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Assembly of sub-10 nm block copolymer patterns with mixed morphology and period using electron irradiation and solvent annealing

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Abstract

Block copolymer self-assembly generates patterns with periodicity in the ~ 10 – 100 nm range, and is increasingly recognised as a route to lithographic patterning beyond the resolution of photolithography. Block copolymers naturally produce periodic patterns with a morphology and length-scale determined by the molecular architecture, and considerable research has been carried out to extend the range of patterns that can be produced from a given block copolymer, but the ability to control the period of the pattern over a wide range and to achieve complex structures with mixed morphologies from a given block copolymer is limited. Here we show how patterns consisting of coexisting sub-10 nm spheres and cylinders and sphere patterns with a range of periods can be created using a combination of serial solvent anneal processes and electron-beam irradiation of selected areas of a film of poly(styrene-block-dimethylsiloxane). These techniques extend the capabilities of block copolymer lithography, enabling complex aperiodic nanoscale patterns to be formed from a single block copolymer thin film.

Keywords: block copolymer, mixed morphology, templated self-assembly, solvent annealing, electron beam, cross-linking, polystyrene-b-polydimethylsiloxane, nanolithography
Block copolymers spontaneously microphase-separate to form periodic features with a length scale of ~10 nm and above\textsuperscript{1,2}. Thin films of these materials can be used as masks for nanolithography and for device fabrication\textsuperscript{3-6}. However, block copolymer self-assembly is generally limited to forming simple patterns such as arrays of dots or lines, determined by the volume fraction of the blocks and the processing conditions, and it is desirable to be able to modify both the period of the patterns and their morphology to form more complex structures useful in devices. Various methods have been suggested to control the orientation,\textsuperscript{7-13} registration\textsuperscript{14,15} and period\textsuperscript{16-18} of microdomains in block copolymer films. The period of well ordered patterns of poly(styrene-\textit{block}-dimethylsiloxane) (PS-\textit{b}-PDMS) or poly(styrene-\textit{block}-methylmethacrylate) (PS-\textit{b}-PMMA) can be varied by up to ~10\% by use of an incommensurate template to strain the microdomain array\textsuperscript{16,17} or by changing the annealing conditions.\textsuperscript{18} Patterns such as isolated lines have been achieved by changing the orientation of lamellar or cylindrical microdomains from out-of-plane to in-plane in specific areas of the substrate using chemical patterns\textsuperscript{7-10} or UV irradiation-induced orientation changes,\textsuperscript{11} and aperiodic patterns such as jogs and zigzags can be templated by chemical patterns\textsuperscript{14} or sparse topographic templates.\textsuperscript{15} In these examples the block copolymer film retains its morphology (i.e. cylinders or lamellae) but the microdomain orientation is locally varied, e.g from in-plane to out-of-plane. Varying the morphology within a given block copolymer film, e.g. from spheres to cylinders, can facilitate production of more complex patterns, but requires a process in which different processing conditions are applied to different regions of the film.

In this article, we present a strategy for the self-assembly of high resolution complex patterns with sub-10 nm features consisting of both lines and dots as well as dot patterns with different periods formed in the same block copolymer film. This is based on a process developed by
Bosworth et al. which formed coexisting line and dot patterns in a block copolymer film by a combination of solvent annealing and cross-linking using UV or electron-beam irradiation,\(^1^9\) forming 95 nm wide regions (~ 4 microdomain periods) of spherical morphology within an untemplated cylindrical-morphology film. In the present article, highly ordered mixed-morphology patterns and patterns with a variation in period and microdomain diameter were made from a PS-\(b\)-PDMS block copolymer film by sequential solvent annealing and electron-beam irradiation as described schematically in Figure 1. The microdomains were finally revealed by etching the film in an oxygen plasma, which removes the PS and oxidizes the PDMS. This approach was used to create isolated or clustered 9 nm wide lines made from oxidized PDMS surrounded by dots; combinations of dots, lines and empty spaces; and dots with a period that varies by ~20\%. Furthermore, by applying this process to a film on a substrate patterned with a sparse array of posts, the long range order of line and dot arrays can be controlled simultaneously within specific substrate areas.

