Mesoscale Metallic Pyramids with Nanoscale Tips

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ABSTRACT

We report a simple procedure that can generate free-standing mesoscale metallic pyramids composed of one or more materials and having nanoscale tips (radii of curvature of less than 2 nm). Mesoscale holes (100−300 nm) in a chromium film are used as an etch mask to fabricate pyramidal pits and then as a deposition mask to form the metallic pyramids. We have fabricated two- and three-layered pyramids with control over their materials and chemical functionality.

This letter reports a parallel method for fabricating free-standing, monodisperse metallic pyramids from different metals with variable thicknesses. The overall size of these pyramids is on the mesoscale (100−300 nm), whereas their tips are on the nanoscale (1−10 nm). We generated these metallic pyramids using a combination of phase-shifting photolithography (PSP), wet-chemical etching, and electron (e)-beam deposition. The key patterning step in this simple procedure is the use of sub-250-nm holes in chromium as both an etch mask and a deposition mask. In addition, we demonstrate how our technique can generate multilayered pyramidal structures by taking advantage of the layer-by-layer capabilities of e-beam deposition. This work shows how top-down nanofabrication methods can produce anisotropic structures that are reasonably monodisperse, highly uniform in shape and size, and multifunctional.

Sacrificial templates are useful for molding the size and shape of interesting free-standing nano- and mesostructures. Typically, solid and supported structures, such as nanometer-sized pores in anodized alumina membranes or micrometer-sized etched pits in silicon, are used as templates. Electrodeposition of conducting materials or molding of polymers is used to reproduce the shape and structure of the template; the templates are then removed by the appropriate etchants. Free-standing structures such as metallic (and multilayered) rods, pyramidal tips for scanning probe applications, and micrometer-sized metallic pyramidal shells can be produced from solid templates.1−5 The pyramidal shells were found to exhibit tips with a radius of curvature r as small as 50 nm.5 Other types of templates, including silica spheres, have recently been used to fabricate metallic structures with unusual shapes. Such structures were generated by e-beam deposition of metal onto silica spheres followed by etching of the sphere template. Submicrometer “half-shells” made from different metals as well as “crescent moon” structures with sharp edges in silver were produced.6,7 The edges of these silver shell structures enhanced the local electromagnetic field, and the Raman scattering of rhodamine 6G from isolated, individual crescent moon structures could be detected.7

The optical properties of noble metals depend critically on their size and shape on the nanoscale. Surface plasmon resonances were first observed in noble metal films, whose thickness and surface corrugation determined how light was absorbed and scattered.8 Solution-phase syntheses provide a flexible route to control the size and shape of metallic nanoparticles, which enables careful tuning of their optical properties. The properties of anisotropic nanoparticles can be quite different from those of spherical particles of similar sizes.9−12 Theoretical studies have shown that very sharp points—tips—in noble metals can concentrate electromagnetic fields, which can dominate the optical properties of nanostructures.13−16 A common drawback of solution-based syntheses of noble metal nanoparticles, however, is the formation of various other shapes in addition to that of the desired product. Besides tunability by size and shape, different material combinations can also be used to control the optical behavior. Core−shell particles composed of layers of different metals or alternating layers of metals and dielectrics exhibit distinct properties as the thickness of each layer is varied.17,18 Although this layer-by-layer synthesis can produce core−shell particles in high yield (e.g., 95% of silica spheres can be converted into core−shell particles19), precise control over the thickness of the layers and the monodispersity of the product remains a challenge.

Recent advances in nanofabrication tools have made access to sub-100-nm feature sizes increasingly routine. We and others have developed a nanopatterning tool kit that can
generate nanostructures in a wide range of materials, on a variety of substrates, over areas greater than cm², and in a parallel manner. Laser-assisted direct imprinting can transfer features of less than 20 nm from a patterned fused-quartz mold into silicon; laser-assisted embossing can generate zL beakers (50–80 nm) in silicon, which can be used for growing nanocrystals.20,21 Nanosphere lithography can produce hexagonally patterned regions as small as 50 nm of different materials.22–24 Nanoimprint lithography and size-reduction lithography can generate metallic nanostructures of less than 20 nm in size.25–27 Soft nanolithography allows significant control over the uniformity, size, shape, and spacing of nanoscale patterns. For example, catalytic metal dots for the growth of ZnO nanowires can be patterned in square, hexagonal, or 1D arrays; 3D multilayered nanostructures can be constructed using nanotransfer printing; and free-standing silicon nanowires can be made in shapes such as rings and lines.28–30 Top-down methods offer several advantages over bottom-up methods for the generation of free-standing, sub-250-nm structures: (i) monodispersity of particle size; (ii) uniformity of particle shape; (iii) increased flexibility to form particles out of more than one material; and (iv) precise control of the thicknesses of materials in multilayer particles.

Figure 1 outlines the procedure for generating metallic pyramids within the etched pits of a Si(100) substrate using a Cr film patterned with sub-250-nm holes as both the etch mask and deposition mask. First, a square array (covering ~1 in.²) of photoresist posts (typical diameters ~250 nm; smallest diameters ~100 nm) was patterned on a Si(100) wafer using PSP. In brief, these posts were formed by exposing photoresist (Shipley 1805) through a h-PDMS mask patterned with a square array of dots28,31,32 and removing the exposed resist with 351 Microposit developer. Cr (20 nm) was deposited by e-beam on these photoresist posts, and lift-off of the resist was achieved by sonicating the pattern in acetone. Round holes, with very smooth edges, were formed in the Cr film (Figure 2A).

