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Resist Free Patterning of Nonpreferential Buffer Layers for Block Copolymer Lithography

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ABSTRACT We report the design of a direct electron beam patternable buffer layer to spatially control the orientation of the microdomains in an overlaying polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer (BCP) film. The buffer layer consists of a surface anchored low molecular weight PS-*b*-PMMA, with the PMMA segment anchored to the surface and a short PS block at the buffer layer/BCP interface. The block architecture of the buffer layer combines the essential features of "bottom up" and "top down" approaches as it functions as a nonpreferential layer to dictate perpendicular orientation of BCP domains from the substrate interface and as an e-beam resist to allow top-down lithographic process to spatially define the buffer layer on the substrate. The composition of the buffer layer can be tuned by changing the relative block lengths to create a nonpreferential surface which effectively induces perpendicular orientation of domains in an overlying BCP film. The grafted block copolymer can be locally shaved by e-beam lithography resulting in spatial control of domain orientation in the BCP film. The direct patterning approach reduces the number of steps involved in forming chemical patterns by conventional lithography.

KEYWORDS: direct patterning · block copolymer · directed assembly · e-beam lithography · neutral surface

Self-assembly of block copolymer materials (BCPs) in bulk and the translation of these ordered domains into thin-films has emerged as a powerful method to create functional nanostructures and templates for various applications.[1−5] The use of ordered BCP domains in thin-film form, known as block copolymer lithography, creates a dense periodic array of nanostructures which are relevant to areas such as bit-patterned media,[6] memory devices,[7] nanowire transistors,[8] and quantum dot arrays.[9] Multiple levels of control over the placement of these nanostructures can be attained by combining the "bottom-up" self-assembling characteristics of the BCP with the "top-down" lithographic processes.[6,10,11]

In thin films, controlling the orientation of domains with respect to the substrate is critical as it dictates the pattern geometry for anisotropic domains such as cylinders and lamellae. While there are several methods such as solvent annealing,[12] the use of rough substrates,[13,14] and chemical modification of the substrate[15−17] to control the orientation of domains in BCP film, we have primarily focused on the use of random copolymers as a nonpreferential buffer layer. The basic principle for achieving perpendicular domain orientation is to balance out the interfacial interactions of each block of the BCP with the substrate (Figure 1a). This has been referred to as a "neutral surface". The concept of surface neutralization with surface anchored polymers was first introduced by Mansky et al.[16] They demonstrated that the interfacial interaction of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) with the substrate can be tuned by controlling the composition of surface grafted polystyrene-*random*-poly(methyl methacrylate) (PS-*r*-PMMA) (Figure 1b). Since then, several advances over the chemistry of these copolymers have been reported. For example, we have synthesized a new type of copolymer to control the interfacial energies for the assembly of BCPs with both small and large differences in surface energies of the blocks, such as polystyrene-*block*-poly(methyl methacrylate) and polystyrene-*block*-poly(2-vinylpyridine) respectively.[18,19] These copolymers have a distribution of hydroxyethyl methacrylate (HEMA) monomer which is capable of multipoint anchoring *via* side groups to the oxide surface creating a cross-linked mat. Further incorporation of photocross-linkable groups[20] allows deposition of these copolymers on atypical substrates such as gold and III−V semiconductors. They offer a number of advantages such as ease of synthesis with readily available monomers, mild cross-linking conditions, and effectiveness in very thin layers.

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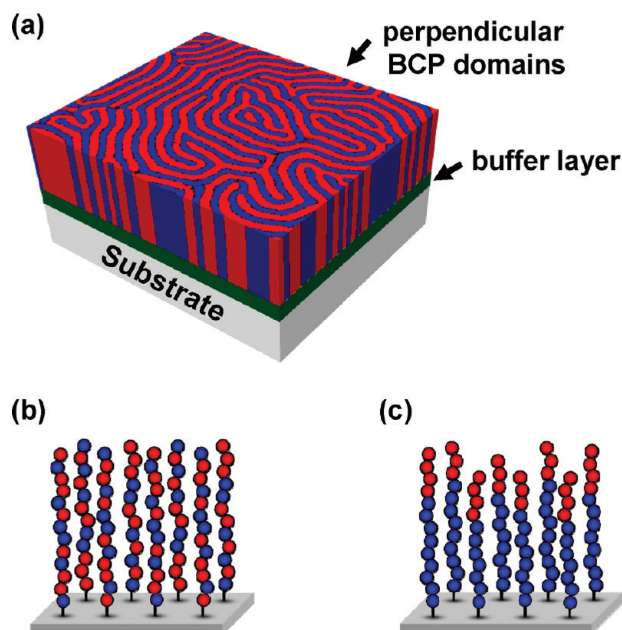

Figure 1. (a) Schematic illustration of thin-film of BCP assembled on a nonpreferential buffer layer, and the architecture of a random copolymer (b) and a block copolymer (c) based buffer layer.