We have previously investigated PS-\(b\)-PDMS block copolymer thin films, which show several advantages for lithographic applications, including a high Flory-Huggins parameter which enables formation of small period patterns with low line-edge roughness, high etch selectivity between PS and PDMS which facilitates pattern transfer,\(^1^5,1^6,1^8,2^0-2^2\) and registration of features using trenches\(^1^6,1^8,2^1,2^2\) or posts.\(^1^5,2^0\) However, PS-\(b\)-PDMS also demonstrates cross-linking under electron-beam irradiation.\(^2^3\) This process can be used on polymeric materials to tune their mechanical, thermal, chemical and other properties by cross-linking or degradation of the polymer chains, and has for example been applied to PS-\(b\)-PMMA block copolymer films to modify their topography.\(^2^4\) In the case of PS-\(b\)-PDMS, the cross-linking yield \(G_x\) per 100 eV of energy deposited in the material is much higher than the scission yield \(G_s\) (\(G_x,\text{PS} = 0.02\) to 0.05, \(G_s,\text{PS} = 0.006\) to 0.02, \(G_x,\text{PDMS} = 0.002\) to 0.01, \(G_s,\text{PDMS} = 0.0001\) to 0.01).
$G_{x,\text{PDMS}} = 2.3$ whereas $G_{x,\text{PS}} = 0.01$ to 0.02, and $G_{x,\text{PDMSS}} = 0$).\textsuperscript{23} This observation suggests that electron-beam irradiation can render the PDMS microdomains of a self-assembled PS-b-PDMS block copolymer stable against subsequent anneal processes which change the morphology of the unirradiated regions.

Solvent annealing is a particularly attractive process to facilitate microphase separation in a block copolymer because the morphology of the microdomains is determined by the selectivity of the solvent molecules between the blocks, and different solvents can therefore produce a range of morphologies which differ from the bulk morphology predicted from the block volume fractions.\textsuperscript{16,25,26} We found previously that films of 16 kg mol\textsuperscript{-1} PS-b-PDMS (11kg/mol-5kg/mol, with a volume fraction of PS, $f_{\text{PS}} = 0.67$, and a bulk cylindrical morphology) show different morphologies upon annealing in acetone and DMF vapors, as seen in Figure 2(a) and (b). Table S1 in the supporting information shows that an acetone solvent vapor swells PS homopolymer films slightly more than PDMS homopolymer films, leading to cylindrical morphology in the swelled block copolymer, but a DMF vapor swells PS significantly more than PDMS producing a spherical morphology. It is notable that the morphology could be switched repeatedly between sphere and cylinder by successive DMF and acetone solvent anneals. Morphological reversibility has also been noted in other polymer/solvent systems.\textsuperscript{19}

We first describe how electron-beam irradiation can be used to stabilize the morphology of the block copolymer. 16 kg mol\textsuperscript{-1} PS-b-PDMS thin films were annealed in acetone or DMF, then irradiated with a 10 kV electron-beam at doses from 10 $\mu$C cm\textsuperscript{-2} (0.624 electrons nm\textsuperscript{-2}) to 100 $\mu$C cm\textsuperscript{-2} (6.24 electrons nm\textsuperscript{-2}), and finally annealed in the other solvent (Figure 2(c)-2(h)). Higher doses (above ~ 30 $\mu$C cm\textsuperscript{-2}) preserved the morphology obtained from the first solvent. At low
doses the film morphology was determined by the second solvent, but an increase in the center-to-center spacing and the diameter of the microdomains was observed. These results are quantified in Fig. 2(i), which presents the period, size and aspect ratio (=length/width) of features formed in the acetone/electron-beam/DMF process as a function of dose for PS-\(b\)-PDMS on two different brush layers. Even a low dose (~ 1 \(\mu\)C cm\(^{-2}\)) led to a significant change in sphere periodicity and size, and an increase of 20 \% in period was found at 16 \(\mu\)C cm\(^{-2}\). Above 20 \(\mu\)C cm\(^{-2}\), coexisting spheres and short cylinders were observed, and doses over 40 \(\mu\)C cm\(^{-2}\) preserved the original cylindrical morphology and periodicity. A complementary behavior was found for the DMF/electron-beam/acetone anneal with a change of 15 \% in the cylinder period at low doses.

