Molecular Transfer Printing Using Block Copolymers

Shengxiang Ji, Chi-Chun Liu, Guoliang Liu, and Paul F. Nealey*

Department of Chemical and Biological Engineering, University of Wisconsin, 1415 Engineering Drive, Madison, Wisconsin 53706

ARTICLE

ABSTRACT Soft lithographic techniques augment or enhance the capabilities of traditional patterning processes and expand the diversity of materials that can be patterned. Realization of robust parallel techniques for creating chemical patterns at the nanoscale has been challenging. Here we present a method for creating and replicating chemical patterns that uses functionalized homopolymer inks that are preferentially segregated into the nanodomains of phase-separated diblock copolymer films. The inks are transferred by reaction to substrates that are brought into contact with block copolymer films, creating chemical patterns on the substrate that mirror the domain structure present at the film surface with high fidelity and resolution. In addition to printing from self-assembled domain structures, we can also direct the assembly of the block copolymer films from which transfer occurs using lithographically defined masters so as to replicate and transfer patterns of inks with controlled and well-defined geometries. The transferred patterns may be at higher resolution than the lithographically defined master, and the process can be repeated to create multiple copies of identical replicas. Transfer of one ink from one block of the copolymer is also possible, and filling the interspatial regions of the pattern with a second ink provides a pathway toward creating patterns with diverse chemical functionalities.

KEYWORDS: block copolymer lithography · transfer printing · directed assembly · nanopatterning · thin films

Fabrication of well-defined chemically patterned surfaces at the micro- and nanoscale is at the heart of many modern scientific and technical fields, including microelectronic devices,[1] microelectromechanical systems,[2] microfluidic devices,[3] photonics,[4] sensors,[5] microarrays,[6] and tissue engineering.[7] Historically, chemical patterning has been enabled by photolithography, a process developed for and by the microelectronics industry to pattern one specific type of material—photoresist. Due to the expense of the lithographic infrastructure when patterning at the nanoscale and the divergence of material and patterning requirements between semiconductor and other applications, a number of alternative techniques have been developed over the past decade. These techniques include microcontact[8,9] and nanoscale transfer printing,[10] and nanoimprint,[11,12] dip-pen,[13] block copolymer,[14] and interference lithography.[15] As fundamental barriers emerge for use of traditional photolithographic materials and processes for patterned features smaller than ~20 nm, however, alternative patterning techniques are now considered even in the context of semiconductor manufacturing. Nanoimprint lithography and directed assembly, for example, are included as potential lithography solutions for the 22 nm node and beyond in the 2007 International Technology Roadmap for Semiconductors.[16] Here we report an approach for replicating geometrically complex patterns over macroscopic areas with feature dimensions on the order of 10 nm. The technique, called "molecular transfer printing" (MTP), takes advantage of patterns in the domain structure at the surface of block copolymer films and transfers those patterns with high fidelity to substrates placed in contact with the copolymer film. In MTP, reservoirs of inks in copolymer domains promote saturation of molecular transfer at the replica surface. Technologically useful patterns may be created from self-assembled block copolymer films or by directing the assembly of block copolymer films on lithographically defined chemical prepatterns. For the latter case, the pattern from which transfer occurs (and thus the resulting pattern by MTP) may be of superior quality (perfection, registration, uniformity of feature dimensions)[17−20] and at higher resolution than the initial lithographically defined prepattern.[21−24]

RESULTS

Description and Demonstration of the MTP Process. A generalized description of the MTP process is shown in Figure 1 and outlined below. MTP starts with the self-assembly or directed assembly of a blend

See the accompanying Perspective by Carter on p 595.

*Address correspondence to nealey@engr.wisc.edu.

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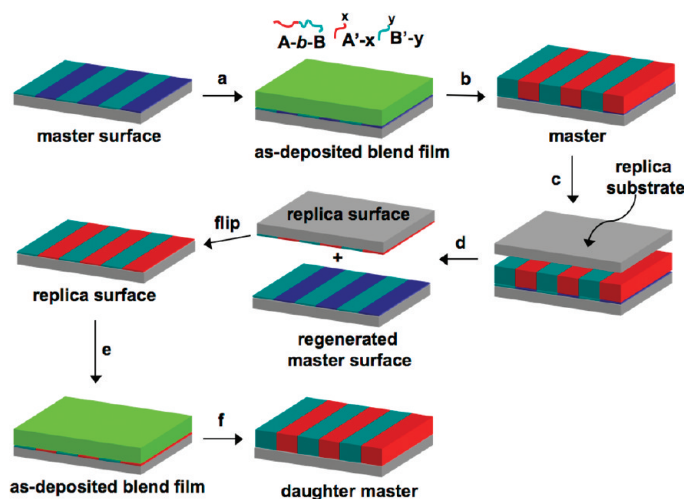

Figure 1. Schematic of molecular transfer printing (MTP). (a) Inks (A′-x and B′-y; x and y are reactive functional groups) are mixed with block copolymers (A-*b*-B) and deposited as a film on the substrate. (b) Blend film is annealed. Inks are compatible with only one block of the copolymer (A′ with A, and B′ with B), and after self- or directed assembly of the film, microphase-separated domains with sequestered inks form a "master" pattern. (c) Second substrate, the replica substrate, is brought in contact with the surface of the assembled film. By designing the inks to react, adsorb, or otherwise interact with the replica surface, inks are transferred in the pattern of copolymer domains present at the master surface to create a chemical pattern of inks on the replica. (d) Master and replica surfaces are separated by dissolving the block copolymer film in solvent to recover the patterned replica and the master surface. The master substrate can be reused multiple times. (e) Second blend film may be deposited on the replica surface and (f) assembled to create a daughter master.

film of a block copolymer and inks on a substrate. During assembly, ink molecules are segregated into their respective block copolymer domains. A replica substrate is then placed in contact with the surface of the assembled film. Upon thermal annealing, the ink molecules are transferred to and react with the replica substrate, creating a covalently bound pattern of ink molecules that mirrors the domain structure of the block copolymer film at the interface. After MTP, the block copolymer and unreacted or excess ink molecules are dissolved in solvents to recover the original master surface and the patterned replica surface.

