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Patterning at the 10 Nanometer Length Scale using a Strongly Segregating Block Copolymer Thin Film and Vapor Phase Infiltration of Inorganic Precursors

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We demonstrate the thin-film assembly of a strongly segregated block copolymer, vapor phase precursor incorporation and pattern transfer to silicon..

ABSTRACT:

1 In this work, we demonstrate the use of self-assembled thin films of the cylinder-forming block
2 copolymer poly(4-*tert*-butylstyrene-*block*-2-vinylpyridine) to pattern high density features at the
3 10 nm length scale. This material's large block interaction parameter facilitates pattern formation
4 at single-digit nanometer dimensions. This block copolymer's accessible order-disorder
5 transition temperature allows thermal annealing to drive the assembly of ordered 2-vinylpyridine
6 cylinders that can be selectively complexed with the organometallic precursor
7 trimethylaluminum. This unique chemistry converts organic 2-vinylpyridine cylinders into
8 alumina nanowires with diameters ranging from 8 to 11 nm, depending on the copolymer
9 molecular weight. Graphoepitaxy of this block copolymer aligns and registers sub-12 nm
10 diameter nanowires to larger-scale rectangular, curved, and circular features patterned by optical
11 lithography. The alumina nanowires function as a robust hard mask to withstand the conditions
12 required for patterning underlying silicon by plasma etch. We conclude with a discussion of
13 some of the challenges that arise with using block copolymers for patterning at sub-10 nm
14 feature sizes.

15
16 KEYWORDS: block copolymer, nanopatterning, block selective infiltration, metal oxides,
17 atomic layer deposition, graphoepitaxy, self-assembly

1 Introduction

2 Block copolymers (BCPs) have a distinctive ability to self-assemble into a variety of
3 morphologies (e.g. spheres, cylinders, gyroid, and lamellae) as a function of the volume fraction
4 of the blocks, the degree of polymerization, and the degree of incompatibility between blocks
5 (characterized by the Flory-Huggins interaction parameter, χ).¹⁻⁴ The use of BCPs in thin-film
6 form to create dense periodic arrays of nanostructures over large areas driven by thermal,^{5, 6}
7 solvent,⁷⁻⁹ chemical, electrical or magnetic forces¹⁰⁻¹² is referred to as directed self-assembly
8 (DSA) of BCPs.^{2, 13-15} The domain structure in thin-film then acts as a template for additive or
9 subtractive pattern transfer to the underlying substrate. As a result, DSA of BCPs has been
10 actively pursued for applications such as bit-patterned media,¹⁶ quantum dot arrays,¹⁷ and for
11 micro- and nano-electronics.^{13, 18} However, transferring the self-assembled BCP features on to a
12 substrate with high fidelity presents additional challenges, especially at the 10 nm length scale.<sup>19-
13 21</sup>

14 One of the most well studied BCP, poly(styrene-*block*-methyl methacrylate) [P(S-*b*-
15 MMA)] is limited to patterning features with periodicity larger than ~ 27 nm²² because of its
16 relatively small interaction parameter, $\chi = 0.03$ at 150 °C.^{8, 23} As a rule of thumb, we estimate
17 the minimum periodicity for a given BCP using the condition defining the copolymer order-
18 disorder transition:^{5, 24}

$$19 \quad \chi N \geq 10.5 \quad (1)$$

20 where N is the copolymer degree of polymerization. The relation between periodicity of
21 the block copolymer pattern (L_0) and degree of polymerization for strongly segregating polymers
22 ^{5, 6, 24} is given by:

$$23 \quad \frac{L_0}{a} = \chi^{1/6} N^{2/3} \quad (2)$$

where a is statistical monomer segment length of the order ~ 1 nm. Combining (1) and (2), reveals a relation:

$$\frac{L_0}{a} \sim \frac{10^{2/3}}{\sqrt{\chi}} \sim \frac{4.6}{\sqrt{\chi}} \quad (3)$$