The change in period indicates considerable sensitivity of the block copolymer to low doses of electron-beam irradiation, which produces a small amount of cross-linking between PDMS chains. During the swelling process, cross-linked polymer chains provide an entropic resistance to expansion of the polymer film network, and thus, cross-linked films swelled less than uncross-linked polymer films.\(^{27}\) Controlling the amount of swelling can affect both the block copolymer microdomain morphology and the period.\(^{18}\) Cross-linking is also expected to affect polydispersity, forming molecules similar to a PS-PDMS-PS triblock copolymer with double the molecular weight of the original diblock copolymer. Simulation\(^{28}\) and experimental\(^{29}\) studies comparing an \(A_nB_{2m}A_n\) triblock copolymer with an \(A_nB_m\) diblock copolymer show that the domain spacing of the \(A_nB_{2m}A_n\) is 5 – 10 \% larger than that of the \(A_nB_m\). This effect can also contribute to an increase in period with cross-linking.

These considerations explain why selective irradiation of regions of the film can produce patterns with a variation in microdomain period or with coexisting spheres and cylinders. Figure
S1 in the Supplementary Information shows examples of films which were solvent annealed, then 3 µm wide rectangles and single-pixel lines were exposed to e-beam irradiation at different doses, followed by a second solvent anneal. For areal exposure doses of 100 µC cm$^{-2}$, or linear doses of 500 pC cm$^{-1}$, sufficient to preserve the morphology created by the first solvent, the boundary between the irradiated and unirradiated regions is distinct, but the features in the unirradiated regions close to the boundary have a larger center-center spacing (e.g. 26.6 nm for spheres) than that (21.6 nm) found far from the boundary. However, for higher doses of 316 and 1000 µC cm$^{-2}$, or a linear dose of 5000 pC cm$^{-1}$, the morphological transition is more diffuse and the unirradiated regions preserved the morphology from the first solvent within ~ 100 nm or more from the boundary.

The electron beam itself has a width of only 5 nm, so the changes in the polymer outside the directly irradiated region are attributed to backscattering of the electron beam in the sample. To quantify this, we plot the period of spheres as a function of distance away from the boundary in Figure 3(a). By comparing this with the data of Fig. 2(i), a calibration of the backscattered dose can be obtained as a function of distance away from the interface, Figure 3(b). This is similar to the calculated backscattered dose profile of HSQ, a well known electron-beam resist material. Unlike HSQ and other resists, the block copolymer has a very low threshold for exposure and is sensitive to very small electron-beam doses. Spreading of the cross-linked pattern dimensions compared to the size of the exposed area was observed in ref. 19.

The best quality of the boundary between spheres and cylinders was obtained using an areal dose of 100 µC cm$^{-2}$ (6.24 electrons nm$^{-2}$) as in Fig. 3 or a linear dose of 200 pC cm$^{-1}$ (125 electrons nm$^{-1}$) in the acetone/electron-beam/DMF process sequence. These conditions were
selected to demonstrate high resolution dual phase patterns in a single film. Figure 4(a) shows a single 9 nm wide line surrounded by hexagonally packed spheres, formed by writing a narrow electron-beam line parallel to aligned block copolymer cylinders formed by the acetone anneal within a topographic template. Figure 4(b) shows an array of 30 nm long parallel line segments surrounded by close-packed dots, made by writing a 30 nm wide electron-beam pattern perpendicular to the cylinder length. Line segments are of interest in SRAM fabrication as well as for patterned magnetic media with a bit aspect ratio exceeding 1. A demonstration of the MIT logo with 80 nm wide characters is shown in Figure 4(c). Figure 4(d) shows a pattern including lines, dots and unpatterned regions simultaneously. The featureless region represents part of the substrate coated with an antireflective coating (ARC) prior to spin-coating the block copolymer. The ARC is removed by the oxygen plasma at the same time as the PS blocks. Low-dose irradiation was also used to produce patterns with a modulation in periodicity and sphere size. In Figure 4(e) a 400 nm × 200 nm rectangular area A was irradiated at 20 μC cm², giving larger diameter and period spheres surrounded by smaller sized spheres in the unirradiated region, area B. Figure 4(f) shows a 100 nm × 100 nm area A irradiated at 40 μC cm² to form line segments, an area B irradiated at 20 μC cm² to form larger spheres, and smaller spheres in unirradiated area C.

