

# Spatial Control of the Self-assembled Block Copolymer Domain Orientation and Alignment on Photopatterned Surfaces

Ji Yeon Kim,<sup>#</sup> Philip Liu,<sup>#</sup> Michael J. Maher,<sup>#</sup> Devon H. Callan, Christopher M. Bates, Matthew C. Carlson, Yusuke Asano, Gregory Blachut, Charles T. Rettner, Joy Y. Cheng, Daniel F. Sunday, R. Joseph Kline, Daniel P. Sanders, Nathaniel A. Lynd, Christopher J. Ellison, C. Grant Willson,<sup>\*</sup> and Carlos R. Baiz<sup>\*</sup>



Cite This: <https://dx.doi.org/10.1021/acsami.0c02997>



Read Online

ACCESS |



Metrics & More



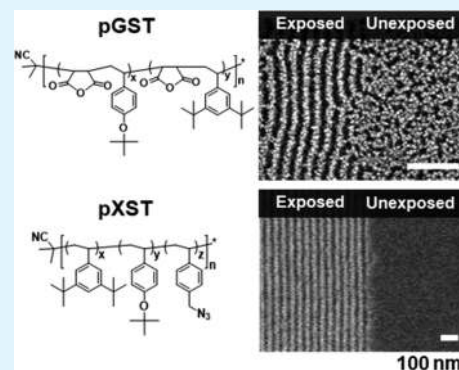
Article Recommendations



Supporting Information

**ABSTRACT:** Polarity-switching photopatternable guidelines can be directly used to both orient and direct the self-assembly of block copolymers. We report the orientation and alignment of poly(styrene-*block*-4-trimethylsilylstyrene) (PS-*b*-PTMSS) with a domain periodicity,  $L_0$ , of 44 nm on thin photopatternable grafting surface treatments (pGSTs) and cross-linkable surface treatments (pXSTs), containing acid-labile 4-*tert*-butoxystyrene monomer units. The surface treatment was exposed using electron beam lithography to create well-defined linear arrays of neutral and preferential regions. Directed self-assembly (DSA) of PS-*b*-PTMSS with much lower defectivity was observed on pXST than on pGST guidelines. The study of the effect of film thickness on photoacid diffusion by Fourier transform infrared spectroscopy and near-edge X-ray absorption fine structure spectroscopy suggested slower diffusion in thinner films, potentially enabling production of guidelines with sharper interfaces between the unexposed and exposed lines, and thus, the DSA of PS-*b*-PTMSS on thinner pXST guidelines resulted in better alignment control.

**KEYWORDS:** photopatterning, block copolymers, directed self-assembly, lithography, photoacid diffusion, thin films, infrared spectroscopy, NEXAFS spectroscopy



## INTRODUCTION

Block copolymer (BCP) self-assembly is currently being explored for high-resolution patterning applications<sup>1,2</sup> because BCPs spontaneously form various morphologies such as lamellae or cylinders with sub-20 nm features of periodic arrays. Precise control over the BCP domain orientation and alignment is critical for it to be integrated into high-volume manufacturing.<sup>3,4</sup> A perpendicular orientation of lamellar domains relative to the underlying substrate can be achieved by tailoring the substrate<sup>5–7</sup> and free interfaces<sup>8–10</sup> with nonpreferential (neutral) polymeric materials. Directed self-assembly (DSA) using topographic guide patterns (i.e., graphoepitaxy)<sup>11–13</sup> or chemical guide patterns (i.e., chemoeptitaxy)<sup>14–18</sup> has been developed to control the alignment of BCP domains to form device-relevant features,<sup>19,20</sup> which have been used to demonstrate patterning of fin field-effect transistors<sup>21</sup> and bit-patterned media.<sup>22</sup> Typically, these guide patterns can be generated by patterning grafting surface treatments (GSTs) or cross-linkable surface treatments (XSTs) via lithography and subsequent reactive-ion etching<sup>23–26</sup> or by using developed photoresist patterns directly as guidelines.<sup>18,27,28</sup> In recent years, DSA has been studied in many other applications including drug delivery<sup>29</sup> and

patterning of sensors,<sup>30</sup> plasmonic materials,<sup>31–34</sup> and scaffolds for tissue engineering.<sup>35–38</sup>

Although DSA offers a large-area patterning capability with sub-optical resolution, it is generally limited to simple and highly periodic patterns.<sup>28</sup> However, advanced microelectronic architectures require creation of complex custom patterns. For example, bit-patterned media are composed of rectangular bits and distinct servo regions,<sup>39</sup> while semiconductors require isolated and discontinuous line/space arrays. These patterns can be achieved using DSA in tandem with other processing steps, including the use of multiple BCP layers,<sup>40</sup> cut masks,<sup>41</sup> imprint,<sup>42,43</sup> and/or select pattern transfer blocking.<sup>28</sup> However, this also means that additional lithographic steps would be necessary. On the other hand, blocking pattern transfer is particularly appealing because it can potentially be achieved by using parallel and perpendicular BCP domains

**Received:** February 16, 2020

**Accepted:** April 29, 2020

**Published:** April 29, 2020

within the same film without additional processes whereby only the perpendicular domains can be pattern-transferred. Achieving control over both perpendicular and parallel domains within the same film has been most commonly explored by altering the surface chemistry at the substrate interface to create selected areas of neutral and preferential surfaces.<sup>44–46</sup> Perpendicular structures appear on neutral interfaces, while parallel structures, which cannot be pattern-transferred, are formed on the preferential interfaces.<sup>47</sup>

Previously, we reported photopatternable grafting surface treatments (pGSTs). These surfaces were used to control the orientation of poly(styrene-*block*-4-trimethylsilylstyrene) (PS-*b*-PTMSS),<sup>48–50</sup> which has high etch selectivity<sup>51</sup> and can be pattern-transferred.<sup>17</sup> The pGSTs contained an acid-labile functional group and were designed to be either inherently neutral or preferential to one of the BCP domains. When exposed to photoacid and baked, the surface chemistry changed in the exposed regions either from neutral to preferential (N2P) or preferential to neutral (P2N). A perpendicular orientation of BCP domains was achieved only on neutral regions, and only a parallel orientation appeared on preferential regions. In both cases, a neutral top coat was used. pGSTs enable spatial control of perpendicular and parallel orientations within the same film and can potentially be used to fabricate guidelines without the use of photoresists and reactive-ion etching that are necessary in chemoepitaxy. As the BCP feature size or domain periodicity ( $L_0$ ) decreases to sub-20 nm, controlling the critical dimension of chemical guidelines to its target width ( $0.5 L_0$  or  $1.5 L_0$ )<sup>23</sup> can be challenging. Thus, avoiding the etch step can be an added advantage. Furthermore, pattern transfer blocking can be achieved in a single photolithographic exposure without involving additional processes. This similar concept of using directly patternable orientation layers was previously demonstrated with patterns created by photolithography,<sup>48,50,52</sup> electron beam,<sup>45,53</sup> and X-ray exposures,<sup>54</sup> but successful DSA of silicon-containing BCPs using photopatternable surface treatments has not yet been demonstrated.

pGSTs, however, require aminopropyltriethoxysilane (APTES)-treated surfaces in order to be grafted to the substrate. The grafted film thickness cannot be easily tuned, and the required pretreatment step may not be “fab-friendly”.<sup>52</sup> Although not all GSTs require surface pretreatment,<sup>55</sup> this is certainly the case for pGSTs studied in this work. On the other hand, photopatternable, cross-linkable surface treatments (pXSTs) can be a more convenient method to prepare photopatterned surfaces because these pXSTs can be spin-coated directly on any substrate without pretreatment.<sup>6</sup> The film thickness can also be tuned by simply changing the spin coating conditions. The same photochemistry used in pGSTs can be incorporated into these pXSTs to provide an alternative route to photopatternable guidelines. DSA using pXSTs would further simplify the overall patterning process and would integrate well with the current infrastructure for microelectronics manufacturing.

