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Directed Self-Assembly of Block Copolymer, No1

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Directed Self-Assembly of Block Copolymer, No1

Summary/Description

The PS-rich and neutral PS-*b*-PMMA block copolymer (BCP) films were spin coated on the neutral random copolymer hydroxyl-terminated PS-*r*-PMMA layers grafted on the native oxide and 50 nm thick PECVD amorphous silicon oxide layers. Relationship between the grafting density of BCP and surface density of hydroxyl moiety on silicon oxide is discussed. Furthermore, optimization of annealing BCP films is reported, and wetted and de-wetted BCP films are shown in optical microscope images. In addition, finger print and nanopore structures of BCP films are also indicated in SEM images.

Keywords

directed self-assembly, block-copolymer, grafting, hydroxylated silicon oxide

Disciplines

Biochemical and Biomolecular Engineering | Biological and Chemical Physics | Membrane Science | Nanoscience and Nanotechnology | Other Chemistry | Physical Chemistry | Polymer and Organic Materials | Polymer Chemistry | Polymer Science

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1. Introduction

Directed self-assembly of block copolymer (BCP) is considered as one of the most promising advanced lithography,[1] and can make nanometer scale patterns on the 6-inch diameter substrate at the same time without expensive cost, using the self-assembly of BCP and guide pattern created by a conventional lithography tool. Up to now, sub-10 nm patterns of high-χ BCP (χ: Flory-Huggins interaction parameter) have been reported.[2,3] The goal of this project is to make this technique available at Quattrone Nanofabrication Facility (QNF).

Figure 1 shows a schematic diagram of multi-layer structure of block copolymer on random copolymer grafted on the Si substrate. In actual devices, a guide pattern is added to the multi-layer structure.[4] The morphology of BCP is controlled by chemical affinity of the underlying random copolymer grafted (or immobilized) on the substrate and by the thickness of BCP film.[5] This report describes a graft (or immobilization) of the random copolymer on the Si substrate and optimization of commensurability between the film thickness of BCP and the polymer domain spacing (or Lamellar spacing).
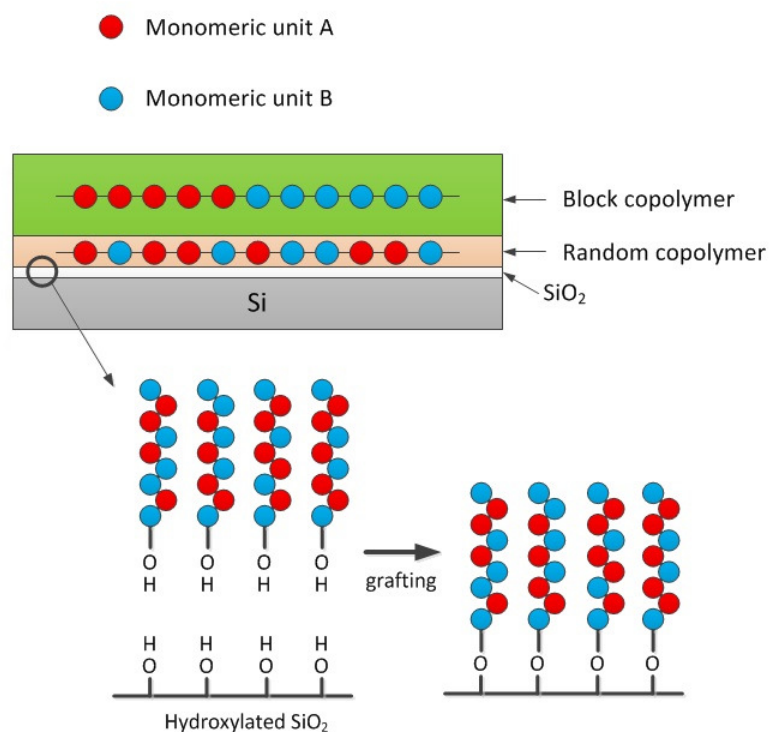
Figure 1. Schematic diagram of multi-layer structure of block copolymer on random copolymer grafted on the Si substrate. The morphology of the block copolymer is controlled by the chemical affinity with the underlying film and by the film thickness.

[1] M. C. Smayling, Proc. SPIE, **9777**, 977702 (2016).

[2] N. Kihara et al., J. Micro/Nanolith. MEMS MOEMS **14**, 023502 (2015).

[3] W. J. Durand et al., J. Polym. Sci., Part A: Polym. Chem. **53**, 344–352 (2015).

[4] C. Liu et al., Macromolecules **44**, 1876 (2011).

[5] J. N. L. Albert and T. H. Epps, Mater. Today, **13**, 24 (2010).

2. Experimental Section

A. Materials

BCP poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) with the average molecular weight M_n of poly-styrene = 15000, M_n of poly-methyl methacrylate = 15000, expressed by 15k-*b*-15k, and PDI[6] ≤ 1.2 was purchased from Sigma-Aldrich. Furthermore, two kinds of BCP PS-*b*-PMMA (poly-methyl methacrylate rich in syndiotactic contents > 78 or 80 %) with M_n of 33k-*b*-33k and 46k-*b*-21k and PDI[6] = 1.09 were purchased from Polymer Source. The three BCPs were used as received.   Hereafter, the BCPs with M_n of 15k-b-15k and 33k-*b*-33k are referred to as "neutral PS(15k)-*b*-PMMA(15k)" and "neutral PS(33k)-*b*-PMMA(33k)", respectively, or simply "neutral PS-*b*-PMMA", where the "neutral" means 50 to 50 mol%, while the BCP with M_n of 46k-*b*-21k is referred to as "PS-rich PS-*b*-PMMA".

