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Perpendicular lamellae induced at the interface of neutral self-assembled monolayers in thin diblock copolymer films

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Abstract

We obtained perpendicular lamellar orientations in thin films of symmetric polystyrene-*block*-poly(methyl methacrylate), PS-*b*-PMMA, on self-assembled monolayers (SAMs) of 3-(*p*-methoxyphenyl)propyltrichlorosilane (MPTS) prepared on silicon wafers. In contrast to completely parallel lamellae on silicon wafers having a native oxide layer, perpendicular lamellae at the MPTS interface with parallel lamellae at the air interface were directly observed by transmission electron microscopy (TEM) in cross-sectional view. The perpendicular lamellae at the MPTS interface were attributed to the non-preferential (neutral) MPTS-covered substrate to both PS and PMMA blocks. The neutrality of the SAMs of MPTS was confirmed by the similar interfacial tension values of the SAMs of MPTS with PS and PMMA, estimated by contact angle measurements. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymer; Thin film; Self-assembled monolayer

1. Introduction

In recent years, there has been intensive research conducted on thin diblock copolymer films due to their tremendous potential for applications in nanofabrication because diblock copolymers microphase-separate to form periodic structures on the tens of nanometer length scale [1–3]. The size and morphology of microphase-separated domains can be easily controlled by the molecular weight and composition of the copolymers [4]. In addition, the nanofabrication technique based on diblock copolymers is a parallel process, resulting in an easy creation of nanopatterns over large areas [1–3].

In order to understand the behavior of diblock copolymers in thin films, a large portion of that research has been directed to symmetric diblock copolymers having lamellar microdomains [3]. For unconfined films of symmetric diblock copolymers on substrates, the relative interfacial energies between each block and the substrate, and the relative surface energy of each block induce a preferential wetting of one block at an interface. Consequently, the lamellar structure is oriented parallel to the plane of the film. Due to commensurability effects of film thickness with a bulk lamellar period (L_o), film thickness is also quantized in values of nL_o for symmetric wetting, i.e. the same block at both interfaces, and $(n + 1/2)L_o$ for asymmetric wetting, i.e. one block at the free surface and the other at the substrate interface. If the initial film thickness is not commensurate with this constraint, terraces (i.e. islands or holes) form on the free surface of the film with a step height of L_o to maintain the natural period of lamellae.

Recently, Russell and coworkers [5–7] showed that the interfacial energies between polystyrene-*block*-poly(methyl methacrylate), PS-*b*-PMMA, and substrates were fine-tuned with end-grafted random copolymer brushes of varying styrene and methyl methacrylate contents. An alternative approach to control interactions between block copolymers and substrates is to employ self-assembled monolayers (SAMs) of alkanethiol on gold [8] or alkylsiloxanes on SiO_x (native oxide layers of silicon wafers) [9]. The use of SAMs has a distinct advantage in the formation of an atomically flat and impenetrable surface due to the crystal-like packing of SAMs. In addition, further modifications on SAM-covered substrates are possible by X-ray or UV exposure to make finely tuned or chemically patterned surfaces [9,10].

In this article, we report the perpendicular lamellae in thin films of symmetric PS-*b*-PMMA at the interface of SAMs of 3-(*p*-methoxyphenyl)propyltrichlorosilane (MPTS) prepared on SiO_x/Si substrates (silicon wafers having a

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native oxide layer). The SAMs of MPTS showed non-selective interactions toward PS and PMMA, i.e. neutral to both PS and PMMA. The neutrality condition for the PS-*b*-PMMA copolymer on the MPTS SAMs was confirmed by contact angle measurements. Since SAMs provide atomically flat and impenetrable surfaces, PS-*b*-PMMA films were effectively detached from the SAMs of MPTS to perform plan-view and cross-sectional TEM. Perpendicular lamellae at the MPTS interface were directly visualized by cross-sectional TEM. At the air interface, however, a parallel orientation was induced due to segregation of the PS block with lower surface energy.

