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A Simple Route to Metal Nanodots and Nanoporous Metal Films

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ABSTRACT

High density arrays of chromium (Cr) and layered gold/chromium (Au/Cr) nanodots and nanoholes in metal films were fabricated by evaporation onto nanoporous templates produced by the self-assembly of poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)) diblock copolymers. The cylindrical microdomains of the asymmetric block copolymer were oriented normal to the surface by balancing interfacial interactions of the blocks with the substrate. By selectively removing either the minor or major component, nanoporous films of PS or nanoscopic posts of PS could be produced. Thus, a template, comprising an array of hexagonally packed pores in a PS matrix or PS posts, was easily fabricated. Evaporation of Cr and Au onto the template, followed by sonication and UV degradation of the PS, left Cr or Au/Cr nanodots or a nanoporous metallic film.

Recently, a variety of new patterning technologies have emerged, which attempt to create nanoscale structures over large areas at low cost.^{1–6} Dot arrays patterned on the nanometer scale hold promise for many applications, such as optical devices,⁷ DNA or protein electrophoresis,^{8,9} and catalysts.¹⁰ Semiconductor quantum dots have been prepared by several techniques such as molecular beam epitaxy,¹¹ metal organic chemical vapor deposition,^{12,13} and electron beam lithography.¹⁴ An ordered array of multiple dots has also been formed by way of alumina membranes as evaporation masks by Masuda et al.,¹⁵ but feature sizes are still larger than 50 nm. Among fabrication methods, self-assembly of diblock copolymers has unique potential to overcome the size scale limitations of conventional lithographic techniques.^{16–23}

Park et al.²⁴ reported a promising route to the fabrication of hexagonally ordered metal dot arrays by combining block copolymer self-assembly and a trilayer pattern transfer technique. In that work, a layer of polyisoprene spheres in a polystyrene film was used to pattern a layer of silicon nitride by reactive ion etching (RIE). The pattern was then transferred by RIE to an underlying layer of polyimide. A

hexagonally ordered array of Ti/Au dots with a diameter of 20 nm and a periodicity of 40 nm were produced by evaporating metals onto the template followed by lifting off the template. Here, we present a simpler, more direct use of block copolymer templates to generate both metal nanodot arrays and nanopore arrays in a metal matrix with high areal density (10^{11} features/cm²) via block copolymer templates with cylindrical microdomains. This method avoids the use of reactive ion etching in order to improve the fidelity with which the pattern can be replicated. We also show that this technique can be applied to produce multilayered metal nanostructures without increasing the number of steps involved.

In this work, we use block copolymers that self-assemble to form periodic structures with well-defined size and periodicity on a scale of tens of nanometers. Asymmetric poly(styrene-*block*-methyl methacrylate) (P(S-*b*-MMA)) diblock copolymers with PMMA volume fractions (ϕ_{PMMA}) of 0.7 and 0.3 were synthesized by standard anionic polymerization techniques in THF at -78 °C. The number average molecular weights were 6.5×10^4 (65 K) and 8.0×10^4 (80 K) with polydispersities of 1.05 and 1.07, respectively. The lattice spacings of the microdomains were ~ 30 and ~ 35 nm, respectively, as measured by atomic force microscopy (AFM).

To prepare P(S-*b*-MMA) diblock copolymer thin films with the cylindrical microdomains oriented perpendicular to

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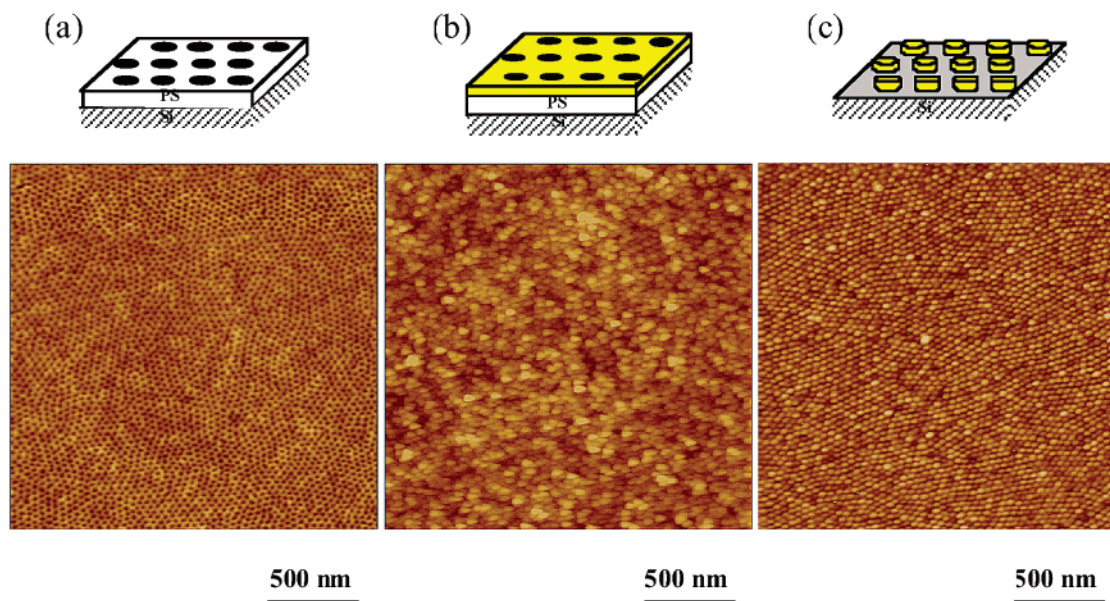