Self-assembled block copolymer films were used in experiments designed to explore and choose appropriate experimental conditions for MTP and to characterize the process. MTP was performed using ternary blends of a diblock copolymer, poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA), and two homopolymer inks: hydroxyl-terminated polystyrene (PS−OH, M_n = 6 kg·mol^{-1}) and hydroxyl-terminated poly(methyl methacrylate) (PMMA−OH, M_n = 6 kg·mol^{-1}). The 6 kg·mol^{-1} hydroxyl-terminated homopolymers were chosen as inks because the molecular weight and chemistry are such that the inks (1) fully segregate into the appropriate PS or PMMA domains, (2) do not swell the block copolymer domains,[25] and (3) form polymer brushes of substantial thickness in regions that are fully functionalized.[26] To investigate transfer from patterns of linear features, a 50 nm thick film of a lamellae-forming blend, L50, consisting of 90 wt % PS-*b*-PMMA (M_n = 52−52 kg·mol^{-1}), 5 wt % PS−OH, and 5 wt % PMMA−OH, was self-assembled on a nonpreferential wetting surface at 190 °C for 24 h such that the lamellar domains were oriented perpendicular to the substrate in a fingerprint pattern with a period, L_B, of 50.3 nm.[26,27] To investigate transfer from patterns of discrete features, a 300 nm thick film of a cylinder-forming blend, C35 [L_B = 34.9 nm (center-to-center), consisting of 90 wt % PS-*b*-PMMA (46−21 kg·mol^{-1}), 7 wt % PS−OH, and 3 wt % PMMA−OH], was self-assembled on a silicon substrate (the native oxide was preferentially wet by PMMA) at 230 °C for 3 h to form arrays of hexagonally packed cylinders oriented normal to the film surface in the near surface region but mixed in orientation throughout the film thickness. The hexagonal arrays of domains had very large grains with long-range order on the surface of the block copolymer film as a result of using a thick film (>200 nm) and a high annealing temperature (~210−250 °C) for which the surface energies of PS and PMMA are balanced (Figure S1 in the Supporting Information).[27]

For all samples, a silicon substrate with a native oxide layer, the replica substrate, was then placed in contact with the surface of the phase-separated block copolymer film. Upon annealing at 160 °C for 24 h, the homopolymer inks diffused toward and reacted with the replica surface by a condensation reaction between the hydroxyl end groups of the homopolymer inks and silanol groups of the native oxide layer. The annealing temperature of 160 °C was chosen to be consistent with previous studies of brush deposition using PS−OH and PMMA−OH materials,[26] but processing at both higher and lower annealing temperatures was also successful. The reacted inks form polymer brushes at the replica surface; PS−OH brushes transfer from PS domains at the interface, and PMMA−OH brushes transfer from PMMA domains at the interface. The result is a pattern of PS and PMMA brushes mirroring the domain structure at the film surface. After MTP, the block copolymer and unreacted homopolymer inks were dissolved in chlorobenzene, and the original master and replica substrates were separated and recovered. The transferred fingerprint patterns and spot patterns of brushes on the replica surfaces were imaged by scanning electron microscopy (SEM), as shown in the left column in Figure 2a,b. The patterned PS and PMMA brushes were densely packed with no pin holes over the entire surface. The continuous lines with complex geometry and the dot arrays had periods of ~50.1 and 34.9 nm, commensurate with the L_B values of L50 (L_B = 50.3 nm) and C35 (L_B = 34.9 nm), respectively, providing a measure of the resolution and fidelity of the technique.

It was also possible to perform MTP if one homopolymer ink in the blends was replaced with its nonreactive analogue or if one homopolymer ink was omit-

ted altogether. Under these circumstances, transfer of ink only occurs from either of the PS or PMMA domains. Analogous blends to L50 and C35 were made in which PMMA−OH was replaced with nonreactive PMMA. After MTP with these versions of L50 and C35, fingerprint or hexagonal array patterns, respectively, consisting of PS brushes and bare substrate areas, were obtained (Figure 2a,b, middle column). In the fingerprint patterns for transfer of PS−OH only, close inspection of the SEM and AFM (Figure 2d) images reveals what appear to be non-uniform widths of PS brushes near defect structures with high curvature. It is unclear whether these deviations in width result from non-uniform swelling and collapse during the solvent wash or occur during MTP, especially near defects where the homopolymer ink concentration is expected to be slightly elevated.[18]

After printing with just the PS−OH ink, PMMA−OH could be used to "fill" the regions of the substrate not patterned in the MTP process (Figure 2a,b, right column). Fill is accomplished by spin-coating a film of PMMA−OH over the pattern of PS−OH brushes, annealing, and removing unreacted PMMA−OH in a solvent wash. SEM images of the print and fill samples appear identical to the images when both inks are transferred by MTP.

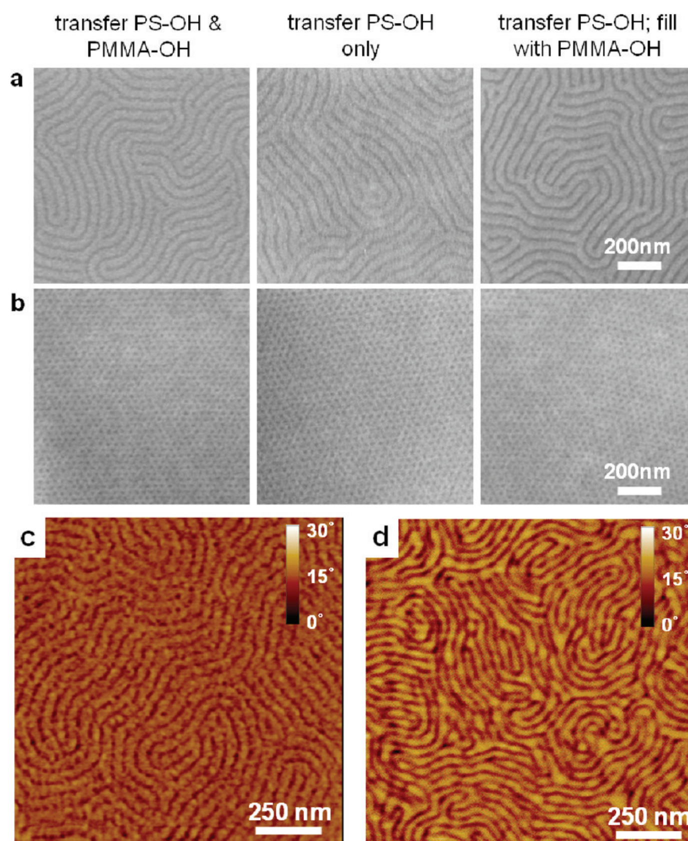

Figure 2. SEM and AFM characterization of brushes transferred by MTP. (a,b) SEM images of patterns of polymer brushes: (left) transferring both PS−OH and PMMA−OH (the brighter and darker regions are from PS and PMMA domains, respectively), (middle) transferring PS−OH only, and (right) transferring PS−OH and filling with PMMA−OH. (c,d) AFM phase images of the pattern of polymer brushes using (c) two inks (PS−OH and PMMA−OH), and (d) one ink (PS−OH and unreactive PMMA) in blend L50. The brighter domains in (c) are PMMAs.

