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Large-area, ordered hexagonal arrays of nanoscale holes or dots from block copolymer templates

Josee Vedrine, Young-Rae Hong, Andrew P. Marencic, and Richard A. Register[a)]
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544, USA

Douglas H. Adamson
Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08540, USA

Paul M. Chaikin
Center for Soft Condensed Matter Research, Department of Physics, New York University, New York, New York 10003, USA

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Hexagonal arrays of nanoscale holes or metal dots (25 nm in diameter and 39 nm in period), with orientational order extending over the entire square-centimeter array area, were fabricated on unpatterned silicon wafer substrates using a shear-aligned sphere-forming diblock copolymer template. Since two or more layers of spherical nanodomains are required to achieve alignment in the block copolymer film, but pattern transfer requires a single layer, a multistep etching process was developed, whereby the top layer of a shear-aligned bilayer was evenly removed, leaving the ordered bottom layer as the fabrication template for hole and dot arrays free from grain boundaries. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2794010]

The growing interest in self-assembled nanostructured systems reflects the desire for low-cost fabrication of features below 100 nm, particularly dense arrays with sub-50 nm period, which are difficult to create by electron beam lithography.[1] Instead, bottom-up self-assembly approaches are being explored to fabricate quantum dot arrays,[2,3] high-density magnetic storage devices,[4–6] nanocrystal flash memory,[7] and air gaps.[8] Asymmetric block copolymers are attractive templates[9] for such arrays, since they spontaneously form uniform-sized spheres of the minority block; in films, thin enough to contain only a single layer of spheres, the spheres pack hexagonally, with a spacing tunable over the typical range of 20–100 nm, set through the length of the polymer chain. However, while the nanodomain periodicity is well-defined, such films normally show no long-range order; the spheres are arranged into micron-scale grains.[10] For some applications, especially those where individual elements of the array are to be addressed, some level of long-range order is required: at a minimum, long-range orientational order should be present,[5] and ultimately translational order.[11] Moreover, removal of the defects which constitute grain boundaries also improves the uniformity of the sphere size, since the distortional field near a defect causes a perturbation of the sphere size.[12]

Graphoepitaxy is an effective method of inducing orientational order in sphere-forming block copolymers.[5,6,11,13] In graphoepitaxy, features (such as troughs) with a length scale typically an order of magnitude larger than the block copolymer nanodomains are prefabricated on the substrate; the domains then spontaneously align with respect to the topographic features (e.g., the (10) planes of a hexagonal nanodomain lattice typically align parallel to trough walls). Alternatively, especially in cases where this larger-scale topography is undesired, shear alignment[14,15] can be employed to align bilayers of hexagonally packed spherical nanodomains, over cm^2 areas with no substrate prepatterning. Unfortunately, films containing only a single layer of spheres cannot be shear aligned, due to the in-plane mechanical isotropy of a hexagonal lattice;[14] moreover, films containing two or more layers of spheres are not directly useful for pattern transfer since the spheres in all layers will contribute during the transfer process, ruining the pattern.

To prepare single-layer films of a sphere-forming block copolymer with long-range orientational order, our approach is to: (1) shear a bilayer film, (2) strip off the top layer (both spheres and matrix) in a nonselective etching process, and (3) use the ordered bottom layer as the template in a selective etching process. The basic process flow is illustrated in Fig. 1, where the selective etching is achieved by selecting a sphere-forming block which can be degraded, leaving spherical voids which provide a mask for reactive ion etching (RIE). While several chemistries and degradation routes are possible,[16] we chose to use a polydiene block [polyisoprene PI] which can be cleaved readily by exposure to ozone (O_3); O_3 exposure simultaneously crosslinks the polystyrene (PS) matrix block. The PS-PI chemistry is attractive here because many RIE processes, including fluorine-based RIE (SF_6 and CF_4), etch PS and PI at very similar rates,[17,18] thus providing a mechanism for nonselective removal of the top half of the bilayer prior to ozonation.

The diblock copolymer employed, PS/PI 68/12, has been described in our previous work;[2,3,10,17,18] with molecular weights of 68 and 12 kg/mol for the PS and PI blocks, respectively, it forms PI spheres of 25 nm in diameter with a 39 nm center-to-center spacing. A 2% solution of PS/PI 68/12 in toluene was spin coated at 1500 rpm onto Si wafers to achieve a bilayer film 96 nm thick. Shearing was conducted on a hot plate at 170 °C, well above the PS block glass transition temperature (100 °C). Because of the poor thermo-oxidative stability of PI, shearing was conducted under a nitrogen atmosphere using a glove bag or glove cham-