2. Experimental

Diblock copolymers: Symmetric polystyrene-*block*-poly(methyl methacrylate), PS-*b*-PMMA, was purchased from Polymer Source Inc. The number average molecular weights of PS and PMMA were 25,000 and 26,000 g/mol, respectively. The polydispersity index was 1.09, and the styrene volume fraction was 0.52. The average bulk period of lamellae (L_o) of PS-*b*-PMMA obtained in TEM and SAXS results was 30 nm.

SiO_x/Si substrates: Silicon wafers having a native oxide layer on the top (ca. 1.5 cm × 1.5 cm) were cleaned in a piranha solution (70/30 v/v of concentrated H_2SO_4 and 30% H_2O_2.) at 90 °C for 20 min, and thoroughly rinsed with deionized water several times, and then blown dry with nitrogen. After cleaning the substrates were extremely hydrophilic (water contact angles less than 10°) and immediately used for the spin coating of copolymers and the deposition of SAMs.

Deposition of self-assembled monolayers: 3-(*p*-methoxyphenyl)propyltrichloro-silane (MPTS, $CH_3OPh(CH_2)_3SiCl_3$, >95%) was purchased from Gelest and used as received. The cleaned SiO_x/Si substrates were immersed in a 1.0 mM anhydrous toluene solution of MPTS in a nitrogen-atmosphere glove box for 48 h that was determined from kinetic studies on the MPTS formation by contact angle and thickness measurements. Then, these substrates were rinsed with anhydrous chloroform several times. After rinsing, the substrates were taken out of a glove box, thoroughly rinsed again with ethanol, then blown dried with nitrogen.

Thin films of diblock copolymers: Thin PS-*b*-PMMA films were spin-coated onto SiO_x/Si or MPTS-covered substrates from a toluene solution. Various film thicknesses were obtained by adjusting spinning speed (1500 ∽ 5000 rpm) and solution concentration (2 ∽ 5 wt%). The film thickness was measured using an Alpha Step 500 profilometer after scraping away some of the film from the substrate with a razor blade. The copolymer films were annealed at 180 °C in a vacuum oven for 36 h.

Contact angle measurements: Advancing contact angles of water, glycerol, and methylene iodide were measured on SAMs of MPTS at room temperature using a Ramé-Hart Model 100 goniometer. In order to measure the contact angles of droplets in dewetted films of PS and PMMA homopolymers on SAMs of MPTS, films of PS ($M_w = 29,000$ g/mol, PDI = 1.09) and PMMA ($M_w = 31,000$ g/mol, PDI = 1.03) with thicknesses of ca. 10 nm were spin-coated on the MPTS-covered substrate, annealed at 200 °C in a vacuum oven for 24 h, then quenched to room temperature. Average height (H) and radius (R) of droplets in each dewetted homopolymer film were measured by atomic force microscopy [11].

Atomic force microscopy: Surface topography of thin films was imaged using an AFM (AutoProbe CP Research, Park Scientific Instruments) in contact mode with Si cantilevers.

X-ray reflectivity: X-ray reflectivity measurements with thin PS-*b*-PMMA films ($5.5L_o$ thick) on both SiO_x/Si and MPTS-covered substrates were carried out in reflection mode with CuK_α radiation supplied by a 18 kW rotating anode X-ray generator (Rigaku) operating at 40 kV and 200 mA.

Small-angle X-ray scattering (SAXS): In order to prepare samples for SAXS measurements perpendicular to the plane of films, thin PS-*b*-PMMA films ($5.5L_o$ thick) were detached from both SiO_x/Si and MPTS-covered substrates as described in Ref. [12]. A thin layer of carbon (ca. 10 nm thick) was first evaporated onto thin PS-*b*-PMMA films on the substrates, and covered with a 25% aqueous solution of poly(acrylic acid), PAA. After drying in air, the PAA/carbon/PS-*b*-PMMA composite was peeled off from the substrates and floated on deionized water with the PAA side down. When the PAA layer was completely dissolved, the floating film was collected onto Kapton films (8 μm thick) and dried. To enhance scattering intensities 16 pieces of the PS-*b*-PMMA/carbon/Kapton films were piled up on the sample holder. SAXS was performed at the 4C1 beamline using synchrotron X-ray radiation sources at the Pohang Accelerator Laboratory in Korea. The wavelength of X-ray source was 1.608 Å. Two-dimensional diffraction data perpendicular to the plane of films were collected with a 2-D CCD camera (Princeton Applied Research).