Finally, we demonstrate a combination of dot and line patterns templated by hydrogen silsesquioxane posts written by electron-beam lithography. Sparse arrays of posts have been used previously to impose long range order and to create complex patterns in block copolymers with either spherical or cylindrical morphologies. Here we extend this process to templating of both lines and dots simultaneously, as shown in Figure 5. The 9 nm wide posts formed a
rectangular array with period $L_x = 45$ nm and $L_y = 78$ nm. These spacings were chosen to be commensurate with the 18 nm period of the in-plane cylinders and with a 26 nm center-to-center spacing (22.5 nm row spacing) of close-packed spheres. The cylinders formed a (1,3) array oriented at 23.4° to the x-axis of the post array within the irradiated area as expected from the commensurability condition. Immediately adjacent to the cylindrical area, the sphere period exceeded the commensurate condition, but further from the interface the spheres formed an ordered lattice with its close-packed direction aligned with the y-axis of the post lattice. In another example, Figure 5(b), an isolated line was formed by electron-beam irradiation at a dose of 500 pC cm$^{-1}$ surrounded by a sphere and post array. The spheres occupy the spaces between posts with a period of $L_x = 48$ nm and $L_y = 42$ nm, though the structure shows defects because the post spacing is incommensurate with the sphere array.

In summary, complex patterns consisting of coexisting ordered lines and dots with sub-10 nm dimensions or dots with varying period in a single block copolymer film were created by sequential solvent annealing and electron-beam irradiation to stabilize particular patterns in selected regions of the film, combined with topographical templating using HSQ posts or removable sidewall templates. The combination of these techniques offers the possibility of forming a wide range of aperiodic pattern geometries useful for devices including single lines or ordered line segments. An even wider range of geometrical arrangements including combinations of lamellae, perforated lamellae, cylinders with different linewidths and spheres may be anticipated from higher-$\chi$ polymers such as P2VP-$b$-PDMS successively annealed in several solvents of different selectivity or vapor pressure. Changes in the period and morphology result from cross-linking of the polymer, which is sensitive to very low doses of electrons. This work
significantly extends the ability of block copolymer lithography to produce patterns essential for nanoscale device fabrication.

**Methods. Substrate and Template Preparation.** Smooth oxidized Si wafers were cleaned in piranha solution (3:1 sulfuric acid and hydrogen peroxide solution by volume) at 120°C for 20 min then spin-coated with hydroxyl-terminated PDMS (0.8 kg mol\(^{-1}\), Polymer Source) or hydroxyl-terminated polyethylene oxide (PEO, 5 kg mol\(^{-1}\), Polymer Source) solution in toluene, annealed at 170°C overnight in vacuum, then rinsed in toluene. Removable sidewall templates were made by spin-coating 30 nm thickness of BARL-i antireflective coating (AZ Electronic Materials) and patterning it to form trenches 25 nm deep and 1.5 \(\mu\)m wide using oxygen reactive ion etching (RIE). The patterns were defined in a Shipley 1813 photoresist overlayer which was exposed with a UV light source (Tamarack Scientific Co., Inc.) through a Cr mask. The post arrays were prepared by electron-beam lithography with negative electron-beam resist, hydrogen silsesquioxane (HSQ) (1% solution, FOx, Dow Corning) on a cleaned Si wafer. The HSQ was exposed using a Raith 150 electron-beam lithography tool at 30 kV then developed by agitating in a 0.25M NaOH/0.7M NaCl aqueous solution for 1 min at room temperature.\(^{33}\) The posts were 19 nm tall and 9 nm wide. These template substrates were also coated by a PDMS brush as described above.

