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# Lithographically directed materials assembly

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## ABSTRACT

We have developed a processing method that significantly reduces the number of steps necessary to yield a surface that directs block copolymer assembly. This methodology employs a single resistless lithography step that directly changes the surface energy without requiring subsequent material deposition or plasma etching steps. The lithographically defined difference in surface energies acts as a template to direct diblock polymer self-assembly into low-defect periodic structures. Our newly developed lithographically directed self-assembly technique can produce sub-45 nm half pitch lines employing poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) and interference lithography. Once assembled into periodic lines of alternating materials, the PMMA block can be removed and the resulting polystyrene features can be used as an etch mask to transfer periodic lines-and-spaces into a silicon substrate.

**Key words:** Block copolymer, directed self-assembly

## 1. INTRODUCTION

Symmetric diblock copolymers have garnered a great deal of attention for their ability to phase separate into lamellar microdomains with dimensions on the order of 10-50 nm.<sup>1</sup> It is possible to use these microdomains to pattern surfaces to critical dimensions smaller than is currently possible with optical lithography.<sup>2-4</sup> Selective removal of one of the blocks<sup>2</sup> results in templates that can be used in the nanofabrication of a variety of devices on the nanoscale, including nanowires<sup>5,6</sup> and magnetic storage media.<sup>7</sup> One of the most studied systems for templating block copolymers has been with poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA).<sup>2,8-15</sup> Two main approaches have been used in templating the block copolymer self-assembly. Graphoepitaxy involves the formation of lithographically predefined topographic features on the substrate surface to guide the assembly of the block copolymer films.<sup>4</sup> The other major approach is chemical nanopatterning of the surface by the selective functionalization of a grafted random copolymer brush<sup>8-10</sup> or self-assembled monolayer.<sup>14</sup> We have developed an improvement on chemical nanopatterning that uses a photoactive alkylsiloxane-modified surface in place of the copolymer brush. On this modified surface, we can directly form a pattern in the polymer by conventional lithographic exposure, e.g., interference lithography.

The advantage of a direct lithographic exposure of an alkylsiloxane-modified silicon surface compared to the conventional polymer brush approach is in terms of the number of processing steps required to form a block copolymer pattern. In the conventional binary approach employed by most groups, a surface modifier such as a polymer brush is grafted to the silicon surface.<sup>8-10</sup> Then, a resist is spun on top, imaged, and developed. The pattern is transferred to the underlying polymer brush through a plasma etching process. The resist is then removed to yield the patterned substrate. Subsequent diblock copolymer deposition followed by thermal annealing results in a pattern that replicates that of the underlying patterned substrate. By modifying the silicon surface with alkylsiloxanes, we are able to directly image a grating pattern using 157-nm interference lithography. It has been shown previously that alkyl- and arylsiloxane self-assembled monolayers can be removed upon exposure to 157-nm irradiation,<sup>16</sup> as well as other exposure techniques including 193-nm irradiation,<sup>17</sup> and e-beam patterning.<sup>18,19</sup> Since the dose delivered to the surface modifying agent varies continuously along the path of the aerial image, areas of hydrophilic and hydrophobic surfaces are separated by areas of intermediate surface energy. Thus, we have a surface with continuously changing surface energy compared to a conventional binary surface energy approach using chemically nanopatterned polymer brushes.

## 2. EXPERIMENTAL

Silicon wafers were cleaned by immersion into CD26 developer for 10 minutes at room temperature to hydroxylate the silicon surface, rinsed with deionized water and blown dry under a stream of nitrogen. CD26 is a commercial 2.38% TMAH based aqueous resist developer from Rohm and Haas. A 1% (v/v) solution of n-butyltrichlorosilane (Gelest) in toluene was prepared and allowed to mature for 10 minutes. The cleaned silicon wafer was immersed in the n-butyltrichlorosilane solution for 10 minutes, rinsed with toluene and blown dry under a stream of nitrogen. Bulk exposure was performed at 157-nm with a laboratory-class projection system employing an F<sub>2</sub> laser. The surface modified silicon wafer was placed on a vacuum chuck of an x-y stepper directly in front of an 8-mm aperture of the laser system. A 6x6 dose matrix was programmed into the computer controller and each spot received an increasing energy dose until the desired final total dose was reached. Once exposed, the wafer was rinsed with deionized water and blown dry with a stream of nitrogen. Contact angle measurements were performed using deionized water and decalin. In a typical measurement, a 1 µL drop of water was placed on the surface being measured using a microsyringe. On a microscope stage equipped with a Boeckler Instruments Microcode II measurement device, the x- and y-diameters were measured and averaged according to  $d = (x^2 + y^2)^{1/2}$ . This diameter value can be converted to a contact angle according to Bikerman's equation<sup>20</sup> (Eq. 1) where d is the diameter of the drop and V is the volume of the drop. After the water and decalin contact angles were determined, the polar and dispersive surface energies for a given surface were calculated by the method of Fowkes.<sup>21,22</sup>

$$\frac{d^3}{V} = \frac{s4 \sin^3 \theta}{\pi(2 - 3 \cos \theta + \cos^3 \theta)} \quad (1)$$

