Dimensions and Shapes of Block Copolymer Domains Assembled on Lithographically Defined Chemically Patterned Substrates

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ABSTRACT: Thin films of a nearly symmetric lamellae-forming diblock copolymer of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) having a bulk repeat period, L_O, were directed to assemble vertically away from chemically nanopatterned striped substrates (having a periodicity L_S) that consisted of alternating stripes that were preferentially wet by the two blocks of the copolymer. The relative widths of the adjacent stripes were systematically varied such that the normalized line width of the chemical surface pattern, defined as the width of the stripe that was wet by the styrene block of the block copolymer, W, divided by the constant chemical surface pattern period, L_s had values between 0.30 and 0.65. On chemical surface patterns with $L_S \approx L_O$ the diblock copolymer domains formed defect-free perpendicular arrays if the normalized line width W/L_S, was between 0.36 and 0.63. On chemical surface patterns with $L_S \neq L_O$, the range of W/L_S capable of inducing defect free arrays decreased as the difference between L_S and L_O increased. Single-chain-in-mean-field (SCMF) simulations provided information on the dimensions and shapes of the block copolymer domains. The SCMF simulations indicated that the widths of the lamellae at half film thickness were $0.47L_S$ independent of W/L_S and the angle of the interface between the vertically oriented domains remained within 11° of the substrate normal over the range of experimentally relevant values of W/L_S.

Introduction

Diblock copolymers are one set of self-assembling materials that are currently being developed for patterning and other applications in nanofabrication to enhance, augment, or exceed the capabilities of current nanomanufacturing processes, often at reduced cost. These materials consist of two chemically different polymer chains connected at one end by a covalent bond and tend to spontaneously form ordered structures at the molecular scale with domain dimensions of 5−50 nm.[1,2] The morphology and the size of the domains in the bulk are dependent on the molecular weight and composition of the copolymer and typically assume geometries of spheres, cylinders, and lamellae. In block copolymer lithography, the domain structure of diblock copolymer thin films is used as a template in subtractive or additive processes to create dense periodic arrays of nanoscale features with uniform dimensions that are difficult or prohibitively expensive to make using traditional lithography.[3] Applications of this technology, each placing different constraints on the uniformity, registration, and long-range order of the periodic arrays, include the fabrication of quantum dots,[3,4] photonic crystals,[5] metallic nanodots,[6] nanocrystal floating gate devices for FLASH memory,[7] and magnetic storage media.[8−10]

Techniques to impart the long-range translational and orientational order required of the block copolymer domains in thin films for many value-added nanomanufacturing applications include electric field alignment,[11,12] nanoimprint lithography,[13] graphoepitaxy,[14−18] directional solidification,[19] solvent annealing,[20−22] shear alignment,[23,24] and chemically nanopatterned substrates.[25−31] We have demonstrated that directed assembly of block copolymers on lithographically defined chemically nanopatterned substrates satisfies some of the essential attributes of the lithographic process such as the ability to generate essentially defect-free patterns,[25,28] precise registration of the pattern features with the underlying substrate,[28] and the ability to generate non-regular device-oriented structures.[30]

One requirement for directing the assembly of symmetric diblock copolymers on chemically nanopatterned substrates is that the bulk lamellar period, L_O, and the chemical surface pattern period, L_S, be commensurate in dimension. Rockford et al.[32] for example, reported that that the degree of alignment of lamellar domains in block copolymer films with nanoperiodic heterogeneous surface patterns was greatest when the periodicity of the chemical surface pattern closely matched L_O. Previously we quantified and modeled the degree of mismatch between L_S and L_O that can be tolerated as a function of the interfacial energy of the underlying chemically patterned substrate and the blocks of the copolymer film to achieve defect-free arrays of lamellae that may be relevant for patterning in nanomanufacturing applications.[25] On chemical surface patterns with weak contrast in interfacial energy of adjacent chemical stripes toward the two blocks of the copolymer, ordered arrays of lamellae were observed only for $L_S = L_O$. On chemical surface patterns with strong contrast in the interfacial energy of adjacent chemical stripes, ordered arrays of lamellae were observed for $L_S = L_O \pm 10\%$. Defect free assembly occurred with the period of the block copolymer stretched or compressed so as to be equal to L_S as long as the total free energy of the block copolymer and the surface and interfacial energy was minimized for the film. The value of L_O can be controlled by the molecular