from which we estimate a minimum $L_0 \sim 27$ nm for P(S-*b*-MMA). The condition (3) implies a minimum $\chi \sim 0.05$ K⁻¹ is required to pattern at sub-20 nm periodicities and sub-10 nm feature sizes. Examples of BCPs with potential for single-digit nanometer resolution include poly(styrene-*block*-2-vinylpyridine) [P(S-*b*-2VP)], poly(cyclohexylethylene-*block*-ethylene oxide), poly(cyclohexylethylene-*block*-methyl methacrylate), and poly(styrene-*block*-dimethylsiloxane).^{8, 25-27} However in order to facilitate pattern transfer in DSA applications, there must be a significant etch contrast between the two blocks of the BCP. Poly(styrene-*block*-dimethylsiloxane) [P(S-*b*-DMS)] (χ of 0.11 at 150 °C) has inherent etch selectivity between the two blocks and can scale to a $L_0 = 14$ nm.^{28, 29} The PDMS domain contains an inorganic siloxane group that can be converted to silicon oxide upon exposure to oxygen plasma.^{7, 8, 28, 29} However, this BCP requires solvent vapor annealing to promote assembly because it does not have a thermally accessible order-disorder temperature.^{8, 30-32} It is beneficial if processing of the material is accomplished with conventional methods such as thermal annealing in order to facilitate scale-up.³³ Gu et al. reported sub-15 nm silicon trenches using P(S-*b*-2VP) by preferentially swelling the VP domain with ethanol and using an optimized cryo-ICP etching to etch 2VP domains faster than the PS matrix.³⁴ Alternatively BCPs which have limited intrinsic etch contrast (e.g. P(S-*b*-2VP)) can be seeded with metal ions to yield metallic nanostructures upon plasma treatment either through a solution deposition or a vapor-phase deposition method.^{25, 35-37} In diluted acids the interaction between the protonated 2VP domains and the metal salts in solution leads to mineralization of the inorganic precursors and formation of metal

1 nanowires. Though metal nanowires in sub-10 nm have been seeded from solution into 2VP
2 domain, pattern transfer using these nanowires as masks has not been demonstrated.^{25, 35} The
3 integrity of the mask created by the inclusion of inorganic precursors from solution become more
4 of an issue in pattern transferring at these small length scales. Similarly, oxides such as iron
5 oxide and aluminum oxide have been seeded in solution into 4VP domains in poly(styrene-
6 *block*-4-vinylpyridine) where subsequent pattern transfer into silicon with sub-12 nm feature
7 sizes has been reported.³⁸

8 We have recently reported the synthesis and characterization of a series of compositions of
9 poly(4-*tert*-butylstyrene-*block*-2-vinylpyridine) [P(tBS-*b*-2VP)], which has $\chi = 0.11$ at 150 °C,
10 and can be thermally annealed to form ordered 2VP cylinders.³⁹ The increased hydrophobicity of
11 4-*tert*-butylstyrene²⁶ compared to styrene increases the χ of this material, calculated to be 1.5
12 times larger when compared to that of its parent, poly(styrene-*block*-(2-vinylpyridine)) [P(S-*b*-
13 2VP)].³⁹ We can leverage specific chemical interactions between vapor phase organometallic
14 precursors and functional groups to selectively infuse one copolymer block with a metal oxide.⁴⁰⁻
15 ⁴² This process, termed sequential infiltration synthesis (SIS), has been used to load aluminum
16 oxide and titanium oxide into the methyl methacrylate domains of P(S-*b*-MMA).^{43, 44} Compared
17 to solution phase infiltration methods the density of the oxide mask can be improved to obtain
18 high fidelity masks as there is no need to protonate the VP domains before precursor
19 incorporation and the amount of precursor incorporated can be controlled by the number of
20 cycles, the cycle time and the partial pressures of the precursor. Trimethylaluminum (TMA) and
21 titanium tetrachloride precursors were incorporated into a self-assembled cylinder-forming P(S-
22 *b*-MMA) film by coordinating with the carbonyl groups in the PMMA domains and nucleate the
23 growth of the oxides. Other groups have demonstrated SIS of alumina into lamellae-forming