Hydroxyl-terminated random copolymer poly(styrene-*r*-methyl methacrylate), α-hydroxyl-ω-tempo moiety terminated, with M_n = 5400 (PS content 60 mol%) and PDI[6] = 1.40 was also purchased from Polymer Source, and used as received. Hereafter, the random copolymer is referred to as "brush-OH" or "PS-*r*-PMMA-OH". The brush-OH with PS content of 60 mol% is considered to be "neutral". A CMOS grade toluene (trace impurity level, 10-200 ppb) was purchased from J. T. Baker, and used as received.

B. Deposition of 50 nm thick silicon oxide film

A (100) Si wafer was sonicated in acetone and isopropyl alcohol (IPA) for 5 min each, and then dried using a nitrogen gun. A 50 nm thick amorphous silicon oxide was deposited on the Si wafer, using Oxford Plasma Lab 100 (Plasma Enhanced Chemical Vapor Deposition (PECVD)).

C. Grafting the brush-OH film on the hydroxylated silicon oxide surface on Si wafer

The 1.2-1.5 nm thick native oxide and the 50 nm thick silicon oxide films were hydroxylated, respectively, by treatment of nitric acid (70 wt%) or piranha solution[7] at 80 °C for 30-40 min.[8] O_2 plasma treatment was not carried out for the hydroxylation, due to possible cross-contamination in the tool frequently used in QNF. The samples hydroxylated were sonicated in de-ionized (DI) water for 2 min, and then dried using nitrogen gun. Furthermore, the samples were dehydrated at ~150 °C for 5 min in a vacuum oven. A ~20 nm thick brush-OH film was spin coated at 4000 rpm on the Si substrate with and without the 50 nm thick silicon oxide film on its surface from the 0.9 wt% toluene solution, and grafted on the hydroxylated silicon oxide by annealing itself in the oven filled with N_2 or in vacuum. The annealing time and temperature are shown later. After annealing, the unreacted brush-OH polymer was removed by repeated 30 min sonication in toluene (3 times).

D. Film preparation of BCPs

Various thick neutral and PS-rich PS-*b*-PMMA films were spin coated at various spin speeds on the brush layers grafted on the Si substrates from 1.2 wt% PS(15k)-*b*-PMMA(15k), 1.7 wt% PS(33k)-*b*-PMMA(33k), and 1.7 wt%

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[6] Polydispersity Index = M_w/M_n, where M_w is the weight average molecular mass and given by the equation, $M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$; M_n is the number average molecular mass, and given by the equation, $M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$; N_i is the number of molecules of molecular mass M_i.

[7] A 3:1 (v/v) mixture of sulfuric acid (H_2SO_4, 95-98 wt%) and hydrogen peroxide (H_2O_2, 30 wt%).

[8] S. Guhathakurta and A. Subramanian, J. Electrochem. Soc. **154**, P136 (2007).

PS(46k)-*b*-PMMA(21k) solutions in toluene. The BCP films were annealed at 190-250 °C for 4-72 hours in the oven filled with N_2, as shown later.

E. Measurements

The BCP films for the thickness measurements were separately spin coated on blank Si wafers. Film thicknesses of silicon oxide, BCP, and brush layer were determined, respectively, using Woollam VASE ellipsometer. Simulation model was Cauchy or SiO_2 models. Scanning electron microscope (SEM) images were measured through a copper (Cu) grid to prevent the polymer films from charging, using JOEL JSM-7500F.   The PMMA portion in the BCP films was removed by O_2 plasma treatment for SEM measurements.

3.   Results and Discussion

3-1. Relationship between grafting density of BCP and surface density of hydroxyl moiety on silicon oxide

Table 1 indicates the hydroxylation and annealing conditions and thicknesses of brush layers grafted on the hydroxylated surfaces of the native oxide and 50 nm thick silicon oxide. The thickness of brush layer grafted <u>on the native oxide</u> was ~3.5 nm even though the samples were annealed for 48 hours, as shown in Table 1. On the other hand, the thicknesses of brush layers grafted <u>on the 50 nm thick silicon oxide</u> hydroxylated with nitric acid and piranha solution were 3.8 ± 0.7 and 4.6 ± 0.4 nm, respectively, for 4 hour annealing, whereas that was 5.5 ± 1.6 nm for 20-24 hour annealing.

Table 1. The hydroxylation and annealing conditions, and average thicknesses and grafting densities σ of brush layers grafted on the hydroxylated surfaces of the native oxide and 50 nm thick silicon oxide.

Hydroxylation of silicon oxide surfaces			Annealing in an oven			Thickness (nm) of brush layer		σ (Chain/nm^2)
solution	Temperature (°C)	Time (Hour)	Temperature (°C)	Time (Hour)	gas	Native oxide	50 nm thick SiO2	
HNO3/piranha	80	30-40	190-250	4	vac/N_2	3.3 ± 0.3	---	0.41
HNO3/piranha	80	30	190	20-48	N_2	3.6 ± 0.4	---	0.44
HNO3	80	30	190	4	vac/N_2	---	3.8 ± 0.7	0.47
piranha	80	30	190	4	vac/N_2	---	4.6 ± 0.4	0.57
HNO3	80	30	190	20-24	N_2	---	5.5 ± 1.6	0.68

The surface coverage Γ (mg/m^2) is given by the following equation:[9]

$$\Gamma = h\rho \qquad (1)$$

where h is the layer thickness (nm), and ρ is density (g/cm^3) of adsorbed molecule. The average density of the brush layer can be estimated to be 1.11 g/cm^3 from the molar fraction and the densities of PS and PMMA of 1.05

