, in which the PS domain that was not cross-linked swelled significantly in the good solvent and rearranged at a molecular-level, thereby preferentially covering the free surface of all of the PMMA domains. Similar reversible surface reconstructions have been caused in thin films by exposure of self-assembled block copolymer nanostructures to a solvent that is selective to a single domain [61–63]. The SEM image in Figure 4.2c characterizes the topographic differences in the surface reconstructed film and, although the lamellar morphology is maintained, the domains appear less clear due to the extensively swollen state of the PS layer even upon drying. The PMMA domain, due its high cross-linking density, remains insoluble and unswollen in the solvent and stabilizes the nanostructures. If the PS domains were also cross-linked, for example by inclusion of epoxide functionalities into both domains of the block copolymer, it is anticipated that the self-assembled nanostructures would not undergo surface reconstruction or otherwise be affected by exposure to solvent. The lamellar morphology and dimension may be recovered or self-healed upon subsequent thermal annealing at 190°C for as short as 30 s as shown in Figure 4.2d. This indicates that the phase separated morphology is the
thermodynamic equilibrium structure and can be regenerated with relatively minimal energy input by thermal treatment.

Figure 4.3. The extent of copolymer cross-linking as reported by the normalized residual film thickness (relative to the initial, as-deposited film thickness) as a function of the thermal annealing temperature and time.

The extent of the epoxide cross-linking reaction in the self-assembled (via solvent annealing) block copolymer thin films was measured as a function of the thermal treatment conditions, as reported in Figure 4.3. The residual film thickness was characterized by ellipsometry after cross-linking by thermal treatment (130 - 230°C for 5 - 60 min) and solvent treatment / sonication to remove unreacted polymer. The normalized residual thickness is reported relative to the as-deposited film thickness and is dependent on both the thermal treatment time and temperature. It is found that the epoxide cross-linking reaction does not occur significantly at 130 or 140°C even for extended treatment times (60 min). Cross-linking is significant and rapid, however, when the epoxide functionalized block copolymers are treated at temperatures of 150°C or higher. Note that the normalized film thickness upon thermal treatment plateaus at ~90%, with this 10% reduction in film thickness being attributed to the densification
of the film upon heating\textsuperscript{[64]} and contractile film stresses upon cross-linking\textsuperscript{[65]}. Even faster cross-linking ($\leq 5$ min) requires more elevated temperatures (190°C or higher). These measurements of cross-linking temperature-dependent kinetics are consistent with our prior observations that the cross-linking reaction effectively outcompetes the self-assembly process at elevated temperatures. This conclusion is further supported by the work of Welander \textit{et al.}\textsuperscript{[66]}, in which directed self-assembly via thermal annealing of lamellar-forming PS-$b$-PMMA systems with molecular weights of $\sim 100$ kg mol$^{-1}$ on chemical surface patterns has been found to occur within times of 40~50 and 4~7 min at 190 and 210°C, respectively, which are thermal conditions at which the epoxide cross-linking reaction would be complete.

\textbf{Figure 4.4.} Schematics of the photopatterning process in a) positive- and b) negative-tones using the cross-linkable block copolymer materials. In the positive-tone system a), the lamellar nanostructures are self-assembled by solvent annealing prior to photopatterning and post-exposure baking that locally cross-links the self-assembled nanostructures, and is followed by a development step to remove the uncross-linked block copolymer nanostructures. In the negative-tone system b), photopatterning and post-exposure baking is performed prior to self-assembly to cross-link the block copolymer in a disordered state, such that subsequent solvent annealing allows self-assembly in only the unexposed regions of the thin film.