P(S-*b*-MMA)⁴⁵ and transferred ~12 nm and ~5 nm wide features into silicon with varying degree of success.^{46, 47}

Here, we selectively infiltrate self-assembled 2VP cylinders through sequential vapor phase exposure to trimethylaluminum (TMA) and water,^{44, 48} transforming polymer patterns into alumina nanowire arrays with diameters in the range of 10 nm. The two P(tBS-*b*-2VP) block copolymers used here have molecular weights of 11.9K– 3.0K and 6.1K - 1.6K, which provide patterns with periodicities of $L_o = 23$ nm and 14 nm respectively. Based on the χ of this material, we use equation (3) to estimate an ultimate size limit of $L_0 = 14$ nm for P(tBS-*b*-2VP), which is slightly larger than the value we measure experimentally using x-ray diffraction ($L_0 = 9.6$ nm) and reflects the simplification of our estimate (3).^{1, 5, 24} The assumption that the statistical segment length is of the order of ~1 nm, is in fact an oversimplification, as most common coil polymers²³ have a smaller statistical segment length. Further, we examine the suitability of the P(tBS-*b*-2VP) material for patterning at sub-10 nm dimensions by transferring features into an underlying silicon layer by plasma etching.

Experimental section

Block Copolymer Thin Film Self-Assembly

Silicon wafers and topographically patterned silicon substrates were cleaned using piranha acid (7:3 H₂SO₄ : 30% H₂O₂, Caution! strongly oxidizing solution) at 75 °C for 20 min then washed copiously with DI water before being dried under air. Topographic trenches with widths varying between 200 nm and 5 μ m and depth ~25 nm were patterned by high-resolution lithography and etching.⁴⁹ Cylinder-forming P(tBS-*b*-2VP) (molecular weight 11.9K–3.0K, respectively, Dispersity = 1.04) with a 2VP minority composition were dissolved in toluene at

0.9 wt % concentration and then spin-coated onto the Si wafers, yielding a 24 nm thick film by ellipsometry (Rudolph Research Auto EL). The lower molecular weight P(tBS-*b*-2VP) (molecular weight 6.1K-1.6K) was dissolved in toluene at 0.6 wt % concentration and spin-coated onto the Si wafers to yield a 14 nm thick film. Lower polymer solution concentrations for both BCP molecular weights were created for the Si topologically patterned substrates. The substrates were annealed at 190 °C for 24 hours under vacuum followed by slow cooling to room temperature. Atomic force microscopy was performed using a Nanoscope III Multimode atomic force microscope (Digital Instruments).

The P2VP domains in P(tBS-*b*-2VP) thin films were selectively infiltrated with alumina in two different atomic layer deposition (ALD) systems. One reactor was a tube furnace (MTI, Co., model MSL-110-NT) operating with nitrogen gas at 40 sccm. The base pressure of the chamber was ~500 mTorr. Silicon substrates were exposed to three sequential cycles of trimethylaluminum for 15 s and water vapor for 0.1 s at a temperature of 85 °C and pressure > 2 Torr. In the other system (Cambridge Nanotech Savannah S100), substrates received three sequential exposures to trimethylaluminum and water vapor for 300 s each at 85 °C at pressures >5 Torr. We removed organic materials after metal oxide infiltration by oxygen plasma (20 W rf power, 100 mTorr O₂) for 2 min (March Plasma CS1701). Line analysis was conducted by measuring over 100 alumina nanowires to procure an average of the nanowire diameter using ImageJ software.

Pattern Transfer by Reactive Ion Etching

Inductively coupled plasma reactive ion etching (ICP-RIE) of silicon using the alumina nanowires as a mask was performed using an Oxford Instruments PlasmaLab 100 with a 100:100:25 sccm ratio of HBr, Cl₂, and O₂ gases (10 mTorr, 60 W rf power, 250 W ICP),

respectively, at room temperature.⁵⁰ The process was initiated with a brief breakthrough step using 20:5 ratio of BCl₃ and Cl₂ (10 mTorr, 100 W rf power, 800 W ICP) for 4-10 s in order to etch the native silicon oxide layer and any residual alumina between nanowires. Scanning electron microscope (SEM) images were acquired using LEO-1550 field-emission scanning electron microscope and a Hitachi S4800 SEM using accelerating voltages between 1 ~ 5 kV.

