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Directed Self-Assembly of Block Copolymers for Nanolithography: Fabrication of Isolated Features and Essential Integrated Circuit Geometries

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ABSTRACT Self-assembling block copolymers are of interest for nanomanufacturing due to the ability to realize sub-100 nm dimensions, thermodynamic control over the size and uniformity and density of features, and inexpensive processing. The insertion point of these materials in the production of integrated circuits, however, is often conceptualized in the short term for niche applications using the dense periodic arrays of spots or lines that characterize bulk block copolymer morphologies, or in the long term for device layouts completely redesigned into periodic arrays. Here we show that the domain structure of block copolymers in thin films can be directed to assemble into nearly the complete set of essential dense and isolated patterns as currently defined by the semiconductor industry. These results suggest that block copolymer materials, with their intrinsically advantageous self-assembling properties, may be amenable for broad application in advanced lithography, including device layouts used in existing nanomanufacturing processes.

KEYWORDS: block copolymers · directed self-assembly · lithography · integrated circuits · thin films

See the accompanying Perspective by Black on p 147.

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Self-assembling materials are being explored actively for patterning and fabricating structures at the nanoscale.[1–24] Block copolymers are particularly attractive due to their ability to assemble into highly ordered lamellar, cylindrical, spherical, and network morphologies with characteristic dimensions of 5–50 nm.[3–6] In addition to patterning dense structures with dimensions below the limits accessible to conventional photolithography, block copolymer assembly provides molecular-level control over the shape and dimensions of the structures that are formed. To date, nanostructures and functional devices fabricated using block copolymers, including quantum dots,[7,8] magnetic storage media,[9,10] flash memory devices,[11] semiconductor capacitors,[12,13] photonic crystals,[14,15] and nanopores,[16–18] have either required or benefited from the highly ordered and periodic nature of the self-assembled material. For many applications of advanced lithography, however, features must be patterned in complex geometries, not just periodic arrays, or alternatively the device layouts must be completely redesigned. The Semiconductor Industry Association's member companies through the Nanoelectronics Research Initiative have defined the essential set of pattern geometries for nanomanufacturing to include long lines, short segments, sharp 90° bends, jogs, T-junctions, periodic arrays of contact openings, and combinations thereof (see Figure 1).[25–27] These features may be required either as dense arrays or as isolated structures with ever decreasing

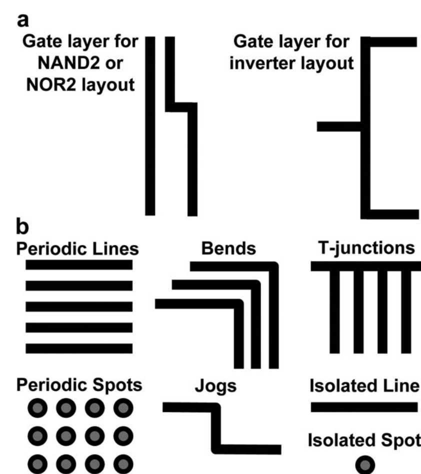

Figure 1. Essential geometries for integrated circuit layouts. (a) The generalized layouts of the gate layer for some of the most basic circuit components, such as those for NAND2, NOR2, and inverter operations, require relatively simple pattern geometries. (b) The essential set of geometries required for fabricating most integrated circuits, as defined by the Semiconductor Industry Association's member companies, includes dense and isolated lines, dense and isolated spots, 90° bends, jogs, and T-junctions.

critical dimensions. The typical gate or polysilicon layer of integrated circuits (see Figure 1a) exemplifies the relevance of these geometries.

