Photopatternable Interfaces for Block Copolymer Lithography

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S *Supporting Information*

ABSTRACT: Directly photopatternable interfaces are introduced that facilitate two-dimensional spatial control of block copolymer (BCP) orientation in thin films. Copolymers containing an acid labile monomer were synthesized, formulated with a photoacid generator (PAG), and coated to create grafted surface treatments (GSTs). These as-cast GST films are either inherently neutral or preferential (but not both) to lamella-forming poly(styrene-*block*-trimethylsilylstyrene) (PS-*b*-PTMSS). Subsequent contact printing and baking produced GSTs with submicron chemically patterned gratings. The catalytic reaction of the photoacid generated in the UV-exposed regions of the GSTs changed the interfacial interactions between the BCP and the GST in one of two ways: from neutral to preferential ("N2P") *or* preferential to neutral ("P2N"). When PS-*b*-PTMSS was thermally annealed between a chemically patterned GST and a top coat, alternating regions of perpendicular and parallel BCP lamellae were formed.
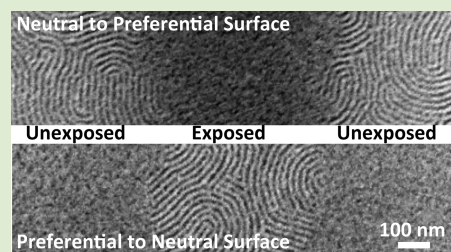
Block copolymers (BCPs) can self-assemble into periodic patterns on the nanometer length scale and have attracted significant interest for diverse applications including ultra-filtration[1] and electrolyte membranes,[2] photonic crystals,[3] and next-generation lithography.[4] Most thin-film applications utilize lamella or cylindrical morphologies and necessitate a perpendicular orientation of the BCP domains relative to the substrate. Domain orientation in BCP thin films is determined primarily by the nature of the interfacial interactions at both the bottom and top interfaces. Preferential interactions between one block and either interface produce parallel BCP domains in the vicinity of that interface, which often propagate through the entire thickness of the film. In contrast, nonpreferential ("neutral") interfacial interactions facilitate the perpendicular orientation of BCP domains.[5] Over the past ca. 20 years, many research groups have established versatile methodologies for producing neutral interfaces. The most successful strategies involve fine-tuning interfacial interactions by careful control of interfacial composition, usually utilizing random copolymers synthesized with an appropriate choice of constituent monomers. Both the substrate[6−8] and top interfaces[9,10] are amenable to functionalization with such copolymers, and composition optimization techniques for both interfaces have now been established.[11−13]

Control of the two-dimensional spatial arrangement of domains in which there are distinct regions of perpendicular and parallel lamellae in a single thin film layer is a critical patterning requirement for many lithographic applications, including production of field effect transistors (FETs),[14] bit-patterned media for hard disk drives,[15] and surface plasmonic waveguides.[16] For example, line-space patterns generated by perpendicular lamellae are important for producing key FinFET features, but individual layers in these devices and other circuit-relevant patterns contain many other pattern motifs, including large featureless regions.[14,17] A methodology that would enable defining both servo information areas and areas of bit-patterned magnetic media in a single lithographic layer through control of the orientation of BCP lamellae would be very valuable for hard disk drive manufacturers.[18−20]

Previous reports have detailed processes designed to produce parallel and perpendicular lamellae in a single BCP layer. These include disordered block copolymers that order in response to light[21,22] and some multistep substrate surface processing protocols, including selective cross-linking,[7,23] electrohydrodynamic jet printing,[24] and reactive ion etching.[25−27] The authors are aware of only three papers detailing directly patternable orientation layers: one is based on inherently electron-beam sensitive materials,[28] a process that lacks scalability due to notoriously slow e-beam patterning rates, and a second is based on self-assembled monolayers,[29] which undergo ill-defined changes in surface chemistry upon exposure to X-rays. A third photopatternable polymer system captures some of the principles embodied in the system reported herein but does not definitively establish (non)preferential interfacial interactions or demonstrate two-dimensional orientation control in a single layer.[30] A material and process that precisely tunes BCP interactions using traditional lithographic practices (e.g., a high throughput and economical process based on optical exposure sources) would therefore be a valuable addition to lithography by directed self-assembly (DSA).[31]