Results and Discussion

Block Copolymer Self-Assembly and Fidelity of their Transformation to Alumina Nanowires

We examined the challenges of replicating sub-10 nm BCP patterns by selectively incorporating aluminum oxide into the self-assembled 2VP domains of the cylinder-forming thin film of P(tBS-*b*-2VP) (mol wt. 11.9K - 3.0K) using sequential infiltration synthesis (Figure 1a).⁴⁴ Thermally annealing these films at 190 °C for 24 hours results in periodic 2VP cylinders oriented parallel to the substrate (Figure 1b). The polarity and lone pair of electrons in the pyridine groups in the 2VP domain allow TMA to specifically coordinate within that domain. Subsequent exposure of the film to water vapor results in conversion of TMA to alumina (ALO).⁴⁴ Finally, exposing infiltrated films to oxygen plasma RIE removes the PtBS and P2VP blocks and also likely oxidizes the ALO, leaving wires whose dimensions mimic that of the initial polymer template (Figures 1c-d, Figure S1 is a low magnification SEM of Figure 1d which shows uniform ALO nanowires over a large area without any dewetting structures). Previous reports have shown that the size of ALO domains can be altered by varying the vapor precursor exposure times and the partial pressure of the precursor.^{43, 44, 46} In addition, the number of cycles of TMA/H₂O also affects the final density and the width of the ALO nanowires.⁴⁴

A total TMA exposure time of 45 s (3 sequential cycles of 15 s each) yields patterns with average ALO nanowire diameters of 10 ± 1 nm (Figure 1c), but 15 min of TMA exposure (3 sequential cycles of 5 min each) saturates 2VP domains with the precursor, resulting in 12 ± 1 nm diameter ALO nanowire diameters (Figure 1d). Longer TMA exposure time increases the wire diameter without significantly broadening the distribution of wire widths for both samples as derived from the statistical analysis of SEM (Figure 1e).

Figure 1. (a) Schematic process of metal organic precursor incorporation into selective domains of a self-assembled BCP film, followed by oxygen plasma RIE. (b-e) Top-down SEM images of self-assembled cylinder-forming P(tBS-*b*-2VP) (mol wt. 11.9K - 3.0K). (b) After polymer film self-assembly (iodine stained for imaging contrast), (c) after a total TMA exposure dose of 45 s, reaction with water vapor, and O₂ RIE, (d) after a total TMA exposure dose of 15 min, reaction with water vapor, and O₂ RIE, and (e) histogram showing average nanowire diameter from 45 s total TMA exposure time (red) and 15 min total TMA exposure (blue).

In order to investigate the resolution limits for using vapor phase infiltration of metal oxides, we employed a lower molecular weight cylinder-forming P(tBS-*b*-2VP) (mol wt. 6.1K - 1.6K, Dispersity 1.04) with a center-to-center distance of 14 nm, with the potential to pattern ~8

1 nm feature sizes or smaller. Atomic force microscope (AFM) characterization of topography
 2 (Figure 2a) and phase (Figure 2b) of the self-assembled cylinders after thermal annealing
 3 confirm the in-plane cylindrical morphology. Infiltrating ALO into these higher-resolution
 4 P(tBS-*b*-2VP) patterns results in nanowires with 9 ± 1 nm average diameter. However, identical
 5 infiltration conditions to that of the higher molecular weight material produce patterns with
 6 distinctly different fidelity (Figure 2c and 2d). Total TMA exposure times of both 45 s and 15
 7 min result in nanowires with 9 nm average diameters, likely due to complete saturation of 2VP
 8 domains within 45 s. However, increased TMA exposure time creates significantly more bridges
 9 between adjacent ALO wires. These imperfect features could result from a non-optimal
 10 TMA/H₂O ratio during exposures, polymer pattern sidewall collapse during O₂ plasma removal
 11 of the organic, or possibly surface reconstruction during the sequential TMA/H₂O infiltration
 12 process, as these conditions can create an environment similar to that of solvent annealing, all of
 13 which are worthy of future study.