We further demonstrated the use of UV to pattern the copolymer mat and hence spatially define the orientation of the overlying BCP domains. For the rest of the manuscript we will refer to the surface grafted polymers as the buffer layer.

In all the above examples, the nonpreferential buffer layer is a surface which has a random distribution of comonomers on the surface so that both the local and global composition is uniformly defined to tune the interactions with the overlying BCP film. However, none of these copolymers have been directly patterned by electron beam lithography (EBL) to spatially define the nonpreferential layer at the submicrometer scale. Instead, patterning of photoresist followed by an etching process has been utilized to create a chemical pattern on the buffer layer.[21−23] In this article, we report the design of a low molecular weight hydroxyl terminated BCP (A-*b*-B−OH) (Figure 1c) anchored to the surface as a nonpreferential buffer layer for the assembly of a higher molecular weight A-*b*-B diblock copolymer in thin films. The advantage of using low molecular weight surface anchored BCP as a nonpreferential buffer layer lies in the fact that (i) hydroxyl terminated low molecular weight BCPs can be readily synthesized for most BCPs relevant to lithography, and (ii) the block architecture, where one of the blocks is intrinsically e-beam sensitive provides sufficient overall sensitivity in these grafted BCPs to enable direct patterning by EBL. As proof of concept we present the first example of a nonpreferential surface created by surface anchored low molecular weight PS-*b*-PMMA for the assembly of both symmetric and asymmetric PS-*b*-PMMA. We also demonstrate the direct patternability of the grafted BCP using EBL to locally remove the buffer layer resulting in spatial control of domain orientation in the overlying BCP film. Thus, essential features of "bottom up" and "top down" approaches are effectively combined in the block architecture of the buffer layer as it functions as a (i) nonpreferential layer to dictate perpendicular orientation of BCP domains from the substrate interface, and (ii) e-beam resist to allow top-down lithographic process to spatially define the nonpreferential layer on the substrate.

RESULTS AND DISCUSSION

Design of the Hydroxyl Terminated PS-b-PMMA Buffer Layer and Surface Modification. Phase separation of symmetric diblock copolymers occurs if χN is greater than 10.5, where χ is the Flory−Huggins interaction parameter and N is the total number of repeat units in the block copolymer.[24] Based on the Flory−Huggins interaction

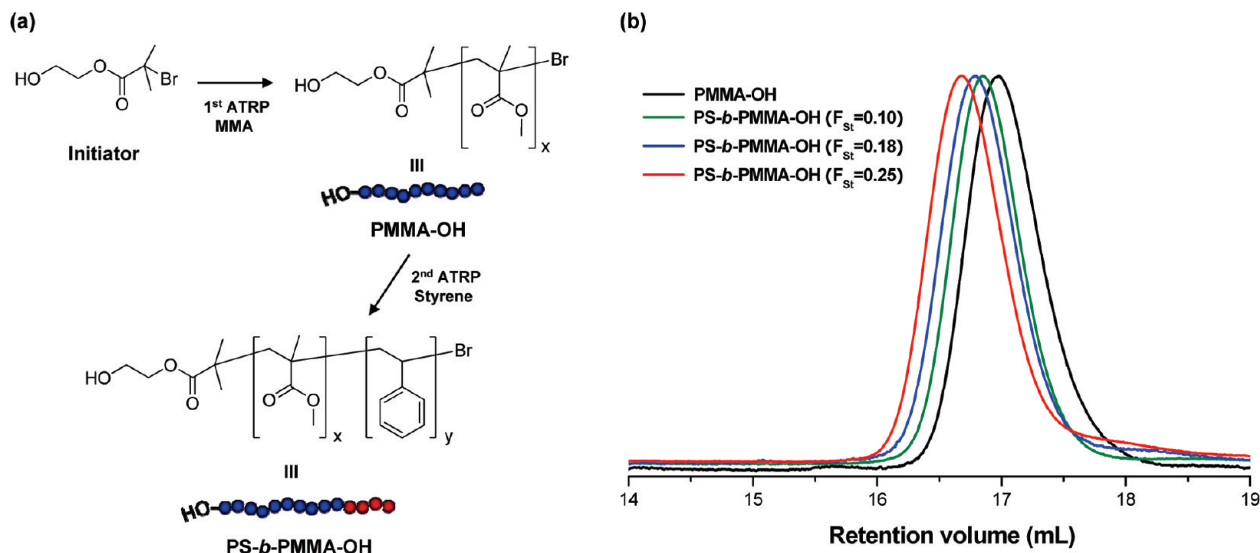

Figure 2. (a) Scheme for the atom transfer radical polymerization of hydroxyl terminated low molecular weight BCP, and (b) GPC traces of the synthesized polymers (styrene fraction in the BCPs was measured by ^{1}H NMR).