Transmission electron microscopy: For plan-view TEM, thin PS-*b*-PMMA films were detached and floated off from both SiO_x/Si and MPTS-covered substrates and onto deionized water as described above, and collected on TEM grids. In order to prepare a sample for TEM in cross-sectional view, a thin layer of carbon (ca. 10 nm thick) was first evaporated onto thin PS-*b*-PMMA films on the substrates, and covered with an embedding epoxy (Araldite 502 Kit, Polysciences, Inc.), then cured at room temperature for 24 h and at 60 °C for 24 h. The epoxy/carbon/PS-*b*-PMMA composite was peeled off from the substrate by immersing the composite in liquid nitrogen. A thin layer of carbon was evaporated again onto the PS-*b*-PMMA side of the detached composite, then covered with epoxy and cured as before. Thin sections (ca. 40 nm thick) from the epoxy/carbon/PS-*b*-PMMA/carbon/epoxy composite

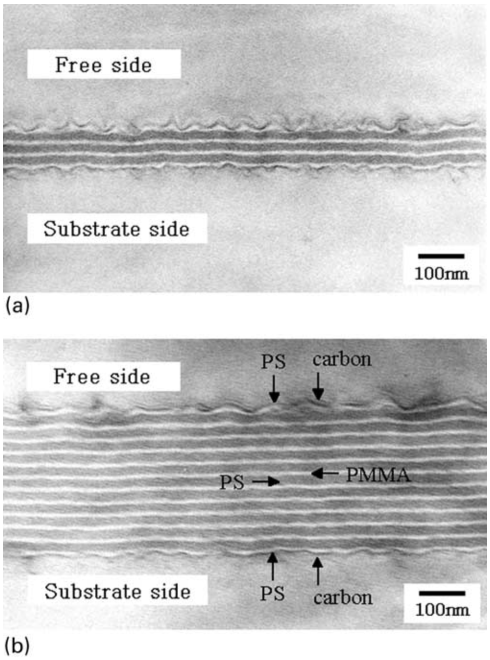

Fig. 1. Cross-sectional TEM images of thin PS-*b*-PMMA films on SiO_x/Si substrates with quantized thicknesses: (a) $4.5L_o$; (b) $12.5L_o$, where L_o is the bulk period of lamellae. PS domains appear as darker regions due to RuO_4 staining. Apparently PS lamellae were thicker than PMMA lamellae due to RuO_4 staining on the PS block and electron-irradiation-induced thinning of the PMMA block.

were obtained using a Reichert Ultra Microtome with a diamond knife. TEM was performed on a JEOL 1200EX operating at 120 kV for both cross-sectional and plan-views. For cross-sectional TEM samples, the films were exposed to RuO_4 (0.5% aqueous solution) for ca. 10 min to stain the PS block selectively. The plan-view image, however, was obtained without RuO_4 staining because electron-irradiation-induced thinning of the PMMA block produced enough contrast [13].

