

Block Copolymer Lithography toward 16-nm-technology Nodes and Beyond

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Abstract

We report a combined top-down/bottom-up approach for nanopatterning using self-assembled domains of a block copolymer. We have successfully demonstrated that these periodic domains with a half-pitch smaller than 16 nm can be ordered by using block copolymers with shorter chain lengths. Moreover, we have devised a new approach for the lateral alignment of the lamellar domains of the diblock copolymer by using a resist pattern as a guide for the alignment. This makes it possible to precisely control the alignment of the self-assembled domains. We are convinced that this approach is promising for high-resolution lithography, which could be applicable to 16-nm half-pitch technology nodes needed in about 2019.

1. Introduction

The remarkable progress in semiconductor fabrication technology has made it possible to manufacture silicon chips using 65-nm process technology. This dramatic advance in miniaturization technology is largely due to progress in lithographic technologies. However, it is becoming difficult to maintain the rapid pace of miniaturization because many difficult challenges need to be overcome, such as critical dimension (CD) control, overlay, defect control, and low cost. The 2005 edition of the International Technology Roadmap for Semiconductors (ITRS Roadmap), which is a fifteen-year assessment of the semiconductor industry's future technology requirements, offered no proposals for potential solutions capable of meeting the requirement for the 16-nm half-pitch technology node generation and beyond. The forecast shows that this requirement should be met by 2019. Therefore, innovative lithographic technologies need to be developed.

Recently, block copolymer lithography [1] has attracted considerable attention as a combined top-down/bottom-up approach to nanopatterning. This method involves the use of microphase-separated

nanometer-sized domains as lithography templates. It is superior in that nanostructures can be fabricated in large quantities with approximately consistent sizes. Its most important feature is that the sizes and periods of the microphase-separated domains involved in this method are determined merely by the chain length of the block copolymer. Therefore, this method has significant potential to exceed the resolution limit of the top-down technologies such as electron-beam (EB) lithography, which is expected to be around 20 nm.

Diblock copolymers comprise two flexible, chemically incompatible and dissimilar polymer chain blocks covalently bonded together at one end, as shown in **Fig. 1**. Due to the incompatibility between the two blocks and connectivity constraints, the chains spontaneously self-assemble into microphase-separated nanometer-sized domains at a certain temperature. In ordered periodic structures, the size of the domains is governed by the dimensions of the chain, which is of the order of tens of nanometers. The shape of the microphase-separated domains depends on the composition of the polymer. Various shapes ranging from spheres, cylinders, and lamellae to inverse spheres (the matrix surrounding spheres of the other material) can be produced by changing the volume fraction of block A, as illustrated in **Fig. 2**. In block copolymer lithography, a monolayer of an ordered structure is used as a patterning template. For example, both spherical domains and vertical cylin-

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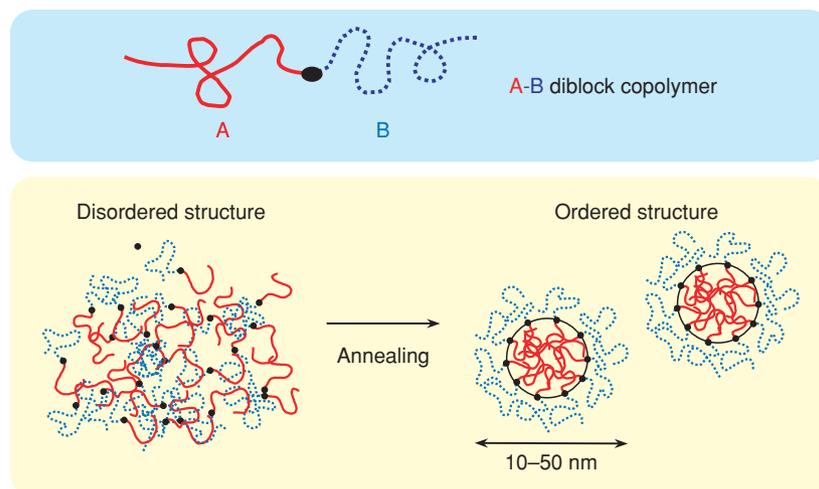


Fig. 1. Self-assembly of diblock copolymer.