Polarity switching from unexposed to exposed regions utilizes the acid-catalyzed thermolysis reaction (or deprotection reaction), which is the same mechanism used in chemically amplified photoresists in current photolithography. One of the key phenomena related to this mechanism is the photoacid diffusion in glassy polymer films. A chemically amplified photoresist consists of a polymer with an acid-labile protecting group and photoacid generators, which generate

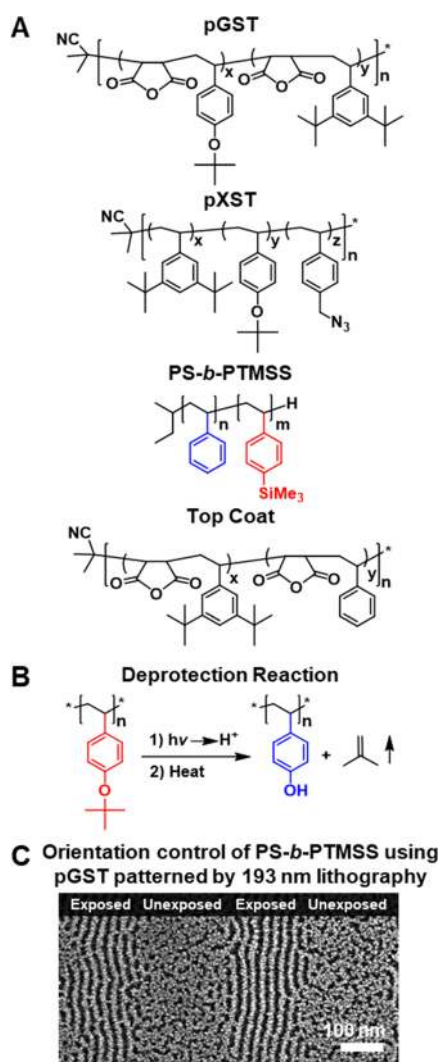
photoacids under the irradiation of light. During the post-exposure bake, the photoacids diffuse and catalyze deprotection reactions and switch the solubility of the polymer resin.<sup>56</sup> There is a tradeoff, however, where the photoacid must be mobile to diffuse and catalyze many deprotection reactions, but the excessive photoacid diffusion from the exposed to unexposed regions can cause an image blur and alter the exposed dimensions or the edge roughness of the photo-patterned regions. Although photoacid diffusion in photoresist films is a well-studied area,<sup>56–60</sup> an understanding of acid diffusion in very thin films is crucial for production of well-defined patterned guides for DSA.

This report is split into two parts. The first part of the paper reports strategies to orient and align PS-*b*-PTMSS with a domain periodicity,  $L_0$ , of 44 nm using pGST and pXST photopatterned by electron beam lithography. The second part of the paper reports the study of the effect of film thickness on photoacid diffusion in patterned poly(4-*tert*-butoxycarbonyloxystyrene) (PTBOC) thin films down to 16 nm by using Fourier transform infrared spectroscopy (FTIR) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and the study offers an additional insight into the effect of pXST film thickness on BCP alignment control. Because the PTBOC homopolymer contains acid-labile groups similar to the pXST, it serves as an analog for the study of acid diffusion behavior in very thin films. The effects of exposure dose and film thickness on the alignment control using photopatterned pXSTs are reported in this study.

## RESULTS AND DISCUSSION

**Description of the DSA Process.** The goal of this study is to compare the quality of DSA patterns prepared using two different surface treatments. Figure 1A shows the primary materials used in this study. pGST is a photopatternable grafting surface treatment consisting of an alternating copolymer of maleic anhydride, acid-labile 4-*tert*-butoxystyrene, and 3,5-di-*tert*-butylstyrene. Covalent bonding between the maleic anhydride and amine-functionalized surface can be achieved by nucleophilic acyl substitution reactions.<sup>48</sup> pXST is a photopatternable cross-linkable surface treatment consisting of a copolymer of 4-*tert*-butoxystyrene, 3,5-di-*tert*-butylstyrene, and 4-vinylbenzylazide. The azide pendant group serves as a cross-linking agent to form a cross-linked surface that is resistant to subsequent thin-film processing. The neutrality of these surface treatments was fine-tuned by the monomer composition. Polystyrene-*block*-poly(4-trimethylsilylstyrene) (PS-*b*-PTMSS) is a silicon-containing BCP with a full pitch,  $L_0$ , of 44 nm.

Figure 2 shows the schematic diagrams of DSA process flows using XST, pGST, and pXST. Figure 2A depicts the DSA process using XST guidelines (i.e., chemoepitaxy),<sup>23–26</sup> and it is shown as a standard process to compare with DSA process flows using pGST and pXST. In this process, XST was spin-coated on a silicon substrate and cross-linked. A photoresist was then spin-coated on top of the XST, post-apply baked, patterned by lithography, and post-exposure baked. The photoresist patterns were developed and used as an etch mask to generate XST guidelines by reactive-ion etching. The photoresist was stripped, and the exposed silicon substrate was then treated with a polymer brush to render the surface neutral. The BCP and neutral top coat were sequentially spin-coated, and they were thermally annealed. The top coat was then removed with a solution of 2-propanol and tetramethy-



**Figure 1.** (A) Primary materials used for photopatternable grafting surface treatment (pGST) and cross-linkable surface treatment (pXST) process flows. pGST consists of an alternating copolymer of maleic anhydride, acid-labile 4-*tert*-butoxystyrene, and 3,5-di-*tert*-butylstyrene, whereas pXST consists of a copolymer of 4-*tert*-butoxystyrene, 3,5-di-*tert*-butylstyrene, and 4-vinylbenzylazide. (B) Acid-catalyzed deprotection reaction of the poly(4-*tert*-butoxystyrene) homopolymer. (C) A scanning electron micrograph of orientation control of PS-*b*-PTMSS on pGST using the preferential-to-neutral (P2N) process. The pitch of the line/space array was 400 nm and was patterned using 193 nm lithography.

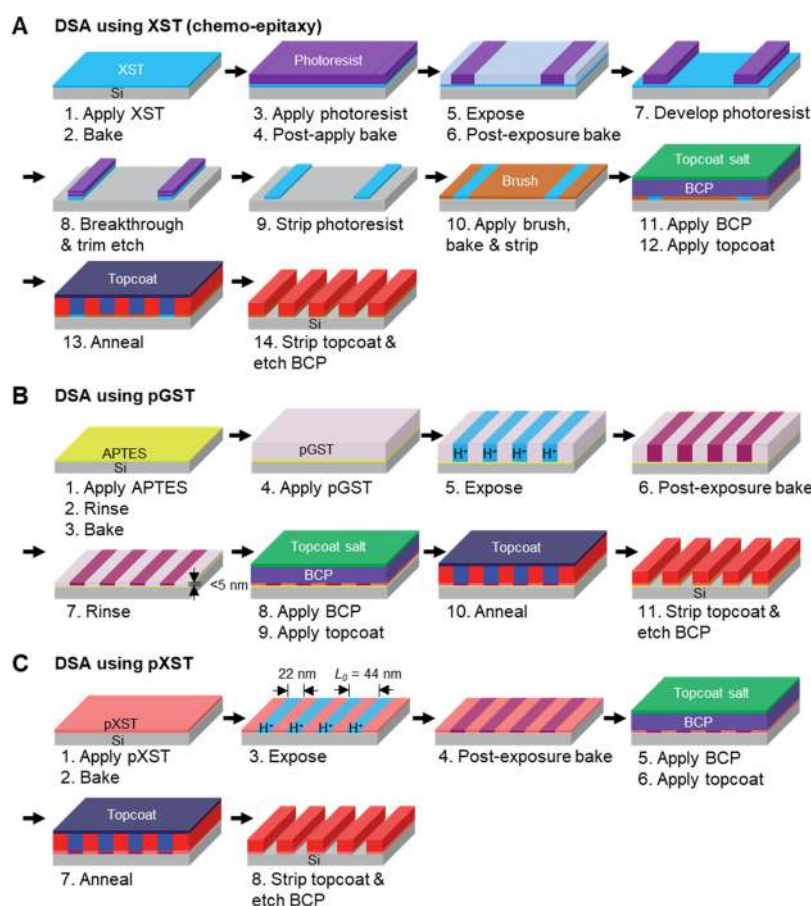
lammonium hydroxide, which solubilizes the top coat but not the BCP film. Finally, the sample was etched using oxygen plasma to remove the polystyrene domains and then imaged via scanning electron microscopy (SEM). For silicon-containing BCPs, as the silicon-containing block is highly preferential to the free (top) air interface and forms a “wetting layer”, a neutral top coat is necessary to achieve a perpendicular orientation that is required for pattern transfer.

Figure 2B shows a representative schematic of the P2N process using pGST. The concept of BCP orientation control by using pGST was previously explored and reported in the literature.<sup>48–50</sup> Figure 1C shows a successful orientation control of PS-*b*-PTMSS on pGST patterned by 193 nm lithography via the P2N process. In this process, a preferential pGST containing a photoacid generator was grafted to the

surface of a silicon wafer that was pretreated with amino-propyltriethoxysilane (APTES). The anhydride functional groups in the pGST formed covalent bonds with the amines on the wafer surface to form imides upon thermal annealing. After grafting, the sample was patterned using electron beam lithography to generate photoacid in the exposed regions that catalyzed the deblocking of the *tert*-butyl groups in 4-*tert*-butoxystyrene monomer units to reveal highly polar phenolic groups.<sup>48</sup> An example of an acid-catalyzed deprotection reaction is shown in Figure 1B. After the deprotection reaction, poly(4-*tert*-butoxystyrene) is converted into poly(4-hydroxystyrene) (PHOST). After patterning and baking, the excess pGST was stripped with an organic solvent, which resulted in a chemically patterned pGST that had a remaining film thickness of approximately less than 5 nm as measured by ellipsometry. The remaining procedure was the same as the abovementioned chemoepitaxial process. For DSA using pGST, spin coating the photoresist, developing photoresist patterns, and reactive-ion etching were not required to generate guidelines. Grafting of the neutral brush was also not required to achieve a perpendicular orientation of BCP domains, hence reducing several processing steps. In other words, the chemical composition of pGST can be tuned such that, before exposure, pGST can behave as chemical guidelines and, after exposure, pGST can act as the neutral brush.

