

Synthesis of Metal Chalcogenide Nanodot Arrays Using Block Copolymer-Derived Nanoreactors

Delia J. Milliron,^{*,†} Marissa A. Caldwell,[‡] and H.-S. Philip Wong[§]

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120,
Department of Chemistry, Stanford University, Stanford, California 94305, and
Department of Electrical Engineering, Stanford University, Stanford, California 94305

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ABSTRACT

Soluble metal chalcogenide precursors are used to fabricate arrays of metal chalcogenide nanodots by spin-coating. Nanodots are formed after thermal decomposition of the precursors, which are collected in patterned nanowell arrays. These arrays are derived from block copolymer patterns and may consist of the polymer itself or result from etching to transfer the pattern to an inorganic substrate. Etching provides enhanced control over nanowell shape and the morphology of the resulting metal chalcogenide array.

A wide range of optical, electronic, and catalytic applications have been demonstrated for inorganic nanoparticles to take advantage of their diverse size-dependent properties. Synthesis within the confines of substrate-bound nanoreactors offers an alternative to solution-phase colloidal synthesis of such nanostructures.^{1–3} Nanoreactor synthesis can be advantageous for some applications because the particles are generated on a substrate, with the possibility of predefined positional order or placement of the particles based on the structure of the template. However, the common approach of impregnating inorganic precursors into organic domains poses severe limitations on the synthetic reactions which can be executed within such nanoreactors. In this work, we instead convert a block copolymer template to an array of nanowells that can be filled with precursors, leading to high-density arrays of well-separated metal chalcogenide nanodots. The nanowells are initially formed in polystyrene but can be transferred to silicon oxide, forming arrays of nanoreactors that are chemically and thermally stable. We demonstrate the synthesis of uniform nanodot arrays by spin-coating single-source precursors into these nanowells, followed by thermal decomposition, to form the metal chalcogenide of choice. Binary or ternary compositions can be achieved in a single step.

Commonly, nanoreactors consist of molecular or dendrimeric micelles that sequester an inorganic precursor on the basis of preferential interaction with the center-facing organic functionality.^{4–6} Similarly, one component of a self-as-

sembled block copolymer micelle^{7–9} or thin film can be impregnated preferentially with an inorganic precursor.^{2,3} In each case, the inorganic precursor is limited in two ways. First, the local precursor concentration is limited based on solubility within the template. Second, reaction temperature must be kept within the stability range of the organic template. Owing to these limitations, such soft templating approaches have been most successful for simple and mild synthetic methods such as the reduction of metal salts to elemental nanoparticles.^{3,4,7} While subsequent chemical transformations can be applied to achieve compositionally more complex products, the limited stability of the templates remains restrictive. The nanowells reported here, which the precursor fills based on physical rather than chemical driving forces, overcome many limitations of micelle-like nanoreactors. Unlimited concentrations of precursor can be achieved and complex precursors or mixtures can be sequestered in one step, simplifying the synthesis of nanostructures with more complex compositions. In addition, nanowells derived from block copolymers are on the same size scale as the targeted nanoscale particles. As compared to filling larger wells with dilute precursor solution,¹ this creates improved control over size and shape distributions and a greater density of nanostructures. Finally, in cases where the polymer walls of the nanowells are incompatible with reaction conditions, the pattern can be transferred to many different inorganic substrates.^{10–12}

Several alternative “top-down” methods can also be used to fabricate arrays of micro- or nanowells, which can serve as templates for nanomaterials fabrication. For example, periodic wells fabricated by interference lithography have

* Corresponding author. E-mail: milliron@us.ibm.com.

† IBM Almaden Research Center.

‡ Department of Chemistry, Stanford University.