The directed assembly of block copolymers on chemical surface patterns is an approach for coupling the advantages of traditional lithographic techniques, including pattern definition and registration, with self-assembling materials.[19–24] Previously lamellar and cylinder-forming block copolymers on chemically patterned surfaces have been assembled defect-free over arbitrarily large areas into dense arrays of lines[21–24] and contact holes,[24] respectively. Nonregular geometries such as arrays of 90° sharp bends have been assembled using a ternary block copolymer–homopolymer blend and benefited from the redistribution of homopolymer within the lamellar domains.[23] Here we show that the directed assembly of block copolymers on chemically patterned surfaces can fabricate almost the entire essential set of geometries required for patterning integrated circuits in both dense and isolated arrangements. Dense geometries of jogs and T-junctions were fabricated, as were isolated segment structures having from 20 segments down to only a single patterned segment. These novel isolated block copolymer structures had neighboring domains controlled to orient parallel and perpendicular to the substrate on chemical surface patterns with mixed and matched length scales, respectively. The resulting self-assembled dense and isolated structures are suitable masks for pattern-transfer processes such as substrate etching. We also introduce a strategy of using multiple exposure steps to chemically pattern surfaces capable of assembling block copolymers into complex, device-oriented structures.

RESULTS AND DISCUSSION

Directed Assembly of Dense Device-Oriented Geometries. The method used to direct the assembly of block copolymers with perfection and in registry with underlying chemical surface patterns is summarized below. A thin imaging layer of self-assembled monolayer[21] or polymer brush[22–24] is chemically grafted to the native oxide of a Si substrate. This surface can be patterned to have regions of distinct chemistry and therefore interfacial energy with respect to the two blocks of the copolymer using traditional top-down lithographic processes, including electron beam lithography and oxygen plasma etching. A block copolymer thin film can be deposited on this chemically patterned surface and thermally annealed such that the different blocks of the copolymer wet the different regions of the surface pattern and equilibrium morphologies are assembled. For this work we have used an end-grafted polystyrene (PS, 9.5 kg mol^{-1}) brush imaging layer and 40–45 nm thick films of a symmetric block copolymer ternary blend with 60 wt % poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA, 104 kg mol^{-1} total, 48 wt % PS), 20 wt % PS homopolymer (45 kg mol^{-1}), and 20 wt % poly(methyl methacrylate) homopolymer (PMMA, 46.5 kg mol^{-1}). This particular blend on neutral wetting surfaces[28] assembles into a lamellar morphology with a periodicity of $L_O \approx 73$ nm. The blend is assembled on chemically patterned surfaces such that the PS domains wet the regions of the PS brush imaging layer that are not chemically modified, while the PMMA domains wet the regions of imaging layer that have been chemically oxygenated in the oxygen plasma etching process. A ternary blend rather than a pure diblock copolymer was chosen to (1) achieve a lamellar-forming block copolymer material with a periodicity accessible to the conventional lithographic techniques used to chemically pattern the substrate and still maintain reasonable kinetics of ordering and (2) facilitate the assembly of defect-free device-oriented geometries through the redistribution of homopolymer within the ordered domains in the thin films.[23]

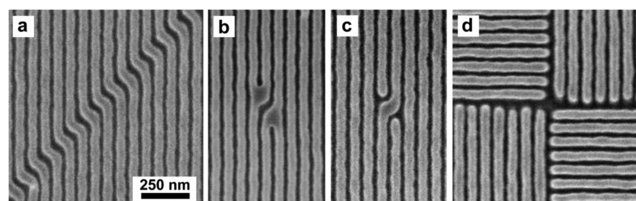

Figure 2. Top-down SEM images of the PS/PMMA ternary blend directed to assemble into (a) nested arrays of jogs, (b) isolated PMMA jogs, (c) isolated PS jogs, and (d) arrays of T-junctions. In all the SEM images, the PS domains are displayed in light gray, while the PMMA domains are dark gray or black.

Figure 2 displays block copolymer structures that were directed to assemble into dense arrays of the jog and T-junction geometries essential for integrated circuit layouts. In Figure 2a, the nested array of jogs demonstrates that these geometries can be assembled with a high degree of perfection and reproducibility. The jogs also can be embedded or isolated within a dense array of lines, as shown in Figure 2b,c, suggesting that complex combinations of the line, jog, bend, and T-junction geometries are possible in dense arrangements. Furthermore, both the PMMA or PS domains can be directed to assemble into the jog structures (see panels b and c of Figure 2, respectively), thereby demonstrating that the domains of symmetric block copolymer systems are interchangeable and that either can be used to fabricate the desired device structure.