The epoxide functionalized PS-$b$-ePMMA block copolymer systems are compatible with optical lithography techniques and may be used as a photoresist material for simultaneously
patterning films at the nano- and micro-scales. Figure 4.4 illustrates processing approaches in which, using the same cross-linkable block copolymer material, the self-assembled nanostructures may be developed in a dual-tone: 1) a ‘positive’-tone in which the nanostructures are generated in the photo-exposed regions and 2) a ‘negative’-tone in which the nanostructures are formed in the unexposed, uncross-linked regions. In the positive-tone system (Figure 4.4a), the lamellar nanostructures are self-assembled by solvent annealing prior to photopatterning and post-exposure baking that locally cross-links the self-assembled nanostructures, and is followed by a development step in a good solvent to remove the uncross-linked block copolymer nanostructures. In the negative-tone system (Figure 4.4b), photopatterning and post-exposure baking is performed prior to self-assembly to cross-link the block copolymer in the unstructured state, such that subsequent solvent annealing allows self-assembly in only the unexposed regions of the thin film. Compared with cross-linking that occurs upon thermal treatment (Figure 4.1-3), cross-linking initiated by a photo-generated acid allows the reaction to proceed at milder conditions (i.e., temperature and time). Here a post-exposure bake of 130°C for 60 min was used to allow the cross-linking reaction to proceed to completion after photopatterning. Unexposed PS-\textit{b}-ePMMA, in comparison, remains relatively uncross-linked under identical thermal treatment conditions (see Figure 4.3). Therefore, cross-linking by photopatterning can be implemented as a distinct process from self-assembly or cross-linking by thermal treatment, thereby enabling the dual-tone nanostructure development.

The combination of block copolymer lithography and optical lithography allows the simultaneous patterning of structures at two distinct length scales - nanostructures through bottom-up self-assembly and microstructures defined through top-down lithography. Figure 4.5 shows top-down optical and SEM images of the positive- and negative- tone patterning, with the
self-assembled nanostructures generated in the exposed regions. The top-down SEM outlined in green of Figure 4.5a proves that the self-assembled PS-\textit{b}-ePMMA lamellae were maintained after cross-linking and development, while the unexposed regions have been fully removed after development in toluene. Higher magnification images of the boundary between the exposed and
Figure 4.5. Optically photo-patterned self-assembled block copolymer thin films in the a) positive-tone after developing in toluene for 30 s and b) negative-tone after solvent vapor annealing: optical microscope images and top-down SEM images at low and high magnifications.

unexposed regions of the lithographical defined micropattern (top-down SEM outlined in blue of Figure 4.5a) indicate some residual nanostructures in the unexposed regions, which likely result from diffusion of the photo-generated acid during the post-exposure bake required for cross-linking, contrast limitations in the block copolymer photoresist material, and a less-than-ideal aerial image provided on the wafer by the exposure tool. Figure 4.5b shows results of the negative-tone patterning process, in which the self-assembled nanostructures were generated in the unexposed regions. There is no topography in this film, unlike the positive-tone system, because there is no material solubilized and removed upon nanostructure development. The UV exposed regions also show a small extent of microphase separation, similar to that observed in the thermally cross-linked thin films shown in Figure 4.1b, which suggests that photo-patterning locks in the material as-deposited.

Figure 4.6. Dose response curves for the PS-\(b\)-ePMMA material with diphenyliodonium hexafluorophosphate photoinitiator under controlled post-exposure baking and standard
development conditions (toluene bath at 22°C for 30 s) as characterized by the normalized residual film thickness.

In the photopatterning experiments, the cross-linkable PS-\textit{b}-ePMMA in thin films was patterned using 365 nm ultraviolet lithography and the cationic photoinitiator diphenyliodonium hexafluorophosphate (DPIHP). Note that for the PS / PMMA system, the use of 365 nm UV exposures is ideal so as to avoid degradation of the PMMA via chain scission that occurs upon exposure to higher energy UV light ($\leq 254$ nm)\textsuperscript{[24,67]}. Figure 4.6 shows photoresist response curves for the PS-\textit{b}-ePMMA material in terms of the normalized residual thickness as a function of exposure dose. Three different post-exposure bake conditions were considered, with a post-exposure bake at 130°C for 60 min showing the highest photoresist sensitivity and contrast. Thus, while the lithographic conditions presented here are useful for a proof-of-concept demonstration, further optimization for higher sensitivity or better resolution may be achieved through the selection of a more sophisticated photoinitiator or different baking conditions. Regardless, the post-apply and post-exposure baking steps remain limited, for the purposes of photopatterning, to conditions under which little thermally induced crosslinking occurs as specified in Figure 4.3.
An example of the fabrication of lamellar nanostructures with different periods was explored by spincast and self-assembly of a smaller symmetric block copolymer onto the toluene developed positive-tone nanostructure. Figure 4.7 shows the top-down SEM image and FFT plots of two self-assembled symmetric block copolymers with distinct periodicities next to each other where the left shows the cross-linked PS-b-ePMMA ($L_0 = 48$ nm) while the right shows the sequentially deposited and self-assembled PS-b-PMMA ($L_0 = 26$ nm). The successful fabrication of this unique type of nanostructure was achieved because positive-tone system has topography that would allow later spincasted smaller symmetric block copolymer flow to the
lower PS-\textit{b}-ePMMA developed neutral surface to micro-phase to form perpendicular lamellar nanostructure. This approach to making nanostructures with different period on the sample wafer enables precise region control of the formation of self-assembled nanostructure with different periods with high through-put because of its great compatibility with conventional optical lithography.

