Improved Block Copolymer Domain Dispersity on Chemical Patterns via Homopolymer-Blending and Molecular Transfer Printing

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ABSTRACT. Herein we have investigated the domain width distributions of block copolymers and their ternary blends after directed assembly on chemically patterned surfaces with and without density multiplication. On chemical patterns with density multiplication, the width of the interpolated block copolymer domains was bimodal. Once blended with the corresponding homopolymers, the block copolymers exhibited unimodal distributions of domain width due to the redistribution of homopolymers in the block copolymer domains. When the block copolymers were blended with hydroxyl-terminated homopolymers, the homopolymers with functional end-groups healed the chemical patterns and facilitated the formation of nanostructures with further improved domain width distributions. Lastly, it is demonstrated that the block copolymers achieved the most improved domain width distributions when directed to assemble without density multiplication on one-to-one chemical patterns generated by molecular transfer printing.

Graphical Abstract

Introduction

Microelectronics and high-density data storage media require patterned templates with a high resolution and well-controlled widths of the critical features, which are defined in terms of the critical dimensions (CD).[1-12] High resolution and well-controlled CD, however, are two competing attributes of patterned templates and improvements in one often come at the sacrifice of the other. Herein we describe a method for narrowing the block copolymer domain width distribution and achieving block copolymer patterns with both high resolution and well-controlled CD.

Previously, the directed assembly of block copolymers on one-to-one chemical patterns (*i.e.*, the ratio of the chemical pattern period, L_s , to the block copolymer period, L_o , is one-to-one) has shown that the block copolymers can form patterned templates with a well-controlled CD in registration with the underlying chemical patterns over arbitrarily large areas.[13-17] The highly controlled CD is thermodynamically governed by the block copolymers because the constituent blocks can equilibrate into microphase-separated domains and the domain size depends on the block copolymer molecular weight.[18-20] The pattern resolution, however, is limited because the feature density in the block copolymer templates is the same as that in the predefined chemical patterns. Later, block copolymer directed assembly with density multiplication was developed to enhance the pattern resolution by interpolating block copolymers on sparse topographic[21-26] or chemical patterns.[25-33] Density multiplication refers to the process of using a predefined pattern to direct the assembly of block copolymers into denser and smaller features than originally defined, and thus enhance the pattern resolution by a factor of n , where n is an integer no less than two. It is shown that block copolymer directed assembly with density

multiplication can partially heal the defects in the underlying chemical patterns,[28] and the resulting block copolymer nanostructures are often complex and three dimensional (3D).[34-38] To achieve defect-free density multiplication, it is required that (i) the thermodynamic energy of the defect-free structures is lower than that of metastable structures, otherwise the block copolymers can be kinetically trapped in metastable states [35, 36, 39-41] and (ii) the width and the wetting properties of the patterned stripes are controlled to an optimal condition to avoid the formation of complex 3D structures.[33-36, 42-45] Based on the previous experiments and simulations, the thermodynamic energies of defective and defect-free nanostructures from lamellae-forming block copolymers do not differ significantly from each other,[35, 36, 39, 40] and block copolymers can form complex structures depending on the boundary conditions.[33-35, 40, 46, 47] Therefore, in principle, the key to the directed assembly of high-quality block copolymer templates is to improve the boundary conditions defined by the underlying chemical patterns.

In this work we investigate the distributions of domain width of lamellar-forming block copolymers that are directed to assemble on chemical patterns. The widths of the interpolated block copolymer domains were bimodal after directed assembly on chemical patterns with density multiplication. To remove the bimodal distributions, the block copolymers were blended with the corresponding homopolymers, either with or without hydroxyl end groups. While the homopolymers without hydroxyl end groups improved the block copolymer domain width distribution after directed assembly, the blends of block copolymers and hydroxyl-terminated homopolymers provided patterned nanostructures with a higher quality. The hydroxyl-terminated homopolymers not only redistributed inside the block copolymers, but also modified the underlying chemical patterns and thus provide better boundary conditions for directed assembly.

To completely remove the bimodal domain distributions, we further employed molecular transfer printing (MTP) to transfer hydroxyl-terminated homopolymers and graft them onto a clean silicon substrate to generate one-to-one chemical patterns. The one-to-one chemical patterns created by MTP ensured that the block copolymers formed nanostructures in full registration with the underlying chemical patterns and provided simultaneous control over resolution and critical dimension.