[9] B. Zdyrko *et al.*, Polymer **47**, 272 (2006).

and 1.20 g/cm^3.[10] The surface coverage is converted into the grafting density, σ (chain/nm^2), using the following equation:[9]

$$\sigma = \frac{(6.023\Gamma \times 100)}{M_n} \tag{2}$$

where M$_n$ (g/mol) is the number average molecular weight of the brush layer grafted. Table 1 also shows the grafting densities of the brush layers, indicating that the grafting densities on the native oxide and 50 nm thick PECVD silicon oxide layers are 0.44 and 0.68 chain/nm^2 for 24 hour annealing, respectively. The hydroxylated native oxide is obviously less reactive than the 50 nm thick hydroxylated silicon oxide. On the other hand, the average brush layer thickness of 5.5 ± 1.6 nm and the grafting density of 0.68 chain/nm^2 are almost the same as the previously reported thickness of 5.8 nm and the grafting density of 0.72 chain/nm^2 for the similar brush layer (M$_n$ = 5400, PS molar fraction = 0.61-0.66), grafted at 250 °C on the 50 nm thick thermally grown silicon oxide, using Rapid Thermal Processing tool.[11]

Figure 2 shows four surface species of silicon oxide reported on hydroxylation.[12,13] Two OH groups of germinal silanol are hydrogen-bonded with adjacent OH groups,[14] as depicted in figure 2. It has been reported that the
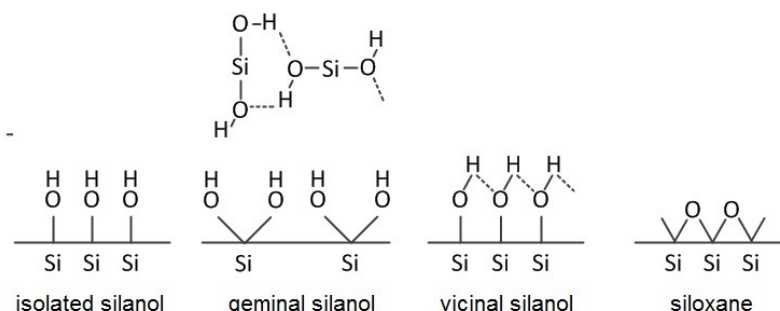

Figure 2. Four surface species of hydroxylated silicon oxide. The OH groups of germinal and vicinal silanols are hydrogen-bonded with adjacent OH groups.

surface density of silanols on the hydroxylated native oxide is 4.6 ± 0.2 OH/nm^2,[12,14] which is almost the same as that on fumed silica highly hydroxylated.[13] In addition, the density of non hydrogen-bonded OH group (isolated silanol) is 1.4 ± 0.1 OH/nm^2, whereas that of hydrogen-bonded OH group (germinal and vicinal silanols) is 3.2 ± 0.1 OH/nm^2. When comparing the grafting density of 0.44 chain/nm^2 of brush layer with the isolated silanol (free OH group) density of 1.4 OH/nm^2 on the hydroxylated native oxide, the brush-OH is likely to be grafted on the 31 % of the isolated silanol sites, although it is possible to react the brush-OH with the hydrogen bonded OH groups and siloxane during the grafting process.[13] It should also be pointed out that the grafting density of 0.44 chain/nm^2 is much lower than the silanol density of 4.6 OH/nm^2 due to the steric hindrance of the polymeric structure of the brush layer.

[10] http://scientificpolymer.com/density-of-polymers-by-density/
[11] K. Sparnacci *et al.,* ACS Appl. Mater. Interfaces **7**, 10944 (2015).
[12] L. T. Zhuravlev, Colloids Surf., A **173**, 1 (2000).
[13] V. Dugas and Y. Chavalier, J. Colloid Interface Sci. **264**, 354 (2003).
[14] V. Masteika *et al.*, ECS J. Solid State Sci. Technol., **3**, Q42 (2014).

On the other hand, the 50 nm thick hydroxylated silicon oxide has the 54 % larger grafting density than the hydroxylated native oxide, as described above. Since the PECVD silicon oxide is amorphous, the distance between oxygen atoms of PECVD silicon oxide should not be as uniform as that of the native oxide on the crystalline Si wafer. In addition, the PECVD silicon oxide should have the dangling bond of Si and defects much more than the native oxide,[15] which increase the reaction sites on the surface. The 54 % larger grafting density should be ascribed to the above situation.

The brush layer thickness also depends on the time when exposing the PECVD silicon oxide into the air. Table 2 indicates a time dependence of hydroxylation that is monitored by the thickness of brush layer grafted. The PECVD silicon oxide films were kept in the air for 4 hours, 1 day, 6 days, and 16 days, respectively, and then the hydroxylation was performed by immersing the samples in nitric acid (70 wt%) at 80 °C for 30 min.   After the treatment and the dehydration at 150 °C, as described above, the brush-OH film was immediately spin coated and annealed at 190 °C for 24 hours in the oven filled with N_2. As can be seen in Table 2, the brush layer thickness and the grafting density decrease with increasing in the time when exposing the samples into the air. The 0.53 chain/nm^2 grafting density for 16 day exposure is 37 % smaller than the 0.84 chain/nm^2 grafting density for 4 hour exposure. On the other hand, the 0.84 chain/nm^2 grafting density on the PECVD silicon oxide in Table 2 is 91 % larger than the 0.44 chain/nm^2 grafting density on the native oxide in Table 1.