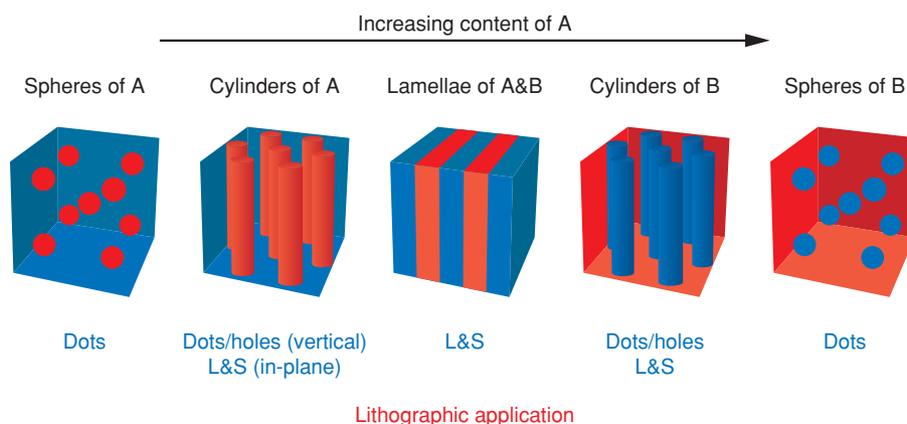


Fig. 2. Various shapes of microphase-separated domains.

der domains can be used to form dot and hole patterns.

With regard to dot and hole patterns, many attempts have been made to apply these domains as dry-etching masks in the semiconductor fabrication process. These structures are reported to have been used to pattern magnetic media [2] and flash memory [3]. On the other hand, research on line-and-space (L&S) patterns has just begun [4]-[6]. For L&S pattern formation, both in-plane cylindrical and lateral lamellar domains can be applied. To apply these domains to L&S pattern formation, the domain alignment should be controlled more strictly.

Here, we report on our recent activity concerning the alignment control of self-assembled domains of diblock copolymers using graphoepitaxy. Graphoepi-

taxy is a technique that uses the surface topography of the substrate to direct epitaxial growth of the block copolymer film.

Section 2 describes the alignment method of in-plane cylindrical domains of an asymmetric diblock copolymer using microtrench patterns. Section 3 reports a new approach to graphoepitaxy using a resist pattern as the guide for alignment; this makes it possible to laterally align the lamellar domain behaviors of symmetric diblock copolymers.

2. Alignment of in-plane cylindrical domains inside a microtrench

2.1 Materials

We used an asymmetric diblock copolymer com-

posed of polystyrene (PS) and poly(ethylene-*alt*-propylene) (PEP). Its chemical structure is shown in **Fig. 3(a)**. The molecular weights of each PS and PEP block were 6100 and 16,500 g/mol, respectively, with a polydispersity of 1.04. The molar ratio of PS:PEP was 0.3:0.7, as shown in Fig. 3(a). In this polymer, self-assembly involves the formation of cylinders of PS embedded in a PEP matrix (**Fig. 3(b)**).

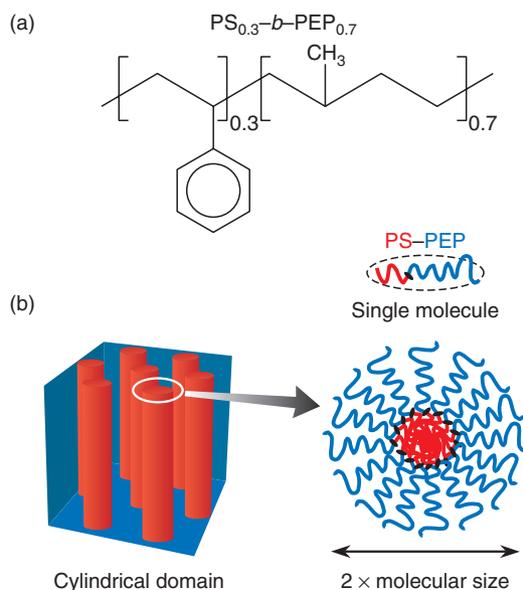


Fig. 3. (a) Chemical structure of PS-*b*-PEP and (b) self-assembled cylinder structure.

