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Yamamoto, Hiroki; Dawson, Guy; Kozawa, Takahiro; Robinson, Alexander

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## Lamellar orientation of block copolymer using polarity switch of nitrophenyl self-assembled monolayer induced by electron beam

Hiroki Yamamoto  
Guy Dawson  
Takahiro Kozawa  
Alex P. G. Robinson

# Lamellar Orientation of Block Copolymer Using Polarity Switch of Nitrophenyl Self-assembled Monolayer Induced by Electron Beam

Hiroki Yamamoto <sup>a</sup>, Guy Dawson <sup>b</sup>, Takahiro Kozawa <sup>a</sup>, Alex. P.G. Robinson <sup>b</sup>

<sup>a</sup> The Institute of Scientific and Industrial Research, Osaka University,  
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

<sup>b</sup> School of Chemical Engineering, University of Birmingham,  
Edgbaston, Birmingham, B15 2TT, UK.

## ABSTRACT

Directed self-assembly (DSA) was investigated on self-assembled monolayers (SAMs) of 6-(4-nitrophenoxy) hexane-1-thiol (NPHT), which were chemically modified by electron beam (EB) irradiation. By irradiating a responsive interfacial surface, the orientation and selective patterning of block copolymer domains could be achieved. We demonstrated that spatially-selective lamellar orientation of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) could be induced via modification of an underlying SAM; for instance the conversion of an NO<sub>2</sub> group to an NH<sub>2</sub> group, induced by EB. The lamellar orientation of PS-*b*-PMMA was controlled by the change in the polarity of different regions of the SAM using EB lithography. The reductive treatment of SAM substrates plays a crucial role in the orientation of block copolymer. This method might greatly simplify block copolymer DSA processes as compared to the conventional multi-step chemo-epitaxy DSA process. By examining the lamellae orientation by EB, we found that the vertical orientation persists only for appropriate an irradiation dose and annealing temperature.

**Keywords:** Block copolymer, lamellar orientation, self-assembled monolayer, polarity switch, electron beam

## 1. INTRODUCTION

With further miniaturization of devices, sub-10 nm feature sizes are anticipated which will not easily be obtained by extreme ultraviolet (EUV) or electron beam (EB) lithography techniques in mass production, due to patterning limitations, tool costs, or low throughput and so on. The combination of top-down and bottom-up approaches to nanopatterning has become an area of research focus because conventional top-down lithographic techniques are now approaching such fundamental limitations. Self-assembly of block copolymers enables the fabrication of features of

sub-20 nm without using an expensive exposure tool. In particular, DSA of block copolymers has attracted significant attention as a promising nanolithography technique to surmount the fundamental limitations of conventional lithography. Block copolymers have the potential to be used in semiconductor manufacturing<sup>1-6</sup> and directed self-assembly (DSA) is currently being considered for future nodes of the ITRS roadmap.<sup>7</sup>

Up to now, a great deal of effort has been devoted to controlling the self-assembly of block copolymers using the techniques of grapho-epitaxy<sup>2,8-11</sup> and chemo-epitaxy.<sup>12-13</sup> Generally, the orientation of block copolymer can be controlled by precisely tuning the chemistry of the interface between the block copolymer and the substrate. The basic method for achieving perpendicular orientation of block copolymer is to balance the interfacial interactions of each block of the block copolymer with the substrate. Neutral surfaces have been shown to induce a perpendicular domain orientation in block copolymer thin films.<sup>14,15</sup> This strategy takes advantage of the inherent versatility of random copolymers, which allows the surface energy or surface characteristics to be tuned by changing the chemical composition of the random copolymer. A more general approach to controlling interfacial and surface interactions using an ultrathin crosslinkable film of a random copolymer has been developed.<sup>16</sup> In addition, there are several methods such as solvent annealing,<sup>17</sup> the use of rough substrates,<sup>18,19</sup> chemical modification of the substrate<sup>15,20,21</sup> and so on to control the orientation of domains in block copolymer films. In particular, surfaces with neutral wettability to the polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymers, such as random styrene-methacrylate copolymer films (PS-*r*-PMMA) or self-assembled monolayer (SAM) modified surfaces have been studied to induce perpendicular orientation for PS-*b*-PMMA self-assembly. Pre-patterned surfaces, consisting of alternating neutral and preferential surfaces, have been prepared by the selective oxidation of a neutral SAM with resist patterns by advanced lithography.<sup>16,18,19</sup> However, current methods for achieving a patterned substrate template are generally complex, involving a large number of steps. In order to simplify and improve DSA processes, several strategies for controlling areas of block copolymer domain orientation using radiation have been reported. Approaches including a photodefinable substrate film,<sup>22</sup> EB sensitive materials,<sup>23</sup> x-ray sensitive self-assembled monolayers,<sup>15</sup> the selective cross-linking of substrate surface treatments via UV light,<sup>24,25</sup> and reactive ion etching<sup>26-28</sup> have all been reported. In addition, disordered block copolymers that order in response to light<sup>29-32</sup> and electrohydrodynamic jet printing<sup>33</sup> have been reported. However, a number of challenges remain with such approaches.

