

One-Dimensional Nanoassembly of Block Copolymers Tailored by Chemically Patterned Surfaces

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ABSTRACT: A symmetric block copolymer was spontaneously assembled into a laterally stacked, one-dimensional lamellar assembly along the chemically stripe patterned surfaces. The lateral dimension of the linear lamellar assembly was in the 20 nm scale, whereas the dimension of the surface stripe pattern directing the linear assembly was in the range of conventional photolithography (70–150 nm). The orientation and shape of the one-dimensional array were varied according to the free-form design of the surface stripe patterns. Our approach provides an opportunity of combining block copolymer assembly with a conventional photolithography to generate well-registered, one-dimensional lamellar assembly that is potentially useful for various nanodevices.

Introduction

A one-dimensional assembly of anisotropic nanostructures is significant for a variety of advanced applications such as plasmonic waveguides,^{1–3} magnetic logic gates,^{4,5} and magnetic data storage.⁶ The assembled structure may give rise to synergistic collective properties, which is hardly anticipated from the individual nanostructure. For example, the linear assembly of anisotropic metal particles may demonstrate interparticle plasmonic resonance as well as a tunable plasmonic resonance frequency. These synergistic properties are potentially useful for plasmonic waveguides that may confine the propagation of visible light through a nanoscale geometry.^{7,8} Owing to the high magnetic coercivity of the anisotropic ferromagnetic elements, the linear assembly of anisotropic ferromagnetic particles may provide a well-defined, ultrahigh-density magnetic nanodomains with an improved in-plane switching field.⁵ Such a structure is highly demanded for ultrahigh-density magnetic storage media and quantum cellular automata.^{4,5}

Various approaches to nanolithography, such as electron beam lithography⁹ or scanning probe lithography,¹⁰ have been used to fabricate one-dimensionally assembled nanostructures with a lateral resolution below 30 nm. However, the serial writing process of those approaches does not allow for a large-scale fabrication process. One alternative approach is self-assembly that relies upon the spontaneous and parallel organization of nanomaterials. Highly specific chemical or biological interactions,^{11,12} anisotropic dipolar/magnetic interactions,^{13,14} or linear molecular templates^{15–19} have been used in the linear assembly of nanoscale building blocks. However, the precise registration of the assembled structure, which is crucial for device application, has remained a formidable challenge.²⁰

Block copolymers have been extensively utilized as template materials for two-dimensional or three-dimensional nanofabrication. The spontaneous assembly of chemically distinctive macromolecular blocks may generate diverse nanoscale morphologies in bulk and thin films.²¹ However, the naturally assembled morphology of block copolymers consists of randomly oriented nanoscale domains with a high density of

defects. For a macroscopically ordered nanoscale morphology, various approaches, such as the application of an external field,^{22–25} topographic confinement,^{26–30} directional solidification,^{31–33} and nanopatterned surfaces,^{34–37} etc., have been exploited. Despite the successful development of strategies for well-ordered self-assembled morphology, block copolymer nanotemplates have been mostly used for two-dimensional or three-dimensional nanofabrication so far.

Here, we demonstrate a tailored assembly strategy of block copolymers to generate one-dimensional nanoassembled structures. A symmetric block copolymer was assembled into a one-dimensional lamellar assembly on chemically stripe patterned surfaces, whose pattern size is larger than the lamellar period of the block copolymer. Tailoring of the orientation and shape of the one-dimensional assembly was achieved by controlling the shape of the surface pattern. The linear assembly consisting of laterally stacked nanoscale lamellae, which has a characteristic length scale of about 20 nm, is beyond the ultimate resolution limit of a conventional lithographic process. In contrast, the surface prepatterns directing the linear assembly had a pattern dimension of about 100 nm that is routinely achievable by means of currently available lithographic processes. Consequently, our novel approach presents a versatile opportunity for hierarchically controlling over the self-assembled nanoscale morphology with a conventional lithographic process.