Figure 1. Schematic diagram of the fabrication process for Cr dot arrays (upper pictures) and height images of tapping mode AFM of each step (lower pictures): (a) nanoscopic holes in cross-linked PS matrix, (b) evaporated Cr onto the PS template, and (c) Cr nanodot arrays. The height range of the AFM images is 10 nm.

the substrate, it is necessary to modify the substrate such that there are no preferential interactions with either polymer block. We used two different methods of substrate neutralization. A random copolymer of poly(styrene-*r*-methyl methacrylate) (P(S-*r*-MMA)) with 58% styrene volume fraction was grafted onto the native silicon oxide of the silicon wafer for use in patterning nanodot arrays.²⁵ The silicon oxide layer was removed by hydrofluoric acid etching for the generation of a nanoporous metal film.²⁶ Polished silicon (100) wafers were purchased from International Wafer Source, Inc., cleaned in sulfuric acid and an inorganic oxidizing bath, then thoroughly rinsed with deionized water before use. P(S-*r*-MMA) random copolymers, with a benzyl alcohol end group, having a styrene mole fraction of 0.58 and a number average molecular weight of 1.0×10^4 were synthesized via nitroxide-mediated controlled free radical polymerization.²⁷ P(S-*r*-MMA) was anchored to the silicon substrate by spin coating from 1% (w/w) solutions in toluene, annealing under vacuum at 165 °C for 3 days, and then washing with toluene. Passivated silicon substrates were initially rinsed in 5% hydrofluoric acid for 3 min, thoroughly washed with deionized water and then air-dried.

A thin (~ 30 nm) film of 65 K P(S-*b*-MMA) ($\phi_{\text{PMMA}} = 0.3$) was spin coated from 1% (w/w) solutions in toluene at 3000 rpm onto the P(S-*r*-MMA) modified substrate, then annealed under vacuum at 170 °C for 2 days. These films, with the PMMA cylinders normal to the surface, were irradiated with UV (5.7 mW/cm²) under vacuum for 35 min, thoroughly rinsed with acetic acid and water, and then allowed to air-dry. A template comprising a hexagonal array of 16 ± 1 nm diameter holes in a cross-linked PS matrix was produced, as shown in Figure 1a. A 10 nm layer of chromium was evaporated onto this nanoporous template at a pressure of 10^{-7} mmHg to cover the top of the template and partially fill the pores in the matrix (Figure 1b).

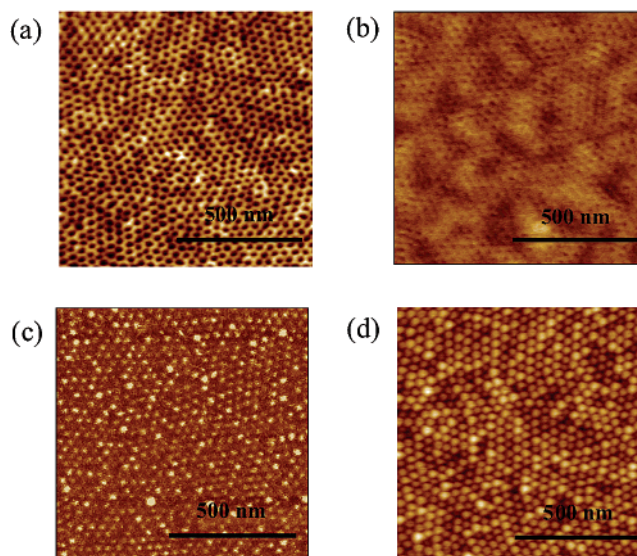


Figure 2. Tapping mode AFM images of layered Au and Cr dot arrays. (a) Block copolymer template etched by UV exposure. (b) Height image and (c) phase image of the Au/Cr evaporated PS template after removing the excess metal. (d) Au/Cr dot arrays after eliminating PS matrix by the irradiation of UV.

