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Fabrication of Free-Standing Metallic Pyramidal Shells

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ABSTRACT

This paper describes a technique for fabricating three-dimensional, metallic, pyramidal microstructures with base dimensions of 1–2 μm, wall thicknesses of ~100–200 nm, and tip-curvature radius of ~50 nm. The procedure begins with the fabrication of pyramidal pits in the surface of an n-doped silicon substrate. An electrically insulating surface layer of SiO_2 covers the regions outside the pits. These pits are patterned using either conventional photolithography or soft lithography and formed by selective anisotropic etching. The resulting topographically patterned silicon serves as the cathode for the selective electrodeposition of metal in the pyramidal pits. Removing the silicon template by etching generates free-standing, pyramidal, metallic microstructures.

This paper describes a technique for fabricating three-dimensional, metallic, pyramidal shells, the walls of which have a thickness of ~100 nm. This method uses as templates pyramidal pits of uniform size formed in n-doped silicon by anisotropic etching; electroplating using the silicon making up the pits as the cathode led to selective growth of the deposited metal. Subsequent dissolution of the silicon substrate released the metallic pyramidal shells into suspension. This work demonstrates a technique for the fabrication of free-standing, metallic, pyramidal shells having a uniform size and provides a route to another class of micro- or nanostructure that is potentially useful for bottom-up self-assembly[1−3] and for other uses in micro- and nanofabrication.

A limited number of shapes, including spheres, hemishells, rods, prisms, and cubes, can be prepared as small metal particles with uniform size.[2−9] The use of templates in the formation of metal structures with different shapes is common: examples include mesoporous silica and zeolites or anodic alumina membranes as template for fabricating nanowires,[4,10−12] nanowires or nanoparticles as templates for fabricating tubular or shell structures,[9,13−16] and others.[17−19] We have described previously the fabrication of metallic half-shells with diameters of 100−500 nm and walls that were 8−15 nm thick by e-beam evaporation deposition of a thin, metal film onto an array of spherical silica colloids, followed by dissolution of the colloidal template.[2]

Anisotropic etching of single-crystal silicon substrates has been used extensively for fabricating sharp tips for atomic force microscopy.[20] Electroplating directly onto a doped silicon substrate without a seed layer has also been used for the fabrication of metallic microstructures for microelectromechanical systems (MEMS).[21−23] The method described here for fabricating free-standing, metallic, pyramidal shells combines patterning and anisotropic etching of silicon with electrodeposition. The method comprises three principal steps: (i) fabrication of the pyramidal pits in the silicon substrate; (ii) deposition of metal on the walls of these pits by electroplating; (iii) dissolution of the silicon template to generate free-standing, pyramidal, metal shells.

Fabrication of Pyramidal Pits on a Silicon Substrate. Step 1 in Figure 1 outlines two methods that we used to generate silicon templates with pyramidal pits. In both methods, we chose an n-doped Si wafer (resistivity ~0.002−0.004 Ω·cm) with a thermally generated SiO_2 layer (~200 nm) as the substrate; the insulating layer of SiO_2 ensured that the electroplating of metal occurred exclusively in the conductive pyramidal pits, not on the top surface of the template.

The first method for fabricating the template is based on conventional photolithography (as shown in Figure 1a). We first exposed the photoresist (Shipley 1805) using a mask patterned with 2-μm-wide lines spaced by 2 μm. We then exposed the photoresist again using the same mask rotated by ~90° to create a grid of 2-μm × 2-μm squares. We coated this substrate with a layer of Ti (5 nm, as an adhesion layer) and Pd (40 nm) using electron-beam physical vapor deposition. We sonicated the sample in acetone to remove the photoresist. This sequence of steps generated a Ti/Pd grid pattern on the SiO_2/Si substrate. We then etched the unprotected areas of SiO_2 anisotropically using a reactive