Scheme 1. Acid-Catalyzed Deprotection of the Materials Used as GSTs and TCs
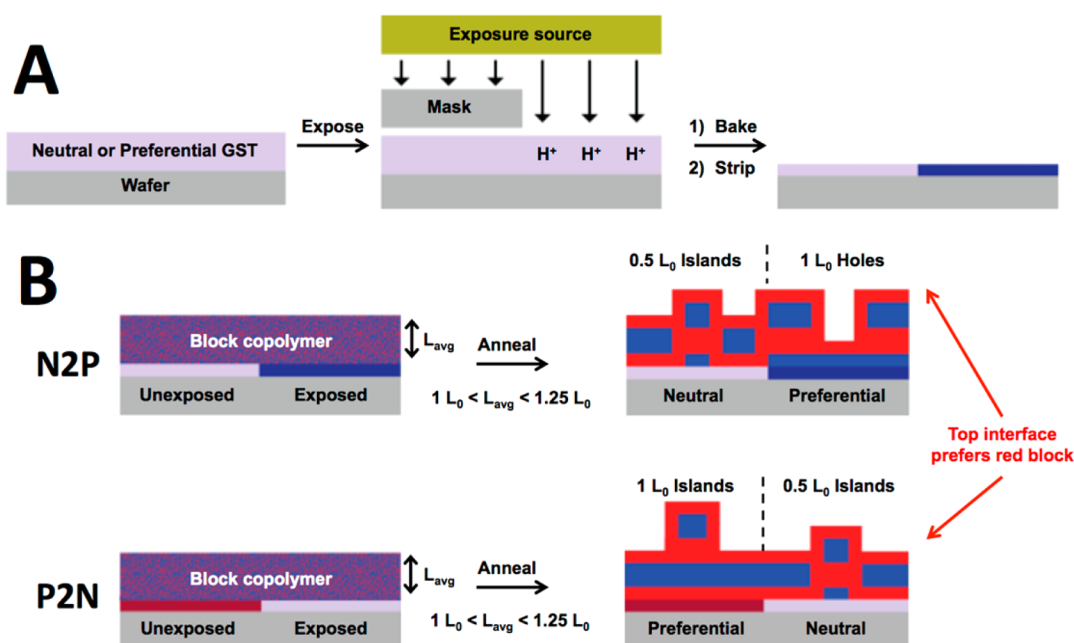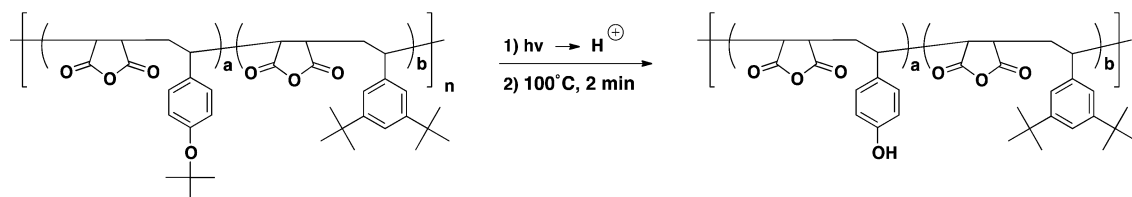

Figure 1. (A) Illustration of the GST patterning process. (B) Illustration of BCP thickness quantization in response to N2P and P2N patterned GSTs. The light purple color is used to represent a neutral interface. A dark red and dark blue surface indicates PTMSS preferential and PS preferential, respectively. The free surface is always PTMSS (red block) preferential.

In this work, photopatternable interfaces are introduced that satisfy the criteria described above. These materials change surface chemistry upon exposure to light in either one of two ways: (1) an inherently neutral surface can be rendered preferential by exposure (herein denoted "N2P") or (2) a preferential surface can be made neutral by exposure ("P2N"). These photopatternable orientation layers follow a previously reported design[11] and are terpolymers composed of maleic anhydride, 4-*tert*-butoxystyrene, and 3,5-di-*tert*-butylstyrene formulated with a photoacid generator (PAG). Maleic anhydride forms alternating copolymers with styrenic derivatives,[32] and the relative ratio of the two styrene derivatives in the terpolymers determines the nature of the interfacial interactions with a BCP.[11] Incorporation of PAG allows for direct photopatterning of these materials because exposure generates a latent image, and subsequent heating induces the acid-catalyzed thermolysis of 4-*tert*-butoxystyrene to generate isobutylene and a more polar phenol (Scheme 1).[33] Covalent bonding of the terpolymer to the substrate surface (grafting) can be accomplished by nucleophilic acyl substitution reactions between the maleic anhydride and amine-functionalized surfaces,[34] which enables these photopatternable materials to function as grafted surface treatments (herein designated "GSTs"). The same terpolymers can be employed as top coats (TCs) by leveraging the polarity-switching, ring-opening and -closing reactions of maleic anhydride,[9] or they can be employed as both GSTs and TCs simultaneously. In this work,