Characterization of Ink Transfer during MTP. A diagnostic of achieving saturated grafting densities for brushes deposited during MTP was comparison of the brush thicknesses obtained from (1) MTP, (2) deposition of homogeneous brushes from binary blends of homopolymer inks in nonfunctional homopolymers of the same chemistry (blanket depositions), and (3) deposition of brushes from films of pure inks. The saturated grafting density was considered to correspond to the maximum thickness that could be obtained for transfer at 160 °C. Blanket depositions of brushes were performed using binary blends consisting of PS−OH (M_n = 6 kg · mol^{-1})/PS (M_n = 50 kg · mol^{-1}, nonfunctional) and PMMA−OH (M_n = 6 kg · mol^{-1})/PMMA (M_n = 50 kg · mol^{-1}, nonfunctional). Nonfunctional PS and PMMA have the same M_n as the PS and PMMA blocks in PS-*b*-PMMA of blend L50. The weight fraction of PS−OH and PMMA−OH in the blends ranged from 1.25 to 15%. The blends were deposited on oxygen-plasma-cleaned silicon substrates from solutions in toluene to yield films with constant thicknesses of ~50 nm. Blend films were annealed at 160 °C for 24 h to graft hydroxyl-terminated homopolymers onto the substrates. The ungrafted polymers were removed by sonication in chlorobenzene. The ellipsometric thicknesses (τ) of brushes increased monotonically with the concentration of hydroxyl-terminated homopolymers in the blends up to 10 wt % (Figure 3a). With further increase of the concentration of hydroxyl-terminated homopolymers, the value of τ remained relatively constant at a value of ~4.1 nm. Under the same annealing conditions, brush deposition from a 40 nm thick film of pure PS−OH (6 kg · mol^{-1}) also results in saturated grafting density corresponding to $\tau \cong$ 4.1 nm.[26]

To ensure that brush deposition was not limited by the chosen annealing time, the grafting kinetics of PS−OH and PMMA−OH on silicon substrates was also investigated using blanket depositions. The amount of PS−OH or PMMA−OH was fixed at 10 wt % in the binary blends, and blend films with thicknesses of ~50 nm were annealed for 2 to 36 h at 160 °C. PS and PMMA brushes reached ~95% maximal thickness within 4 and 12 h, respectively (Figure 3b). MTP was therefore performed at 160 °C for 24 h to induce maximal grafting densities of PS and PMMA homopolymer inks on substrates.

The thickness of the transferred brushes by MTP depended on the concentration of homopolymer inks in a nearly identical manner to the blanket depositions described above. Ternary blends of PS-*b*-PMMA (M_n = 52−52 kg · mol^{-1}) with varying amount of PS−OH (M_n = 6 kg · mol^{-1}) and PMMA−OH (M_n = 6 kg · mol^{-1}) were prepared with the total weight fraction of homopolymer inks (50:50) ranging from 2.5 to 12.5 wt %.

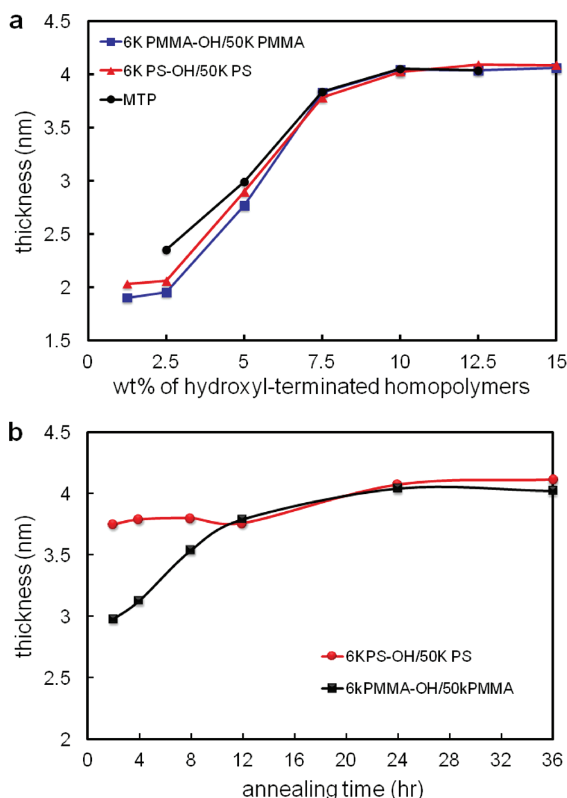

Figure 3. Brush thicknesses *versus* (a) the content of hydroxyl-terminated homopolymers in binary homopolymer blends and ternary blends used for MTP, and (b) the annealing time with fixed 10 wt % hydroxyl-terminated homopolymers in binary homopolymer blends. The standard deviation was ~0.1 nm for all data points and omitted for clarity.

The blends were cast on nonpreferential substrates (film thickness ≈ 50 nm) and annealed at 190 °C for 24 h to form fingerprint patterns of lamellar domains orientated perpendicular to the substrates.[25,26,28] The PS and PMMA domains contained 2.5 to 12.5 wt % of their respective homopolymer inks. MTP was performed at 160 °C for 24 h. After MTP, τ of the transferred brushes had almost the same thickness as a function of ink concentration as those in the blanket depositions of brushes from the binary blends. The thickness increased monotonically for concentrations of homopolymer inks up to 10 wt % and then leveled off at the same maximum value of ~4.1 nm (Figure 3a). For the 50 nm thick master films used throughout this work, homopolymer ink concentrations of 10 wt % were sufficient to form brush layers with saturated grafting densities. If transfer of inks was performed using thicker blend films, however, either in MTP or blanket depositions, saturated brush thicknesses could be obtained using ink concentrations below 10%.

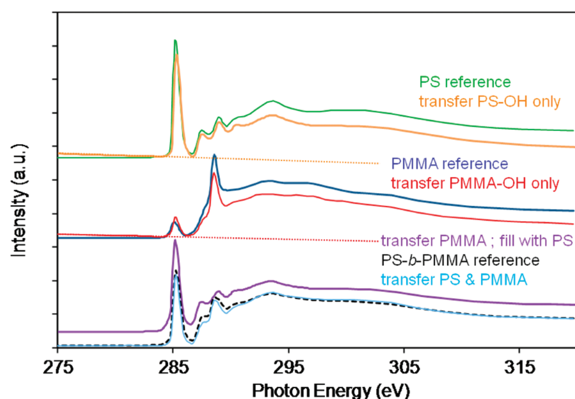

Figure 4. NEXAFS characterization of the transferred brushes from MTP using blend L50 films. NEXAFS spectra are shifted vertically for clarity. The linear dashed lines correspond to nonhorizontal baselines for samples for which only one ink was transferred.