Directed Assembly of Isolated Geometries. Unlike dense pattern layouts which benefit from a uniform block copolymer domain orientation and the length scale inherent to the material,[22] semi-dense and isolated structures demand the assembly of neighboring block copolymer structures with domain orientations both parallel and perpendicular to the substrate. For example, in Figure 2, all of the PS/PMMA interfaces and domains are oriented perpendicular to the substrate, and the periodicity of the assembled structures is commensurate with L_O. The self-assembly of isolated structures useful for top-down pattern-transfer processes,

ARTICLE

however, will require that large areas of the film be uniform in composition, either at the free surface or at the substrate interface.

The schematics in Figure 3 detail the directed assembly of structures formed from lamellar-forming block copolymers, or from blends of block copolymers and homopolymers, on chemically patterned surfaces and the application of such structures as pattern-transfer masks. Block copolymers form parallel-oriented domains on homogeneous surfaces preferentially wet by one block of the copolymer or on chemically patterned surfaces with $L_S \gg L_O$ (see Figure 3a).[3,29–31] Island or hole morphologies may be generated in copolymer films with thicknesses greater than L_O to maintain both the copolymer's equilibrium lamellar periodicity (L_O) and the favored wetting of the substrate and the air or free surface by the copolymer domains.[29–31] In the case of PS and PMMA systems, the lower surface energy PS component preferentially wets the free surface. Films with thicknesses less than L_O, such as those used in this work, often maintain uniform film thicknesses and do not form island or hole morphologies.[30,32] It is important to note that parallel-oriented block copolymer structures uniformly protect the substrate from etching, as there exists a continuous layer of resistant material (PS in this case). Figure 3b shows the scheme for the directed assembly of dense block copolymer structures on chemical surface patterns with $L_S = L_O$. In this case, the blue or PMMA domains can be removed from the assembled film and the pattern directly transferred to the substrate by reactive ion etching.

The fabrication scheme for isolated block copolymer features used in this work is shown in Figure 3c and combines the concepts of perpendicular and parallel domain orientations on the substrate. Any number of PMMA-preferential lines or segments with a periodicity of L_O (*e.g.*, two lines in Figure 3c) can be chemically patterned in the PS brush imaging layer. The block copolymer domain interfaces assembled in these areas orient perpendicular to the substrate, and the domains are registered with the surface pattern. The lack of surface pattern outside of the PMMA-preferential lines leaves a homogeneous, PS-preferential surface that induces a parallel block copolymer domain orientation. The assembled line patterns can be transferred to the substrate after selective removal of one of the copolymer domains. Figure 3c demonstrates the removal of the PMMA domains and the transfer of a two-line pattern to the substrate. Alternatively, the PS domains could be removed, leading to the transfer of a single isolated line to the substrate.

Figure 4 demonstrates the directed assembly of PS/PMMA block copolymers into isolated segment geometries that were 1 μm in length and ~35 nm in width.