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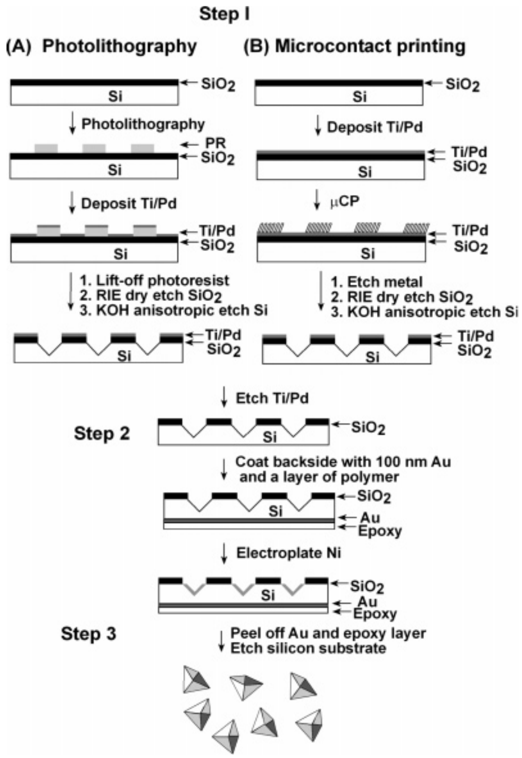

Figure 1. Scheme for the fabrication of metallic pyramidal shells, using (A) photolithography and (B) soft lithography.

ion etch (a Nexx-Cirrus 150 RIE with CF_4 plasma at 15 mTorr for 240 s). The pattern of SiO_2 formed in this step served as a mask for the anisotropic etching of the underlying silicon in KOH/i-PrOH.[24−26]

The second method used to generate the pyramidal pits on the SiO_2/Si substrate started with soft lithography (Figure 1B).[27,28] We first deposited a layer of Ti/Pd (5 nm/40 nm) onto a SiO_2/Si surface using physical vapor deposition. We then used a PDMS stamp patterned with 2-μm wide parallel lines to print a SAM of hexadecanethiol ($C_{16}SH$) on the palladium surface, keeping the stamp in contact with the surface for 5 s. We removed the stamp and placed it back into contact with the surface with the orientation of the pattern rotated by ~90° from the first printing. These two steps produced a square grid of the thiol ink. Chemical etching with iron(III)-based etchant (Palladium Etch TFP from Transene, Inc., Danvers, MA) removed the palladium/titanium (Ti/Pd) film in the areas not coated by the thiol.[29] Anisotropic RIE of SiO_2 with CF_4 and of silicon with KOH, generated pits with pyramidal shapes in the silicon substrate. Immersion of the substrate in an aqua regia solution (HCl/HNO_3 = 3:1) for 10 s removed the remaining Ti/Pd film from the surface. Figure 2A,B shows pits with a pyramidal shape in a silicon substrate, fabricated using photolithography and soft lithography, respectively.

Electroplating Metal on the Exposed Conductive Silicon Surface. We used the n-doped silicon substrate with pyramidal pits as the cathode for the electrodeposition of metals (e.g., nickel, gold, or palladium). Coating the backside of the silicon cathode with a 200-nm thick gold layer was necessary to achieve uniform electrodeposition across the

