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Ultralarge-Area Block Copolymer Lithography Enabled by Disposable Photoresist Prepatterning

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ABSTRACT We accomplished truly scalable, low cost, arbitrarily large-area block copolymer lithography, synergistically integrating the two principles of graphoepitaxy and epitaxial self-assembly. Graphoepitaxy morphology composed of highly aligned lamellar block copolymer film that self-assembled within a disposable photoresist trench pattern was prepared by conventional I-line lithography and utilized as a chemical nanopatterning mask for the underlying substrate. After the block copolymer film and disposable photoresist layer were removed, the same lamellar block copolymer film was epitaxially assembled on the exposed chemically patterned substrate. Highly oriented lamellar morphology was attained without any trace of structure directing the photoresist pattern over an arbitrarily large area.

KEYWORDS: block copolymer · self-assembly · lithography · graphoepitaxy · nanopatterning

Patterning densely packed nanoscale features is of great research interest in the numerous areas of nanotechnology. Block copolymers are self-assembling materials that spontaneously microphase separate into the densely packed periodic arrays of nanodots, nanowires, and interconnected networks, whose characteristic length scales are typically tunable to within 5−50 nm.[1−10] Block copolymer lithography utilizes the self-assembled morphology of block copolymer thin films as a lithographic mask for large-area, scalable nanopatterning.[11] This self-assembly-based nanolithography has progressed as a viable nanolithography to overcome the intrinsic resolution limit of conventional photolithography. Nevertheless, the spontaneously assembled block copolymer thin films suffer from the randomly oriented nanodomains with a high density of defects. The accomplishment of lateral ordering by a cost-effective and "conventional-lithography-compatible" approach has been a longstanding technological challenge thus far.

To date, various directed self-assembly approaches utilizing chemically and topographically prepatterned substrates or external fields have been exploited for the lateral ordering of self-assembled morphology.[12−27] Among them, graphoepitaxy and epitaxial self-assembly are two major successful approaches (Figure 1). As illustrated in Figure 1a, graphoepitaxy utilizes a topographic substrate pattern to guide the self-assembly of block copolymer thin films.[16−24] The topographic confinement from the side walls enforces the lateral ordering of block copolymer nanodomains within the pattern trenches. In this approach, the maximum area of the laterally ordered nanodomain array is intrinsically limited by the trench width of the substrate pattern.[28] Moreover, the substrate pattern frequently remains even after pattern transfer (usually *via* selective etching or deposition) and, thus, prevents a further overlay process for multilayered device architecture. In contrast, epitaxial self-assembly utilizes chemically patterned surfaces (Figure 1b).[12−14] The epitaxial assembly of block copolymers on the topography-free chemical patterns enables a laterally ordered periodic nanodomain array over an arbitrarily large area. However, an ultrafine nanoscale chemical pattern is required that is commensurate with the block copolymer self-assembled morphology. Such an ultrafine prepatterning is generally unattainable by conventional photolithographies, such as I-line lithography or ArF lithography. Instead, it requires high-cost, serial lithography such as E-beam or scanning probe lithography. This practically impedes large-area nanofabrication.

Herein, we introduce a cost-effective and truly scalable directed block copolymer assembly for ultralarge-area nanopatterning. We succeeded in the synergistic integration

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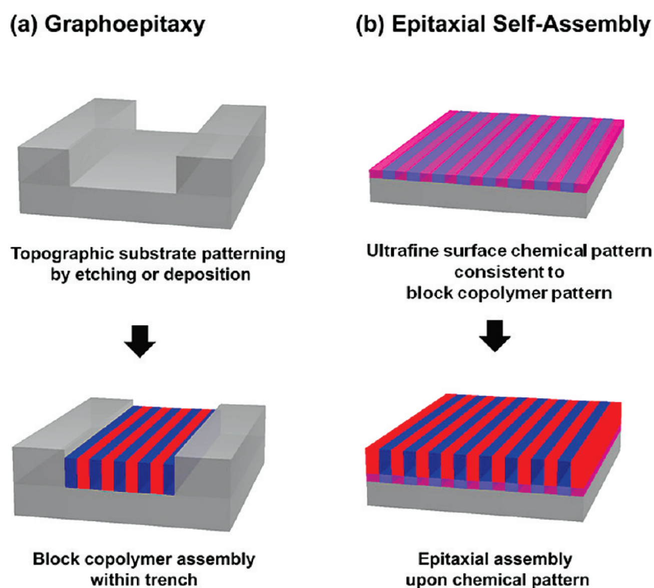


Figure 1. Graphoepitaxy vs epitaxial self-assembly. (a) Graphoepitaxy utilizes topographic substrate pattern for directed block copolymer assembly. The substrate pattern remains in the finally formed nanopatterned morphology. (b) Epitaxial self-assembly utilizes nanoscale chemical pattern to register block copolymer assembly. Ultrafine chemical patterning requires e-beam lithography or other high-cost lithography such as EUV.

