

Directed self-assembly of block copolymers

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Abstract

Block copolymers in the strong segregation regime self-assemble to form regular periodic nanopatterns that are applicable as the templates for nanofabrication or nanoprocessing such as the etching masks for nanolithography. However, self-assembly of block copolymers alone usually results in poly-grain structures. Directed self-assembly is an excellent technique developed rapidly in the past decade. Directed self-assembly either by graphoepitaxy with topographical guides or chemical registration with chemically patterned surfaces enabled us to control orientation and alignment of block copolymer microdomains in thin film on a substrate. It is expected that this technique will further extend the resolution limit of the conventional photolithography. This article briefly reviews the directed self-assembly techniques.

Introduction

Extremely regular and fine nanopatterns that block copolymers (bcp) exhibit in ultrathin films are a promising candidate as the etching masks for the new and facile approach for downsizing in nanolithography. The major problem is to solve the problem how to align the bcp microdomains in a single-crystal-like array with the minimum defects. The solution is the directed self-assembly (dsa) in which the microdomain formation of the bcp is guided by

the patterns prefabricated on the substrates by the top-down techniques. Here we review the two techniques of dsa, one is graphoepitaxy and the other is chemical registration. The former uses physically patterned guides such as trenches and the latter uses the chemically patterned substrates, the surface of which are grafted with self-assembled monolayer (sam) or polymer chains and patterned by lithographic techniques. Some review papers are also available [1-5].

Graphoepitaxy

Graphoepitaxy was originally developed by Smith et al. [6,7] to control orientation of crystal growth in thin films with topographically patterned surfaces in contrast to classical heteroepitaxial growth of thin crystal films on single crystal surfaces. Siegalman et al. [8*] first applied graphoepitaxy to align spherical microdomains of polystyrene-*block*-poly(2-vinylpyridine) bcp (PS-*b*-P2VP) in a thin film with the thickness of a single layer of the spheres. The film coated on the flat surface of Si substrate with SiO₂ surface layer exhibited a polycrystalline pattern even after extensive annealing while a single crystal pattern of hexagonally packed spheres was formed on the regularly spaced long rectangular mesas formed on the substrate by a lithographic technique. Since the epitaxial growth of the hexagonal lattice is nucleated by the edges of the mesas, the persistence of the alignment is limited by the width of the mesas. Cheng et al. [9], on the other hand, demonstrated the regular alignment of spherical microdomains of polystyrene-*block*-polyferrocenyldimethylsilane bcp (PS-*b*-PFS) in the trenches prepared by interference lithography on the SiO₂ surface. Alignment of single layer of spherical microdomains can be directed by physical confinement by the trenches as shown in Figure 1a. Again the persistence of the alignment is limited by the width of the grooves. Naito et al. [10*] applied this technique to prepare bit patterned media for magnetic data storage (2.5-inch hard disk), which requires size uniformity and position accuracy.

For the purpose to use bcp self-assembled patterns as the etching masks in preparation of bit patterned media for high density data storage, cylindrical microdomains perpendicularly aligned to the substrate surface are preferred to spherical microdomains due to the larger aspect ratio. PS-*b*-PMMA with cylindrical microdomains was shown to be a good candidate because of the high etching contrast between PS and PMMA domains [11-13]. However, due to the lower interfacial energy between PMMA and SiO₂ surfaces of Si substrates than PS and SiO₂ PMMA cylinders tend to orient parallel to the trenches as shown in Figure 1b. By chemically modifying the surface of the trenches for neutral wetting, long-range order of cylindrical domains in hexagonal arrays oriented perpendicular to the substrate was attained [11]. The neutral surface can be attained by grafting random copolymer of PS and PMMA. Blending two PS-*b*-PMMA with different molecular weights is a simpler technique to induce the perpendicular orientation of the cylinders [13]. Hexagonally close-packed cylinders have interstitial space of a concaved triangular shape in the center of the adjacent three cylinders. The block chains of the major component must be stretched to fill the triangular interstitial space resulting in reduction of the conformational entropy. If the blended longer block chains of the higher molecular weight preferentially fill this space to avoid stretching of the shorter chains, it would stabilize hexagonal packing of the cylinders, which can be realized by perpendicular orientation of the cylinders. In this case, film thickness must be adjusted not to be an integer multiple of the domain spacing.