Experimental Section

The silicon wafer was cleaned by acid treatment. The wafer was immersed in a piranha solution (7:3 mixture of H₂SO₄ and H₂O₂) for 1 h at 110 °C and then washed several times with deionized water. After cleaning, a polystyrene-*r*-poly(methyl methacrylate) (PS-*r*-PMMA) brush (M_n 16 500 g mol⁻¹) was grafted onto the wafer surface to form a homogeneous neutrally modified surface.³⁸ A 110 nm photoresist (poly(methyl methacrylate), 950 kg mol⁻¹, Microchem Corp.) film was then spin-coated on the neutrally treated surface and baked at 130 °C for 10 min to remove any residual solvent. The positive photoresist was patterned by using electron beam lithography (Hitachi S-4300, 30 keV). The resulting topographic pattern of the photoresist was transferred to a chemical pattern in the neutral PS-*r*-PMMA brush layer by oxygen plasma etching at 5 mTorr of O₂ and a power of 50 W for 10 s. The neutral brush layer in the region that was not covered by the photoresist underwent selective oxidation at this stage, whereas that protected by the remaining photoresist did not undergo any chemical

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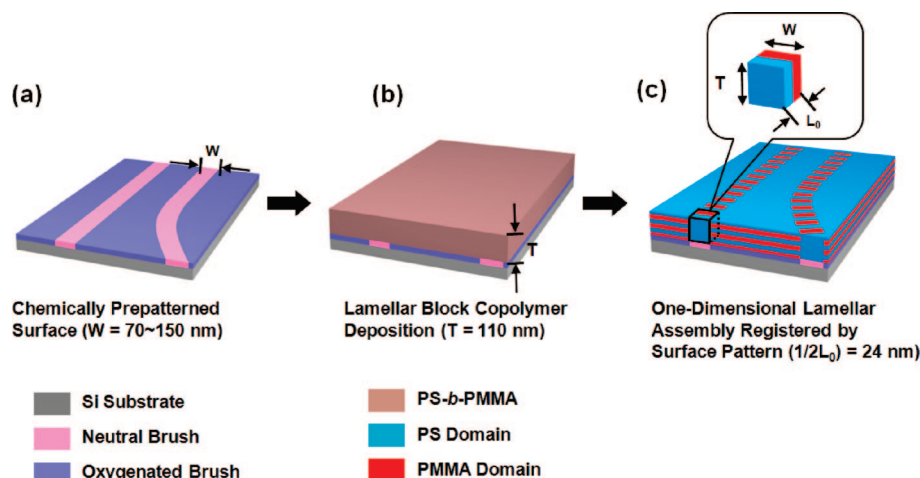


Figure 1. Schematic representation for tailored one-dimensional assembly process. (a) Preparation of chemical stripe pattern, whose pattern width ($W = 70\text{--}150\text{ nm}$) was larger than the lamellar thickness ($L = 24\text{ nm}$), by selective oxidation of neutral brush surface using electron beam lithography and subsequent reactive ion etching process. (b) Spin-casting of a block copolymer thin film, whose thickness (T) is about 110 nm . (c) 20 nm scale, one-dimensional assembly of lamellae following the neutral stripes of the underlying surface pattern after a sufficient thermal annealing. The inset shows the dimensions of the one-dimensional assembly.