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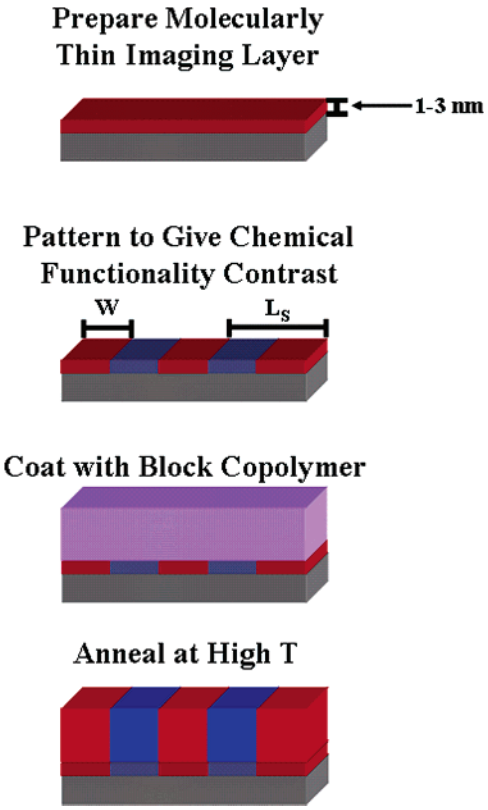


Figure 1. Schematic diagram of the insertion of block copolymers into the lithographic process. An ultrathin organic imaging layer is prepared on a silicon substrate and patterned using standard lithographic procedures at a period, L_S. The width of the stripes that are wet by the minority block of the block copolymer is denoted by W. The chemical surface pattern is then coated with a block copolymer having a bulk repeat period L_O and annealed above the glass transition temperature of the two blocks to direct the assembly of the block copolymer domains in registry with the underlying chemical surface pattern. One of the domains is then selectively removed resulting in a template that can be used to resist subsequent processing.

weight of the block copolymer or by using binary blends of diblock copolymers and ternary blends of diblock copolymers with homopolymers of the constituent blocks to match the period of block copolymer materials to L_S.[33,34]

In the current paper, we continue the investigation of the directed assembly of diblock copolymers with respect to the details of the underlying chemical surface pattern. Our process for inserting block copolymers in the lithographic process is shown schematically in Figure 1. A molecularly thin imaging layer, comprised here of polymer brushes, is deposited and subsequently patterned with regions of different chemical functionality using advanced lithographic techniques. The geometry of the pattern is striped and the chemistry is such that alternating stripes are preferentially wet by the styrene block and the methyl methacrylate block of the copolymer, respectively. A lamellae-forming (PS-*b*-PMMA) diblock copolymer thin film is then spin-coated on the chemically patterned substrate and annealed. The block copolymer domains assemble in registration with the underlying chemical surface pattern. In contrast to our previous work that focused on the commensurability of the block copolymer bulk period, L_O with the period, L_S of the surface pattern and its chemistry, in this paper we explore how changing the relative widths of the stripes of the chemical surface pattern impacts the assembly of the block copolymer film. Here, the width of the stripe that is wet by the styrene block of the diblock copolymer is defined as W (see Figure 1) and the ratio W/L_S is termed the normalized line width. Using advanced lithographic tools we vary W/L_S systematically and examine the resulting block copolymer domain structure. We find that when $L_S = L_O$, the diblock copolymer domains exhibit significant process latitude and form defect-free arrays on chemical surface patterns with normalized linewidths in the range $0.36 < W/L_S < 0.63$. When L_S and L_O are incommensurate process latitude decreases. Single-chain-in-mean-field (SCMF) simulations provide information regarding the dimensions and shapes of the diblock copolymer domains as a function of W/L_S, information that is difficult to gather experimentally. The SCMF simulations indicate that the width of the polystyrene domains at half film thickness, normalized to the substrate pattern period are invariant for a given value of L_S over the experimentally relevant range of W/L_S. Moreover, the SCMF simulations indicate that the angle of the interface between the block copolymer domains does not vary by more than 11° with respect to the substrate normal. The implications of these experimental and simulation results are discussed with respect to the motivation to insert block copolymers into advanced lithographic processes to meet challenges facing traditional imaging materials related to dimensional control over patterned resist features at the nanoscale.

Experimental and Simulation Methods

Materials. All materials were used as received. Unless otherwise noted, materials were purchased from Sigma-Aldrich, Milwaukee, WI.