When just PS−OH ink was transferred by MTP, then τ = 2.9 ± 0.2 nm (blend L50) and 3.2 ± 0.1 nm (blend C35), corresponding to the expected partial coverage of the patterns described above (50% for lamellae and 70% for cylinders). After print and fill, τ again reached the saturated value of ~4.1 nm.

The chemical specificity of the transfer process was characterized using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Figure 4 shows the spectra from brushes transferred in the MTP process for fingerprint patterns for which (1) both PS−OH and PMMA−OH inks were transferred, (2) only PS−OH or PMMA−OH inks were transferred, and (3) PMMA−OH ink was transferred and PS−OH ink was deposited to fill the interspatial regions. The PS contents of the transferred brushes from masters containing both PS−OH and PMMA−OH inks from lamellae- and cylinder-forming systems were determined to be 48.7 ± 0.7 and 66.3 ± 1.1 wt %, respectively. These values are consistent with the expected area fraction of PS domains at the interface, equal to the volume fraction of PS and PMMA in the block copolymer films. The volume fractions of PS domains in blends L50 and C35 are ~53 and ~71 vol %, respectively. If only one ink was transferred during MTP, only peaks corresponding to the corresponding homopolymer reference spectra were observed.[29] NEXAFS data thus confirmed the chemical specificity of the MTP process; only inks were transferred to the replica surfaces during MTP. The integrated areas of the absorption peaks of the brushes after transfer using only one ink are smaller than those of the corresponding homopolymer ink reference because of the partial coverage of the substrate. The nonhorizontal baselines of the spectra taken for single ink transfer are due to the high-energy tail of Si 2p edge of the exposed silicon regions. For the print and fill sample (transfer PMMA−OH, fill with PS−OH), the NEXAFS spectra show the presence of both PMMA−OH and PS−OH brushes on the replica surface. The PS content of the print and fill brush is ~55.7 ± 0.9 wt %. This value is 7% higher than the PS content in brushes transferred using both inks for the fingerprint pattern and is due primarily to the partial insertion of PS−OH into PMMA−OH regions during fill.[30]

Replication of Patterns Using Directed Assembly of Block Copolymer Films. MTP allows for the transfer of lithographically defined device-oriented patterns with high degrees of perfection if combined with techniques to direct the assembly of the domain structure at the surface of block copolymer thin films. Chemically nanopatterned substrates were prepared using advanced lithographic tools and used to create well-defined patterns in block copolymer films upon equilibration.[17−19] These device-oriented pattern geometries, including arrays of bends, jogs, T-junctions, and spots, are useful for the fabrication of elements of integrated circuits.[17−19,21] The left column of Figure 5 shows SEM images of patterns of resist (prepattern, defined by electron-beam lithography, pattern periods of 50 nm for lines and 45 nm for spots) on the top of uniformly deposited PS−OH brushes. The samples were exposed to oxygen plasma, and then the resist was stripped to create chemically nanopatterned substrates. Regions protected by the resists were preferentially wet by PS, and the oxygen-plasma-treated regions were preferentially wet by PMMA. Films of blends L50 and C45 [L_B = 45.6 nm, consisting of 90 wt % PS-*b*-PMMA (50−21 kg · mol^{-1}), 7 wt % PS−OH (6 kg · mol^{-1}), and 3 wt % PMMA−OH (6 kg · mol^{-1})] were directed to assemble on the chemical prepatterns to realize high aspect ratio block copolymer domains throughout the thickness of the film (Figure 5, second column). After MTP from these masters, the patterned brushes on replica surfaces and block copolymer domains that were directed to assemble on replicas were in the exact mirror images of the lithographically defined masters, with no missing or partially printed features (Figure 5, third and right columns).

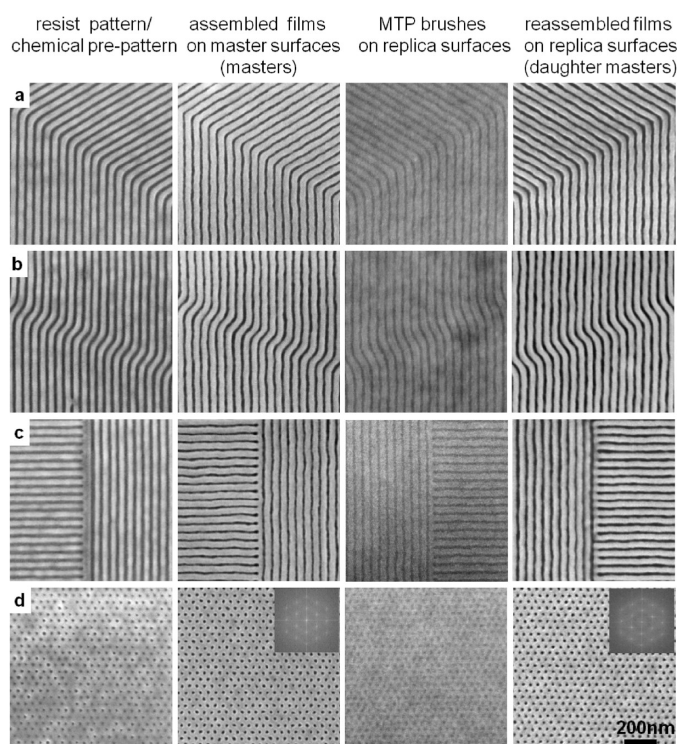

Figure 5. Demonstration of MTP of different pattern geometries using ternary blends of block copolymers. (a−d) SEM images of the photoresist pattern, indicative of chemical prepatterns, blend films assembled on the master surfaces (masters), transferred brushes on replica surfaces, and reassembled blend films on replica surfaces (daughter masters). MTP replicates arrays of (a) 120° bends, (b) jogs, (c) T-junctions, and (d) dot arrays with high fidelity. The patterns of the brushes transferred by MTP and the daughter masters are mirror images of the masters. The insets in (d) are fast Fourier transforms (FFTs) of the images.

