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# Directed Self-Assembly of Cage Silsesquioxane Containing Block Copolymers via Graphoepitaxy Techniques

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## 1. Introduction

Block copolymers (BCPs) consist of two or more chemically distinct polymer chains covalently bonded at one end. Immiscible segments in the blocks spontaneously induce to create microphase-separated nanostructures with periodic features of spherical, cylindrical or lamellar microdomains of the length ranging from approximately 5 to 50 nm, which can be controlled by the volume fraction and molecular weight of the blocks [1]. Recently, BCP thin films have attracted a great interest because the features of oriented and aligned microdomains can provide a potential application of nanolithography as a variety of patterned templates such as a high density data storage, photonics, sensors, catalysts and tissue engineering etc [2].

Precise control of the orientation and alignment of nanostructures is essential for the patterned templates. Russell *et al.* reported a creation of vertically oriented BCP nanostructures by using a neutral layer, which is a modified substrate with hydroxyl terminated PS-*r*-PMMA random copolymer brushes [3]. They also succeeded to build up a method of solvent vapor annealing for a vertically orientation of PS-*b*-PEO nanostructures in the thin films [4]. Nealey *et al.* developed a method of chemical registration which can provide the formation of long range and well-ordered nanostructures of BCPs based on a

chemically modified line or dot patterned substrate [5]. On the other hand, it is known a graphoepitaxy technique as a straightforward pathway for controlling the ordering of BCP domain. Kramer *et al.* reported the formation of well-ordered hexagonally packed spheres on a trench substrate prepared by conventional lithographic technology [6]. Epitaxial growth of BCP microdomains is nucleated by the edges of the mesas.

In the next step process of the nanolithography, it is normally necessary the dry etching with O<sub>2</sub> plasma for the well-ordered microphase-separated structures of BCPs to provide the patterned templates. In order to obtain the patterns with a high aspect ratio, developing the suitable BCP with a high contrast of the etch resistance is essential. Because most of the conventional BCPs such as poly(styrene)-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) composed of all of organic segments in both polymer blocks, namely organic-organic BCPs, show insufficient contrast in the etch resistance. Furthermore, the relatively smaller Flory-Huggins interaction parameters  $\chi$  limit to miniaturizing the sizes of the periodic domains. In contrast, there have been only a few reports of BCPs composed of a metal and/or silicon-containing segment in the blocks, even though they are expected not only higher contrast of the etch resistance, but also larger  $\chi$  parameter in comparison to those of the organic-organic BCPs.

Ross *et al.* reported the formation of well-ordered nanostructures of poly(styrene)-*b*-poly (ferrocenylsiloxane) (PS-*b*-PFS) and poly(styrene)-*b*-poly(dimethylsiloxane) (PS-*b*-PDMS) in the thin films through the graphoepitaxy technique [7-8]. The metal and/or silicon-containing polymer domains showed good etch resistance to the PS domains. In case of PS-*b*-PFS, however, the metal-ion contaminants derived from PS-*b*-PFS should be considered in the final products. A tedious multi-step etching process including a short etching with CF<sub>4</sub> plasma should be needed for the patterning of PS-*b*-PDMS thin films because the top layer is covered with PDMS in the films.

We recently reported the creation of polyhedral oligomeric silsesquioxane (POSS)-containing BCPs such as poly(methyl methacrylate)-*b*-poly(methacrylate POSS) (PMMA-*b*-PMAPOSS) and PS-*b*-PMAPOSS [9-10]. POSS is a very attractive organic-inorganic hybrid material because of the molecular sized cage structure, flexible functionality based on the substituents on the silicon atoms, and highly etch resistance to oxygen plasma. In our previous study, the POSS-containing BCPs showed the formation of well-ordered microphase-separated nanostructures with the chemically heterogeneous surfaces covered with the both polymers in the films by solvent vapor annealing with carbon dioxide (CS<sub>2</sub>). Therefore, the thin film patterning based on the microphase-separated nanostructures was carried out by a simple etching with only oxygen plasma. However, the study of long range ordering of the microphase-separated nanostructures for the POSS-containing BCPs has not been attempted so far.