Table 2. Time dependence of hydroxylation that is monitored by the thickness of brush layer grafted. The 50 nm thick PECVD silicon oxide films were kept in the air for 4 hours, 1 day, 6 days, and 16 days, respectively, and then the hydroxylation was performed by immersing the samples in nitric acid (70 wt%) at 80 °C for 30 min.

Hydroxylation starting time after preparing PECVD 50 nm thick SiO2 film	Thickness (nm) of brush layer	σ (chain/nm^2)
4 hours	6.8 ± 0.3	0.84
1 day	5.9 ± 0.2	0.73
6 days	5.1 ± 0.2	0.63
16 days	4.3 ± 0.1	0.53

The time dependence of hydroxylation should also be attributed with the non-uniform distance between oxygen atoms, the dangling bond of Si, and the defects on the surface, as discussed above. Some species such as H_2O and CO in the air must make a bond (hydrogen-bond or covalent bond) with, or be trapped in those deficiencies on the PECVD silicon oxide surface during the air exposure, resulting in decreasing in the grafting density of the brush layer. As described below, BCP films were prepared on the 5-7 nm thick brush layer grafted on the 50 nm thick PECVD silicon oxides.

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[15] L. He and S. Hasegawa, Jpn. J. Appl. Phys. **40**, 4672 (2001).

3.2. Annealing BCP film in the oven

Figure 3 shows optical microscope images of 42 nm thick neutral PS-*b*-PMMA films annealed at 190 °C in the oven filled with N_2 for 20, 25, 45, and 72 hours, respectively, indicating that the BCP film becomes wet completely by 3 day annealing.
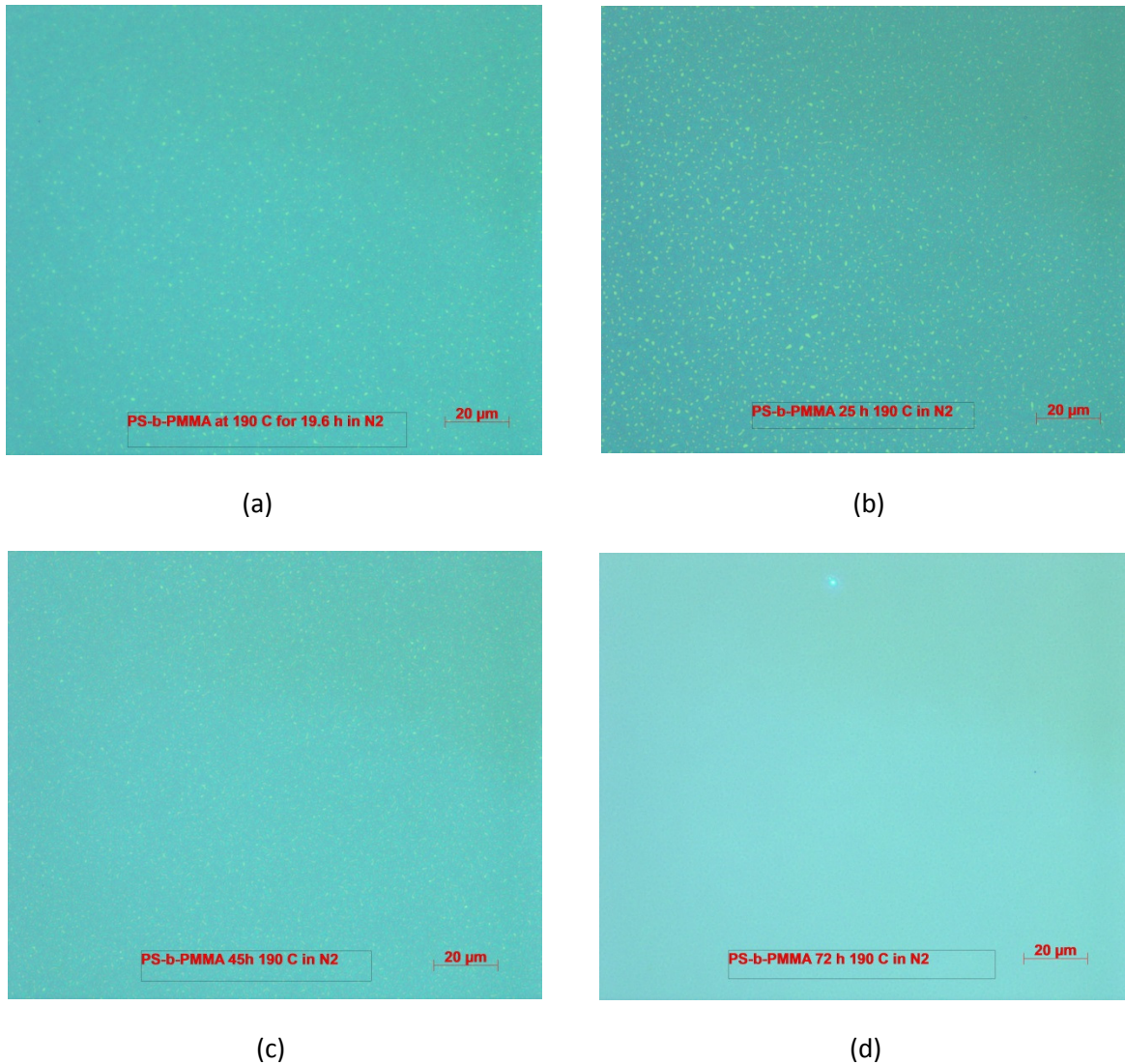

(a)

(b)

(c)

(d)

Figure 3. Optical microscope images of 42 nm thick PS(33k)-b-PMMA(33k) films annealed at 190 °C in N_2 for (a) 20 hours, (b) 25 hours, (c) 45 hours, and (d) 72 hours, respectively. BCP films were spin coated on the neutral brush layer grafted on the 50 nm thick silicon oxide layers.