Figure 2C shows a representative schematic of the P2N process using pXST. The pXST process is similar to the pGST process, but the pXST containing a photoacid generator was spin-coated directly onto the silicon wafer and thermally cross-linked. This process did not require the pretreatment using APTES and the rinse step after post-exposure baking, further simplifying the DSA process. Unlike the pGST process, the thickness of pXST can be also controlled by simply changing the spin coating conditions.

**DSA Using pGST.** In an attempt to demonstrate DSA using the P2N process, a 1:1 line/space array with a full pitch of 44 nm was patterned on pGST using electron beam lithography. Figure 3A shows a graph of the DSA score, a measure of BCP alignment quality, of BCP on electron-beam-patterned P2N pGST as a function of exposure dose. The DSA score near 0 describes a randomly oriented fingerprint pattern, while the DSA score near 1 describes a perfectly aligned pattern in the direction of the guideline. The DSA score was quantified by analyzing SEM micrographs following the procedure described in Figures S1–S3. The DSA score was below 0.1 and had no observable trend below the exposure dose of 2000  $\mu\text{C}/\text{cm}^2$ . Above 2000  $\mu\text{C}/\text{cm}^2$ , the DSA score increased with increasing exposure dose and plateaued at approximately 3000  $\mu\text{C}/\text{cm}^2$ . A maximum DSA score was observed at 3100  $\mu\text{C}/\text{cm}^2$ , and Figure 3B shows the SEM image of BCP self-assembled on pGST exposed at that dose. The line/space exposure was performed in the vertical direction. DSA in the exposed direction was seen, but defectivity was very high. Both fingerprint-like and parallel regions can be observed in the sample. We hypothesize that the proximity effect of electron beam lithography,<sup>61</sup> i.e., forward scattering of electrons from the air/pGST interface into the pGST/Si interface and the backscattering of electrons from Si into the pGST/Si interface, caused acid generation in unintended regions at the critical pGST/Si interface. The production of acid by scattered electrons could result in deprotection in the unexposed regions. This would create a decrease in chemical contrast between the exposed and unexposed regions of the thin grafted



**Figure 2.** DSA process flows using (A) XST (chemoepitaxy), (B) pGST, and (C) pXST.

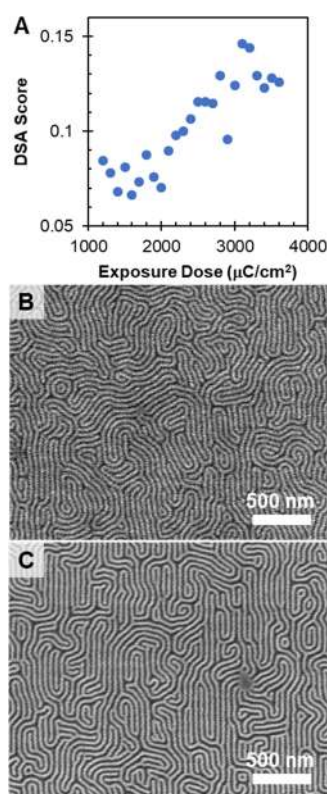
layer of pGST (<5 nm) at the silicon surface (after the rinse step) and result in poorly defined line/space patterns, which is suspected to be the cause of poor DSA quality.

**DSA Using pXST.** Due to the sensitivity of the pGST/Si interface to the electron beam proximity effect, pXST, which cross-links at elevated temperatures and does not require a rinse step, was synthesized. This means that only the polymer/air interface was important to the DSA performance on the pXST and would allow us to circumvent the potential proximity effect at the polymer/Si interface. pXST of various film thicknesses can be placed directly on the silicon wafer, and if the pXST film is sufficiently thick, only the top surface of the pXST is critical to the DSA process. Additionally, for the P2N process, the pXST contains more 4-*tert*-butoxystyrene (38%) than the pGST (24%). Since a larger percentage of the pXST changes from hydrophobic to hydrophilic after exposure and baking, the pXST may potentially have a larger inherent chemical contrast between the unexposed and exposed regions. DSA on the patterned pXST had an overall DSA score greater than that on pGST. The maximum DSA score seen in the pGST sample was approximately 0.15, which was lower than the minimum DSA score observed in the pXST sample of around 0.3 (Figure 3C).

**Photoacid Diffusion in Thin Films.** Although the DSA score of the preliminary pXST sample was better than that of the pGST, dislocation defects were still evident. In order to improve the DSA performance further, one factor to consider is the quality of the photopatterned guidelines. Previous work suggests that sharp and precisely defined guidelines<sup>62</sup> and specific dimensions of guidelines enable better DSA.<sup>23</sup> A

hypothesis was made that film thickness can impact photoacid diffusion and that thinner films can possibly result in more clearly defined interfaces, which are important for BCP alignment control.<sup>63</sup> It is well documented that thin-film confinement can induce changes in physiochemical properties of thin polymer films such as the orientation of polymer chains and glass transition temperature, and transport properties such as diffusion coefficient.<sup>60,64,65</sup> As the spatial resolution of photopatterned pXST is dependent on the extent of photoacid diffusion from exposed to unexposed regions, the effect of film thickness on photoacid diffusion was studied by Fourier transform infrared spectroscopy (FTIR) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. In order to study acid diffusion in very thin films, we used the poly(4-*tert*-butoxycarbonyloxystyrene) (PTBOC) homopolymer instead of pXST. This polymer was chosen because only a fraction of pXST contained 4-*tert*-butoxystyrene monomer units, and the intensity of C–O stretching was very weak (Figure S4). O–H stretching could potentially be used as a probe to measure the extent of deprotection reaction, but the O–H peak was broad and overlapped with the C–H stretching peaks, which could complicate the analysis and introduce errors. Hence, the PTBOC homopolymer was used as a model to measure the extent of acid diffusion in thin films. The deprotection reaction of PTBOC is similar to that of poly(4-*tert*-butoxystyrene) (Figure 4A), but PTBOC has a characteristic sharp carbonyl stretching at  $1756\text{ cm}^{-1}$ , which can be used as a probe to measure the extent of deprotection reaction (Figure 4B).

PTBOC films of various film thicknesses were patterned by photolithography to expose equal lines and spaces at a large



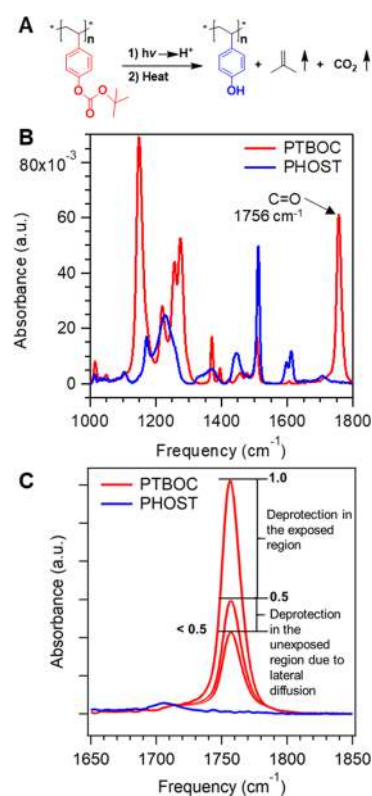
**Figure 3.** (A) DSA score as a function of exposure dose for DSA on a 1:1 line/space array with a pitch of 44 nm ( $1 L_0$ ) on pGST. (B) An SEM image of DSA on pGST with a maximum DSA score of around 0.15. (C) An SEM image of DSA on pXST with a minimum DSA score of around 0.3. The DSA score was quantified by analyzing SEM micrographs following the procedure described in Figures S1–S3.

exposure dose of  $150 \text{ mJ}/\text{cm}^2$  to generate enough photoacid in the exposed regions to deprotect all PTBOC during the post-exposure bake (Figure S5). The amount of carbonyl groups remaining after exposure and baking was normalized with respect to that of the unexposed region. The deprotection level was calculated by eq 1, where  $A_{\text{C=O,Patterned}}$  and  $A_{\text{C=O,Unexposed}}$  are the absorbances of carbonyl groups of patterned and unexposed samples, respectively. The absorbance was measured by taking the area under the curve of the infrared absorption spectra of the carbonyl peak centered at  $1756 \text{ cm}^{-1}$ .

$$\text{deprotection level} = 1 - \frac{A_{\text{C=O,Patterned}}}{A_{\text{C=O,Unexposed}}} \quad (1)$$

In an attempt to decouple the effect of lateral and vertical photoacid diffusion, unpatterned PTBOC samples were exposed at the same dose, and it was determined that, at that dose, the PTBOC samples were almost completely deprotected regardless of film thickness (Figure S6). Hence, any deviation of the deprotection level with film thickness was assumed to be mainly contributed by the change in lateral diffusion only.

