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Ordered Patterns of Microimprinted Bilayer Polymer Films with Controlled Dewetting and Layer Inversion

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Control of the polymer self-assembly based on dewetting and partial layer inversion on a microscopic length scale is immensely important for realizing the possibility of adapting polymer processing technologies to fabricate cheap devices with desired patterns over large area, which do not necessarily rely on high-cost lithographic techniques. Dewetting of thin polymer blend films has been performed on deliberately tailored chemically heterogeneous substrates fabricated using several techniques such as microcontact printing,[1−5] vapor deposition,[6] and photolithography.[7] While many studies have been focused on using chemically patterned substrates, mostly by modification of self-assembled monolayers (SAMs),[1−5] very few have been studied to use topographically patterned substrates (i.e., patterns consisting of height variation on a chemically homogeneous substrate) for controlling the dewetting and partial layer inversion of polymer thin films.

Here, we demonstrate a very simple and fast route to fabricating ordered micropatterns over large areas on various substrates by using dewetting and partial layer inversion of *topographically* patterned polymeric films *without* a prepatterned substrate. Our method is based on utilizing microimprinting to induce the local thickness variation of an initially inverted bilayer which allows the controlled dewetting and partial layer inversion upon subsequent thermal annealing. As illustrated schematically in Figure 1, the microimprinting generates a topographically heterogeneous bilayer film as the imprinted areas by a poly(dimethylsiloxane) (PDMS) mold are thinner than the rest of areas. The subsequent annealing above the glass transition temperatures of the constituent polymers induces the initiation of dewetting of the top layer selectively at thinner regions, leading to the localized dewetting of the top layer and the partial layer inversion of two layers. The kinetically driven, nonlithographical pattern structures were easily fabricated over large area by this approach.

For the preparation of an inverted layer, a 2 wt % polystyrene (PS) solution in toluene was first spin-coated onto a silicon substrate and subsequently a poly(4vinylpyridine) (P4VP) solution (2 wt %) in ethanol was spin-coated on the PS film. Both polymers were purchased from Polymer Source Inc., Doval, Canada. The molecular weights of PS and P4VP are 45 800 and 48 000 g/mol, respectively, and the polydispersity of both polymers is about 1.05. The spin-coating (SPIN 1200 Midas-system, Korea) was carried out at the 2000 rpm for 1 min for each polymer. The thicknesses of PS and P4VP film were approximately 80 and 100 nm respectively measured by atomic force microscope (AFM).

The spin-coated P4VP/PS bilayer was topographically patterned with a house-made microimprinting apparatus (See Supporting Information). The microimprinting of the bilayer with a PDMS master pattern was performed for 15 min at 150 °C. The topographically micropatterned bilayer was annealed at 250 °C on a thermal stage (Linkem THMSE 600) to induce the dewetting of top P4VP layer and partial layer inversion of the bilayer in the selective areas. The dewetting of the P4VP layer occurred within a few minutes only in the thinner regions and unique micropatterns were observed. The sample was annealed at 250 °C for more than 100 h, as the reference

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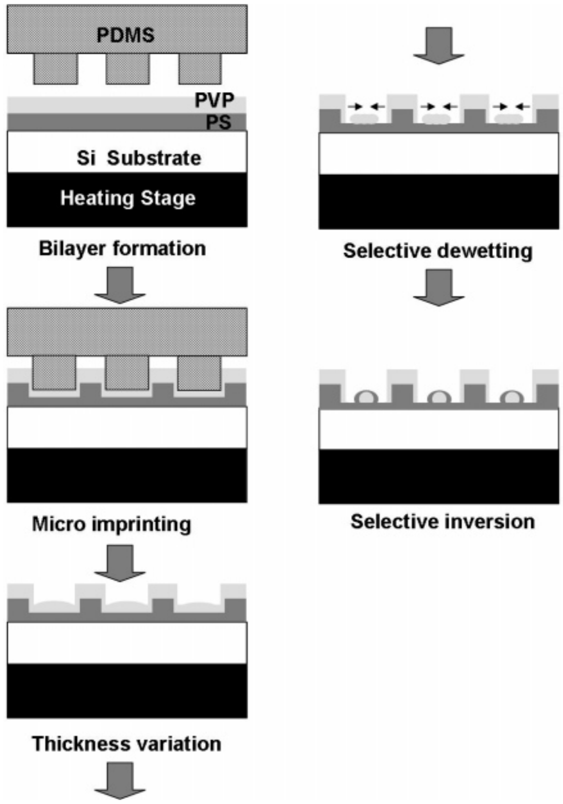

Figure 1. Procedure of the controlled dewetting and partial layer inversion. Microimprinting on a P4VP/PS bilayer induces thickness variation. The subsequent temperature annealing confines the dewetting of the P4VP layer only in the thinner regions. The partial layer inversion occurs by prolonged heat treatment, leading to a topographically and chemically modified micropatterned surface.

suggested, in order to have the partial layer inversion occur.[8] The procedure of our patterning method is schematically depicted in Figure 1. The micropatterns were characterized with a SEM (Hitachi: S-2700) at 10 kV and an AFM (Nanoscope III Digital Instruments) in tapping mode.