as-synthesized neutral (GST-N) and preferential (GST-P) GSTs are reported that enable N2P and P2N processes, respectively. Two-dimensional control over the spatial orientation of BCP domains is demonstrated using lamella-forming poly(styrene-*block*-trimethylsilylstyrene) (PS-*b*-PTMSS) with a periodicity (L_0) of 22 nm.

This report is split into two parts. First, the wetting behavior of PS-*b*-PTMSS in both the exposed and unexposed regions was established for both the N2P and P2N processes. These experiments leveraged the unique tendency of parallel lamellae to spontaneously form surface topography[35−37] ($1L_0$ and/or $0.5L_0$ "islands" and/or "holes"), which can be interpreted to report the preferential (or nonpreferential) interactions of BCP blocks with an interface. These analyses rely on a single block preferentially wetting one interface.[29,38−40] For instance, Si-containing blocks generally segregate to the free surface.[41] The experimental methodology and associated interfacial wetting implications have recently been described in detail.[11,40]

The second part of this report demonstrates two-dimensional orientation control with both N2P and P2N processes by confining PS-*b*-PTMSS between a patterned GST and an appropriate TC. Figure 1 illustrates the N2P and P2N patterning processes with the GSTs. A solution of a GST (either neutral or preferential, Tables S1 and S2 and Figures S1−S6, Supporting Information) containing PAG was deposited onto an amine-functionalized wafer. The film was then annealed to chemically graft the GST to the surface.
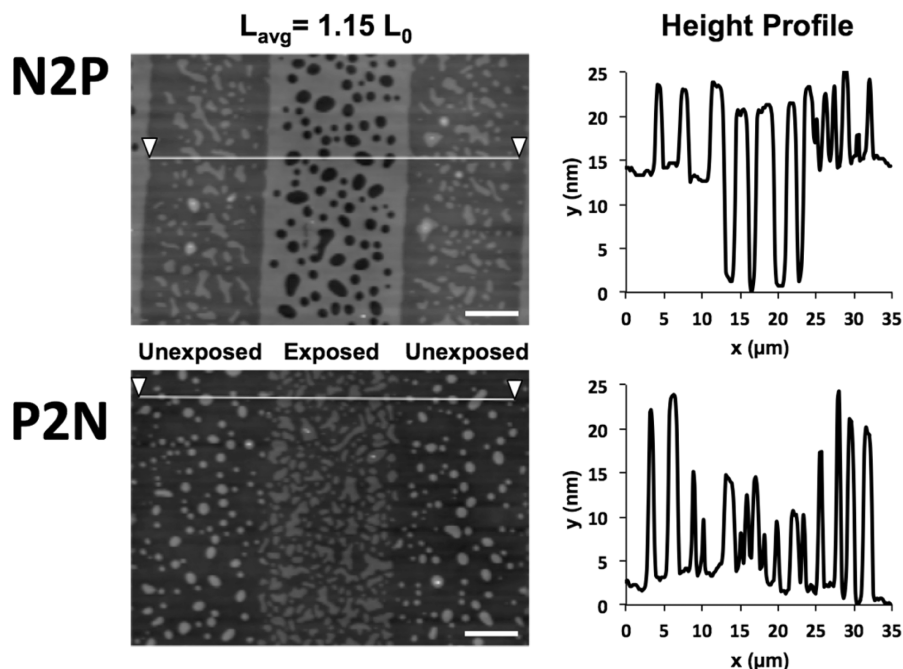
Figure 2. N2P and P2N processes: Atomic force micrograph height (left) and height profile (right) of PS-*b*-PTMSS (L_0 = 22 nm, L_{avg} = 1.15 L_0) annealed at 180 °C for 10 min on chemically patterned GST. Scale bars are 5 μm.
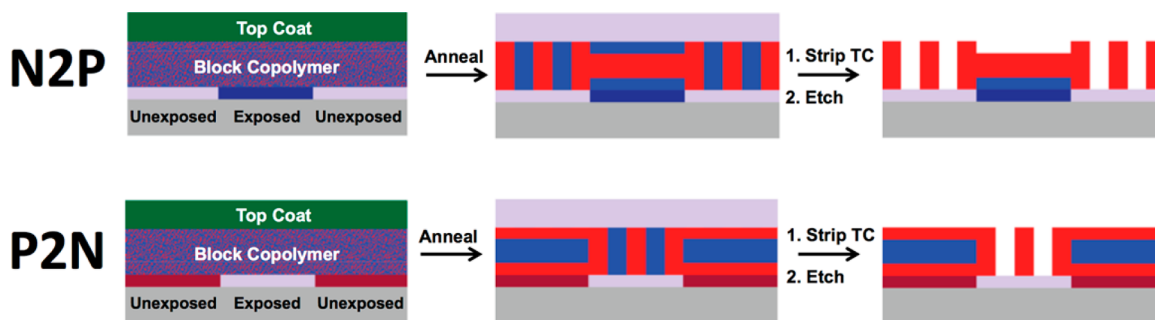
Figure 3. Illustration of two-dimensional spatial control of block copolymer orientation using the N2P and P2N processes. Top: a chemically patterned GST-N with neutral unexposed regions and PS-preferential exposed regions. Bottom: chemically patterned GST-P with PTMSS-preferential unexposed regions and neutral exposed regions. In both processes, the BCP is annealed under a near-neutral TC.