As illustrated in Figure 4C, if there was no lateral photoacid diffusion into the unexposed regions, the deprotection level would remain at 0.5 since the equal line/space array was exposed on the film. However, if the photoacid diffused into the unexposed regions and catalyzed the deprotection reaction, the deprotection level would be greater than 0.5, and the normalized absorbance of carbonyl stretching would be less

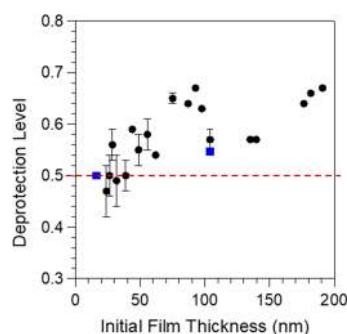


**Figure 4.** (A) Acid-catalyzed deprotection reaction of poly(4-tert-butoxycarbonyloxystyrene) (PTBOC). (B) FTIR spectra of PTBOC and PHOST homopolymers. The carbonyl group absorbed at  $1756 \text{ cm}^{-1}$  has a clean baseline that can be used to measure the extent of deprotection reaction in thin films. (C) An illustration of the carbonyl peak in the FTIR spectra as a probe to measure the extent of photoacid diffusion. The absorbance of carbonyl stretching in the patterned film is normalized to that in the unexposed film.

than 0.5. It has to be noted that a deprotection level of 0.5 is an ideal case where the aerial image is a perfect binary profile of the line/space array. However, photolithography using a contact mask is prone to diffraction-limited edges if perfect contact is not fulfilled. Blurred and overexposed lines may result in a larger deprotection level and variance of sample data. Interference effects may also have an effect on the deprotection level for thicker films but not so much for thinner films. Hence, rather than quantifying the acid diffusion length, a general trend of the deprotection level with film thickness was observed and analyzed to gain a qualitative understanding of the effect of film thickness on photoacid diffusion behavior.

Figure 5 shows the graph of the deprotection level against initial film thickness of the PTBOC resist films. Films with thicknesses ranging from 16 to 191 nm were spin-coated and patterned by photolithography with a constant exposure dose of  $\sim 150 \text{ mJ}/\text{cm}^2$ . The data with error bars are measurements from two or more independently prepared samples. The general trend of lower deprotection level with smaller film thicknesses suggested that there was less deprotection reaction in the unintended (unexposed) regions, possibly due to less acid diffusion.

FTIR was used as a convenient and quick measurement method for the analysis of the deprotection level in thin resist films down to 24 nm, but FTIR was not able to measure resist films less than 24 nm with reasonable accuracy due to a low signal-to-noise ratio. In order to further corroborate the

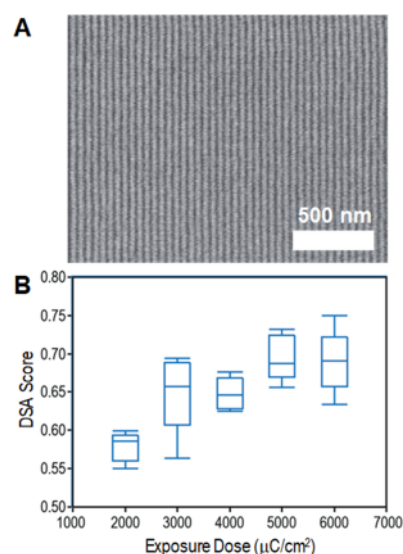


**Figure 5.** Deprotection level against film thickness on patterned PTBOC samples. Black circles are measured deprotection levels from FTIR measurements. Blue squares are measured deprotection levels from the near-edge X-ray absorption fine structure (NEXAFS) measurements.

behavior of acid diffusion in very thin films, we explored near-edge X-ray absorption fine structure (NEXAFS) transmission absorption spectroscopy as an alternative technique for measuring even thinner films with a reasonable signal-to-noise ratio. Control tests were performed to ensure that there was minimal X-ray beam damage on the PTBOC films. The deprotected fractions of patterned films were calculated by linear combinations of NEXAFS spectra of adjacent blanket regions of exposed and unexposed PTBOC. The linear combination was done across the carbon edge from 284 to 300 nm. Figure S7 shows the exposed and unexposed fractions, the comparison of the NEXAFS for the patterned film and the total of the fractions of the blanket measurement, and the residual. The deprotection levels at the two film thicknesses are plotted in Figure 5 in blue square data points and were consistent with the general trend from the FTIR study. In summary, the general trend of a lower deprotection level with thinner films is apparent, and the deprotection levels of very thin films reach  $\sim 0.5$  suggesting that there may be slower acid diffusion in the thinner films. A similar observation of the transition of acid diffusion behavior with film thickness was reported by Goldfarb et al.,<sup>66</sup> who observed that the velocity of the reaction front in PTBOC was significantly reduced in film thicknesses less than 60 nm.

Another possible reason for this transition could be free volume expansion in the films. The portion of the film at the substrate interface does not expand as much as at the air interface. In very thin regimes, the substrate has a greater confinement effect on the film. This was seen in cross-linked polymer films studied by Lenhart and Wu.<sup>67</sup> They documented that cross-linked epoxy network films with thicknesses between 20 and 40 nm exhibited smaller thermal expansion behavior that was independent of the substrate surface treatment. A decrease in thermal expansion implies a decrease in the change in free volume during the post-exposure bake, and the diffusivity of the photoacid in the polymer film is a direct function of the change in free volume.<sup>68</sup>

**Effect of Film Thickness on BCP Alignment Control.** Leveraging the findings from the photoacid diffusion study in very thin films that thinner pXST films could potentially result in more well-defined guidelines, the film thickness of pXST film was reduced, and the DSA was performed again. Lowering the film thickness of pXST films from 40 to 20 nm gave a significant improvement in the DSA score from 0.3 to 0.65 (Figure S8). Figure 6A shows an SEM image of high-quality



**Figure 6.** (A) SEM image of resulting DSA on the 20 nm-thick pXST film exposed 1:1 line/space pattern with a dose of  $6000 \mu\text{C}/\text{cm}^2$ . (B) DSA score as a function of exposure dose for DSA using a 1:1 line/space array on pXST with a film thickness of 20 nm.

DSA on a pattern-wise exposed pXST sample by electron beam lithography, and it has a DSA score of 0.69. As the random noise in SEM also contributes to the overall DSA score, a good DSA generally has a maximum DSA score of  $\sim 0.8$ . Here, we clearly observed that the DSA quality on the pXST was better than that on the pGST with much lower defectivity, and the DSA on the thinner pXST was improved compared to that on the thicker pXST. One possible argument for the improved performance seen in thinner pXST films is due to slower photoacid diffusion creating more well-defined boundaries between the unexposed and exposed regions. Although a wide range of pXST film thickness was not explored, there may exist an optimal pXST film thickness, which is thicker than the grafted pGST ( $< 5$  nm) but not too thick, and the DSA score could be improved further. pXST therefore provides access to the ideal range of film thickness that can potentially maximize the DSA score.

**Effect of Exposure Dose on BCP Alignment Control.** As previously shown in Figure 3A, the exposure dose has an observable effect on the DSA score on pGST, so one would expect that the same would be true for the pXST. Figure 6B shows a plot of DSA score as a function of exposure dose. An increase in DSA with increasing exposure dose can be seen. A large increase in DSA quality occurred from 2000 to  $3000 \mu\text{C}/\text{cm}^2$ . From there, the average increase in DSA was not as dramatic.

A dose of  $5000 \mu\text{C}/\text{cm}^2$  required for low-defectivity DSA is higher than expected. At this dose, degradation of the protecting group is possible through thermolysis. Thus, control experiments were performed to confirm that the changes in the surface wetting behavior were caused by an acid-catalyzed deprotection pathway and not by a simple thermolysis reaction. pXST films with and without photoacid generator were exposed to the same exposure pattern and dose. Good DSA patterns were observed only on the exposed pXST film containing a photoacid generator. Therefore, the DSA shown in Figure 6A was due to acidolysis and not just thermolysis. The details of the control experiment are included in Figure S9.

Besides exposure dose, there are other process parameters such as BCP annealing temperature and time that can influence the overall BCP alignment<sup>24</sup> and DSA score. Fully optimizing BCP annealing conditions is beyond the scope of this work. Nevertheless, the current strategy offers a simple alternative to achieving DSA using directly photopatterned pXST surfaces.

