

Fabrication of nanostructures with long-range order using block copolymer lithography

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(Received 8 April 2002; accepted 13 September 2002)

Block copolymer lithography makes use of the self-assembling properties of block copolymers to pattern nanoscale features over large areas. Although the resulting patterns have good short-range order, the lack of long-range order limits their utility in some applications. This work presents a lithographically assisted self-assembly method that allows ordered arrays of nanostructures to be formed by spin casting a block copolymer over surfaces patterned with shallow grooves. The ordered block copolymer domain patterns are then transferred into an underlying silica film using a single etching step to create a well-ordered hierarchical structure consisting of arrays of silica pillars with 20 nm feature sizes and aspect ratios greater than 3. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519356]

Fabrication of large-area periodic nanoscale structures using self-organizing systems is of great interest because of the simplicity and low cost of the process.¹ The typical sub-100 nm length scales of self-assembled block copolymers make these materials attractive for potential applications in electronic, optoelectronic, and magnetic devices. Block copolymers which microphase-separate into a monolayer of densely packed, periodic, cylindrical or spherical structures on a surface can be used for patterning or templating various thin film materials. Recently, many high density nanostructures, such as posts or holes in silicon, germanium, silicon oxide, diamond, GaAs, and cobalt, have been made by etching, electroplating, or chemical reactions using block copolymer lithographic templates.¹⁻⁸ In these nanostructures, the feature size and feature spacing are primarily controlled by the molar mass and chemistry of the block copolymer which is well defined by the polymer synthesis route. However, these nanostructures lack long-range order because the typical "grain size" over which the block copolymer features are ordered is in the submicron range. Many practical applications such as patterned magnetic recording media⁹ require nanostructures with long-range positional order. There is, therefore, an interest in developing fabrication methods for long-range ordered nanostructures from these self-assembled systems.

An artificial topographic pattern on the substrate can be used to orient the growth of a thin film in a process known as graphoepitaxy.¹⁰ This has been used to orient crystals grown from solution or vapor^{10,11} or to induce alignment in liquid crystals.¹² Recently, similar schemes have been used for ori-

enting block copolymer systems. Long-range alignment of cylindrical domains in polystyrene (PS)-*block*-polyisoprene thin films has been observed following directional solidification of a polymer solution on a patterned substrate.¹³ Patterned substrates were also employed to improve the in-plane order of polystyrene-*block*-poly(2-vinylpyridine) (PS/PVP) thin films by floating precast, 1-monolayer-thick polymer films onto patterned substrates, followed by annealing.¹⁴ The PS/PVP block copolymer formed single grains with very low defect levels over lengths of up to 5 μm adjacent to substrate steps.

Combining block copolymer self-assembly with long-range ordering methods would allow nanostructures to be lithographically fabricated in precise positions on a substrate. In this letter, we present a graphoepitaxy method for orienting self-assembled block copolymers using substrates patterned by interference lithography over areas of several cm^2 . We transfer the resulting patterns into an underlying layer of silica to form an ordered array of high-aspect-ratio silica posts with a hierarchical structure. This method can be generalized to the patterning of a wide range of materials using processes discussed earlier.⁸

The key to the lithographic process is the use of a block copolymer with good chemical selectivity between its two constituents, so that one may be removed and the other remain to act as an etch mask to pattern an underlying film. We employed a polystyrene (PS)-*block*-polyferrocenyldimethylsilane (PFS) diblock copolymer,¹⁵⁻¹⁷ in which the organometallic PFS component is resistant to an oxygen plasma that removes the PS.^{8,18} In the following experiments the polymer had a molecular weight of 30 kg/mol for PS and 12 kg/mol for PFS, denoted PS/PFS 30/12, so that the volume fraction of PFS is approximately 20% and the equilibrium morphology consists of PFS spheres within a PS

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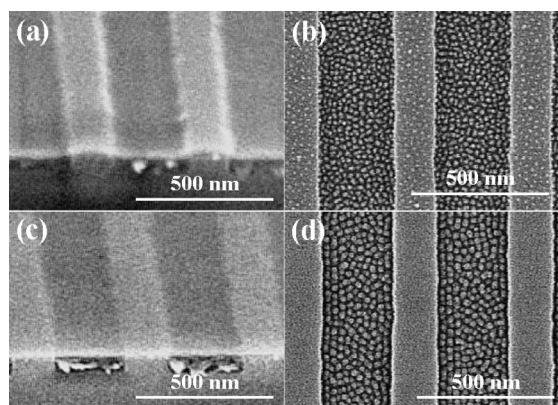


