

Fabrication of Size-Tunable Large-Area Periodic Silicon Nanopillar Arrays with Sub-10-nm Resolution

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Here, we present a fabrication procedure that can produce large-area, size-tunable, periodic silicon nanopillar arrays, using metal templates that are created via nanosphere lithography. The size of the silicon nanopillars can be systematically controlled by an oxidation and etching process. The smallest size of nanopillars fabricated via this method is ~ 9 nm, and the area covered with nanopillars is > 1 cm². Using this approach and nanoimprint lithography, it is possible to pattern sub-10-nm metal nanoparticles with a particle density as high as 1×10^9 particles/cm².

One of the most important research directions in the development of nanotechnology is to explore our capability of fabricating ever-smaller nanostructures over a large area, possibly in a cost-effective way. Both fundamental research and industrial applications will benefit from our ability of making nanostructures with features < 10 nm in size. It is known that the metal particle size can affect the electronic structure of a metal particle for sizes < 5 nm. Using metal nanoclusters as catalysts, the structure sensitivity of turnover rates and production distribution has been observed in the partial oxidation of ethylene on silver, as well as in the dehydrogenation, hydrogenolysis, and dehydrocyclization of hydrocarbons on platinum.^{1–3} If we can systematically control the metal catalyst surface structure, the size of the metal catalyst, and the interparticle distances between metal particles, it will allow us to access the most needed information for making heterogeneous catalysis with a high reaction rate and high selectivity. Currently, electron beam lithography is the most commonly used technique to create nanostructures with a high degree of control. However, the generation of secondary electrons during electron bombardment makes it difficult to achieve sub-10-nm patterning.⁴ It is also impractical to utilize electron beam lithography to pattern large areas, because it is a sequential patterning technique. Scanning-probe-based lithographic techniques^{5–7} have also been used to pattern nanostructures with a very high degree of control. However, it is also time-consuming for scanning-probe-based lithography to create large-area patterns at the nanometer scale. Recent development in the “spacer lithography” also permits the creation of sub-40-nm wires, starting from 600-nm features that have been produced by photolithography.^{8–10} Using size reduction techniques, 20-nm-wide single-crystal silicon nanowire arrays have been obtained. Further oxidation of the silicon nanowires and etching in HF solution reduced the dimensions to sub-10 nm.¹¹ It has been demonstrated that 7×10^8 nanowires on a 4 in. silicon wafer can be fabricated with the total patterned surface area of ~ 1 cm². However, the nanostructures produced

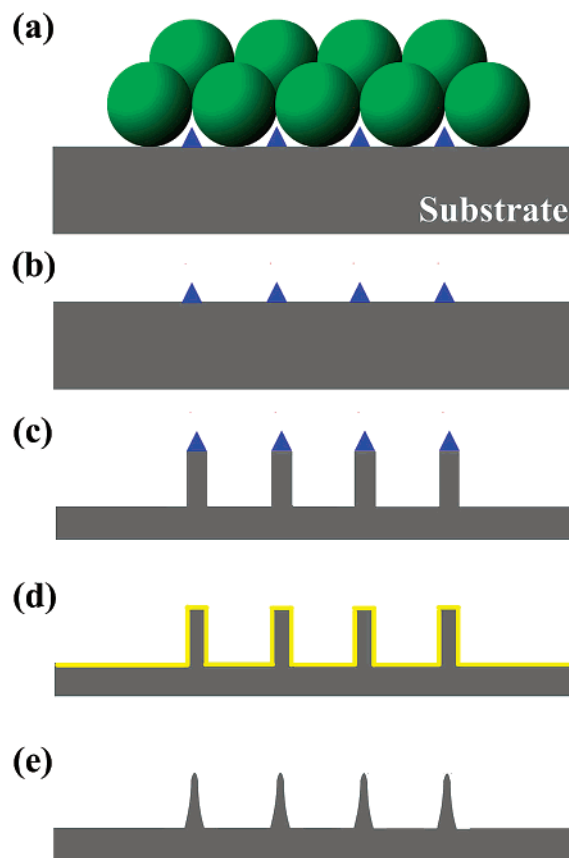


Figure 1. Scheme of the fabrication of large-area, periodic sub-10-nm silicon nanopillar arrays. Panel a shows the silicon substrate coated with a double layer (DL) of polystyrene beads by nanosphere lithography, and a chromium film is deposited on top of the polystyrene nanospheres. In panel b, after the lift-off process, periodic chromium nanoparticle arrays are formed on the substrate surface, and these metal nanoparticles work as etching masks in a reactive-ion-etching process. In panel c, after the reactive ion etching, silicon nanopillar arrays are formed. Panel d shows that chromium nanoparticles on top of the nanopillars are removed by a chromium etchant, and the silicon nanopillar arrays are oxidized in an oven that has been purged with oxygen. Panel e shows that the size of the nanopillars can be reduced by removing the oxide layer in a BOE solution.