3. Results and discussion

3.1. Parallel lamellae on SiO_x/Si substrates

In thin films of symmetric PS-*b*-PMMA on SiO_x/Si substrates, i.e. silicon wafers having a native oxide layer, multilayer structures can be generated [3,4]. The PMMA block prefers polar native oxide layers of silicon wafers and the PS block has a lower surface energy than the PMMA block. Thus, thin PS-*b*-PMMA films on SiO_x/Si substrates always have lamellae parallel to the plane of films with asymmetric wetting. The cross-sectional images of parallel lamellae in thin PS-*b*-PMMA films with quantized thicknesses of $4.5L_o$ and $12.5L_o$ are shown in Fig. 1(a) and (b), respectively. PS domains appear as darker regions due to RuO_4 staining. These images clearly show the multilayer structure of lamellae parallel to the plane of films. Apparently PS lamellae were thicker than PMMA lamellae due to RuO_4 staining and additional thinning of the PMMA block by electron irradiation [13]. Carbon coating and epoxy embedding procedures presumably caused undulations of the lamellae next to the carbon coatings, especially for the top PS layer. $1/2L_o$-thick lamellae (a half-thick PS lamella and a half-thick PMMA lamella) were absent on the substrate sides in Fig. 1, because the copolymer film was not completely detached from the SiO_x/Si substrate due to strong adhesions of the PMMA block to the substrate. Since the PMMA block is covalently linked with the PS block, the PS block could be pulled off together, resulting in the missing $1/2L_o$-thick lamellae on the substrate side. In addition, the surface of the SiO_x/Si substrate after removing the copolymer film was much rougher than that of an original SiO_x/Si substrate in AFM measurements. Similar results of incomplete detachments of $1/2L_o$-thick lamellae were also observed with thin films of polystyrene-*block*-poly(4-vinylpyridine) on SiO_x/Si substrates [14].

3.2. Perpendicular lamellae at the interface of SAMs of MPTS

Surface characteristics of SiO_x/Si substrates can be easily modified with self-assembled monolayers (SAMs) of chemisorbed alkylsilane derivatives on SiO_x. The functional head structure of alkylsiloxane formed on SiO_x/Si substrates determines the surface characteristics [15]. Therefore, interactions between PS-*b*-PMMA and SiO_x/Si substrates can be changed by a careful selection of the SAMs. But the physical characteristics of SiO_x/Si substrates can be maintained after SAM formation because SAMs still provide an atomically flat and impenetrable surface [15]. We selected 3-(*p*-methoxyphenyl)propyltrichlorosilane (MPTS) to form SAMs on SiO_x/Si substrates. After complete formation of the SAMs, the value of advanced contact angle of water on them was 76° with a small hysteresis between advancing and receding values. The thickness of SAMs of MPTS measured by an ellipsometer was ca. 13 Å. The surface roughness of the SAMs was almost the same as that of Si wafers in AFM measurements. Since MPTS has a similar functional head structure (*p*-methoxyphenyl group) to poly(phenylene oxide), a well-known miscible polymer with PS homopolymers [16], we can deduce that MPTS-covered SiO_x/Si substrates have better interactions with PS blocks than the original SiO_x/Si substrates, although SAMs of MPTS can also have preferences to PMMA blocks through polar interactions.

In reflection optical micrographs of thin PS-*b*-PMMA films annealed at 180 °C for 36 h on SAMs of MPTS (not shown), the copolymer films were optically smooth with no distinguishable features, regardless of film thickness, in contrast to hole and island formation as in the case of copolymer films on SiO_x/Si substrates. These results imply that at least lamellae in the PS-*b*-PMMA films on the SAMs of MPTS are not parallel to the substrate from the

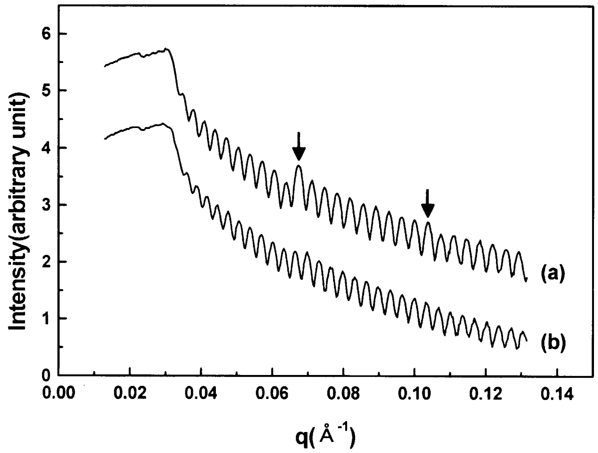

Fig. 2. X-ray reflectivity profiles of thin PS-*b*-PMMA films (5.5L_0 thick): (a) on SiO$_x$/Si substrates; (b) on SAMs of MPTS. Third and fifth order reflections were evident with films on SiO$_x$/Si substrates (indicated by the arrows). With the film on SAMs of MPTS, however, Bragg peak reflections were not appreciable from the Kiessig fringes.

top to the bottom of the film, because a complete parallel orientation of lamellae in thin copolymer films having an incommensurable thickness with $(n + 1/2)L_0$ should generate holes or islands on the free surface of the films.