TABLE 1. Summary of the Molecular Weight, Polydispersity Index and Composition of the Synthesized Hydroxyl Terminated BCPs and the Resulting Thicknesses of the Buffer Layer on the Modified Substrates

polymer	M_n[a]	PDI	F_{St} (by ^{1}H NMR)	thickness[b] (nm)
PMMA−OH	11 500	1.08	0	4.7
PS-*b*-PMMA−OH	14 400	1.08	0.10	5.2
PS-*b*-PMMA−OH	15 300	1.07	0.18	5.3
PS-*b*-PMMA−OH	16 200	1.09	0.25	5.5

[a] M_n was measured by GPC using monodispersed PS standards. [b] Dry film thickness of the polymer layer measured by ellipsometry.

parameter of PS-*b*-PMMA at 190 °C,[25] molecular weights lower than ~20 kg/mol will result in disordered state. Therefore, we designed the hydroxyl terminated PMMA macro initiator with a molecular weight of 11.5K whereas the second PS block is relatively short (3 to 5K) to suppress the phase separation and keep the surface composition homogeneous. Hydroxyl terminated PMMA was synthesized by atom transfer radical polymerization (ATRP) using hydroxyl containing initiator and used as a macro initiator for the polymerization of styrene as the second block (Figure 2a). The chain length of the PS block was tuned to get the desired surface chemical composition of styrene and MMA in the copolymer. The molecular weight of the BCP and hence the increase in PS fraction was monitored by GPC and NMR. As shown in Figure 2b, the polymerization is well controlled and the molecular weight increases with the reaction time.

Silicon substrates were modified by grafting the PS-*b*-PMMA−OH by thermal annealing. The hydroxyl groups on the native oxide react with the end-hydroxyl group in the block copolymer to create the buffer layer. Table 1 summarizes the molecular weight and PDI of these copolymers and the resulting thickness of the buffer layer. As expected, the thickness of the buffer layer increases with the length of PS chain. The surface morphology of grafted BCP examined by AFM does not show phase separation after thermal annealing at 190 °C. (Figure S1 in Supporting Information). The root-mean-square (rms) roughness of buffer layer was between 0.13 and 0.18 nm, which is comparable to those observed for a grafted random copolymer.[18]

Evaluation of the Nonpreferentiality. We evaluated the compositional dependence of the nonpreferentiality of the buffer layer to the overlying symmetric or asymmetric PS-*b*-PMMA. On the modified substrates, either 45 nm thick lamella-forming (52K−52K) or 32 nm thick of PMMA cylinder-forming (50K−20K) BCPs were deposited, followed by thermal annealing at 190 °C under vacuum. Top view SEM images of assembled BCPs (Fig-

