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Fabrication of Thin Film Surface Templates from Two Immiscible Polymers by Phase Separation and Phototethering

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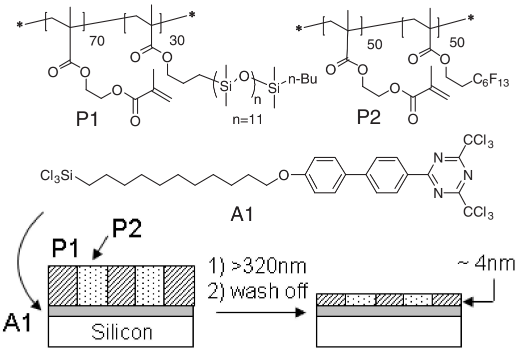
Thin layer surface templates were fabricated by spin coating two immiscible polymers onto a photoreactive substrate, followed by photoirradiation and removal of the unreacted polymer with solvent. Phase-separation occurs during the spin coating process and the separated structure was tethered onto the substrate surface by photoirradiation, to yield a thin surface pattern on the substrate. The surface patterns thus obtained were robust, applicable to large areas, and could be tuned at will by designing component polymers.

Surface patterning for the fabrication of structures at micrometer and/or nanometer scale is receiving great attention, particularly for its increasing use in surface-directed phase separation. In this technique, the domains of a phase-separating mixture of polymers in a thin film can be guided into arbitrary structures onto a surface by designing a prepatterned variation of surface energies. This allows these surface patterns to be readily transferred to a two-component polymer film.[1,2] This approach might provide a simple means for fabricating polymer-based microelectronic circuits and is expected to play an important role in future technological applications.[1,3–8] For instance, Friend et al. have reported a control of the phase separation of conjugate polymer blends by introducing a chemical pattern onto the substrate for surface energy modification, which has led successfully to improved LED performance.[9,10]

Various methods can be used to produce periodic patterns of chemically heterogeneous substrates. The most versatile are those of microcontact printing,[1,2,4,5,9] or a phase-separated Langmuir–Blodgett (LB) film.[11–14] These procedures are capable of covering a metal substrate with patterns of thin (ca. 2 nm) self-assembled monolayers (SAMs). However, in order to realize their potential, it is necessary to have the ability to fabricate the surface pattern over a larger area, more simply and with polarity and morphological control.

In this letter, we report a new method for preparation of surface templates that utilizes phase separation of two immiscible polymers and phototethering onto a photoreactive substrate surface.

Scheme 1 shows the structures of the compounds used in this study and the immobilization process used to prepare a phase-separated polymer thin film onto a photoreactive silicon wafer. As shown in Scheme 1, two copolyacrylates, **P1** ($M_w = 34700$, $M_w/M_n = 1.7$) and **P2** ($M_w = 27300$, $M_w/M_n = 1.4$), each having a polymerizable unsaturated pendant group, were prepared.[15] A silicon substrate was treated to immobilize a photoinitiator onto the substrate by dipping a silicon wafer in a 0.1 wt % toluene solution of **A1** for 3 h.[16] The experimental procedure was simple: the two polymers were dissolved in a common solvent (1 wt % in 2-butanone), a drop of the solution was placed onto the substrate, and the film was prepared by spin-coating (1500 rpm, 20 s) to form a layer about 30 nm thick. As most chemically different polymers are immiscible due to the their much reduced entropy of mixing compared to their low molecular weight analogs, demixing takes place during the spin-coating procedure.[4,17–19] By then photoirradiating the film for 10 s through a glass filter (transparent over 320 nm, 32 mW at 365 nm), a radical was generated from the photoinitiator on the substrate and this reacted with an unsaturated group of the polymer next to the substrate, causing phototethering. After removal of unreacted polymers with a solvent, an ultrathin polymer film (ca. 4 nm) was fixed onto the silicon surface. If the polymers next to the substrate have a phase-separated structure, that structure will be fixed onto the surface of the substrate after removing unreacted polymers.



Scheme 1. Schematic representation of surface pattering of phase-separated polymers.

Experimental results are as follows. As **P1** and **P2** are strongly incompatible, coexisting phases of the almost pure polymer components were formed after spin-coating. (Figure 1a, as a reference). After photoirradiation and removing unreacted polymers (Figure 1b), the AFM image revealed almost the same morphology, but a flatter, planar structure was observed, as evident from surface average roughness (R_a). The ellipsometric thickness of the spin cast film (Figure 1a) was 26 nm, whereas that of the irradiated film (Figure 1b) was much thinner, estimated about 4 nm by ellipsometry (DHA-XA/S4, Mizojiri Opt Co.). These results indicate that the radicals photogenerated on the surface reacted with the unsaturated pendant group of the polymers next to the substrate, resulting in the formation of a thin layer between the substrate and the polymers. Because of the phase-separated structures in the polymer layer, a thin layer structure next to the substrate was transferred and fixed on the surface.