Interference exposure was performed at 157-nm with a laboratory-built two-beam 157-nm interference system based on a Jamin interferometer. This system is capable of forming periodic lines and spaces with a 91-nm pitch. The surface modified silicon wafers were exposed to a 4x3 exposure dose matrix, then rinsed with deionized water and dried under a stream of nitrogen before diblock copolymer deposition. Extreme ultraviolet (EUV) open frame exposures were performed at the EUV reflectometry beamline facility at NIST (Gaithersburg, MD). The EUV lithography exposures were performed at the Lawrence Berkeley National Laboratory on a 0.30 NA microfield exposure tool.

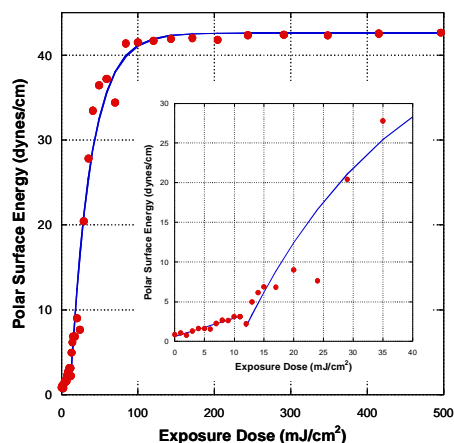
Symmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymers were purchased from Polymer Source Inc. and had molecular weights of (105-*b*-106) kg/mol and (130-*b*-133) kg/mol with polydispersity indices of 1.13 and 1.1, respectively, and bulk lamellar repeat periods of  $L_{087} = 87$  nm and  $L_{096} = 96$  nm. Thin films of PS-*b*-PMMA were spin coated onto the desired substrate to give films that were approximately 45 nm thick. The thicknesses of the films were determined using a Gaertner Scientific Corporation L115BLC Dual Wavelength Ellipsometer using a He-Ne laser ( $\lambda=632.8$  nm) at an incident angle of 70° relative to the surface normal of the substrates. The polymer films were then annealed at 260 °C for 2 hrs on a hotplate in a nitrogen-filled glove box. After annealing, the films were imaged using a LEO-982 field-emission scanning electron microscope (SEM) at an accelerating voltage of 1 keV.

PMMA block removal was accomplished photochemically either with a 193-nm laser with a 500 mJ/cm<sup>2</sup> exposure dose or a 157-nm laser with a 31 mJ/cm<sup>2</sup> exposure dose. The PMMA was then immersed in a 1:1 methyl isobutyl ketone:isopropanol developer. PMMA was also removed by reactive ion etching using an oxygen etch for 1 minute at 10 mTorr (15 sccm flow rate) with 100 V bias in a Perkin Elmer Reactive Ion Etcher. Pattern transfer into silicon was accomplished using the PS masks and etching using a 95:5 SF<sub>6</sub>:O<sub>2</sub> mixture at 10 mTorr (15 sccm flow rate) with a 60 V bias.

## 3. RESULTS AND DISCUSSION

Diblock copolymer compositions forming lamellar phases will tend to form in parallel lamellar orientation when one block preferentially wets the surface. In the case of PS-*b*-PMMA, on a cleaned silicon dioxide surface (SiO<sub>2</sub>), the PMMA block will be attracted to the surface and will form a uniform wetting layer.<sup>23</sup> An alkylsiloxane-modified silicon surface will have a much lower surface energy than that of silicon with a native oxide layer, and this surface will be preferentially wetted by the PS block of PS-*b*-PMMA. In order to orient these lamellae perpendicularly to the surface, the surface must be neutral to both the PS and PMMA blocks. Traditionally, this is achieved by coating the