Both PS-*b*-PMMA films (5.5L_0 thick) on SiO$_x$/Si and MPTS-covered substrates were investigated using X-ray reflectivity measurements (Fig. 2).[1] Third and fifth order Bragg peaks (indicated by arrows) were evident with the film on SiO$_x$/Si substrates [17], providing evidence of parallel lamellae that were directly observed by cross-sectional TEM of Fig. 1. In contrast, Bragg peaks were not appreciable from the Kiessig fringes for the copolymer film on the MPTS-covered substrate. Since PS blocks have a lower surface energy than PMMA blocks, parallel lamellae can be induced near the air interface even for the copolymer film on SAMs of MPTS. However, if they exist only in a small portion of the film, intensities of Bragg reflections may be too weak for detection. In any case, these reflectivity results again provide complementary evidence that at least lamellae in the PS-*b*-PMMA on SAMs of MPTS are not entirely parallel to the substrate.

SAXS patterns with incident beams normal to the plane of thin PS-*b*-PMMA films (5.5L_0 thick) on SiO$_x$/Si and MPTS-covered substrates were also obtained after removing the substrates (Fig. 3). As expected, no scattering was detected with the film on SiO$_x$/Si substrates because all lamellae were parallel to the plane of the film. However, the first order ring, corresponding well to the bulk period of lamella L_0, was obtained with the film on SAMs of MPTS. This SAXS pattern provides strong evidence that some portions of lamellae in the copolymer film on the SAMs of MPTS must be perpendicular to the plane of films.

These perpendicular lamellae were also investigated in plan-view TEM as shown in Fig. 4. PMMA domains appear as brighter regions due to electron-irradiation-induced thinning. These alternating bright and dark domains confirm lamellae perpendicular to the substrate. The lamellar period estimated from this image is ca. 30 nm, the same value as L_0. In order to visualize internal structures of PS-*b*-PMMA films on SAMs of MPTS, cross-sectional TEM images were obtained as shown in Fig. 5. Since SAMs provide atomically flat and impenetrable surfaces, PS-*b*-PMMA films were effectively detached from the SAMs of MPTS as described in the experimental section. After removing the copolymer film from the MPTS-covered substrate, the surface roughness of the substrate was not much different from that of the original MPTS-covered substrate in AFM measurement. This result suggested that the copolymer films were almost completely removed from the substrate in contrast to the case of SiO$_x$/Si substrates. The images in Fig. 5 were obtained with RuO$_4$ staining, resulting in darker PS lamellae. The electron-irradiation-induced thinning of the PMMA block reduced its lamellar thickness. In Fig. 5, perpendicular lamellae at the MPTS interface were clearly visible, in contrast to the completely parallel lamellae on SiO$_x$/Si substrates (Fig. 1). The lower surface energy of the PS block compared to the PMMA block resulted in parallel lamellae at the air interface [18], although the top PS lamella in all images was wavy as before due to TEM sample preparations. Whereas the perpendicular lamellae at the MPTS interface were attributed to the non-preferential (neutral) MPTS-covered substrate to both PS and PMMA blocks.[2]

3.3. Neutrality of SAMs of MPTS

The neutrality of SAMs of MPTS to the PS-*b*-PMMA copolymer was examined by interfacial energies between PS and PMMA homopolymers and MPTS-covered substrates [9,19]. First, the interfacial energy $\gamma_{\text{k-MPTS}}$ between the homopolymer k (k = S or M for PS and PMMA, respectively) and the SAMs of MPTS were calculated from a combination of the modified Fowkes and Young equations.[3] Using glycerol and methylene iodide as polar and non-polar test liquids, we estimated

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[1] Incomplete interception of the incident beam by the substrate resulted in the gradual increases in reflectivity below the critical angles. A fitting based on the electron density profile in the copolymer film was not pursued.