In addition to PS-*b*-PMMA other bcps such as polystyrene-*block*-polyethyleneoxide (PS-*b*-PEO) [14-18], PS-*b*-PFS [19], polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS) [19-26] and PS-*b*-P2VP [8,27-29] are also used for bcp dsa by graphoepitaxy. The characteristics of these bcps is that the segregation power between two blocks is much larger than PS-*b*-PMMA so that much smaller domain sizes are available while it is more difficult to attain the perpendicular orientation of cylinders. As small as 8 nm feature width [24] or 15 nm

spacing [26] of the line pattern was reported for PS-*b*-PDMS.

In practical applications formation of defects of the patterns should be avoided. The effect of trench walls to align cylindrical microdomains in an array dissipates with increasing the distance from the walls. Utilizing the short-range interaction can eliminate defects in the self-assembled patterns more effectively. A good solution is to employ an array of nanoscale topographical elements (posts) that have a long-range order given by a lithographic technique and act as surrogates for the minority domains of the bcp instead of trenches. Bitar et al. [20**] demonstrated that the substrate having a sparse 2D array of posts created by scanning-electron-beam lithography successfully arranged the PDMS spherical microdomains of spin-coated PS-*b*-PDMS thin film in a hexagonal array with one third of the spacing of the posts as shown in Figure 2, where the case of the posts grafted with PS is shown. Since the domain spacing of the spheres is a third of the spacing of the posts, the self-assembled array of the spheres has nine times higher density of the substrate pattern. Therefore, this technique will be useful in nanolithography applications such as the formation of high-density microelectronic structures. Recent advancement [22*] was reported for cylinder-forming PS-*b*-PDMS for which an array of carefully spaced and shaped posts, prepared by electron-beam patterning of an inorganic resist, can be used to template complex patterns including bends, junctions and other aperiodic features in specific locations. With this method linear patterns can be directed by a sparse template occupying only a few percent of the area of the final self-assembled pattern. In addition, the method can be used to selectively and locally template complex linear patterns.

Preparation of prepatterned surface for graphoepitaxy in an area as large as the wafer surface is limited by the employed top-down techniques. A novel technique [16**,18] was proposed to prepare ordered arrays of cylindrical microdomains 3 nanometers in diameter, with areal densities in excess of 10 terabits per square inch for PS-*b*-PEO. They used

commercially available defect-free sapphire (α -Al₂O₃) wafers and created faceted surfaces with a sawtooth topography, which was obtained by the cutting single crystals along specific crystallographic planes to create unstable surfaces and subsequent annealing. The unidirectional ridges of the sawtoothed topography provides the guide to direct the cylinders by the entropic driving force and surface defects such as dislocations can be amended by the self-assembly of the bcp.

Topographic patterns to direct self-assembly of bcps in graphoepitaxy are sometimes unfavorable for applications to various nanomaterials and nanodevices. Jeon et al. [30] proposed “soft graphoepitaxy”, in which a mild cleaning process can easily dispose of the photoresist pattern directing nanoscale bcp assembly. Therefore, it may be useful in the nanolithography for complex device architectures requiring multilayer overlay processing.

To reduce the feature sizes of the self-assembled patterns of bcps it is necessary to reduce their molecular weights. Reduction of the molecular weights in turn reduces the segregation power and leads to the order-disorder transition. Therefore, a bcp with highly incompatible blocks must be employed for dsa.

Poly(2-vinylpyridine)-*block*-polydimethylsiloxane (P2VP-*b*-PDMS) is one of such bcps.