3. Conclusion

The work presented here demonstrates the potential of epoxide functionalized block copolymer materials to simultaneously fabricate structures across multiple length scales. The incorporation of reactive groups capable of cross-linking, in response to thermal- or photo-initiation, allowed the self-assembling materials to be integrated as a photoresist for optical lithography. Interestingly a dual-tone nanostructure development process fabricated patterns with opposite tone in a single material, with ~25 nm nanostructures being selectively self-assembled in either the exposed or unexposed regions. Deposition and self-assembly of smaller symmetric block copolymer in thin films on top of the developed positive-tone nanostructure allows the fabrication of lamellar nanostructures with different periods on a same wafer with high through-put. Enabling to all of the fabrication was the design of unique process conditions capable of decoupling block copolymer self-assembly from thermal cross-linking from photo-initiated cross-linking. Future implementations of this combined bottom-up and top-down fabrication approach may be improved by drawing upon existing knowledge of conventional chemically amplified photoresists and optical lithography tools to yield materials with higher sensitivities, higher contrast, better resolution, or improved etch resistance.
Additionally, the cross-linking of self-assembled block copolymer thin films makes possible the layer-by-layer assembly of stable three-dimensional structures, including those with controlled sidewall profiles useful for pattern transfer processes.

4. Experimental Section

Synthesis of cross-linkable block copolymer.

The PS-b-P(MMA-r-GMA) block copolymer was synthesized via sequential atom transfer radical polymerization (ATRP). The monomers styrene (Sigma-Aldrich, stabilized, 99%) and methyl methacrylate (Acros, stabilized, 99%) were purified by distillation under reduced pressure. The catalyst copper (I) bromide was purified as reported previously[68]. All other chemicals and solvents were used as received. The polymerization started by synthesizing a polystyrene (PS) macroinitiator with bromine at one end, using the purified styrene monomer, (1-bromoethyl)benzene (Sigma-Aldrich, 97%) as the initiator, copper (I) bromide as the catalyst, and \( N,N,N',N'',N''\)-pentamethyldiethylenetriamine as the stabilizing ligand in the absence of solvent at 100°C. The PS macroinitiator (M.W. = 47.3 kg mol\(^{-1}\), PDI = 1.04) was used as the initiator to grow the second block. The symmetric block copolymers PS-b-PMMA (99.5 kg mol\(^{-1}\), PDI = 1.14, volume fraction of PS \( \phi_{PS} = 50.4\% \)) and PS-b-P(MMA-r-GMA) (93.7 kg mol\(^{-1}\), PDI = 1.11, \( \phi_{PS} = 53.4\% \), GMA: 4.5 mol\%) were prepared by polymerizing in anhydrous THF at 50°C the purified methyl methacrylate and glycidyl methacrylate (MP Biomedicals, 99%) monomers, using copper (I) chloride as the catalyst and using \( N,N,N',N',N''\)-pentamethyldiethylenetriamine as the ligand\(^{69}\). The composition of the block
copolymers and the PS macroinitiator were characterized by $^1$H NMR as shown in the spectra of Figures 4.S2-S4.