Experimental Section

Materials: PS-*b*-PMMA ($M_n = 37\text{-}b\text{-}37$ and $52\text{-}b\text{-}52$ kg·mol⁻¹, denoted as SMMA1 and SMMA2, respectively, polydispersity index (PDI) = 1.04-1.06), PS-OH ($M_n = 6$ kg·mol⁻¹, PDI = 1.05), PMMA-OH ($M_n = 6$ kg·mol⁻¹, PDI=1.06), PS ($M_n = 6$ kg·mol⁻¹, PDI=1.04), and PMMA ($M_n = 6$ kg·mol⁻¹, PDI = 1.06) were purchased from Polymer Source, Inc. PMMA photoresist ($M_n = 950$ kg·mol⁻¹) was purchased from MicroChem, Inc. All solvents were purchased from Sigma-Aldrich and used as received.

Directed Assembly of Block Copolymers on Lithography-Defined Chemical Patterns with Density Multiplication: PS-OH was spin-coated on silicon substrates with native silicon oxide and annealed at 160 °C for 24 h to form a layer of ~5 nm-thick PS brush. The PS brush was subsequently covered with a ~50-nm-thick film of PMMA photoresist and patterned with electron beam lithography or x-ray interference lithography. The resulting patterns had periodic stripes with a spacing of $L_S = 90$ or 100 nm. The widths of the patterned stripes were controlled by the dose of electrons or x-rays delivered to the substrates. After development, the photoresist patterns were exposed to an oxygen plasma, which converted the unprotected PS brush to be preferentially wet by PMMA. The remaining photoresist was removed by repeated sonication in

chlorobenzene, resulting in lithography-defined chemical patterns for directed assembly of block copolymers and the ternary blends. All ternary blends had 90 wt.% block copolymers and 5 wt.% each the corresponding homopolymer. The film thicknesses were controlled to match the block copolymer natural period (L_0). The thin films of block copolymers and ternary blends were annealed at 230 °C for 3 days.

Directed Assembly of Block Copolymers on MTP Patterns: Firstly, thin films of block copolymers blended with hydroxyl-terminated homopolymers (SMMA2/PS-OH/PMMA-OH) were applied on lithography-defined chemical patterns. The thin films were subsequently covered with clean silicon substrates and annealed at 190 °C for 24 h. The hydroxyl-terminated homopolymers grafted to the clean substrates and formed MTP patterns with a feature density matching that of the block copolymers.[48] Afterwards, SMMA2 with a thickness of L_0 was spin-coated on the MTP patterns and annealed at 230 °C for 24 h.

Instrumentation and image analysis: The block copolymers and their ternary blends were imaged using SEM (LEO 1550VP) at an accelerating voltage of 1 kV. To analyze the domain width distribution, we used an automated program that was developed in-house to collect the line edges and analyze the statistics. First, SEM images were passed through a band filter to remove high and low frequency noises. Afterwards, the grayscale images were converted to black and white images using Otsu's method. The edges of the PS and PMMA domains were identified using algorithms provided by the image processing toolbox in MATLAB. Finally, the PS and PMMA domain widths were calculated by measuring the distance between the identified domain edges.

Results and Discussion

Two types of chemical patterns, *i.e.*, lithography-defined chemical patterns ($L_S=2L_o$) (Figure 1A) and MTP patterns ($L_S=L_o$) (Figure 1B), were used for the directed assembly of block copolymers and their ternary blends. The polymers used here included (a) pure block copolymers (Figure 1a), (b) ternary blends of block copolymers and homopolymers without hydroxyl end-groups (Figure 1b), and (c) ternary blends of block copolymers and homopolymers with hydroxyl end-groups (Figure 1c). The chemical patterns were prepared as follows. First, a ~5-nm-thick PS brush on a silicon wafer was converted to chemical patterns using lithographic and oxygen plasma processes. The chemical patterns had a period of $L_S=2L_o$ and consisted of alternating PS- and PMMA-wetting stripes. The width (W) of PMMA-wetting stripes was controlled to be either $W=L_o/2$ or $3L_o/2$. To multiply the feature density and enhance the pattern resolution by a factor of two, polymers (a), (b), and (c) were applied on the lithography-defined chemical patterns to form lamellae-like structures (Figure 1A). After directed assembly with density multiplication, polymers (c) were sandwiched and annealed between the patterned surface and another clean silicon substrate. Hydroxyl-terminated homopolymers were grafted onto the top silicon substrate to form an MTP chemical pattern with feature density twice that of the original lithography-defined chemical pattern, following the procedures in a previous report.[48] Once separated from the original chemical pattern and rinsed thoroughly, the MTP chemical pattern could be used to direct the assembly of block copolymers into patterned nanostructures with a high resolution (Figure 1B).