§ Department of Electrical Engineering, Stanford University.

been used to template nanorings and nanowires.¹³ However, standard interference lithography produces relatively large scale periodicity, from hundreds of nanometers to micrometers. Finer nanoscale features require either a soft X-ray light source (extreme ultraviolet or EUV)¹⁴ or immersion lithography with high-energy ultraviolet laser illumination.¹⁵ In contrast, block copolymer nanowells can be prepared with only a spin-coater and an oven and can be transferred to an inorganic substrate with a standard etch tool. Nanoimprint lithography is capable of generating nearly arbitrary patterns down to ca. 20 nm (10 nm in exceptional cases) when the imprint template is fabricated using electron beam lithography.¹⁶ However, imprinting large areas requires expensive large area templates and repeated imprinting steps. Large areas of 10–20 nm feature size may be patterned simultaneously using block copolymers without the need for expensive templates. When precise positioning of nanoscale features is required, combining top-down techniques with block copolymer patterning¹⁷ ultimately offers the greatest potential for control over the nanowell template pattern and therefore over the arrangement of the eventual nanostructures. In this approach, low-resolution lithography dictates the placement and arrangement of features while the nanometer scale feature size is generated by self-assembly, resulting in a patterning process that is both inexpensive and scalable.

Nanowells formed from the block copolymer polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) were used as a template for the synthesis of uniform arrays of ternary metal chalcogenide nanostructures. GeSbSe alloy films have recently been prepared by spin coating a mixture of Ge–Se and Sb–Se precursors from solution, followed by low-temperature thermal decomposition.¹⁸ This material exhibits a thermally induced amorphous-crystalline phase transition, which may be useful for advanced memory applications. Dense but well-separated arrays of GeSbSe nanodots were prepared on silicon substrates patterned with polystyrene nanowells generated from a PS-*b*-PMMA film (Figure 1). To form the template, a brush layer of PS-PMMA random copolymer was first deposited on the silicon surface. Then, a layer of block copolymer was spin-coated and annealed to facilitate self-assembly. The PS block is longer than the PMMA block so that PS forms the matrix. The random copolymer neutralized the interaction of the two components with the substrate, inducing the PMMA cylinders to orient vertically in the thin film.¹⁰ The PMMA can then be displaced by submerging in acetic acid, leaving an array of nanowells with a thin layer of random copolymer at their base. Finally, this layer was removed with a mild oxygen plasma etch, opening the wells to the silicon substrate below. The same mixed precursor solution used for the deposition of GeSbSe thin films was spin-coated onto the template, filling the nanowells. Following thermal decomposition of the precursors at 180 °C, the PS template was removed by liftoff, taking any superficial inorganic material with it. The resulting GeSbSe nanodots have a slightly tapered shape in cross section (Figure 1d), implying that the template walls have a slight reverse taper. SEM of the cleaved template (Figure 1b) shows some evidence for this shape, which likely results

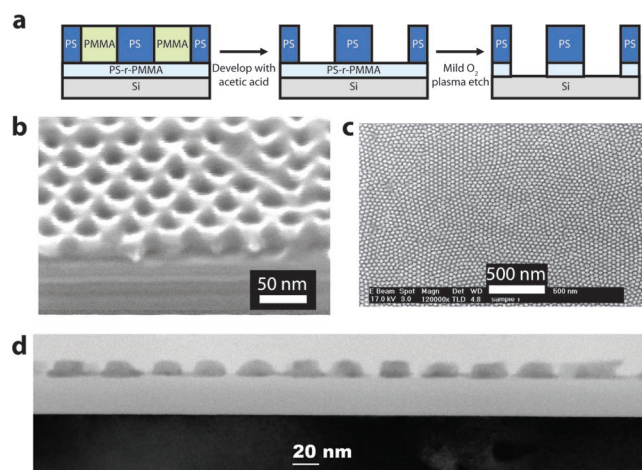


Figure 1. Synthesis of free-standing GeSbSe nanodot arrays using a PS-*b*-PMMA template. (a) Scheme of template fabrication illustrating self-assembly, selective removal of PMMA, and etching to remove the random copolymer layer from the nanowells. (b) SEM of a completed PS nanowell template (tilt = 55°). (c) SEM of the nanodot array after template removal. (d) Cross-sectional bright-field TEM of the nanodot array demonstrating size and shape uniformity.