Experimental Data. The 2,2,6,6-tetramethylpiperidin-1-yl oxide (TEMPO) based initiator used to synthesize hydroxy terminated polystyrene was synthesized according to techniques already presented in the literature.[35,36] Using the TEMPO based initiator polymerization of the hydroxy terminated polystyrene was performed as described elsewhere and had a molecular weight M_N = 5.4 kg/mol and PDI = 1.3.[37] Thin films of this polymer were spin-coated onto piranha solution (***Caution!***) cleaned silicon substrates from a 1.5 wt % solution in toluene at 6000 RPM to give films approximately 40 nm thick. The polystyrene was then grafted to the silicon substrate by annealing at 160 °C for 48 h under vacuum before quenching to below 80 °C over a 2 h period. The ungrafted portions of the thin film were then removed using sonication in warm toluene to yield a brush ($\sigma \approx 0.5$ chains/nm^2) that was approximately 4 nm thick (as determined by ellipsometry) with water contact angles of 93° (advancing) and 79° (receding). A thin film of photoresist (poly(methyl methacrylate), 950 kg mol^{-1}, Microchem Corp.) was spin-coated from chlorobenzene on top of the polymer brush and exposed with extreme ultraviolet interferometric lithography as described previously.[38] After exposure the photoresist was developed using a 3:1 mixture of isopropyl alcohol and methyl isobutyl ketone for 30 s, rinsed extensively with isopropyl alcohol, and blown dry in a stream of nitrogen to give lines and spaces in the photoresist with pattern periods of 65−80 nm in 2.5 nm increments. Two matrices of doses were created on a single wafer with one matrix being used for SEM analysis on the PMMA patterns and one matrix used to direct the assembly of the block copolymer domains, since scanning electron microscopy will damage the underlying polystyrene layer when long dwell times are used. The sample that was used to align the block copolymer domains was exposed for 10 s to an oxygen plasma to incorporate polar oxygen containing moieties in the polystyrene brush. The remaining PMMA was removed by repeated sonication in chlorobenzene. Block copolymer (poly(styrene-*b*-methyl methacrylate), M_N = 85-*b*-91 kg/mol, PDI = 1.12, Polymer Source Inc.) was cast from a 1.5 wt % toluene solution at 6000 rpm to give a 42 nm thick film as determined by ellipsometry. The sample was then annealed for 330 h at 190 °C under vacuum in a chamber that had been repeatedly flushed with argon. The block copolymer domains and PMMA patterns were imaged using a LEO 1550 VP FE-SEM with an accelerating voltage of 1 kV. The linewidths were determined by thresholding images of the PMMA patterns according to brightness and matching the resulting pixel intensity with the appropriate line width.

Single-Chain- in-Mean-Field (SCMF) Simulations

To describe the diblock copolymer we utilized a discretized Edwards-Hamiltonian with $N = 32$ segments per molecule, 15 PS segments and 17 PMMA segments. A short-range repulsion of strength $\chi N = 63.2$ acted between PS and PMMA segments. The segment density was fixed to $8930/R^3$ to match the experimental polymer density; i.e., each configuration contained several million segments. Fluctuations of the total segment density were controlled by a Helfand-compressibility term with reduced compressibility, $\kappa N = 50$ or 75.[39] In the SCMF simulations, the lamellar period of the diblock copolymer was $L_O \approx 1.8R$ (R, being the root-mean-square end-to-end distance of the diblock copolymers). Comparing this result with the experimental observation, $L_O = 80$ nm we identify the length scale in the simulations. The surface to the air was treated as a hard, neutral wall. Periodic boundary conditions were applied in the two lateral directions. The substrate pattern symmetrically attracted/repelled PS and PMMA segments with a short-range interaction that falls off with a length scale of $dz = 0.15R$. Fields and densities were calculated on a grid with a spatial resolution of $\Delta \approx R/11$ or $\Delta \approx R/110$ for the three- and two-dimensional calculations, respectively. The molecular conformations evolved through random, local displacements of segments, the translation of the center of mass of each polymer, and head-to-tail flips of diblock copolymers. All configurations were prepared by a quench from a disordered state and annealed on the patterned substrate from $\chi N = 0$ to $\chi N = 63.2$. The SCMF simulation was implemented as scalable, parallel MPI code.

The dimensions and shapes of the block copolymer domains were determined from equilibrium two dimensional SCMF calculations. The widths of the polystyrene domains and the angle of the styrene methyl methacrylate interface with respect to the substrate normal were measured by hand at the half-thickness of the film using printouts of the contour plots of the equilibrated morphologies from two-dimensional calculations. Two measurements were taken for the angle of the styrene-methyl methacrylate interface, one for each side of the domain. The reported values are the average of those two measurements.

Results and Discussion

Chemically patterned surfaces consisting of alternating stripes of different chemical functionalities with varied dimensions and periods were prepared as shown in Figure 2A. A polystyrene brush (thickness = 4 nm, $M_N = 5.4$ kg/mol) was grafted on a silicon wafer by reacting hydroxy-terminated polystyrene with a hydroxy terminated silicon wafer at high temperature (160 °C). The silicon wafer with polystyrene brush was then coated with a thin film of a positive-tone photoresist. Extreme ultraviolet lithography was used to pattern the photoresist with lines and spaces having pattern periods, L_S, that varied from 65 to 80 nm in increments of 2.5 nm. The widths of these photoresist lines, W, and the normalized line width, which we define as the ratio of the width of the photoresist lines to the pattern period (W/L_S), depend on the exposure dose. For each type of pattern two identical samples were processed simultaneously on a single wafer using the same exposure and processing conditions. Metrology (scanning electron microscopy, SEM) was performed on one set of samples to quantify the values of W. The second set of samples were subjected to an oxygen plasma such that areas of the polystyrene brush not protected by photoresist were chemically modified to incorporate highly polar, oxygen containing moieties and remove part of the polystyrene brush.[40] The remaining photoresist was then stripped by repeated sonication in chlorobenzene, leaving behind a chemically patterned substrate consisting of alternating stripes of the polystyrene and oxygenated polystyrene brushes.