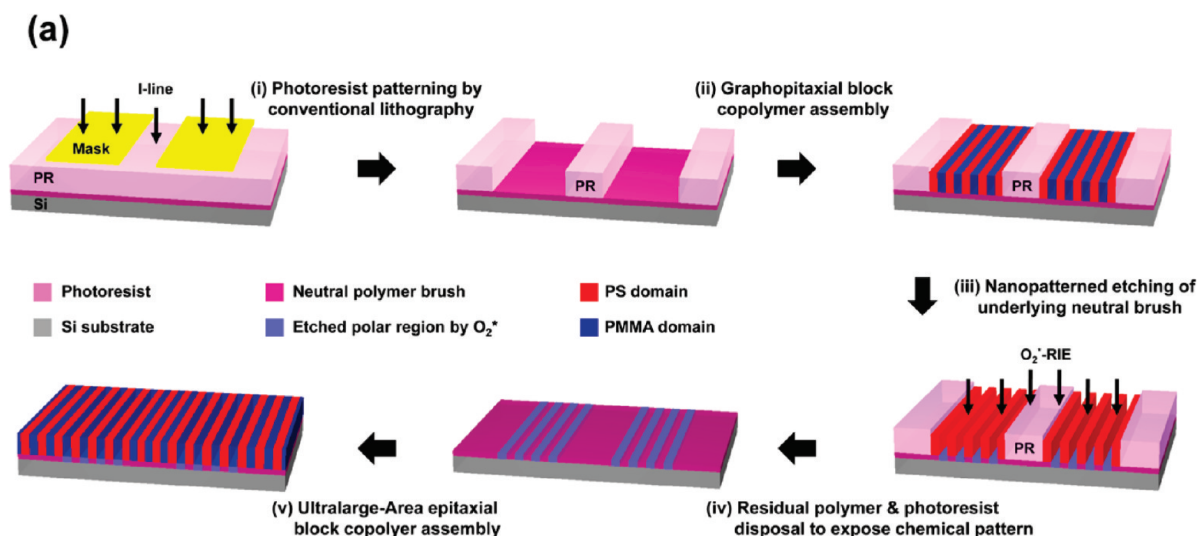
of two directed self-assembly principles of graphoepitaxy and epitaxial self-assembly. In this approach, an arbitrarily large-area block copolymer lamellar pattern without any trace of a structure directing prepattern has been attained from conventional photolithography prepatterning (Figure 2a). In the first step, a parallel photoresist trench pattern with a pattern period of 600−1000 nm was prepared by I-line lithography (Instead, any other conventional photolithography, such as ArF lithography, can be employed). A symmetric block copolymer thin film was graphoepitaxially assembled within the parallel photoresist trenches to generate hierarchically ordered lamellar morphology. This graphoepitaxy morphology composed of block copolymer film and a photoresist pattern was utilized as the pattern master for the chemical patterning of the underlying surfaces. Oxygen plasma etching over the entire area resulted in the masked etching of underlying surface *via* graphoepitaxy morphology. After polymer and photoresist layer were disposed, a thin film of the same lamellar block copolymer was epitaxially assembled on the chemically patterned surface. Highly aligned lamellar morphology was attained without any trace of a structure directing photoresist pattern. We note that although the substrate surface under the photoresist layer remained unpatterned, the lamellae on this region were aligned along the neighboring lamellae epitaxially assembled on the chemically patterned region. 22-nm-thick lamellar arrays have been readily produced from a 600 nm scale photoresist pattern (15-fold increase in pattern density). Taking advantage of the large-area patternability of conventional I-line lithography, we achieved ultralarge-area lamellar patterns over a 5 mm × 5 mm area without any elaborate process optimization.

