NANOTEMPLATES FROM VERSATILE DOMAIN MORPHOLOGIES IN PS-*b*-PFS BLOCK COPOLYMER FILMS

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INTRODUCTION

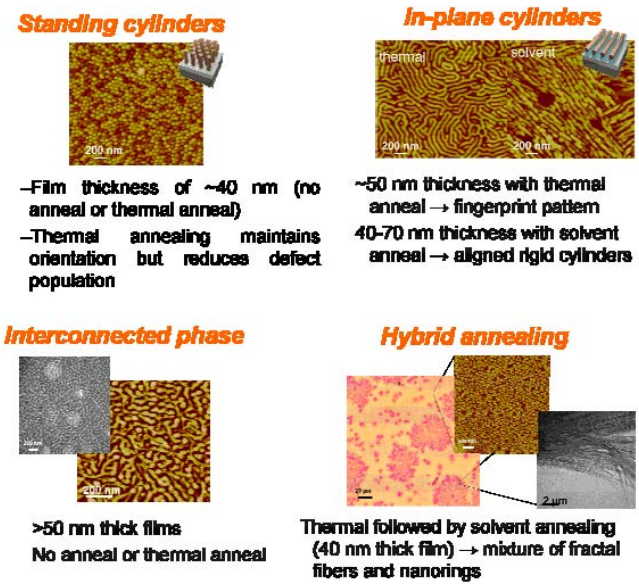
Block copolymers are composed of covalently bonded sequences of chemically distinct repeated units. Because of the incompatibility, block copolymers usually microphase separate into well-ordered nanoscale structures below an order-disorder transition temperature.1 The segregation strength is primarily determined by the enthalpy and entropy and usually described as χN, the product of the Flory-Huggins parameter (χ) between the blocks and the total degree of polymerization (N) of the copolymer.2 The existence of some morphologies are theoretically predicted within self-consistent field theory on the basis of the volume fraction of the components, the number of segments in the copolymer, and the Flory-Huggins interaction parameter, as is the case for the spherical, cylindrical, gyroid, and lamellar phases, which have been observed in the simplest amorphous diblock copolymers.3

In this work, we show that thin films of a metal-containing diblock copolymer namely polystyrene-*block*-poly(ferrocenyldimethylsilane) (PS-*b*-PFS) exhibit a variety of nanostructures including nanorings and cylinders. These nanostructures as well as their orientations are obtained simply by varying the film thickness and annealing conditions without varying the χN. Scanning force and electron microscopes were used to characterize these structures. Use of these nanostructures as nanoscale etch masks (nanotemplates) to develop periodic nanoarrays onto virtually any material, including metals, semiconductors and insulators is outlined.

EXPERIMENTAL

PS-*b*-PFS with an overall molecular weight (Mn) of 90,000 g mol-1 (PS block 60,000 g mol-1) was purchased as a custom synthesis from Polymer Source, Inc. (Dorval, Québec) and used as received. A 1.0 w/w% solution was prepared in toluene to be used in all sample preparations. This solution was spin cast onto Si3N4 and metal-coated Si3N4 substrates. Spin speed and polymer concentration determines the film thickness. Besides film thickness, thermal and solvent annealing were used to induce specific domain morphologies. A Veeco MultiMode V scanning probe microscope via tapping mode was used to image the domain structures.

Transmission and scanning electron microscopes were also employed for structural characterizations. Reactive ion etching (RIE) was used to transfer the patterns onto solid substrates.



RESULTS

As spin cast, without any annealing, films of approximately 40 nm thickness exhibit standing cylinders of PFS in a PS matrix. Increasing the film thickness to 50 nm results in the formation of in-plane cylinders. Ordering of the in-plane cylinders is influenced by the type of annealing i.e. thermal annealing induces fingerprint-like patterns whereas solvent annealing induces rigid in-plane cylinders.4 Increasing the thickness beyond 50 nm results in the formation of an interconnected phase. Hybrid annealing involving first thermal and then solvent annealing results in the formation of macroscale dendrite patterns. AFM imaging on top of the dendrite shows rigid cylinders whereas ring structures are seen at the non-dendrite areas.5

One of the advantages of having these patterns is to use them as an etch mask/template wherein one transfers these patterns onto a given substrate. Unlike many other copolymers, PS-*b*-PFS wets a wide variety of substrates such as metals (Au, Cr, Nb), semiconductors (Si, Si3N4, UNCD), and insulators (glass, mica) in a similar manner. We have successfully transferred some of these nanopatterns onto substrates by utilizing an anisotropic reactive ion etching process. The etching gas/plasma and conditions are chosen such that it preferentially etches the open areas (areas free of polymeric domain) leaving the domain shape of the material unetched. Finally, the polymer mask was removed by solvent and piranha cleaning.

This simplified way of creating nanostructures challenges the conventional lithographic processes in terms of resolution, cost and time.6 Potential applications of these patterns include high capacity magnetic data storage, sensing, nanofluidics, and biomedical devices.

REFERENCES

1. F. S. Bates and G. H. Fredrickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).
2. M. J. Fasolka and A. M. Mayes, Annu. Rev. Mater. Res. **31**, 323 (2001).
3. I. W. Hamley, *The Physics of Block Copolymers* (Oxford University Press, Oxford, 1998).
4. M. Ramanathan, E. Nettleton and Seth B. Darling to be submitted.
5. M. Ramanathan and Seth B. Darling manuscript in preparation.
6. Craig J.Hawker and Thomas P. Russell MRS Bulletin, **30**, *952* (2005).