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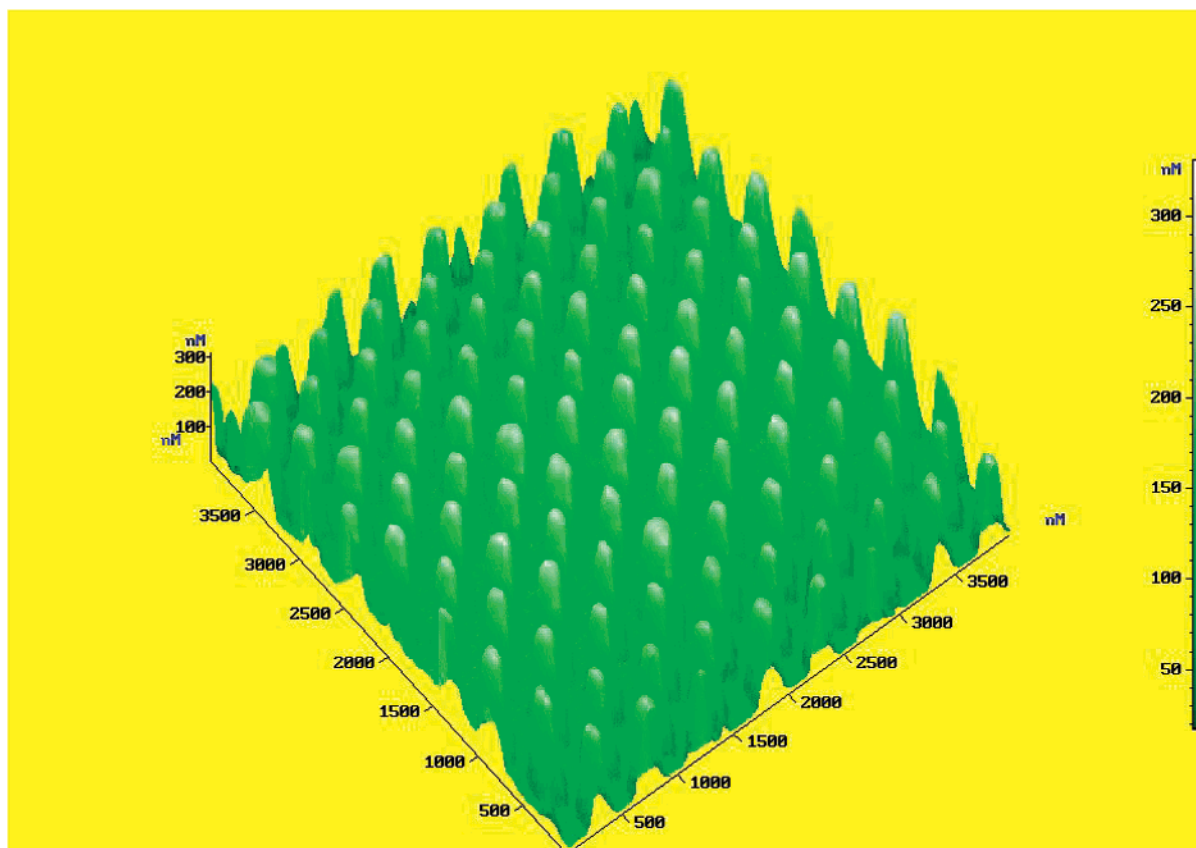


Figure 2. AFM image of silicon nanopillar arrays formed by a 440-nm DL polystyrene template. Reactive-ion-etching conditions were as follows: CHF_3 flow rate, 20 sccm; O_2 flow rate, 2 sccm; pressure, 100 mTorr; power, 80 W.

by this method currently are continuous nanowires, whereas most applications, such as sensors and catalysts, favor nanostructures in a nanoparticle format.

