Application of Thermal Gradients to Achieve Orientational Order in Block Copolymer Thin Films*

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INTRODUCTION

The development of methods that permit control over the long-range order and orientation of microdomains in block copolymer (BCP) thin films for “bottom-up” approaches to nanoscale surface patterning is of great interest for many applications, including microelectronics and data storage devices.[1,2] One such method recently reported,[3] a type of zone refinement called cold zone annealing (CZA) in which the BCP film is passed across a thermal gradient, was shown to result in long-range orientational order. CZA is a versatile technique that can be combined with other approaches, such as chemical or topographic substrate patterning. Here, we utilize a combination of Rotational Small Angle Neutron Scattering (R-SANS) and specular neutron reflectivity (SNR) to investigate the mechanism and driving forces behind CZA. These unique techniques are used to characterize the 3-dimensional structural properties of zone annealed BCP films, revealing the previously unreported role of thermal gradients in controlling the kinetics and orientation of block copolymer films.

EXPERIMENTAL

Poly(styrene-b-methyl methacrylate) (PS-b-PMMA) with a total relative molecular mass of 47.7 kg/mol and a mass fraction of PS of 0.74 was purchased from Polymer Source, Inc.[4] Poly(deutero-styrene-b-methyl methacrylate) (dPS-b-PMMA) with a total relative molecular mass of 77.5 kg/mol and a mass fraction of dPS of 0.74 was synthesized at Oak Ridge National Laboratory. Films of PS-b-PMMA and dPS-b-PMMA were spin-coated from solutions in toluene. Films were baked overnight in a vacuum oven at 60 °C prior to characterization and/or further processing. Zone annealing of films was carried out as previously described.[3]

Height and phase AFM images were obtained on an Asylum MFP-3D scanning force microscope in tapping mode, using silicon cantilevers with a nominal force constant of 48 N/m (NanoWorld AG, Neuchatel, Switzerland).

Rotational SANS (R-SANS) measurements were conducted using the NG7-SANS instrument at the NIST Center for Neutron Research (NCNR) at the National Institute of Standards and Technology, using an incident wavelength of 6.0 Å and a wavelength divergence of 0.11. Samples were mounted on a rotational stage, and SANS measurements were collected at multiple incident angles. Q_x-Q_z scattering images were reconstructed from the raw data as previously described.[5] Neutron reflectivity experiments were conducted using the NG7 horizontal reflectometer at the NCNR, utilizing a 4.76 Å collimated neutron beam with a wavelength divergence of 0.18 Å. The angular divergence of the beam was varied through the reflectivity scan, providing a relative q resolution dq/q of 0.04, where $q = 4\pi \sin(\theta)/\lambda$, and θ is the incident and final angle with respect to the surface of the film.

RESULTS AND DISCUSSION

Figure 1 (left) shows a phase AFM image of a film of dPS-b-PMMA deposited on a topographically patterned silicon substrate consisting of channels 400 nm wide and 200 nm deep and then zone annealed, with the temperature of the hot zone reaching 220 °C. This image reveals the long-range order of the hexagonally-packed cylindrical PMMA domains oriented perpendicular to the substrate surface within the channels. Additionally, a high degree of orientational order is observed for the grains within the channels, with the (100) plane oriented parallel to the channel walls.

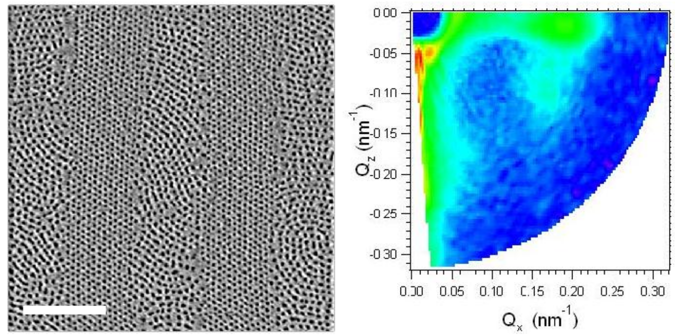

Figure 1. Left: An AFM phase image of a cold zone annealed film of cylinder-forming dPS-b-PMMA on a patterned substrate (see text) reveals hexagonal packing and orientational order of cylindrical domains in the channels. Scale bar = 500 nm. Right: The Q_x-Q_z plot of neutron scattering of the same film obtained by rotational SANS yields information about the 3-dimensional film structure.

While AFM yields structural information only at the surface of the film, Rotational SANS permits characterization of the 3-dimensional film structure. In this technique, multiple transmission SANS measurements are made on a single sample at varying incident angles as the sample is rotated. Figure 1 (right) shows a 2-dimensional slice of the 3-dimensional map of scattered intensity. Plotted is intensity in the Q_x-Q_z plane, a plane oriented normal to the substrate plane. These data indicate that while the majority of cylinders are oriented perpendicular to the substrate, a small sub-population of cylinders oriented parallel to the substrate exists as well. The results of additional experiments investigating the role of thermal gradients in CZA will be discussed.

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4. Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.
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