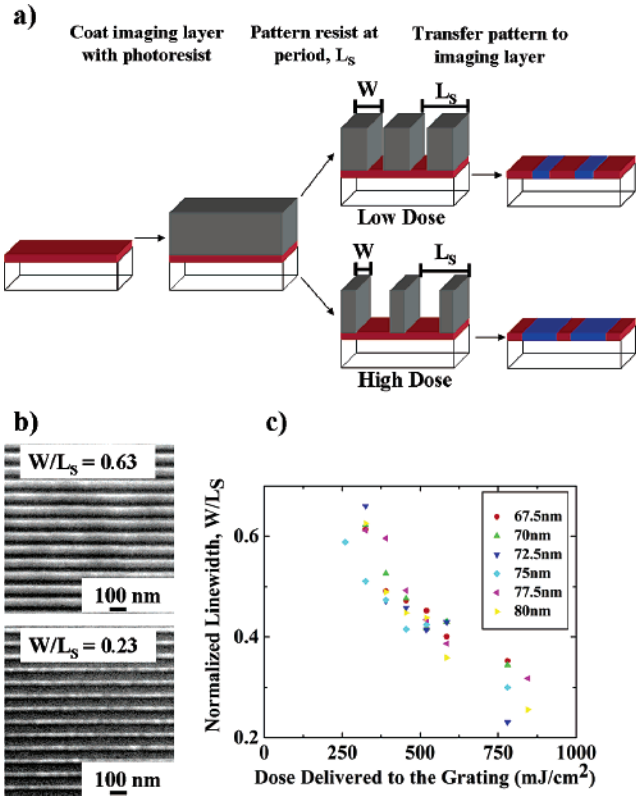
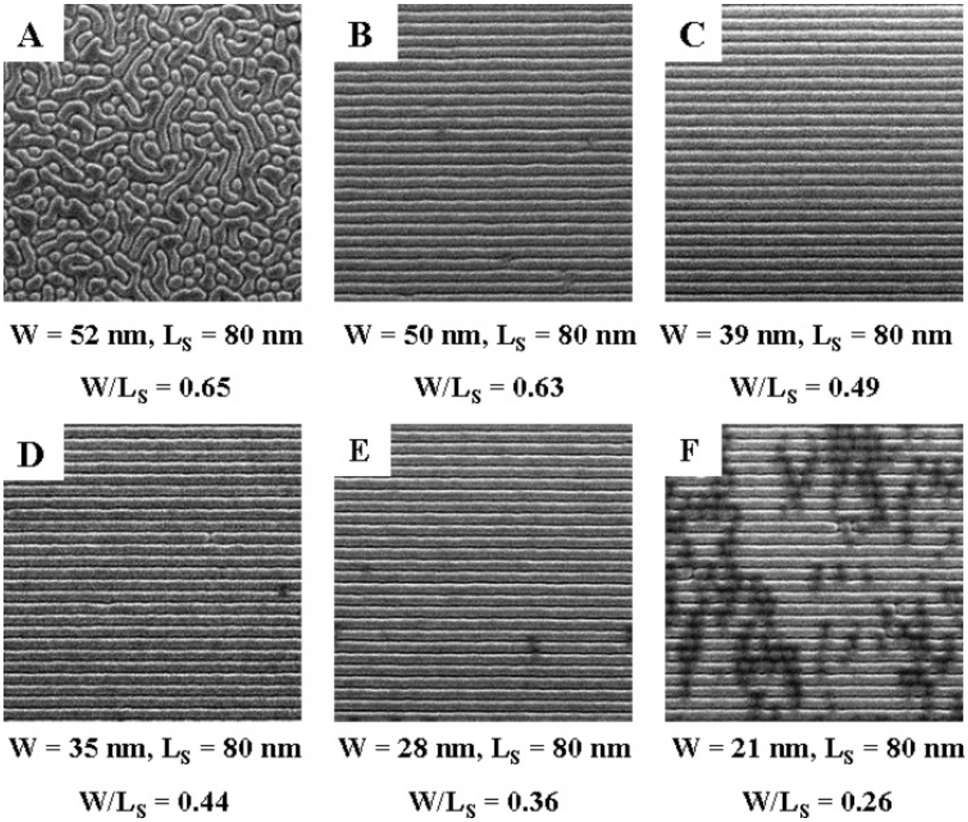