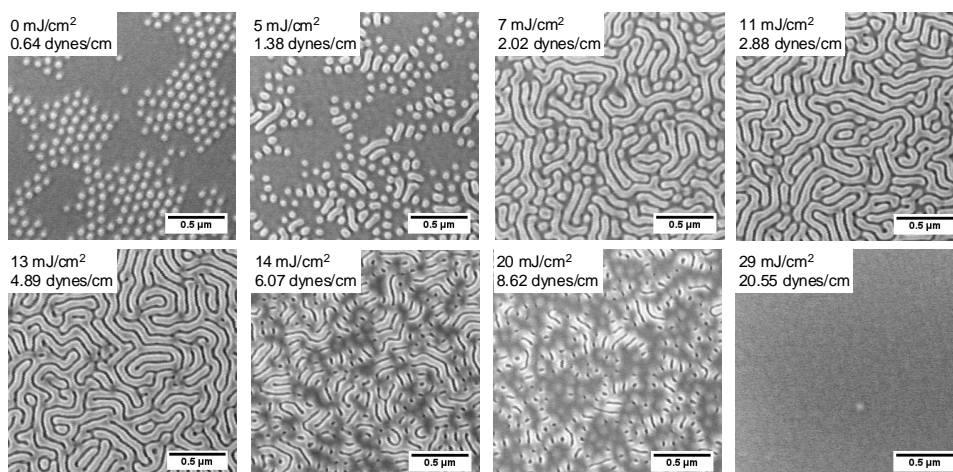
silicon surface with a thin film of a random PS-PMMA copolymer before coating with the block copolymer. The same result can be achieved using alkylsiloxane-modified surfaces in which we can control the polar surface energy. Exposure to 157-nm light will cleave the Si-C bond, with the Si quickly reacting with water to form SiOH.<sup>16</sup> The amount of alkylsiloxane that is removed is a function of the exposure dose at 157 nm. A plot of polar surface energy as a function of exposure dose at 157 nm for an n-butylsiloxane-modified (nBS) silicon wafer is shown in Figure 1. At very low exposure doses ( $< 10 \text{ mJ/cm}^2$ ), there is little change in the polar surface energy from the initial 0.6 dynes/cm. However, as the exposure dose increases past  $12 \text{ mJ/cm}^2$ , there is rapid increase in the polar surface energy of the substrate. This increase continues until nearly all of the nBS is removed upon exposure of  $75 \text{ mJ/cm}^2$  and the surface energy approaches that of bare SiO<sub>2</sub> (ca. 42 dynes/cm).



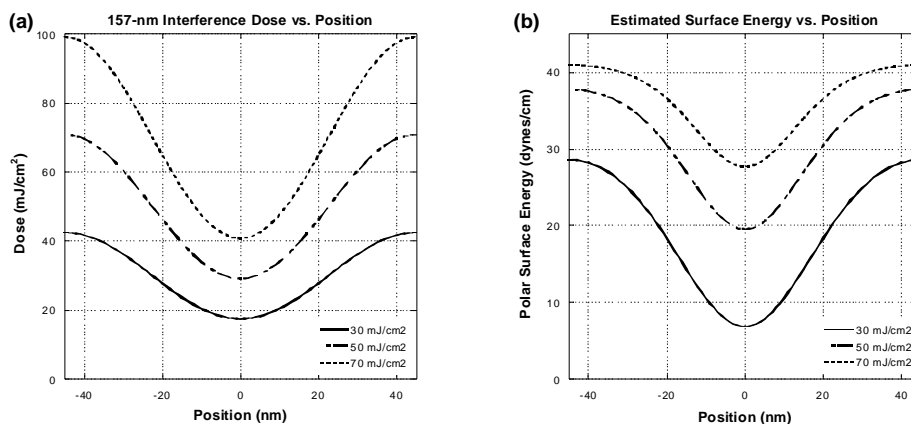
**Figure 1.** 157-nm contrast curve for an nBS-modified silicon surface showing polar surface energy changes as a function of exposure dose. Inset: Low dose region of the contrast curve highlighting little change in surface energy at low exposure doses.

A 45-nm thick film of 211 kDa PS-*b*-PMMA was deposited onto an nBS-modified silicon wafer in which various degrees of surface modifier were removed and then baked for 2 hr at 260 °C on a hot plate in a nitrogen-filled glove box. As demonstrated in Figure 2, at low doses ( $< 7 \text{ mJ/cm}^2$ ), the PS blocks preferentially wet the substrate and small, random islands of polystyrene (light areas in the SEM image) are observed on top of the darker PMMA lamella. Once the surface energy approaches a point that is "neutral" to both PS and PMMA ( $11 \text{ mJ/cm}^2$ ), the lamellar orientation flips to perpendicular and the characteristic fingerprint pattern of light PS and darker PMMA domains is observed. The exposure dose window for this orientation is  $11 - 13 \text{ mJ/cm}^2$  (2.9 – 4.9 dynes/cm). Defects begin to appear at  $14 \text{ mJ/cm}^2$  (6 dynes/cm), indicating the beginning of a transition to a PMMA-preferential parallel lamellar orientation. The block copolymer film is fully parallel at higher surface energies ( $> 20 \text{ dynes/cm}$ ).