RESULT AND DISCUSSION

We used the polystyrene-*block*-poly(methylmethacrylate) ((PS-*b*-PMMA), M_n 48K mol^{-1}−46K kg mol^{-1}) with a lamellae period (L_o) of 44 nm as self-assembling block copolymers.[29,30] Silicon substrate surfaces were neutrally modified with a P(S-*r*-MMA) random copolymer brush to have a identical, well-balanced, surface tension for PS and PMMA components.[8,31,32] The symmetric PS-*b*-PMMA thin film self-assembled on the neutrally modified substrate to form surface perpendicular lamellae due to thin film confinement. We note that this neutral brush layer is selectively etched to form a neutral/polar chemical pattern in the following process. Despite the well-controlled vertical lamellar orientation on the neutral substrate surface, the lateral ordering of lamellae in the film plane reveals random orientation with a high density of structural defects.[33]

The lateral ordering of block copolymer lamellae could be remarkably enhanced by graphoepitaxy with a photoresist pattern (Figure 2b). We note that, unlike usual graphoepitaxy methods, utilizing inorganic substrate patterns, our approach employing photoresist patterns (SU8 negative tone resist) enables complete disposal of topographic confinement after pattern transfer.[29,30] As mentioned above, the photoresist trench patterns were prepared by I-line lithography (Figure 2b, inset). When a PS-*b*-PMMA thin film was graphoepitaxially assembled within the photoresist trenches, the trench side walls were preferentially wet by the PS component, inducing the trench parallel alignment of neighboring lamellae. As such, this highly aligned graphoepitaxial morphology was used as a selective etching mask for the underlying neutral polymer bush layer. Since the etching resistivity of PMMA is significantly lower than that of PS or SU8 for oxygen plasma treatment, a mild oxygen etching over the entire area selectively etched the neutral brushes underneath the PMMA lamellae. This created a chemical nanopattern consisting of polar (bare substrate or oxygenated brush) stripes and neutral (unetched brush) stripes underneath the block copolymer film. Meanwhile, the brush layer under the photoresist layer remains unpatterned and neutral. Therefore, the finally obtained substrate pattern constitutes a hierarchical nanopattern of the alternate chemically nanopatterned region (typically 400−800 nm width) and uniform neutral region (typically 200−600 nm width). After this pattern transfer, the residual polymer and photoresist remaining on the substrate surface was thoroughly washed by a mild sonication in an organic solvent.

For a successful large-area nanopatterning, the random copolymer brushes under the photoresist layer