from a slight overetch of the PMMA-containing random copolymer at the base. The high surface density of the GeSbSe nanodots facilitated X-ray diffraction characterization of their crystallization temperature, which is reduced in comparison to a continuous thin film.¹⁸ Meanwhile, intimate contact with the substrate and the surfactant-free surface of the nanostructures open the possibility of low-resistance electrical contact for further characterization in the future.

In many cases, high temperatures or other process conditions, which are not compatible with organic templates, are required for the synthesis of the targeted or highest quality nanoparticles. In this case, the nanowell pattern can be transferred to an inorganic substrate, forming a more robust array of nanoreactors. For this purpose, PS nanowells were formed on a ca. 30 nm thick thermally grown silicon oxide layer on a silicon substrate. The ca. 20 nm diameter nanowells could be etched into the silica with an anisotropic etch based on CHF₃/Ar reactive ion etching (RIE).¹¹ Upon spin-coating a solution of Ge–Se precursor and thermal decomposition, the silica nanowells were completely filled with GeSe₂ and the surface planarized (Figure 2a). By reducing the concentration of the spin-coating solution, the nanowells were again completely filled, but the thickness of the conformal layer connecting the nanodots was reduced (Figure 2b). A low spin speed was required to slow the drying rate in order to enhance the preference for filling the wells. Hence, nearly isolated nanodots in partially filled wells were achieved at low concentration and slow spin speeds (Figure 2c). When too fast a spin rate (2500 rpm and above) was used with such a low-viscosity solution, rapid drying induced instabilities that led to nonuniform coating of the template (Figure 2d). Such nonuniformities were never observed for higher viscosity solutions (50 mg/mL or greater) at least up to spin speeds of 4000 rpm.

To achieve completely isolated metal chalcogenide nanodots, we etched the silicon oxide into broader nanowells,

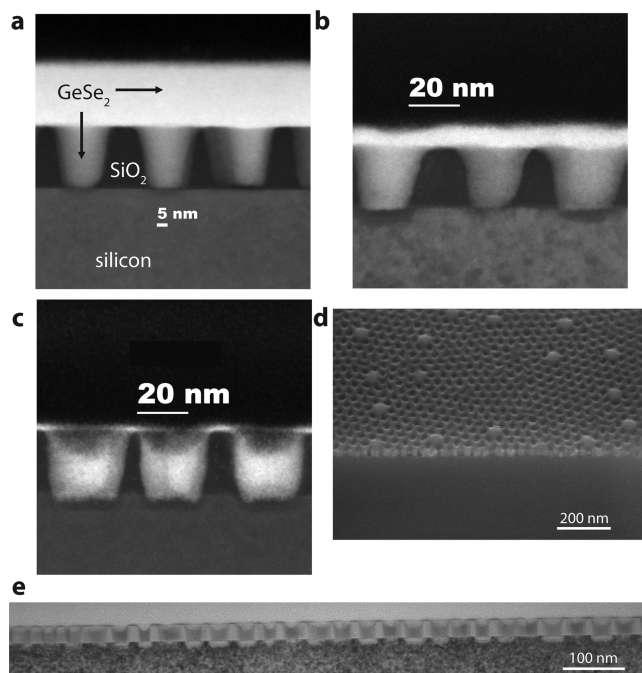


Figure 2. Synthesis of GeSe_2 nanodot arrays within silicon oxide templates. (a) Cross-sectional z -contrast TEM of a silica template completely filled and planarized with GeSe_2 using a 90 mg/mL precursor solution at a spin speed of 1500 rpm. (b) TEM of a silica template filled with GeSe_2 with a significant conformal coating (50 mg/mL; 4000 rpm). (c) TEM of a partially filled template with minimal conformal coating (25 mg/mL; 1500 rpm). (d) SEM of a partially filled template with apparent nonuniform dewetting (tilt = 45°) (25 mg/mL; 2500 rpm). (e) Bright-field TEM at low magnification, demonstrating the uniformity of partial filling in the sample captured in (c). Some damage of the silicon substrate due to overetching is visible as dark contrast in the z -contrast TEM images (a–c) and as light contrast in the bright-field TEM image (e).