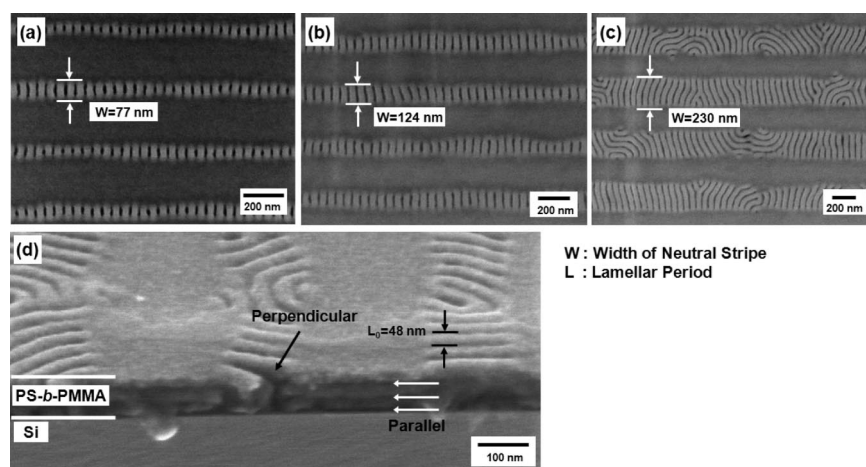


Figure 2. Scanning electron microscopy (SEM) images of the one-dimensional block copolymer assembly ($L_0 = 48\text{ nm}$, film thickness $T = 110\text{ nm}$). The well-ordered one-dimensional assembly is formed upon the neutral stripes having widths of (a) 77 nm and (b) 124 nm . (c) When the width of neutral stripe was 230 nm , defects such as disclinations and dislocations appeared. (d) The tilted SEM image for the cross-sectional morphology of an assembled block copolymer film. The lamellar domains were alternately oriented parallel and perpendicular to the underlying surface. The black arrow points to the poorly ordered region revealing surface perpendicular lamellar orientation, while the white arrows indicate three dark layers alternately arranged with three bright layers in the surface parallel lamellar region.

modification. The resulting chemically modulated patterns consisting of alternate neutral and PMMA preferential surfaces showed a good fidelity in terms of the pattern transfer process. A symmetric diblock copolymer, polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), whose number-average molecular weight (M_n) was 72 kg mol^{-1} ($L_0 = 36\text{ nm}$) or 104 kg mol^{-1} ($L_0 = 48\text{ nm}$), was spin-coated from a 3 wt % toluene solution to a prepatterned surface and subsequently annealed at $190\text{ }^\circ\text{C}$ in a vacuum for sufficiently long time. The resulting film thickness measured by ellipsometry was $\sim 110\text{ nm}$. The nanoscale self-assembled morphology of the block copolymer thin film was imaged by a field emission SEM (Hitachi S-4800). No sample treatment was applied prior to characterization with SEM. Note that in the SEM images of the symmetric lamellae the darker PMMA domains appear narrower than the bright PS domains.³⁹

Results and Discussion

Figure 1 briefly describes our tailored one-dimensional assembly process. A PS-*b*-PMMA with a high molecular weight (M_n ; 104 kg mol^{-1} ; $L_0 = 48\text{ nm}$) was used as self-assembling material. Electron beam lithography and subsequent oxygen

plasma etching were applied to prepare a chemically prepatterned surface, allowing the free-form design of the surface pattern.³⁶ The chemically patterned surface consists of alternate neutral stripes and PMMA preferential stripes, which induce a surface-perpendicular and a surface-parallel lamellar morphologies, respectively. We note that the widths of surface prepatterns were large enough ($70\text{--}150\text{ nm}$) to be achievable by means of current industrial photolithographic processes, even though it has been written by e-beam lithography in our work, which enabled the free-form design of surface pattern. Block copolymer thin film with a uniform thickness was spin-coated on the prepatterned surface and thermally annealed to direct the self-assembly. The resultant block copolymer morphology demonstrates the one-dimensionally assembled lamellae, well-registered along the neutral stripes of the underlying surface patterns.

Scanning electron microscopy (SEM) images of the prepared one-dimensional assembly are presented in Figure 2. The plane views in Figure 2a,b show a well-ordered linear assembly. PS and PMMA lamellae appear as bright and dark stripes, respectively.³⁹ The lamellar assembly maintained their equilibrium