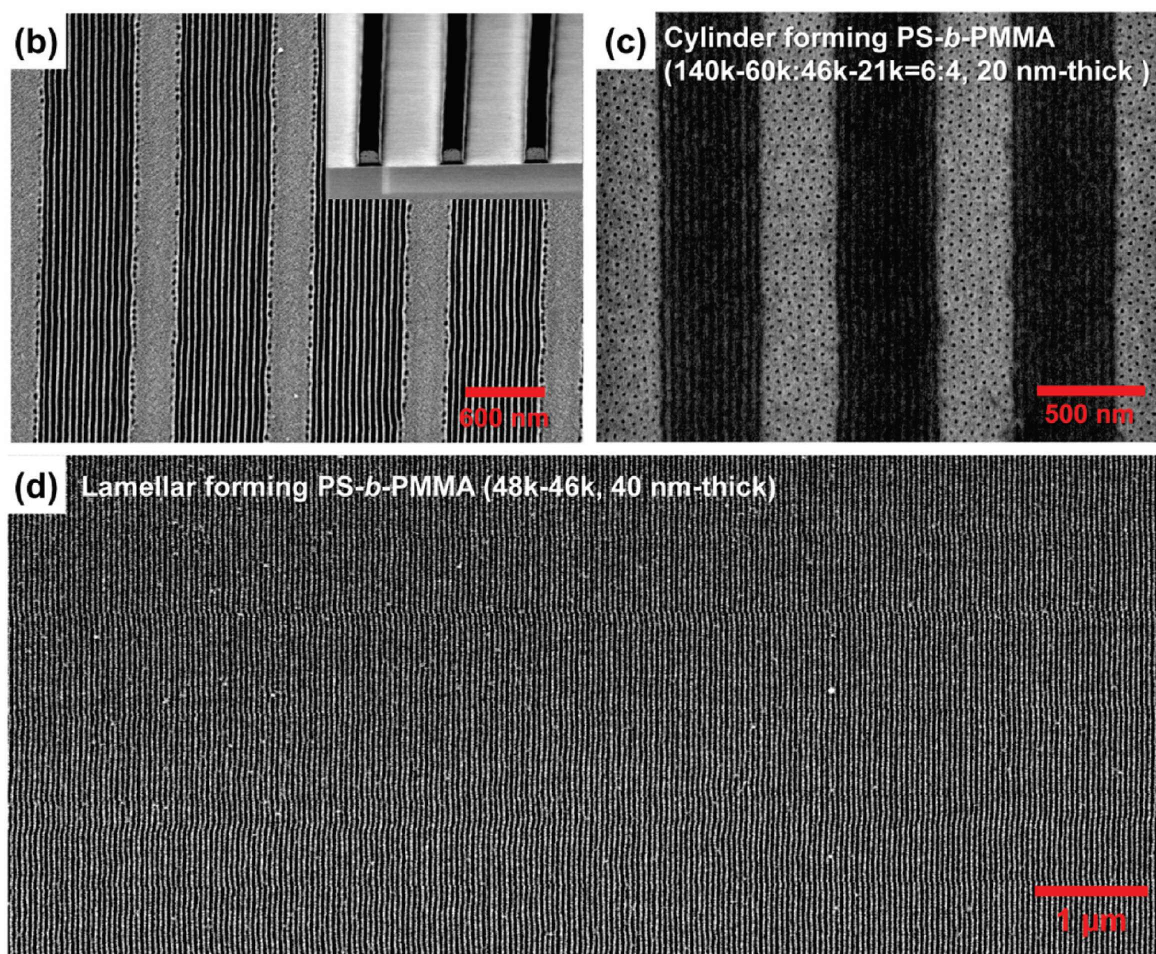


Figure 2. (a) Schematic illustration of ultralarge-area block copolymer lithography procedure. (i) Photoresist patterning by I-line lithography on a neutral polymer-brush-treated Si substrate. (ii) Graphoepitaxy of block copolymers within photoresist confinement. (iii) Polymer brush layer chemical patterning by selective etching *via* graphoepitaxy morphology. (iv) Residual photoresist and polymer disposal to expose a chemically nanopatterned substrate. (v) Ultralarge-area epitaxial assembly of block copolymers. (b) Graphoepitaxy morphology of lamellar block copolymers within photoresist trenches. Inset: photoresist pattern prepared by I-line photolithography. (c) Cylindrical block copolymers assembled on a chemically patterned substrate. (d) Lamellar block copolymer assembled on chemically patterned substrates (10 μm × 5 μm).

must maintain the chemical neutrality during the entire chemical patterning process. If the brush layer is damaged during the photopatterning or subsequent disposal of the photoresist layer, block copolymer