Next, we anisotropically etched the exposed silicon with a KOH/isopropyl alcohol (IPA) solution to form pyramidal pits underneath the Cr nanoholes (Figure 2B). We took advantage of this undercutting to fabricate pyramids smaller than the size of the etched pyramidal pits and defined by the size of the Cr hole. The smoothness and circular symmetry of the nanoholes in the Cr etch mask are crucial in forming symmetrical (square) pyramidal pits. Oblate or rough Cr holes produced rectangular or irregularly shaped pyramids. We then used the Cr mask as a deposition mask and evaporated a 50-nm Ni film (1–4 Å/s) onto these patterns (Figure 2C). The patterned samples were placed in the evaporator so that they were in the line of sight of the evaporation source; the film thickness was monitored with a quartz crystal microbalance. Finally, we etched the Cr film with a commercial etchant (Transene Corp., Danvers, MA) to reveal Ni pyramids (50 nm thick and ~250 nm across their base) situated within the centers of the silicon pyramidal pits (Figure 2D). The monodispersity of the pyramids was estimated by the differences in the sizes of the Cr holes. From SEM images taken at over seven different and representative locations (>10⁶ holes) over a 1-in.² sample, we estimate a monodispersity of <10%.

To release the Ni pyramids from the silicon template, we etched this pattern with KOH/IPA (Figure 3A). For our patterned area (pyramids spaced 2 μm × 2 μm over 1 in.²), we generated ~10⁸ pyramids/in.². These mesoscale pyramids can be isolated using an ~1-T SmFeB magnet or centrifugation (3000 rpm for 5 min). Because Ni is a hard magnetic material, the 50-nm-thick pyramids isolated by the strong magnet tended to clump together or to align into chains.
Chains formed when the Ni pyramids were magnetized in the silicon mold; after release, their remnant magnetization assisted in their alignment. Importantly, a majority (>99.9%) of the pyramidal tips that we observed had a radius of curvature of $r < 10$ nm (Figure 3A, right inset). The facets of the Ni pyramids are remarkably smooth. We propose that the exposed crystalline Si(111) planes of the pyramidal pits assist in molding and merging the nickel grains as they are deposited onto the surface.

We also used this procedure to fabricate pyramids with much thicker side walls; 150 nm of nickel was deposited through the Cr mask of holes (Figure 3B). Certain distinct features of these arrowlike particles indicate the mechanism of pyramid formation: (i) the ridges or notches along the shaft of the arrow reproduce the granular structure of the Cr deposition mask exactly (Figure 3B, left inset); (ii) the diameter of the shaft becomes smaller along the length of the particle, which indicates that the Cr holes are decreasing in size; and (iii) the interior of the shaft is grainy because the metal is no longer depositing directly against a smooth surface. Because of their unique shape, these types of 3D particles would be difficult to fabricate by other nanofabrication routes. In addition to Ni pyramids, we fabricated 50-nm-thick gold pyramids using our method (Figure 3C). The smoothness of the facets and the sharpness of the tips (we observed tips with $r < 8$ nm) make them ideal structures for studying the local electromagnetic field enhancement of noble metal tips.

One of the greatest advantages (besides creating nanoscale tips) of our nanofabrication procedure is our ability to control both the materials and chemical functionality of these pyramids. We have used the layer-by-layer feature of e-beam deposition to create multilayered pyramids of gold and nickel with variable thicknesses. To create two-layered pyramids, we evaporated 25 nm of Au and then 25 nm of Ni through the same Cr-deposition mask (Figure 4A). The inset image...
(tilted 15°) shows a Au/Ni pyramid before it was removed from the etched Si pit. Such mesostructures can be manipulated with magnetic fields because of their magnetic interior and can easily be chemically functionalized on their outer shell. Also, we formed three-layer pyramids (Au/Ni/Au, similar to core–shell structures) that responded to a magnetic field and can have two different or orthogonal types of chemical functionality. Figure 4B shows a 10-nm layer of Ni sandwiched between 25-nm layers of Au (25/10/25). The inset highlights the boundaries between the Ni and Au layers. Trilayer pyramids with different thicknesses of Au and Ni were also fabricated (Figure 4C); remarkably, in these mesostructures, pyramidal tips exhibited radii of curvature of \( r < 2 \text{ nm} \) (inset).

In summary, we have developed a simple procedure for fabricating free-standing mesoscale metallic pyramids with nanoscale tips. Our current method produces \( \sim 10^8 \text{ pyramids/in.}^2 \) (limited only by the size of our \( h \)-PDMS mask), and hence the density of the mesostructures can easily be scaled up. It is possible to improve the monodispersity (\( \sim 1\% \)) of the pyramids by using high-quality masters prepared by other approaches such as interference lithography. Limitations of our technique for pyramid formation include the following: (i) materials must be compatible with the postprocessing steps (e.g., etching the Si template) and (ii) multilayered pyramids can have irregular edge structures. The use of other release methods (e.g., mechanical pressure or molding) and the deposition of materials at different rates and temperatures should overcome these drawbacks. Because the overall size of these structures is determined by the diameters of the Cr holes in the deposition mask, decreasing these diameters can result in sub-100-nm pyramids. In addition, we anticipate that our ability to generate multilayered pyramids with different types of functionality (including insulating materials) can be useful in investigations of certain biological systems. The production of free-standing and isolated noble metal particles with well-defined ultrasharp tips now also enables detailed studies of their optical properties (e.g., localized surface plasmon resonance) and their use as substrates for surface-enhanced Raman spectroscopy. Multifunctional anisotropic mesostructures with nanoscale features have potential in a broad range of applications from cancer therapy to subwavelength optics.

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