Solvent annealing with P2VP-*b*-PDMS can provide an extraordinarily large degree of tunability both in geometry and dimension of the self-assembled patterns when the vapors of various selective solvents were used [31*]. Various morphologies such as spheres, cylinders, hexagonally perforated lamellae, and lamellae from the same sample. This methodology is particularly useful because a broad range of geometries and sizes can be obtained with a single block copolymer without changes in molecular weight or volume fraction.

Chemical registration

In chemical registration, the bcp microdomains is registered by chemically

pre-patterned templates with surface energy contrast. Figure 3 shows schematic illustration of chemical registration for PS-*b*-PMMA forming hexagonally-close-packed (hcp) cylinder microdomains of PMMA as an typical example of chemical registration [32*].

The dots placed on hexagonal lattice are prepared on the surface of a substrate. The size of dots and the domain spacing d_{pre} of chemical patterns are identical with those of the microdomain structure of PS-*b*-PMMA, d_{block} . The surface of dots is designed to have lower surface energy to PMMA, while the surrounding matrix is tuned for preferential wetting by PS. When PS-*b*-PMMA self-assembles the microdomain structure, the PMMA cylinders are registered on the dots regions to minimizing the free energy of the film.

Rockford et al. first reported the control of the orientation of the microdomain of bcp thin film by using chemical registration [33]. They made the surface having stripe patterns consisting of alternate silicon oxide and Au. The difference of the affinity in silicon oxide and Au directed the orientation of the lamellar microdomain structure of PS-*b*-PMMA. Then, Nealey et al. have successfully directed lamellar- and cylinder-forming bcp self-assembled microdomains in registration with the lithographic pattern defined in the chemically modified surfaces with a one-to-one correspondence [34**-36].

It is well-known that bcp can form well-aligned microdomain structures with long range order during their self-assembling process. These self-assembly can restore the short-range errors in pattern prepared by conventional lithography. Tada et al. demonstrate that the defect-free pattern of the microdomain structure of hcp cylinder in PS-*b*-PMMA thin film can be obtained on the chemical patterns having significant defects, indicating that variations in pattern position and point defects in the resist pattern can be corrected by the bcp self-assembly. This restoration effect has also been reported to be effective in reducing the line-edge roughness effect of the resist patterns [37,38] and in correcting the width variations of the line-and-space patterns [39]. As critical dimensions reach smaller dimensions,

conventional lithographic techniques are approaching their resolution limits. In such cases, quality of the pattern may have significant amount of errors and variations.

Though the application of the chemical registration was described for one to one correspondence or $d_{\text{pre}} = d_0$ above, the technique can also be applied to density multiplication $d_{\text{pre}} = nd_0$ (n : integer) or frequency multiplication of sparse chemical template patterns [32,40,41*]. Figure 4 shows the nine-fold density multiplication ($d_{\text{pre}} = 3d_0$) of a hexagonal lattice pattern [41*]. As shown in Figure 4(a), the chemical template was prepared by EB resist pattern with $d_{\text{pre}} = 72$ nm corresponding to three times of $d_0=24$ nm. Figure 4(b) shows the self-assembled structure of PS-*b*-PMMA thin film on the chemical template. The self-assembled structure with long-range order is directed by the template pattern without defects. The domain spacing d_0 of the microdomain structure of the thin film on the template was 24 nm, which was a third of the lattice spacing, $d_{\text{pre}} = 72$ nm, of the chemical template. The self-assembling ability of bcp can induce interpolation of the chemical pre-patterns and achieve a nine-fold density multiplication. It should be noted that the density multiplication process is a promising technique to break through the limitations in current lithographic techniques to reach smaller dimensions.

Though chemical registration of self-assembling structures of bcp was discussed mainly for hcp patterns with perpendicularly oriented cylindrical domains, chemical registration can also be applied to arrange spherical microdomains on hcp patterns [42,43] . In addition it is possible to align perpendicularly oriented lamellar microdomains [34*,38,39,44,45] or cylindrical microdomains oriented parallel to the substrate surface [35] to form line-and-space patterns. Moreover, it has been reported that changes in morphology can be induced by chemical heteroepitaxy [46,47]. Furthermore, chemical heteroepitaxy has also been successfully applied to complex patterns, such as bent lines, isolated lines, and junctions, which basically demonstrate that the method can be applicable in patterning semiconductor

logic circuits [48*-51*].