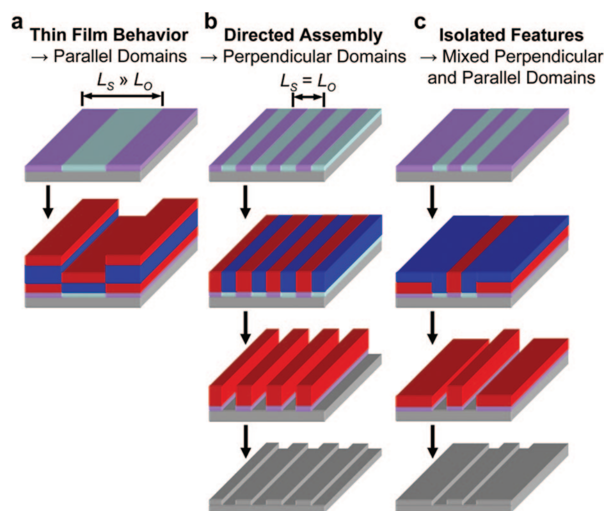

Figure 3. Fabrication scheme for directing the assembly of block copolymers into dense and isolated features using chemically patterned surfaces. The top row of images in each case represents the chemically patterned surface (purple, PS-preferential; light blue, PMMA-preferential; gray, substrate), while the second row demonstrates the orientation of the block copolymer domains (red, PS domains; blue, PMMA domains) assembled on these surfaces. (a) Block copolymer domains orient parallel to the substrate when the chemical surface pattern has a periodicity $L_S \gg L_O$. (b) The directed assembly of dense arrays of block copolymer domains occurs perpendicular to the substrate and in registry with the surface pattern when $L_S = L_O$. (c) Isolated structures can be directed to assemble in block copolymer films using mixed perpendicular and parallel orientations on surfaces that were chemically patterned at both $L_S = L_O$ and $L_S \gg L_O$ length scales. The perpendicular domains in panels b and c can be selectively removed (in this case, the blue domains) to provide a suitable mask for etching or depositing material on the substrate. The bottom row demonstrates the dense and isolated structures that could be reactive-ion-etched into the substrate using the self-assembled layer as a mask.

Sets of 10, 5, 3, 2, and 1 PMMA segments were fabricated in the block copolymer film, as shown from left to right in Figure 4a. The isolated segment structures appear as vertical, dark gray lines and are sandwiched between light gray lines. The PMMA domains were selectively removed in Figure 4b and created a PS template suitable for selective etching or deposition processes. Ultraviolet irradiation was used to degrade the PMMA polymer and cross-link the PS domain such that the degraded PMMA material could be removed by an acetic acid rinse.[33] Figure 4c demonstrates the transfer of these isolated segment patterns from the PS template to a silicon oxide substrate using HF wet etching techniques.

Two types of morphologies were found to arise in the parallel-oriented regions of the block copolymer film during the assembly of isolated structures. First, numerous PS spots on the top surface of the film were observed away from the patterned segments. The chemical surface in these regions was strongly PS-preferential, and it might be expected for this film thickness of ~$0.5L_O$ that parallel PS and PMMA layers would uniformly wet the substrate and the free surface, respectively. Instead, PS necks arise from the PS bottom layer

and propagate to the free surface. The PS/PMMA interface is, in reality, not perfectly parallel to the substrate and has significant fluctuations in contour, but nevertheless, the PS domain uniformly wets the PS brush substrate. The minimum thickness of the PS layer wetting the substrate in these parallel-oriented regions has been estimated from reactive-ion etching tests to be between 5 and 8 nm. It is suggested that these PS necks form as a result of the lower surface energy of the PS component and its slight preference for wetting the free surface of the film. The block copolymer/homopolymer blend system in these thin-film and symmetric wetting conditions, in contrast to thick-film and pure block copolymer systems, favors the formation of the PS necks to mitigate the unfavorable PMMA/free surface interactions rather than island and hole morphologies that have non-uniform film thicknesses. Similar hybrid perpendicular/parallel morphologies have been observed previously for pure block copolymer systems in films of thicknesses less than L_O and with comparable interfacial interactions.[32]

The second type of morphology that arose were PS ridges along the lengthwise edges of the patterned isolated structures. For example, three PS lines (light gray) rather than the expected single PS line were observed in the case of two PMMA lines (dark gray) shown in Figure 4a. These PS ridges are larger and less regular in shape than the PS necks but are also connected to the underlying PS layer that is registered with the chemical surface pattern.

Figure 4d shows predictions from single-chain-in-mean-field (SCMF) simulations[34,35] of the directed assembly of two-PMMA-line isolated structures. The PS ridges are readily predicted by the SCMF simulations and have a three-dimensional shape that connects to the underlying PS layer that wets the substrate (see Figure 4d, left). In this case, the simulation reproduced the experimental conditions using a block copolymer/homopolymer blend that was symmetric in composition with 60 wt % PS-*b*-PMMA, 20 wt % PS, and 20 wt % PMMA. The SCMF simulations also predict that the ridges may be eliminated if the block copolymer/homopolymer blend were made asymmetric in composition. A blend system more heavily enriched in PMMA homopolymer than PS homopolymer could serve to (1) match the relative volumes required for formation of isolated structures free of PS necks and ridges and (2) reduce the stresses associated with the sharp interface transition between perpendicular- and parallel-oriented lamellae that is similar in nature to T-junction grain boundary defects in bulk block copolymer systems.[36] A blend with a composition of 60 wt % PS-*b*-PMMA, 11 wt % PS, and 29 wt % PMMA is predicted to form the two-PMMA-line structures and to prohibit the formation of PS ridges (see Figure 4d, right). Blend compositions with less than 11 wt % PS homopolymer, however,