2.2 Self-assembly on a flat substrate

First, we investigated the behavior of the self-assembly of this diblock copolymer on a flat substrate. Thermal annealing quantizes the film thickness of the block copolymer by separating it into terraces (i.e., islands and holes). An optical microscope image exhibiting a hole morphology is shown in **Fig. 4(a)**. From thickness measurements of the hole and surrounding regions, we found that the block copolymer film on the silicon oxide surface exhibited asymmetric wetting: a PS block preferentially wet the oxide surface, whereas a PEP block covered the free surface. The quantized thickness corresponds to odd half-integer multiples of L , that is, $(2n + 1)L/2$, where n is an integer and L is the thickness of a single layer of the cylinders.

A topographic image of the region near the boundary between the $L/2$ and $3L/2$ terraces is shown in **Fig. 4(b)**. In the $3L/2$ terraces, a fingerprint pattern can be clearly observed. This implies that the cylinders lay parallel to the substrate. Although a PS cylinder was embedded in a PEP matrix, the cylinder structures were observed even in the topographic image because the surface immediately above the PS cylinder swelled up to a height of approximately 1 nm.

The phase image corresponding to the topographic image of Fig. 4(b) is shown in **Fig. 4(c)**. Phase imaging is a standard technique for mapping the spatial variation in surface elasticity. The cylinder structures

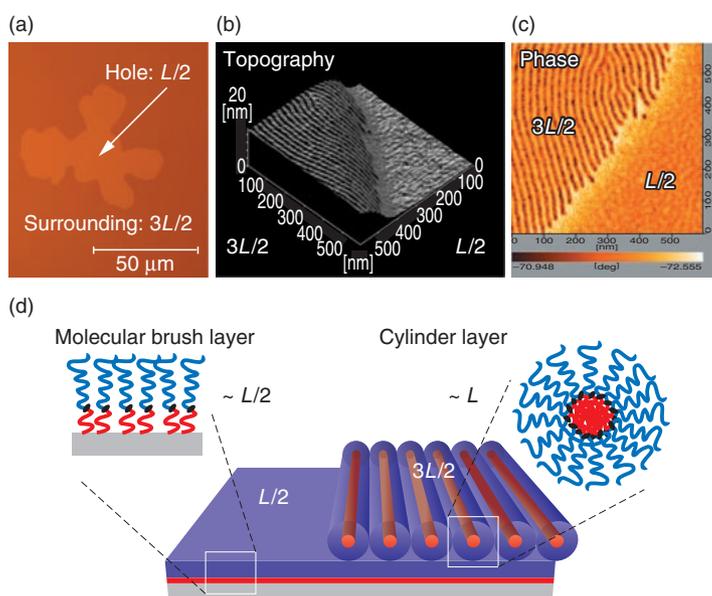


Fig. 4. In-plane cylindrical structure: (a) optical microscope image, (b) AFM topological image, (c) AFM phase image, and (d) schematic diagram.

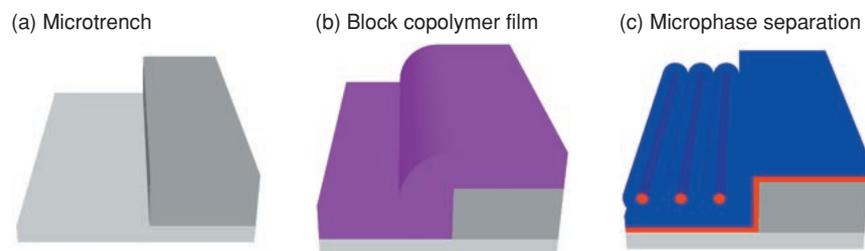


Fig. 5. Alignment process of cylindrical domains inside microtrench.

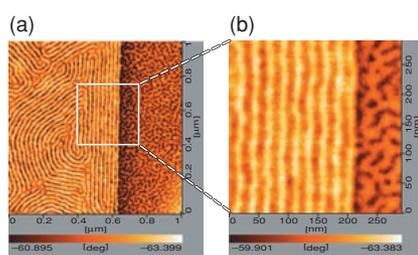


Fig. 6. AFM phase images of cylindrical domains near the edge region of a trench.

can be observed due to the difference in elasticity between the PS and PEP domains. The dark region in the phase image corresponds to a PS cylinder domain that is less elastic than a PEP domain. Neither the topographic images nor the phase images showed any specific structures due to the self-assembly on the $L/2$ terrace. This is because a self-assembled monolayer, in which the PS block wets the substrate and the PEP block faces the polymer/air interface, was formed on the $L/2$ terrace. These results confirmed that the block copolymer film on a flat surface covered with silicon dioxide was quantized in units of odd half integers and had a layer period L of about 20 nm, as illustrated in Fig. 4(d).