Deterioration of the BCP film was also found when applying the temperature more than 210 °C in the oven. Figure 4 shows optical microscope images of PS-rich and neutral BCP films annealed at (a) 190, (b) 210, (c) 230, and (d) 250 °C for 3 days. As can be seen in figure 4, some spots start emerging in the films at the temperature more than 210 °C. On the other hand, some articles reported the annealing at the temperature more than 210 °C for a short time: *e.g.* 250 °C for 1 hour[4] and 310 °C for 60 sec.[11] It is assumed that their annealing tools, which are a hot plate in a

globe box or Rapid Thermal Processing tool, make a difference from this result, although some articles have not shown the annealing tools explicitly.
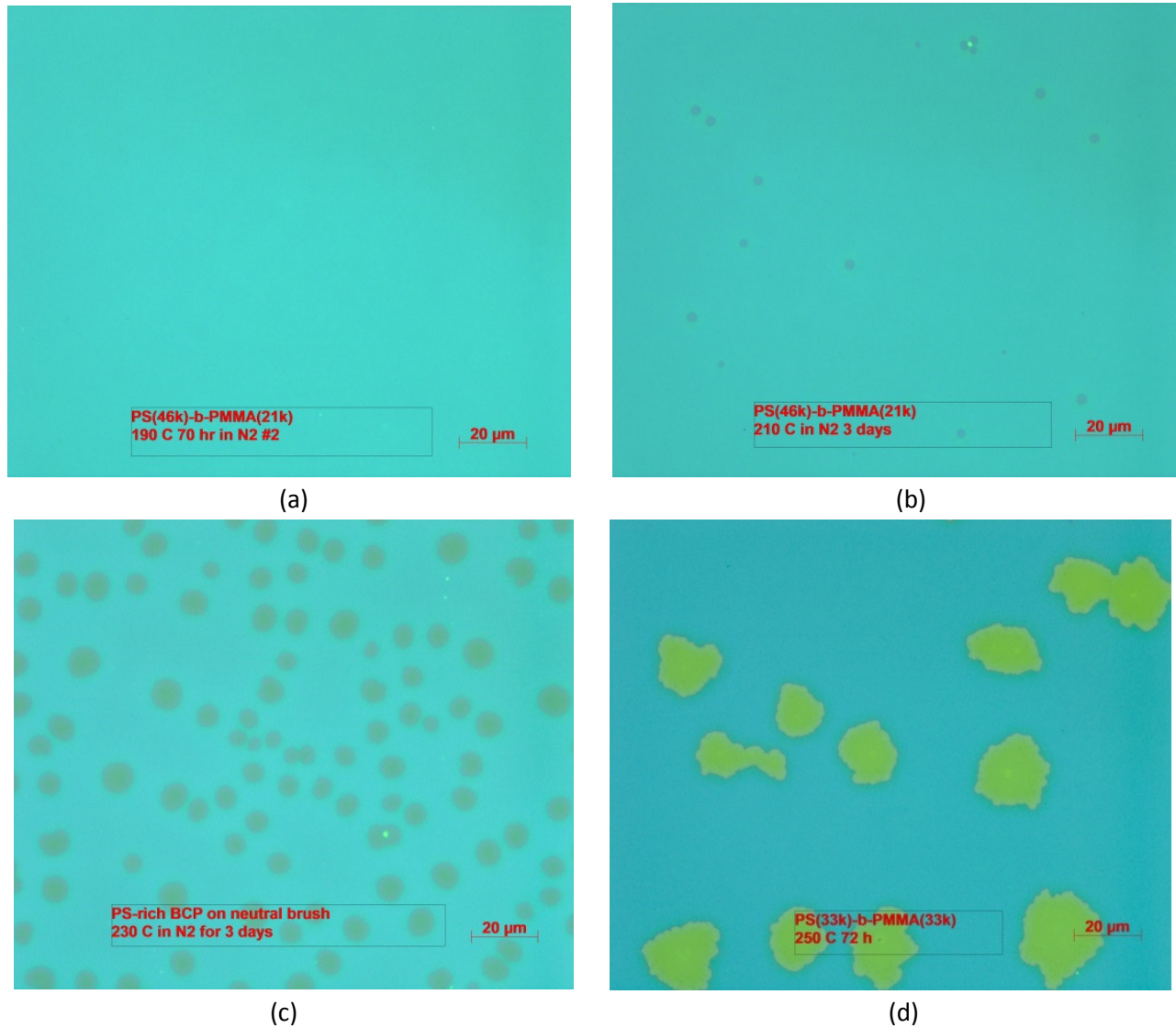

Figure 4. Optical microscope images of 42 nm thick PS-rich PS(46k)-*b*-PMMA(21k) and neutral PS(33k)-*b*-PMMA(33k) films on the neutral brush layer annealed at (a) 190, (b) 210, (c) 230, and (d) 250 °C in an oven filled with N_2 for 3 days. (a) to (c) are PS-rich PS-*b*-PMMA films, while (d) is neutral PS-*b*-PMMA film.