**Figure 4.S2.** Partial $^1$H NMR spectrum of PSBr in CDCl$_3$ at 22 °C $^1$H NMR (300 MHz, CDCl$_3$, δ): 7.32-6.67 (br, 3H, ArH), 6.67-6.20 (br, 2H, ArH), 2.06-1.65 (br, 3H, CH3), 1.64-1.22 (br, 2H, CH2).
Figure 4.S3. Partial $^1$H NMR spectrum of PS-$b$-P(MMA-$r$-GMA) in CDCl$_3$ at 22 °C $^1$H NMR (300 MHz, CDCl$_3$, δ): 7.37-6.85 (br, 3H, ArH), 6.84-6.28 (br, 2H, ArH), 4.37-4.25 (m, 1H; CH$_2$), 3.88-3.71 (m, 1H, CH$_2$), 3.70-3.44 (br, 3H, CH$_3$), 3.27-3.17 (m,1H, CH), 2.90-2.82 (br, 1H, CH$_2$), 2.69-2.60 (m, 1H, CH$_2$), 2.11-1.65 (br, 3H, CH$_3$), 1.62-1.24 (br, 2H, CH$_2$), 1.11-0.95 (br, 1H, CH), 0.95-0.64 (br, 2H, CH$_2$).
Self-assembly and thermally-activated cross-linking.

A neutral Si wafer substrate for the self-assembly of lamellar-forming PS-b-PMMA block copolymers with perpendicular orientations in thin films was prepared by coating with a poly(styrene-random-methyl methacrylate-random-glycidyl methacrylate) brush [P(S_{0.58-r-MMA_{0.31}-r-GMA_{0.01}}) in mole fractions]^{[44,56,70]}. The random copolymer was synthesized by free-radical polymerization by heating up a mixture of styrene, methyl methacrylate, glycidyl methacrylate and azobisisobutyronitrile (AIBN) in toluene to 80°C for 8 hrs and purified by precipitating in methanol and filtration. The composition of the random copolymer was characterized by \(^1\)H NMR. Silicon wafers were purchased from Montco Silicon Technologies, Inc.
and piranha treated with a mixture of 30% H₂O₂ / 70% H₂SO₄ (v/v) at 70°C for 20 min. The cleaned Si substrates were rinsed sequentially with distilled water, acetone (Fisher, 99%), and toluene (Fisher, 99%). A 0.3 wt% solution of the P(S₀.₅₈-r-MMA₀.₃₁-r-GMA₀.₀₁) brush in anhydrous toluene (EMD Chemicals, 99.8 wt%) was prepared, which was then spin cast on the clean Si wafers to a film thickness of 10 nm. Annealing at 170°C for 4 hrs cross-linked the random copolymer onto the substrate, and subsequent sonication in toluene removed any unreacted polymer.

Thin films (~50 nm) of uncross-linkable PS-b-PMMA or cross-linkable PS-b-(PMMA-r-GMA) block copolymer were spincast onto the prepared neutral substrates. Block copolymer solutions in anisole (Sigma-Aldrich, anhydrous 99.7%) were prepared at a concentration of 1.5 wt% by weighing out dry polymer and adding the solvent dropwise. Photo-sensitive systems of cross-linkable block copolymer were prepared at a concentration of 1.425 wt% PS-b-P(MMA-r-GMA) and 0.075 wt% diphenyldonium hexafluorophosphate in anisole.

Self-assembly of the uncross-linkable and cross-linkable block copolymer morphologies in thin films was performed using either solvent vapor or thermal annealing. Solvent vapor annealing used a saturated vapor of mixed solvents consisting of acetone and cyclohexane (Fisher, 99%) achieved by adding 30 mL each to the bottom of a glass desiccator (1.5 L volume). The block copolymer samples were suspended and sealed in the solvent-rich environment for 4 hrs, thereby allowing the thin films to swell significantly [71–73]. The solvent vapor annealing process was terminated by opening the chamber to vacuum to remove the solvent vapor and by allowing the thin films to further dry in air prior to SEM imaging.
Thermal annealing of uncross-linkable block copolymer materials led to the self-assembly of lamellae in thin films (typical conditions of 190°C for 24 hrs under ~10 Torr vacuum). Cross-linkable block copolymer materials that were thermally treated under similar conditions were cross-linked and unable to microphase separate into well-developed lamellar morphologies. Note, however, that thermal annealing (190°C for 1 hr under ~10 Torr vacuum) was used to complete the cross-linking reaction in the self-assembled morphologies of the cross-linkable block copolymer achieved by solvent vapor annealing. The thermal-activated cross-linking conditions (130 - 230°C for 5, 10 or 60 min) were studied by annealing block copolymer nanostructures self-assembled by solvent annealing. The thermally treated samples were sonicated in a toluene bath at 22°C for 3 min and thermally annealed at 190°C for 1 hr. The residual film thickness was measured by ellipsometry and reported relative to the thickness of an as-deposited block copolymer thin film.