## CONCLUSIONS AND OUTLOOK

In this work, electron beam lithography was used to expose photopatternable pGST and pXST containing photolabile 4-*tert*-butoxystyrene to create well-defined, high-resolution areas of perpendicular and parallel domains in the same BCP film. pXST was found to be more versatile than pGST because it does not require pretreatment, and its film thickness can be easily tuned. Successful BCP alignment with low defectivity was achieved with 1:1 line/space patterns in pXST compared to pGST, and the quality of the DSA was dependent on pXST film thickness and exposure dose. The extent of deprotection reaction was measured in patterned films of various film thicknesses by FTIR and NEXAFS down to 16 nm, and these data suggested that there may be less acid diffusion in much thinner films, which is consistent with previous reports.<sup>66,69</sup> Defectivity decreased as the XST film thickness decreased, potentially due to less acid diffusion in thinner films and thereby creating sharper patterned edges enabling better alignment control. The proposed DSA strategy using pXST provides a simple alternative method that does not require (1) a series of photolithography steps to produce chemical guidelines, (2) a neutral brush, and (3) substrate pretreatment, and it is easily transferrable to the current lithography process. The techniques and materials used in this work can potentially enable routes to complex custom patterns for microelectronic devices in a single photolithographic exposure. The simplified DSA strategy is not just amenable to future semiconductor applications, but it can potentially be used to create ordered nanoarrays for controlled drug delivery,<sup>29</sup> large-area nano-patterns that can serve as scaffolds to promote cell alignment for tissue engineering,<sup>35–38</sup> high-resolution metal nanoparticle arrays for sensors,<sup>30</sup> and patterned plasmonic nanostructures for photovoltaic applications.<sup>31–34</sup> With further studies of other process parameters and optimization, the proposed DSA strategy could help advance BCP lithography and make it a more attractive patterning technology.

## METHODS

**Instrumentation. Patterning of pGST and pXST.** Electron beam patterns were generated with a JEOL 6000 FSE<sup>4</sup> electron beam lithography tool operating in 5th lens mode at 50 kV. Direct writing was performed using a spot size of approximately 2 nm and a beam current of 100 pA. SEM micrographs were captured on a Hitachi S-4500 with a working distance of 5 mm and an accelerating voltage of 1.5 kV.

**Patterning of Thin PTBOC Films.** A Canon contact aligner (PLA-501F-FA), equipped with a filter that passes ultraviolet light with 254 nm and longer wavelengths, was used for patterning thin PTBOC films. A standard 6 in. photomask containing areas of 10  $\mu\text{m}$  lines and spaces and unexposed and exposed regions was employed (Photronics, Inc.).

**Characterization of PTBOC Films.** Ellipsometry was used to measure the film thickness of resist films before and after exposure and baking, and measurements were performed with a J. A. Woollam Co., Inc. M-2000 V ellipsometer with 382 to 984 nm wavelengths and a 65° angle of incidence. FTIR (Vertex 70, Bruker Optics) with a

liquid nitrogen cooled mercury cadmium telluride (MCT) detector was used to record the spectra of the unexposed, exposed, and patterned resist films at an 8  $\text{cm}^{-1}$  resolution with an average scan of 512 scans or more. The patterned PTBOC films on double-sided polished silicon wafers were mounted on an FTIR sample holder and were measured in the transmission mode. The transmission near-edge X-ray absorption fine structure (NEXAFS) measurements were performed at the beamline 6.3.2 at the Advanced Light Source. PTBOC films were on freestanding 100 nm silicon nitride membranes fabricated as described in the Materials section. The measurements were conducted in a transmission geometry with the sample at normal incidence to the beam using a photodiode detector. A combination of a 60 nm Ti filter and a triple mirror order suppressor was used to eliminate contributions from higher-order light. Reference spectra from an empty SiN window were collected in order to account for contributions from the substrate. Spectra were collected between 270 and 320 eV with 500 points.

**Materials.** Lamellar-forming poly(styrene-*block*-4-trimethylsilylstyrene) (PS-*b*-PTMSS) with a domain periodicity,  $L_0$ , of 44 nm was used for DSA using pGST and pXST. The neutral top coat contained 48% maleic anhydride, 21% 3,5-di-*tert*-butylstyrene, and 26% styrene. The top coats were converted to their trimethylamine salts before use. Full synthetic details and characterization data for the BCP and top coat are reported elsewhere.<sup>9</sup> The preferential-to-neutral (P2N) pGST consisted of 50% maleic anhydride, 24% 4-*tert*-butoxystyrene, and 26% 3,5-di-*tert*-butylstyrene. Full synthetic details on pGSTs can be found elsewhere.<sup>48</sup> The P2N pXST consisted of 5% 4-vinylbenzylazide, 38% 4-*tert*-butoxystyrene, and 57% 3,5-di-*tert*-butylstyrene (feed ratio), and it was synthesized by free-radical polymerization with azobisisobutyronitrile. Neutral and preferential compositions were identified using island/hole methods as described previously.<sup>70</sup> Poly(4-*tert*-butoxycarbonyloxystyrene) (PTBOC) was synthesized by free-radical polymerization with azobisisobutyronitrile following the procedure described by Frechet et al.<sup>71</sup> The 4-*tert*-butoxycarbonyloxystyrene monomer was a generous gift from TriQuest Chemical Co. Molecular weight measurements were performed using an Agilent 1100 Series isopump and autosampler with a Viscotek Model 302 TETRA detector platform and three Viscotek Viscogel (I-MBMMW-3078) columns using tetrahydrofuran as an eluent. The number-average molecular weight of PTBOC used in this study was  $\sim 60$  kDa with a polydispersity index of  $\sim 1.9$  using polystyrene standards.

**Sample Preparation. DSA Using pGST and pXST.** For pGST, the native oxide on the surface of silicon wafers was first treated with APTES to produce a surface with free amines.<sup>48,51</sup> The P2N pGST was grafted via the reaction between the anhydride functional groups in pGST and surface amines. This process chemically modifies the surface by covalently grafting a thin layer ( $<5$  nm) of pGST. To produce the amine-enriched surfaces, a silicon wafer was covered with neat APTES and allowed to react for 30 s at room temperature. The wafer was then rinsed with tetrahydrofuran and baked at 100 °C for 30 s. Then, a solution of P2N pGST (1 wt % polymer in methyl isobutyl ketone with 10 wt % triphenylsulfonium nonaflate relative to the polymer mass) was spin-coated at 1500 rpm and annealed at 180 °C for 1 min. This resulted in a film of approximately 25 nm. For P2N pXST, a solution of pXST (1 wt % polymer in methyl isobutyl ketone with 10 wt % triphenylsulfonium hexafluoroantimonate relative to the polymer mass) was spin-coated directly on an untreated silicon wafer at 1500 rpm and annealed at 250 °C for 5 min to cross-link the pXST.<sup>7</sup> This also resulted in a film of approximately 25 nm.

Samples were then directly patterned with electron beam radiation with doses of 100 to 4000  $\mu\text{C}/\text{cm}^2$  and post-exposure baked at 100 and 165 °C/1 min for pGST and pXST samples, respectively, during which the acid-catalyzed deblocking of the *tert*-butyl ethers occurred.<sup>48</sup> The pGST samples were then rinsed with methyl isobutyl ketone to remove excess ungrafted pGST. After rinsing, the final film thicknesses of grafted pGST were between 3 and 5 nm. The pXST samples required no further processing.

PS-*b*-PTMSS was spin-coated out of methyl isobutyl ketone to form films approximately 1  $L_0$  (44 nm) in thickness. A neutral top

coat trimethylamine salt was spin-coated out of methanol and annealed at 180 °C for 10 min.<sup>9</sup> The top coat was removed by immersing the samples in a solution of three parts 0.26 N tetramethylammonium hydroxide solution and one part 2-propanol (by volume). Samples were rinsed with deionized water and dried with a gentle stream of nitrogen. Samples were etched with oxygen plasma (Harrick PDC-32G) at 500 mtorr for 60 s.

**Photoacid Diffusion Measurements of Thin PTBOC Films.** Various concentrations of PTBOC solutions in propylene glycol monomethyl ether acetate were prepared with 10 wt % triphenylsulfonium hexafluoroantimonate relative to the polymer mass. The PTBOC solution was spin-coated under a flow of air that was passed through an active carbon filter to minimize the base contamination effect. Resist films with various film thicknesses were prepared on 4 in. double-sided polished silicon wafers and were post-apply baked at 100 °C for 2 min to remove any residual casting solvent. The resulting films were then exposed and patterned by photolithography using a contact mask with a constant dose of ~150 mJ/cm<sup>2</sup> to ensure that most of the photoacid generators were activated and then post-exposure baked at 80 °C for 5 min to fully deprotect the exposed regions. For NEXAFS measurements, PTBOC films were spin-coated on 100 nm silicon nitride films on silicon and were patterned by the previously described photolithography method. Windows were etched in the back of the sample using KOH at 80 °C for about 3 h until silicon nitride was exposed. PTBOC films were on freestanding silicon nitride membranes.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c02997>.