To create large-area, high-resolution nanostructures, various alternative techniques have been developed. The use of so-called "soft materials" to pattern nanostructures is one of the most active research areas in today's materials science community.¹² There are many advantages of using "soft materials" for building nanostructures, including lower cost, higher speed, more flexibility, and easier implementation. It has been shown that soft materials such as colloidal particles,^{13–23} block copolymers,^{24–27} DNAs,^{28,29} and proteins^{30,31} can be used to create templates for patterning nanostructures through self-assembly processes. Despite the fruitful achievements of patterning nanostructures using soft materials, it is not always easy to control the size of the nanostructure, which is normally achieved using different sizes or compositions of the soft materials. Very often, the conditions of forming well-ordered self-assembled nanostructures vary when the size and composition of the patterning materials change, and the degree of tunability is also limited by the available materials. To control the size of the nanostructure systematically, one may choose to start with a single template and tailor the size of the nanostructures using other techniques. It has been reported recently that large-area periodic nanostructures can be obtained by transferring the patterns formed by the self-assembled nanospheres into silicon substrates that form nanopillar arrays and replicating the nanostructures using nanoimprint lithography.³² The size of the silicon nanopillars can be trimmed by oxidation and etching processes; therefore, this approach provides an excellent way to produce size-controllable nanostructures. In this letter, we report a simple fabrication process for producing large-area, size-tunable, periodic nanopillar arrays with a lateral resolution of <10 nm.

Figure 1 illustrates the scheme for fabricating size-tunable, periodic silicon nanopillars. The first step in this process is to create metal masks that can be used in the reactive etching process. To create periodic nanostructures, nanosphere lithography is used to form close-packed structures, which serve as the templates for metal deposition. By adjusting the concentration of nanospheres in solution, both single-layer (SL) and double-layer (DL) close-packed structures can be obtained on the substrate surfaces. Figure 1a shows an illustration of what happens when a DL nanosphere template is used in the metal deposition process. After deposition of a layer of chromium, and a lift-off process, large-area periodic chromium nanoparticles can be obtained (see Figure 1b). The pattern formed by periodic chromium nanoparticles can be transferred to silicon by reactive ion etching, producing periodic silicon nanopillar arrays (as depicted in Figure 1c). After the chromium nanoparticles have been removed in a chromium etchant, the substrate is placed in an oven that has been purged with pure oxygen, to form a layer of silicon oxide on the surfaces of nanopillars (see Figure 1d). The thickness of the oxide layer can be precisely controlled by the oxidation time. After the oxide has been removed in the oxide etching solution, silicon nanopillars with smaller lateral dimensions can be obtained (as shown in Figure 1e). Using this approach, it is possible to reduce the size of the nanopillars systematically to the sub-10-nm regime.

In this experiment, nanosphere lithography is used to prepare large-area metal particles. The detailed description of nanosphere lithography can be found in the literature.^{16,17,32} In brief, silicon substrates of several square centimeters were cut from *n*-doped silicon (100) wafers (Gredmann). To clean these silicon substrates, piranha solution was used. (Caution: The piranha solution, whose composition is 3:1 concentrated H_2SO_4 :30% H_2O_2 , is explosive.) After sonication in the piranha solution for

30 min, the silicon substrates were rinsed repeatedly with ultrapure water (18.2 M Ω , Millipore Simplicity), acetone, and methanol. To form large-area metal nanoparticles, the silicon substrates were first coated with the solution, which contained the monodisperse polystyrene beads (Bangs Laboratories, Inc. Fishers, IN), Triton X-100 (Aldrich), and methanol (1:400 by volume). By adjusting the speed of the spin coater (800–3600 rpm) and the surfactant concentration, both SL and DL large-area (up to a few square centimeters) close-packed structures have been obtained. These two-dimensional periodic colloidal arrays were then used as the deposition templates for the periodic metal nanoparticle arrays. In this experiment, we prepared chromium nanoparticle arrays by sputtering a layer of chromium (~ 50 nm) on the top of polystyrene templates in an ULVAC sputter deposition system. The deposition rate was ~ 2 nm/min at a total pressure of 1×10^{-3} Pa. After the deposition process, the polystyrene beads were removed by sonicating the substrates in the CH_2Cl_2 solution for 2–4 min. After this process, the chromium particles sitting in the interstices of the polystyrene template remained on the surface, forming large-area, periodic triangular chromium nanoparticle arrays.