3-3. Wetted and de-wetted BCP films

Figure 5 shows optical microscope images of (a) "wetted" and (b) "de-wetted" neutral PS-*b*-PMMA films on the neutral brush layers. The morphology of BCP film strongly depends on the surface interaction, the film thickness, and the polymer domain spacing (L_0) (or lamellar spacing).[5] Polymer chain compression and stretching are controlled by incommensurability between the film thickness and the polymer domain spacing, and are released by the formation of islands and holes or by the formation of cylinders or lamellae, depending on the chemical affinity with the substrate surface. When the film thickness is commensurate with the polymer domain spacing, the wetted BCP film is obtained. Otherwise, the de-wetted BCP film is observed.
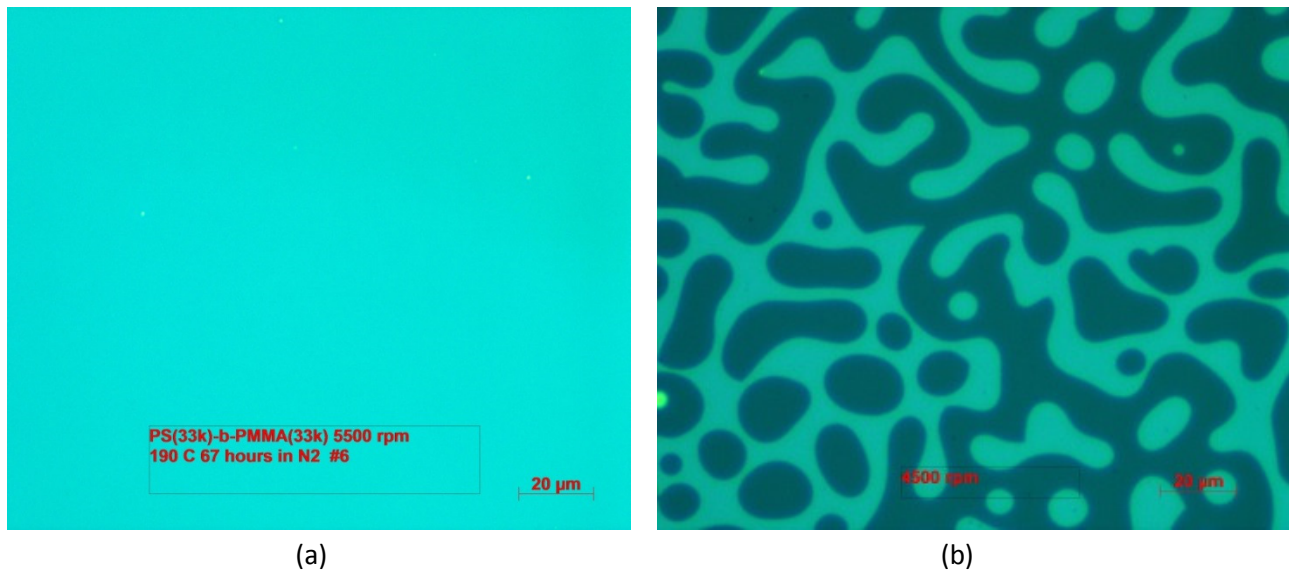

(a)   (b)

Figure 5. Optical microscope images of (a) 42 nm thick "wetted" PS(33k)-b-PMMA(33k) film and (b) 38 nm thick "de-wetted" PS(15k)-b-PMMA(15k) film. The neutral BCP films were spin coated on the neutral brush layer grafted on the 50 nm thick silicon oxide layers, and annealed at 190 °C in N_2 for 3 days.

The commensurable thickness *h* of BCP film is given by the following equation:[5,16]

$$h = n \cdot L_0 \tag{3}$$
$$L_0 \propto N^{2/3} \tag{4}$$

where L_0 is the polymer domain spacing, and N is degree of polymerization. n is given by m (an integer) for symmetric wet, while given by m + 1/2 for anti-symmetric wet. Symmetric wet means that "A" or "B" block of "AB" block copolymer preferentially wets both of the top and bottom of the BCP film, whereas anti-symmetric wet means that "A" block wets the top, but "B" block wets the bottom, or vice versa. When commensurability is achieved, no islands and holes were observed on the top of the film.

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[16] C. T. Black *et al*., IBM J. Res. Dev. **51**, 605 (2007).

Table 3 indicates degree of polymerization, polymer domain spacing (or Lamellar spacing), commensurable thickness, and wettable thickness window of PS-*b*-PMMAs in this report. It has been reported that

Table 3. Degree of polymerization, polymer domain spacing (or Lamellar spacing), commensurable thicknesses, and wettable thickness window of BCP PS-*b*-PMMAs in this report.

Molecular weight of PS-*b*-PMMA (g/mol)	Degree of polymerization[a]	Polymer domain spacing (nm)	Commensurable thickness (nm): $h = n \cdot L_0$ Symmetric wet: n = m (m: integer) Anti-symmetric wet: n = m + 1/2 (m: integer)				Wettable thickness window (nm)
			n				
	N	$L_0 = 0.425 \cdot N^{2/3}$ [b]	1	1.5	2	2.5	$\Delta h = \delta \cdot L_0$
30000 (15k-*b*-15k)	294	18.8	18.8	28.2	37.6	47.0	4.3 ± 1.3 ($\delta = 0.23 \pm 0.07$)[c]
66000 (33k-*b*-33k)	646	31.8	31.8	47.7	63.5	79.4	8.9 ± 1.0 ($\delta = 0.28 \pm 0.03$)[c]
67100 (46k-*b*-21k)	652	32.0	32.0	48.0	63.9	79.9	9.0 ± 1.0 ($\delta = 0.28 \pm 0.03$)[c]

a. Degree of polymerization is estimated by the number of monomer units of styrene and methyl methacrylate.
b. 0.425 is estimated using the equation $L_0 \propto N^{2/3}$ in Ref. 16 and the parameters in Ref. 17.
c. δ of $M_n = 26k$ in Ref. 17 is used for δ of $M_n = 30k$, while δ of $M_n = 51k$ in Ref. 17 is used for δs of $M_n = 66k$ and 67.1k.