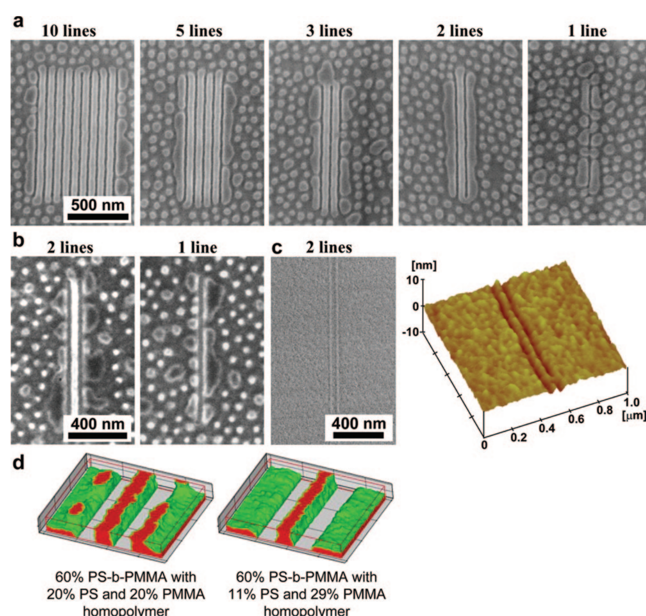

Figure 4. Directed assembly of the PS/PMMA ternary blend into isolated segment structures. (a) Top-down SEM images of isolated segment structures are shown for 10, 5, 3, 2, and 1 lines that have $L_S = 70$ nm and are 1 μm in length. The number of lines represents the number of PMMA-preferential lines in the surface pattern and therefore the number of perpendicular PMMA domains that were assembled on the surface pattern. The isolated PMMA segment structures are dark gray or black and are sandwiched between light gray PS domains. (b) Top-down SEM images of the PS structures formed after selective removal of the PMMA domains from the block copolymer blend films. (c) Top-down SEM and atomic force microscopy height images of defect-free isolated segment structures etched into a SiO_2 substrate using a PS template and HF wet etching. The etch depth in the patterned segments was 5–10 nm, and the root-mean-square roughness outside of the segments was <0.4 nm, comparable to that of the as-deposited SiO_2 layer. (d) SCMF simulations have been performed for the directed assembly of 60:20:20 (left, reproducing the experimental blend) and 60:11:29 (right) PS-*b*-PMMA:PS:PMMA blends on chemical surface patterns with two PMMA-preferential lines. Cuts through the PS domain are shown in red, and the interfaces between the PS and PMMA domains are displayed in green. The PMMA component has been removed from each film for visualization purposes.

are predicted to be unable to assemble into the unbroken PS line required between the two PMMA lines.

The SCMF simulations suggest that tailoring the blend composition to be slightly asymmetric may enhance the perpendicular-to-parallel transitions and eliminate certain edge structures. The blend composition required to prevent the PS ridge structures cannot be directly compared between the experimental isolated structures and the simulation predictions due to the periodic boundary conditions and finite box size used in the simulations. In the experiments, the isolated line structures were separated from the nearest neighboring structures by many micrometers of distance, while in comparison the line structures examined in the simulations were periodic and separated by only a few hundred nanometers, as set by the box size. The homopolymer can redistribute within the films such that the distance between structures is expected to influence the local blend composition and thus the mor-

phologies that are formed. Furthermore, the SCMF simulated systems form fewer PS necks than in the experiments, but this difference likely results from the estimated strengths of the polymer/substrate and polymer/air interactions implemented in the SCMF simulations.