To fabricate silicon nanopillar arrays, substrates with chromium nanoparticles were placed in a reactive ion etcher (Oxford Plasmalab 80 Plus). After the etcher was evacuated to $<2 \times 10^{-3}$ Pa, the substrates were cleaned with oxygen plasma (50 mTorr, 80 W) for 30 s, and then a mixture of CHF_3 (20 sccm) and O_2 (2 sccm) at a total pressure of 100 mTorr was used for 25 min. To measure the size and height of the silicon nanopillar, a Solver P47 scanning probe microscope (NT-MDT, Moscow, Russia) with a silicon cantilever (NSG 11, force constant of 11.5 N/m, NT-MDT) was used. Figure 2 shows an AFM image of periodic silicon nanopillar arrays that was fabricated using a DL 440-nm-diameter polystyrene template. This template should produce periodic nanoparticles with a lateral dimension of ~ 60 nm, according to the geometry constraint set by the physical contact of a DL close-packed structure.¹⁶ However, the lateral dimension of the nanopillar shown in the AFM image is >60 nm (~ 100 nm), because of the AFM tip convolution for measuring high-aspect-ratio objects. To measure the lateral dimension of the nanopillar, scanning electron microscopy (SEM) images were taken with a LEO model 1154 scanning electron microscope (5–20 kV). The size of the nanopillar measured in the SEM images is ~ 60 nm, which agrees with their geometry constraint. Figure 2 shows that nanopillar arrays with a very high aspect ratio over a large domain can be produced via this method. The size of a typical perfect domain is $\sim 100\text{--}400 \mu\text{m}^2$. However, the entire substrate surface is covered with domains of nanopillar arrays. The overall defect concentration is estimated to be $<10\%$ of the overall area. The quality of these nanopillar arrays is good enough for various printing experiments, such as nanoimprinting and micro-contact printing, as reported previously.³² To reduce the size of the nanopillars, the chromium mask was first removed by dipping the substrate into a CR7 (Transene) solution for 4 min. The remaining silicon nanopillars were then oxidized in an oven purged with oxygen at 800°C . The silicon oxide on the outside wall of the nanopillars was subsequently removed by an oxide etchant (BOE solution, J.T. Baker) for 10 s. The thickness of the silicon oxide on the nanopillars can be controlled by the oxidation time. Figure 3a shows the size-reduced silicon nanopillar arrays after oxidizing in an oven for 60 min. The size of nanopillars was measured to be 50 nm, which was smaller than those shown in Figure 2. As the oxidation time increased to 90 min, the size of nanopillars was further reduced