Controlling the surface chemistry of specific regions, to locally change the orientation of block copolymer domains by top-down lithography, is very valuable. In particular, EB lithography is suitable for the modification of the substrate surface, and has the advantage that it is easily possible to fabricate feature size patterns as small as 20 nm. In addition to high resolution, EB lithography makes it possible to fabricate complex patterns by adjusting the irradiation dose and so on. One strategy to induce lamella to form perpendicular to the substrate with controlled orientation in the plane of the film is the nanopatterning of substrates with alternating regions that are wetted differently by the different blocks of copolymer. In particular, tuning the polarity of the SAM-covered surface can control the wetting behavior of block

copolymer films. It has been reported that such a surface pattern could be transferred to films of poly(styrene-*b*-2-vinylpyridine) (P(S-*b*-2VP)) by using striped SAMs of CH<sub>3</sub>- and HO-terminated alkanethiols on gold.<sup>34-36</sup> Also, it has been reported that the wetting behavior of polymer was controlled by the functionality, or surface chemistry of the SAMs such as patterned striped SAMs of CH<sub>3</sub>- and COOH-terminated alkanethiols on gold,<sup>37,38</sup> and patterned stripes of gold and SAMs of CH<sub>3</sub>-terminated alkanethiols on gold.<sup>39</sup> Moreover, the surface chemistry of the SAMs was modified by exposure to x-rays in air to incorporate oxygen into polar function groups on the surface of the SAMs.<sup>40</sup> However, none of these SAMs have been directly patterned by EB reduction of the SAM to fabricate alternating regions that are wetted by the different blocks of copolymer. Instead, patterning of photoresist followed by an etching process has been utilized to create a chemical pattern on the buffer layer.<sup>26,27</sup> In addition to orientation control, photopatternable interfaces have been used to define trenches that guide self-assembly via grapho-epitaxy using photolithography<sup>2</sup> and to make directing guidelines for chemo-epitaxy with lithography in tandem with other processes.<sup>13,41-45</sup>

In this study, we demonstrate that lamella orientation of PS-*b*-PMMA films can be performed using EB induced change of SAMs, such as the conversion of a NO<sub>2</sub> group to an NH<sub>2</sub> group upon electron irradiation. Also, we fabricated surface topography by EB lithographic patterning and reactive plasma etching of silicon. DSA onto such pre-patterned Si substrates modified with PS-*r*-PMMA results in subdivision of the lithographic patterns into line and space patterns or hexagonally packed hole arrays. Furthermore, we present experiments investigating the difference in the direction of a diblock copolymer thin film in contact with a chemically patterned substrate surface and surface topography.

## 2. EXPERIMENTAL

Gold was deposited onto silicon substrates in a sputter coater (Edwards 306 auto), using an argon pressure of 1 Pa, and sputtering power 100w, to a thickness of 100nm, (measured on a sacrificial sample using a surface profiler (Dektak 3st). The gold coated samples were then cleaned in piranha solution (30:70 v/v solution of 30% hydrogen peroxide and concentrated sulfuric acid) for 5 m at room temperature. 6-(4-nitrophenoxy) hexane-1-thiol (NPHT) was prepared as detailed elsewhere.<sup>46</sup> To deposit the SAMs a 10mmol solution of NPHT was created in ethanol solvent, and the gold samples submerged in the solution for 48 h. Deposition was terminated using a 15 s rinse in the solvent and the samples were then dried with nitrogen. The rinse and dry was repeated twice to ensure maximum removal of physisorbed multilayers.