Exposure with UV light through a mask generated acid in the exposed regions of the film, and subsequent heating induced acid-catalyzed thermolysis of the *tert*-butyl ether (Scheme 1 and Figures S7 and S8, Supporting Information). In the N2P process, the GST-N became preferential in the area that was exposed; in the P2N process, the GST-P became neutral in the exposed regions, vide infra. The ungrafted GST was then stripped with solvent to leave a chemically patterned surface with an average thickness of ca. 3 nm (N2P) or 4 nm (P2N) and no significant topography between the exposed and unexposed regions (Figure S9, Supporting Information). After patterning and rinsing the GST, the BCP was deposited with a thickness (L_{avg}) between $1.0L_0$ and $1.25L_0$ and thermally annealed. Since L_{avg} was incommensurate to both symmetric and asymmetric wetting [$L_{avg} \neq nL_0$ and $L_{avg} \neq (n + 0.5)L_0$], thickness quantization generated topography on the surface of the film, which was inspected by optical microscopy and atomic force microscopy (AFM).[35,36]

Under these experimental conditions, three possible topographies are expected after annealing: $1L_0$ islands, which imply preferential PTMSS (symmetric) wetting, $1L_0$ holes, which

reports preferential PS (asymmetric) wetting, and $0.5L_0$ islands, which indicate a neutral surface.[40] Thus, for the N2P process, $0.5L_0$ islands (neutral) should occur in the *unexposed* regions of the film and $1L_0$ holes (PS wetting) in the *exposed* region (qualitatively, since PS has a higher surface energy than PTMSS and the GST becomes more polar after deprotection, the GST should preferentially wet the more polar PS block). For the P2N process, $1L_0$ islands (PTMSS wetting) are expected in the *unexposed* region and $0.5L_0$ islands (neutral) in the *exposed* region of the film.

Figure 2 shows the BCP thickness quantization results for both the N2P and P2N processes that are outlined in Figure 1. AFM evaluation of BCP films annealed on patterned GST-N (containing 50% 4-*tert*-butoxystyrene) confirmed that the unexposed regions exhibit $0.5L_0$ islands, while exposed regions produced $1L_0$ holes. GST-N is neutral in the unexposed regions, but PS is preferential in the exposed regions and thus exhibits N2P behavior. In contrast, GST-P (containing 24% 4-*tert*-butoxystyrene and 26% 3,5-di-*tert*-butylstyrene) forms $1L_0$ islands (PTMSS preferential) in the unexposed regions and $0.5L_0$ islands (neutral) in the exposed regions. Thus, GST-P

enables P2N patterning. Optical micrographs and exposure control experiments can be found in the Supporting Information (Figures S10−S13) and are fully consistent with these conclusions.