In this study, we describe the alignment of the microphase-separated nanostructures for the PMMA-*b*-PMAPOSS thin films by combining the solvent vapor annealing and the graphoepitaxy technique. To investigate the effect of the substrate for formation of the long range ordered microphase-separated nanostructures, two different kinds of trench patterned substrates consistent with Si/Si (bottom/side wall) and Si/Si<sub>3</sub>N<sub>4</sub> (bottom/side wall) were attempted for the graphoepitaxy. The wettability of each block segment to the side walls (Si or Si<sub>3</sub>N<sub>4</sub>) was investigated by observation under the scanning electron microscopy (SEM).

## 2. Experimental Section

### 2.1. Materials

3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo[9.5

.1<sup>3,9</sup>.1<sup>5,15</sup>1<sup>7,13</sup>]octasiloxan-1-yl)propyl methacrylate (MAPOSS) was purchased from Hybrid Plastics Inc., and used after recrystallization with methanol. The other reagents and solvents were purchased from Aldrich. Methyl methacrylate (MMA) and 1,1-diphenylethylene (DPE) were dried with triethylaluminum and *n*-butyllithium and then distilled, respectively. PMMA-*b*-PMAPOSS was synthesized by anionic polymerization of MMA and MAPOSS. The polymerization was conducted in tetrahydrofuran solution with lithium chloride (LiCl), DPE and *sec*-butyllithium as an initiator at -78 °C. To afford the target polymers with several different molecular weights and compositions, the anionic polymerization with various monomer loadings was performed. The polymers described as below were used in this study. PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub>: molecular weight ( $M_n$ ) = 16,200, polydispersity index ( $M_w/M_n$ ) = 1.04, volume fraction of PMAPOSS ( $\phi_{\text{PMAPOSS}}$ ) = 0.83, morphology (bulk): PMMA cylinder. PMMA<sub>262</sub>-*b*-PMAPOSS<sub>23</sub>:  $M_n$  = 47,700,  $M_w/M_n$  = 1.08,  $\phi_{\text{PMAPOSS}}$  = 0.45, morphology (bulk): lamella.

### 2.2. Film Preparation

The substrate with trench patterns consistent with Si bottom and wall (Si/Si) was prepared by a conventional photolithography process. The trench width is varied from 150 to 500 nm. The substrate of trench patterns consistent with Si bottom and Si<sub>3</sub>N<sub>4</sub> wall (Si/Si<sub>3</sub>N<sub>4</sub>) was prepared by deposition of Si<sub>3</sub>N<sub>4</sub> on Si wafer and subsequently conventional e-beam lithography. The trench patterns consist of wide range of width of 30 nm to 5  $\mu$ m. The polymer thin films were prepared from 1 wt% PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub> solution in cyclopentanone by spin casting onto flat Si, Si/Si and Si/Si<sub>3</sub>N<sub>4</sub> trench patterns at 4,000 rpm for 60 sec. The thickness of polymer films on flat Si substrate was 13.5 nm measured by atomic force microscopy (AFM). Solvent annealing for the thin films obtained was performed in desiccator (1 L) with 20 mL of CS<sub>2</sub> at r.t. Samples for cross sectional observation under SEM were prepared from the PMMA<sub>262</sub>-*b*-PMAPOSS<sub>23</sub> solution in cyclopentanone by spin casting onto the Si and Si<sub>3</sub>N<sub>4</sub> substrate and subsequently thermal annealing at 160 °C for 24 h and then argon milling to generate clean cross section surface.

### 2.3. Measurements

Surface morphologies of the BCP thin films and the film thickness were measured by using a Seiko model SPA 400 AFM. Cross sections of the thin