Samples were then irradiated with EB to produce a patterned SAM layer. They were patterned at exposure doses of 50 mC/cm<sup>2</sup>. PS-*b*-PMMA block copolymer was purchased from Polymer Source, Inc. and used as received. PS-*b*-PMMA block copolymer was spin-coated from propylene glycol mono methyl ether acetate (PGMEA) solutions onto the patterned SAM layer coated substrates after EB irradiated. Subsequently, they were annealed at 150 °C, 190 °C, and 250

°C in a vacuum for a sufficiently long time. The annealed film was also treated with an oxygen reactive ion etching (RIE) process in order to selectively remove the PMMA domains and form PS patterns on the substrate. After selective removal of one of the blocks, the remaining pattern can be obtained. A thin layer of tungsten was sputter-coated on the sample to prevent charging. The resulting morphology was recorded using a field emission-scanning electron microscope (FE-SEM, Hitachi-hitec S-5500) operated with an acceleration voltage of 1 kV.

Deep topographic features were also fabricated in silicon (Si) using EB lithography and plasma etching techniques. The surface of the lithographically defined templates was coated with PS-*r*-PMMA by spin-coating from a suitable solvent, and the samples were baked on a hotplate at 110 °C for 90 s. After baking, PS-*b*-PMMA block copolymer was spin-coated from PGMEA solutions onto the samples, which were then annealed at 190 °C for 24 h. After self-assembly of the PS-*b*-PMMA block copolymer, the sample was subjected to an oxygen plasma to remove the PMMA domains. The resulting morphology was recorded using FE-SEM after tungsten coating.

### 3. RESULTS AND DISCUSSION

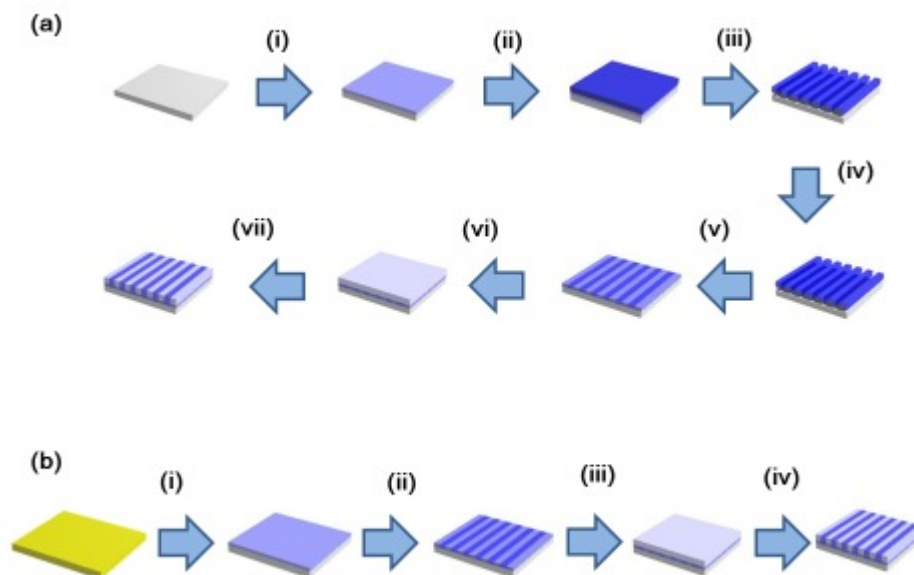


Figure 1. Schematic presentation of block copolymer DSA process using (a) a conventional chemically patterned surface process and (b) a directly chemically patternable SAMs method.

Figure 1(a) shows a schematic of the typical lithographic patterning method used to chemically pattern a SAM surface, in order to subsequently induce directed self-assembly via chemo-epitaxy. The method typically proceeds by patterning of SAMs or grafted polymer monolayers using lithographically defined resist patterns as a mask. However, these approaches require a number of complex processes such as resist coating, exposure, development, etch, the difficulty of

surface neutrality, and so on. Compared to the complex processes used for traditional chemo-epitaxy, a directly chemically patternable SAMs would greatly simplify the process as shown in Figure 1 (b). Thus, the number of steps can be reduced in the DSA process. In addition, this method reduces the probability for defectivity, for instance caused by residual resist on the patterned SAM.