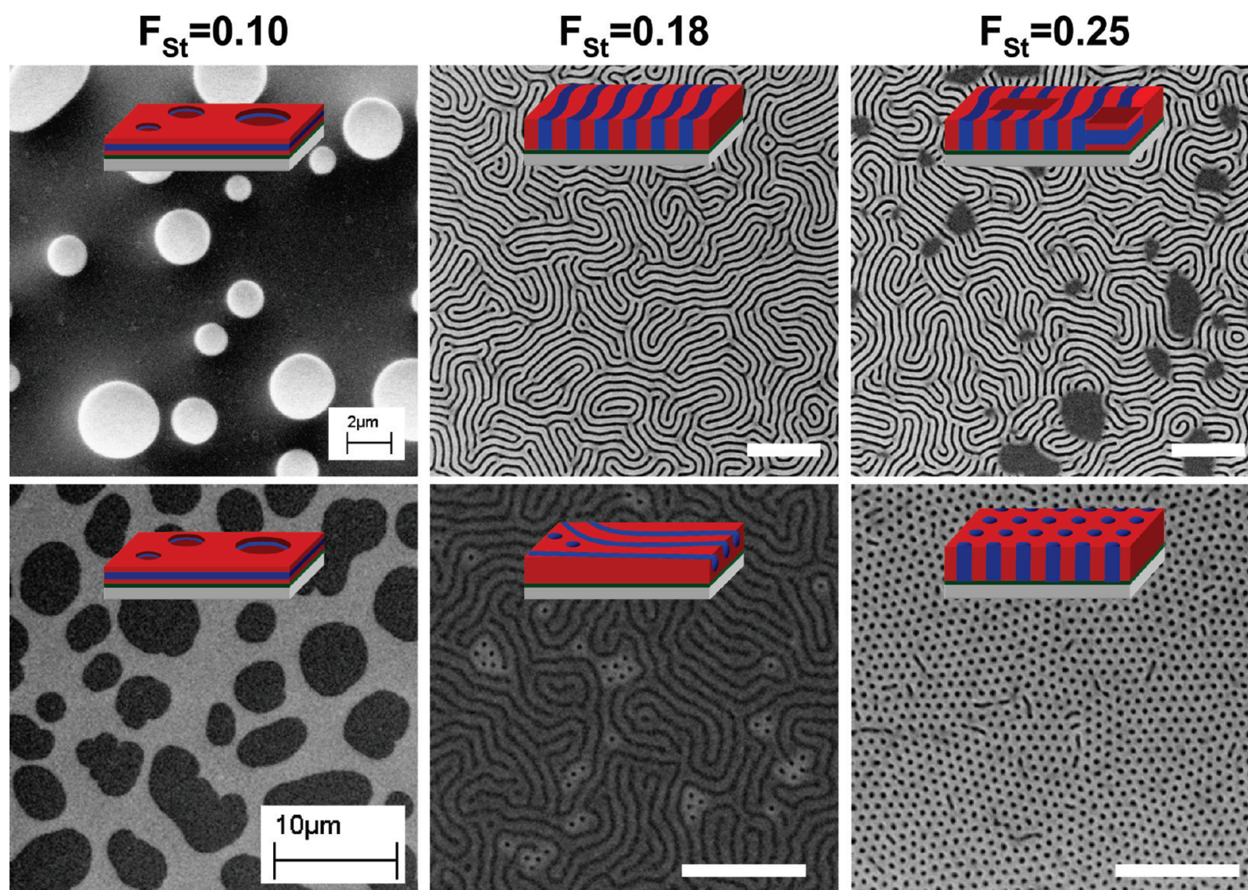

Figure 3. Top view SEM images of lamella-forming BCP (first row) and PMMA cylinder-forming BCP (second row) on block copolymer grafted substrates. The numbers on the top indicate the mole fraction of styrene in the grafted block copolymer measured by ^{1}H NMR (white scale bar = 200 nm).

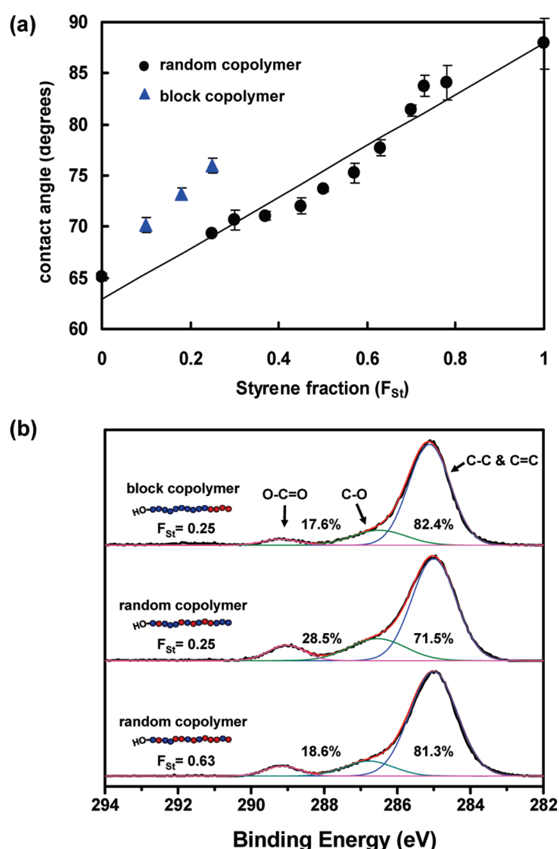

Figure 4. (a) Water contact angles measured as a function of F_{St} for buffer layer consisting of block copolymer are significantly higher than those for random copolymer with comparable styrene content, and (b) surface chemical composition estimated by XPS by comparing the C_{1s} peaks at 289.1 eV and 286.8 eV for select compositions of block and random copolymer modified substrates. Error bars show the standard deviation of each measurement.

ure 3) on the buffer layer show that the composition of the grafted block copolymer can be effectively tuned to create nonpreferential substrates. The buffer layer having $F_{St} = 0.10$ induced parallel orientation of domains with terraced structures confirming preferential wetting characteristics for both symmetric and asymmetric PS-*b*-PMMA. As the PS fraction of the buffer layer increased to 0.18, typical fingerprint morphology from the perpendicular orientation of domains was observed for the lamella forming PS-*b*-PMMA, whereas the PMMA cylinders in asymmetric BCP were oriented parallel to the substrate. As the PS fraction was further increased to 0.25, mixed (parallel and perpendicular lamellae) morphology was observed for the symmetric BCP, whereas predominantly perpendicular cylinders were obtained for the asymmetric BCP.