We generated cylindrical holes on the bilayer surface by employing a PDMS mold containing cylindrical posts with 2 μm in diameter arrayed with a 4*mm* symmetry. The square arrays of patterns generated by imprinting clearly display the thickness variation in the optical microscope (OM) in Figure 2a and the height contrast AFM image in the inset. The maximum height of the noncontact region was measured as approximately 250 nm, and that of the punched region was approximately 80 nm (each layer has approximately 40 nm in thickness). The scheme in Figure 2b depicts the imprinted bilayer structure.

The thickness variation of the bilayer depends on temperature, time of microimprinting, applied pressure, and its positional distribution under the mold.[9,10] Typical polymer melts similar to our cases under confined pressure result in a thinner film at pattern edge regions than center regions. The thinner pattern edge at which the dewetting initiates arises from the local capillary flow at the vicinity of pattern boundary as previously reported by L. J. Heyderman et al.[11] (see also Supporting Information). The thickness variation results in selective dewetting and layer inversion, giving rise to a submicrometer pattern selectively in the punched regions as shown in Figure 2, parts c and d, respectively. Indeed, the initiation of the dewetting was restricted at the circular interfaces, thus the dewetting P4VP layer was converged toward the center of the circle, leading to hemispherical submicrometer dots with the diameter of approximately 500 nm.

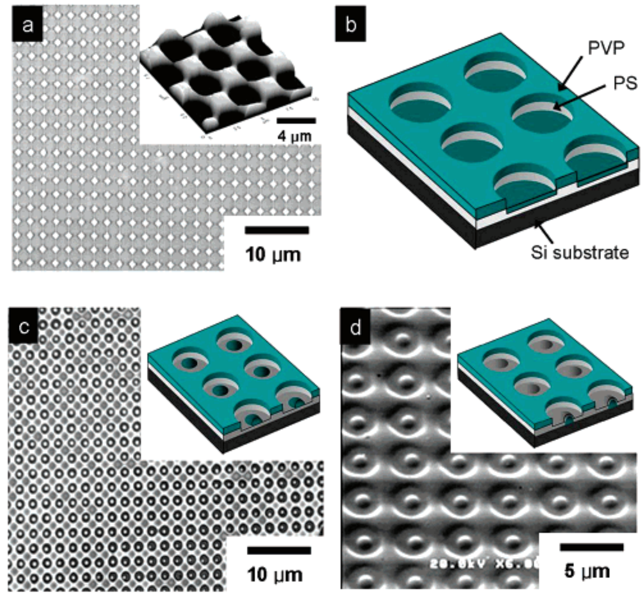

Figure 2. Dewetting and partial layer inversion of a microimprinted P4VP/PS bilayer film on a Si substrate with a PDMS mold that has cylindrical posts with 4*mm* square symmetry. (a) OM and AFM (inset) images and (b) schematic of the imprinted P4VP/PS bilayer. (c) OM image and schematic (inset) of the P4VP/PS bilayer after dewetting. (d) SEM image and schematic (inset) of the P4VP/PS bilayer after partial layer inversion.

The etching of either PS or P4VP layer after heat treatment with the selective solvents confirmed the selective dewetting and partial layer inversion. (See Supporting Information.) It should be pointed out that the viscosity of the P4VP used in this study is higher than that of the PS[8] so that more viscous upper liquid layer dewets less viscous *liquid* layer. As reported by Char et al., in this case the lower liquid layer becomes deformed as the dewetting of upper layer proceeds, which is eventually followed by a layer inversion between two initially placed layers.[8] We also observed a layer inversion but only within the imprinted patterns. This selective layer inversion induced by the film topography therefore could be used to as a potential route to chemically patterned surfaces.

One should note, however, that the pattern structure we obtained may be thermodynamically unstable, but kinetically driven. According to Brochard-Wyart et al.[12.13], the thickness (h_i), below which an upper layer (e.g., the A-layer) is unstable against capillary wave fluctuations (i.e., spinodal instability) on a substrate (e.g., the B-layer) is given as $h_i = [-A/(2\pi\rho g)]^{1/4}$where A is the effective Hamaker constant, ρ is the density of the A-layer, and g is the gravitational constant. Furthermore, the rise time of such unstable mode (τ_m) in the case of liquid/liquid dewetting takes the form of $\tau_m \sim h^6\eta_B(1/\gamma_{A/Air}+1/\gamma_{A/B})^{-1}$-$(L|A|^2)^{-1}$ where η_B is the viscosity of the liquid substrate, $\gamma_{\alpha/\beta}$ is the α/β interfacial tension, and L is the thickness of the substrate. A rough estimation based on the parameters for PS/P4VP/Air system at the experimental condition gives $A \approx -2 \times 10^{-20}$ J, $h_i \approx 750-1000$ nm, and $\tau_m \sim O(10^5)$ s at the elevated region. Therefore, it is very likely that the P4VP layer deposited on PS layer at the elevated region with approximately $h = 130$ nm and $L = 120$ nm shown in Figure 2a will dewet the substrate eventually at a certain time scale. Nevertheless, for the experimental conditions in this study, the dewetting did not occur at the elevated region and the structure remains nondeformed when it was vitrified below the glass transition temperatures of both polymers. (See Supporting Information.)