*Photopatterning block copolymer nanostructures in positive- and negative-tones.*

The cross-linkable block copolymer was photopatterned in a positive-tone as follows: Block copolymer lamellae with 5.0 wt% diphenyliodonium hexafluorophosphate photoinitiator were self-assembled in thin films on neutral substrates via solvent annealing and then exposed to UV light (Karl Suss MJB4 Mask Aligner at $\lambda = 365$ nm and an exposure dose of 12 J/cm$^2$) through a chrome photomask. A post exposure bake was performed at 130°C for 1 hr. The samples were then developed in toluene for 30 s to remove uncross-linked material from the unexposed region. The cross-linkable block copolymer was photopatterned in a negative-tone as follows: First, the as spincast cross-linkable block copolymer thin films with 5.0 wt% photoinitiator were exposed UV light (Karl Suss MJB4 Mask Aligner at $\lambda = 365$ nm and an
exposure dose of 12 J/cm$^2$) through a chrome photomask. The exposed thin film samples were baked at 130°C for 1 hr, followed by solvent annealing for 4 hrs.

The photoresist dose response curves for PS-$b$-ePMMA with 5.0 wt% photoinitiator (130 - 230°C for 5, 10 or 60 min) were studied by exposing (2.79 - 39.06 J/cm$^2$ at 365 nm) and post-exposure baking (110°C for 60 min, and 130°C for 5 or 60 min) the nanostructures self-assembled in thin films by solvent annealing. The UV exposed and post-baked samples were developed in a toluene bath at 22°C for 30 s and thermally annealed at 190°C for 5 min. The residual film thickness was measured by ellipsometry and reported relative to the thickness of an as-deposited block copolymer thin film.

Thin films (~26 nm) of small block copolymer PS-$b$-PMMA (51 kg mol$^{-1}$, PDI = 1.06, $\phi_{PS} = 51.9\%$) were spincast onto the developed photopatterned PS-$b$-ePMMA thin film on top of neutral substrate. The thin film sample was treated by a process of 2 hrs solvent annealing under the vapor of saturated acetone and cyclohexane to allow the small block copolymer to form self-assembled lamellar nanostructures.

Nanostructure characterization.

The block copolymer morphology in thin films was imaged by scanning electron microscopy (SEM) using a JEOL JSM-7401F. Top-down SEM images were collected at an accelerating voltage of 1 kV and a gun emission current of ~10 mA in gentle-beam mode. All film thicknesses were measured by ellipsometry (J.A. Woollam VASE-VB 250, angle: 70°, wavelength: 500~800 nm).
Acknowledgements

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Chapter 5 Interfacial Roughness of Self-assembled Lamellae in Block Copolymer Thin Films

Abstract

Biblock copolymers are attractive for fabricating structures with 5-50 nm dimensions. The ability of such materials to self-correct or ‘heal’ nanoscale defects is of importance for future lithographic applications. Reduced interfacial roughness and enhanced dimensional control have been demonstrated to occur at the molecular-level when the block copolymers are directed to self-assemble on chemically patterned surfaces or in topographic structures. Here we demonstrate that the self-assembling methods can also significantly influence interfacial roughness. Lamellar-forming block copolymer / homopolymer blends, were directed to self-assemble on chemically patterned substrates and processed by solvent-annealing at room temperature. The lamellae were subsequently thermally-processed in a step distinct from the self-assembly process. Spectral analysis of the interfacial roughness was compared between the solvent-annealed and thermally annealed block copolymer materials, and the thermally annealed sample was quantified to have lower interfacial roughness due to a higher surface tension and stronger coupling between neighboring interfaces. Solvent annealing reduces the interfacial tension and interface-interface coupling leading to high interfacial roughness. Thermal annealing recovers low interfacial roughness.
Introduction