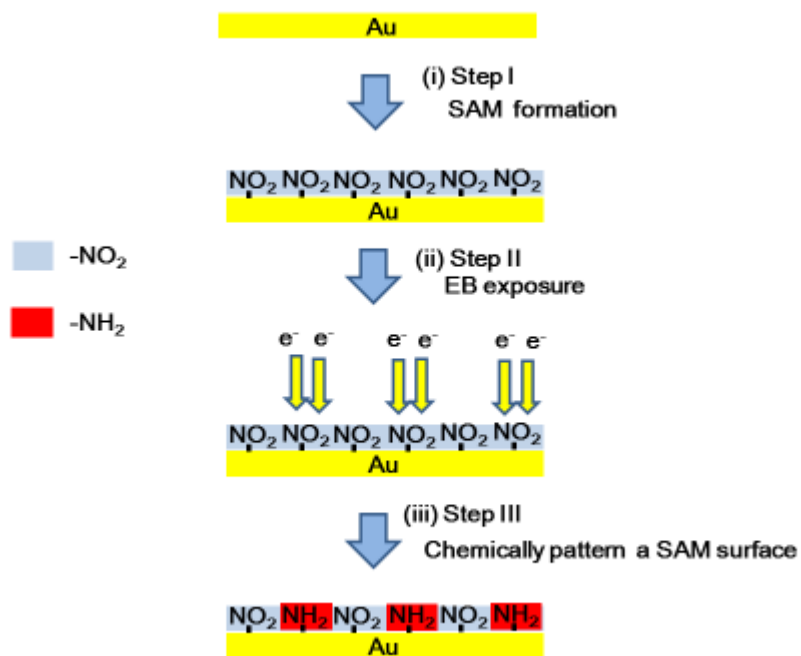


Figure 2. A scheme of the experimental steps. (Step I) SAM formation, (Step II) Patterning of SAM with EB lithography, and (Step III) EB patterning of a SAM, which induces conversion of the SAM terminal functional aromatic  $\text{NO}_2$  moieties to aromatic  $\text{NH}_2$  moieties..

EB patterning was chosen for manipulating block copolymer features since EB lithography tools can pattern areas nearly as small as block copolymer. By exposing a responsive interfacial surface of SAMs to EB, selective orientation of block copolymer domain can be achieved. In other words, after EB irradiation the SAMs underwent selective reduction. It has previously been reported that EB lithography and x-ray irradiation can induce conversion of the SAM terminal function aromatic nitro ( $\text{NO}_2$ ) moieties to aromatic amino ( $\text{NH}_2$ ) moieties.<sup>46-53</sup> Thus, EB irradiation results in a chemically striped patterned substrate consisting of alternating stripes of SAM with an aromatic  $\text{NO}_2$  terminal functionality and SAM with aromatic  $\text{NH}_2$  terminal functionality, as shown Figure 2. Patterning of SAMs was performed by EB lithography for all features with various periods. SAMs were patterned at doses of  $40 \text{ mC/cm}^2$ . The exposed electron dose in this study is comparable to the dose of  $35000 \mu\text{C/cm}^2$  required to carry out the large-scale nitro reduction on biphenyl based  $\text{NO}_2$  terminated SAM on gold.<sup>54</sup>

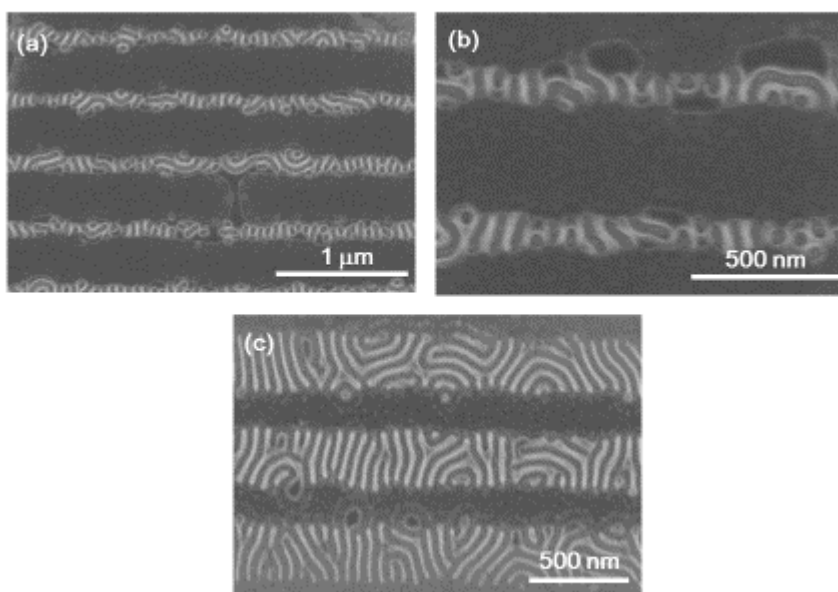


Figure 3. SEM images of PMMA etched lamellar PS-*b*-PMMA block copolymer on Au deposited silicon substrates pre-coated with self-assembly monolayer (SAM). The widths of alternating stripes of SAMs were (a) 150 nm, (b) 150 nm and (c) 300nm , respectively.