Additional details on analysis of the DSA score, FTIR spectra of pXST and PTBOC, an illustration of photoacid diffusion experimental setup, NEXAFS spectra and analysis of patterned PTBOC samples, and optical micrographs of pXST samples with and without a photoacid generator (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

**C. Grant Willson** – McKetta Department of Chemical Engineering and Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0002-2072-3981](https://orcid.org/0000-0002-2072-3981); Email: [cbaiz@cm.utexas.edu](mailto:cbaiz@cm.utexas.edu)

**Carlos R. Baiz** – Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0003-0699-8468](https://orcid.org/0000-0003-0699-8468); Email: [willson@che.utexas.edu](mailto:willson@che.utexas.edu)

### Authors

**Ji Yeon Kim** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0001-7068-0871](https://orcid.org/0000-0001-7068-0871)

**Philip Liu** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States

**Michael J. Maher** – Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States; IBM Research - Almaden, San Jose, California 95120, United States; Department of Chemical Engineering and Material Science, University of Minnesota Twin Cities, Minneapolis, Minnesota 55455, United States; [orcid.org/0000-0003-0577-3726](https://orcid.org/0000-0003-0577-3726)

**Devon H. Callan** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0002-8562-8141](https://orcid.org/0000-0002-8562-8141)

**Christopher M. Bates** – Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States;

[orcid.org/0000-0002-1598-794X](https://orcid.org/0000-0002-1598-794X)

**Matthew C. Carlson** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States; Department of Chemical Engineering and Material Science, University of Minnesota Twin Cities, Minneapolis, Minnesota 55455, United States

**Yusuke Asano** – Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States

**Gregory Blachut** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0002-8539-4840](https://orcid.org/0000-0002-8539-4840)

**Charles T. Rettner** – IBM Research - Almaden, San Jose, California 95120, United States

**Joy Y. Cheng** – IBM Research - Almaden, San Jose, California 95120, United States

**Daniel F. Sunday** – Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States; [orcid.org/0000-0002-6840-535X](https://orcid.org/0000-0002-6840-535X)

**R. Joseph Kline** – Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

**Daniel P. Sanders** – IBM Research - Almaden, San Jose, California 95120, United States

**Nathaniel A. Lynd** – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States; [orcid.org/0000-0003-3010-5068](https://orcid.org/0000-0003-3010-5068)

**Christopher J. Ellison** – Department of Chemical Engineering and Material Science, University of Minnesota Twin Cities, Minneapolis, Minnesota 55455, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsami.0c02997>

### Author Contributions

#J.Y.K., P.L., and M.J.M. contributed equally.

### Author Contributions

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

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank Nissan Chemical Industries, Lam Research, the ASTC, and the National Science Foundation Nanomanufacturing Systems for mobile Computing and Energy Technologies (NASCENT) (Grants EECS-1120823 and EEC-1160494) for financial support. P.L. thanks the National Science Foundation Graduate Research Fellowship for financial support. M.J.M. thanks the IBM Ph.D. Fellowship Program and the National Science Foundation Graduate Research Fellowship (Grant No. DGE-1110007) for financial support. G.B. thanks the Paul D. Meek Endowed Graduate Fellowship in Engineering for support. C.J.E. thanks the Welch Foundation (grant #F-1709) for partial financial support. C.R.B. thanks the Welch Foundation (grant #F-1891) and the National Science Foundation (CHE-1847199) for financial support. C.G.W. thanks the Rashid Engineering Regents Chair and the Welch Foundation (Grant #F-1830) for financial support. The authors also thank the Advanced Light Source,



Lawrence Berkeley National Laboratory. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-05CH11231. R.J.K. and D.F.S. thank the National Institute of Standards and Technology for financial support. The authors thank Subhrangsu Mukherjee for assistance with the etching of the wafers for NEXAFS measurements and Eric Gullikson for assistance with setting up NEXAFS measurements. The authors also thank Drs. Dustin Janes, Lisa Lofano, Hoa Truong, Amy Bowers, and Christopher Soles for their insightful ideas, Alison Pawlick from Oak Ridge National Laboratory for initial AFM-IR measurements, and Ron Synockwicki from J. A. Woollam for initial ellipsometry patterning measurements.

## ABBREVIATIONS

- BCP, Block copolymer  
DSA, Directed self-assembly  
GST, Grafting surface treatment  
NEXAFS, Near-edge X-ray absorption fine structure spectroscopy  
N2P, Neutral-to-preferential  
P2N, Preferential-to-neutral  
XST, Cross-linkable surface treatment  
PHOST, Poly(4-hydroxystyrene)  
PTBOC, Poly(4-*tert*-butoxycarbonyloxystyrene)

## ADDITIONAL NOTE

<sup>a</sup>Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

## REFERENCES

- (1) Bates, C. M.; Maher, M. J.; Janes, D. W.; Ellison, C. J.; Willson, C. G. Block Copolymer Lithography. *Macromolecules* **2014**, *47*, 2–12.
- (2) Luo, M.; Epps, T. H., III Directed Block Copolymer Thin Film Self-Assembly: Emerging Trends in Nanopattern Fabrication. *Macromolecules* **2013**, *46*, 7567–7579.
- (3) Doerk, G. S.; Liu, C. C.; Cheng, J. Y.; Rettner, C. T.; Pitera, J. W.; Krupp, L. E.; Topuria, T.; Arellano, N.; Sanders, D. P. Pattern Placement Accuracy in Block Copolymer Directed Self-Assembly Based on Chemical Epitaxy. *ACS Nano* **2013**, *7*, 276–285.
- (4) Doerk, G. S.; Liu, C.-C.; Cheng, J. Y.; Rettner, C. T.; Pitera, J. W.; Krupp, L.; Topuria, T.; Arellano, N.; Sanders, D. P. Measurement of Placement Error between Self-Assembled Polymer Patterns and Guiding Chemical Prepatterns. *Proc. SPIE* **2012**, *8323*, 83230P.
- (5) Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. A Generalized Approach to the Modification of Solid Surfaces. *Science* **2005**, *308*, 236–239.
- (6) Bang, J.; Bae, J.; Löwenhielm, P.; Spiessberger, C.; Given-Beck, S. A.; Russell, T. P.; Hawker, C. J. Facile Routes to Patterned Surface Neutralization Layers for Block Copolymer Lithography. *Adv. Mater.* **2007**, *19*, 4552–4557.
- (7) Bates, C. M.; Strahan, J. R.; Santos, L. J.; Mueller, B. K.; Bamgbade, B. O.; Lee, J. A.; Katzenstein, J. M.; Ellison, C. J.; Willson, C. G. Polymeric Cross-Linked Surface Treatments for Controlling Block Copolymer Orientation in Thin Films. *Langmuir* **2011**, *27*, 2000–2006.
- (8) Bates, C. M.; Seshimo, T.; Maher, M. J.; Durand, W. J.; Cushen, J. D.; Dean, L. M.; Blachut, G.; Ellison, C. J.; Willson, C. G. Polarity-Switching Top Coats Enable Orientation of Sub-10-Nm Block Copolymer Domains. *Science* **2012**, *338*, 775–779.
- (9) Maher, M. J.; Bates, C. M.; Blachut, G.; Sirard, S.; Self, J. L.; Carlson, M. C.; Dean, L. M.; Cushen, J. D.; Durand, W. J.; Hayes, C. O.; et al. Interfacial Design for Block Copolymer Thin Films. *Chem. Mater.* **2014**, *26*, 1471–1479.
- (10) Ramírez-Hernández, A.; Suh, H. S.; Nealey, P. F.; De Pablo, J. J. Control of Directed Self-Assembly in Block Polymers by Polymeric Topcoats. *Macromolecules* **2014**, *47*, 3520–3527.
- (11) Segalman, R. A.; Yokoyama, H.; Kramer, E. J. Graphoepitaxy of Spherical Domain Block Copolymer Films. *Adv. Mater.* **2001**, *13*, 1152–1155.
- (12) Xiao, S.; Yang, X.; Edwards, E. W.; La, Y. H.; Nealey, P. F. Graphoepitaxy of Cylinder-Forming Block Copolymers for Use as Templates to Pattern Magnetic Metal Dot Arrays. *Nanotechnology* **2005**, *16*, S324–S329.
- (13) Bitá, I.; Yang, J. K. W.; Jung, Y. S.; Ross, C. A.; Thomas, E. L.; Berggren, K. K. Graphoepitaxy of Self-Assembled Block Copolymers on Two-Dimensional Periodic Patterned Templates. *Science* **2008**, *321*, 939–943.
- (14) Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. Epitaxial Self-Assembly of Block Copolymers on Lithographically Defined Nanopatterned Substrates. *Nature* **2003**, *424*, 411–414.
- (15) Ruiz, R.; Kang, H.; Detcheverry, F. A.; Dobisz, E.; Kercher, D. S.; Albrecht, T. R.; De Pablo, J. J.; Nealey, P. F. Density Multiplication and Improved Lithography by Directed Block Copolymer Assembly. *Science* **2008**, *321*, 936–939.
- (16) Cheng, J. Y.; Rettner, C. T.; Sanders, D. P.; Kim, H.-C.; Hinsberg, W. D. Dense Self-Assembly on Sparse Chemical Patterns: Rectifying and Multiplying Lithographic Patterns Using Block Copolymers. *Adv. Mater.* **2008**, *20*, 3155–3158.
- (17) Cushen, J.; Wan, L.; Blachut, G.; Maher, M. J.; Albrecht, T. R.; Ellison, C. J.; Willson, C. G.; Ruiz, R. Double-Patterned Sidewall Directed Self-Assembly and Pattern Transfer of Sub-10 Nm PTMSS-b-PMOST. *ACS Appl. Mater. Interfaces* **2015**, *7*, 13476–13483.
- (18) Maher, M. J.; Rettner, C. T.; Bates, C. M.; Blachut, G.; Carlson, M. C.; Durand, W. J.; Ellison, C. J.; Sanders, D. P.; Cheng, J. Y.; Willson, C. G. Directed Self-Assembly of Silicon-Containing Block Copolymer Thin Films. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3323–3328.
- (19) Stoykovich, M. P.; Kang, H.; Daoulas, K. C.; Liu, G.; Liu, C. C.; De Pablo, J. J.; Müller, M.; Nealey, P. F. Directed Self-Assembly of Block Copolymers for Nanolithography: Fabrication of Isolated Features and Essential Integrated Circuit Geometries. *ACS Nano* **2007**, *1*, 168–175.
- (20) Stoykovich, M. P.; Müller, M.; Kim, S. O.; Solak, H. H.; Edwards, E. W.; de Pablo, J. J.; Nealey, P. F. Directed Assembly of Block Copolymer Blends into Nonregular Device-Oriented Structures. *Science* **2005**, *308*, 1442–1446.
- (21) Tsai, H.; Pitera, J. W.; Miyazoe, H.; Bangsaruntip, S.; Engelmann, S. U.; Liu, C. C.; Cheng, J. Y.; Bucchignano, J. J.; Klaus, D. P.; Joseph, E. A.; et al. Two-Dimensional Pattern Formation Using Graphoepitaxy of PS-b-PMMA Block Copolymers for Advanced FinFET Device and Circuit Fabrication. *ACS Nano* **2014**, *8*, 5227–5232.
- (22) Albrecht, T. R.; Arora, H.; Ayanoor-Vitikkate, V.; Beaujour, J. M.; Bedau, D.; Berman, D.; Bogdanov, A. L.; Chapuis, Y. A.; Cushen, J.; Dobisz, E. E.; et al. Bit-Patterned Magnetic Recording: Theory, Media Fabrication, and Recording Performance. *IEEE Trans. Magn.* **2015**, *51*, 1–42.
- (23) Liu, C. C.; Ramírez-Hernández, A.; Han, E.; Craig, G. S. W.; Tada, Y.; Yoshida, H.; Kang, H.; Ji, S.; Gopalan, P.; De Pablo, J. J.; et al. Chemical Patterns for Directed Self-Assembly of Lamellae-Forming Block Copolymers with Density Multiplication of Features. *Macromolecules* **2013**, *46*, 1415–1424.
- (24) Doise, J.; Koh, J. H.; Kim, J. Y.; Zhu, Q.; Kinoshita, N.; Suh, H. S.; Delgado, P. R.; Vandenberghe, G.; Willson, C. G.; Ellison, C. J. Strategies for Increasing the Rate of Defect Annihilation in the