The microelectronics industry constantly strives to improve the operation speed of microprocessors and the storage density of memory devices to continue their historical pace indicated by the so-called “Moore’s law”. However, advanced lithographic techniques and photoresist materials are rapidly reaching their extremes in patterning the ever-decreasing dimensions required for semiconductor devices like transistors in integrated circuits (e.g., in microprocessor units (MPU)) and dynamic random access memory (DRAM). The semiconductor industry specified the requirements for photoresists and lithographic exposure tools at future technology milestones in the International Technology Roadmap for Semiconductors (ITRS) as in Table 1. Particularly challenging has been the incapability of conventional photoresist materials to achieve the critical dimension control (CD referring to the dimension of the smallest patterned feature of importance, e.g., the transistor gate length in MPUs) and line edge roughness (LER) requirements, both of which should have been at sub 3 nm levels by the year 2012. The frequency of the line edge roughness as well as the magnitude of the LER are important considerations for the devices to be fabricated and affects the operation of transistors, interconnect wire resistances, and dopant concentration profiles. Block copolymers self-assembly approaches are actively being studied as a next generation lithography technique, not only due to the ability of these materials to spontaneously form large arrays of lamellar or cylindrical structures at the necessary resolution, but also because the molecular-level control over the structure dimensions and interfaces is possible. For symmetric block copolymers, line and space structures can be fabricated with line edges defined by the interfaces between lamellar domains. The width and structure of the interfaces are governed by system parameters such as the Flory-Huggins interaction parameter and the degree of polymerization.
Self-assembly of lamellar structures into arrays with long-range order is complicated by low energy penalty defects such as disclinations, dislocations, and bending of the domain interfaces with relatively large radii of curvatures compared to the domain periodicity.

Table 5.1. Fabrication requirements for industrial semiconductor devices given by ITRS

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<td>28</td>
<td>25</td>
<td>23</td>
<td>20</td>
<td>18</td>
<td>16</td>
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<td>MPU/ASIC metal ½ pitch (nm)</td>
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<td>18</td>
<td>17</td>
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<td>14</td>
<td>13</td>
<td>12</td>
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<tr>
<td>MPU gate in resist length (nm)</td>
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<td>25</td>
<td>22</td>
<td>20</td>
<td>18</td>
<td>16</td>
<td>14</td>
<td>10</td>
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<tr>
<td>Gate CD control (max, 3σ)</td>
<td>1.9</td>
<td>1.8</td>
<td>1.7</td>
<td>1.6</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
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<tr>
<td>Low frequency line width roughness (nm, 3σ) &lt;8% of CD</td>
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<td>2.0</td>
<td>1.8</td>
<td>1.6</td>
<td>1.4</td>
<td>1.3</td>
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<td>Correlation length (nm)</td>
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<td>15.5</td>
<td>12.6</td>
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<td>6.9</td>
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Directed self-assembly of block copolymers on chemical surface patterns\textsuperscript{[11,12]} is an attractive approach to self-assembling structures with long-range order and a high degree of perfection that are positioned precisely on the substrate and in geometries relevant to the patterning of semiconductor devices. \textsuperscript{[12,13]} The preferential wetting of the block copolymer domains on the chemical patterns in this approach greatly increases the energetic penalty of common block copolymer defects and therefore prohibits their formation. However, most these studies on directed self-assembly of block copolymer were carried out by thermal annealing. Here we present the directed self-assembly of block copolymer blends in thin films on nanopatterned substrate and experimental characterizations of that the annealing method have direct effects on the line edge roughness in block copolymer lamellae.
Results and Discussion

A general step-by-step approach to conduct directed self-assembly is illustrated in Figure 5.1 which describes the process block copolymer self-assembled in registration with nanopatterned designed features by extreme ultraviolet (EVU) lithography or electron beam lithography\textsuperscript{[11–14]}. The top left Figure 5.2 shows a top-down SEM image of a typical finger-print nanostructure of the block copolymer self-assembly on neutral surface and the directed self-assembly on nanopatterned structure. When the self-assembly of block copolymer happened on a neutral surface, all kinds of low free-energy defects (disclination, dislocation and bending with radii higher the period \( L_0 \)) are presented. These defects can be viewed as some type of “interfacial roughness” with different frequency or wavelengths. As shown in the bottom three top-down SEM images of Figure 5.2, the interfacial roughness of low frequency or higher wavelengths can be removed by directed self-assembly with patterned substrate where energy penalty is minimized. However, the interfacial roughness at high frequency or lower wavelength have maintained because this level of roughness were controlled by the molecular-level thermodynamic fluctuation.
Figure 5.2. The influence of directed self-assembly on different frequency interface defects.