We generated hexagonal posts on the surface by applying another PDMS mold containing hexagonal holes arrayed with

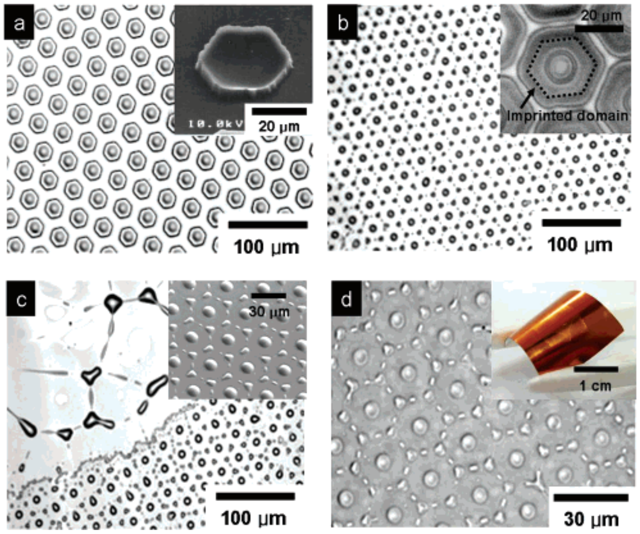

Figure 3. Dewetting and partial layer inversion of a microimprinted P4VP/PS bilayer film on a Si substrate with a PDMS mold that has hexagonal holes with 6*mm* hexagonal symmetry. OM (a) and SEM (inset) images of the imprinted P4VP/PS bilayer pattern. OM (b−d) images of the imprinted P4VP/PS bilayer pattern after the thermal annealing. (c) Boundary regions between randomized and controlled microstructure. (d) Microstructure formed on a polyimide substrate. Inset of part b displays the captured OM image during dewetting of the P4VP layer. Inset of part c is a SEM image of the elevated hemispherical and triangular features. Inset of part d is a photograph of the micropattern on a flexible polyimide substrate.

6*mm* hexagonal symmetry. The size of the hexagon and the periodicity of the mold were 20 and 40 μm, respectively. As shown in Figure 3a, the imprinting on a P4VP/PS bilayer with the PDMS mold produced well-defined hexagonal arrays. SEM image in the inset shows that the top boundary of each hexagonal domain is concave due to the insufficient material filling and both inside and outside boundaries of a hexagonal domain are minimal in thickness. Therefore, the subsequent dewetting of the P4VP layer occurred simultaneously in both inside and outside of the domains. In the inside of the posts, the dewetting began at the boundary and propagated toward the center, resulting in hemispherical dots very similar to ones observed with the square array (Figure 2c). In outer regions the dewetting initiated at the boundary of the posts was guided by the presence of the arrays of the hexagonal domains.

A honeycomb shape polygon structure of the dewetting P4VP layer (the inset of Figure 3c) was broken into ellipsoids and triangular droplets with 6*mm* symmetry during further heat treatment (Figure 3b−d). Again the prolonged heat treatment at 250 °C induced the partial layer inversion between the P4VP and the PS layer. The hemispheres surrounded by the ellipsoids and triangular dots are shown in the inset of Figure 3b. Figure 3c illustrates the boundary between the controlled regions and the randomized ones. The regions where the dewetting and partial layer inversion randomly occurred are very similar to ones demonstrated the results reported previously. [8]

In summary, we demonstrate a simple and fast patterning method which gives ordered micropatterns over large areas. Our method is advantageous in three aspects. First of all, the method can easily produce the circular shape pattern arrays with submicrometer dimensions without any complicated, high-cost lithographical treatments (Figure 2). In principle, the application of a PDMS mold with submicrometer pattern size allows us to produce much smaller circular patterns. Second, our method enables us to fabricate micropatterns with both topographical and chemical contrasts. The selective partial layer inversion in the imprinted areas resulted in the top PS and bottom P4VP layer on the Si substrate, while the rest of the areas remained with the top P4VP and bottom PS layer. The third is that, more importantly, our method does not require any effort to generate prepatterns. Furthermore, the method is applicable to a variety of substrates including Si, glass, Mica and even polymer substrate. The P4VP/PS bilayer prepared on an oxygen plasma treated polyimide film was successfully converted into an ordered micropattern by the dewetting and partial layer inversion. As shown in Figure 3d and inset, the controlled micropattern was successfully obtained on the flexible polyimide substrate through the heat treatment over large area ($\sim 1 \times 1$ cm^2).

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Supporting Information Available: Text giving experimental details including microimprinting lithography, with a figure showing the experimental equipment, capillary flow at the edge of the micropattern, with a figure showing the surface profile, partial layer inversion, with a figure showing the top layers of the samples, and dynamics of dewetting, with a figure showing the dewetting speed. This material is available free of charge via the Internet at http://pubs.acs.org.

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