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Figure Captions

- Figure 1 AFM images of (a) spherical microdomains and (b) cylindrical microdomains of PS-*b*-PMMA aligned in trenches by graphoepitaxy.
- Figure 2 A top-view scanning electron micrograph of PS-*b*-PFS diblock copolymer aligned by graphoepitaxy with the posts as illustrated in the drawings.
- Figure 3 Schematic illustration demonstrating block copolymer lithography process taking vertically oriented cylindrical microdomain as an example of block copolymer microphase separated structure.
- Figure 4 (a) A top-view scanning electron micrograph of EB resist employed to pattern PS graft layer on Si wafer surface for a chemically pre-patterned template with $d_s = 72\text{nm}$. (b) A top-view scanning electron micrograph of cylinder structures of PS-*b*-PMMA with $d_o = 24\text{nm}$ self-assembled perpendicularly on the chemically pre-patterned template.

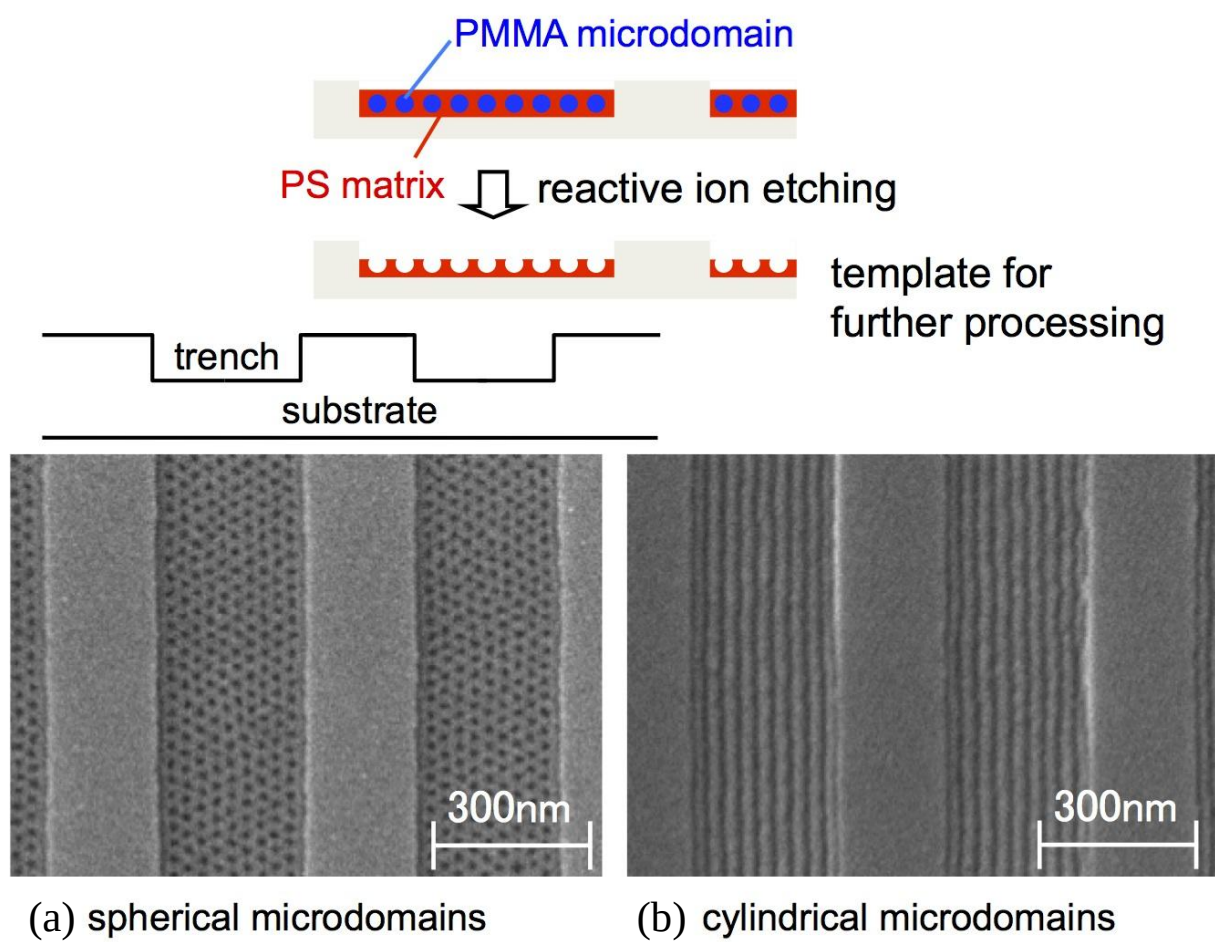


Figure 1

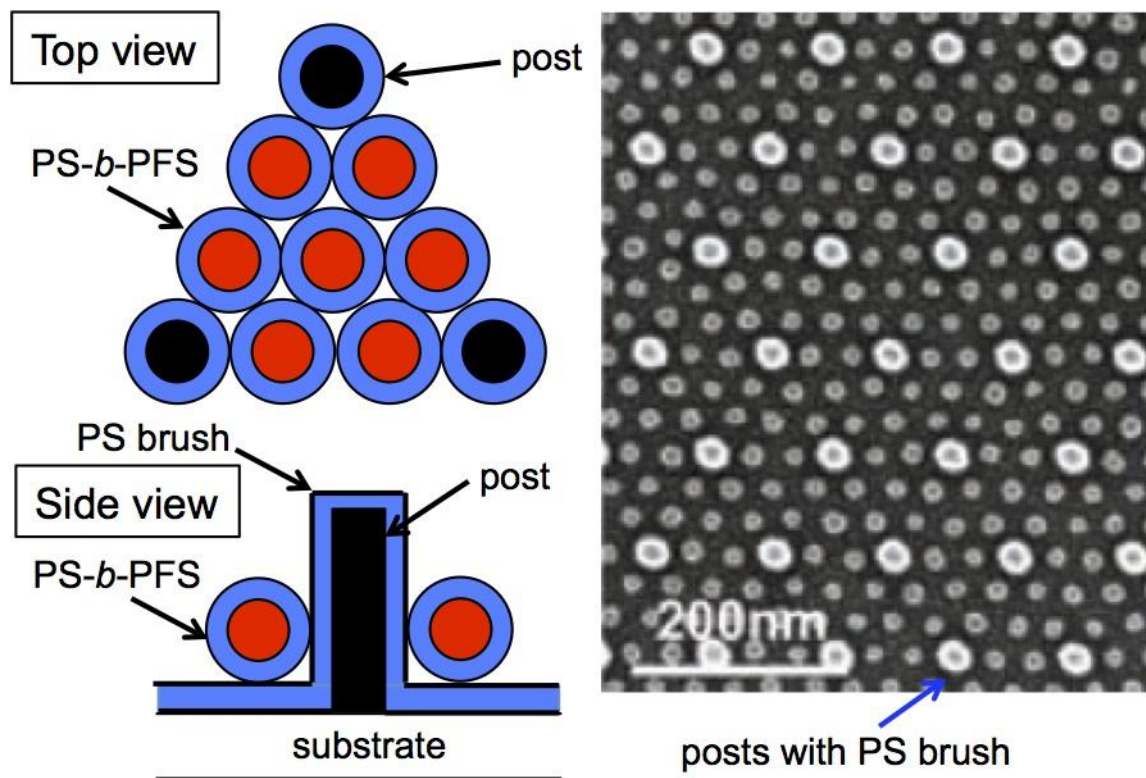


Figure 2

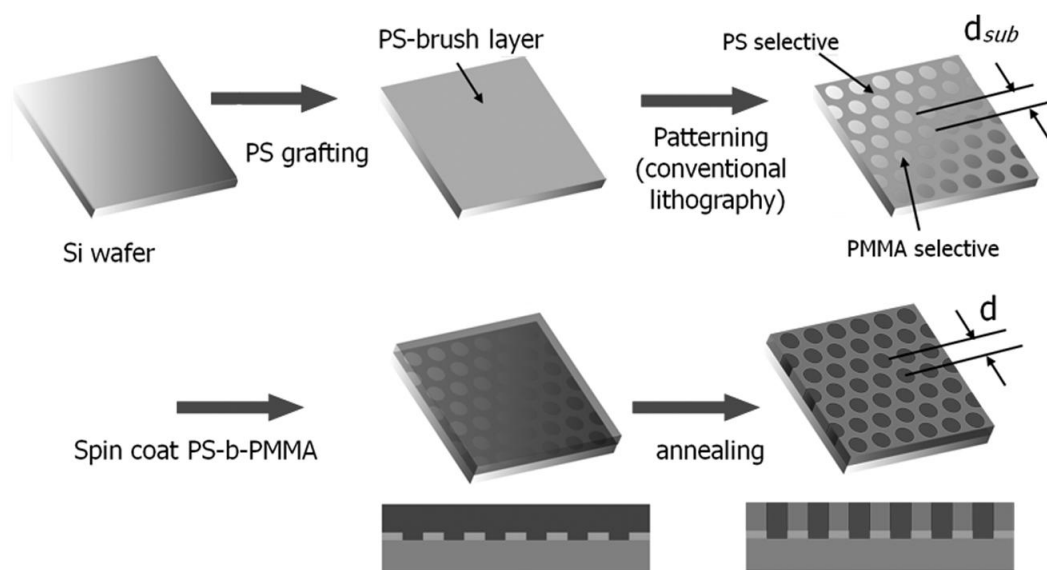


Figure 3

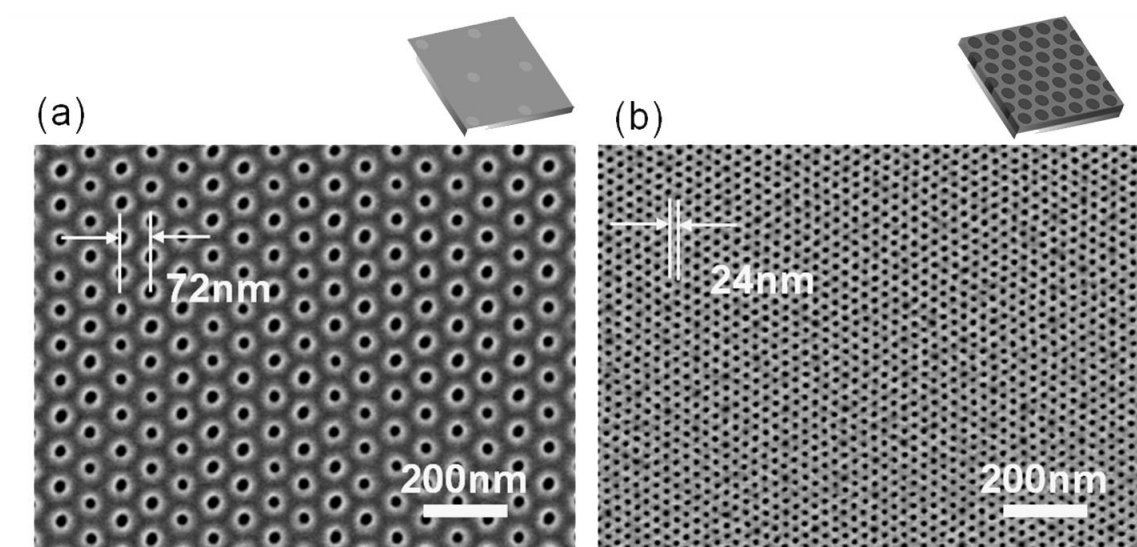


Figure 4

Highlights