Figure 5.3 shows the effect of thermal treatment (190°C for 4 hours) on the LER of directed self-assembled block copolymer nanostructure by solvent annealing. In Figure 3, the items in red indicates shows the results of directed self-assembly of block copolymer blend in thin by solvent annealing while the ones in blue presents the results after thermal treatment. By comparing the top-down SEM images of the solvent-annealed block copolymer on nanopatterned substrate, the microdomains line in images of solvent-annealed shows visible line-width-roughness and line-edge-roughness compared with the top-down SEM images after thermal annealing. The visible difference in SEM image was quantitatively proved by the calculation of their LER and LWR. The calculation of LER and LWR is detailed in literature.\cite{15}

In solvent vapor annealing processes, the solvent molecules penetrating into polymer thin films
leads to not only lower the glass transition temperature of the polymer blocks but also allow mobility of the polymer chain. However, the existence solvent molecules in the polymer thin film reduces the interfacial tension and interface-interface coupling and result in high interfacial roughness.

**Figure 5.3.** The LER recovery by thermal annealing from directed self-assembly on nanopatterned surface by solvent annealing. The SEM images in red box and the legend in red are the sample solvent annealed at 22°C, while the ones in blue is the sample thermally treated afterwards.
Conclusion

In this short note, we demonstrate that block copolymer interfaces have significant roughness over wide range of spatial frequencies. Interfacial roughness is a function of block copolymer thermodynamics, processing conditions and directing fields. In order to be applied for next-generation lithographic templates, LER at all spatial frequencies will need to be reduced.

Experimental Section

Directed Self-assembly on Chemical Surface Patterns

A generalized approach to carrying out the directed assembly of block copolymers on chemical surface patterns is shown in Figure 5.1. In the first step, chemical surface patterns were fabricated in a polystyrene (PS, 9.5 kg mol$^{-1}$) brush imaging layer covalently grafted on silicon substrates such that the alternating stripes had distinct chemistries and surface energies. The fabrication process used electron beam lithography to define the surface pattern in a photoresist film that subsequently acted as a mask for an oxygen plasma treatment that chemically modified the PS brush (details for this procedure can be found in refs 22 and 34). The periodicity of the chemical surface pattern ($L_S$) was chosen to closely match the periodicity of the block copolymer / homopolymer blend lamellae ($L_o$), such that in this case $L_S=55$ nm. The microphase separated lamellar domains that assembled preferentially wet the different stripes of the surface pattern and were oriented perpendicular to the substrate. In addition, the lamellae were ordered without dislocation and disclination defects over greater than 2$\mu$m by 2$\mu$m areas, and were spatially registered with the underlying surface pattern. A symmetric ternary blend of 60 wt % poly(styrene-block-methyl methacrylate) (PS-b-PMMA, 107 kg mol$^{-1}$ total, 48 wt % PS), 10 wt %
PS homopolymer (21.8 kg mol\(^{-1}\)), and 10 wt % poly(methyl methacrylate) homopolymer (PMMA, 20.5 kg mol\(^{-1}\)) was used here, but this copolymer system behaves similarly to a pure symmetric diblock copolymer in thin films and on chemical surface patterns.\(^{[16]}\) The polymers were used as received from Polymer Source, Inc. (Dorval, Canada).

Self-assembly of the block copolymer / homopolymer blends in thin films was conducted using either solvent vapor or thermal annealing. Solvent vapor annealing used a saturated vapor of mixed solvents consisting of acetone and cyclohexane (Fisher, 99%) achieved by adding 30 mL each to the bottom of a glass desiccator (1.5 L volume). The block copolymer samples were suspended and sealed in the solvent-rich environment for 4 hrs, thereby allowing the thin films to swell significantly\(^{[17,18]}\). The solvent vapor annealing process was terminated by opening the chamber to vacuum to remove the solvent vapor and by allowing the thin films to further dry in air prior to SEM imaging. Thermal treatment (190\(^{\circ}\)C for 4 hours under ~10 Torr vacuum) of block copolymer / homopolymer blends in thin film led to the recovery of low interfacial roughness.