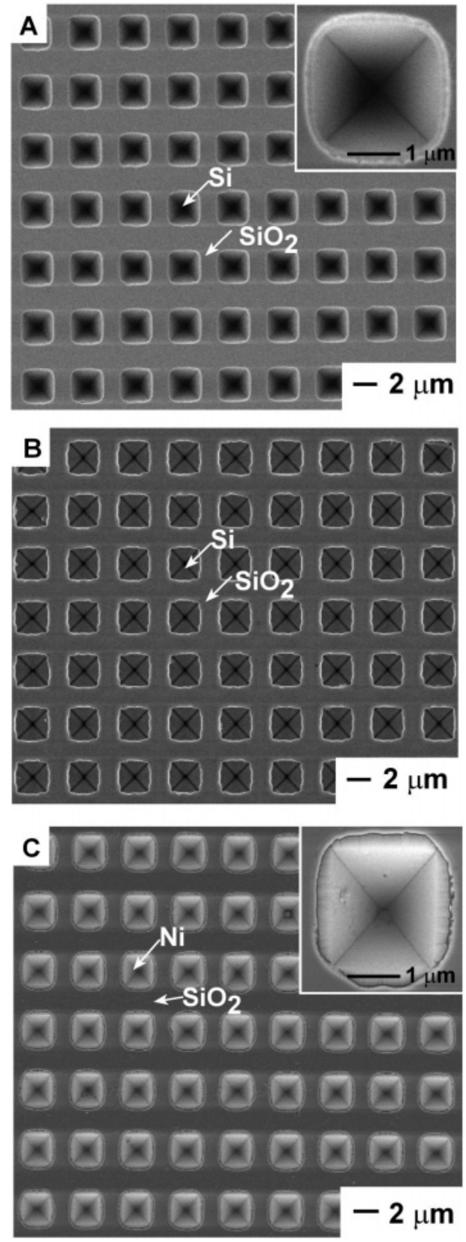

Figure 2. Scanning electron micrographs (SEMs) of (A) the anisotropically etched silicon substrate with pyramidal pits fabricated using photolithography; (B) the anisotropically etched silicon substrate with pyramidal pits fabricated using soft lithography; (C) pits coated with electroplated nickel.

whole silicon substrate;[23,30] we assume that adding the conducting backplane minimized IR drops across the wafer and equalized the potential in all of the pits. Before electroplating, we pretreated the silicon substrate with 1% HF solution for 1 min. This treatment improved the uniformity of the initiation of metal deposition on the silicon surface (perhaps by removing a SiO_2 surface layer). The electroplating occurred exclusively in the pits; the thick SiO_2 layer successfully insulated the top surface of the substrate. Figure 2C is an SEM image of the silicon substrate with pyramidal pits filled with nickel after electroplating at 15 mA/cm^2 (calculated for the entire area of the substrate, not just the surface of the pits) for 30 s using a commercially

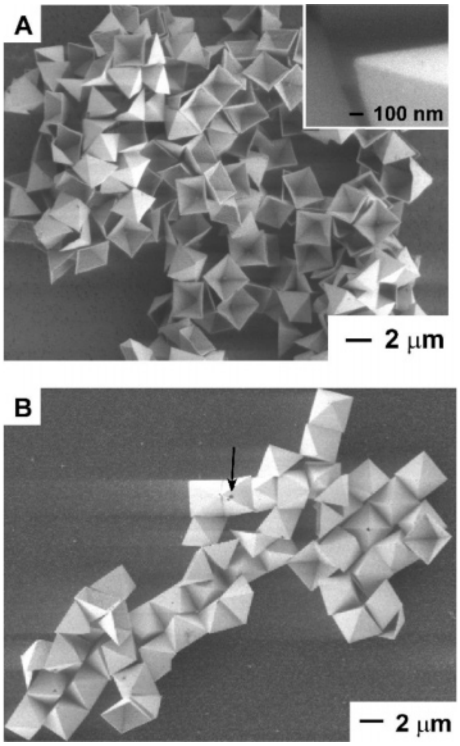

Figure 3. SEMs of free-standing (A) nickel, and (B) gold pyramidal shells. Inset of (A) shows the tips of the nickel pyramidal shells having a radius of curvature ∼50 nm.

available electroplating solution (RTU Nickel Sulfamate from Technic Inc., Cranston, RI).

Removal of the Silicon Template by Etching and Generation of Free-Standing Pyramidal Metallic Structures. We dissolved the silicon substrate completely in KOH solution, leaving the metallic pyramidal shells intact. The sample was then centrifuged and washed four or five times in water. Figure 3A shows an SEM image of nickel pyramidal shells with a wall thickness of ∼200 nm; the thickness of the walls can be modulated by controlling the electroplating time and current density. Figure 3B shows an SEM image of free-standing gold pyramidal shells with a wall thickness of ∼100 nm; these shells formed by electroplating at a current density of 0.5 mA/cm^2 for 60 s using a commercially available electroplating solution (Orotemp 24 from Technic Inc., Cranston, RI). Some defects (most noticeably, holes) occur in the walls of the shells; we attribute these defects to nonuniform nucleation, perhaps due to the presence of less-conductive regions of the exposed silicon surface, during electroplating. The arrow in Figure 3B shows a representative defect.