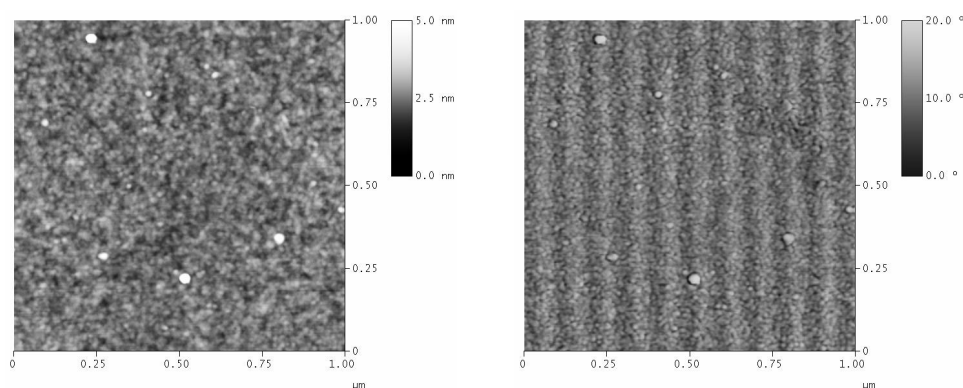
Alignment of PS-*b*-PMMA into ordered arrays is accomplished by thermally annealing them on well-defined surfaces of different interfacial (surface) energy. Typically, chemically nanopatterned substrates employ a polymer brush that has alternating areas that have been exposed to an oxygen plasma to generate sufficient surface energy contrast. Figure 3 shows how the surface energy of an nBS-modified silicon wafer can be modified using 157-nm interference lithography. From the known normalized aerial image of our home-built 157-nm interference exposure system, the delivered dose at any point along the 91-nm pitch can be calculated relative to the nominal dose. For example, a nominal exposure dose of  $50 \text{ mJ/cm}^2$  will actually deliver between  $29 \text{ mJ/cm}^2$  and  $70 \text{ mJ/cm}^2$  along the x-axis. Combining this information with the 157-nm contrast curve data for an nBS-modified silicon surface (Fig. 1) allows for the estimation of polar surface energy along the x-axis as a function of nominal exposure dose (Fig 3b). Thus, we can create areas with distinctly different polar surface energies and have a continuum of surface energy states between them. Confirmation that the surface energy has been changed can be seen in the AFM images of a patterned substrate. Figure 4 shows the height and phase images of an nBS-modified silicon substrate patterned at a nominal exposure dose of  $50 \text{ mJ/cm}^2$ . No differences in height between the high- and low-exposure regions were observed. However, the phase image reveals an ordered pattern on the substrate surface due to the difference in elasticity between the nBS surface modifier and the SiO<sub>2</sub> substrate.



**Figure 2.** SEM micrographs of 45 nm thin films of 211 kDa PS-*b*-PMMA showing changes in lamellar orientation as a function of surface energy.

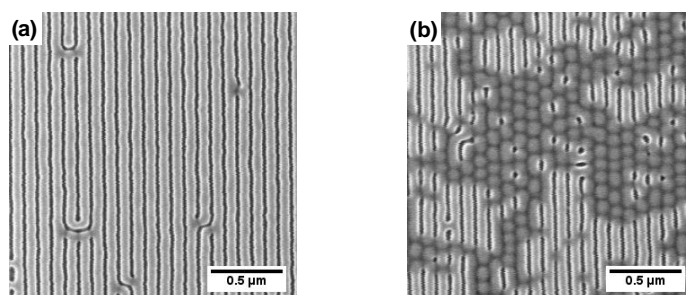


**Figure 3.** (a) Calculated exposure dose vs. position for one period of our 157-nm interference exposure system for three nominal exposure doses. (b) Conversion of exposure dose into polar surface energy vs. position along one period.