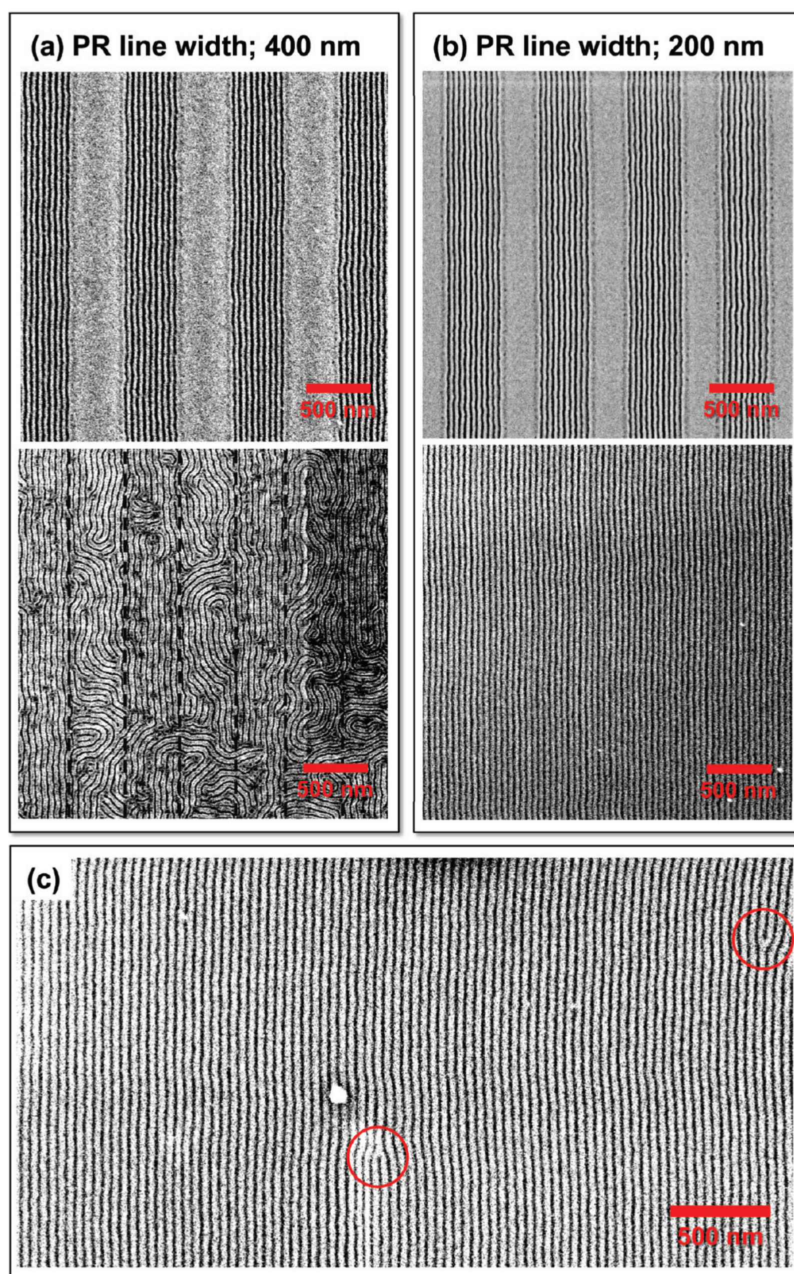


Figure 3. Graphoepitaxy morphology and the corresponding lamellar pattern prepared from the photoresist patterns with mesa and trench widths of (a) 400 and 400 nm, and (b) 200 and 400 nm, respectively. (c) Dislocation defect morphology of a large-area lamellar pattern.

lamellae would lie parallel to the substrate surface due to the preferential segregation of a particular component to the non-neutral substrate surface.[8] This morphology without chemical modulation in the film plane is useless as a nanolithographic mask. For a straightforward evaluation of the stability of a brush layer, a thin film of asymmetric PS-*b*-PMMA block copolymer blends (4:6 blends of PS-*b*-PMMA1 with PS block M_n, 46.1 kg/mol; PMMA block M_n, 21 kg/mol; PDI = 1.08; and PS-*b*-PMMA2 with PS block M_n, 140 kg/mol; PMMA block M_n, 60 kg/mol; PDI = 1.09) was deposited on the chemically patterned surfaces and thermally annealed. The center-to-center distance between neighboring cylinders matches with the period of the surface chemical pattern. As shown in Figure 2c, the nanocylinder orientation exhibited distinct transition depending on the surface chemistry. While the cylinders were epitaxially assembled in the horizontal direction on the nanopatterned region, they aligned vertically in the uniform neutral region. This assembly behavior confirms that the neutrality of brush layer is well-maintained during brush layer chemical patterning and subsequent photoresist disposal.[8]

Given that the chemically patterned substrate has been successfully prepared, ultralarge-area block copolymer lamellar alignment was simply achieved by

spin-casting the same lamellar PS-*b*-PMMA block copolymer thin film (40 nm thickness) and epitaxial self-assembly upon thermal annealing. As mentioned above, the self-assembled morphology yielded highly oriented lamellae on the uniform neutral surface region as well as on the chemically patterned region. Figure 2d shows the in-plane scanning electron microscopy (SEM) image demonstrating laterally ordered lamellae over a 10 μm × 5 μm area. This highly ordered morphology was obtained provided that the widths of neutral region and chemically nanopatterned region were 400 and 200 nm, respectively (Figure 3a,b). In contrast, when the width of the neutral region reached 400 nm, lamellae exhibited poor alignment (Figure 3a). Structural defects such as high strength disclinations as well as dislocations were observed among the poorly ordered lamellae. Those defects even penetrated into the lamellar array in the chemically patterned region, indicating that the lamellar orderings in the nanopatterned region and uniform neutral region mutually interact. Meanwhile, this behavior is inconsistent with the morphology evolution in graphoepitaxy with hard cross-linked photoresist confinement, where no significant deterioration of lamellar alignment is observed up to a trench width of ~700 nm (Figure 2b).