Chromium (Cr) and gold (Au) pellets ($>99.95\%$ purity) were purchased from Electronic Space Products International. Sonication of the sample in toluene mechanically removed the excess chromium and much of the underlying cross-linked PS matrix. The adhesion of the template to the underlying brush was also weakened significantly by this step. UV irradiation of the sample under vacuum for 40 min and subsequent washing with toluene for 5 h was sufficient to remove most of the remaining cross-linked PS. After drying, a final oxygen RIE for 3 s ensured complete removal of all remaining polymer. Densely packed chromium dots with regular diameters of 16 ± 1 nm and center-to-center

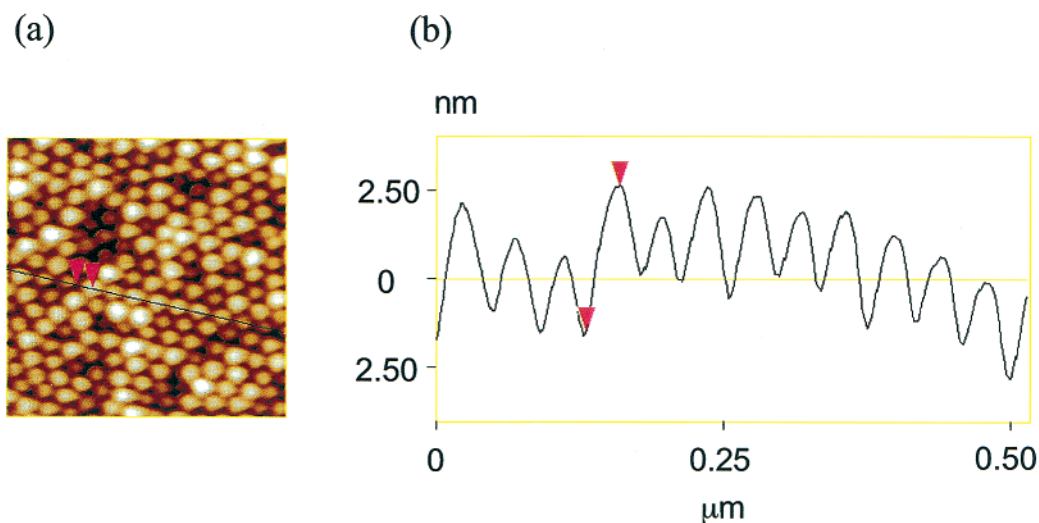


Figure 3. Two-dimensional and cross-sectional AFM images of layered Au and Cr dot arrays. (a) Height contrast AFM image of selected area in Figure 2d. (b) Cross-sectional AFM profile.