[a)]Electronic mail: register@princeton.edu

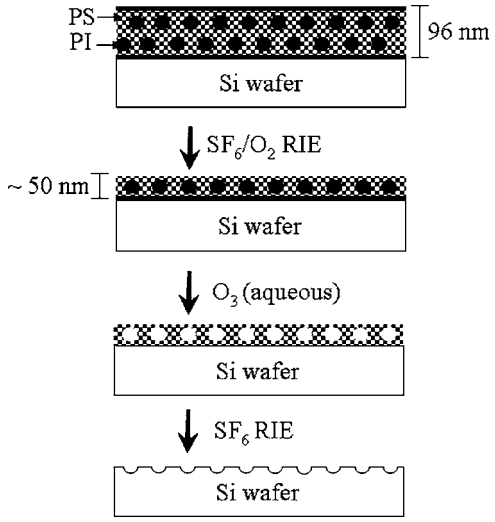

FIG. 1. Fabrication process sequence for ordered nanohole array, starting with a shear-aligned bilayer of block copolymer spherical nanodomains (PI spheres in a PS matrix). A fluorine-based RIE, nonselective for PS vs PI, evenly removes the top layer. The remaining bottom layer is treated with O_3 to remove the PI, creating spherical nanovoids in a cross-linked PS matrix. A second RIE step transfers the void pattern into the Si substrate as an ordered array of holes.

ber. A polydimethylsiloxane (PDMS) (Dow Corning Sylgard 184) shearing pad, minimum 1×1 cm^2, was placed on the supported bilayer film. Stress was imparted either through a weight-over-pulley assembly as previously described,[19] or more simply (but less flexibly) by inserting an angled aluminum block (angle $\alpha\approx5°$) between the sample and the hotplate, and placing a weight on top of the PDMS pad to impart both normal and shear stress simultaneously (in a ratio of $\cos\alpha/\sin\alpha$). Typically, shear stresses of 2–6 kPa were employed for 30 min. Occasionally, removing the PDMS pad appeared to cause some surface roughness, which was reduced by a 3 min postannealing at 120 °C. The top half of the bilayer was removed by a nonselective etching with SF_6/O_2 (8/2 v/v) or CF_4 [PlasmaTherm 790, 15 mTorr, 10 SCCM (SCCM denotes cubic centimeter per minute at STP)], resulting in an ordered monolayer ~50 nm thick. The specimen was then exposed to an aqueous solution of O_3, previously described.[17,18] O_3 cleaves the PI double bonds, leaving spherical voids (25 nm in diameter and 39 nm in periodicity) inside the now-crosslinked PS matrix. A second fluorine-based RIE (SF_6 or CF_4) was performed using the PS mask to introduce holes into the Si substrate to a depth of 20–25 nm.

Figure 2 shows a scanning electron microscope (SEM) image of a section of a 1.6×1.9 cm^2 hole array. Only a small portion of the array is shown so that the individual holes can be resolved, but the general orientation of the lines of spheres [(10) planes of the hexagonal macrolattice] persisted over the entire 3 cm^2 sheared area. The quality of the orientational order was assessed through the hexagonal orientational order parameter ψ_6,

$$\psi_6=\langle\cos[6(\theta-\theta_0)]\rangle,$$

where θ is the angle of the bond between nearest neighbors and θ_0 is the shearing direction.[15] The average is over all bonds in the image. For the image in Fig. 2, $\psi_6=0.70$; analysis of several images shows an average $\psi_6=0.68$, with a dislocation density of 24 per 1000 spheres.

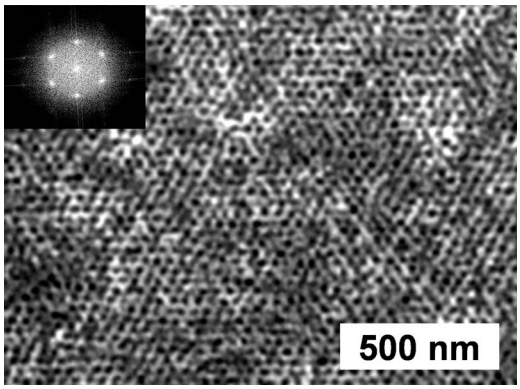

FIG. 2. Plan-view SEM image of an oriented nanohole array in Si. Shear direction for the block copolymer film template from which this array was fabricated is horizontal (from left to right). Inset in the upper left corner is the fast Fourier transform of the image, clearly showing the six first-order spots expected for an ideal hexagonal lattice.

By incorporating additional steps into the process flow, more complicated structures can be prepared, such as supported arrays of metal dots with long-range orientational order. Evaporation provides a wide palette of metals to choose from, such as magnetic Co (Ref. 6) and Ni,[20] or Au, which can readily be conjugated with proteins to immobilize them.[21] Figure 3 shows the process flow for the fabrication of an ordered array of Au dots, combining the shear alignment and successive etch steps of Fig. 1 with the trilayer transfer technique previously reported.[3] First, a 52 nm layer of polyimide (Fujifilm Durimide 284) was spin coated onto a Si wafer pretreated with QZ adhesion promoter (Arch Chemicals) and baked for 3 hr at 250 °C. An 8.5 nm layer of silicon nitride (SiN_x) was then deposited by plasma enhanced chemical vapor deposition (PlasmaTherm 790). A bilayer film (96 nm thick) of PS/PI 68/12 was then spin coated and shear aligned; the top layer was removed by nonselective CF_4 RIE, the bottom layer ozonated, and the pattern transferred into the SiN_x layer by CF_4 RIE, all as described above. Etching was continued until the SiN_x underlying the spheres in the original bottom layer was completely removed. These perforations were then etched through to the bottom of the