14
 15 Figure 2. AFM height (a) and phase (b) images of self-assembled cylinder-forming P(tBS-*b*-
 16 2VP) (mol wt. 6.1K-1.6K) after thermal annealing. Top-down SEM images (c) after a total

TMA exposure dose of 45 s, reaction with water vapor, and O₂ RIE, (d) after a total TMA exposure dose of 15 min, reaction with water vapor, and O₂ RIE.

Pattern Registration and Long-Range Ordering in Lithographically Defined Topographic Trenches

Alumina nanowires with 11 nm average diameter (45 s of total exposure) conform to the geometry of larger-scale, lithographically patterned rectangular, U-shaped, and circular trenches due to graphoepitaxy of the P(tBS-*b*-2VP) film (Figures 3a-c). We observed some interconnectivity between ALO wires (as shown in Figure 3b). Since, the infiltration temperature is 85 °C which is lower than the copolymer glass transition temperature, it is unlikely that the bridging is caused by thermally driven mobility of the polymer.³⁹

For the lower molecular weight composition (6.1K - 1.6K), the ALO nanowires with a 9 nm average diameter (45 s of total exposure) show qualitatively less alignment to larger-scale topographic patterns as well as increased bridging between them (Figures 3d-f). We surmise that the low molecular weight BCP can be more sensitive to processing conditions such as the film thickness not meeting the commensurability requirements inside the graphoepitaxial trench.^{51, 52} Figure 3d and Figure 3e show that the cylinders in the immediate vicinity to the trench walls are aligned parallel to the trench walls compared to those in the center of the trench that are aligned perpendicularly to the trench walls. This effect is most likely from the initial flow during the polymer deposition and annealing as well as having the film thickness inside the trench greater than one monolayer.⁵¹⁻⁵³ In general it is challenging to control the thickness of low-molecular weight BCPs in graphoepitaxial trenches (see Figure S2) to result in a monolayer of cylinders. Since the BCP is significantly lower in molecular weight and confined within very large trenches

compared to the size of the microdomains, the kinetics of microdomain alignment could be improved with additional annealing or in narrower trenches.^{52, 54} Despite the lower fidelity of the ALO cylinders for this particular molecular weight and composition, we still observe some degree of alignment suggesting that with further study and optimization this BCP can be utilized in templated substrates.

Figure 3. SEM images of 11 nm aligned ALO nanowires (a-c) with long-range ordering within ~20 nm deep trenches on silicon: (a) U-shaped channels with width of 410 nm, (b) rectangular channels of 200 nm, and (c) circular trench with diameter of 510 nm. SEM images of 9 nm aligned ALO nanowires (d-f) within ~20 nm deep trenches on silicon: (d) rectangular channel with width of 410 nm, (e) narrower rectangular channels with 250 nm width, and (f) circular trench with diameter of 510 nm.

Pattern Transfer of Alumina Nanowire Arrays to Silicon by Reactive Ion Etch

Alumina nanowires formed by precursor infiltration into self-assembled P(tBS-*b*-2VP) thin films are suitable for high-resolution patterning at 10 nm dimensions by reactive plasma etch. Here, we transfer the ALO nanowire patterns to the underlying silicon using two sequential inductively-coupled plasma reactive-ion etch (ICP-RIE) steps, the first one clears residual material from between the nanowires and breaks-through the top oxide layer using a mixed ratio of BCl₃ and Cl₂ gases. The second step involves etching ~50 nm of Si using a mixture of HBr, Cl₂, and O₂ gases.⁵⁰ Careful control of the initial ‘breakthrough’ step limits the amount of ALO nanowires consumed during this process. The silicon etch produces patterned nanostructures with nearly vertical sidewalls (sidewall angle of ~77°), due to the slow lateral etch rate of this process (Figure 4).⁵⁰ Alumina nanowires formed from shorter total TMA vapor exposures times (45 s) were narrower, with better-defined space between wires, and therefore resulted in higher fidelity pattern transfer (Figure 4a). Longer total TMA exposure times (15 min) result in wider ALO wires and, we presume more ALO between wires, which in this experiment yielded lower fidelity transfer into the silicon (Figure 4b). Low magnification SEM images can be found in the SI section as FigureS3.