[2] Ambiguities of defect structures in the interfaces between parallel and perpendicular lamellae made it difficult to draw complete schematics. It would be possible to define $s_{1/2}$ and $s_{-1/2}$ disclinations comprised of either PS or PMMA cores at a certain interface, especially in Fig. 5(b). But these structures were not clear enough to be analyzed completely.

[3] $\gamma_{\text{k-MPTS}} = \gamma_{\text{k}} + \gamma_{\text{MPTS}} - 2(\gamma_{\text{k}}^{\text{d}}\gamma_{\text{MPTS}}^{\text{d}})^{1/2} - 2(\gamma_{\text{k}}^{\text{p}}\gamma_{\text{MPTS}}^{\text{p}})^{1/2}$ and $(1+\cos\theta_{\text{t-MPTS}})\gamma_{\text{t}} = 2(\gamma_{\text{t}}^{\text{d}}\gamma_{\text{MPTS}}^{\text{d}})^{1/2} + 2(\gamma_{\text{t}}^{\text{p}}\gamma_{\text{MPTS}}^{\text{p}})^{1/2}$, where $\gamma_{\text{k}}(= \gamma_{\text{k}}^{\text{d}} + \gamma_{\text{k}}^{\text{p}})$, $\gamma_{\text{MPTS}}(= \gamma_{\text{MPTS}}^{\text{d}} + \gamma_{\text{MPTS}}^{\text{p}})$, and $\gamma_{\text{t}}(= \gamma_{\text{t}}^{\text{d}} + \gamma_{\text{t}}^{\text{p}})$ are the surface tensions of the homopolymer, the MPTS-covered substrate, and the test liquid, respectively. γ^{d} and γ^{p} are the dispersion and polar components of each surface tension, respectively. $\theta_{\text{t-MPTS}}$ is a measured contact angle of a test liquid on the SAMs of MPTS.

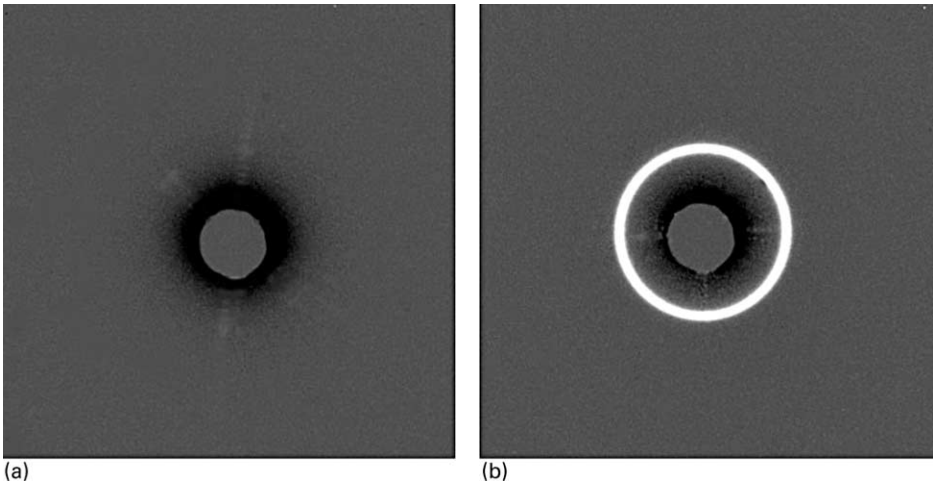

Fig. 3. Small-angle X-ray scattering patterns perpendicular to the plane of thin PS-*b*-PMMA films ($5.5L_o$ thick): (a) on SiO_x/Si substrates; (b) on SAMs of MPTS. To enhance scattering intensities, the films were stacked after removing the substrates. No scattering was detected with films on SiO_x/Si substrates, whereas a first order ring was obtained with films on SAMs of MPTS.