The distinct compositional ranges of the buffer layer for inducing perpendicular orientation in symmetric and asymmetric BCPs in this study agrees very well with our earlier publication.[26,27] We reported the compositional windows for various types of random copolymers that induce perpendicular orientation of lamella-, PMMA cylinder- and PS cylinder-forming PS-*b*-PMMA. Typically BCPs ($\approx L_0$ thickness) that form PMMA cylinders require higher styrene fraction in the underlying random copolymer brush compared to those that form lamellae or PS cylinders. This is primarily due to the fact that the free energy of these surface equilibrated BCP films is dependent not only on the interfacial interactions of the two blocks with the substrate but also the relative volume fraction of two blocks and the interaction of the two blocks with the free surface.[27]

The styrene fraction (Figure 1c) required for the buffer layer to be nonpreferential is significantly lower for the grafted BCPs compared to the grafted random copolymers[23] (Figure 1b). For example, hydroxyl terminated PS-*r*-PMMA having F_{St} of 0.45−0.60 induces perpendicular lamellae in a symmetric BCP with a film thickness $\approx L_0$[27] whereas the hydroxyl terminated BCP with a F_{St} as low as 0.18 is equally effective. Since we did not alter other experimental parameters such as the molecular weight, the film thickness of BCP, or the annealing temperature from our earlier work, the difference in compositional range is clearly attributable to the difference in the architecture of the buffer layer itself.

In the case of the buffer layer based on the random copolymer, although there is a possibility of slight compositional drift during polymerization, the distribution of styrene and MMA monomers in the polymer chain is almost random. In contrast, in the block copolymer based buffer layer, the sequence of polymerization sets one block as a surface rich component. Since the block

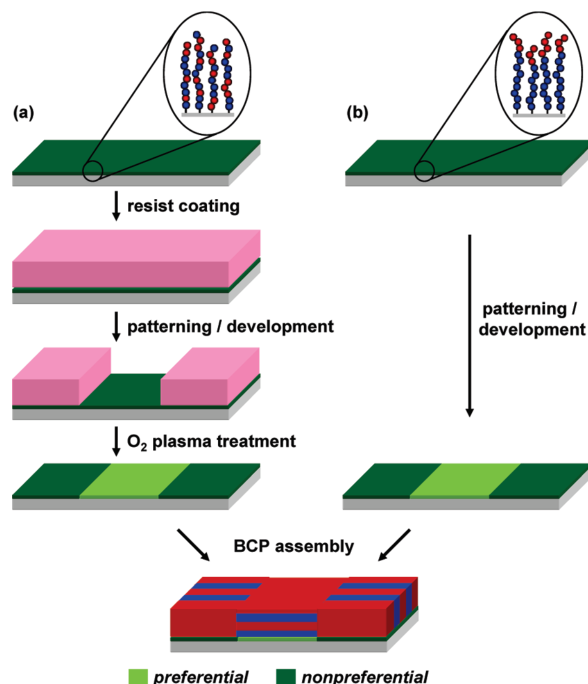

Figure 5. Schematic illustration of (a) the traditional approach for fabricating chemical patterns from random copolymer anchored to surfaces and (b) our approach of direct chemical patterning of e-beam sensitive block copolymer anchored to surfaces.

copolymer is grafted to the substrate through the hydroxyl group on the PMMA chain end, the short PS block is predominantly located at the BCP/buffer layer interface. As a result, the effective PS fraction at the BCP/buffer layer interface is higher when the buffer layer is a grafted block copolymer compared to a grafted random copolymer. Indeed this can be confirmed by both water contact angle measurements and the surface compositional analysis by XPS.

Water contact angles were measured for the buffer layers created from both the grafted block copolymers as well as the random copolymers, to assess the relative surface compositions. It is well-known from the literature that the hydrophobicity of PS-*r*-PMMA grafted surface is a function of styrene fraction.[16] As shown in Figure 4a, the contact angles of the buffer layers composed of random copolymers increases monotonically with the F_{St}. The contact angles of the block copolymer based buffer layers follow similar trend but the values are significantly higher for equivalent F_{St}. For example, the contact angle of buffer layer based on block copolymer having $F_{St} = 0.25$ is similar to those of random copolymer having F_{St} of 0.57−0.63. XPS results in Figure 4b shows similar trends. The intensity of C_{1s} peaks at 289.1 and 286.8 eV originating from MMA of block copolymer is comparable to those for random copolymer with higher F_{St}. The water contact angles and XPS results confirm that the short PS block presents a higher effective styrene content at the buffer layer/BCP interface compared to same composition of a random copolymer and effectively prevents microphase separation leading to the desired homogeneous distribution of MMA and styrene on the surface. This leads to a nonpreferential wetting behavior at significantly lower styrene content compared to the random copolymer buffer layer.