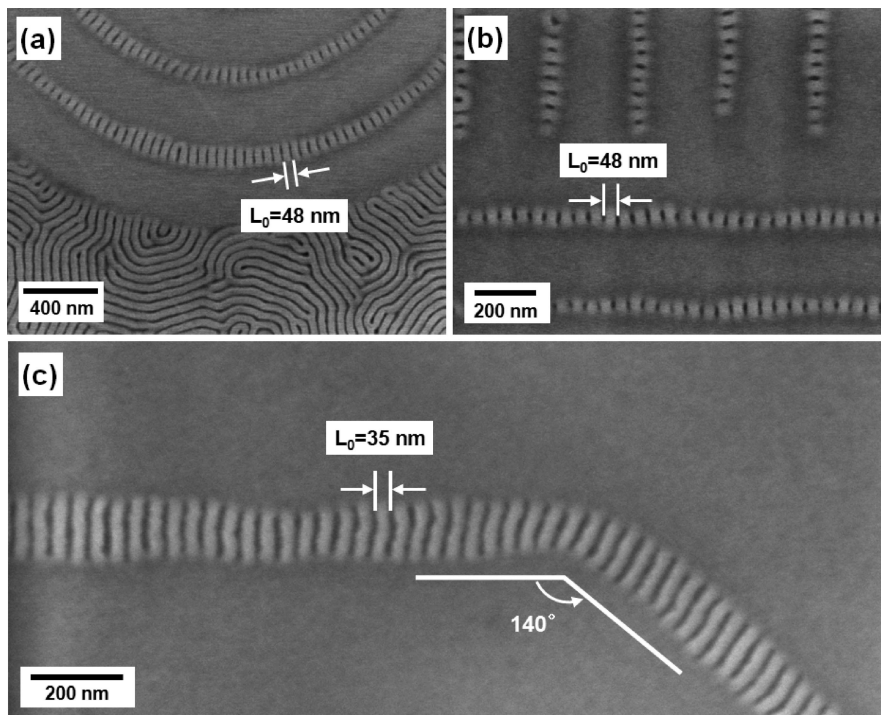


Figure 3. Scanning electron microscopy (SEM) images of the tailored assembly registered by the various shapes of surface patterns. The free-form design of e-beam lithography allowed for the diverse pattern shapes. Plane view of the linear assembly on (a) curved stripes, (b) sets of vertically oriented linear arrays, and (c) isolated angled stripe.

periodicity in bulk (~ 48 nm), which is far beyond the resolution limit of conventional photolithography. The widths of the assembled stripes (77 and 124 nm) were consistent with those of the neutral stripes of the underlying surface patterns (80 and 125 nm). This striking one-dimensional assembly behavior is a purely spontaneous process. Without any chemical modulation along the long axes of the surface pattern, the lamellae spontaneously organized themselves into a linear assembly. The linear assembly revealed a low degree of ordering if the surface prepattern width was too large. As shown in Figure 2c, the assembly included a high density of defects, when the surface stripe pattern was wider than 200 nm. Figure 2d clearly demonstrates the morphology inside the linearly assembled block copolymer thin film. Owing to the poor ordering of the insufficiently annealed sample, it is clearly seen that the lamellae are oriented in surface-perpendicular (as indicated by the black arrow) and surface-parallel direction (as indicated by the white arrows) alternately. The linear assembly observed at the film surface evidently resulted from the surface-perpendicular lamellar orientation. The three alternately arranged bright (PS) and dark (PMMA) layers, which are indicated by white arrows, are clearly observed in the surface-parallel lamellar region. We note that, since the block copolymer film thickness (110 nm) was close to the equilibrium quantized thickness above a PMMA preferential surface (asymmetric wetting condition), there is no island or hole morphology at the surface of the parallel lamellar region.⁴⁰

Figure 3 shows SEM images of the tailored assembly registered by the various shapes of the surface patterns. Diverse pattern shapes were accomplished by taking advantage of the free-form design of the e-beam lithography.³⁶ In Figure 3a, the linear assembly was registered by the curved stripes with a high degree of perfection. The well-ordered assembly clearly contrasts with the randomly oriented lamellae observed at the lower part of the image. In Figure 3b,c, the linear assembly was well-registered along the orthogonally arranged lines and an isolated angled stripe. As shown in Figure 3c, the periodicity of linear assembly was reduced into 36 nm, if a block copolymer with

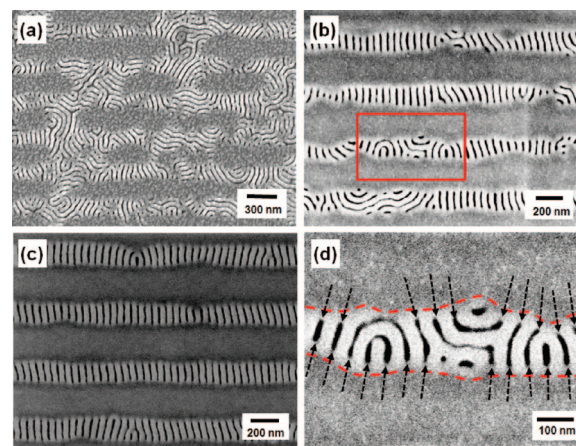


Figure 4. Scanning electron microscopy (SEM) images of PS-*b*-PMMA film observed at the various stages of annealing time of (a) 1, (b) 14, and (c) 48 h. (a) In the beginning of thermal annealing, the lamellar domains were irregularly distributed in the film plane. (b) As the annealing proceeded, the surface perpendicular morphology was gradually registered by the underlying pattern, and the defects in the lamellar assembly reduced also. (c) Well-ordered linear assembly fully registered the underlying stripe patterns was formed. (d) A part of lamellar domain as marked square in (b) is magnified. Despite the low degree of ordering, lamellae were preferentially aligned normal to the domain boundary.