Directed Self-Assembly of High- $\chi$  Block Copolymers. *ACS Appl. Mater. Interfaces* **2019**, *11*, 48419–48427.

(25) Delgadillo, P. A. R.; Gronheid, R.; Thode, C. J.; Wu, H.; Cao, Y.; Neisser, M.; Somervell, M.; Nafus, K. Implementation of a Chemo-Epitaxy Flow for Directed Self-Assembly on 300-Mm Wafer Processing Equipment. *J. Micro/Nanolithogr., MEMS, MOEMS* **2012**, *11*, No. 031302.

(26) Pathangi, H.; Chan, B. T.; Bayana, H.; Vandenbroeck, N.; Van Den Heuvel, D.; Van Look, L.; Rincon-Delgadillo, P.; Cao, Y.; Kim, J.; Lin, G.; et al. Defect Mitigation and Root Cause Studies in 14 Nm Half-Pitch Chemo-Epitaxy Directed Self-Assembly LiNe Flow. *J. Micro/Nanolithogr., MEMS, MOEMS* **2015**, *14*, No. 031204.

(27) Cheng, J. Y.; Sanders, D. P.; Truong, H. D.; Harrer, S.; Friz, A.; Holmes, S.; Colburn, M.; Hinsberg, W. D. Simple and Versatile Methods to Integrate Directed Self-Assembly with Optical Lithography Using a Polarity-Switched Photoresist. *ACS Nano* **2010**, *4*, 4815–4823.

(28) Doerk, G. S.; Cheng, J. Y.; Singh, G.; Rettner, C. T.; Pitera, J. W.; Balakrishnan, S.; Arellano, N.; Sanders, D. P. Enabling Complex Nanoscale Pattern Customization Using Directed Self-Assembly. *Nat. Commun.* **2014**, *5*, 5805.

(29) Lo, K. H.; Chen, M. C.; Ho, R. M.; Sung, H. W. Pore-Filling Nanoporous Templates from Degradable Block Copolymers for Nanoscale Drug Delivery. *ACS Nano* **2009**, *3*, 2660–2666.

(30) Yap, F. L.; Thoniyot, P.; Krishnan, S.; Krishnamoorthy, S. Nanoparticle Cluster Arrays for High-Performance SERS through Directed Self-Assembly on Flat Substrates and on Optical Fibers. *ACS Nano* **2012**, *6*, 2056–2070.

(31) Lalander, C. H.; Zheng, Y.; Dhuey, S.; Cabrini, S.; Bach, U. DNA-Directed Self-Assembly of Gold Nanoparticles onto Nanopatterned Surfaces: Controlled Placement of Individual Nanoparticles into Regular Arrays. *ACS Nano* **2010**, *4*, 6153–6161.

(32) Shin, D. O.; Mun, J. H.; Hwang, G. T.; Yoon, J. M.; Kim, J. Y.; Yun, J. M.; Yang, Y. B.; Oh, Y.; Lee, J. Y.; Shin, J.; et al. Multicomponent Nanopatterns by Directed Block Copolymer Self-Assembly. *ACS Nano* **2013**, *7*, 8899–8907.

(33) Mistark, P. A.; Park, S.; Yalcin, S. E.; Lee, D. H.; Yavuzcetin, O.; Tuominen, M. T.; Russell, T. P.; Achermann, M. Block-Copolymer-Based Plasmonic Nanostructures. *ACS Nano* **2009**, *3*, 3987–3992.

(34) Botiz, I.; Darling, S. B. Optoelectronics Using Block Copolymers. *Mater. Today* **2010**, *13*, 42–51.

(35) Aubin, H.; Nichol, J. W.; Hutson, C. B.; Bae, H.; Sieminski, A. L.; Crokek, D. M.; Akhyari, P.; Khademhosseini, A. Directed 3D Cell Alignment and Elongation in Microengineered Hydrogels. *Biomaterials* **2010**, *31*, 6941–6951.

(36) Zhao, G.; Bao, X.; Huang, G.; Xu, F.; Zhang, X. Differential Effects of Directional Cyclic Stretching on the Functionalities of Engineered Cardiac Tissues. *ACS Appl. Bio Mater.* **2019**, *2*, 3508–3519.

(37) Qing, H.; Jin, G.; Zhao, G.; Huang, G.; Ma, Y.; Zhang, X.; Sha, B.; Luo, Z.; Lu, T. J.; Xu, F. Heterostructured Silk-Nanofiber-Reduced Graphene Oxide Composite Scaffold for SH-SY5Y Cell Alignment and Differentiation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 39228–39237.

(38) Lim, J. Y.; Donahue, H. J. Cell Sensing and Response to Micro- and Nanostructured Surfaces Produced by Chemical and Topographic Patterning. *Tissue Eng.* **2007**, *13*, 1879–1891.

(39) Lille, J.; Ruiz, R.; Wan, L.; Gao, H.; Dhanda, A.; Zeltzer, G.; Arnoldussen, T.; Patel, K.; Tang, Y.; Kercher, D.; et al. Integration of Servo and High Bit Aspect Ratio Data Patterns on Nanoimprint Templates for Patterned Media. *IEEE Trans. Magn.* **2012**, *48*, 2757–2760.

(40) Tavakkoli, K. G. A.; Gotrik, K. W.; Hannon, A. F.; Alexander-Katz, A.; Ross, C. A.; Berggren, K. K. Templating Three-Dimensional Self-Assembled Structures in Bilayer Block Copolymer Films. *Science* **2012**, *336*, 1294–1298.

(41) Ruiz, R.; Dobisz, E.; Albrecht, T. R. Rectangular Patterns Using Block Copolymer Directed Assembly for High Bit Aspect Ratio Patterned Media. *ACS Nano* **2011**, *5*, 79–84.

(42) Yang, X.; Xiao, S.; Hu, W.; Hwu, J.; Van De Veerdonk, R.; Wago, K.; Lee, K.; Kuo, D. Integration of Nanoimprint Lithography with Block Copolymer Directed Self-Assembly for Fabrication of a Sub-20 Nm Template for Bit-Patterned Media. *Nanotechnology* **2014**, *25*, 395301.