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Chapter 6 Current Collaborations and Future Work

This chapter presents three projects of current research and preliminary data is shown in the areas that we have made progress on. These projects include current work and collaborations with other groups, and will likely be continued on by graduate students who are currently in the group.

1. Regional tuning of block copolymer periodicity in thin films using photopatternable block copolymer

It is an important goal for the block copolymer self-assembly studies to achieve the precise periodicity control in different area of block copolymer on a single wafer. Photopatternable block copolymer discussed in Chapter 4 is used in current work to explore the possibility to have regional tuning of block copolymer periodicity. We firstly solvent annealed photopatternable block copolymer in thin films to enable the self-assembly. The solvent annealed thin films were then photopatterned to cross-link specific regions of the thin film. A layer of homopolymer blend of PS and PMMA was spin-cast on the photopatterned block copolymer thin film and solvent annealed. Figure 6.1 shows preliminary data on the work. Figure 6.1a shows microemulsion formed because the mixing happened between the top layer (~0.5$L_0$) of homopolymer blend and the uncross-linked block copolymer. Figure 6.1b shows the cross-linked block copolymer kept the lamellar structure because the cross-linked lamellar nanostructure doesn’t mix with the top deposited homopolymer blend. Further study on this can lead to precise control of periodicity of unpatterned region by changing the thickness of the deposited top homopolymer blends or more than two periods on one wafer by multiple times of homopolymer deposition and photopatterning.
**Challenge:** The dewetting of homopolymer blends on cross-linked block copolymer thin film region.

![Image](image_url)

**Figure 6.1.** Homopolymer solvent annealed on patterned cross-linkable block copolymer: a) Microemulsion formed from PS / PMMA top layer homopolymer mixed with underlying uncross-linked block cocopolymer, b) Lamellar nanstructure of cross-linked block copolymer

2. **Cross-linking effect on line edge roughness of interfaces of self-assembled block copolymer**

In order to be applied for next-generation lithographic templates, LER at all spatial frequencies will need to be reduced. Block copolymer has been studied to control the LER propagation from nanopatterned substrate. Directed block copolymer can effectively diminish low spatial frequency roughness and out-of-phase roughness.\(^1\) However, the high spatial frequency roughness controlled by the thermodynamics at the molecular level is less effectively reduced. The in-phase roughness is very stable. The higher interfacial tension and interface-interface coupling lead to lower interfacial roughness. The cross-linkable block copolymer can induce stress during the cross-linking process which can potentially reduce the interfacial roughness.

**Challenge:** The available nanopatterned substrate and the resolution of available SEM equipment.
3. **Dense directed carbon nanotube growth with Fe nanodots on quartz patterned from block copolymer**

The thermal treated quartz with certain crystallinity was proved to help the guided carbon nanotube growth with Fe dots as catalyst.\[^{2-4}\] Block copolymer self-assembly coupled with photopatterning is applied to fabricate the Fe nanodots in specific regions of thermally treated quartz substrate. **Figure 6.2** shows Fe nanodots in desired regions.

*Challenge:* regular Fe nanodot array in desired regions and in the same time no Fe nanodot in the designed open area.

![Figure 6.2: Patterned Fe nanodots on Si wafer.](image)

4. **Homopolymer and block copolymer mixing effects and wetting phenomena on their self-assembly in thin films**

Interesting morphologies depending on the molecular weights of homopolymer were observed in annealing homopolymer on self-assembled block copolymer. **Figure 6.3a** shows that the mixing of top layer of low molecular weight (2kDa) homopolymer with underlying self-assembled block copolymer results in cylinders in the lamellar domains while **Figure 6.3b** presents that the mixing of top layer of molecular weight (54.3kDa) homopolymer close to that of one block with
underlying self-assembled block copolymer result in a mix of lamellar and unclear bumps with almost all edges perpendicular to the line direction of block copolymer microdomain.

**Figure 6.3.** Mixing of top layer of homopolymer (a: 2kDa, b: 54.3kDa) with underlying self-assembled block copolymer PS-b-PMMA (47kDa:53kDa) by thermal annealing (190°C for 24 hours)

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