low molecular weight (M_n : 72 kg mol⁻¹; $L_0 = 36$ nm) was used. The well-registered linear assembly following the diverse shapes of the surface patterns is an essential feature of device-oriented nanofabrication.

To gain an insight into the mechanism of one-dimensional assembly, we observed the evolution of the morphology at various stages of thermal annealing. These observations are shown in Figure 4. In the early stage of annealing, the lamellar morphology was rarely registered by the underlying surface pattern. The surface-perpendicular lamellar domains were irregularly located in the film plane, revealing a poor lateral

ordering of lamellae inside the domains (Figure 4a). As the annealing proceeded, the lamellar domains became gradually registered by the underlying surface pattern, and the lateral ordering of lamellae inside the domains was remarkably improved (Figure 4b). After 48 h of annealing, the well-ordered linear lamellar assembly was formed along the neutral stripes in the underlying surface pattern (Figure 4c). These experimental findings demonstrate that the one-dimensional assembly occurred gradually from randomly oriented lamellae upon the thermal annealing process. In Figure 4d, a part of the lamellar domain presented in Figure 4b is magnified. Despite the low degree of ordering that resulted from insufficient annealing time, it is clearly observed that lamellae were preferentially aligned normal to the domain boundary. This behavior, together with the poor lamellar ordering observed on a wide stripe pattern whose pattern width is larger 200 nm (Figure 2c), suggests that the boundary interface between the surface perpendicular and surface parallel lamellae should be playing a significant role in the spontaneous linear assembly.

Our approach to one-dimensional lamellar assembly shares the advantage of the graphoepitaxial approach, where the pattern density of a top-down process can be remarkably enhanced by block copolymer self-assembly. In the graphoepitaxial approach, a topographically patterned surface with a pattern scale much larger than the nanoscale morphology of a block copolymer may induce lateral ordering of the nanodomains in block copolymer thin films.^{26–30} The vertical edge of a topographically patterned surface imposes lateral confinement on block copolymer thin films, causing self-assembled nanodomains to become well-ordered along the edge of the pattern. Owing to the self-assembly of nanodomains, the boundary confinement successively propagates over the neighboring arrays of nanodomains to yield a well-ordered nanoscale morphology over a large area after sufficient thermal annealing.⁴¹ We note that neutral chemical modification of a topographically patterned surface may induce a linear lamellae array along the topographic pattern. Chemically neutral surfaces at the vertical edge and at the bottom surface simultaneously impose a surface-perpendicular alignment of lamellae, producing a linear lamellar assembly along the topographic pattern. This morphological evolution resembles the one-dimensional lamellar assembly achieved in our work.⁴² However, our approach does not require any topographic confinement, which is advantageous for preparing large-area, uniform block copolymer nanotemplate by means of a spin-coating process.

Since neither chemical nor topographic modulation existed along the neutral stripe pattern, the spontaneous linear lamellar assembly could be hardly driven by the underlying surface pattern. Here we suggest a model for this striking linear assembly based on the boundary interfacial energy difference with respect to the orientation of surface perpendicular lamellae. Figure 5 schematically depicts two representative morphologies of the grain boundary interfaces with respect to the in-plane orientation of the surface-perpendicular lamellae. As observed in the cross-sectional SEM image in Figure 2d, the part of lamellae assembled on neutral stripe was oriented in the surface perpendicular direction, while that assembled on PMMA preferential stripe was oriented in the surface parallel direction. If the surface perpendicular lamellae are oriented along the underlying stripe pattern, the grain boundary geometry should form a 90° tilt boundary, and the resulting interfacial morphology is a T-junction tilt boundary (Figure 5a).^{43,44} Although T-junction tilt boundary is known as the stable interfacial morphology in this boundary geometry, it disrupts the continuity of the lamellar domains across the grain boundary. The terminated lamellae form semicylindrical caps at their ends, where the high curvature of the interface as well as the large