Figure 3 shows SEM images of PMMA etched lamellar PS-*b*-PMMA block copolymer on Au coated silicon substrates pre-coated with SAM. It is known that the PMMA block preferentially wets on SAMs that contain polar groups. The surface NO<sub>2</sub> groups of the NPHT become reduced upon EB exposure and are converted to NH<sub>2</sub> groups to which the PS block preferentially wets. Thus, DSA of PS-*b*-PMMA block copolymer film on a stripe pattern was expected. However, the lamellar assembly of PS-*b*-PMMA was observed on the surface pattern of SAM irradiated by EB after 24h of annealing. The reason why DSA was observed is thought to be for the following two reasons. First was the control of stripe width. It has been reported that the amount of defects increased as the density multiplication factor, and the ratio of the chemical pattern period to the block copolymer period, increased.<sup>55</sup> Also, it is known that if the periods of the surface and block copolymer don't agree within approximately 10%, the morphology of the block copolymer films will not be perfect.<sup>13</sup> The second reason is that Au surfaces are difficult to modify with thiol monolayers because our annealing temperatures are 190 °C, which is much greater than the dissociation temperature of the Au-thiol bond. The resulting chemical patterns provide neutral surface layers for lamella orientation of PS-*b*-PMMA domains. Figure 4 shows SEM images of PMMA etched lamellar PS-*b*-PMMA block copolymer on Au deposited silicon substrates pre-coated with SAM at the annealing temperature of (a) 150 °C and 250 °C, respectively. While the self-assembly of PS-*b*-PMMA didn't occur at the annealing temperature of 150 °C, dissociation temperature of the Au-thiol bond would occur at the annealing temperature of 250 °C. This result indicated the vertical orientation conditions required the appropriate annealing temperature. To our knowledge, this is the first example of a neutral layer using reductive treatment of EB irradiation,



and this work provides insights on tuning the neutral layer and the vertical orientation conditions for appropriate irradiation dose and annealing temperature. The main obstacle for this process is controlling the alignment of the domains to accomplish DSA. An understanding of the process variables that control this alignment is crucial. Further work is required to fully characterize and understand all the mechanisms at play during the fabrication procedure and understand in detail the key  $\text{NO}_2$  to  $\text{NH}_2$  conversion threshold required to control the alignment of the domains in order to give DSA.

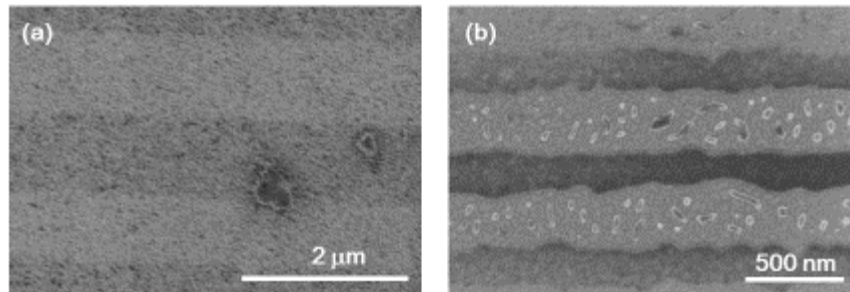


Figure 4. SEM images of PMMA etched lamellar PS-*b*-PMMA block copolymer on Au deposited silicon substrates pre-coated with SAM at the annealing temperature of (a) 150 °C and 250 °C, respectively.

Also, we created surface topography by EB lithographic patterning and reactive plasma etching of silicon. Our research has focused on self-aligned self-assembly of PS-*b*-PMMA block copolymer thin film patterns of both line and space patterns and hexagonal hole arrays and compared with our simple DSA process. Figure 5 shows SEM images of PMMA etched PS-*b*-PMMA block copolymer patterns on silicon substrates pre-coated with PS-*b*-PMMA. Line widths on these topographically patterned substrate were (a) 300 nm, (b) 100 nm, and (c) 300 nm, respectively. We successfully fabricated the DSA of PS-*b*-PMMA block copolymer onto pre-patterned surfaces resulting in subdivision of the lithographic patterns into line and space patterns. The spaces shown in the SEM images in Figure 5 correspond to perpendicular PMMA domain orientation within various trenches, and clearly demonstrates that perpendicular orientation of PS-*b*-PMMA was achieved. It can be seen that the confinement topography induced excellent microphase segregation within the trenches irrespective of the channel width with lamella domains orientating perpendicular to the substrate surface. However, these patterns lacked long-range alignment. Although the SEM micrograph is not shown here, feature sizes of less than 30 nm and other shape of PS-*b*-PMMA patterns could be easily achieved.