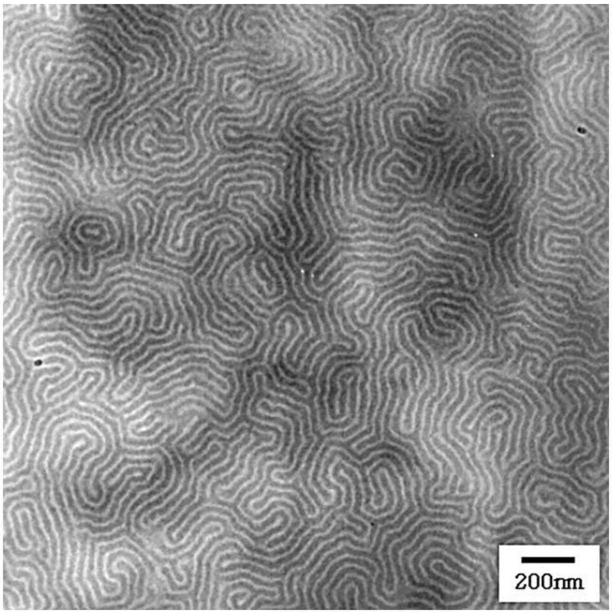

Fig. 4. Plan-view TEM image of a thin PS-*b*-PMMA film ($2.1L_o$ thick) on SAMs of MPTS. The image was obtained without RuO_4 staining. PMMA domains appear as brighter regions due to electron-irradiation-induced thinning.

$\gamma_{\text{S-MPTS}} = 2.21$ mJ/m^2 and $\gamma_{\text{M-MPTS}} = 2.19$ mJ/m^2.[4] The close values of estimated $\gamma_{\text{S-MPTS}}$ and $\gamma_{\text{M-MPTS}}$ interfacial energies can provide an explanation for the neutral behavior of the MPTS-covered substrate toward the PS-*b*-PMMA copolymer.[5]

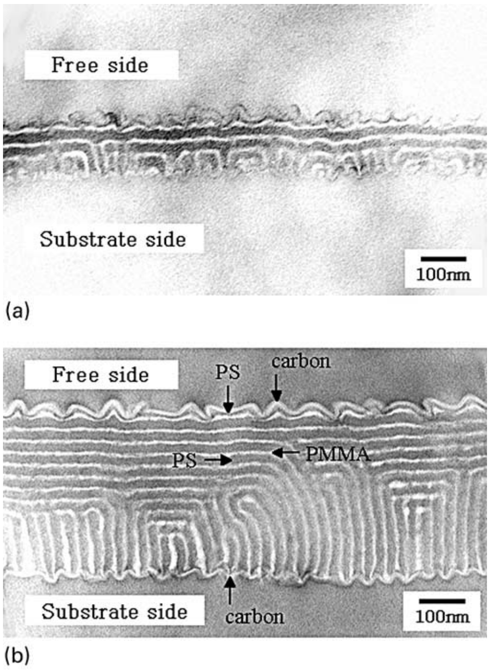

Fig. 5. Cross-sectional TEM images of thin PS-*b*-PMMA films on SAMs of MPTS: (a) $3.7L_o$ thick (b) $13.4L_o$ thick. The images were obtained with RuO_4 staining, resulting in darker PS lamellae. The electron-irradiation-induced thinning of the PMMA block reduced its lamellar thickness.

Alternatively, according to the Young equation ($\gamma_{\text{k-MPTS}} = \gamma_{\text{MPTS}} - \gamma_{\text{k}}\cos\theta_{\text{k-MPTS}}$), the condition of $\cos\theta_{\text{S-MPTS}}/\cos\theta_{\text{M-MPTS}} \approx \gamma_{\text{M}}/\gamma_{\text{S}}$ should be satisfied for neutrality, i.e. $\gamma_{\text{S-MPTS}} \approx \gamma_{\text{M-MPTS}}$. Though $\gamma_{\text{M}} > \gamma_{\text{S}}$ over the temperature range between 100 and 225 °C, γ_{M} and γ_{S} differ by at most a few percent [5]. Thus, the $\theta_{\text{S-MPTS}}$ value must be close to that of $\theta_{\text{M-MPTS}}$ to satisfy the neutrality condition. To find $\theta_{\text{S-MPTS}}$ and $\theta_{\text{M-MPTS}}$, we measured the contact angles of the droplets in dewetted films of PS and PMMA homopolymers on SAMs of MPTS [5,11]. Thin films (ca. 10 nm

