Notes

Imaging the Substrate/Film Interface of Thin Films of Diblock Copolymers on Chemically Patterned Surfaces

Xiao M. Yang,[†,‡] **Richard D. Peters,**[†] **and Paul F. Nealey***

Department of Chemical Engineering and Center for Nanotechnology, University of Wisconsin, Madison, Wisconsin 53706

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Introduction

Epitaxial techniques using chemically patterned surfaces have been shown to guide the self-assembly of block copolymer films[1−8] and the phase separation of homopolymer blend films.[9−11] A major challenge in using block copolymer films for nanofabrication is controlling the perfection of ordering and orientation of the domains over macroscopic dimensions, i.e., several cm^2. The epitaxial techniques have shown promise for achieving the desired macroscopic ordering as well as registration of the block copolymer domains with the substrate.[1,3,4] These techniques depend on controlled wetting of the different blocks of the copolymer on the different chemical regions of the patterned surface and amplification of the surface pattern through the thickness of the polymer film. An important area of study of polymer films on chemically patterned surfaces is the analysis of defects and the origin of defects in the polymer domain structure, specifically at the substrate/film interface. Scanning probe microscopy,[12−18] including the use of multiple mode force microscopy to distinguish between surface chemistry and topography,[1,3,19] and electron microscopy[17,20−26] are the two principal methods of imaging block copolymer domains with in-plane ordering in thin films. A variety of sample preparation techniques for both cross-sectional and top-down imaging of block copolymer films have been used, including thin sectioning with ultramicrotomy,[7,27,28] focused ion beam milling with lift-out,[29] and depth profiling.[20,21,30] A common disadvantage with each technique mentioned above is the inability to image clearly the interface between the polymer film and the substrate. Knowledge of the behavior of the polymer film at this interface is critical for understanding surface-guided self-assembly of block copolymer films and phase separation of polymer blend films. In this paper, we report a technique for imaging the surfaces of polymer films originally in contact with chemically patterned substrates. The technique was used to verify that different blocks of a copolymer wet adjacent regions of a chemically patterned surface with fidelity, resulting in easily interpreted topography at the free surface of the film associated with the quantization of thickness for symmetric and asymmetric wetting of block copolymer films.

Experimental Section

A 50 nm thick layer of SiO$_2$ was deposited onto Si ⟨100⟩ wafers by plasma-enhanced chemical vapor deposition at 350 °C with a gas flow having a composition of 64.8% N$_2$O (405 sccm) and 35.2% SiH$_4$ (2%, 220 sccm). Self-assembled films of octadecyltrichlorosilane (OTS) were deposited on the SiO$_2$/Si wafers following a previously published procedure.[1,31] Values of $105 \pm 3°$ and $85 \pm 3°$ were measured for the advancing and receding contact angles of deionized water on OTS, respectively. OTS-covered wafers were exposed to X-rays at a dose of 2800 mJ/cm^2 through an X-ray mask in a chamber with a pressure of 1 Torr of air.[32] Thin films of P(S-*b*-MMA) (M_n = 51 200 g/mol, $L_0 \sim 30$ nm) were deposited onto patterned OTS by spin-coating, and an initial thickness of 70 nm ($\sim 2.3L_0$) for the films was determined using ellipsometry. The polymer films were annealed at 180 °C in a vacuum oven for 24 h. P(S-*b*-MMA) films were floated off the substrate by dissolution of the sacrificial SiO$_2$ layer with dilute solutions of hydrofluoric acid (20% v/v). The Si/SiO$_2$/P(S-*b*-MMA) multilayered samples were partially dipped into the HF solution to allow a portion of the P(S-*b*-MMA) film to float on the surface of the HF solution and to allow a portion of the film to remain on the substrate. The floating portion of the film was collected on top of the portion of the film that remained attached to the substrate. The films were imaged by atomic force and lateral force microscopy in contact mode.