2.3 Alignment of cylindrical domains inside microtrench

Next, we investigated the graphoepitaxy of self-assembled cylindrical structures on a micropatterned substrate [7]. In graphoepitaxy, the self-assembled structures are aligned with the sidewalls of the patterns.

A schematic diagram of the alignment process in this approach is shown in Fig. 5. First, the microtrench is formed on the substrate. A SiO_2 layer with a thickness of a few tens of nanometers is formed on the Si substrate by thermal oxidation in a

dry oxygen ambient. A 1.5- μm L&S pattern of the oxide is made by contact photolithography and subsequent reactive ion etching (Fig. 5(a)). Next, the block copolymer film is formed over trenches (Fig. 5(b)). The spin-coated film is then annealed in an oven at 130°C under a nitrogen atmosphere for 15 h to enable sufficient microphase separation (Fig. 5(c)). The self-assembled domains are observed using an atomic force microscope (AFM) in the dynamic force mode.

AFM phase images of a self-assembled block copolymer film near the edge region of a trench with a depth of 26 nm and width of 1.5 μm are shown in Fig. 6(a). It is clear that the cylinder structure was formed only within the trench. This is due to the formation of a $3L/2$ terrace within the trench and an $L/2$ terrace on the mesa resulting from height quantization. To confine the formation of cylinders within a trench, a certain minimum height, which is probably greater than L , is required. It is noteworthy that the cylinder structure is aligned with the sidewall of the trench that is 800 nm long and 200 nm wide. A magnified view of Fig. 6(a) is shown in Fig. 6(b). We can clearly see that the bright domain corresponding to the PS block is in contact with the sidewall of the trench. This implies that a self-assembled monolayer was formed on the sidewall of the trench as well as on the bottom surface of the trench. This monolayer formation is the key to inducing the lateral alignment of the cylinder structures. Moreover, it is clear that the cylinders having a 23-nm pitch are separated from each other, although the lines that they form are not completely straight.

We have demonstrated that cylindrical domains with a pitch of 23 nm were aligned inside the oxide trench. This already surpasses the resolution of the 16-nm half-pitch technology generation and confirms that block copolymer lithography has significant potential for high-resolution lithography.

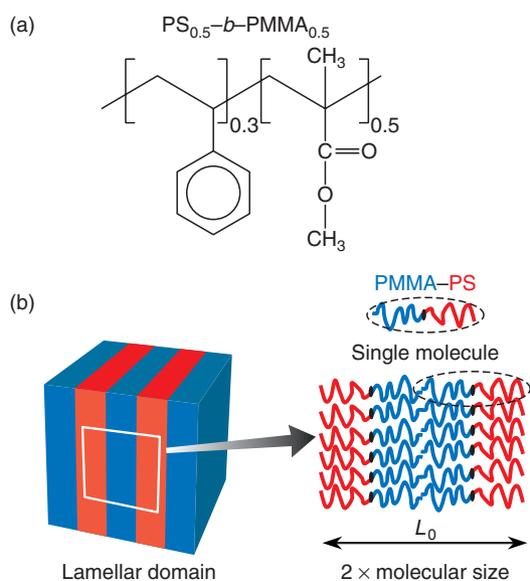


Fig. 7. (a) Chemical structure of PS-*b*-PMMA and (b) self-assembled lamellar structure.

3. Alignment of lateral lamellar domains in confined spaces between resist patterns

From the viewpoint of pattern transfer processes such as dry etching, lateral lamellar domains are preferable to in-plane cylindrical domains because in their case, an aspect ratio of at least 2 can be obtained. Kim *et al.* successfully demonstrated that the lamellar domain made of symmetric poly(styrene-*b*-methylmethacrylate) could be perfectly aligned on chemically nanopatterned substrates [4]. However, in this method, lateral lamellar domains having a pitch smaller than that of the chemically nanopatterned substrates formed by conventional lithography can never be aligned. To obtain a smaller pitch than the guide pattern, the graphoepitaxy technique should also be used to align the lateral lamellar domain. Therefore, we devised a new approach for graphoepitaxy using a resist pattern as the guide for alignment [8].