The PS neck and ridge structures in the parallel-oriented regions are connected to a substrate-wetting PS layer and do not have a negative effect upon the application of such self-assembled structures as masks for selective etching or deposition processes. The underlying parallel-oriented PS layer serves as a mask regardless of the PS domain morphology present at the top of the film. Figure 4b shows the PS mask generated after removal of the PMMA domains and displays the neck and ridge structures. The pattern transferred from the PS mask into the substrate using wet etching techniques, as shown in Figure 4c, does not display any of the necks or ridges observed in the block copolymer structures. Reactive-ion etching with a high etch selectivity between the substrate and the polymer mask also should be capable of transferring the isolated patterns from the PS mask into a Si substrate with perfection. Although the PS mask self-assembled here may be too thin and have too low an aspect ratio for application in industrial pattern-transfer processes,[37] the PS component of the block copolymer could be replaced with a highly etch-resistant iron-[9,38] or silicon-containing[39] component. Pattern-transfer processes involving metal hard masks[40,41] are also being considered for industrial applications and would enable the use of thin, polymeric masks such as those assembled from block copolymers.

Complex Self-Assembled Structures on Surface Patterns Fabricated with Multiple Overlapping Exposures at Different Length Scales. Figure 5 shows an alternative approach for directing the assembly of block copolymers into isolated, device-oriented geometries. A multiple-exposure process can be used to fabricate the chemically patterned surface, as shown in the schematic in Figure 5a. First, large areas of the surface can be chemically patterned at the desired critical dimension and with a high degree of periodicity using a high-resolution but low-cost lithographic step, *e.g.*, using interference lithography.[42–45] Next, a relatively low-resolution lithographic step, *e.g.*, using optical lithography, can be applied to the pre-existing chemically patterned surface to isolate the desired structures. In theory, any number of patterning steps or lithography techniques could be used to generate the chemically patterned surface. Block copolymers directed to assemble on the final patterned surface can form dense, semi-dense, or isolated feature geometries.

Dense arrays of segments assembled by the lamellar-forming PS/PMMA blend on a chemical surface pattern generated with multiple overlapping exposures at different length scales are displayed in the top-down SEM image in Figure 5b. These particular patterned structures could be used to fabricate nanowire field effect transistors.[46] There is an important difference between the parallel-oriented domains assembled in Figure 5b and those in Figure 4. The multiple-exposure process used to chemically pattern the surface in Figure 5b resulted in the wide vertical stripes being PMMA-preferential, whereas the parallel-orienting areas of the chemically patterned surface in Figure 4 were PS-preferential. The large areas of PMMA-preferential surfaces resulted in lamellar domains oriented parallel to the substrate, with a PMMA layer wetting the substrate and a PS layer wetting the free surface. No PS neck structures are observed in the parallel wetting regions in Figure 5b because the free or air interface was already favorably wet by a PS layer.

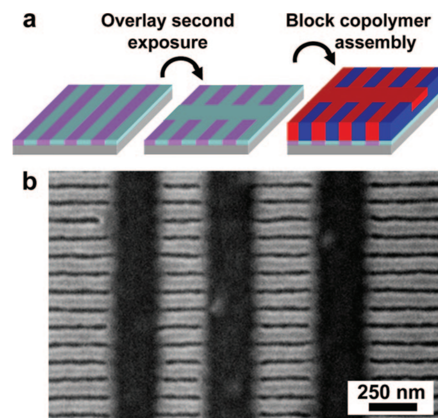

Figure 5. Multiple-exposure approach to the directed assembly of dense, semi-dense, or isolated device-oriented geometries. (a) A second chemical pattern can be exposed and overlaid on a surface with a pre-existing chemical pattern. Directed assembly of the block copolymer should follow the final chemical surface pattern regardless of the layouts of the individual pattern exposures. (b) The PS/PMMA blend with L_O = 73 nm was assembled on a chemical surface pattern fabricated using the two-step exposure process shown in panel a. Neighboring regions of perpendicular (patterned with dense arrays of horizontal lines with $L_S = L_O$) and parallel (uniform, large vertical stripes) orientations of the block copolymer domains were achieved. The PS and PMMA domains in the dense arrays in this top-down SEM image are shown in light and dark gray, respectively, while in the larger vertical stripes the PS is present at the flat top surface (appears in dark gray because of the image contrast).