Figure 1. (A) Directed assembly of polymer systems of (a) PS-*b*-PMMA, (b) PS-*b*-PMMA/PS/PMMA ternary blends, and (c) PS-*b*-PMMA/PS-OH/PMMA-OH ternary blends on lithography-defined chemical patterns with density multiplication ($L_S = 2L_0$). PS brush (pink) on a Si substrate is covered with photoresist (PR) and subjected to lithography to create alternating PS-wetting (pink) and PMMA-wetting (light blue) stripes. When $W = L_0/2$, PMMA domains of polymers (a), (b), and (c) after directed assembly have different shapes and widths due to different boundary conditions. (B) Directed assembly of PS-*b*-PMMA on MTP-defined chemical patterns without density multiplication ($L_S = L_0$, $W = L_0/2$). PS-*b*-PMMA/PS-OH/PMMA-OH on a lithography-defined chemical pattern is covered with a clean Si substrate. PS-OH and PMMA-OH are transferred to the clean Si substrate to generate an MTP pattern, which is subsequently used for directed assembly of PS-*b*-PMMA without density multiplication.

We used scanning electron microscopy (SEM) to analyze the domain width distributions of PS-*b*-PMMA after directed assembly on lithography-defined chemical patterns and MTP patterns. SMMA1 had a natural period of $L_0 = 45.8$ nm and the lithography-defined chemical patterns had a period of $L_S = 90$ nm. The sparse chemical patterns directed the assembly of

SMMA1 into asymmetric vertical lamellae[35][35] and multiplied the feature density by a factor of two. On the lithography-defined chemical patterns with $L_S=2L_o$ and $W=L_o/2$ (Figure 2A top), some of the PMMA domains were in registration with the underlying PMMA-wetting stripes, and the rest were interpolated on the PS-wetting stripes. Due to the incompatibility between PMMA and the underneath PS-wetting stripes, the interpolated PMMA domains could not completely wet the substrate and were repelled away from the PS-wetting stripes to form 3D structures (Figure 2C top). Under the electron microscope the interpolated PMMA domains appeared wider than the non-interpolated ones. As a result, PMMA domains alternated between wide and narrow, which is in agreement with the molecular simulations and cross-sectional views of similar structures in the previous report.[36] Similarly, on the lithography-defined chemical patterns with $L_S=2L_o$ and $W=3L_o/2$ (Figure 2A middle), the interpolated PS domains on the PMMA-wetting stripes appeared wider than those non-interpolated ones on the PS-wetting stripes. The interpolated and non-interpolated PS domains showed different brightness. Different from the lithography-defined chemical patterns, the periodicity of the chemically patterned stripes in the MTP patterns matched that of the block copolymer features. PS and PMMA domains were in registration with the underlying PS- and PMMA-wetting stripes, respectively. After directed assembly, all domains exhibited similar widths and the domain width distributions were narrower than those of the block copolymer domains on chemical patterns with density multiplication (Figure 2A bottom).

Figure 2. (A) Top-down SEM images, (B) domain width distributions of PS (left) and PMMA (right), and (C) the corresponding proposed cross-sectional views of SMMA1 on chemical patterns: (Top) $W=L_o/2$, $L_S=2L_o$; (middle) $W=3L_o/2$, $L_S=2L_o$; and (bottom) $W=L_o/2$, $L_S=L_o$. The scale bar applies to all SEM images. Pink, PS-wetting surface; light blue, PMMA-wetting surface; red, PS; blue, PMMA.