Coupling the photopatternable GST substrate surfaces with a proper top coat provides the ability to produce areas of arbitrary shape which contain perpendicular lamellae, while the lamellae in the rest of the film are oriented parallel to the substrate. Figure 3 illustrates the strategy used to produce alternating regions of perpendicular and parallel lamellae by both N2P and P2N patterning processes. The N2P process produced perpendicular lamellae only in the unexposed region. In contrast, the P2N process produced perpendicular lamellae in the exposed regions. Figure 4 shows scanning electron
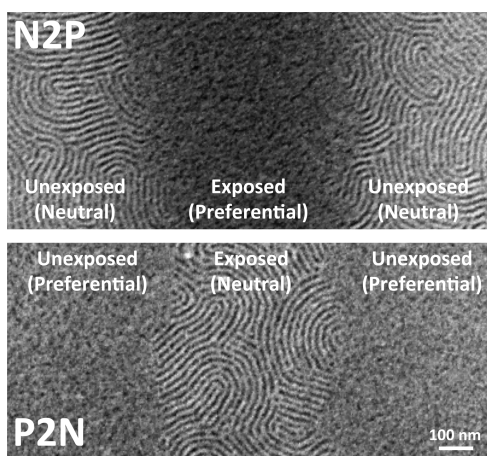
Figure 4. Scanning electron micrographs of PS-*b*-PTMSS (L_0 = 22 nm, L_{avg} = $3L_0$) annealed at 180 °C for 10 min confined between the top coat TC-24 and chemically patterned GST-N (top) or GST-P (bottom). The top coat was stripped, and the samples were etched with O_2 plasma.

micrographs of PS-*b*-PTMSS annealed between patterned GST-N or GST-P and a near-neutral top coat. The films were patterned with a contact photomask to yield submicron line-space patterns. PS-*b*-PTMSS with a thickness of $3L_0$ was deposited and annealed under a near-neutral top coat (containing 24% 4-*tert*-butoxystyrene). The near-neutral TC was slightly PTMSS preferential (Figures S14 and S15, Supporting Information) and was chosen to promote the formation of parallel lamellae in regions of the film overlaying preferential GST. A perfectly neutral top coat did not completely orient lamellae parallel at the top interface in as-designed preferential regions, as a consequence of its nonpreferential BCP interactions. Unexposed regions (for N2P with GST-N) and exposed regions (for P2N with GST-P) produced perpendicular lamellae since the BCP was confined by one neutral and one near-neutral interface. These perpendicular features are independent of film thickness (Figure S16, Supporting Information), and a vast majority appear to span the entire film thickness, even at $3L_0$, when confined between exposed GST-P (neutral) and a near-neutral top coat (Figure S17, Supporting Information). In contrast, the exposed regions (for N2P with GST-N) and unexposed regions (for P2N with GST-P) are featureless, suggestive of parallel BCP domains that form in the presence of a strongly preferential interface. The boundaries between the exposed and unexposed regions are ill defined along the interface, which

is most likely an artifact of the crude, low-resolution contact printing methodology used to generate the patterns. The line-edge roughness is anticipated to decrease with the use of higher-resolution exposure tools.

The spatial control of block copolymer thin film orientation was demonstrated with lamella-forming PS-*b*-PTMSS. Photo-patternable interfacial materials were employed as grafted substrate surface treatments. The methodology is amenable to producing either preferential or neutral regions upon exposure with no topographical distinction between exposed and unexposed regions. These materials should be compatible with the existing industrial lithographic infrastructure and could find use in next-generation processes that demand suboptical lithography resolution. Experiments exploiting these materials in combination with well-established approaches to directed self-assembly[42] are ongoing and will be the subject of future reports.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Instrumentation, reagents, GST and TC synthesis, GST characterization, TC TMA salt formation, wafer preparation, IR sample preparation, N2P and P2N patterning processes, confined island and hole tests, SEM sample preparation, Tables S1−S2, and Figures S1−S17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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