FIG. 1. Scanning electron micrographs of PS/PFS 50/12 polymer films on patterned substrates. (a) As-spun film, showing conformal coverage; (b) the same film after oxygen plasma etching, showing PFS features on the mesas and valleys of the topography; (c) film spun then annealed at 140 °C for 4 h, showing a smooth surface as the polymer flows into the valleys; (d) the same film after oxygen etching, showing PFS features present only in the valleys and partially aligned with the steps.

matrix. When a 1.5% toluene solution of the copolymer is spun onto a flat substrate and annealed at 140 °C, it forms a monolayer of close-packed PFS spheres in a PS matrix on a thin brush layer at the substrate surface where the PFS layer preferentially wets the silica surface. On a smooth substrate, the average sphere diameter is 20 nm, the average center-to-center distance between the spheres is 29 nm and the average grain size is around 280 nm.

The topographical relief structures for graphoepitaxy were made by interference lithography.^{19,20} The substrates were 10-cm-diam silicon wafers which were thermally oxidized to form a 150-nm-thick surface layer of silica. A trilayer resist stack consisting of a 200-nm-thick anti-reflection coating layer (ARC, AZ BARLi), a 30-nm-thick evaporated silica interlayer then a 200-nm-thick photoresist layer (PFI-88 from Sumitomo) was deposited sequentially over the oxidized wafer. A 325 nm wavelength HeCd laser was used to expose grating structures in the resist with a periodicity that was varied from 200 to 1500 nm. After exposure the resist was developed and the pattern transferred down through the interlayer, the ARC and into the thermal oxide using a series of reactive ion etch steps. After removing the residual ARC, a square-wave grating topography remains in the thermal oxide. The width of the grooves and the depth of the steps are adjusted by controlling the exposure time and etch process. Three different gratings with 50 nm step height were used in this work: a 700 nm period grating with 500 nm groove width, a 440 nm period grating with 320 nm groove width, and a 440 nm period grating with 240 nm groove width.

To study the graphoepitaxy of the block copolymer films, a 1.5% PS/PFS toluene solution was spin cast onto patterned silica substrates using various spin rates. As-spun films exhibit conformal coverage [Fig. 1(a)]. Etching of the film using an oxygen plasma removes the PS to reveal PFS spheres, which exhibit short-range order on both the mesas and valleys of the grooves [Fig. 1(b)]. However, the morphology of the polymer is significantly altered by annealing. After a 4 h 140 °C anneal the top surface of the polymer film is smooth and flat [Fig. 1(c)]. The appearance of the fracture

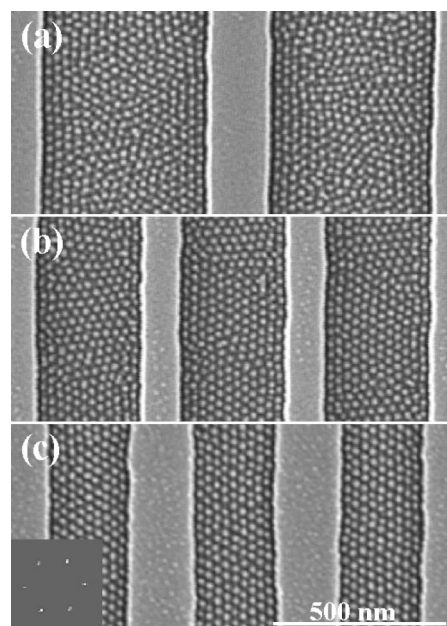


FIG. 2. Scanning electron micrographs of 48 h annealed and plasma-treated PS/PFS 50/12 films spun at 3500 rpm on silica gratings with (a) 500-nm-wide grooves, (b) 320-nm-wide grooves; (c) 240-nm-wide grooves. The inset is the Fourier transform of the plan-view pattern showing sixfold symmetry. Comparison of (c) with Fig. 1(d) shows the improvement of ordering with annealing time.

surface indicates that polymer is present only in the valleys. Etching of the film in oxygen shows an array of PFS spheres in the valleys but not on the mesas. Moreover, the rows of spheres in the valleys are partially aligned with the step edges [Fig. 1(d)]. The gap present between the first row of spheres and the step edges shows that there is a thin PFS-PS brush layer present at the groove edge and groove bottom where PFS wets the silica surface. This surface-induced thin layer provides the driving force to align the PS-PFS copolymers and results in PFS features parallel to the groove edges.^{21,22} Interestingly, analysis of plan-view images shows that the diameters of spheres adjacent to the sidewalls are slightly smaller than those in the center of the groove. This indicates that the free energy gain from the surface lamellar layer is larger than the cost of additional conformational energy for adjusting the domain size from the bulk value.²³