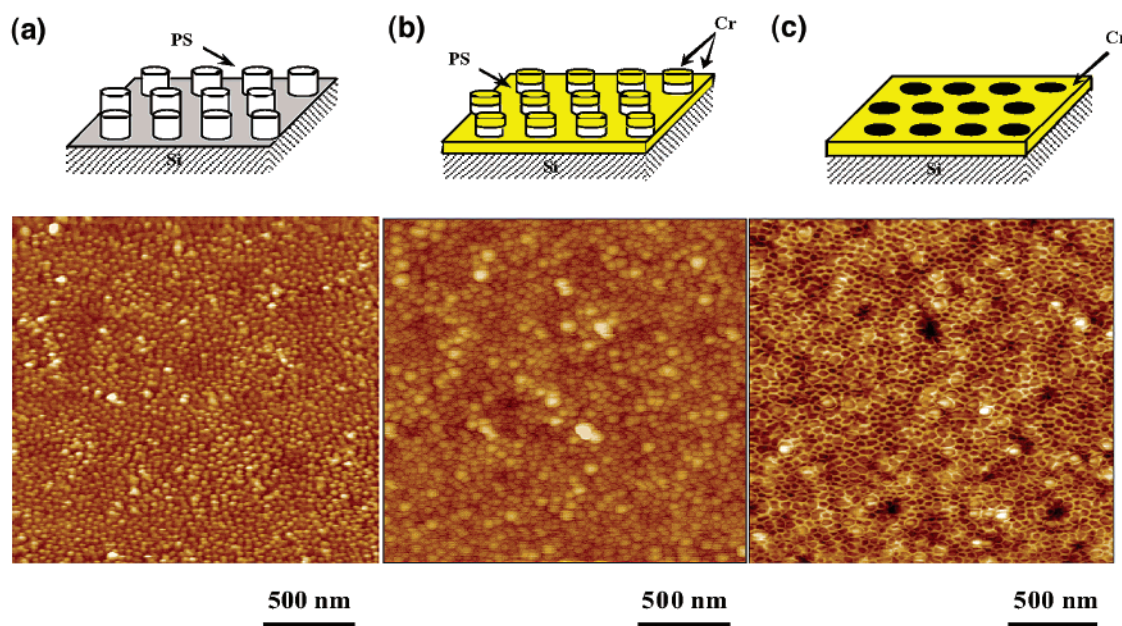


Figure 4. Schematic diagram of the fabrication of nanometer-sized holes in a thin Cr film (upper pictures) and tapping mode AFM height images of each step (lower pictures). (a) PS posts array. (b) Evaporated Cr aggregates onto the PS posts array. (c) Holes in a Cr matrix after eliminating excess Cr and PS posts.

spacings of 34 ± 1 nm are clearly visible in the height image of the tapping mode atomic force micrograph (Figure 1c).

Multilayered nanodots were also prepared by the sequential evaporation of Au onto Cr. The original nanoporous PS template is shown in Figure 2a. Sequential evaporation of Au onto Cr with subsequent sonication and toluene rinsing produced metal bilayer dots. The height and phase AFM images of the template after the sequential evaporation of 9 nm Au onto 3 nm Cr and after sonication of the sample in toluene are shown in Figures 2b and 2c, respectively. As before, sonication mechanically removed the Au/Cr on the surface of the template, while leaving the metal bilayer within the pores unchanged. In the height image (Figure 2b), the pores in the PS template are dark (lower), indicating that the pores have not been completely filled with metal. In the phase image (Figure 2c), however, bright spots are observed

due to the greater hardness of the Au/Cr bilayers than the PS matrix and consequently, the image is the inverse of Figure 2b. The Au/Cr multilayered nanodots form a hexagonal array on the surface as shown in Figure 2d.

The cross-sectional profile of the surface of layered Au/Cr dot arrays is shown in Figure 3. A distinct dot array with hemispherical-shaped cap is clearly observed over a selected area. The average height of each dot is measured to be ~ 3.5 nm, which is lower than the thickness of evaporated metal. This discrepancy is attributed to the size of the AFM tip, which causes the shape of the tip to be convoluted with the surface features.

An array of nanoholes in thin films of metal was obtained as follows. Thin films (~ 30 nm) of 80 K P(S-*b*-MMA) with $\phi_{\text{PMMA}} = 0.7$ were spin coated onto passivated silicon substrates. The films were annealed under vacuum for 3 days

at 180 °C. PS cylinders, oriented normal to the film surface, in a PMMA matrix were produced. Exposure of the diblock copolymer film to UV irradiation under vacuum, followed by sequential rinsing in acetic acid and water, produced PS posts on the surface (Figure 4a). The posts have diameters of 21 ± 1 nm and center-to-center spacing of 42 ± 1 nm. The PS cylinders are in direct contact with the substrate, which is crucial for the retention of the PS nanodots during subsequent fabrication. A 15 nm layer of Cr was then evaporated over the entire surface at 10^{-7} mmHg, and the AFM image is shown in Figure 4b. The films were then sonicated in toluene for 20 min to remove the excess Cr. UV exposure degraded the remaining PS. After rinsing with toluene, a hexagonal array of 21 ± 1 nm diameter holes in a 15 nm thick film of Cr (Figure 4c) was produced.

In summary, very simple routes to generate nanoscopic arrays of metal dots and nanoporous metal films are presented. Filling the block copolymer templates by metal evaporation grants quite a few advantages over using the template as an etching mask. This nondestructive technique ensures the fidelity of replication to produce more well-defined features, without the cumbersome optimization of multiple etching steps. This is an important aspect of any technique that may be applied to further reductions in feature size. The process described here expands the use of block copolymer templates to include those having cylindrical microdomains, which have the advantage of application both as negative and positive templates. The formation of pores or posts is controlled simply by appropriate selection of compositional asymmetry in the copolymer. Variation of the molecular weight of the copolymer enables control over the size and periodicity of the cylindrical microdomains and therefore of the resulting metallic structures. Furthermore, varying the total thickness of metal deposited onto the film, rather than etching parameters, controls the aspect ratio of the metal nanostructures. Although we demonstrate only the formation of gold and chromium nanostructures, this method may be applied to the deposition of many other metals available for evaporative deposition. For these reasons, this route to the generation of arrays of nanostructures is particularly attractive in terms of simplicity and flexibility.

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