Figure 2. (A) Schematic diagram illustrating how a positive-tone photoresist can be patterned to vary the width of photoresist features, W, at a given pattern period, L_S. (B) Top down SEM images of $L_S = 80$ nm PMMA patterns created using EUV Lithography at exposure doses of 260 mJ/cm^2 and 910 mJ/cm^2. The micrographs have normalized linewidths, W/L_S, of 0.63 and 0.23, respectively. (C) Results of an image analysis on PMMA structures used to create chemical surface patterns to direct the assembly of block copolymer thin films presented as W/L_S vs dose.

The widths of photoresist lines, W, and W/L_S, for each pattern over which block copolymer films were directed to assemble depends on the exposure dose as quantified in Figure 2, parts B and C. The plan-view SEM images of PMMA structures having the periodicity, $L_S = 80$ nm, shown in Figure 2B were created with exposure doses of 260 and 910 mJ/cm^2 and had normalized lines widths, as determined by an image analysis, of 0.63 and 0.23, respectively. Figure 2C is a plot of W/L_S as a function of exposure dose for all of the patterns used in the experiments. The reproducible and monotonic decrease in normalized line width with increasing dose for all periods is indicative of our ability to systematically investigate these parameters. This experimental protocol highlights problems that are encountered in processing traditional photoresists. The density of structures can be precisely controlled (e.g., periodicity of lines and spaces; also termed pitch), but it is difficult to control the dimensions of the individual structures (widths of the lines; also termed critical dimension).[41]

Photoresist structures, such as those shown in Figure 2B, were used as a lithographic mask to pattern the underlying polystyrene-coated silicon substrate, generating a chemical surface pattern that was used to investigate the behavior of a lamellae forming diblock copolymer. The resulting chemically nanopatterned substrates were coated with a $D = 42$ nm thick diblock copolymer film of poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA), ($M_N = 85$-*b*-91 kg/mol, PDI = 1.12, $L_O = 80$ nm) and annealed under vacuum at 190 °C for 14 days. At 42 nm, the films are thick enough to be applicable for many pattern transfer processes and still ensure that the directed self-assembly



W = 52 nm, L_S = 80 nm W/L_S = 0.65

W = 50 nm, L_S = 80 nm W/L_S = 0.63

W = 39 nm, L_S = 80 nm W/L_S = 0.49

W = 35 nm, L_S = 80 nm W/L_S = 0.44

W = 28 nm, L_S = 80 nm W/L_S = 0.36

W = 21 nm, L_S = 80 nm W/L_S = 0.26

Figure 3. Plan-view SEM images of PS-*b*-PMMA domains annealed on chemical surface patterns with $L_S = 80$ nm for 14 days at 190 °C. The normalized linewidths of the PMMA structures used to create the chemical surface patterns are (A) 0.65, (B) 0.63, (C) 0.49, (D) 0.44, (E) 0.35, and (F) 0.26. All micrographs image a 2 μm by 2 μm area.

of the block copolymer domains is dominated by the interfacial interactions between the blocks of the copolymer and the chemically nanopatterned substrates. The polystyrene block of the block copolymer preferentially wets the polystyrene brush in the regions previously protected by the photoresist and the methyl methacrylate block of the block copolymer preferentially wets the chemically modified, oxygenated polystyrene brush. The resulting domain structures were analyzed in plan-view using SEM.

On chemical surface patterns that had a pattern period that was approximately equal to the bulk lamellar period of the block copolymer ($L_S = L_O$), the block copolymer domains assembled into defect-free arrays over large areas, in registration with the underlying chemical surface pattern over a broad range of normalized linewidths, from $W/L_S = 0.36$ to $W/L_S = 0.63$. This is shown in a series of plan-view SEM images of a lamellar PS-*b*-PMMA block copolymer with a bulk repeat period L_O = 80 nm annealed on chemical surface patterns with a period L_S = 80 nm presented in Figure 3. When photoresist structures with $W/L_S > 0.65$ were used to generate chemical surface patterns the block copolymer domains exhibited behavior that was identical to the behavior of block copolymer domains on uniform, unpatterned polystyrene brushes. In these samples the photoresist was not completely removed throughout the entire film and no chemical surface pattern was created during the oxygen plasma etch. When photoresist structures with $W/L_S <$ 0.30 were used to generate chemical surface patterns the block copolymer domains exhibited intermittent defects in the aligned lamellae. In these samples, the photoresist pattern is overexposed or overdeveloped, resulting in localized breaks in the line structures that are subsequently transferred to the chemical surface pattern during the oxygen plasma etch.