CONCLUSIONS

In conclusion, this work demonstrated the directed assembly of block copolymers on chemically nanopatterned surfaces to form most of the essential set of pattern geometries required for integrated circuit layouts (*e.g.*, lines, segments, jogs, and T-junctions as shown in Figure 1). The block copolymers were directed to assemble into structures with ~35 nm critical dimensions and ranging in density from highly dense (1:1) to isolated, as typically needed in the fabrication of memory and microprocessor units, respectively. The only essential pattern geometries not presented here were sharp block copolymer bends that have been detailed else-

where[23] and contact holes that would benefit from the use of asymmetric, cylinder-forming block copolymer materials.[24] Although this work has focused on the use of symmetric, lamellar-forming block copolymer systems for the fabrication of dense line and isolated segment geometries, molecular-level simulations predict that tuning the blend composition is important for achieving defect-free structures. The optimal blend composition will depend upon the desired structure geometry and density of features.

On the basis of the results presented here, it is reasonable to expect that the directed assembly of block copolymers on lithographically defined, chemically nanopatterned surfaces should enable the fabrication of the entire set of essential geometries for the manufacture of integrated circuits, especially in light of current design trends in the semiconductor industry.[47] The motivation for using self-assembling materials in this context relates to improved control over the shapes and dimensions of the patterned features. It remains to be shown that these essential features patterned by self-assembled materials and techniques can be integrated to define devices, but these results point to the feasibility of patterning current device layouts as well as designs that are significantly simplified and more regular in geometry.

METHODS

Fabrication of Chemically Patterned Surfaces. A hydroxy-terminated polystyrene (PS, 9.5 kg mol^{-1}, Polymer Source, Inc.) brush imaging layer was chemically grafted to the native oxide of a piranha-treated Si substrate by annealing under vacuum at 160 °C for ≥48 h. Ungrafted polymer was removed using sonication in warm toluene for >10 min total. The PS imaging layer was then chemically nanopatterned using traditional lithographic and pattern-transfer techniques. A 50 nm thin film of photoresist (poly(methyl methacrylate), PMMA, 950 kg mol^{-1}) was spin-coated on the PS brush-grafted substrate and baked at 160 °C for 60 s. Electron beam lithography (LEO 1550-VP field emission scanning electron microscope (SEM) operating with a J. C. Nabity pattern generation system) was performed with an accelerating voltage of 20 keV, a beam current of ~20 pA, and an array of line doses centered at 0.6–1.0 nC/cm. All samples were developed for 30 s in a 1:3 solution of methyl isobutyl ketone:isopropyl alcohol (IPA), followed by a 30 s rinse in IPA and nitrogen drying. The pattern in the photoresist was subsequently transferred to a chemical pattern in the PS brush imaging layer by oxygen plasma etching at 10 mTorr of O_2 for 10 s. The PS imaging layer exposed to the oxygen plasma was chemically modified to include oxygen-containing groups and had a higher surface energy than the chemically unmodified PS brush.

Directed Assembly of Block Copolymers on Chemically Patterned Surfaces. Ternary blends of a lamellar-forming poly(styrene)-*block*-poly(methyl methacrylate) (PS-*b*-PMMA, 50 kg mol^{-1} PS and 54 kg mol^{-1} PMMA, PDI 1.04) diblock copolymer and its corresponding homopolymers (PS, 45.0 kg mol^{-1}, PDI 1.05; PMMA, 46.5 kg mol^{-1}, PDI 1.04) were prepared as 0.8 or 1.5 wt % solutions in toluene. This symmetric blend contained 60 wt % block copolymer and 20 wt % of each homopolymer and formed a lamellar phase with a periodicity of ~73 nm.[28] The polymers were acquired from Polymer Source, Inc. and used as received. The ternary blend was spin-coated on the chemically patterned surface to a thickness of 40–45 nm, as measured by ellipsometry (Rudolph Auto EL). Thermal annealing was performed under vacuum at 190–195 °C for 3–7 days and was sufficient to achieve equilibrium self-assembled morphologies. The PMMA and PS domains of the block copolymer preferentially wet the chemically oxygenated and the unmodified PS brush regions of the chemical surface pattern, respectively.