Previously, we and others have shown that, in comparing the lithographically defined prepatterns to the assembled structures in the overlying block copolymer film, resolution may be enhanced by factors of four or more,[21−24] and the dimensional uniformity and control of feature size and shape may be vastly improved.[31,32] Figure 6 illustrates that, in combining MTP with the directed assembly of block copolymer films, the patterns of transferred inks from MTP may also share these highly desirable properties. Figure 6a shows an SEM image of the patterned resist with ~20 nm lines on a 110 nm pitch on top of a cross-linked PS brush. After transforming the pattern in the resist into a chemical prepattern, a lamellae-forming ternary blend L30 [L_B = 29.6 nm; 90 wt % PS-*b*-PMMA (18−18 kg · mol^{-1}), 5 wt % PS−OH (6 kg · mol^{-1}), and 5 wt % PMMA−OH (6 kg · mol^{-1})] film was directed to assemble on the surface, resulting in lamellae oriented perpendicular to the surface with a period of 27.5 nm and with a high degree of perfection (Figure 6b). In this case, assembly resulted in multiplying the feature density of the chemical prepattern by a factor of 4, and the feature dimensions correspond to one-half of the period for the lamellae over the preferential wetting stripe in the prepattern or over the interspatial regions of the prepattern (the interpolated features) alike. After MTP from this master film, the transferred pattern of inks consisted of alternating lines of PS and PMMA brushes with a period of 27.5 nm, matching the resolution of the master film (Figure 6c). Although it is difficult to characterize the patterned polymer brushes at this sublithographic length scale, the patterns subsequently directed the assembly of another film of blend L30 (Figure 6d) with very high degrees of perfection.

An attractive capability of MTP is that a single master can be replicated time and again to create large numbers of copies or daughter masters. For patterns such as those presented in Figures 5 and 6, the expensive, difficult, and time-consuming step of creating chemical prepatterns by lithography needs to be performed only once. We have used a single master as many as 20 cycles to regenerate identical master patterns 20 times and create 20 identical replicas (Figure 7). Chemical prepatterns consisting of arrays of stripes with L_S of 45, 47.5, and 50 nm were written by EUV-IL.[33] Films of blend L50 were directed to assemble on the master surfaces, accommodating incommensurability between L_S and L_B for the smaller periods.[18,32,34] After MTP, the master and replica surfaces were subsequently used to direct the assembly of freshly deposited

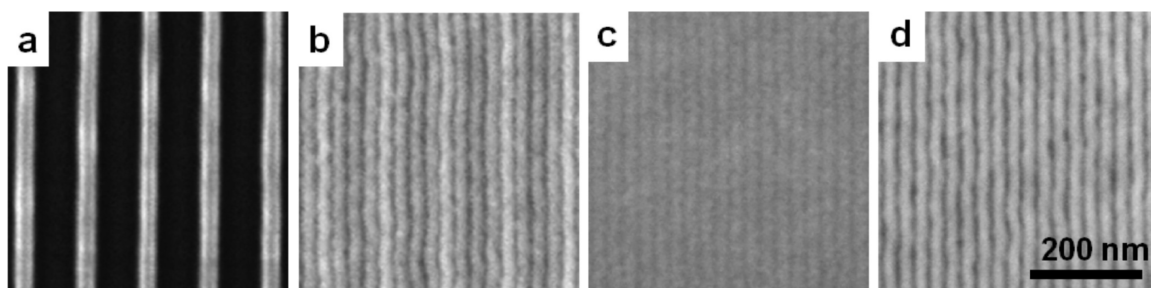

Figure 6. Combination of density multiplication and MTP to create chemical patterns with higher feature density than lithographically defined prepatterns. SEM images of (a) the photoresist pattern, indicative of chemical prepattern, (b) the master (blend L30), assembled with a factor of 4 higher feature density compared to the prepattern, (c) the patterned brush transferred by MTP, and (d) the reassembled blend L30 film on the replica surface. Every fourth PS domain in (b) appears brighter due to the presence of underlying cross-linked PS stripe from the prepattern.

films of blend L50. FFT analysis of the SEM images of the brushes on the 20th replica and the assembled films on both the master surface after the 20th cycle and the 20th replica surface revealed high pattern transfer fidelity; the PS and PMMA domains had essentially identical periods on masters and replicas alike, for both commensurate ($L_S = L_B$) and incommensurate ($L_S < L_B$) pattern periods.

Using lithographically defined chemical prepatterns and directed assembly of block copolymer films such as those shown in Figures 5 and 7, the appearance of defects was vanishingly small and did not offer the opportunity to easily explore the limits of MTP with respect to the defect formation or pattern fidelity. To find and compare master patterns and mirror image replica patterns that were not identical, we revisited the extremely complex fingerprint patterns formed by self-assembly and probed the capability of MTP to replicate the mirror image of such complex morphologies. (The spontaneously generated fingerprint pattern represents a convenient method to create a library of complex and technologically important features such as jogs, T-junctions, terminations, disclinations, acute and obtuse bends, and sharp radii of curvature at dimensions and spacing beyond that possible by traditional means.[16,19,35]) MTP was used to create a "master" fingerprint pattern, the first-generation replica, of PS and PMMA brushes transferred from a 100 nm thick L30 film assembled on a nonpreferential surface.[26] This master pattern was then used to direct the assembly of a newly deposited 50 nm thick film of blend L30.[35] The MTP process was repeated to create a daughter master (the second-generation replica). Blend L30 was then directed to assemble on both the master and daughter master, and top-down SEM images of the patterns in the block copolymer films from complementary areas were compared side-by-side (see Figure 8). Nearly exact replication of complicated structures with ~15 nm feature dimensions at 30 nm pitch was obtained from assembled block copolymer films on the master and daughter master alike. Rare defects were observed at regions of high curvature, as shown in Figure 9b. Unfortunately, when these differences in the patterns

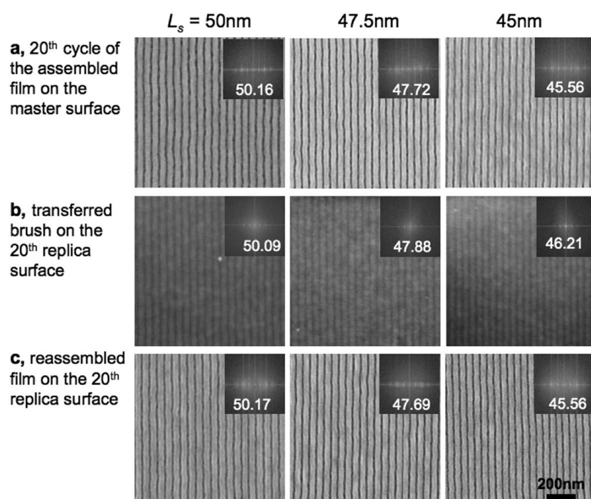

Figure 7. Demonstration of using a single master prepattern to produce multiple replicas. (a) SEM images of the 20th reassembled blend L50 film on the same EUV-IL patterned master surface. (b,c) SEM images of the transferred brushes and the reassembled blend L50 film on the 20th replica surface. The insets are the FFTs of the images and the corresponding calculated periods of the patterns. The calculated periods matched the periods of the underlying chemical patterns.