Our ultralarge-area block copolymer lithography utilizes a hierarchical substrate pattern that includes a neutral homogeneous region. Accordingly, the finally prepared large-area lamellar pattern may have structural defects, particularly in this neutral region. As shown in Figure 3c, the typically observed defects are edge dislocations with the least distortion of surrounding lamellar alignment. No disclination with a high distortion was observed. Previously, similar defects have been observed when lamellae are assembled upon an incommensurate surface pattern.[12,21,33] In the present work, the commensurability between lamellar thickness and the width of neutral stripe region may influence the defect density. We note that, without significant effort for process optimization, the defect density could be substantially lowered such that highly ordered lamellar arrays were observed throughout the entire sample area of 5 mm ×5 mm (see Supporting Information, Figure 1S).

CONCLUSION

We have demonstrated a cost-effective, ultralarge-area block copolymer nanopatterning enabled by disposable photoresist prepatterning. Graphoepitaxy within the disposable photoresist trench was utilized for the chemical patterning of the underlying surface. The epitaxial block copolymer assembled upon the chemically patterned surface generated a highly oriented lamellar array over an arbitrarily large area. Our approach comprises low-cost, parallel processes from the conventional projection-type I-line lithography to the eventual block copolymer self-assembly. Therefore, it realizes the true scalability of nanolithography that had rarely been achieved so far. The employment of I-line lithography and chemical etching also ensures the high compatibility with a standard device fabrication process. Furthermore, the vertical side-wall profile of a surface-perpendicular lamellar array provides facile pattern transferability into a metal or semiconductor nanowire array *via* a lift-off or etching process.[8,29,30] These advantages together with the pattern rectifying and low line edge roughness of block copolymer self-assembly offer enormous potential for nanomanufacturing.[14,34]

METHODS

Substrate Preparation. A silicon substrate was cleaned by immersion in piranha solution (7:3 mixture of H_2SO_4 and H_2O_2) for 1 h at 110 °C and rinsed with deionized water. The cleaned substrate surface was neutrally modified by the covalent functionalization with polystyrene-*r*-poly(methyl methacylate) (P(S-*r*-MMA)) copolymer brush layer. End-functional P(S-*r*-MMA) was spin-cast from an organic solution and thermally reacted to the substrate surface at 160 °C for 48 h in a vacuum. Unreacted polymers were thoroughly spin washed with toluene.

Photoresist Prepatterning. A negative tone photoresist, SU8-2000.5 (MicroChem Corp. US) was used to prepare a topographic pattern for the direct block copolymer assembly. A 100 nm thick photoresist layer was spin-cast on a neutrally modified substrate and soft baked at 65 °C for 20 s. The photoresist was exposed to a I-line source (Midas/MDA-6000 DUV, KR; wavelength, 365 nm; 9.5 mW/cm^2) through a pattern mask and postbaked at 110 °C for 20 s to selectively cross-link the exposed portion. The pattern development was performed by immersion in propylene glycol methyl ether acetate (PGMEA) for 40 s.

Ultralarge-Area PS-b-PMMA Lamellar Patterning. After photoresist patterning, a thin film of diblock copolymer was spin-coated over the topographic pattern. A PS-*b*-PMMA block copolymer (M_n of 48K kg mol^{-1}−46K kg mol^{-1} for PS and PMMA blocks), films were spin-cast from a toluene solution onto the photoresist patterned substrate. Thermal annealing at 250 °C for 24 h in a vacuum accomplished the graphoepitaxy. The PMMA lamellae were selectively removed from the PS-*b*-PMMA block copolymer film by dry-etching with O_2 plasma (plasma power, 50 W; O_2 gas flow, 40 sccm; process pressure, 7 × 10^{-2} Torr; etching time, 40 s). The resultant polystyrene nanowire arrays located within the photoresist trench were employed as an etching mask for the chemical patterning of the underlying neutral brush layer.[35] After pattern transfer, residual polystyrene, and photoresist layer were washed by mild sonication for 1 h in toluene solution. The same lamellar PS-*b*-PMMA block copolymer or binary blends of cylinder-forming PS-*b*-PMMA block copolymers (PS-*b*-PMMA1 PS block M_n, 46.1 kg/mol; PMMA block M_n, 21 kg/mol; PDI = 1.08 and PS-*b*-PMMA2 PS block M_n, 140 kg/mol; PMMA block M_n, 60 kg/mol; PDI = 1.09) thin film was spin-cast from a toluene solution onto the chemically patterned surface. Thermal annealing conducted at 250 °C for 24 h in a vacuum achieved the directed assembly into ultralarge-area lamellar nanopatterning.

Characterization. The nanoscale morphology of block copolymer thin films and photoresist patterns were imaged using a Hitachi S-4800 SEM with a field emission source at 1 kV.

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Supporting Information Available: Extensive figures. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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