leaving narrow, sharp walls between them. To achieve this shape of nanowells, we employed a less selective etch based on SF_6 RIE chemistry¹⁹ (Figure 3a). In this case, the mixed Ge–Se and Sb–Se precursor entirely dewetted the barrier between wells, leading to isolated GeSbSe nanodots without a liftoff step (Figure 3b). The spin speed and therefore drying rate are the same as in the case of the thin conformal layer (Figure 2c and e), and concentrations were selected that yield blanket films of comparable thickness (around 5 nm), implying that the solution viscosities are comparable. The key difference is the shape of the oxide barriers that separate adjacent nanowells. The walls in Figure 2c,e are fairly narrow, yet the top surface of the oxide remains unetched and therefore flat, with a very large local radius of curvature. In contrast, the oxide film in Figure 3a has been largely etched away so that the radius of curvature at the top of the remaining walls is below 5 nm. The surface energy cost of maintaining wetting over these sharp features is too great and, as the solvent evaporates, the film of solution becomes discontinuous, wetting only the depressions.²⁰ These arrays were further characterized by tapping mode AFM. The sharp walls were broadened through convolution with the shape of the AFM tip, but the topographic image otherwise echoes the SEM observations (Figure 3c). The phase image,

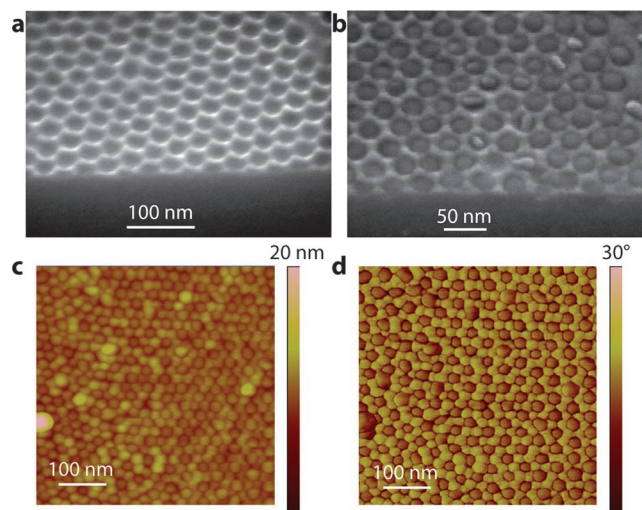


Figure 3. Isolation of GeSbSe nanodots by controlled dewetting. (a) SEM of silicon oxide etched into broad wells with sharp walls. (b) SEM of nanodots in a sharp-walled template (30 mg/mL; 1500 rpm). (c) Tapping mode AFM topography of the same sample. The sharp walls are artificially broadened by convolution with the shape of the tip. (d) AFM phase image collected simultaneously with (c). The material contrast between the GeSbSe and the silica reflects the isolation of each nanodot from its neighbor.

however, shows contrast between the barriers and the nanodots, indicating a difference in interaction of the tip with each region of the surface (Figure 3d). Such contrast is strong evidence for clean silicon oxide barriers, separating isolated GeSbSe nanodots.

