Quick Formation of DSA Neutralization Polymer Layer Attached by Reactive Self-Assembled Monolayer

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The Neutralization layer for Directed self-assembly (DSA) was quickly formed by using polystyrene-polymethylmethacrylate random copolymer (PS-r-PMMA) immobilized by two different kinds of reactive self-assembled monolayers (SAMs). Two different kinds of reactive SAMs, one was photo-reactive and the other was thermal reactive, were covalently bound to PS-r-PMMA by the photo exposure or thermal annealing, respectively. The surface energy for the neutralization layer was easily controlled by the composition ratio of PS-r-PMMA. The lamellar-forming PS-PMMA block copolymer was perpendicularly aligned on the neutralization layers.

Keyword: Directed Self-Assembly, Block Copolymer, Neutralization Layer, Reactive Self-Assembled Monolayer, Quick Polymer Immobilization

1. Introduction

Directed self-assembly (DSA) lithography has recently attracted much interest as an alternative technique to overcome the resolution limit of conventional optical lithography [1-4]. DSA lithography is by using block copolymer cylindrical and lamellar microdomains with periods of the order of 5-50 nm.

Perpendicularly oriented microdomain of the block copolymer in thin films is required for lithographic pattern. The surface energy of the underlying substrate influences the microdomain orientation of the block copolymer.

Mansky et al. showed controlling the surface energy by random copolymer brush [5]. By the composition ratio of the polystyrene-polymethylmethacrylate random copolymer (PS-r-PMMA), the surface energies could be easily controlled, and PS-PMMA block copolymer (PS-b-PMMA) microdomains were aligned perpendicularly on the end-hydroxy functionalized PS-r-PMMA brush [6]. Controlling the surface energy by random copolymer is simple technique and versatile for various block copolymers. However, the long annealing time is needed for the random copolymer brush formation.

The immobilization of the polymer layer by using the reactive self-assembled monolayer (SAM) have been reported recently [7-10]. In these simple methods, the polymers can be quickly immobilized by using multipoint reaction with reactive SAM. Additionally, variety of polymers can be used for immobilization by reactive SAMs. Therefore, the method for polymer immobilization by reactive SAMs is effective for formation of DSA neutralization layer.

In this study, we investigated quick formation of neutralization layers by immobilization of random copolymer using
two different kinds of reactive SAMs. Then, we demonstrated self-assembled structures of block copolymer on our neutralization layers.

2. Experimental

2.1. Materials

Dehydrated toluene, cyclohexanone, acetone, triethylamine (TEA), propylene-glycol monomethylether acetate methoxypropyl acetate (PGMEA) were purchased (Kanto Chemical Co., Ink. and Wako Pure Chemical Industries). PS-r-PMMA, PS homopolymer and PS-b-PMMA were purchased (Polymer Source Inc.). Characteristics of PS-r-PMMA and PS were listed in Table 1. The number-average molecular weight ($M_n$) of PS-b-PMMA was 46.9 and 39.6 kg/mol for the PS and the PMMA blocks with polydispersity index ($M_w/M_n$) of 1.08.

Table 1. Characteristics of PS-r-PMMA and PS homopolymer.

<table>
<thead>
<tr>
<th>molar fraction of PS</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.54</td>
<td>68</td>
<td>1.60</td>
</tr>
<tr>
<td>0.59</td>
<td>7.0</td>
<td>1.20</td>
</tr>
<tr>
<td>0.63</td>
<td>17</td>
<td>1.22</td>
</tr>
<tr>
<td>0.82</td>
<td>68</td>
<td>1.45</td>
</tr>
<tr>
<td>1.00</td>
<td>116</td>
<td>1.10</td>
</tr>
</tbody>
</table>

4-(3'-chlorodimethylsilyl)propoxybenzophenone (CSBP) and 4-(3'-chlorodimethylsilyl)propoxybenzene-sulphonylazide (CSBSA) were synthesized following the procedure according to previous reports, respectively [7, 10]. The chemical structures of CSBP and CSBSA are shown in Figure 1.

![Chemical structures of (a) photo-reactive SAM (CSBP) and (b) thermal reactive SAM (CSBSA).](image)

2.2. Reactive SAMs formation

Two different kinds of reactive SAMs were used, one was photo-reactive (CSBP) and the other was thermal reactive (CSBSA), respectively. They were dissolved in dehydrated toluene (30 mM) and dropped on UV-cleaned Si substrates, respectively. Then, TEA as a catalyst was dropped into the solution puddle on the Si substrates. The Si substrates were left for 1 min and removed the solution puddle by rotation at 1500 rpm. The Si substrates were rinsed by toluene, methanol, and acetone for 5 min, consequently. As a result, two different kinds of reactive SAMs were formed on Si substrates.