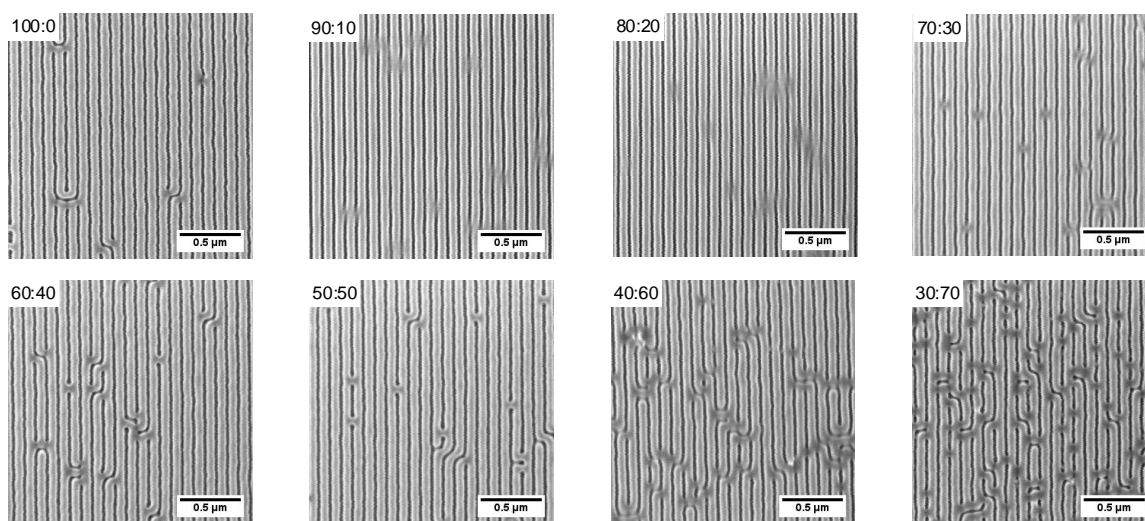
**Figure 4.** Height (left) and phase (right) AFM images of an nBS-modified silicon surface after imaging with a 157-nm interference laser.

The ability of an interference lithography imaged nBS-modified surface to direct block copolymer self-assembly was investigated using thin films of PS-*b*-PMMA having molecular weights of 211 kDa and 263 kDa. The bulk lamellar period of the polymers was  $L_{O87} = 87$  nm and  $L_{O96} = 96$  nm, respectively. The period of the imaged surface is 91 nm. Spin coating thin films of LO87 and LO96 on the imaged surface followed by thermal annealing for 2 hr at 240 °C resulted in the directed assembly of lamellar domains with periods of 91 nm. Figure 5 shows 45-nm thick LO87 and LO96 films on an nBS-modified surface that was imaged at an exposure dose of 47 mJ/cm<sup>2</sup>. Both of these samples show numerous defects, but also give indications that the imaged surface will direct polymer self-assembly. The defects are most likely caused by the large mismatch of the polymer lamellar spacing and the substrate period. This effect has been observed by others investigating polymer self-assembly on chemically nanopatterned surfaces of mismatched periods.<sup>15,24,25</sup>



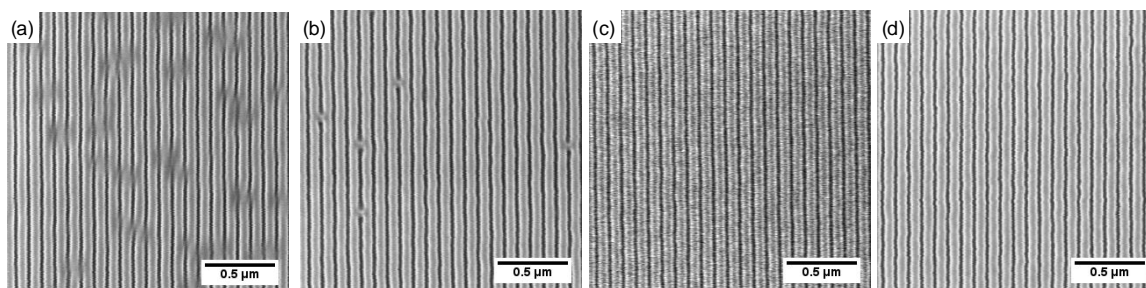
**Figure 5.** SEM micrographs of 45-nm thick films of (a) 211 kDa PS-*b*-PMMA (LO87) and (b) 263 kDa PS-*b*-PMMA (LO96) on nBS-modified silicon surfaces at an exposure dose of 47 mJ/cm<sup>2</sup> and having a substrate period of 91 nm.

In order to obtain defect-free lamellar self-assembly, the periods of the block copolymer films need to more closely match the underlying nBS-modified substrate period. One way to accomplish this has been demonstrated by Nealey by blending two polymers of close molecular weights to obtain a polymer lamellar period of the blend that is between the two original polymers.<sup>15</sup> We followed the same approach by preparing a series of blends based on LO87 and LO96. Figure 6 shows blends prepared on substrates that were imaged at an exposure dose of 47 mJ/cm<sup>2</sup>. Blends that are rich in LO96 PS-*b*-PMMA still have numerous defects, but not to the same extent as the LO96 copolymer alone. As we approach a 90:10 blend of LO87:LO96 (LB91), we obtain SEM images that have far fewer defects than any of the other blends. This was used as a basis for further processing optimization.