**Self-Assembly of Block Copolymer Thin Films and Electron-Beam Irradiation.** PS-\(b\)-PDMS diblock copolymer (16 kg mol\(^{-1}\), PDI = 1.08, \(f_{PS} = 0.69\)) was purchased from Polymer Source, Inc. 0.7 wt % PS-\(b\)-PDMS solution dissolved in cyclohexane was spin-coated at 6000 rpm on PDMS brush coated flat or patterned substrates. Solvent annealing was carried out at
room temperature using 1 ml of acetone in a 9.3 ml volume of glass chamber with a controlled leak until the solvent was fully evaporated, or 1 ml of DMF for 3 hrs. Electron-beam irradiation was performed in a Raith 150 electron-beam lithography tool at 10 kV. To reveal the microdomains, an etch process consisting of 2 s CF$_4$ RIE followed by 12 s O$_2$ plasma etching was used to first remove the surface layer of PDMS, then to remove the PS while oxidizing the PDMS microdomains.

**Characterization.** The morphology of the block copolymer patterns was observed by Field Emission-Scanning Electron Microscope (FE-SEM, Zeiss/Leo Gemini 982) operated at 5 kV and Raith 150 SEM operated at 10 kV. The samples were coated with a thin Au-Pd alloy film in order to avoid charging effects. To measure the thickness of films of PS homopolymer (1350 kg mol$^{-1}$, Polymer Source Inc.), PDMS homopolymer (100,000 cSt, 139 kg mol$^{-1}$ Aldrich Inc.) and block copolymer film during solvent annealing, a Filmetrics F20-UV (Filmetrics Inc.) instrument was used through a quartz window attached to the solvent annealing chamber. The original film thickness before solvent annealing was approximately 70 nm.

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**Supporting Information Available.** Additional information showing swelling ratio of polymer films during solvent annealing and the effects of selective irradiation of regions of polymer films. This material is available free of charge via Internet at http://pubs.acs.org.
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Figure captions

**FIGURE 1.** Schematics of the formation of dual morphologies in PS-\(b\)-PDMS block copolymer thin films resulting from solvent annealing, electron-beam irradiation and a subsequent solvent anneal. The PS-\(b\)-PDMS film forms a cylinder morphology in acetone and spheres in DMF vapor. After a first anneal the films were selectively irradiated with a electron-beam, then annealed in the other solvent to change the morphology in the unirradiated regions. The orientation of the sphere or cylinder array is determined by a topographical template (not shown) enabling the electron beam irradiation to be aligned with the microdomains.

**FIGURE 2.** Effects of electron-beam irradiation with sequential solvent annealing on morphology. SEM images of PS-\(b\)-PDMS block copolymer films annealed in (a) acetone to form cylindrical line patterns and (b) DMF solvent vapors for spherical dot patterns. (c-h) Solvent annealed films exposed to electron-beam followed by annealing in a different solvent. In acetone/electron-beam/DMF treated films: (c) 10 \(\mu\)C cm\(^{-2}\) was ineffective at cross-linking the PDMS and the film formed spheres; (e) 31.6 \(\mu\)C cm\(^{-2}\) caused partial cross-linking leading to the coexistence of short cylinders and spheres; (g) 100 \(\mu\)C cm\(^{-2}\) caused sufficient cross-linking to maintain the cylindrical morphology of acetone even after the DMF anneal. DMF/electron-beam/acetone treated samples showed a similar trend: (d) 10 \(\mu\)C cm\(^{-2}\) dose, spheres; (f) 31.6 \(\mu\)C cm\(^{-2}\), short cylinders and spheres; (h) 100 \(\mu\)C cm\(^{-2}\), spheres. (i) Principal domain spacing, sphere size, aspect ratio (length/width) and morphology of acetone/electron-beam/DMF treated 16 kg mol\(^{-1}\) PS-\(b\)-PDMS block copolymer thin films on PDMS or PEO brush-coated substrates vs.
electron-beam irradiation dose. The principal domain spacing $d^*$ was calculated from a fast Fourier transform of the SEM images. The spacing between cylinders is equivalent to $d^*$, and the nearest-neighbor spacing of spheres is $(4/3)^{1/2} d^*$.

