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Ordering of lamellar block copolymers on oxidized silane coatings

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ABSTRACT

Thin films of lamellar poly(styrene-b-methyl methacrylate) (PS–PMMA) block copolymers are widely investigated for surface patterning. These materials can generate dense arrays of nanoscale lines when the lamellar domains are oriented perpendicular to the substrate. To stabilize this preferred domain orientation, we tuned the substrate surface energy using oxidation of hydrophobic silane coatings. This simple approach is effective for a broad range of PS–PMMA film thicknesses when the oxidation time is optimized, which demonstrates that the substrate coating is energetically neutral with respect to PS and PMMA segments. The lamellar films are characterized by high densities of defects that exhibit a strong dependence on film thickness: in-plane topological defects disrupt the lateral order in ultrathin films, while lamellar domains in thick films can bend and tilt to large misorientation angles. The types and densities of these defects are similar to those observed with other classes of neutral substrate coatings, such as random copolymer brushes, which demonstrates that oxidized silanes can be used to control PS–PMMA self assembly in thin films.

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1. Introduction

Block copolymers can spontaneously self-assemble into dense arrays of nanoscale domains. In a thin film, these systems have been used for patterning nanowire arrays [1], nanoscale sensors [2], and nanoscale devices for integrated circuits [3,4]. Most examples of block copolymer patterning use vertically-oriented lamellar or cylindrical domains to produce nanoline or nanodot templates, respectively. The most common block copolymer chemistry for patterning is the diblock copolymer poly (styrene-b-methyl methacrylate) (PS–PMMA) [3,5]. The advantages of this system include commercial availability, easy pattern development, and simple methods to create "neutral" interfaces that do not preferentially attract the PS or PMMA segments. Neutral interfaces are critical for stabilizing a vertical domain orientation over a broad range of film thickness [6,7].

Neutral substrate coatings are usually required for PS–PMMA patterning. The most popular coating materials are based on random copolymers of styrene and methyl methacrylate [5,8–15]. In these systems, the optimal proportion of styrene to methyl methacrylate is determined by the composition of the block copolymer [5,7–10], as well as the coating thickness and density [12–15]. While there are a few types of commercially-available random copolymer coating materials, most are

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synthesized in a university laboratory to target a specific composition and molecular weight. Furthermore, parameters like coating thickness and density are partially controlled by the deposition process and can be difficult to accurately characterize. Therefore, an easy process that tunes substrate properties with commercial materials and simple instrumentation could be very valuable for block copolymer patterning.

In this manuscript, we report a simple approach to generate neutral interfaces for PS–PMMA lamellae. We employ high temperature processing to suppress the formation of PS wetting layers at the free surface [7,13], and we create neutral substrates through oxidation of hydrophobic organo-silane coatings. Organo-silanes are commercially-available small molecule hydrocarbons that spontaneously assemble on the native oxide of a clean silicon wafer [16]. There are several literature studies that used silanes to engineer surface interactions for block copolymer self-assembly. As examples, silane mixtures that mimic the chemistry of each segment can produce a neutral or preferential boundary [17–19], and patterned silane coatings can serve as epitaxial templates for directed self-assembly [20]. The use of silane *oxidation* to generate neutral coatings is less studied. One work demonstrated the potential of this approach using ultrathin films of PS–PMMA cylindrical and lamellar phases on oxidized hydrophobic silanes [21]. Herein, we demonstrate that vertical lamellar domains can be stabilized across a broad range of film thicknesses when the oxidation time is optimized, but mixed domain orientations are observed at certain film thicknesses if the oxidation time is too short or too long. Furthermore, using microscopy and X-ray scattering, we demonstrate that lamellar defect structures on oxidized silane coatings are similar to those encountered with the more common neutral polymer coatings. Therefore, we conclude that oxidized silanes can replace other neutral coatings for PS–PMMA patterning.

2. Experimental procedures

2.1. Materials

The diblock copolymer used for these studies is a lamellar poly(styrene-b-methyl methacrylate) (PS–PMMA) with 53 vol% PS, $M_n = 98$ kg/mol, and $Đ = 1.12$. This material was purchased from Polymer Source and independently characterized at the University of Houston with nuclear magnetic resonance spectroscopy and gel permeation chromatography. The equilibrium lamellar periodicity (L_0) for this PS–PMMA copolymer is 46 nm (measured with grazing-incidence small angle X-ray scattering). The segregation strength for this polymer is $\chi N \simeq 45$ and approximately independent of temperature [22]. Substrates were 3-in. diameter, p-type (100)-oriented silicon wafers with standard resistivity and thickness. Self-assembled monolayers were prepared with octyldimethylchlorosilane (ODS), which has a very low vapor pressure of 6.7 kPa at room temperature. ODS was purchased from Gelest.

2.2. Substrate functionalization

Silicon substrates were cleaned with a UVOCS ultraviolet/ozone system (wavelengths of 185–254 nm, and intensity of 2.5 mW/cm^2) for 20 min to destroy organic contamination and grow a thin oxide layer. ODS was vapor deposited on the oxidized silicon using low vacuum and ambient temperature. The deposition time ranged from 48–60 h. This excessive deposition time generates a thick coating of ODS on the wafer, meaning there is a film on top of the surface-attached monolayer, and the extra material is removed through the following stages: First, the samples were gently sonicated in a 50:50 (vol/vol) mixture of water and chloroform for 5 min. Second, the wafers were gently sonicated in toluene for 2 min. Third, the wafers were gently sonicated in isopropyl alcohol for 1 min. Finally, the wafers were gently sonicated in deionized water for 1 min, and then dried under a nitrogen stream. The thickness of the ODS coating was measured with a J.A. Woollam spectroscopic ellipsometer. Each data set consists of the parameters Ψ and Δ that describe the change in polarization state of light. These data were modeled with a predetermined refractive index for native oxide and bulk silicon, and the refractive index of the silane was modeled with the Sellmeier relation $n(\lambda) = a + b\lambda^2/(\lambda^2 - c^2) - d\lambda^2$, where λ is the wavelength of incident light. The oxide thickness was constrained to 1 nm, and the Sellmeier constants and ODS film thickness were adjustable parameters for regression analysis. Typical values of the Sellmeier constants are $a = 2.35$, $b = 0.29$, $c = 0.35$ μm, and $d = 0.06$ μm^{-2}. The ODS thickness determined with this approach was approximately 1 nm for all samples, which is consistent with a self-assembled monolayer. The substrate surface energy was tuned by oxidizing ODS in the UVOCS system for up to 60 s.

2.3. Surface energy

The surface energies of functionalized wafers (ODS and oxidized ODS) were calculated from equilibrium contact angle measurements based on Wu's harmonic method [23,24]. Two liquids were used, diiodomethane (non-polar) and deionized water (polar), and equilibrium contact angles were recorded from at least three points on the substrate using a DataPhysics OCA 15EC goniometer.

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