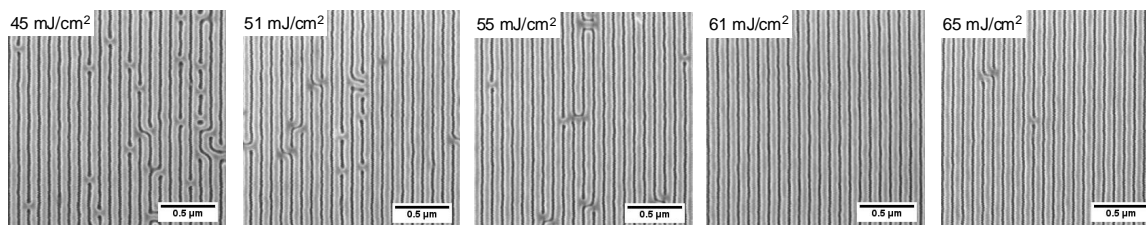
**Figure 6.** SEM micrographs of blends of 45-nm thick LO87 and LO96 PS-*b*-PMMA films on nBS-modified silicon surfaces imaged at an exposure dose of 47 mJ/cm<sup>2</sup> and having a substrate period of 91 nm. The ratios given are LO87:LO96.

Due to the large molecular weights of the polymers required to obtain lamellar periods approaching 91 nm, thermal annealing times and temperatures that are longer and higher than for lower molecular weights polymers are required. Nealey and coworkers have shown previously that for 104 kDa PS-b-PMMA films deposited onto chemically nanopatterned surfaces, directed self-assembly of the lamellae occurred on the order of minutes at high temperatures ( $> 220\text{ }^{\circ}\text{C}$ ) to 50 minutes at normal processing temperatures ( $190\text{ }^{\circ}\text{C}$ ) on a hot plate in a nitrogen atmosphere.<sup>13</sup> Figure 7 shows films of LB91 thermally annealed on a hot plate under nitrogen and the effect of time and temperature. All of the samples shown were processed on nBS-modified substrates that were imaged at an exposure dose of  $61\text{ mJ/cm}^2$  in order to ensure that the aerial image was consistent throughout. At  $240\text{ }^{\circ}\text{C}$  for 2 hr, there are some dislocation defects observed indicating incomplete pattern registration. Increasing the time did not considerably help remove these defects. Increasing the temperature to  $260\text{ }^{\circ}\text{C}$  brought about noticeable changes in the SEM micrographs. After 30 minutes, most of the bridging and dislocation defects have been eliminated. Annealing for 1 hr resulted in nearly defect-free patterns, while the best conditions were found to be annealing for 2 hours.



**Figure 7.** SEM micrographs of 45-nm thick LB91 films on nBS-modified silicon surfaces imaged at an exposure dose of  $61\text{ mJ/cm}^2$  and having a substrate period of 91 nm. The films were thermally annealed on a hot plate under nitrogen at (a)  $240\text{ }^{\circ}\text{C}$  for 2 h, (b)  $260\text{ }^{\circ}\text{C}$  for 30 min, (c)  $260\text{ }^{\circ}\text{C}$  for 1 hr and (d)  $260\text{ }^{\circ}\text{C}$  for 2 hr.

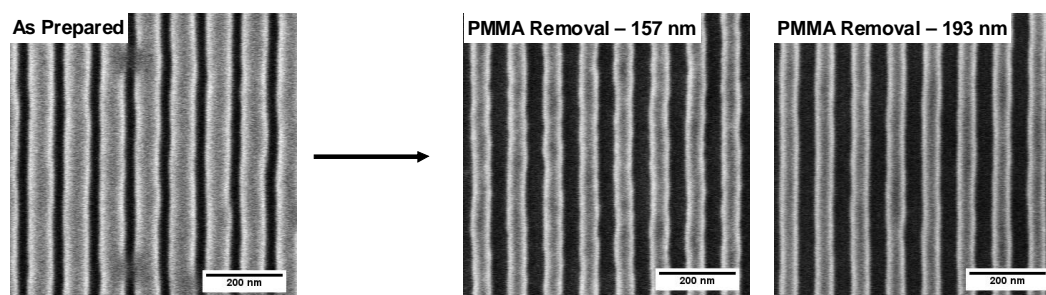
The exposure latitude for the nBS-modified surface was also probed. The freshly-prepared nBS-modified silicon surface was exposed to a matrix of exposure doses ranging from  $10\text{ mJ/cm}^2$  to  $120\text{ mJ/cm}^2$ . After exposure, a 45-nm thick film of LB91 was deposited and the substrates were annealed on a hot plate under nitrogen at  $260\text{ }^{\circ}\text{C}$  for 2 hrs. A subset of this matrix is shown in Figure 8. As the exposure dose increased from 10 to  $40\text{ mJ/cm}^2$  (not shown) the polymer film begins to self-assemble into a periodic structure with many defects. Increasing the exposure dose from 45 to  $55\text{ mJ/cm}^2$  reduces the number of dislocation defects and finally a uniform periodic lamellar film is seen on a surface patterned at  $61\text{ mJ/cm}^2$ . Increasing the exposure dose beyond  $63\text{ mJ/cm}^2$  shows defects beginning to reform, with many appearing at doses  $> 70\text{ mJ/cm}^2$ . We speculate that at lower doses, the more hydrophilic regions are not commensurate with the PMMA domain width and these surfaces behave similar to a random copolymer brush. When the hydrophilic and hydrophobic stripes are of nearly equal size, complete registration of the block copolymer film is observed. Increasing beyond this ideal range of exposure doses, wider areas of hydrophilic surfaces are formed and are less able to perfectly direct the block copolymer self assembly.