3.1 Materials

Diblock copolymers of PS and poly(methylmethacrylate) (PMMA), whose chemical structure is shown in Fig. 7(a), is the most suitable materials for block copolymer lithography. This is because the PS domain has a high dry-etching durability and the PMMA domain can be easily removed by exposure to deep-ultraviolet light and subsequent development. The self-assembly of the symmetric diblock copoly-

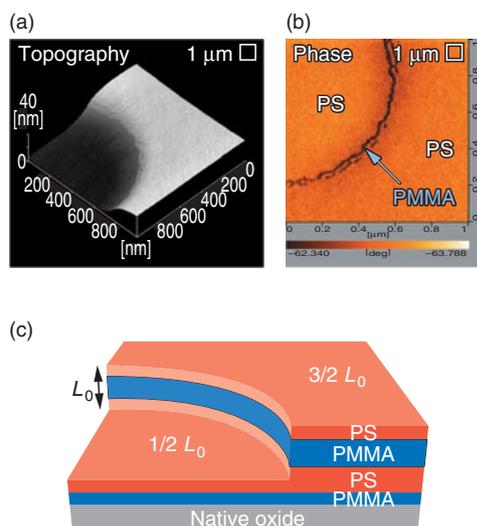


Fig. 8. Parallel lamellar structure: (a) AFM topographic image, (b) AFM phase image, and (c) schematic diagram.

mer made of PS and PMMA with the same molar ratio involves the formation of a lamellar structure composed of alternating stacked layers of PS and PMMA domains, as shown in Fig. 7(b). The lamellar period L_0 is twice the size of the molecule.

3.2 Self-assembly on a flat substrate

First, we investigated the behavior of the self-assembly of this diblock copolymer on a flat substrate. Generally, the parallel lamellar structure of this block copolymer, in which the lamellar interface is parallel to the substrate surface, is formed on the silicon substrate. This is because a PMMA block preferentially wets the substrate surface, which has a strong affinity with a PMMA block, whereas a PS block covers the free surface because its surface tension is lower than that of a PMMA block. As a result, the block copolymer film is separated into terraces during annealing. Moreover, the block thicknesses are quantized in odd half-integer multiples of L_0 , that is, $(2n + 1)L_0/2$, where n is an integer. In particular, at an incommensurate initial thickness, an island or hole structure is clearly formed with a step height of L_0 . Therefore, we only need to measure the height of these terraces to determine the value of L_0 .

A topographic AFM image of the region near the boundary between the $L_0/2$ and $3L_0/2$ terraces of the self-assembled structures on a flat surface is shown in Fig. 8(a). The figure shows that the terrace surfaces were completely flat and exhibited no morphology.

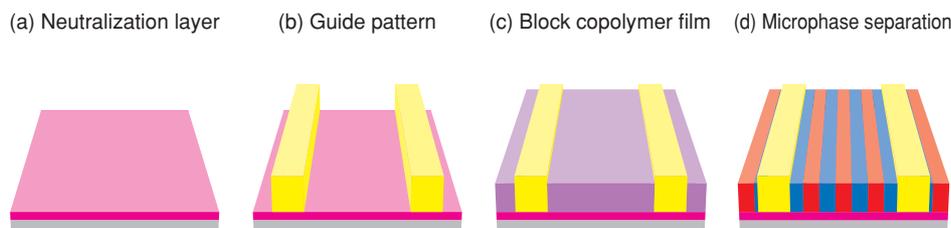


Fig. 9. Alignment process of lamellar domains.

The phase image corresponding to the topographic image in Fig. 8(a) is shown in Fig. 8(b). The bright and dark regions correspond to the PS and PMMA domains, respectively. It is clear that the PS domain covered all the terraces, regardless of whether they were $L_0/2$ or $3L_0/2$ terraces. On the other hand, the PMMA domain appeared only as a streak around the boundary of a step. This is good evidence that parallel lamellae do actually form, as illustrated in Fig. 8(c). From the topographic image, we determined that the average step height between the $L_0/2$ and $3L_0/2$ terraces was approximately 28 nm. This implies that this block copolymer should form L&S patterns with a pitch of 28 nm.

3.3 Alignment of lamellar domains

As described above, a parallel lamellar structure of this block copolymer, in which the lamellar interface is parallel to the substrate surface, was formed on the silicon substrate. To align the lamellar domains laterally, we should align the lamellar interface in two directions, i.e., perpendicular to the substrate surface and parallel to the sidewall surface of the guide pattern. To achieve this, it is essential to create a difference between the surface affinities on the substrate surface and the sidewall surface of the guide pattern; in other words, the surface free energies of both the surfaces must be controlled independently.