As the block copolymer lamellar period and the substrate pattern period became increasingly incommensurate ($L_S < L_O$), the range of W/L_S over which defect-free directed assembly occurred decreased as shown in Figure 4. At $W/L_S = 0.47$ the block copolymer domains formed defect free arrays for the range $0.84\ L_O < L_S \leq L_O$. However, for $W/L_S = 0.42$ or $W/L_S = 0.51$, defect-free block copolymer domains were only found over the range $0.94\ L_O < L_S \leq L_O$. These results are consistent with our previous work in which defect free assembly was observed for $L_S = L_O \pm 10\%$ using chemical surface patterns with strong contrast in the interfacial energy of adjacent chemical stripes, even though the block copolymer used in this study had an L_O = 80 nm whereas the block copolymer used in our previous study had an L_O = 48 nm.

Information about the three-dimensional structures of the individual block copolymer domains annealed on chemical surface patterns that were mismatched with the desired domain structures is difficult to gather experimentally and was obtained from SCMF simulations,[39] a particle-based self-consistent field method. Self-consistent field theory[42] has been employed previously to successfully predict block copolymer self-assembly in the bulk,[43] under confinement,[44] and in mixtures with homopolymers on chemically nanopatterned substrates.[30,45,46] The simulation requires as inputs values for χN and L_O where χ is the Flory–Huggins interaction parameter of the block copolymer, N is the degree of polymerization, and L_O is the block copolymer bulk lamellar period. The morphology and degree of long-range order in the block copolymer domains depends on the strength of the surface interactions. The surface interactions in the simulations were chosen to produce defects at large asymmetry of W/L_S or incommensurability, L_S/L_O, in qualitative agreement with experiments. The results indicate that