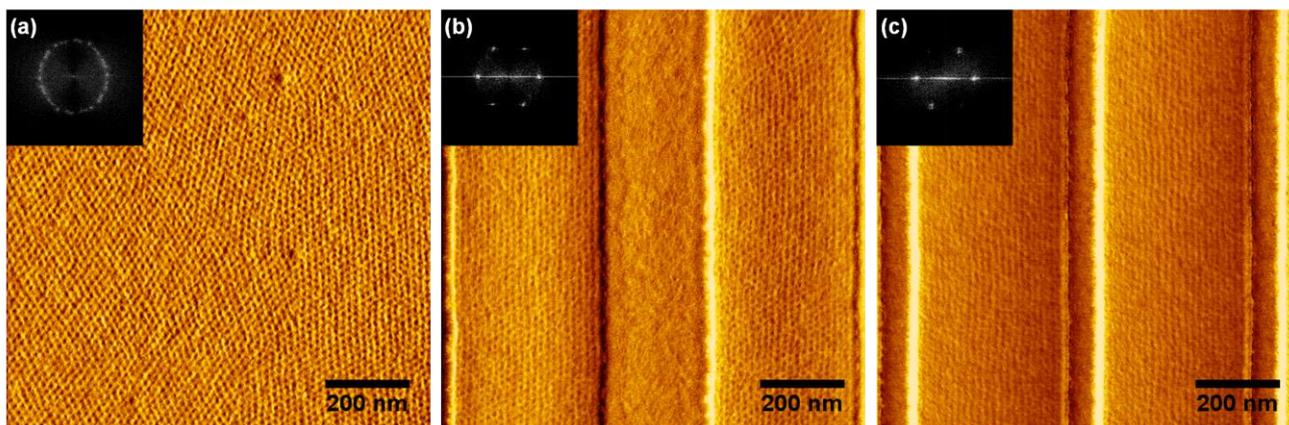


Figure 1. AFM phase images and FFT images of PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub> thin films after CS<sub>2</sub> solvent annealing for 4 h on flat Si substrate (a), Si/Si trench pattern and (b) Si/Si<sub>3</sub>N<sub>4</sub> trench pattern (c).

films were measured by using a Hitachi S-4800 SEM.

### 3. Results and Discussion

In the previous study, we revealed that PMMA-*b*-PMAPOSS forming PMMA cylinder in the bulk shows the formation of polycrystalline hexagonal PMMA dot patterns in the thin film on a flat Si substrate by solvent vapor annealing with CS<sub>2</sub>. The pattern formation and the *d*-spacing of PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub>, which is the sample in this study, were first investigated by AFM measurement. Note that the molecular weight (*M<sub>n</sub>*) and volume fraction of PMAPOSS ( $\phi_{\text{PMAPOSS}}$ ) are 16,200 and 0.83, respectively, and the bulk morphology is the PMMA cylinder with *d* spacing of 14.1 nm measured by small angle X-ray scattering (SAXS). The thin film annealed by solvent vapor with CS<sub>2</sub> for 4 h indicated the formation of the high density hexagonally packed dot pattern with *d* spacing of 14.9 nm measured by 2D fast Fourier transform (FFT) image. The *d*-spacing is slightly larger than that of the bulk, indicating the swelling of the polymer with CS<sub>2</sub> during the solvent vapor annealing. No hexagonal dot spots were observed in the FFT image. This indicates that the resulting dot structures form polycrystals with the hexagonally packed microphase-separated nanostructures. For a long range alignment of the dot structures, the trench patterned substrates with the side walls/bottoms of Si/Si and Si/Si<sub>3</sub>N<sub>4</sub> were used. Figure 1b shows AFM phase image of PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub> thin film on the flat Si/Si trench pattern (width: 330 nm) annealed with CS<sub>2</sub> vapor for 4 h. This image shows more aligned hexagonal dot patterns than that of the flat Si substrate. This result indicates that the PMMA dots aligned along by the

Si walls and propagated to the center of trench to create large area ordering. Although most of dot structures formed a hexagonally packed structure in the trench patterns, poly crystals with some of grain boundaries were also observed (see figure 1b upper right). On the other hand, the thin films on the Si/Si<sub>3</sub>N<sub>4</sub> trench pattern substrates (width: 350 nm) casted and annealed with same conditions displayed well-aligned and nearly perfect single crystal of hexagonally packed dots over several micrometers length scale as shown in Figure 1c. The *d* spacings between the dot structures with Si/Si and Si/Si<sub>3</sub>N<sub>4</sub> substrates were 14.7 and 15.0 nm, respectively, which are good agreement with those of the flat substrates. The number of the lines aligned the dots in the trench patterns with the Si/Si (width: 330 nm) and Si/Si<sub>3</sub>N<sub>4</sub> (width: 350 nm) walls substrates were 22 and 23 lines, respectively. They exhibited good agreement with the estimated numbers of the lines which