Results and Discussion

OTS-covered substrates were patterned with regions of different chemical functionality (arrays of 5 μm diameter circles) by proximity X-ray lithography. The circles correspond to unexposed regions of the patterned OTS; the mask consisted of 5 μm diameter circles of Au as absorber regions on a SiN membrane mask. The X-rays induced chemical modification of the exposed regions of OTS such that the initial methyl-terminated surface was converted to oxygen-containing aldehyde, carboxylic acid, and hydroxyl surface groups.[33] Thin films of P(S-*b*-MMA) were deposited on the chemically patterned substrates and annealed. Figure 1a shows an AFM image of the topography present on the free surface of a P(S-*b*-MMA) film. On the basis of our previous work, we interpreted the formation of topography as follows: P(S-*b*-MMA) exhibits symmetric wetting on unexposed OTS with the PS block preferentially wetting the substrate and asymmetric wetting on exposed OTS with the PMMA block preferentially wetting the substrate (the PS block is always present at the free surface).[31,34] On chemically patterned surfaces, a difference in film thickness of $^1/_2L_0$ is observed over adjacent unexposed and exposed regions of the OTS due to the quantization of film thickness of nL_0 and $(n + {}^1/_2)L_0$ for symmetric and asymmetric wetting of the block copolymer, respectively.[1] Figure 1b, a cross-

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[†] These authors contributed equally to this report.

[‡] Current address: Seagate Research Center, River Park Commons, Suite 550, 2403 Sidney St., Pittsburgh, PA 15203-2116.

* Corresponding author: e-mail nealey@engr.wisc.edu.

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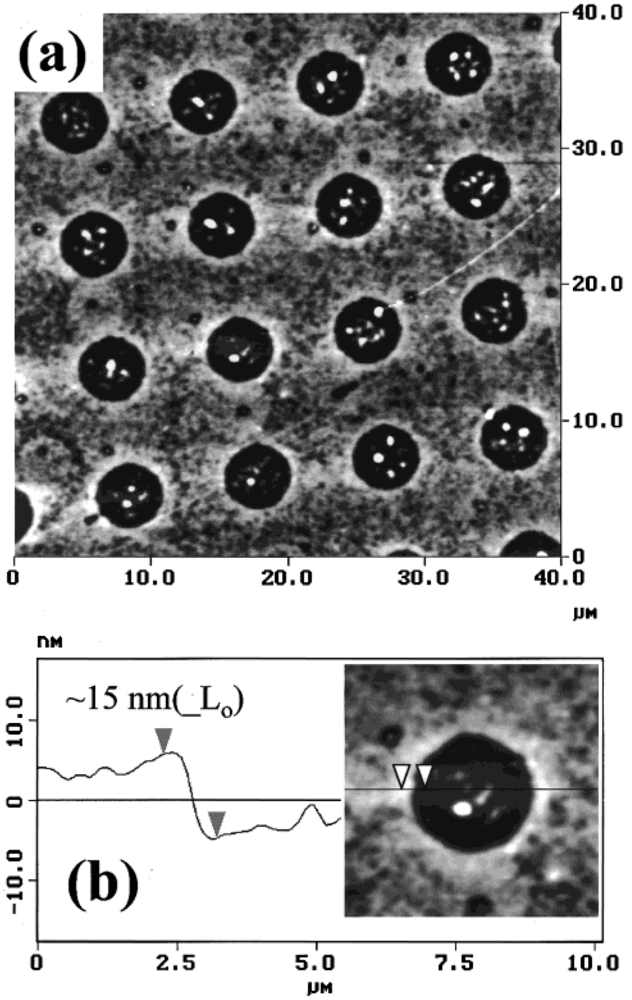

Figure 1. (a) AFM image of the surface of patterned P(S-*b*-MMA) film. The initial film thickness was $\sim 2.3L_0$ (70 ± 2 nm). The topography of the P(S-*b*-MMA) film on patterned regions replicated the underlying pattern of the OTS due to different wetting behavior on adjacent regions. Depressions occur over unexposed regions of the SA film. (b) AFM image of an individual circle with cross section, showing a depth of ~15 nm ($^1/_2L_0$).

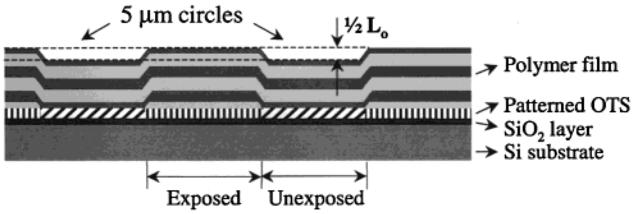

Figure 2. Schematic of lamellar structure in P(S-*b*-MMA) film on the chemically patterned surface. The darker shaded regions correspond to PS, and the lighter shaded regions correspond to PMMA. The PS block preferentially wets unexposed regions of OTS, and the PMMA block preferentially wets exposed regions of OTS. The alternating wetting behavior on adjacent exposed and unexposed regions of the SA film results in thickness differences of $^1/_2L_0$ on the surface of the film, where the thickness undulations follow the underlying surface pattern.