the commensurable thickness of neutral PS-*b*-PMMA film is observed in the case of anti-symmetric wet.[17] As indicated in Table 3, it is expected that the commensurability is achieved at the thickness of 28 or 47 nm for PS(15k)-b-PMMA(15k), and at the thickness of 48 or 79 nm for PS(33k)-*b*-PMMA(33k), respectively. In addition, the wettable thickness windows of PS(15k)-b-PMMA(15k) and PS(33k)-*b*-PMMA(33k) are expected to be 4 and 9 nm, respectively. As shown in figure 3, the "wet" BCP film of PS(33k)-*b*-PMMA(33k) is achieved at the thickness of 42 nm, owing to the wettable thickness window. The "de-wetted" BCP film of PS(15k)-*b*-PMMA(15k) is observed at the thickness of 38 nm, although it is almost the same as the symmetric wet thickness in Table 3. This is consistent with the previously reported result.[17]

Figure 6 shows optical microscope images of "wetted" PS-rich PS-*b*-PMMA films with the thicknesses of (a) 42 and (b) 68 nm, respectively. Any island/hole structure is not observed in both of figures 6(a) and 6(b). On the other hand, anti-symmetric and symmetric wet thicknesses are calculated to be 48 and 64 nm, respectively, as indicated in Table 3, strongly suggesting that both of the anti-symmetric and symmetric wet PS-rich PS-*b*-PMMA films should be revealed at the thicknesses of 42 and 68 nm. This will be discussed later with SEM images.

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[17] A. P. Smith *et al*., Phys. Rev. Lett. **87**, 015503 (2001).

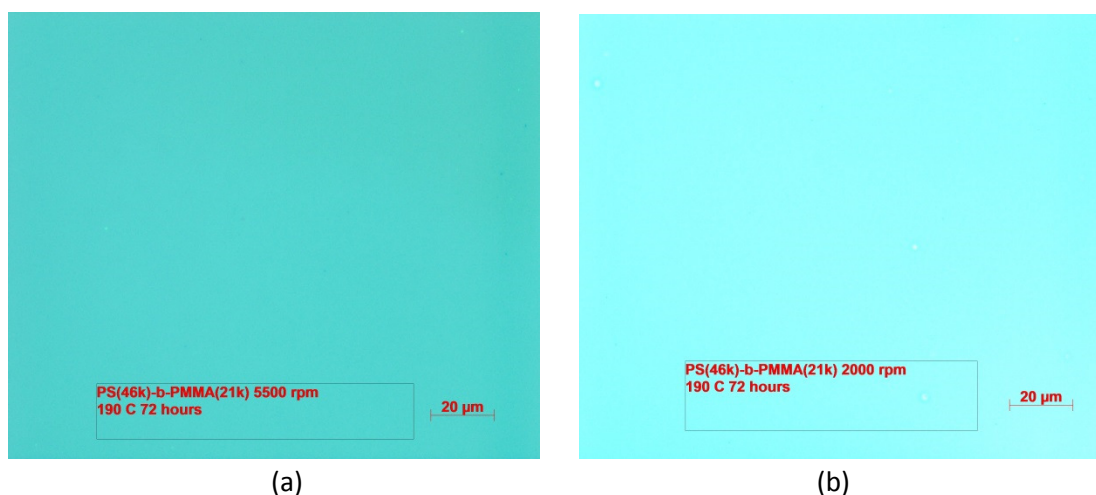<table>
<tr><td>(a)</td><td>(b)</td></tr>
</table>

Figure 6. Optical microscope images of "wetted" PS(46k)-b-PMMA(21k) films with the thicknesses of (a) 42 and (b) 68 nm, respectively. The PS-rich BCP films were spin coated on the neutral brush layer grafted on the 50 nm thick silicon oxide layers, and annealed at 190 °C in N_2 for 3 days.

3.4. Finger print and nanopore structures

Figure 7 shows SEM image of 42 nm thick "wetted" neutral PS-*b*-PMMA film, indicating a finger print structure, which is also consistent with the previously reported results.[2-5,11,16,17]
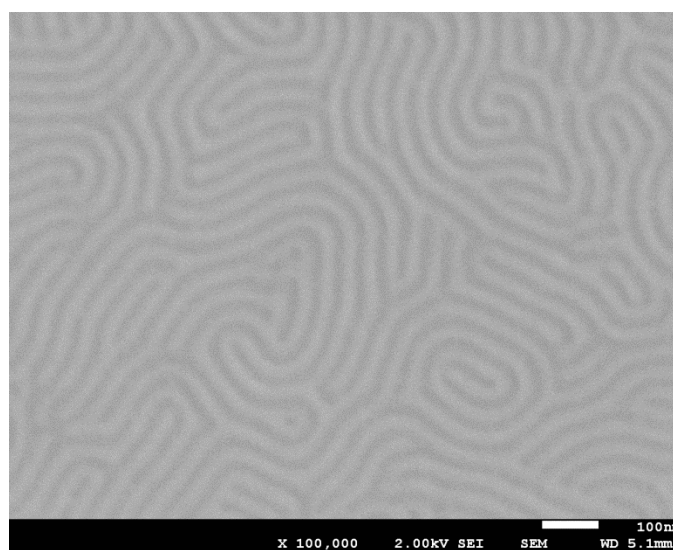

Figure 7. SEM images of 42 nm thick "wetted" neutral PS(33k)-b-PMMA(33k) film spun on the neutral brush layers. The neutral BCP film was spin coated on the neutral brush layer grafted on the 50 nm thick silicon oxide layers, and annealed at 190 °C in N_2 for 3 days. The PMMA portion is removed by O_2 plasma treatment.