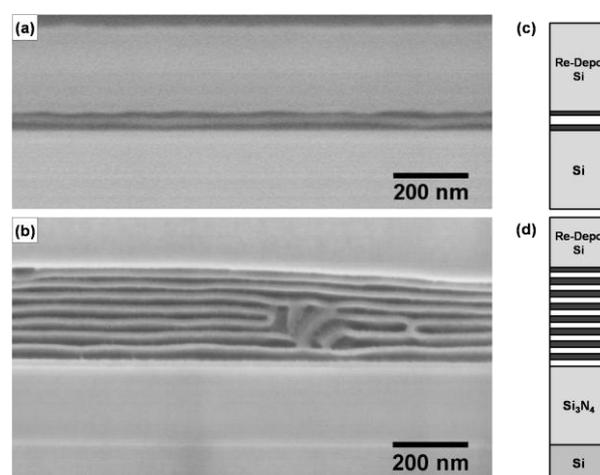


Figure 2. Cross section SEM images (a, b) and schematic illustration (c, d) of PMMA<sub>262</sub>-*b*-PMAPOSS<sub>23</sub> thin films on Si (a, c) and (b) Si<sub>3</sub>N<sub>4</sub> (b, d) substrate. Brighter and darker region are PMAPOSS and PMMA domains respectively.

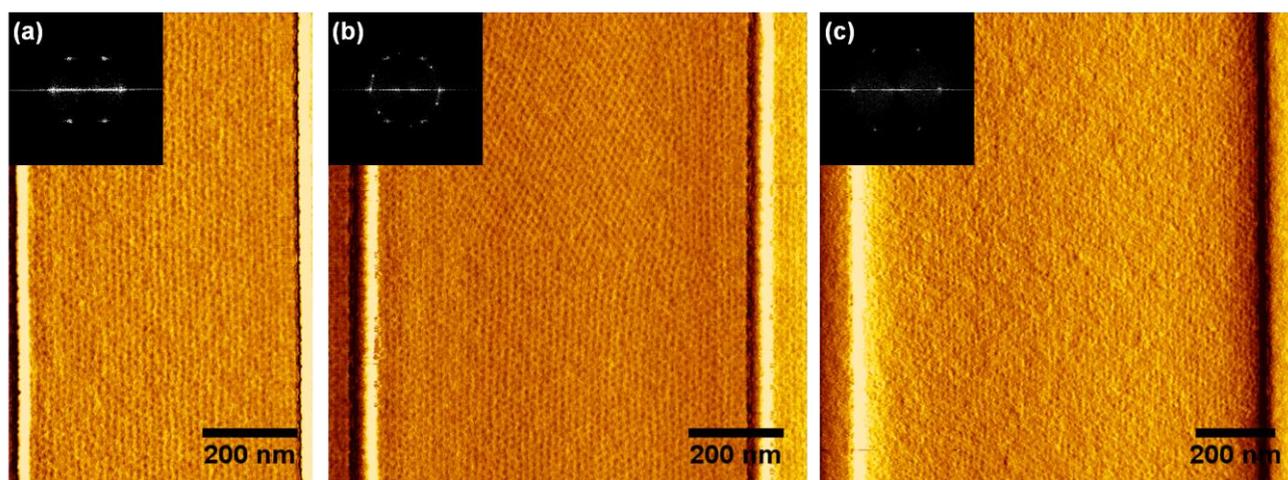


Figure 3. AFM phase images and Fourier transform images of PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub> thin films on Si/Si<sub>3</sub>N<sub>4</sub> trench patterns after CS<sub>2</sub> solvent annealing for 4 h (a, b), and 8 h (c). The trench pattern widths are (a) 560 nm, (b) 770 nm and (c) 1000 nm.

calculated from the *d* spacing and trench pattern width.