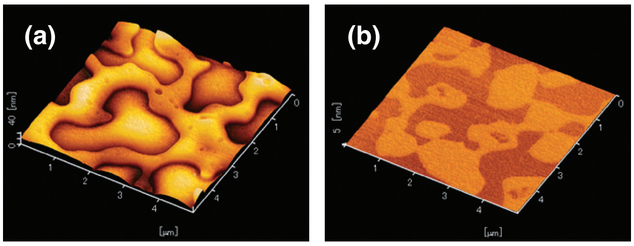


Figure 1. AFM images of phase-separated films. (a) As spin-cast (reference). Thickness: 26 nm, R_a: 4.9 nm. (b) Surface pattern obtained after photoirradiation (>320 nm) of spin-cast film and removal of unreacted upper layer by washing in 2-butane. Thickness: 5 nm, R_a: 1.2 nm. Scanned area 5 μm × 5 μm. AFM: E-seep/NanoNavi, SII-NT Co.

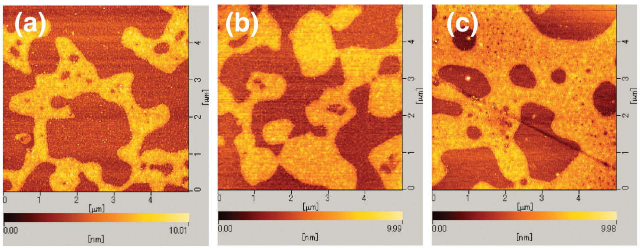


Figure 2. AFM images (5 μm × 5 μm) of surface pattern at various weight ratio in **P1**:**P2** after spin-coating, photoirradiation and solvent washing: (a) 2:1, (b) 1:1, and (c) 1:2. The area ratios of the darker and the brighter portions are 7:3, 5:5, and 3:7, and ellipsometric thickness is 3.9 ± 0.3, 4.3 ± 0.1, and 4.8 ± 0.1 nm, respectively.

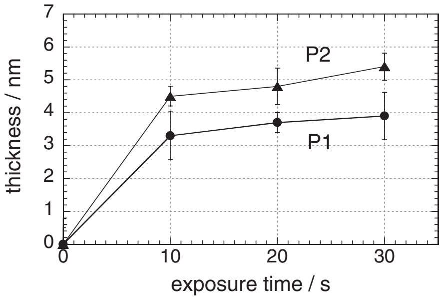
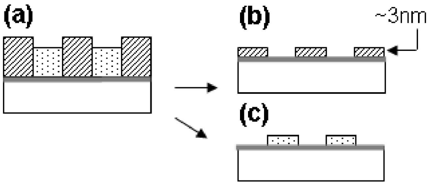


Figure 3. Ellipsometric thickness of individual polymers (**P1** or **P2**) after irradiation (>320 nm) and washing with a solvent.



Scheme 2. Fabrication of opposite surface patterns (b), (c), from a phase-separated polymers film. (a) as spin-coated, (b), (c) after phototethering. Surface pattern depends on which polymer has reactive pendant group.

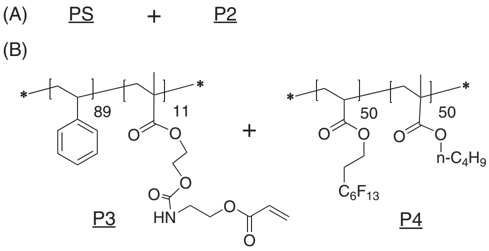


Figure 4. Structures of polymers for surface patterning.

Figure 2 shows the AFM topographic images (5 μm × 5 μm) of thin films obtained from the mixed polymers with different weight fractions. The brighter portions were about 2 nm higher than the darker portions. The mixing ratios of **P1**:**P2** in Figures 2a, 2b, and 2c were 2:1, 1:1, and 1:2, respectively. By measuring the area of darker and brighter portions by a threshold method using the grain analysis function generated by computer software (SPIWin), the area ratios were found to be 7:3, 5:5, and 3:7, respectively, which were in good agreement with the weight fraction of the component polymers. This result indicates that brighter regions correspond to **P2** and darker portions correspond to **P1**.

The layer thickness of the individual polymers was confirmed (Figure 3). Either **P1** or **P2** formed a uniform thin layer and the thickness was slightly higher for **P2** than for **P1**, in accord with the results obtained in Figure 2.