We collected a population of more than 10,000 domain widths to analyze the width distributions. After directed assembly of SMMA1 with density multiplication on chemical patterns with $L_S=2L_o$ and $W=L_o/2$ (Figure 2 top row), all PS domains had the same boundary conditions and were monodisperse, while PMMA domains had two different boundary conditions (on either PMMA- or PS-wetting stripes) and revealed a bimodal distribution (Figure 2B top-right). Full width at half maximum (FWHM) was chosen to describe the characteristics of the bimodal peaks instead of the traditionally used *sigma*, which is accurate only for single-peak

Gaussian distributions and not applicable here. The PMMA domain width distribution had a peak at 19.0 nm and a FWHM of 8.0 nm. The bimodal distribution was fitted by two Gaussian distributions with their peaks at 18.5 and 24.3 nm, and FWHM of 4.7 and 5.8 nm, respectively. Similarly, on the chemical patterns with $L_S=2L_0$ and $W=3L_0/2$ (Figure 2 middle row) the PS domains had a bimodal distribution while the PMMA domains were unimodal. The PS domain width distribution (peak at 23.6 nm, FWHM=15.6 nm) was fitted by two Gaussian distributions with their peaks at 23.3 and 31.9 nm, and FWHM of 6.3 and 7.1 nm, respectively. We note that, on chemical patterns with either $W=L_0/2$ or $W=3L_0/2$, the two fitted Gaussian peaks had approximately the same integral area, indicating that half of the domains were interpolated and half were not. In contrast, on the MTP chemical patterns all PS and PMMA domains had the same boundary conditions and the bimodal distributions disappeared. The monodisperse PS and PMMA domains had their peaks at 25.6 and 19.4 nm, and the FWHMs were reduced to 4.6 and 4.3 nm, respectively (Figure 2B bottom).

We chose a large molecular weight SMMA2 to evaluate the improvement in pattern quality after adding homopolymers or using MTP. SMMA2 was blended with PS and PMMA or hydroxyl-terminated PS-OH and PMMA-OH. **Figure 3** shows the SEM images of SMMA2, SMMA2/PS/PMMA, and SMMA2/PS-OH/PMMA-OH after directed assembly with density multiplication on lithographically defined chemical patterns ($L_S=2L_0$ and $W=L_0/2$), as well as SMMA2 after directed assembly on MTP chemical patterns ($L_S=L_0$ and $W=L_0/2$). The corresponding PMMA domain width distributions are analyzed and summarized in **Figure 4**. For comparison, we normalized the height of all peaks and centered them at 21.4 nm. After directed assembly with density multiplication, the PMMA domains of pure SMMA2 had a broad distribution (FWHM=7.4 nm) with an apparent shoulder at high domain widths (Figure 4A).

Similar to SMMA1, the curve was fitted by two Gaussian distributions indicating that the PMMA domains were bimodal. When PS and PMMA homopolymers were added, the right shoulder disappeared and the domain width became monodisperse, resulting in a FWHM of 5.2 nm which indicates a narrower distribution than the pure block copolymers (Figure 4B). This phenomenon is attributed to the redistribution of homopolymers in the block copolymer domains to minimize the free energy penalty in defective structures, an effect similar to the redistribution of homopolymers in sharp corners that facilitates the formation unnatural structures as reported previously.[13, 29, 49] Although the PMMA domains appear to be bimodal in the SEM images, the domain width distributions were improved by the homopolymers. Although it is likely that there are two peaks that can be quantified, the two peaks are too close to each other to be distinguished and the overall distribution becomes unimodal. It is important that the molecular weight of the homopolymers is small in these blended systems so that they uniformly distribute in the block copolymer domains, otherwise defective structures arise.[20, 50] We note that hydroxyl-terminated homopolymers not only were redistributed in the domains, but also penetrated the initial brush and modified the surface[51] so that the underlying patterned stripes could be preferentially wetted by the polymers above them. Furthermore, the increased polymer brush density also contributed to the minimization of defective structures.[52] As a result, the hydroxyl-terminated homopolymers healed the boundary conditions for density multiplication and further narrowed the domain width distribution (FWHM = 4.8 nm, Figure 4C). After directed assembly on one-to-one chemical patterns from MTP, SMMA2 formed nanopatterns with highly controlled domain width distribution (FWHM = 4.1 nm, Figure 4D). The domain edges became smooth after PMMA removal by exposing to UV light and subsequently rinsing with acetic acid. The FWHM of the distribution of the widths of the resulting PMMA lines was

further narrowed down to 2.3 nm (Figure 4E). The narrow FWHM after removing the PMMA domains is a common phenomenon in lithographic etching. Due to isotropic etching, the etchant erodes the domain edges and smooths the line, resulting in a narrow distribution of domain width.