A schematic diagram of the alignment process in this approach is shown in Fig. 9. First, a neutralization layer [9] is formed on the substrate (Fig. 9(a)). Using a neutralization layer is an effective method of aligning the lamellae perpendicularly. It prevents the other block domains from preferentially wetting the substrate because the surface affinity of the neutralization layer is approximately half that of either domain of the block copolymer. This facilitates the perpendicular alignment of the lamellae to the substrate. We used a 10-nm-thick film of a cross-linked alternating copolymer of α -methyl styrene and methylmethacrylate as the neutralization layer.

Second, the resist pattern for the alignment guide is formed on the neutral surface (Fig. 9(b)). We used hydrogen silsesquioxane (HSQ), which is an EB negative-tone resist [10], as the resist pattern guide. An HSQ pattern with a width of 25 nm and height 40 nm was delineated by 100-kV EB lithography. Since the surface free energy of the HSQ pattern composed of siloxane is close to that of the PMMA domain, this domain preferentially wets the sidewall surface of the resist pattern guide. Therefore, lateral alignment of the lamellar domain could be achieved.

Third, the block copolymer film is formed over the resist pattern guide (Fig. 9(c)). We used symmetric poly(styrene-*b*-methylmethacrylate) with a molecular weight of 36,000 g/mol. A 30-nm-thick block copolymer film was prepared by spin coating on the substrates.

Finally, the film is baked to induce microphase separation (Fig. 9(d)). It is then annealed in an oven at 175°C under a N_2 atmosphere for 16 h.

AFM phase images of the microphase-separated domains near the boundary between a flat region and a guide pattern region are shown in Fig. 10. The left-hand image shows a magnified view of the flat region. Although the alignment here was random, a lateral lamellar domain had formed. This indicates that the lamellae were aligned vertically on the neutralization layer. The right-hand image shows a magnified view of the guide pattern regions. The arrows indicate the positions of the guide patterns with pitches in the range from 104 to 108 nm. In the confined space between the guide patterns, two dark PMMA domains had partially formed parallel to the guide pattern. Unfortunately, we could not observe a PMMA domain directly wetting the sidewall because there was a difference of approximately 10 nm in the height between the top of the pattern and the surface of the film. These images demonstrate that the HSQ patterns function as guides for lateral alignment.

We investigated how the degree of alignment depends on the pitch of the guide pattern. AFM phase

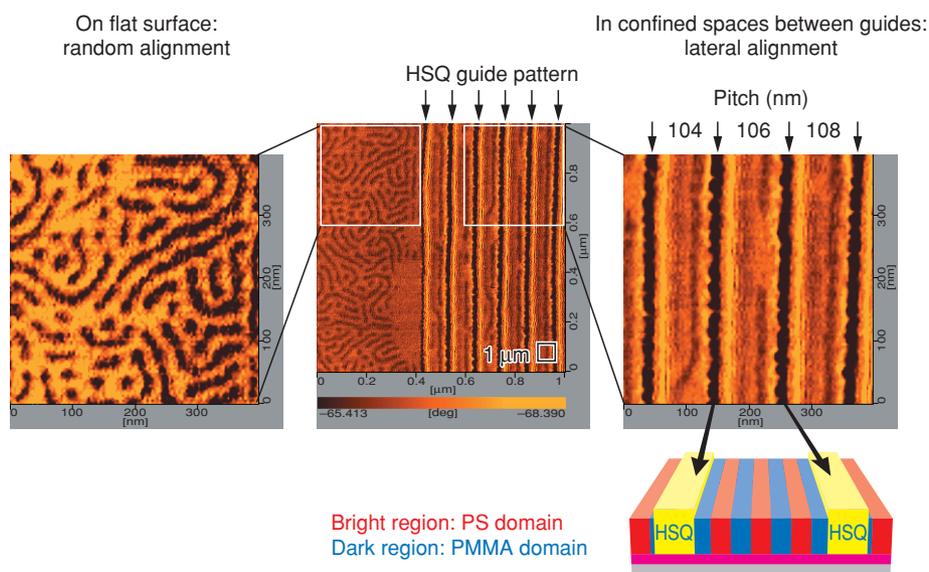


Fig. 10. Lateral alignment in confined spaces between guides.