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[4] $\gamma_{\text{S}} = 40.3$ mJ/m^2, $\gamma_{\text{S}}^{\text{d}} = 40.3$ mJ/m^2, $\gamma_{\text{S}}^{\text{p}} \approx 0$ mJ/m^2, $\gamma_{\text{M}} = 41.1$ mJ/m^2, $\gamma_{\text{M}}^{\text{d}} = 32.8$ mJ/m^2, $\gamma_{\text{M}}^{\text{p}} = 8.3$ mJ/m^2, $\gamma_{\text{glycerol}} = 64.0$ mJ/m^2, $\gamma_{\text{glycerol}}^{\text{d}} = 34.0$ mJ/m^2, $\gamma_{\text{glycerol}}^{\text{p}} = 30.0$ mJ/m^2, $\gamma_{\text{CH}_2\text{I}_2} = 50.8$ mJ/m^2, $\gamma_{\text{CH}_2\text{I}_2}^{\text{d}} = 48.5$ mJ/m^2, and $\gamma_{\text{CH}_2\text{I}_2}^{\text{p}} = 2.3$ mJ/m^2 in Ref. [19] were used with measured values of $\theta_{\text{glycerol-MPTS}} = 67°$ and $\theta_{\text{CH}_2\text{I}_2\text{-MPTS}} = 37°$.

[5] When water and methylene iodide were used as polar and non-polar test liquids, $\gamma_{\text{S-MPTS}} = 1.9$ mJ/m^2 and $\gamma_{\text{M-MPTS}} = 2.1$ mJ/m^2 were obtained.

thick) of PS and PMMA homopolymers having a similar molecular weight to each block of the PS-*b*-PMMA copolymer were annealed on the MPTS-covered substrate to induce autophobic dewetting. At 180 °C, the temperature at which the copolymer film was annealed, both homopolymer films dewetted the MPTS-covered substrate but irregular shapes of droplets were obtained even with prolonged annealing, which cannot be used for contact angle analysis with AFM. Thus, assuming a similar temperature dependency in surface tensions of PS, PMMA, and SAMs of MPTS between 180 and 200 °C, both homopolymer films were annealed at 200 °C to form droplets with nearly circular shapes. Although some of both homopolymer droplets were still in irregular shapes after annealing, droplets only with circular shapes were analyzed to obtain contact angles of homopolymers on the SAMs of MPTS using AFM. The droplets were quite similar in both PS and PMMA cases, although the size of PS droplets was larger than that of PMMA droplets. The contact angles were calculated using $\tan(\theta/2) = H/R$, where H and R are the droplet height and radius, respectively [11]. We obtained $\theta_{\text{S-MPTS}} = 13.0°$ and $\theta_{\text{M-MPTS}} = 14.3°$ after averaging at least 10 different droplets. The similar contact angles of the droplets imply $\gamma_{\text{S-MPTS}} \approx \gamma_{\text{M-MPTS}}$ as explained above. Therefore, these contact angle results can be further evidence of the neutrality of SAMs of MPTS toward PS and PMMA blocks.

4. Conclusions

We first confirmed parallel lamellae of symmetric PS-*b*-PMMA on SiO_x/Si substrates, i.e. silicon wafers having native oxide layers, directly by cross-sectional TEM. In order to induce a different ordering of the lamellae by changing interactions between the copolymer and the substrate, the chemical characteristics of SiO_x/Si substrates were modified with SAMs of chemisorbed MPTS on SiO_x, keeping the physical characteristics of the substrates, i.e. atomically flat and impenetrable surfaces. On the MPTS-modified substrate, perpendicular lamellae at the MPTS interface were observed regardless of film thickness, because of the neutrality of the SAMs of MPTS toward PS and PMMA blocks. Thus, we demonstrated a successful example of the changing of lamellar orientations by altering the interaction between copolymers and substrates with careful selection of chemisorbed SAMs on silicon wafers.

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