Self-assembly of PMMA-*b*-PMAOSS in the thin films on the trench patterned substrate with Si and Si<sub>3</sub>N<sub>4</sub> walls under CS<sub>2</sub> solvent vapor annealing exhibited differences over the ability of long range alignment. To reveal the influence of the wall materials, we investigated the wettability of PMMA and PMAPOSS with Si and Si<sub>3</sub>N<sub>4</sub>, respectively. The film samples were prepared from the PMMA<sub>262</sub>-*b*-PMAPOSS<sub>23</sub> solution in cyclopentanone by spin-casting and subsequently thermal annealing at 160 °C for 24 h, which forming lamellae on the Si and Si<sub>3</sub>N<sub>4</sub> substrates. The cross-sectioned structures were observed in the SEM images. The images shown in Figure 2 indicate the brighter and darker regions are corresponding to PMAPOSS and PMMA, respectively, due to be the high electron density of PMAPOSS domains. Top layer of the thin films was covered by deposited Si due to argon milling process during the sample preparation. In case of the Si substrate, it was revealed that the PMMA<sub>262</sub>-*b*-PMAPOSS<sub>23</sub> thin film formed PMMA half layers on the substrate, which indicates PMMA is able to wet to Si substrate. On the other hand, PMAPOSS half layer was obtained on the Si<sub>3</sub>N<sub>4</sub> substrate. This indicates selective wetting of PMAPOSS on the Si<sub>3</sub>N<sub>4</sub> substrate. From these results, it was found that the PMAPOSS domains are preferentially contacted to the Si<sub>3</sub>N<sub>4</sub> walls and the selective wet property leads to a long range alignment of the PMMA dot structures along by the line of walls in the Si/Si<sub>3</sub>N<sub>4</sub> trench patterns, while the PMMA domains are difficult to face the Si walls perfectly because of the lower volume

fraction of PMMA in PMMA<sub>27</sub>-*b*-PMAPOSS<sub>14</sub>.

Effect of the annealing time for the long range alignment was investigated in a variety of widths of the trench patterned Si/Si<sub>3</sub>N<sub>4</sub> substrates. Figure 3a and b show the AFM images of the samples annealed with CS<sub>2</sub> solvent vapor annealing for 4 h on the substrates with the trench width of 560 and 770 nm, respectively. Nearly perfect alignment of dot structures along by the edge lines of the trench patterns was obtained in the substrate with 560 nm width, while some of the defects which are grain boundaries were observed in the film on the substrate with 770 nm width. Figure 3c shows the long range alignment on the substrate with 1000 nm width annealed with a longer time for 8 h, exhibiting the well-ordered hexagonally packed dot nanostructures. This indicates that the alignment of dot structures is positively affected by time of solvent vapor annealing, even in case of using more widely patterned substrate. This is due to occurring the self-assembly of hexagonally packing of dots from both sides of the walls toward the center of trench. By using the suitable substrates and optimizing the annealing conditions, it was eventually achieved nearly perfect hexagonally packed dot structures with several micrometer length scales for the PMMA-*b*-PMAOSS, which corresponding to more than the density of 2.5 Tb/inch<sup>2</sup>.

#### 4. Conclusion

Directed self-assembly of organic-inorganic hybrid block copolymers bearing polyhedral oligomeric silsesquioxane, PMMA-*b*-PMAPOSS, was performed via combining techniques of graphoepitaxy and solvent vapor annealing. The

solvent vapor annealing exhibited the effect of the formation of well-aligned dot structures in the thin film with Si/Si<sub>3</sub>N<sub>4</sub> trench patterns over some micrometers length scale, while a small amount of defects appeared in the case of the Si/Si trench patterns. The SEM images of the cross-sectioned films indicated selective wet properties of PMMA with Si and PMAPOSS with Si<sub>3</sub>N<sub>4</sub>, respectively. It was found that optimizing the annealing time is also important to the long range alignment of the dot structures. The nearly perfect long range alignment of PMMA dot structures was achieved on the Si/Si<sub>3</sub>N<sub>4</sub> trench patterned substrate by combining the solvent vapor annealing with CS<sub>2</sub> for 8 h, which the diameter of 7 nm and the distance between the dots of 17.0 nm corresponding to the dots density of 2.5 Tb/inch<sup>2</sup>.

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