The mechanism of polymer dewetting and three-dimensional distribution of phase-separated structure by spin-coating was extensively studied by Steiner et al.[18] They observed different structures on an air surface (e.g., islands and plateaus consisting of two polymers) and next to the substrate (e.g., a homogeneous thin layer consisting of either polymer), due to the difference of the surface energy of two polymers. Taking this into consideration, it is interesting to note here that a domain structure that was proportional to the feed ratio of the two component polymers was observed at the near surface (ca. 4 nm) of the substrate in our experiments.

In order to confirm the robustness of the thin films, ultrasonic washing for extended period of time (ca. 10 min) in 2-butanone was carried out repeatedly, with no apparent damage to the polymer surface pattern. The remarkably stable surface and strong anchoring of these polymer patterns to the substrate are a manifestation of the covalent bonding between the polymers and the substrate.

Our methodology can be extended to control the morphology and polarity of surface patterns. As shown in Scheme 2, a phase-separated film consisting of two immiscible polymers (Scheme 2a) can form a surface pattern (b) or reversed pattern (c) after photoirradiation and washing with a solvent, depending on which polymer has a reactive pendant group.

Our idea was realized by designing new polymers. As shown in Figure 4, a combination of polystyrene (PS, Aldrich, $M_w = 194000$, $M_w/M_n = 1.3$) and a fluoro-polymer having an unsaturated reactive pendant group **P2** (weight ratio 1:2, case A) and a combination of polystyrene having the unsaturated reactive group **P3** ($M_w = 143000$, $M_w/M_n = 2.2$) and fluoropolymer **P4** ($M_w = 13600$, $M_w/M_n = 1.9$, weight ratio 1:2, case B) were employed. In both cases, two polymers are dissolved in a common solvent (2-butanone, 1 wt %) and spin-coated onto a photoinitiator-tethered silicon wafer.

The AFM image of spin-casted film of PS/**P2** combinations (1:2 weight ratio, Figure 5a) showed a column-like structure

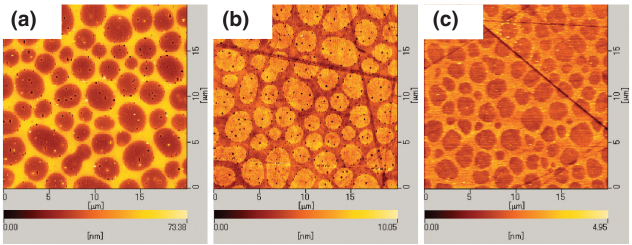


Figure 5. AFM images (20 μm × 20 μm). (a) PS + **P2** (1:2): as spin-cast; reference. (b) PS + **P2** (1:2): spin-casting, photoirradiation (>320 nm, 30 s) and washing by 2-butanone. (c) **P3** + **P4** (1:2): same procedure as in (b). Vertical scale is 73, 10, and 5 nm respectively.

with PS existing in the brighter, peripheral regions, as suggested by the increased peripheral region with an increase of PS content (PS/**P2** = 1:1). The peripheral region was higher than the circular region at about 30 nm. Upon photoirradiation of this film and removing the unreacted polymers by ultrasonication in 2-butanone, a reversed column-like structure appeared, with relatively flat shape (Figure 5b). The height of the circular domains was 3 nm higher than the surrounding regions. Because only **P2** had a reactive pendant group, it is reasonable to assume that the circular domain consisting of the fluoro-polymer **P2** was tethered onto the surface of the substrate by chemical bonds and the excess **P2** and the unreacted PS were removed by the solvent treatment.

A reversed pattern would be expected by changing the unsaturated pendant group from the fluoro-polymer to PS (case B, in Figure 4). As shown in Figure 5c, after photoirradiation and dissolution of a spin-cast film (**P3** + **P4**, 1:2 weight ratio), a thin peripheral structure (ca. 1 nm height) of PS, which is reversed pattern of Figure 5b, was revealed on the substrate surface. These results indicate that the morphology of a surface pattern could be tuned simply by designing the reactivity of two polymers.

In conclusion, we demonstrated a novel method of fabricating patterned-polymer thin films using separation of two immiscible polymers followed by photografting of the polymers on the solid surface. Our methodology has the following advantages: (1) The surface patterns are robust, due to the covalent bonding between the polymer and the substrate. (2) The method can be applied to a large area with a short processing time, due to the rapid spin-coating process. (3) The size and shape of the domains can be tuned by designing component polymers and the mixing ratio. This technique will be important in the fabrication of patterned materials at the micrometer or nanometer scale for application to electronic devices, sensors, and for protein adsorption. Further study to extend our approach to a large number of binary polymer pairs on a variety of different substrates is in progress.

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