Figure 2 shows how the long-range order of the pattern changes with the width of the grooves. The samples were spin cast at 3500 rpm and annealed at 140 °C for 48 h. Within a 500-nm-wide groove, about three rows of close-packed PFS features are aligned parallel to the sidewall [Fig. 2(a)]. In the 320 nm grooves, some regions show a close-packed pattern extending across the groove but there is a significant number of defects in the pattern [Fig. 2(b)]. However, the alignment is nearly perfect in 240-nm-wide grooves, in which the groove width is comparable to the typical polymer grain size. An area of $4 \mu\text{m} \times 4 \mu\text{m}$ (not shown here) typically contains fewer than ten defects, and almost no high-angle grain boundaries are observed. The features have a sixfold symmetry and the superposed fast Fourier transforms of the images of several grooves [Fig. 2(c)] show that the pattern in each groove has the same orientation. The rare domain packing defects are apparently generated from the edge roughness of the grooves. The quality of

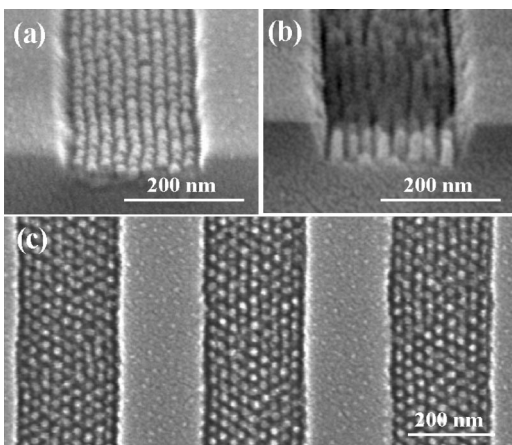


FIG. 3. Pattern transfer from an ordered PS/PFS 50/12 polymer to form an array of ordered silica nanostructures. (a) Side view of the PFS pattern in 240-nm-wide grooves corresponding to Fig. 2(c). (b) Side view and (c) plan view of the pattern after it has been transferred into an underlying silica layer by reactive ion etching. The silica posts in (c) have the same spatial organization as the originating PFS features of Fig. 2(c), and aspect ratios exceeding 3.

the alignment increases with annealing time, as misaligned grains are observed to reorder to bring close-packed rows parallel to the groove sidewalls. The number of aligned rows increases as the annealing time increases. This can be seen by comparing Fig. 1(d) (4 h anneal) with Fig. 2(c) (48 h anneal).

The period and feature size of the patterns can be changed by varying the molecular weight of the polymer. A block copolymer with molecular weights of 91 kg/mol PS and 21 kg/mol PFS showed a similar tendency to align on the same patterned substrates, forming, for instance, five rows of PFS spheres across the width of a 240-nm-wide groove, but the lower diffusivity of this polymer leads to poorer alignment. In addition, the quality of ordering is affected by the geometry of the sidewalls. The block copolymer does not align well along a tapered sidewall (in which the sidewall angle of the grating is smaller than 40°) because these gratings do not provide sufficient lateral confinement of the polymer. Alignment is also poor if the grating has undercut sidewalls. Therefore flat, vertical sidewalls are essential to achieve good ordering.

The well-ordered domain patterns [Fig. 3(a)] were transferred into the underlying silica using a reactive ion etch process with a CHF_3 plasma. This produced ordered arrays of silica posts with aspect ratios of 3 or higher [Fig. 3(b)]. The silica posts have uniform widths of 20 nm which is consistent with the PFS sphere size, though some height variations exist, presumably due to erosion of the PFS caps on top of each silica pillar. Ordered nanostructures of other materials such as cobalt can be formed by transferring the silica pattern into underlying films such as W/Co bilayers, as described previously,⁸ making this lithography method appli-

cable to a wide range of materials. The good aspect ratios available in the patterned silica structures are particularly advantageous for pattern transfer to other layers. The aspect ratio in this experiment can be further improved by tuning reactive ion etch conditions. This combination of graphoepitaxy and block copolymer lithography therefore provides a powerful method for precise placement of a variety of nanoparticles on a surface. Control of the nanostructure locations in two dimensions is expected to be possible by using a substrate patterned, for instance, with two sets of grooves oriented at 60° to each other.

The support of the NSF and the MIT Center for Materials Science and Engineering is gratefully acknowledged. The authors thank Mike Walsh for assistance with interference lithography.

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