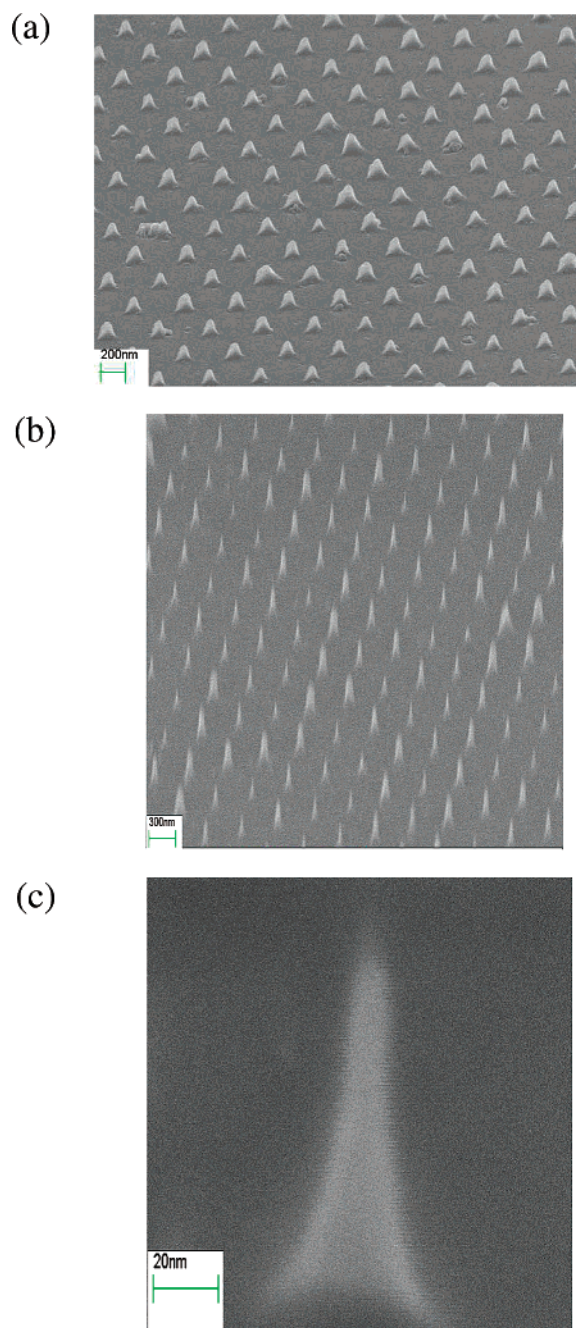


Figure 3. SEM images (45°) of the size-reduced nanopillar arrays. In panel a, the nanopillar arrays were formed using a 440-nm DL polystyrene template, and the oxidation time was 60 min. The lateral dimension of the nanopillar is ~ 50 nm. In panel b, nanopillar arrays were formed using a 440-nm DL polystyrene template, and the oxidation time was 90 min. The lateral dimension of nanopillar is ~ 40 nm. Panel c shows that a sub-10-nm nanopillar can be obtained, using a smaller polystyrene template and longer oxidation time. This last panel of the figure depicts a 9-nm nanopillar formed using a 280-nm DL template and an oxidation time of 150 min.

to 40 nm, as shown in Figure 3b. To obtain sub-10-nm silicon nanopillars, smaller-diameter polystyrene templates and longer oxidation times were used. Figure 3c shows a silicon nanopillar that was fabricated using a 280-nm-diameter polystyrene template, and the oxidation time for the material in the figure was 150 min. The lateral dimension (the size at half-height) of this nanopillar was measured to be 9 nm.

We have systematically fabricated periodic silicon nanopillars with different lateral dimensions using two different templates: 280- and 440-nm-diameter double-layer (DL) polystyrene

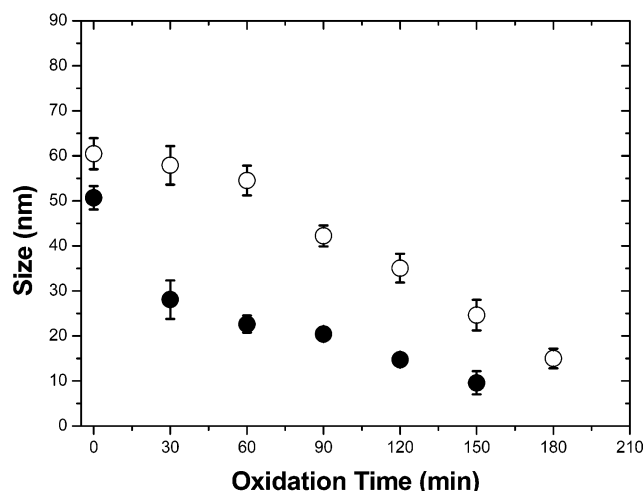


Figure 4. Relationship between the lateral dimension of the nanopillars and the oxidation time ((●) nanopillars fabricated by 280-nm DL templates and (○) nanopillars formed on 440-nm DL templates).

templates. The measured lateral dimensions of the silicon nanopillars are plotted as a function of the oxidation time in Figure 4. The oxidation rate for the silicon nanopillar is estimated to be 0.3 nm/min, which indicates that the size of the nanopillars can be precisely controlled. Note that, as the oxidation time increases, the uniformity of the nanopillar arrays becomes poorer, which is due to severe undercutting in the prolonged oxidation and etching process. Also, note that the density of the nanopillar array is $\sim 1 \times 10^9/\text{cm}^2$ when a DL 280-nm-diameter polystyrene template is used. If the nanopillar arrays are used as the stamp in nanoimprint lithography, such as those demonstrated in a previous study,³² it is possible to create sub-10-nm metal nanoparticles over a large area with a particle density as high as $1 \times 10^9/\text{cm}^2$. Higher-density nanopillar arrays can be achieved using smaller-diameter polystyrene beads or utilizing templates that have been formed by a block copolymer,²⁴ where an array density as high as $\sim 10^{11}/\text{cm}^2$ has been demonstrated.

In summary, we have developed a low-cost, high-throughput fabrication process for producing large-area, well-ordered periodic nanopillar arrays with a feature size of <10 nm. By adjusting the oxidation time, the size of silicon nanopillars can be precisely controlled. The periodic nanopillar arrays fabricated by this method can be used to produce nanoparticles via printing lithography methods such as nanoimprinting lithography.

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