In conclusion, this procedure provides a route to fabricate metallic shells with a pyramidal structure, the tips of which have a radius of curvature of ∼50 nm. The uniformity of the template fabricated by photolithography or soft lithography ensures the uniformity in shape and size of the pyramidal shells. These pyramid-shaped microobjects are potentially useful for exploring bottom-up self-assembly. We believe that the sharp tip from the metallic pyramidal shells will produce strong enhancements in optical and magnetic fields that will be useful in studies involving surface plasmons or magnetic field concentrators.

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References

(1) Sun, S.; Murray, C. B.; Doyle, H. *MRS Sym. Proc.* **1999**, *577*, 385−398.
(2) Love, J. C.; Gates, B. D.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Nano Lett.* **2002**, *2*, 891−894.
(3) Love, J. C.; Urbach, A. R.; Prentiss, M. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12696−12697.
(4) Martin, C. R. *Science* **1994**, *266*, 1961−1966.
(5) Haynes, C. L.; McFarland, A. D.; Smith, M. T.; Hulteen, J. C.; Van Duyne, R. P. *J. Phys. Chem. B* **2002**, *106*, 1898−1902.
(6) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176−2179.
(7) Sun, Y.; Mayers, B.; Xia, Y. *Nano Lett.* **2003**, *3*, 675−679.
(8) Puntes, V. F.; Zanchet, D.; Erdonmez, C. K.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, *124*, 12874−12880.
(9) Metraux, G. S.; Cao, Y. C.; Jin, R.; Mirkin, C. A. *Nano Lett.* **2003**, *3*, 519−522.
(10) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712.
(11) Scott, B. J.; Wirnsberger, G.; Stucky, G. D. *Chem. Mater.* **2001**, *13*, 3140−3150.
(12) Martin, B. R.; Dermody, D. J.; Reiss, B. D.; Fang, M.; Lyon, L. A.; Natan, M. J.; Mallouk, T. E. *Adv. Mater.* **1999**, *11*, 1021−1025.
(13) Jackson, J. B.; Halas, N. J. *J. Phys. Chem. B* **2001**, *105*, 2743−2746.
(14) Oldenburg, S. J.; Westcott, S. L.; Averitt, R. D.; Halas, N. J. *J. Chem. Phys.* **1999**, *111*, 4729−4735.
(15) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711−714.
(16) Sun, Y.; Wiley, B.; Li, Z.-Y.; Xia, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9399−9406.
(17) Yang, H.; Love, J. C.; Arias, F.; Whitesides, G. M. *Chem. Mater.* **2002**, *14*, 1385−1390.
(18) Melosh, N. A.; Boukai, A.; Diana, F.; Gerardot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112−115.
(19) Xu, Q.; Gates, B.; Whitesides, G. M. *J. Am. Chem. Soc.* **2004**, *126*, 1332−1333.
(20) Albrecht, T. R.; Akamine, S.; Carver, T. E.; Quate, C. F. *J. Vac. Sci. Technol. A* **1990**, *8*, 3386−3396.
(21) Herino, R.; Jan, P.; Bomchil, G. *J. Electrochem. Soc.* **1985**, *132*, 2513−2514.
(22) Gobet, J.; Cardot, F.; Bergqvist, J.; Rudolf, F. *J. Micromech. Microeng.* **1993**, *3*, 123−130.
(23) Sander, D.; Hoffmann, R.; Relling, V.; Mueller, J. *J. Microelectromech. Syst.* **1995**, *4*, 81−86.
(24) Kim, E.; Kumar, A.; Whitesides, G. M. *J. Electrochem. Soc.* **1995**, *142*, 628−633.
(25) Xia, Y.; Mrksich, M.; Kim, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 9576−9577.
(26) Petersen, K. E. *Proc. IEEE* **1982**, *70*, 420−457.
(27) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550−575.
(28) Gates, B. D.; Xu, Q.; Love, J. C.; Wolfe, D. B.; Whitesides, G. M. *Annu. Rev. Mater. Res.* **2004**, *34*, 339−372.
(29) Love, J. C.; Wolfe, D. B.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 1576−1577.
(30) Tien, J.; Terfort, A.; Whitesides, G. M. *Langmuir* **1997**, *13*, 5349−5355.

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