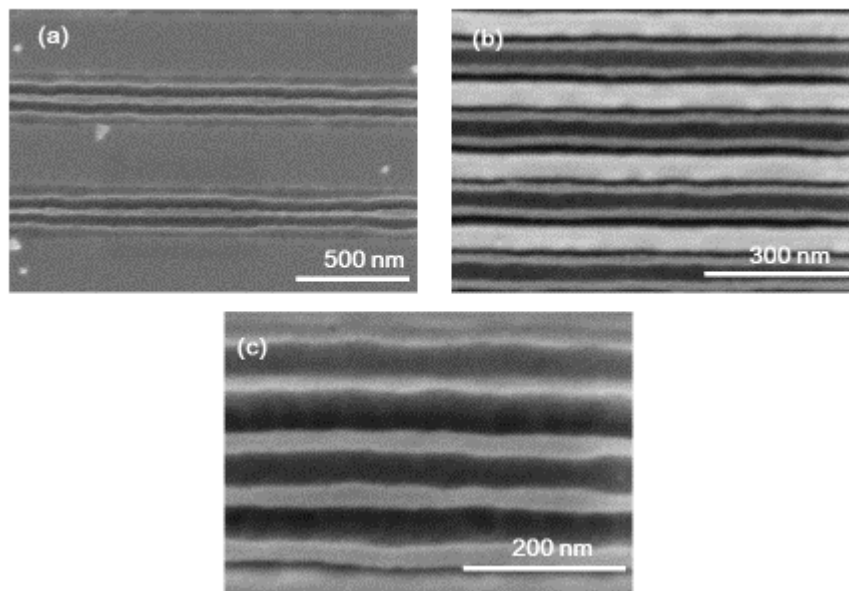


Figure 5. SEM images of PMMA etched lamellar PS-*b*-PMMA block copolymer on silicon substrates pre-coated with PS-*b*-PMMA. Line widths on these topographically patterned substrate were (a) 300 nm, (b) 100 nm, and (c) 300 nm, respectively.

We have demonstrated a novel strategy for the one-dimensional lamellar assembly of block copolymers by chemically patterned surfaces. We confirmed a process that uses directly EB patternable interfaces using chemical reduction of SAMs to simplify the current DSA schemes and avoid additional processing steps. In this work, the direct method has been shown to be effective in inducing microphase separation such as lamella in block copolymer thin film on striped pattern of SAMs, but further work is required to optimize the process. Experiments exploiting novel SAM materials and block copolymers are ongoing in order to accomplish directed self-assembly by this method. Generally, the silane/silicon interface is stronger than the thiol/gold interface. Also, patterning on oxidized silicon wafers is more compatible with conventional lithography technology. Additionally, the electron dose required for the patterning on SiO<sub>2</sub> is much lower than required for a SAM on Au. It has been reported that the difference in EB lithography behavior between SAMs on Au and Si is related to the differing film thicknesses and electron scattering characteristics of the two underlying surface.<sup>56,57</sup> Therefore the reduction of SAMs on SiO<sub>2</sub> substrate by EB and following DSA are in progress and they will be the subject of future reports.

#### 4. CONCLUSION

We conclude that lamellar orientation of PS-*b*-PMMA block copolymer could be performed using the change of SAMs such as the conversion of the NO<sub>2</sub> group to an NH<sub>2</sub> group induced by EB. The reductive treatment of SAM substrate plays a crucial role in the ordering. By examining the lamellae orientation by EB, we found that the vertical state persists

only for appropriate irradiation dose and annealing temperature. Future applications may benefit from or required the synthesis of sensitive and chemically specific imaging layers that change functionality directly upon lithographic exposure. Our method has the potential to greatly simplify block copolymer DSA processes as compared to the multi-step guiding layer fabrication procedures currently used.

## ACKNOWLEDGEMENTS

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