(43) Wan, L.; Ruiz, R.; Gao, H.; Patel, K. C.; Albrecht, T. R.; Yin, J.; Kim, J.; Cao, Y.; Lin, G. The Limits of Lamellae-Forming PS-*b*-PMMA Block Copolymers for Lithography. *ACS Nano* **2015**, *9*, 7506–7514.

(44) Shin, D. O.; Kim, B. H.; Kang, J. H.; Jeong, S. J.; Park, S. H.; Lee, Y. H.; Kim, S. O. One-Dimensional Nanoassembly of Block Copolymers Tailored by Chemically Patterned Surfaces. *Macromolecules* **2009**, *42*, 1189–1193.

(45) Han, E.; Leolukman, M.; Kim, M.; Gopalan, P. Resist Free Patterning of Nonpreferential Buffer Layers for Block Copolymer Lithography. *ACS Nano* **2010**, *4*, 6527–6534.

(46) Liu, G.; Thomas, C. S.; Craig, G. S. W.; Nealey, P. F. Integration of Density Multiplication in the Formation of Device-Oriented Structures by Directed Assembly of Block Copolymer-Homopolymer Blends. *Adv. Funct. Mater.* **2010**, *20*, 1251–1257.

(47) Walton, D. G.; Kellogg, G. J.; Mayes, A. M.; Lambooy, P.; Russell, T. P. A Free Energy Model for Confined Diblock Copolymers. *Macromolecules* **1994**, *27*, 6225–6228.

(48) Maher, M. J.; Bates, C. M.; Blachut, G.; Carlson, M. C.; Self, J. L.; Janes, D. W.; Durand, W. J.; Lane, A. P.; Ellison, C. J.; Willson, G.; et al. Photopatternable Interfaces for Block Copolymer Lithography. *ACS Macro Lett.* **2014**, *3*, 824–828.

(49) Lane, A. P.; Maher, M. J.; Willson, C. G.; Ellison, C. J. Photopatterning of Block Copolymer Thin Films. *ACS Macro Lett.* **2016**, *5*, 460–465.

(50) Maher, M. J.; Bates, C. M.; Durand, W. J.; Blachut, G.; Janes, D. W.; Cheng, J. Y.; Sanders, D. P.; Willson, C. G.; Ellison, C. J. Interfacial Layers with Photoswitching Surface Energy for Block Copolymer Alignment and Directed Self-Assembly. *J. Photopolym. Sci. Technol.* **2015**, *28*, 611–615.

(51) Durand, W. J.; Blachut, G.; Maher, M. J.; Sirard, S.; Tein, S.; Carlson, M. C.; Asano, Y.; Zhou, S. X.; Lane, A. P.; Bates, C. M.; et al. Design of High- $\chi$  Block Copolymers for Lithography. *J. Polym. Sci. Part A Polym. Chem.* **2015**, *53*, 344–352.

(52) Cheng, J.; Lawson, R. A.; Yeh, W.-M.; Tolbert, L. M.; Henderson, C. L. Developing Directly Photodefinable Substrate Guiding Layers for Block Copolymer Directed Self-Assembly (DSA) Patterning. *Proc. SPIE* **2011**, 7972, 79722I.

(53) Yamamoto, H.; Dawson, G.; Kozawa, T.; Robinson, A. P. G. Lamellar Orientation of a Block Copolymer via an Electron-Beam Induced Polarity Switch in a Nitrophenyl Self-Assembled Monolayer or Si Etching Treatments. *Quantum Beam Sci.* **2020**, *4*, 19.

(54) Peters, R. D.; Yang, X. M.; Kim, T. K.; Sohn, B. H.; Nealey, P. F. Using Self-Assembled Monolayers Exposed to X-Rays to Control the Wetting Behavior of Thin Films of Diblock Copolymers. *Langmuir* **2000**, *16*, 4625–4631.

(55) Peeters, E.; Ketelaars, W. S. M. M.; Wuister, S. F.; Koole, R.; Van Heesch, C. M.; Brizard, A. M. A.; Boots, H. M. J.; Nguyen, T. T.; Yildirim, O. Methods of Providing Patterned Chemical Epitaxy Templates for Self-Assemblable Block Copolymers for Use in Device Lithography. U.S. Patent 9,235,125, Jan 12, 2016.

(56) Lin, E. K.; Soles, C. L.; Goldfarb, D. L.; Trinquet, B. C.; Burns, S. D.; Jones, R. L.; Lenhart, J. L.; Angelopoulos, M.; Willson, C. G.; Satija, S. K.; et al. Direct Measurement of the Reaction Front in Chemically Amplified Photoresists. *Science* **2002**, *297*, 372–375.

(57) Wallraff, G.; Hutchinson, J.; Hinsberg, W.; Houle, F.; Seidel, P. Kinetics of Thermal and Acid-Catalyzed Deprotection in Deep-UV Resist Materials. *Microelectron. Eng.* **1995**, *27*, 397–400.

(58) Stewart, M. D.; Schmid, G. M.; Postnikov, S. V.; Willson, C. G. Mechanistic Understanding of Line End Shortening. *Proc. SPIE* **2001**, 4345.

(59) Kang, S. H.; Prabhu, V. M.; Vogt, B. D.; Lin, E. K.; Wu, W.-L.; Turnquist, K. Effect of Copolymer Composition on Acid-Catalyzed

Deprotection Reaction Kinetics in Model Photoresists. *Polymer* **2006**, *47*, 6293–6302.

(60) Kang, S.; Wu, W. L.; Choi, K. W.; De Silva, A.; Ober, C. K.; Prabhu, V. M. Characterization of the Photoacid Diffusion Length and Reaction Kinetics in EUV Photoresists with IR Spectroscopy. *Macromolecules* **2010**, *43*, 4275–4286.

(61) Chang, T. H. P. Proximity Effect in Electron-Beam Lithography. *J. Vac. Sci. Technol.* **1975**, *12*, 1271.

(62) Doise, J.; Mannaert, G.; Suh, H. S.; Rincon, P.; Koh, J. H.; Kim, J. Y.; Zhu, Q.; Vandenberghe, G.; Willson, C. G.; Ellison, C. J. Defect Mitigation in Sub-20nm Patterning with High-Chi, Silicon-Containing Block Copolymers. *Proc. SPIE* **2019**, *10960*, 109600Y.

(63) Stoykovich, M. P.; Daoulas, K. C.; Müller, M.; Kang, H.; De Pablo, J. J.; Nealey, P. F. Remediation of Line Edge Roughness in Chemical Nanopatterns by the Directed Assembly of Overlying Block Copolymer Films. *Macromolecules* **2010**, *43*, 2334–2342.

(64) Frank, C. W.; Rao, V.; Despotopoulou, M. M.; Pease, R. F. W.; Hinsberg, W. D.; Miller, R. D.; Rabolt, J. F. Structure in Thin and Ultrathin Spin-Cast Polymer Films. *Science* **1996**, *273*, 912–915.

(65) Soles, C. L.; Lin, E. K.; Lenhart, J. L.; Jones, R. L.; Wu, W.-L.; Goldfarb, D. L.; Angelopoulos, M. Thin Film Confinement Effects on the Thermal Properties of Model Photoresist Polymers. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom.* **2001**, *19*, 2690.

(66) Goldfarb, D. L.; Angelopoulos, M.; Lin, E. K.; Jones, R. L.; Soles, C. L.; Lenhart, J. L.; Wu, W.-L. Confinement Effects on the Spatial Extent of the Reaction Front in Ultrathin Chemically Amplified Photoresists. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom.* **2001**, *19*, 2699–2704.

(67) Lenhart, J. L.; Wu, W. L. Deviations in the Thermal Properties of Ultrathin Polymer Network Films. *Macromolecules* **2002**, *35*, 5145–5152.

(68) Byers, J. D.; Smith, M. D.; Mack, C. A.; Biafore, J. J. Modeling Soft-Bake Effects in Chemically Amplified Resists. *Proc. SPIE* **2003**, 5039.

(69) Soles, C. L.; Douglas, J. F.; Lin, E. K.; Lenhart, J. L.; Jones, R. L.; Wu, W.-L.; Goldfarb, D. L.; Angelopoulos, M. Incoherent Neutron Scattering and the Dynamics of Thin Film Photoresist Polymers. *J. Appl. Phys.* **2003**, *93*, 1978–1986.

(70) Kim, S.; Bates, C. M.; Thio, A.; Cushen, J. D.; Ellison, C. J.; Willson, C. G.; Bates, F. S. Consequences of Surface Neutralization in Diblock Copolymer Thin Films. *ACS Nano* **2013**, *7*, 9905–9919.

(71) Fréchet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. Poly(p-Tert-Butoxycarbonyloxystyrene): A Convenient Precursor to p-Hydroxystyrene Resins. *Polymer* **1983**, *24*, 995–1000.