sectional AFM profile of one circle, confirms the difference in thickness between exposed and unexposed regions was 15 nm ($^1/_2L_0$). The bright spots in the center of the circles in Figure 1a are islands with a step height of 30 nm = L_0. If the dimensions of the patterned regions are of order 1 μm or greater, island or hole topography

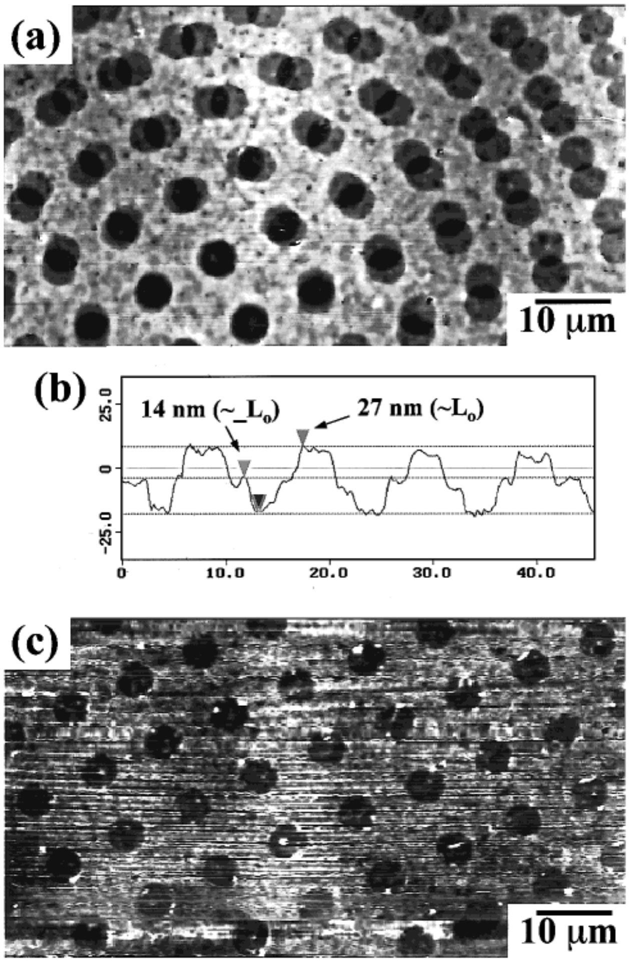

Figure 3. (a) AFM image of P(S-*b*-MMA) film after floating off substrate and collecting on top of itself. The AFM image shows relief structures associated with circles from the underlying film and from the floated film. (b) Cross-sectional profile of AFM image showing $^1/_2L_0$ and L_0 step heights for partially overlapping circles. (c) LFM image of P(S-*b*-MMA) film collected simultaneously as the AFM image in (a). Both (a) and (c) are images of the surface of the film that was in contact with the patterned OTS interface during annealing. The LFM image shows contrast due to the different blocks of P(S-*b*-MMA) wetting exposed and unexposed regions. The dark circles correspond to the PS block that wets unexposed regions of OTS, and the light background corresponds to the PMMA block that wets exposed regions of OTS.

may be observed within each region.[35] Islands formed because the initial film thickness was 70 nm ($\sim 2.3L_0$). Figure 2 shows a schematic of the probable lamellar structure of the P(S-*b*-MMA) film, ignoring the presence of islands or holes. This schematic shows the parallel orientation of the lamellae in the polymer film. The PS block preferentially wets unexposed regions of OTS and the free interface, and the PMMA block preferentially wets exposed regions of OTS. Dislocations in the lamellar structure at the substrate/film interface at the pattern boundaries result in thickness differences of $^1/_2L_0$ between regions of the polymer films over adjacent unexposed and exposed areas of OTS.