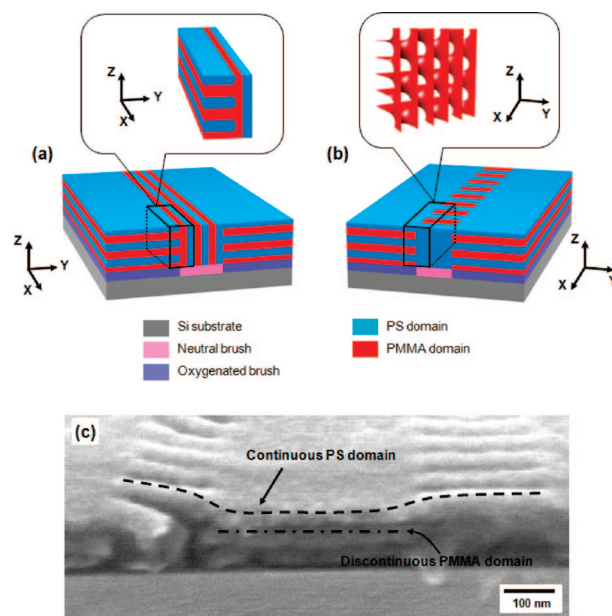


Figure 5. Schematic representation for two possible grain boundary morphologies according to the orientation of lamellar assembly. (a) T-junction tilt boundary; only one domain is continuous along the grain boundary, and the other domain is terminated and forms a semicylindrical cap. (b) 90° Scherk surface twist grain boundary; lamellar domains are continuous across the grain boundary with the minimized interfacial area. (c) Cross-sectional SEM image of linear lamellar assembly showing a continuous PS domain and a discontinuous PMMA domain across the domain boundary.

interfacial area gives rise to a high-energy penalty.^{43,44} In general, the T-junction morphology is considered a high-energy grain boundary morphology and has rarely been experimentally observed.⁴⁴ By contrast, if the lamellar microdomains are oriented across the underlying striped pattern, the grain boundary should form a 90° twist boundary. In this geometry the stable interfacial morphology is known as Scherk surface morphology (Figure 5b).^{45,46} This morphology is generated by smoothly joining two sets of planes that are aligned normally with respect to each other. The interface consisting of a doubly periodic array of the saddle-surface region allows for the continuity of lamellae across the grain boundary and the minimizes interfacial area. The resulting energy penalty at the grain boundary can be minimized also. It has been suggested that Scherk surface with the twist angle of 90° is the stable boundary interface morphology of block copolymer thin films, where lamellae are allowed to orient either in surface perpendicular or in surface parallel direction due to the substrate/film interaction.^{43,44} For the block copolymer films assembled on alternate neutral and preferential stripe patterns that has been investigated in our work, the surface perpendicular lamellae assembled on neutral stripes may favor the orientation across the neutral stripes, since the resulting boundary interface morphology of Scherk surface minimizes the energy penalty at the boundary interface and thereby minimizes overall energy of the block copolymer thin films. The cross-sectional SEM image of lamellar assembly in Figure 5c shows that a PS domain is continuous throughout surface perpendicular and parallel lamellar region, while a PMMA domain is not continuous at a cross section, which closely resembles the cross-sectional morphology described in Figure 5b.

Conclusion

We have demonstrated a novel strategy for the one-dimensional lamellar assembly of block copolymers directed by chemically patterned surfaces. The linear assembly was fully

registered by the underlying free-form designed surface pattern, allowing the diversity of the assembled shapes. Our approach represents that self-assembling materials, which generically form two-dimensional or three-dimensional periodic structures, can be directed to engage in one-dimensional assembly by hybridizing with a top-down process.^{15–18} The applied prepatter dimension is within the range of conventional photolithography. Thus, further development of our approach in conjunction with conventional lithography may provide a useful large-scale one-dimensional lamellar assembly process. Furthermore, the development of a pattern transfer technique generally applicable to various functional materials would provide a valuable nanolithographic process for various nanodevices.^{47,48}

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