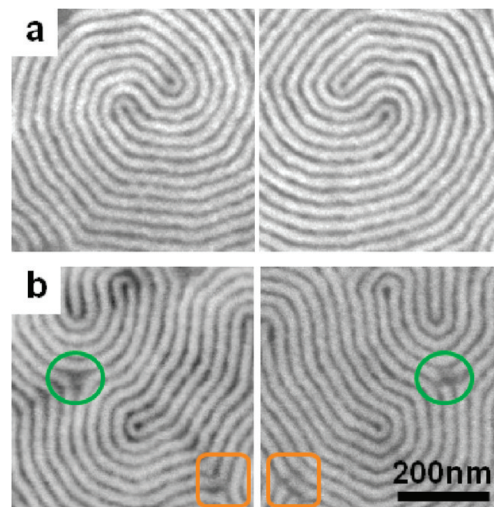

Figure 8. (a,b) SEM images of blend L30 films from complementary areas after reassembly on the master (left) and the daughter master (right), respectively. The squares and circles in (b) highlight defects.

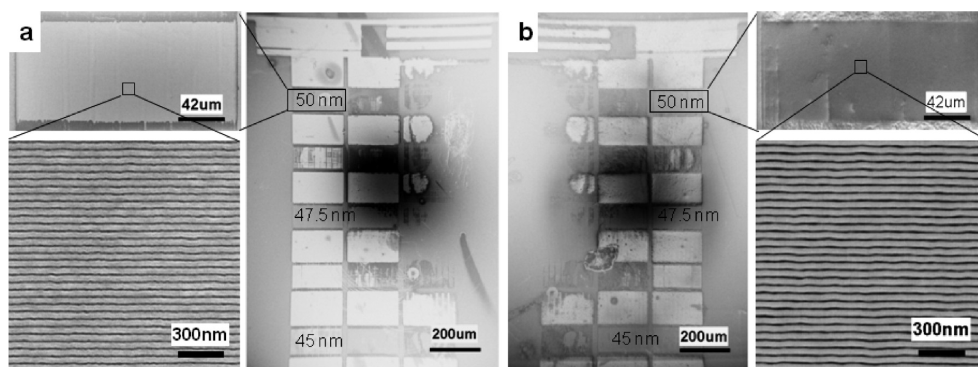

Figure 9. Large area printing using a conformal coating of silicon oxide as the replica. (a,b) SEM images of blend L50 films assembled on (a) the EUV-IL master surface and (b) its thin oxide replica (supported on a carrier silicon substrate) surface, respectively. The low magnification images show one of nine exposure fields of a EUV-IL master. The replica pattern is a mirror image of the master. The medium and high magnification images are from the patterned areas with L_S = 50 nm. The numbers in the low magnification images indicated the regions with the indicated pattern periods. The round dark areas in low magnification images are due to the charging effect of SEM imaging.

were observed, we could not differentiate between defects in the patterns of brushes that result from the MTP process or defects that occur in assembly of the block copolymer films on the patterned brushes.

Large Area Printing. A technological challenge in implementing MTP is achieving conformal contact between the surface of the master and the replica over large areas. In most of the samples described above, the process step of bringing the replica surface into conformal contact with the surface of the block copolymer film was done using rather crude clamping devices. Transfer of inks to the replica surface occurred only in regions of contact, and the area of contact was limited at times by the planarity of master and replica substrates. To demonstrate the principles of MTP, clamping by hand was sufficient, but it is anticipated that using more sophisticated equipment, for example, tools created for nanoimprint lithography, would produce even better results than those described here. Here we outline a strategy to achieve contact over large areas that may be particularly amenable for MTP—conformal deposition of a replica surface on top of the block copolymer film. Choice of replica films and surfaces includes numerous organic and inorganic, flexible and rigid materials. In a first demonstration, we used a 30 nm thick silicon oxide layer that was deposited on the master block copolymer film by chemical vapor deposition (Telemark eBeam evaporator; vacuum = 10^{-6} Torr, deposition rate = 6 nm/min). During MTP, inks reacted with the silicon oxide to form chemical patterns at the film−oxide interface. Using wafer bonding technology,[36] the oxide layer could be manipulated on a carrier substrate for further processing. In this way, much larger areas of pattern transfer could be routinely achieved compared to those obtained using the clamping devices, although fracture of the oxide layer during processing remained an issue. Figure 9 shows low-resolution SEM images (size = 1.0 mm × 1.4 mm) of a L50 film assembled over one exposure field of a EUV-IL patterned master and over the complementary area on a thin oxide replica supported on a carrier wafer. The corresponding high-resolution images show the 50 nm pitch patterned areas (80 μm × 200 μm) on both master and replica surfaces. In this case, the total area of successful replication was ~1 cm × 1 cm and contained nine exposure fields.

DISCUSSION

Comparison of MTP to other technologically important massively parallel techniques for creating and replicating patterns at the nanoscale highlights the advantages and disadvantages of different strategies for transfer of materials with respect to patterning capabilities, fidelity, and resolution. In microcontact printing (μCP),[8] nanoscale transfer printing (nTP),[10] affinity contact printing (αCP),[37] and supramolecular nanostamping (SuNS),[38,39] master patterns are typically written by traditional lithography, and contact of the master surface with a second substrate is required for transfer of materials and pattern replication. In μCP and nTP, inks and inorganic materials, respectively, are transferred from the tops of topographic features that have been molded into elastomeric stamps. Limitations in the mechanical stability and ease of deformation of the relief structures may limit the resolution and fidelity of pattern transfer at the nanoscale.[40] In αCP and SuNS, transfer of inks (proteins and DNA) occurs from planar substrates, but preparation of the template and the single molecule layer coverage of the template and subsequent transfer to the replica surface limit transfer efficiency, resolution, and quality of the patterns at the nanoscale.[38,39] In MTP, the amount of ink required for saturated deposition during transfer does not need to reside on a surface or at the transfer interface. Rather, the inks are sequestered in reservoirs, the block copolymer domains, and despite being initially distributed throughout the domain volume, readily access the transfer surface as necessary. In our experiments using 6 kg · mol^{-1} PS, for example, we estimate the diffusion coefficient of the ink in the PS domain at the temperature of transfer (160 °C) to be approximately 10^{-12} cm^2/

s.[41] During MTP, inks may diffuse across the entire ~50 nm thickness of the block copolymer film, the master, within just 10 s. Conformal contact between the replica and the film is facilitated when the film is in the melt, and unfavorable thermodynamics of mixing at interfaces between domains must prevent lateral mass transfer of inks during printing. The result is saturated ink transfer and very high pattern transfer fidelity.