Direct Patterning of the Buffer Layer. Defining the buffer layer on a substrate by "top-down" patterning methods enables spatial control of the domain orientation in an overlaying BCP film. Earlier, photocross-linkable random copolymers have been developed to spatially direct the orientation of the overlying BCP at the micrometer scale.[20,28] For patterning the buffer layer into submicrometer dimensions, chemical resists for advanced lithography have been employed.[21−23] Generally, the physical pattern of resist layer generated by lithographic process is translated to a chemical pattern by exposure to oxygen plasma environment (Figure 5a). By doing so, the nonpreferential layer in the unexposed region is protected by the remaining overlaying resist while exposed region becomes more polar.

PMMA is a well-known resist for deep UV, e-beam, and X-ray lithography.[29] Recently, Rastogi et al. reported a detailed general study evaluating the patterning of various methacrylate based polymer brushes including PMMA and PHEMA grafted on silicon substrate using EBL.[30] In our system, instead of a homopolymer

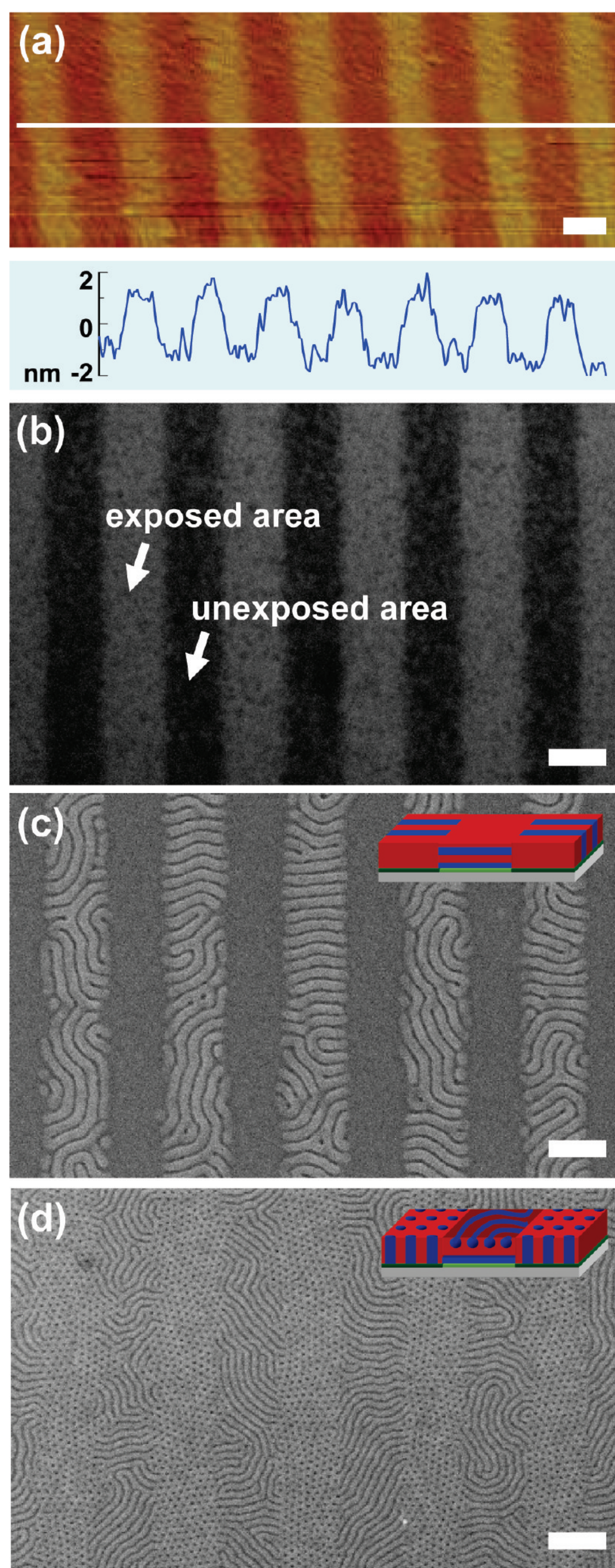

Figure 6. (a−b) E-beam patterned block copolymer ($F_{St} = 0.18$) buffer layer showing difference in height by AFM (a) and color contrast by SEM (b) between the patterned and unpatterned regions. Top view SEM image of (c) the lamella forming BCP (over $F_{St} = 0.18$), and (d) PMMA cylinder forming BCP (over $F_{St} = 0.25$) assembled on the patterned buffer layer, showing perpendicular microdomains on the unexposed region and parallel microdomains on the exposed region (white scale bar = 200 nm).