2.3. Immobilization of PS-r-PMMA by reactive SAM

PS-r-PMMA dissolved in PGMEA (0.5 wt%) was spuncoated on reactive SAMs, respectively. Then, the PS-r-PMMA thin films were baked at 110 °C for 90 s. PS-r-PMMA thin films with the photo-reactive SAM were exposed by high pressure mercury lamp. The exposure condition was 6 J/cm² at $\lambda = 365$ nm. In the case of thermal reactive SAM, PS-r-PMMA thin films were annealed at 200 °C for 10 min under the air. Finally, the resulting films were rinsed by cyclohexanone to remove PS-r-PMMA unreacted with reactive SAMs.

2.4. Phase separation of block copolymer

A PS-b-PMMA solution dissolved in PGMEA was spin-coated onto the PS-r-PMMA thin films immobilized by the photo-reactive SAM and the thermal reactive SAM, respectively. To form block copolymer nanopatterns, the PS-b-PMMA film was annealed on the hot plate at 250 °C for 1 min under the air. The patterns were observed by the phase mode of an atomic force microscope (AFM, Nanoscope III Dimension, Digital Instruments).

3. Results and Discussion

3.1. The Neutralization layer formation

As shown in Figure 2, the neutralization layers were formed by immobilization of PS-r-PMMA with reactive SAM. CSBP and CSBSA were absorbed quickly on UV-cleaned Si substrate in Figure 2(a). The contact angles of photo-reactive SAM and thermal reactive SAM were 66° and 54°, respectively.
PS-r-PMMA thin films were immediately immobilized by using two different kinds of reactive SAMs in Figure 2(b). In the case of photo-reactive SAM, PS-r-PMMA reacted with benzophenone group by one shot exposure, 6 J/cm² at $\lambda = 365$ nm. The benzophenone group shows an absorption of UV light at around 345 nm caused by a $\pi, \pi^*$ transition in the carbonyl group. It is covalently bonded with $\pi$-position carbon of the PS chain [7, 8]. On the other hand, the thermal reactive SAM containing the sulphonyl azide group reacted with PS-r-PMMA by annealing at 200 °C for 10 min. By thermal annealing, the sulphonyl azide group decomposes under releasing a nitrogen to produce a nitrene group. The nitrene group reacted with $\alpha$-position carbon of PS chain [9, 10]. As a result, PS-r-PMMA was quickly immobilized with two different kinds of reactive SAMs.

The contact angles of PS-r-PMMA and PS thin films after immobilization by two different kinds of reactive SAMs are shown in Figure 3. The same results were obtained in spite of the different SAM, the photo-reactive SAM and the thermal reactive SAM. Because the processing method for immobilization of PS-r-PMMA by these reactive SAMs is only difference between exposure and annealing, two different kinds of reactive SAMs can be separately used as the situation demands. Then, the contact angle was changed from 71° to 93° in the dependence of PS molar fraction. This result means the surface energy was controlled by the composition ratio of PS-r-PMMA, which is easily synthesized by radical polymerization.

3.2. PS-b-PMMA nanopatterns

PS-b-PMMA patterns were formed on the neutralization layers. PS-r-PMMA with PS molar fraction of 0.63 was immobilized by two difference kinds of reactive SAMs, respectively. The film thicknesses of PS-r-PMMA were ~2.4 nm. PS-b-PMMA thin films with thickness of 50 nm were annealed at 250°C for 1 min. Figure 4 shows AFM images of PS-b-PMMA nanopatterns on our neutralization layers. From AFM images, we observed that PS-b-PMMA block copolymers formed perpendicular lamellar structure. The half-pitch of lamellar microdomains was 25 nm. The PS-b-PMMA nanopatterns could be perpendicularly aligned on neutralization layer which is fabricated by immobilization of optimized PS-r-PMMA by reactive SAM.
4. Conclusion

The neutralization layers for DSA were immediately formed by immobilization of PS-r-PMMA with photo-reactive SAM and thermal reactive SAM. By composition ratio of PS-r-PMMA, the surface energy for neutralization layer would be controlled easily. The perpendicular lamellar structure of PS-b-PMMA block copolymer was obtained on the neutralization layer. PS-b-PMMA block copolymer would be aligned by graphoepitaxy or chemical guide on our neutralization layers.

References