The resolution of MTP also compares favorably to the other printing techniques because it is correlated directly to the dimensions of block copolymer domains, not necessarily the capabilities of the lithographic tools and materials used to fabricate the original masters. In performing MTP in conjunction with directed assembly of block copolymer films on lithographically defined chemically patterned substrates as masters, the assembled master films and transferred patterns may be not only at higher resolution than the chemical prepattern but also with improved control over the shapes and dimensions of pattern features (Figure 6). MTP was first developed and demonstrated using PS-*b*-PMMA because it is a special material. The blocks of the copolymer have nearly equal surface energies at annealing temperatures used for self-assembly and directed assembly,[27] facilitating presentation of both types of domains in desired patterns at the surface. Large differences in surface energy tend to induce parallel orientation of domains at the free surface and preclude pattern transfer.[42] Unfortunately, the use of PS-*b*-PMMA limits the resolution of MTP to dimensions of 10 to 12 nm due to the relatively weak value of the Flory−Huggins interaction parameter, χ, for this material. Other block copolymer systems, for example, poly(styrene-*block*-ethylene oxide) plus salts,[43] with higher values of χ are known to form domains with dimensions of 5 nm and below. It may be possible to further improve the resolution of MTP using such materials. One particularly promising approach is to assemble these materials by solvent annealing, as has been demonstrated in the literature,[44] to induce the presentation of patterned domain structures at the film surface, and to attempt to transfer inks by MTP from the solvent-annealed templates.

It is also germane to discuss MTP in the context of nanoimprint lithography (NIL).[11,12] NIL is similar to μCP and nTP in that master templates are topographic in nature, but different than μCP, nTP, SuNS, and MTP in that topographic rather than chemical patterns are replicated on the second substrate by molding or embossing. A strength and weakness of NIL is that the fidelity of pattern transfer even at the scale of a few nanometers is remarkable for desired features and defects alike. It does not share the self-healing and defect rejecting character of directed assembly of block copolymers. A major challenge in the development of NIL is the fabrication of large, high-quality, and high-resolution templates. We anticipate that NIL and MTP may be synergistic. MTP may be enabling for fabrication and replication of NIL templates, and tools developed for NIL may be useful in bringing surfaces together in the MTP process, perhaps with specific orientation or registration with one another. The synergy to create topographic masters for NIL relates to an important function of the patterned PS and PMMA brushes—the ability to direct the assembly of another block copolymer film on the replica surface. The patterned brushes themselves are not ideal for pattern transfer into the underlying substrate as they are molecularly thin. The reassembled block copolymer films provide the means of effective pattern transfer to the underlying substrate as the PMMA domains may be easily removed, leaving behind the relatively high aspect ratio PS domains as a soft etch mask for reactive ion etching.[45]

A disadvantage of MTP with respect to μCP, nTP, αCP, SuNS, and NIL relates to limitations in the geometries of patterns that can be replicated. Although there has been great progress over the past few years in expanding the variety and complexity of patterns that can be created using block copolymers, and further developments in this area are expected, it is unlikely that block copolymer lithography and therefore MTP will ever match the capabilities of top-down lithographic processes. These tools have the capability to pattern arbitrarily shaped features with widely varying dimensions and, therefore, impart this flexibility in pattern generation to μCP, nTP, αCP, SuNS, and NIL, as well.

Finally, we envision pathways to diversify the chemistry of materials patterned using MTP even if the starting point remains self-assembly or directed assembly of PS-*b*-MMA films. For consistency in brush thickness measurements and NEXAFS analysis, in this paper, we demonstrated printing PS−OH or PMMA−OH followed by filling with PMMA−OH or PS−OH. It is not only possible, but often preferable, to fill with inks that are completely different in chemistry than either block of the master copolymer film. Direct printing of inks that are chemically different from either block of the block copolymer may be also possible to create patterns with diverse functionalities if the inks are compatible with and segregated into just one block in the master film.

CONCLUSIONS

We have demonstrated a technique for creating and replicating chemically nanopatterned surfaces using block copolymer films impregnated with reactive inks. Technologically important patterns of high fidelity and resolution result from the following principal concepts: (1) printing from masters that incorporate reservoirs of inks promotes saturated transfer of ink to the replica surface; (2) the resolution correlates directly with the dimensions and spacing of domains in block copolymer films; (3) the molecular weight and composition of masters provide ready access to a range of feature shapes and dimensions; (4) pattern geometries

and layouts include those that can be obtained from self-assembly and directed assembly of block copolymer films; (5) massively parallel processing is possible with masters and daughter masters so as to efficiently create large numbers of copies of the same pattern; and (6) pathways enabled by print and fill strategies in addition to direct ink transfer allow for the diversification of the types and chemistries of materials that can be patterned. The ease of this technique to produce well-defined nanoscale patterns over macroscopic areas holds potential for many applications across the physical, engineering, and life sciences.

METHODS

Materials. PS-*b*-PMMA (M_n = 52-52, 50-21, 46-21,18-18, and 5-5 kg·mol^{-1}, polydispersity index (PDI) = 1.04−1.06), PS−OH (M_n = 6 kg·mol^{-1}, PDI = 1.05), PMMA−OH (M_n = 6 kg·mol^{-1}, PDI = 1.06), PS (M_n = 50 and 6 kg·mol^{-1}, PDI = 1.04), and PMMA (M_n = 50 and 6 kg·mol^{-1}, PDI = 1.06) were purchased from Polymer Source, Inc. PMMA photoresist (M_n = 950 kg·mol^{-1}, 4 wt % in chlorobenzene) was purchased from MicroChem, Inc. All solvents were purchased from Aldrich and used as received. Hydroxyl-terminated poly(styrene-*ran*-methyl methacrylate) (PS-*r*-PMMA−OH, M_n = 12.5 kg·mol^{-1}, PDI = 1.25) was synthesized by nitroxide-mediated polymerization according to the reported procedure.[27] The styrene fraction was determined to be 50 mol % by ^{1}H NMR analysis. The cross-linkable PS (M_n = 30.5 kg·mol^{-1}, PDI = 1.22) was synthesized by nitroxide-mediated copolymerization of styrene and glycidyl methacrylate and contained ~4 mol % of cross-linkable epoxy groups.