Figure 4. SEM cross-sectional images of pattern transfer into ~50 nm of silicon by plasma etch. (a) ALO nanowire mask formed by 45 s total TMA exposure (b) ALO nanowire mask formed by 15 min of TMA exposure.

Alumina wires formed from self-assembly of the lower molecular weight P(tBS-*b*-2VP) (6.1K- 1.6K) have average diameters of 9 nm, and are also robust enough for plasma etch pattern transfer to silicon. Cross-sectional SEM images of the etch structures reveal that the <10 nm thick ALO etch mask withstands etching 50 nm of silicon (Figures 5a, low magnification SEM images can be found in the SI section as FigureS4). The resulting trapezoidal silicon wires have a 9 nm width at the top and flare to ~20 nm at the bottom. Because these ALO films are < 15 nm thick, it is important to minimize the initial etch breakthrough step to preserve as much mask as possible. For example, doubling the breakthrough etch time from 4 s to 8 s results in insufficient remaining ALO mask, with resulting increased etch non-uniformity (Figure 5b). Recently, Ghoshal et al. reported the use of a solvent annealed poly(styrene-*block*-ethylene oxide) thin film to fabricate a 4 nm thick iron oxide nanowire hard mask, which was subsequently used to etch into silicon to create low aspect ratio features. Their studies also showed discontinuity between the wires likely due to over etching of their hard mask or mechanical weakness of the samples.⁵⁵ With the SIS combined with a thermally processable highly phase segregated polymer, we have shown that the integrity of the hard mask can be substantially improved to pattern transfer high aspect ratio features into silicon.

Figure 5. SEM cross-sectioned samples demonstrating pattern transferring ~50 nm into Si substrate from BCP/ALO nanowire template with (a) short oxide breakthrough (4 s etch) (b) extended oxide breakthrough exhibiting pattern degradation (8 s etch).

Conclusions

We have demonstrated the ability of a self-assembled, cylinder-forming P(tBS-*b*-2VP) to form uniform patterns at the 10 nm length scale by thermal annealing, due to its large block interaction parameter and thermally accessible order-disorder transition temperature. The copolymer patterns were transformed to alumina nanowires by vapor phase infiltration, which serves as a hard mask to transfer to silicon by reactive ion etch. These studies underline the utility of combining organometallic precursor infiltration with soft templates for pattern transfer from high- χ BCPs, as well as the challenges associated with fabricating sub-10 nm patterns from these hybrid templates.

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Notes

The authors declare no competing financial interest.

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3

Supporting Information

Patterning at the 10 Nanometer Length Scale using a Strongly Segregating Block Copolymer Thin Film and Vapor Phase Infiltration of Inorganic Precursors.

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Figure S1. Low magnification SEM image of the ALO nanowires showing no island/hole structures.

Figure S2. SEM image of P(tBS-*b*-2VP) (mol wt. 6.1K-1.6K) in a 410 nm rectangular shaped trench showing a change in microdomain alignment. This can be explained by the thickness of the film being one monolayer in the top portion then a region of bilayer of cylinders in the bottom half. This is consistent with the report by Hammond et al. and Mishra et al. where a monolayer of a 2VP cylinder forming PS-*b*-2VP inside a graphoepitaxial trench displayed a lower degree of alignment within a trench compared to a bilayer. The authors explain that it is most likely because a bilayer film is closer to the bulk ODT of the BCP, whereas a monolayer exhibits a depression in ODT.[1, 2].

Figure S3. Low magnification SEM image of 11.9K-3.0K pattern transferred film.

Figure S4. Low magnification SEM image of 6.1K-1.6K pattern transferred film.

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