Ordered Polymer Nanostructures Induced by Controlled Dewetting

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Introduction

Control of the polymer self assembly based on dewetting, partial layer inversion and microphase separation on both micro and nanoscopic 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 microcontact printing[1], vapor deposition, and photolithography[2], leading to self organized microarrays of polymer thin films with careful control of experimental parameters. For nanometer scale ordered polymer patterns, block copolymers have been extensively investigated due to their capability of spontaneous nanostructure formation under directional external fields including electric, magnetic and surface one[3]. Further utilization of the polymer micro and nanostructures requires the combination of block copolymer self assembly with advanced dewetting techniques.

Here, we demonstrate two very simple and fast routes to fabricating ordered micro/nanopatterns of polymers over large areas on various substrates using controlled dewetting. The first 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. In the second method, the self assembly of block copolymer was controlled on a chemically micropatterned surface produced by microcontact printing, being combined with its solvent vapor treatment. The kinetically driven, non-lithographical nanopattern structures were easily fabricated over large area by these approaches.

Experimental

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(4vinyl pyridine) (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 g/mol 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 1min for each polymer. The thicknesses of PS and P4VP film were approximately 80nm and 100nm respectively measured by atomic force microscope (AFM).

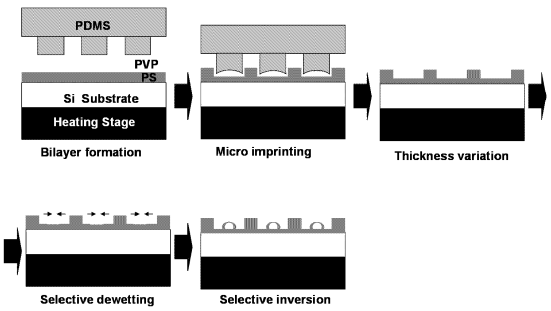

Figure 1. Procedure of controlled dewetting of a polymer bilayer

The spin-coated P4VP/PS bilayer was topographically patterned with a house-made micro-imprinting apparatus. 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 hours. The procedure of our patterning method is schematically depicted in Figure 1.

Results and discussion

Figure 2a shows the optical micrograph of P4VP/PS bilayers micro-imprinted by PDMS molds with stripe geometry. The width of each line in the stripe is 2 μm, and its periodicity is 4 μm. The micro-imprinting caused contact areas of the bilayer with the PDMS mold to be thinner than the non-contact ones. The maximum height of the elevated region is approximately 250 nm, and that of punched, thinner region is approximately 80 nm; each layer has approximately 40 nm in thickness measured by AFM. The thickness variation of the bilayer depends on applied pressure, temperature and time of microimprinting. The selective dewetting produced an interesting sub-micron pattern selectively in the thinner regions where a broken line pattern was observed with approximately 400 nm in width as shown in Figure 2b and 2c. Another example of micropatterned arrays of polymer thin film is obtained using controlled dewetting (Figure 2d). Figure 2e displays nanoscale polymer dot arrays with 70 nm in diameter induced by controlled dewetting on a topographic pre-pattern.

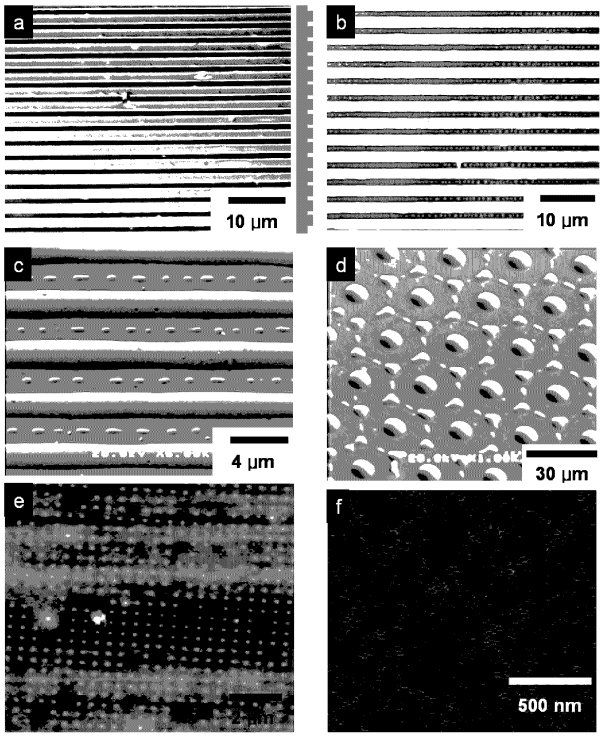

Figure 2. Micro/nanopatterned polymer thin films produced by controlled dewetting

A highly ordered block copolymer nanostructure is shown in Figure 2f. The structure results from the combination of block copolymer assembly with the selective dewetting on a chemically modified surface.

Conclusions

We demonstrated various ways to fabricate self organized micro/nanostructures of polymers mainly by utilizing confined dewetting either in micro-imprinted films or on chemically modified surfaces. Globally ordered pattern structures are potentially useful for many nanotechnological applications.

References

[1] A. M. Higgins, R. A. L. Jones, *Nature* **2000**, *404*, 476.
[2] M. Böltau, S. Walheim, J. Mlynek, G. Krausch, U. Steiner, *Nature* **1998**, 391,877.
[3] C. Park, J. S. Yoon, E. L. Thomas *Polymer* **2003**, *44*, 6725.