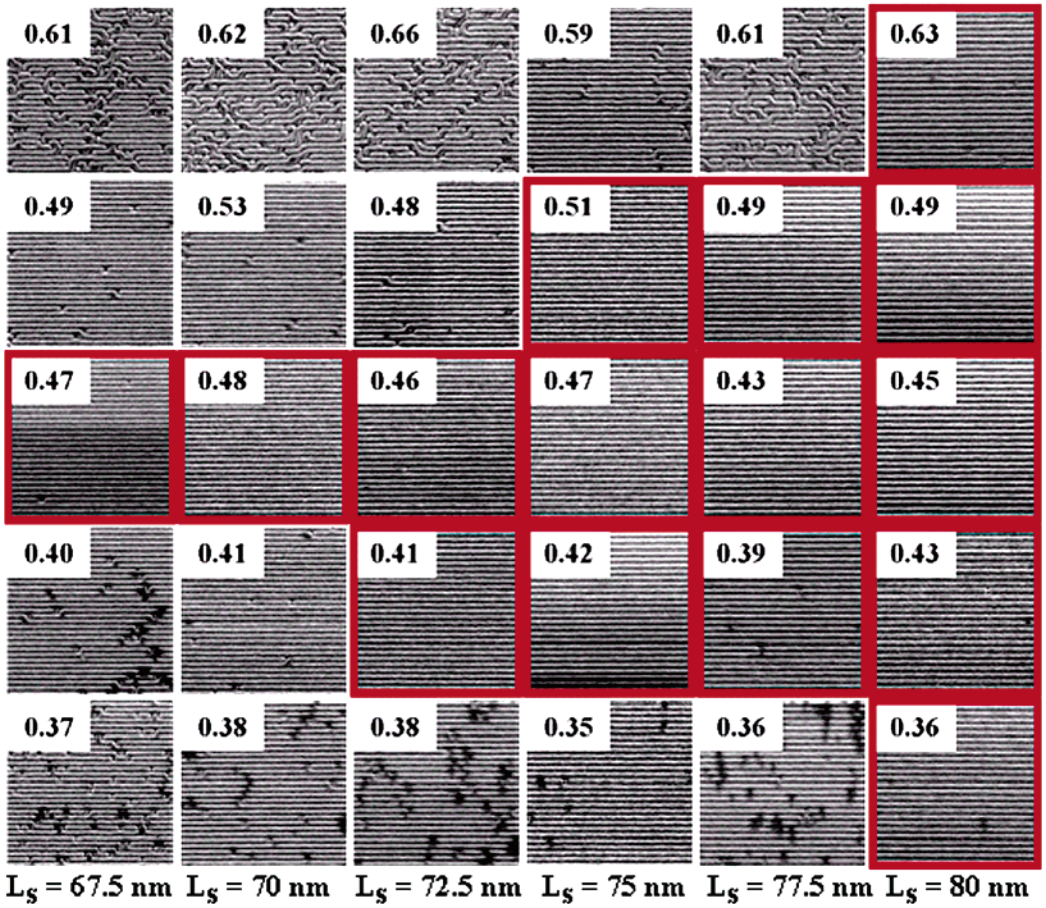


Figure 4. Plan-view SEM images of block copolymer domains directed to assemble over chemically nanopatterned substrates with varied normalized linewidths and substrate pattern periods. The micrographs are presented with the pattern period, L_S, increasing in the rows from 67.5 to 80 nm in 2.5 nm increments from left to right. In the columns the normalized linewidths, W/L_S of the PMMA structures used to create the chemical surface patterns decreases from top to bottom as shown in the upper left of each micrograph. Red boxes are placed around micrographs that show defect-free ordering in the block copolymer domains. All micrographs image a 2 μm by 2 μm area.

it is feasible to choose surface interactions sufficiently strong to achieve registration of the block copolymer morphology with the patterned substrate and weak enough not to excessively tilt the block copolymer interface with respect to the surface normal for a range of asymmetry. Figure 5A presents contour plots of the final three-dimensional morphology of block copolymer films with $\chi N = 63.2$ on a chemically patterned substrate with $L_S = L_O = 80$ nm and different values of W/L_S, after starting from a disordered state. Contour plots of two-dimensional calculations are presented as insets. On chemical surface patterns with a value of W/L_S of approximately 0.50, the block copolymer structures orient perpendicular to the substrate throughout the film. As W/L_S is shifted from 0.50 the block copolymer domains stretch and compress at the substrate and free interface creating trapezoidal structures to accommodate the underlying chemical surface pattern. The width of the polystyrene domains at half-height, W_{PS}, as determined from the SCMF simulations, normalized by the substrate pattern period, L_S, are plotted in Figure 5B. The self-assembling nature of the block copolymer domains results in normalized polystyrene domain widths, W_{PS}/L_S, of 15/32 ± 0.01, consistent with the simulated chain segment lengths of $N_{PS} = 15$ and $N_{PMMA} = 17$. The same result was observed for simulations in which the block copolymer with a bulk lamellar period, $L_O = 80$ nm was equilibrated on chemical surface patterns with periods, L_S, that were 70 and 80 nm.

The shape of the block copolymer domains impacts the value of templates created from block copolymer films for nanofabrication. The angle, θ, between the PS and PMMA domain interfaces and the surface normal may relate to the profile of the sidewall of patterned polymer structures after removal of one block of the copolymer domains and, subsequently, to dimensional fidelity during pattern transfer. Figure 5C is a plot of θ as a function of W/L_S, as determined from the SCMF simulations. The values of θ in Figure 5C do not deviate by more than 11° for any of the values of W/L_S investigated experimentally. The lines in Figure 5C represent the angle of the block copolymer interface with respect to the surface normal that would result based on conservation of volume arguments if the block copolymer domains formed ideal trapezoids that were pinned by the underlying chemical surface pattern. The self-healing nature of the block copolymer domains results in values of θ that are closer to the surface normal than those calculated based on this simple geometric estimate, resulting in a broad process window of chemical surface patterns with $0.45 < W/L_S < 0.55$ that are capable of directing the assembly of domains with less than 5° of tilt.

The insertion of block copolymers into the lithographic process is motivated by the need for improved dimensional and shape control of patterned resist structures. Chemically amplified resists, the type of resists used ubiquitously in advanced lithographic processes, have an ultimate resolution of approximately 30 nm,[47] but do not at present meet manufacturing requirements in terms of dimension control and line edge roughness even at much larger feature dimensions (ca. 54 nm).[48−50] According to the resist section of the most recent edition of the International Technology Roadmap for Semicon-