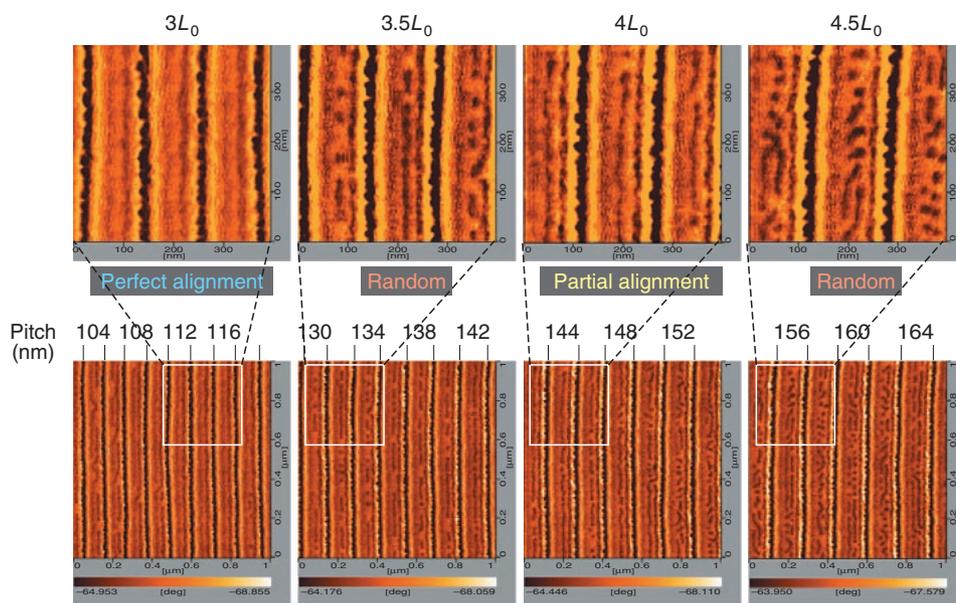


Fig. 11. Pitch dependence of self-assembly.

images of the microphase-separated domains in the confined spaces between the guide patterns with various pitches are shown in **Fig. 11**. The lower images are the original images covering a scan area of $1 \mu\text{m}$ square and the upper ones are magnified views covering an area 400 nm square. For pitches in the range from 112 to 116 nm, which corresponds to approximately $3L_0$, two PMMA domains were distinctly separated from each other. The repetition period of later-

al lamellar domains P_L was about 29 nm, which was obtained as $P_L = (P_g - W_g)/N$, where P_g is the pitch of the guide patterns (25 nm), and N is the repetition number. This value is consistent with the step height of parallel lamellar domains $L_0 = 28 \text{ nm}$. In addition, we can see that these domains were successively aligned over a distance of $1 \mu\text{m}$. For pitches in the range from 142 to 144 nm, which corresponds to approximately $4L_0$,

three PMMA domains were nearly aligned with each other; however, defects interrupted the continuity. On the other hand, at an incommensurate pitch such as $3.5L_0$ or $4.5L_0$ many defects appeared; consequently, disordered domains were formed.

This result indicates that the degree of alignment strongly depends on the pitch of the guide pattern and that lamellae with a thickness of at least $3L_0$ can be aligned laterally in the confined spaces between the guide patterns under the experimental conditions used in this study.

4. Conclusion

Block copolymer lithography is a powerful technique as a combined top-down/bottom-up approach to exceed the resolution limit of conventional top-down lithography. We have succeeded in the graphoepitaxy of a 23-nm-pitch cylindrical domain of asymmetric diblock copolymer PS-*b*-PEP inside microtrenches made of silicon dioxide. The value of this pitch is approximately equal to the current resolution limit of electron-beam lithography. We have also devised a new approach for the graphoepitaxy of the lamellar structures of a symmetric diblock copolymer PS-*b*-PMMA by using a resist pattern as a guide for alignment. We have successfully demonstrated lateral alignment of lamellae in confined spaces with a thickness of at least $3L_0$ between the straight guide patterns composed of an HSQ resist on a neutral surface. This approach has the significant advantage of differentiation between the surface affinities on the substrate surface and the sidewall surface of the guide pattern, which makes it possible to achieve strict control of the alignment of self-assembled domains. We believe that the combination of the artificial layout of the guide patterns and the best choice of polymer materials could lead to a new type of high-resolution lithographic technology.

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