Figure 8 displays SEM images of (a) 42 nm and (b) 68 nm thick "wetted" PS-rich PS-*b*-PMMA film. As discussed above, the PS-rich PS-*b*-PMMA films revealed both of the anti-symmetric and symmetric wet, while the neutral PS-*b*-PMMA film shows the anti-symmetric wet only. This suggests that the anti-symmetric wet induces the finger print structure, whereas the symmetric wet forms the nanopore structure. K. Sparnacci *et al.*[11] reported that the finger print structure was well separated from the nanopore structure. However, figure 8(a) indicates that the finger print and nanopore structures are mixed together. Further investigation is needed to elucidate it.
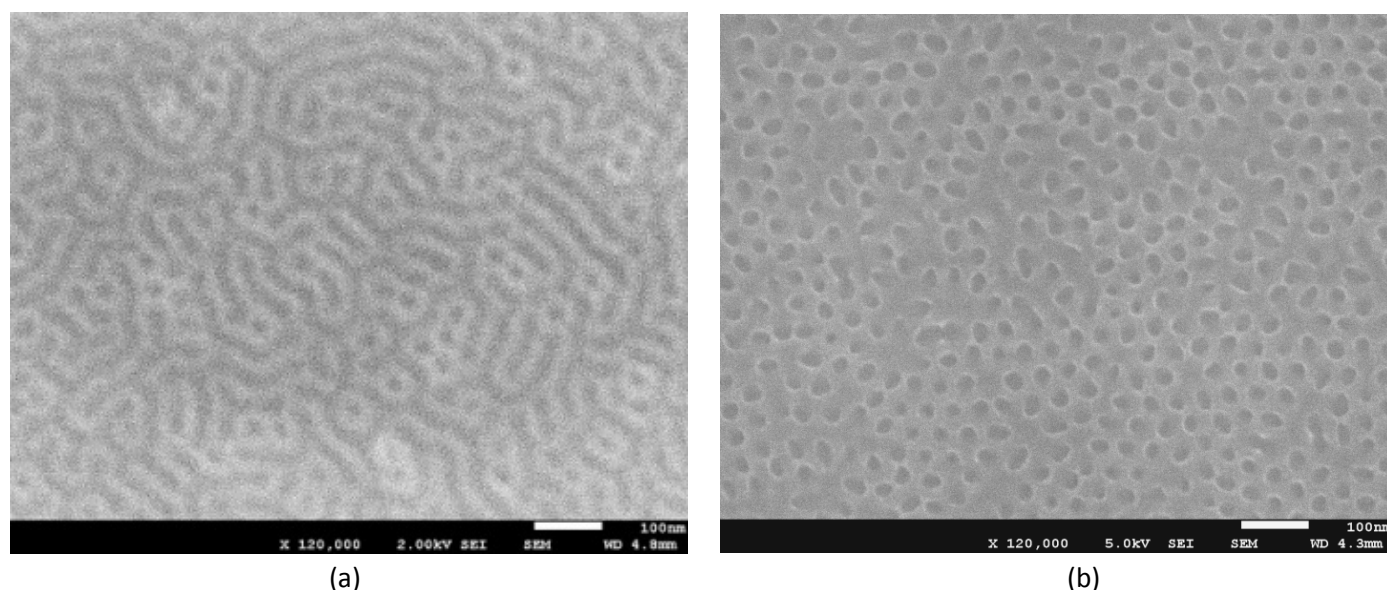

(a)　　　　　　　　　　　　　　　　(b)

Figure 8. SEM images of (a) 42 nm and (b) 68 nm thick "wetted" PS-rich PS(46k)-*b*-PMMA(21k) film spun on the neutral brush layers. The BCP films were spin coated on the neutral brush layer grafted on the 50 nm thick silicon oxide layers, and annealed at 190 °C in N_2 for 3 days. The PMMA portion is removed by O_2 plasma treatment.

4.   Summary

Directed Self-Assembly of BCP was performed for the goal of making this technique available at QNF. The PS-rich and neutral PS-*b*-PMMA films were spin coated on the neutral random copolymer hydroxyl-terminated PS-*r*-PMMA (brush-OH) layers grafted on the native oxide and 50 nm thick PECVD amorphous silicon oxide layers. The thickness and grafting density of brush layer on the native oxide hydroxylated was ~3.5 nm and 0.4-0.5 chain/nm^2, respectively, for 24 hour annealing at 190 °C, while those on the 50 nm thick silicon oxide hydroxylated was 5-7 nm and 0.7-0.8 chain/nm^2, respectively, for the 24 hour annealing. The reactivity of the 50 nm thick silicon oxide hydroxylated with the brush-OH decreased with the time when exposing it into the air, due to bond formation of some species in the air with the dangling bond of Si and other deficiencies, and/or due to trapping of the species in the surface defects of the amorphous silicon oxide. The annealing condition of BCP films using the oven was optimized at 190 °C in N_2 for 3 day. The deterioration of BCP film was also observed when annealing at the temperature more than 210 °C for 3 days. The "wetted" neutral PS-*b*-PMMA film was obtained at the anti-

symmetric wet thickness of 42 nm. On the other hand, the "wetted" PS-rich PS-*b*-PMMA film was acquired at both of the anti-symmetric wet thickness of 42 nm and the symmetric wet thickness of 68 nm.   Furthermore, the SEM images indicated that the anti-symmetric wet film has the finger print structure, whereas the symmetric wet film has the nanopore structure.