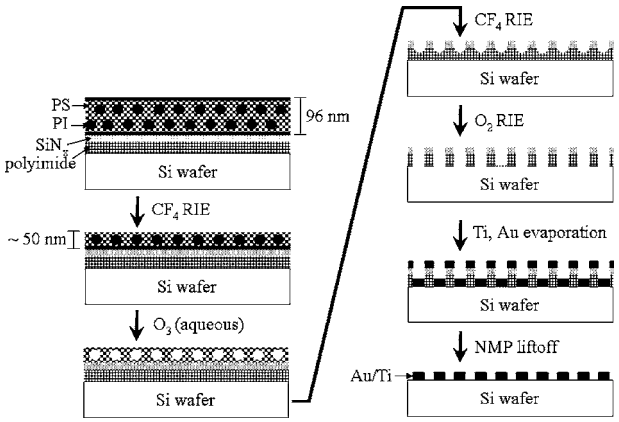

FIG. 3. Fabrication process sequence for an ordered metal (Au/Ti) nanodot array. The left portion of the sequence is identical to Fig. 1, except that the Si substrate is first coated with layers of polyimide and SiN_x. Once the pattern is transferred through the SiN_x, the RIE gas is changed to O_2, which completely etches the polyimide but not the SiN_x. Blanket metal evaporation followed by lift-off to remove excess polyimide, SiN_x, and metal leaves the ordered dot array.

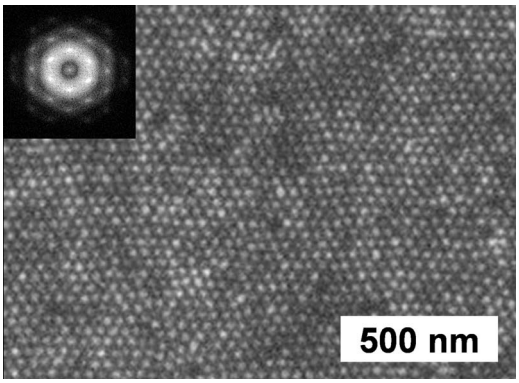

FIG. 4. Plan-view SEM image of an oriented Au dot array. Inset in the upper left corner is the fast Fourier transform of the image, clearly showing the first four orders of spots expected for an ideal hexagonal lattice.

polyimide layer using oxygen RIE (15 mTorr, 10 SCCM). Subsequently, a 2.7 nm Ti adhesion layer and a 12.3 nm Au layer were deposited sequentially by electron-beam evaporation (Denton DV-502A). The remaining polyimide and SiN_x, along with the excess metal on top of the SiN_x, were removed by lift-off in *N*-methylpyrrolidone, resulting in a densely packed array of ordered Au dots on the substrate.

Figure 4 shows a plan-view SEM image of a small portion of the 1.0×1.0 cm^2 dot array. No grain boundaries were observed in the array, as expected for macroscopic orientational order. The only defects observable in Fig. 4 are a few dislocations, which are present in the block copolymer film template,[14,15] and a few vacancies (missing dots), which result from fabrication imperfections (holes not etched through the SiN_x or not etched to the bottom of the polyimide, or inadequate adhesion by the Ti layer).[3] Quantitative analysis of the image in Fig. 4 yielded $\psi_6 = 0.83$; an average over several such images yielded $\psi_6 = 0.77$ and a dislocation density of 11 per 1000 spheres. The higher value of ψ_6 and lower dislocation density found here, versus those for the hole arrays illustrated in Fig. 2, may reflect the higher stress employed (6 kPa vs 2 kPa).[15] We note that the ψ_6 and the dislocation density values found for these Au dot arrays are quite similar to the values found for the top layer of spheres in a sheared bilayer of a different block copolymer[22] in the high-stress limit, where ψ_6 becomes independent of stress. Since the Au dot arrays are replicas of the bottom layer of spheres, this similarity indicates that shear is equally effective in aligning both the top and bottom layers in the bilayer film, as expected.

In this letter, we have shown that shear-aligned bilayers of sphere-forming block copolymers can be employed as templates for the fabrication of macroscopic (cm^2) arrays of nanoscale holes and dots, with orientational order extending over the entire array. The hole/dot diameter and period are set by the lengths of the blocks in the PS/PI template, and thus are readily controlled during polymer synthesis. While the fabrication examples we have presented here have been limited to holes in Si and to Au dots, we note that the block copolymer nanolithography process is quite flexible in the choice of substrate or dot materials, through modifications of the process flow shown in Fig. 3. For example, Ge,[18] GaAs,[23] and SiO_2 (Ref. 24) substrates have also been employed, and dots have been prepared from GaAs/InGaAs,[2] SiO_2,[25] and Ni,[20] among others. Moreover, in many cases, it is possible to transfer the pattern directly into a thin supported layer of the material of interest,[4–6,21] rather than depositing the material after patterning. Thus, the process we have presented here is readily extendable to the fabrication of supported, ordered arrays comprising a broad range of dot materials and substrates.

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