Figure 3a shows an AFM image of a P(S-*b*-MMA) film that was (1) deposited and annealed on a chemically patterned substrate, (2) partially floated on a dilute solution of hydrofluoric acid, and (3) folded back on the portion of the film still attached to the substrate. A moiré pattern formed due to overlapping circles from the underlying, attached portion of the film and the

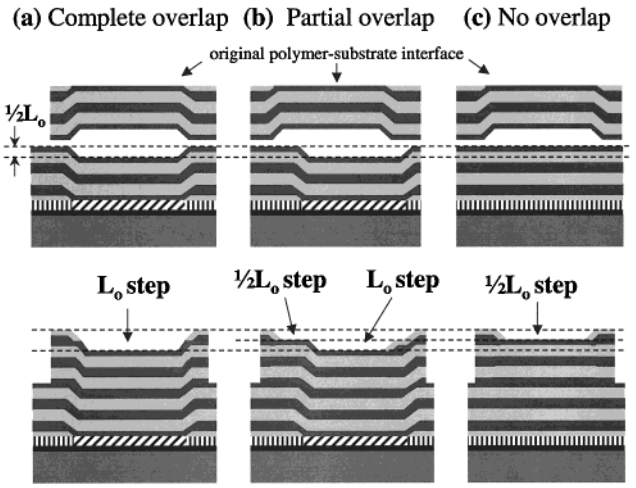

Figure 4. Schematic of film structures obtained after floating and collecting patterned P(S-*b*-MMA) film. The darker shaded regions correspond to PS, and the lighter shaded regions correspond to PMMA. Three regions were observed: (a) completely overlapping regions, (b) partially overlapping regions, and (c) no overlapping regions. The top schematics are before conformal wetting, and the bottom schematics are after conformal wetting. The floated film conformally wets the underlying film such that the depressions in the underlying film are transferred through the floated film.

floated portion of the film. Figure 3b shows a cross-sectional profile of the film shown in Figure 3a. Figure 3c shows an LFM image collected simultaneously as the AFM image shown in Figure 3a. The AFM and LFM images in Figure 3 are images of the surface of the film that was in contact with the chemically patterned OTS interface during annealing. The contrast in the LFM image is due to differences in chemical composition. The dark circles correspond to the PS block that preferentially wets the unexposed regions of OTS. The surrounding lighter regions correspond to the PMMA block that preferentially wets exposed OTS.[1] The observed contrast in the LFM image confirms the preferential wetting of the different blocks of the copolymer on adjacent unexposed and exposed regions of the SA film of OTS. This image verifies a high fidelity of pattern transfer from the substrate to the first layer of the polymer film.

The presence of overlapping circles in the AFM image shown in Figure 3a is due to conformal wetting of the floated portion of the film on the underlying, attached portion of the film. This conformal wetting is expected since the thickness of the polymer film is very thin compared to 5 μm diameter of the circles. From the cross-sectional profile, there are two depths for the overlapping circles, 14 nm ($\sim{}^1/_2L_0$) and 27 nm ($\sim L_0$). Figure 4 contains a schematic showing the structure of the floated and collected assembly for complete overlapping (a), partial overlapping (b), and no overlapping (c) circular regions of the floated and collected film. (The possibility of the presence of islands within the circular regions is ignored.) For complete overlapping of a circle in the floated portion of the film with a circle in the underlying film, the floated film conforms to the surface undulations of the underlying film and results in a circle with a depth of $\sim L_0$. For partial overlapping, the center region where the circles have overlapped has a depth of $\sim L_0$, and the regions where the two circles do not overlap have depths of $\sim{}^1/_2L_0$. For the case of no overlapping of either a circle in the floated portion of the film (shown in Figure 4c) or a circle in the underlying portion of the film (not shown in schematic), a circle with a depth of $\sim{}^1/_2L_0$ results. In each case of complete, partial, or no overlapping, the alternating PS and PMMA blocks that wet the alternating unexposed and exposed regions of the patterned OTS are still present and detectable in the LFM image at the free surface of the floated and collected assembly.

We have presented a technique to image the substrate/film interface of a polymer film annealed on a chemically patterned surface. This float-and-collect technique allows one to investigate the in-plane ordering in two dimensions of structures in the film specifically at the substrate/film interface and is complementary to other techniques such as cross-sectional TEM and depth profiling. The findings presented in this paper support our previous results where we used the formation of topography, the initial film thickness, and the value of L_0 to infer the wetting behavior of block copolymer films on chemically patterned substrates.[1,2,32] This technique will be most useful for studying epitaxial techniques for guiding the self-assembly of block copolymer films or polymer blend films on chemically patterned surfaces, specifically for analyzing defect formation to determine fidelity of pattern transfer for pattern dimensions less than 100 nm. Both LFM and phase imaging with tapping mode AFM can be used to image the block copolymer domains. Phase imaging generally results in better contrast than LFM, and the resolution of LFM may be limited below 100 nm.[32] To improve contrast and resolution, it may be necessary to insert a secondary hard surface between the floated portion of the film and the underlying, connected portion to eliminate any interactions between the two portions of the film.

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