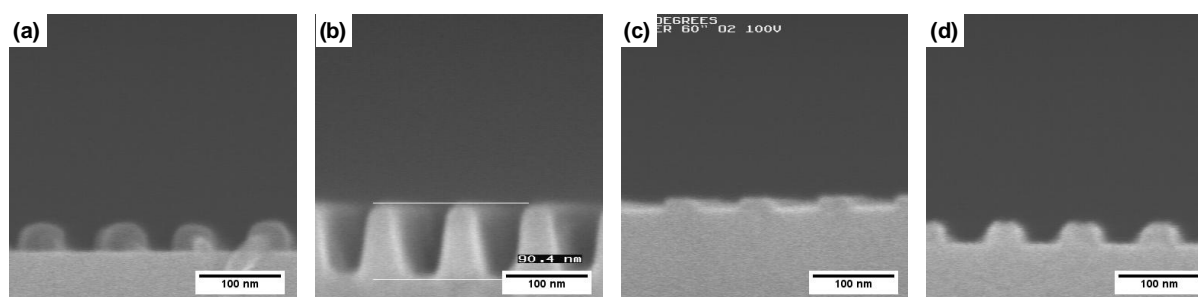
**Figure 8.** SEM micrographs of 45-nm thick LB91 films on nBS-modified silicon surfaces. The surfaces were imaged at the listed exposure doses and then the spin coated LB91 films were thermally annealed on a hot plate under nitrogen at  $260\text{ }^{\circ}\text{C}$  for 2 hr

Block copolymer films can be used as etch masks for pattern transfer into a silicon substrate. This was first demonstrated by Park and coworkers using cylindrical domains of poly(butadiene) in a poly(styrene) matrix.<sup>2</sup> One

block was preferentially removed by reactive ion etching (RIE) to create a mask and then transfer that image to the underlying substrate. Russell and coworkers created poly(styrene) etch masks from PS-*b*-PMMA by first irradiating the PMMA with UV light and then removing the degraded material with an appropriate solvent to create a positive mask.<sup>26</sup> We have looked at both approaches to create PS etch masks. Exposing the aligned PS-*b*-PMMA films to 39 mJ/cm<sup>2</sup> of 157-nm irradiation or 500 mJ/cm<sup>2</sup> of 193-nm irradiation followed by development in a 1:1 mixture of MIBK:IPA resulted in the complete photolytic removal of the PMMA block (Fig. 9). In both cases, we obtain films with ~46 nm wide PS lines, which is what we would expect from a symmetric block copolymer. The as-prepared image shows an uneven distribution of PS/PMMA linewidths; however, this is an artifact of the SEM image. A cross-section of a photolytically processed PS etch mask is shown in Figure 10a. As seen in the cross-section, the PS pattern has roughly equal lines and spaces. This mask was then placed into a reactive ion etch chamber and the underlying silicon was etched for 2.5 minutes using a 95:5 SF<sub>6</sub>:O<sub>2</sub> mixture at 10 mTorr (15 sscm flow rate) with a 60 V bias. We found that using this etching mixture allowed for a more anisotropic etch into the silicon and allowed for a > 2:1 etch selectivity of silicon:PS. As seen in Figure 10b, using a 45 nm initial block copolymer film, we were able to etch a grating pattern into silicon that is 90 nm deep. In addition to the photolytic removal of PMMA, we also investigated its O<sub>2</sub> plasma removal. Subjecting an aligned PS-*b*-PMMA film to an oxygen etch for 1 minute at 10 mTorr (15 sscm flow rate) with a 100 V bias completely removed the PMMA block. However, it also had the effect of greatly thinning the PS block. Thus, the initial 45 nm thick PS-*b*-PMMA film gave a 13 nm thick PS mask after the initial PMMA removal (Fig. 10c). This mask was used in similar fashion as with the photolytically generated mask with the exception that the silicon etching was stopped after 1 minute to yield a grating pattern in the silicon that was 34 nm deep.