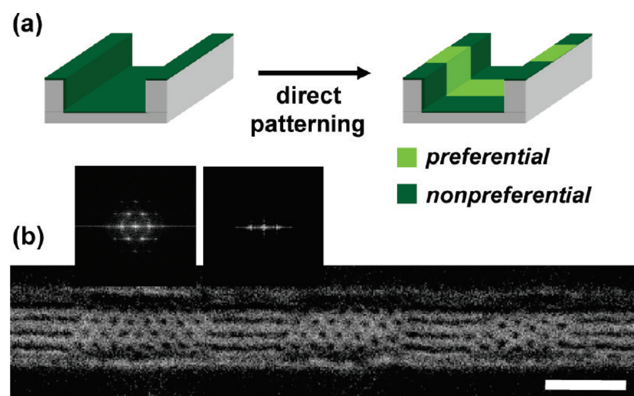

Figure 7. (a) Schematic illustration of the assembly of PMMA cylinder forming BCP in a trench modified with the buffer layer (F_{St} = 0.25) and directly patterned with e-beam to create a chemical pattern and, (b) top view SEM images of the assembled BCP showing alternating line (on exposed region) and dots (on unexposed region) arrays within the trench (scale bar = 200 nm).

brush we conducted the e-beam patterning of the grafted PS-*b*-PMMA. Upon exposure to e-beam, PMMA block in the buffer layer undergoes well-known chain scission reaction[29] resulting in the cleavage of the block copolymer from the substrate upon subsequent washing (Figure 5b). Grafted block copolymers were directly patterned by e-beam with doses ranging from 34 to 340 $\mu C/cm^2$ which is comparable to those reported earlier for homopolymer PMMA brush.[30] Since we intentionally designed the block copolymer to have a majority of PMMA block (75−82%) anchored to the substrate and a small fraction of PS block at the surface, the overall block copolymer showed similar sensitivity toward e-beam as homopolymer PMMA brush. Direct patterning of the buffer layer results in its removal from the exposed region. Both the height differences seen from AFM (Figure 6a) and the contrast in the SEM (Figure 6b) confirm the pattering of the buffer layer. Assembly of both cylinder- and lamella-forming BCP on the e-beam patterned buffer layer shows clear switching of wetting behavior toward the overlying BCP from nonpreferential (block copolymer) to preferential (cleaved PMMA) as shown in Figure 6c and d. Patterning the buffer layer (200 nm line width) induced alternation in the domain orientation from perpendicular to parallel.

In a control experiment, we tested the direct patterning of random copolymer based buffer layer (F_{St} = 0.60). We varied e-beam dose from 34 to 9500 $\mu C/cm^2$. However, we did not observe any changes in domain orientation as a result of direct patterning. This is attributable to the random distribution of MMA monomer along the copolymer chain which does not provide enough sensitivity for the random copolymers toward e-beam.

Direct Patterning of the Buffer Layer to Create Chemical Patterns on Topographic Substrates. Perpendicular lamellar domains are mainly used for creating line arrays while cylinder-forming BCP can be used to create either line or dot arrays. Therefore, by alternating the wetting behavior of the substrate from preferential to nonpreferential, both line and dot pattern can be generated side by side using cylinder-forming BCP as shown in Figure 6. Alternating line and dot arrays using a single BCP was reported earlier by Bosworth et al.[31] They used a multistep process involving sequential solvent annealing to reversibly switch the morphology of poly(α-methylstyrene)-*block*-poly(4-hydroxystyrene) (PαMS-*b*-PHOST) from cylinder to sphere[32] and cross-linking the PαMS-*b*-PHOST to fix the morphology.

Although direct patterning of grafted block copolymer can successfully control the orientation of BCP domain with respect to the substrate, the grains are still randomly oriented resulting in poor lateral ordering of the domains (Figure 6c and d). To impose high degree of lateral order, we utilized graphoepitaxy technique. Graphoepitaxy uses a submicrometer groove as a substrate, where spatial confinement of BCP within the grooves induces nucleation and propagation of microdomains from the confining hard walls.[33] This process provides resolution enhancement as we go from a submicrometer groove to few tens of nanometers using BCP assembly. Previously, perpendicular domain orientation of PS-*b*-PMMA within a topographic pattern was achieved by modifying the surface with nonpreferential layer.[34,35] However, side by side location of perpendicular and parallel cylinders within a single topographic pattern has not been demonstrated so far. We first modified a topographic substrate by surface grafting block copolymer based buffer layer (F_{St} = 0.25), followed by e-beam patterning to create a chemical pattern within the trench. Directed assembly of cylinder forming BCP using the resulting chemically and topographically patterned substrate created both aligned line and dot arrays within the trench (Figure 7b). Thus, the e-beam sensitivity of these buffer layers can be effectively combined with known methods such as graphoepitaxy to achieve lateral ordering of domains as well as enhanced resolution.