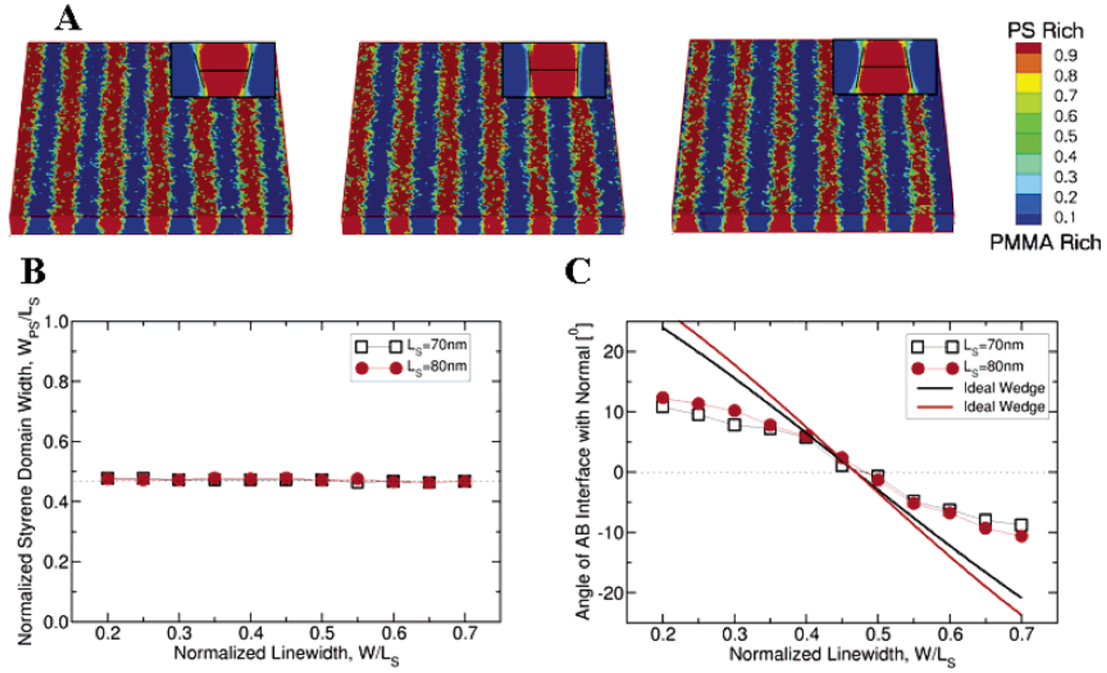


Figure 5. Results of single-chain-in-mean-field (SCMF) simulations of diblock copolymer thin films on chemically nanopatterned substrates with varying normalized linewidths. (A) Three-dimensional snapshot (large) and two-dimensional contour plots (inset) of SCMF simulations with $W/L_S = 0.30$, 0.45, and 0.65, from left to right, and $L_S = L_O = 80$ nm. Red domains are styrene and blue domains are methyl methacrylate. (B) Normalized width of polystyrene domains at half-height, W_{PS}/L_S, on chemically nanopatterned substrates with normalized linewidths, W/L_S of 0.2 to 0.7 with L_S equal to 80 (●) and 70 nm (□). (C) Sidewall angle Θ (angle of the styrene/methyl methacrylate interface) at half-height with respect to the substrate normal for the same range of normalized linewidths. The ideal wedge behavior is given by $\tan \Theta = (L_S f - W)/D$.

ductors (ITRS), lithographic processes and materials exist for generating 50 nm photoresist features for the 2010 benchmarks, but there are no known manufacturable solutions for controlling the dimensions of the features to within 2.1 nm for gate devices at these length scales. Moreover, there are no known manufacturable solutions for controlling the dimensions of 70 nm photoresist features to within 2.9 nm for patterning gate structures according to the 2007 benchmarks. In this study, we have purposefully created photoresist structures with systematic dimensional variations that emulate dimensional control problems (albeit magnified in some cases by an order of magnitude) in standard lithographic resists, and we used those resist structures to create chemical surface patterns. The block copolymer domains assembled over those chemical surface patterns exhibit a self-healing character. Defect-free and registered arrays of block copolymer domains could be obtained with dimensions and shapes that correct for the variations in the underlying chemical surface pattern that may be inherent to patterning with advanced lithographic tools. The dimensions of the block copolymer domains at half-film thickness were invariant with respect to the changes in the underlying chemical surface pattern indicating the potential to offer dimensional control to within 1 nm. Moreover, the sidewall angles of the block copolymer domains, an important parameter when considering the development of pattern transfer processes, were more perpendicular than would be expected from conservation of volume arguments. Although it remains to be seen whether pattern transfer processes can be developed to take advantage of the self-assembling attributes of the diblock copolymers, there is certainly the potential for block copolymers in the lithographic process to address these key problems.

Conclusions

The domain structure of block copolymer films can be directed to assemble on chemically nanopatterned surfaces to form defect-free arrays that are in registry with the underlying lithographically defined substrate. In contrast to previous studies in which lamellae were directed to assemble vertically, away from the surface pattern in an epitaxial manner (e.g., the width of the chemically patterned stripes matched the widths of the block copolymer domains), here we demonstrated that defect-free assemblies can be achieved even in the presence of substantial differences between the dimensions of the lamellae and the dimensions of the underlying chemical surface pattern. Moreover, the self-assembling nature of the block copolymer domains resulted in shapes that are more perpendicular, relative to the surface normal, on mismatched dimension stripes, than would be expected from conservation of volume arguments, thus delineating a process window over which the distortions in shape associated with the non-epitaxial assembly may not be severe enough to impact subsequent pattern transfer strategies. The technological importance of these findings relates to the insertion of block copolymers into the lithographic process for enhanced control over the dimensions and shapes of resist features.

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