**Figure 9.** SEM micrographs of 45-nm thick LB91 films on nanopatterned nBS-modified silicon surfaces having a substrate period of 91 nm showing the effect of photolytic PMMA exposure and development.

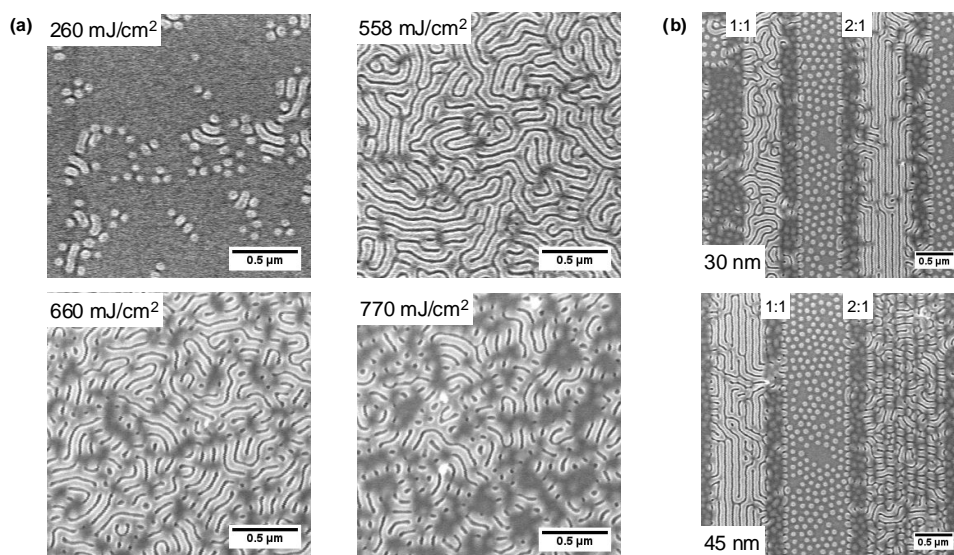


**Figure 10.** Cross sectional SEM micrographs of polystyrene etch masks after (a) photolytic and (c) RIE PMMA removal. Images of pattern transfer into silicon using these masks are shown in (b) and (d), respectively

In order to see how well this technique can extend to other imaging wavelengths, an extreme ultraviolet (EUV) exposure matrix was performed on an nBS-modified silicon substrate. After exposure, the wafers were coated with 45 nm of 211 kDa PS-*b*-PMMA and annealed on a hot plate under nitrogen for 2 hrs at 260 °C. As can be observed in Figure 11a, much higher exposure doses are required to induce a change in surface energy to direct perpendicular lamellae formation. The directed self-assembly of LB91 films on EUV-patterned substrates was also investigated. An nBS-modified silicon wafer was patterned at an exposure dose of 300 mJ/cm<sup>2</sup> with a projection microstepper. The mask included a number of pitches and line-space patterns. Once patterned, the substrates were coated with 45 nm of LB91



and annealed at 260 °C for 2 hrs. Figure 11b shows the best results that were obtained at the edge of the focus range. In areas that were not exposed, the typical parallel lamellar orientation with random islands is observed. However, in patterned areas, we do observe perpendicular lamellae and in some cases there is a directional orientation to these lamellae. In the case of 30 nm imaged lines (Fig 11b, top) 1:1 line-to-space ratios result in random lamellae formation, but when the pitch is increased to 90 nm, a more ordered domain ensues. Similarly, 45 nm lines at a 90 nm pitch also resulted in the formation of ordered lamellae with numerous dislocation defects, while a 135 nm pitch yielded only disordered perpendicular lamellae. These initial results are intriguing and would require further optimization of the exposure dose and focus, but also point to the utility of EUV patterning as a way to obtain decreased feature sizes through the use of lower molecular weight diblock copolymers.



**Figure 11.** (a) SEM micrographs of 45 nm thin films of 211 kDa PS-*b*-PMMA showing changes in lamellar orientation as a function of surface energy. (b) SEM micrographs of LB91 films on nBS-modified silicon surfaces imaged at an EUV exposure dose of 300 mJ/cm<sup>2</sup> and having imaged lines of 30 and 45 nm width at line-to-space ratios as indicated.

#### 4. SUMMARY

Silicon wafers coated with surface modifying agents can be directly imaged by 157-nm interference lithography to produce surfaces to direct the self-assembly of PS-*b*-PMMA films. Once assembled, the PMMA blocks can be removed either by a secondary photolytic exposure and develop or by a direct oxygen plasma etching process, both of which leave behind PS lines for use as an etch mask. Pattern transfer of the opened lines into silicon was demonstrated. Preliminary patterning using EUV resulted in the formation of directed self-assembled block copolymer films; however, further optimization is needed.

#### 5. ACKNOWLEDGMENTS

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