CONCLUSIONS

In summary, we have reported the first example of a direct e-beam patternable nonpreferential buffer layer for BCP lithography. We demonstrated the use of low molecular weight surface anchored BCPs as a nonpreferential layer for the assembly of the corresponding BCP in thin film. The block copolymer has a PMMA segment anchored to the surface and a short PS block at the buffer layer/BCP interface. This allows homogeneous control of the surface composition. Nonpreferentiality of this buffer layer can be controlled for both symmetric and asymmetric PS-*b*-PMMA by changing the PS block length. Due to the block architecture, the buffer layer showed similar sensitivity to e-beam as the traditional PMMA homopolymer resist. We have also shown that the buffer layer can be directly patterned

by e-beam lithography to spatially control the domain orientation in the overlying BCP film at submicron length scale. The direct patterning approach reduces the number of steps involved in forming chemical patterns by conventional lithography. Furthermore, the functionality and chemistry of the patterned region can be diversified by designing new di- or triblock copolymers with an intrinsically patternable component.

METHODS

Materials. Styrene and methyl methacrylate were purchased from Aldrich and distilled under reduced pressure. Hydroxyl containing ATRP initiator was synthesized according to the literature.[36] BCPs were purchased from Polymer Source Incorporated (Dorval, Quebec, Canada) and used without further purification: symmetric PS-*b*-PMMA (PS 52 kg/mol, PMMA 52 kg/mol) and asymmetric PMMA cylinder forming PS-*b*-PMMA (PS 50.5 kg/mol, PMMA 20.9 kg/mol).

Synthesis of Hydroxyl Terminated PS-b-PMMA. (i) ATRP of MMA. In a 20 mL Schlenk flask, OH-ATRP initiator (0.1 g, 0.48 mmol), CuBr (0.068 g, 0.48 mmol), $CuBr_2$ (0.0053 g, 0.0024 mmol), PMDETA (0.0825 g, 0.48 mmol), MMA (4.77 g, 48 mmol), and anisole (4 mL) were placed and the reaction mixture was degassed by two freeze−pump−thaw cycles. The flask was placed in a thermostatic oil bath at 80 °C. Polymerization was stopped after 40 min by cooling to room temperature and opening the flask to air. The mixture was then dissolved in THF and passed through neutral alumina and reprecipitated from THF into methanol. **(ii) ATRP of styrene.** In a 20 mL Schlenk flask 1 g of OH-PMMA, CuBr (0.03 g, 0.21 mmol), PMDETA (0.036 g, 0.21 mmol), and styrene (10 mL) were placed. The mixtures was stirred until the solution became homogeneous, and degassed by two freeze−pump−thaw cycles. The flask was placed in a thermostatic oil bath at 110 °C. Samples were removed from the reaction flask at the different time intervals during the polymerization (40 min for $F_{St} = 0.10$, 70 min for $F_{St} = 0.18$, and 90 min for $F_{St} = 0.25$). The samples were diluted with THF and passed through neutral alumina and reprecipitated from THF into methanol. White powder was dried in a vacuum oven at 60 °C for one day.

Surface Modification and BCP Deposition. Solutions of hydroxyl terminated PS-*b*-PMMA in toluene (1% w/w) were spin-coated at 2000 rpm onto silicon wafers and then annealed under vacuum at 160 °C for 2 days. The substrates were sonicated in toluene to remove ungrafted block copolymer and rinsed with fresh toluene. On these BCP grafted wafers, solutions of lamellae-forming PS-*b*-PMMA in toluene (1.5% w/w) or PMMA-cylinder forming PS-*b*-PMMA in toluene (1% w/w) were spin-coated at 4000 rpm to produce films with thicknesses of 45 and 32 nm, respectively. All BCP films were annealed at 190 °C for 24 h under vacuum to attain the equilibrium morphology prior to imaging. For graphoepitaxy, topographically patterned Si substrate (trench width 150 nm and trench depth 60 nm) was used.

Characterization. For each synthesized BCP, a ^{1}H NMR spectrum was recorded in solution ($CDCl_3$) with a Bruker AC+ 300 (300-MHz) spectrometer. Molecular weight of polymers was measured with GPC. THF was used as an eluent and monodisperse polystyrene standards were used for calibration. The film thicknesses of the brush and BCP layers were measured by ellipsometry (Rudolph Research Auto EL). Static contact angles of sessile drops were measured to characterize the hydrophobicity of the surface layers with a Dataphysics OCA 15 Plus goniometer. (All samples were thermally annealed at 190 °C for 12 h before surface characterization) Top-down scanning electron microscope (SEM) images of the BCP microdomains were acquired with a LEO-1550 VP field-emission instrument using an accelerating voltage of 1 kV. The surface topography of buffer layers was examined using a Nanoscope III Multimode atomic force microscope (Digital Instruments) in tapping mode.

E-Beam Patterning. The electron beam lithography was performed with a LEO 1550-VP field emission scanning electron microscope (SEM) operating with a J.C. Nabity pattern generation system. The exposure used an accelerating voltage of 20 kV, a beam current of ~30 pA, and area doses varied from 34 to 340 μC/cm^2. Development was done by immersing patterned substrate in THF for 60 s, followed by rinsing fresh THF and drying.

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Supporting Information Available: AFM analysis of grafted block copolymers. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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