Synthesis of metal chalcogenide nanostructures in block copolymer-derived nanowells provides a route to uniform, surfactant-free nanodots arranged in high-density arrays. Because the nanodots are on the same size scale as the wells, their spacing and position is closely determined by the template pattern. In addition, block copolymer self-assembled patterns can be induced to order over large length scales,^{17,21} or to align to lithographically patterned features,^{17,22–24} so that this approach could be directly applied to synthesize metal chalcogenide nanostructures in predefined arrangements or locations. Even beyond the binary and ternary metal chalcogenide structures demonstrated here, this method could be leveraged to make a variety of more complex nanostructured materials. First, a wide range of inorganic materials can be etched using block copolymer etch masks to serve as the matrix material.^{11,12,14} Second, the tunable partial filling of the nanowells reported here opens the possibility that vertical heterostructures of multiple metal chalcogenide materials could be fabricated within each nanowell, further expanding the range of functionality that could be achieved in the final nanocomposite film. Considering the generality of the synthetic approach, from precursor synthesis to template filling and decomposition, a very broad range of functional nanocomposite materials can be prepared. Employing only the class of single-source precursors used in this work, p- and n-type semiconductors with band gaps ranging from the infrared to the ultraviolet could be prepared in nanodot arrays.^{25–28} Furthermore, the use of thermally and chemically stable silicon oxide templates allows the pos-

sibility for reactive synthesis to be carried out in the nanowells. We have therefore demonstrated a generalized method for synthesizing arrays of metal chalcogenide nanostructures using block copolymer-derived nanoreactor arrays.

Preparation of Block Copolymer Nanowell Arrays.

Block copolymer nanowell arrays were prepared using PS-*b*-PMMA and PS-PMMA random copolymer from Polymer Source by a previously described process.²⁹ Briefly, a 1% (w/w) toluene solution of random copolymer was spin-coated onto a silicon wafer and annealed for 2 days at 180 °C, then rinsed to remove excess polymer. Then a 1% toluene solution of the block copolymer (MW = 67 000 g/mol, 70:30 PS:PMMA) was spin-coated and annealed at 180 °C to permit self-assembly. Following development with glacial acetic acid, the random copolymer was removed with a mild isotropic oxygen plasma (30 sccm O₂, 6 mTorr, 300 mW ICP).

Preparation of Silicon Oxide Nanowell Arrays. Block copolymer nanowells were prepared on ca. 30 nm thermally grown silicon oxide, omitting the final oxygen plasma etch. The oxide was etched using CHF₃ and Ar plasmas (typically: 20 and 5 sccm, respectively, 15 mTorr, 100 W) for 3–4 min utilizing the PS as the etch mask. Finally, the residual polymer was removed with a 60 min UV–ozone clean.

Broad oxide nanowells were prepared similarly. The oxide was etched using SF₆ plasma (typically: 20 sccm, 15 mTorr, 200 W) for 30–45 s, with the PS serving as the etch mask. No residual polymer was observed by SEM.

Synthesis of Metal Chalcogenide Nanostructure Arrays.

The Sb–Se and Ge–Se precursors were synthesized as previously reported.¹⁸ Characterization by thermal gravimetric analysis (TGA) guided the selection of thermal profile used to decompose them within the nanowell templates. All nanostructured arrays were prepared in an inert atmosphere. Precursor solutions were prepared by stirring in a 5:3 volumetric mixture of dimethylsulfoxide and ethanolamine at room temperature. The solution was passed through a 0.2 μm filter, then used to flood the nanowell templates, which were spun at the reported rate for 90 s, at which point the films appeared dry. For reported rates lower than 3000 rpm, a final spin step at 3000 rpm for 15 s was added in order to dry any remaining droplets at the edges of the wafer before removing it from the spinner. Nanostructured films were then immediately dried at 100 °C for 5 min, followed by thermal decomposition of the precursor. For GeSbSe nanostructures, the final decomposition was carried out at 180 °C for 10 min, while GeSe₂ nanostructures were annealed at 150 °C for 20 min, then 260 °C for 20 min. A final liftoff step was accomplished for free-standing nanodots by sonicating in toluene for 30 min.

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