Self-Assembly of Fingerprint Patterns on Nonpreferential Substrates. The nonpreferential substrate was prepared by (1) depositing a 40 nm thick film from a 1 wt % ternary blend solution of 60 wt % PS-*b*-PMMA (5-5 kg·mol^{-1}), 20 wt % PS−OH (6 kg·mol^{-1}), and 20 wt % PMMA−OH (6 kg·mol^{-1}) in toluene by spin-coating on an oxygen-plasma-cleaned silicon substrate, (2) annealing the film at 160 °C for 24 h, and (3) removing unreacted homopolymers and copolymers by sonication in toluene.[26] Solutions of 1.5 wt % blends L50 and L30 in toluene were spin-coated on nonpreferential substrates to yield films with thicknesses of ~100 nm. The films were annealed at 190 °C for 24 h under vacuum. The lamellar domains formed a fingerprint pattern on the film surface and oriented perpendicular to the substrate.[25,26,28]

Self-Assembly of Hexagonal Arrays of Cylinders with Long-Range Order on Silicon Substrates. A 300 nm thick film of blend C35 was spin-coated onto a silicon substrate from a 7 wt % toluene solution. The film was then annealed at 230 °C for 3 h under vacuum to form arrays of perpendicular cylinders with large grain sizes on the film surface. The sizes of some "single crystal" grains are as large as 5−6 μm^2 (Supporting Information Figure S1a). The orientational correlation length (ξ), a measure of grain size, of the perpendicular cylinders on the surface of the 300 nm thick film was estimated to be ~1 μm (Figure S1b).

Fabrication of Chemical Prepatterns by Electron Beam Lithography (EBL). We start with the deposition of a PS brush. A 40 nm thick PS−OH (6 kg·mol^{-1}) film was spin-coated on an oxygen-plasma-cleaned (PE-200 Benchtop Plasma System, Plasma Etch, Inc.) silicon substrate and annealed at 160 °C for 24 h under vacuum. Excess PS−OH was removed by sonication in toluene to form a PS brush layer with a thickness of ~4.1 nm. A 50 nm thick PMMA photoresist (950 kg·mol^{-1}) film was deposited onto the PS brush from a 1.2 wt % chlorobenzene solution and baked at 160 °C for 60 s. Patterns of jogs, bends, and T-junctions with periods, L_S, of 50 nm, and cylinders with L_S = 45 nm (Figure 5) were exposed on the resists using EBL. EBL was performed on a LEO 1550 VP SEM equipped with a J. C. Nabity pattern generation system with an acceleration voltage of 20 kV.[19,46] Exposed substrates were developed with a 1:3 (v/v) mixture of methyl isobutyl ketone/isopropanol (MIBK/IPA) for 60 s and rinsed with IPA. The resulting resist pattern was transformed into a chemical prepattern on the PS brush by exposing the sample to an oxygen plasma followed by stripping the PMMA photoresist in warm chlorobenzene. The plasma-modified regions are preferentially wet by PMMA domains of the copolymers, and the unmodified PS brush regions are wet by PS domains.

Fabrication of Chemical Prepatterns by Extreme Ultraviolet Interference Lithography (EUV-IL). Grating chemical prepatterns on PS brushes with L_S of 45, 47.5, and 50 nm were fabricated by EUV-IL at the Synchrotron Radiation Center (SRC) at the University of Wisconsin—Madison. The patterns were exposed on the resists using a transmission membrane interferometric mask.[33] The exposed resists were developed with 1:3 MIBK/IPA. The resulting resist pattern was transformed into a chemical prepattern on the PS brush by exposing the sample to oxygen plasma followed by stripping the PMMA photoresist in warm chlorobenzene.

A grating chemical prepattern with L_S = 110 nm was fabricated by EUV-IL on cross-linked PS brushes. A 5 nm thick film of cross-linkable PS was spin-coated onto an oxygen-plasma-cleaned silicon substrate from a 0.25 wt % solution in toluene and cross-linked at 190 °C for 2 days under vacuum. The uncross-linked PS was rinsed away by sonication in toluene. A 50 nm thick PMMA photoresist film was deposited on the cross-linked PS brush, patterned with EUV-IL, and developed in 1:3 MIBK/IPA to create a grating resist pattern consisting of ~20 nm wide parallel lines with a L_S of 110 nm (Figure 6a). The cross-linked PS layer not protected by photoresist was etched with an oxygen plasma to yield parallel cross-linked PS stripes spaced by trenches free of brushes. After removal of the photoresist with warm chlorobenzene, a 20 nm thick film of PS-*r*-PMMA−OH with 50 mol % of styrene content was spin-coated from a 0.5 wt % toluene solution onto the patterned substrate. The substrate was then annealed at 190 °C for 4 h to graft the brush into the exposed regions between the cross-linked PS stripes. Excess PS-*r*-PMMA−OH was removed by sonication in toluene to yield a grating pattern of alternating PS and PS-*r*-PMMA stripes.

Directed Assembly of Blends on Lithographically Defined Chemical Prepatterns. Blend L50 films (~50 nm) were deposited on the chemical prepatterns of (1) bends, (2) jogs, (3) T-junctions, and (4) 45−50 nm gratings from a 1.5 wt % toluene solution and annealed at 190 °C for 24 h under vacuum. A 50 nm thick blend C45 film was deposited on the chemical prepattern of spot arrays from a 1.5 wt % toluene solution and annealed at 190 °C for 24 h under vacuum. After directed assembly, the copolymer domains faithfully registered on the chemical prepatterns and oriented perpendicular to substrates (Figure 5).[17−19]

A 50 nm thick blend L30 film was deposited on the chemical prepattern with L_S of 110 nm from a 1.5 wt % toluene solution and annealed at 250 °C for 1 h under a nitrogen atmosphere. The lamellar domains assembled on the chemical prepatterns and oriented perpendicular to the substrate with a period of 27.5 nm, multiplying the feature density by a factor of 4 (Figure 6).[21,22]

Molecular Transfer Printing (MTP). An oxygen-plasma-cleaned silicon substrate was placed in contact with the master film surface. The sandwiched structure was clamped by a parallel four-screw clamp, annealed at 160 °C for 24 h under vacuum, and separated by dissolving block copolymers and unreacted homopolymers by repeated sonication in chlorobenzene to create a replica (and regenerate the master chemical prepattern). Transfer of inks to the replica surface occurred only at the region in contact, and the area of contact is limited by the planarity of master and replica substrates. Use of thick films facilitated the contact between the master and replica substrates, and large area replication was achieved. The transferred brushes on replicas were then used to direct the assembly of block copolymer films.

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Supporting Information Available: (1) NEXAFS characterization and (2) generation of hexagonal arrays of cylinders with long-range order. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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