Pattern Transfer using Block Copolymer Templates. Pattern transfer of the isolated segment structures (Figure 4) was accomplished by fabricating a PS template from the block copolymer structures *via* removal of the PMMA domains. An ultraviolet exposure with a wavelength of 254 nm and a dose of 0.875 J/cm^2 was used to degrade the PMMA and partially cross-link the PS domains.[33] An acetic acid wash and deionized water rinse for 1 min each removed the degraded PMMA domains. Reactive-ion etching (PlasmaTherm Unaxis 790) for 4 s with an oxygen plasma (50 W, 10 mTorr, and a PMMA etch rate of 100 nm/min) was used to etch through the PS brush imaging layer. The resulting PS templates were suitable masks for the wet etching of isolated structures into substrates consisting of a 100 nm SiO_2 layer deposited on Si wafers using plasma-enhanced chemical vapor deposition (PlasmaTherm PT70); the fabrication of the chemical surface pattern and the block copolymer assembly process were identical to those used for Si substrates as described previously. Structures ~5–10 nm in depth were etched into the SiO_2 substrate with a solution of 50:1 deionized water: hydrofluoric acid (HF, 49%). The remaining PS templates were removed by an oxygen plasma etching process (3 min at 50 W and 10 mTorr).

Structure Characterization. The structures self-assembled by the block copolymer were imaged using scanning electron microscopy (LEO 1550-VP field emission SEM). No special procedures were required to obtain contrast between the PS and PMMA domains. The patterns etched into the SiO_2 substrate were characterized by SEM and atomic force microscopy operating in tapping mode with a Si tip (Digital Instruments Nanoscope IIIa).

Single-Chain-in-Mean-Field (SCMF) Simulations. SCMF simulation is a particle-based technique that retains the efficiency of self-consistent mean-field theory while providing an accurate approximation of fluctuations.[34,35,48] A bead-spring model describes the molecular architecture with $N = 15 + 17$ beads for the PS-*b*-PMMA, and $N_{PS} = 12$ and $N_{PMMA} = 13$ for the two homopolymers. The interactions are described by a coarse-grained density functional, $F[\{\varphi_a\}]$, where $\{\varphi_a\}$ denotes the PS and PMMA volume fractions. The PS/PMMA incompatibility is considered with a Flory–Huggins approach using $\chi N = 37.6$, and polymer compressibility is captured *via* Helfand's potential.[49] Polymer–substrate interactions are short-ranged in the x direction, normal to the substrate, and are described[50] *via* a potential of the form $\Lambda[f(y,z)R_e/\varepsilon]\exp[-x^2/2\varepsilon^2]$; $\varepsilon = 0.15R_e$ sets the interaction range, and $f(y,z)$ encodes the pattern geometry, taking values 1 or -0.6, depending on whether the considered y,z point on the substrate prefers PMMA or PS segments. $\Lambda N = 3$ sets the interaction strength, which can be estimated only approximately due to the complex experimental preparation of the substrate. The polymer–air interface is modeled as a neutral, hard wall. All lengths are measured in units of the bulk end-to-end distance of the diblock molecule, R_e, and the length scale is identified by comparing the lamellar spacing, $L_O = 2.26R_e$, of bulk SCMF simulations with the experimental value, $L_O = 73$ nm. The polymer chain number density, Φ, is matched to the experiments yielding an invariant polymerization degree of $\bar{N} = (\Phi R_e^3)^2 = 16\,384$.

SCMF simulations consider an ensemble of independent chains in fluctuating external fields, $W_a = \Phi\delta F/\delta\varphi_a$, acting on "a"-type segments. These fields approximate the instantaneous interactions of a chain with its surroundings and are frequently recalculated from the spatial segment distribution. Between updates, the fields are considered stationary and the chains evolve *via* a short Monte Carlo (MC) simulation. The decoupling of chains (*i.e.*, a quasi-instantaneous field approximation[48]) allows for a highly efficient parallel implementation. Recalculating the fields from the density distribution of the ensemble recovers the correlations between molecules. In the limit that the W_a fields follow the spatial distribution instantaneously, SCMF simulations become exact.

ARTICLE

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