**FIGURE 3.** (a) Principal domain spacing of 16 kg mol$^{-1}$ PS-$b$-PDMS block copolymer thin films in the vicinity of 3 μm long rectangular areas of the film treated in acetone, irradiated at 100 μC cm$^{-2}$ then annealed in DMF as a function of distance from the interfaces of the irradiated region. The spacing between spheres is $(4/3)^{1/2} d^*$. Inset shows a SEM image of the sample. (b) Dose profiles as a function of distance from the irradiation interface obtained by comparing the effect of dose on period from Figure 3(i) and the data in Fig. 3(a). The expected dose profile is also shown which was calculated based on backscattering of electrons from writing a 3 μm rectangular shape at 100 μC cm$^{-2}$ dose using 10 kV acceleration voltage for a 30 nm HSQ film on Si substrate.

**FIGURE 4.** High Resolution patterns with mixed morphology and period. SEM images of (a) isolated 9 nm wide single line and (b) 9 nm × 30 nm line segments surrounded by close-packed spherical dot patterns selectively irradiated with 200 pC cm$^{-1}$ line dose. (c) 80 nm wide MIT logo composed of 9 nm line patterns, surrounded by dots. (d) coexisting dots, lines and a featureless area achieved using electron-beam irradiation with 100 μC cm$^{-2}$ area dose. (e,f) Patterns showing different size and period of spheres. (e) larger size dots in a 400 nm × 200 nm area A irradiated at 20 μC cm$^{-2}$ surrounded by smaller size dots in unirradiated area B, and (f) line patterns in a 40
μC cm⁻² irradiated 100 nm × 100 nm area A, larger size dot patterns in 20 μC cm⁻² irradiated area B and smaller size dots in unirradiated area C. The films were firstly treated in acetone vapor, followed by electron-beam irradiation, then reannealed using DMF solvent vapor. Approximate boundaries of the irradiation are indicated.

**FIGURE 5.** Dual phase patterns combined with post templating. SEM images of dual phase block copolymer patterns combined with post templates with a period of (a) 45 nm × 78 nm, commensurate with cylinders angled at 23° to the post lattice and a 26 nm center-to-center sphere array aligned along the y axis, and (b) 48 nm × 42 nm to form a single line in a square-symmetry sphere array.
Figure 1 (Son et al.)
Figure 2 (Son et al.)
Figure 3.
Figure 4 (Son et al.)

Figure 5 (Son et al.)
Supporting Information

Assembly of sub-10 nm block copolymer patterns with mixed morphology and period using electron irradiation and solvent annealing

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TABLE S1. Swelling ratio of the PS homopolymer, PDMS homopolymer and PS-b-PDMS (11k-5k) block copolymer thin films during solvent annealing after \( \sim 30 \) min exposure to the solvent vapor. The film thicknesses before solvent annealing were approximately 70 nm. The last two columns represent the swelling ratio and volume fraction calculated for the block copolymer during solvent annealing, based on the homopolymer swelling rates. The 16 kg mol\(^{-1}\) PS-b-PDMS itself swelled slightly less than the volume-averaged homopolymer results suggest, which may be a result of the geometrical constraint on swelling provided by the connectivity of the blocks. The homopolymer swelling ratios suggest that the volume fraction of PS in the acetone-swelled PS-b-PDMS increased to 0.70, maintaining the cylindrical morphology until the solvent was fully evaporated, while the PS volume fraction in the DMF-swelled PS-b-PDMS was 0.77, leading to the formation of a spherical morphology.

|                | PS      | PDMS   | Experimental 16k PS-b-PDMS \((f_{PS} \sim 0.67)\) | Estimated PS-b-PDMS \((f_{PS} \sim 0.67)\) | PS-b-PDMS \(f_{PS}\) during SA and PDMS morphology |
|----------------|---------|--------|-----------------------------------------------|--------------------------------------------|-----------------------------------------------|
| Acetone        | 1.62    | 1.44   | 1.46                                          | 1.56                                       | 0.70 cylindrical                             |
| DMF            | 1.85    | 1.15   | 1.48                                          | 1.62                                       | 0.77 spherical                               |
FIGURE S1. By irradiating selected areas of the film, combinations of lines and dot arrays were formed in a single block copolymer film. Examples are given of films which were annealed in (a,b) acetone, (c,d) DMF, then (a,c) 3 µm wide rectangles and (b,d) single-pixel lines were exposed to electron-beam irradiation at different doses, followed by a second anneal in the other solvent. The approximate boundaries of the electron-beam written areas and lines are indicated.