Figure 3. Top-down SEM images of (A) SMMA2, (B) SMMA2/PS/PMMA, and (C) SMMA2/PS-OH/PMMA-OH on chemical patterns with density multiplication ($W=L_o/2$, $L_S=2L_o$). The inset is a magnified view to illustrate PMMA bimodal distribution. Top-down SEM images of (D) SMMA2 on MTP patterns without density multiplication ($W=L_o/2$, $L_S=L_o$). (E) PMMA

was etched from (D) to illustrate the removal of bimodal distribution of PMMA domains. All scale bars, 100 nm.

Figure 4. PMMA domain width distributions after directed assembly of block copolymers and block copolymer-homopolymer ternary blends on chemical patterns. For comparison, the domain widths are centered at 21.4 nm and the counts are normalized. (A-E) correspond to the (A-E) in Figure 3. Although the PMMA domains in Figure 3(B) appeared to be non-uniform under scanning electron microscopy, the width distribution analysis shows a unimodal distribution.

The use of hydroxyl-terminated homopolymers and MTP chemical patterns is the key to improving block copolymer pattern quality. First, hydroxyl-terminated homopolymers not only redistribute in the block copolymer domains to facilitate the formation of thermodynamically favored nanostructures, but also chemically modify the substrate[51] and heal the boundary

conditions to accommodate the directed assembly of block copolymers. The healing effect of the hydroxyl-terminated homopolymers on the boundary conditions is in agreement with the previous reports on polymer brush insertion[51] and polymer molecular transfer printing,[48] in which the substrate can be modified with functional homopolymers even if there is an initial layer of polymer brush. Second, MTP patterns is an attractive way to provide one-to-one chemical patterns, which can improve boundary conditions for the directed assembly of block copolymers and enable better control over the nanostructures than in density multiplication. Previous reports have shown that the directed assembly of lamellar-forming block copolymers on one-to-one chemical patterns provide some tolerance to the pattern periodicity, stripe width, and line edge roughness.[15, 53, 54] Density multiplication, however, requires more stringent boundary conditions, otherwise complicated and unintended morphologies arise.[35, 36] The one-to-one chemical patterns generated from MTP avoid the process of density multiplication; they can direct the assembly of block copolymers into thermodynamically favored structures without ambiguity. Third, MTP patterns are advantageous over sparse patterns in terms of processing time. It is shown that density multiplication requires longer annealing times to reach equilibrium than directed assembly on one-to-one chemical patterns.[40, 55, 56] The MTP patterns eliminate the need for density multiplication and shorten the time for directed assembly.

Conclusion

We have investigated the domain width distributions of PS-*b*-PMMA and its ternary blends on chemically patterned surfaces with and without density multiplication. The interpolated domains were bimodal in domain widths, while the non-interpolated domains had widths that were always monodisperse. To mitigate the bimodal domain width distributions, homopolymers with and without hydroxyl-terminating groups were added to the block copolymers. Homopolymers

without hydroxyl-terminating groups redistributed in the block copolymer domains and partially improved the domain width distributions. Hydroxyl-terminated homopolymers healed the chemical pattern boundary conditions and further improved the domain width distributions. Besides homopolymers, molecular transfer printing was used to generate one-to-one chemical patterns and to significantly improve the block copolymer domain width distribution. Since metastable structures are typically formed in the course of block copolymer self-assembly,[57] the findings herein provide methods for removing metastable structures and improving the block copolymer pattern quality by adding functional homopolymers or introducing MTP into the process flow for directed assembly. These methods enable the fabrication of nanopatterned templates with high-density, high-resolution, and high-uniformity for semiconductor and magnetic data storage media.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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TOC.

Improved Domain Dispersity of Block Copolymers on Chemically Patterned Surfaces via Homopolymer-Blending and Molecular Transfer Printing

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