Size- and Shape-Controlled Fabrication of Large-Area Periodic Nanopillar Arrays

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A simple process for the fabrication of large-area well-ordered periodic nanopillar arrays have been developed based on a combination of colloidal lithography and etching techniques. Large-area nanopillar arrays have been successfully fabricated by this approach. The lateral dimensions of nanopillars as small as 40 nm and the aspect ratio as high as 7:1 have been achieved. Our results indicate that it is possible to control the size, shape, and height of nanopillar arrays by fine-tuning the etching recipes. These periodic nanopillar arrays can be used as stamps for nanoimprinting lithography and contact printing lithography to produce more complex periodic nanostructures.

Introduction

One of the most important issues in the development of nanotechnology is to fabricate nanostructures with size and shape control because it allows us to modify the optical, magnetic, catalytic, and electrical transport properties of materials. To realize such opportunity in various applications, the first step is to develop cheap, high-resolution, high-throughput lithographic methods. Current approaches for fabricating sub-100-nm nanostructure mainly rely on the e-beam lithography, which provides precise size and shape control. However, it is impractical to employ e-beam lithography for the large-scale fabrication because of its high cost and slow speed. In the past few years, various alternative cost-effective, high-throughput fabrication processes have been investigated.5–6 Among these approaches, many promising results7 have been demonstrated using colloidal lithography. It has been shown that both two-dimensional8–13 and three-dimensional14–18 nanostructures can be produced by colloidal lithography.

The basic principle for colloidal lithography is to utilize the templates formed by monodisperse colloidal spheres for the construction of nanostrutures.17,18 Since monodisperse colloidal spheres are used in colloidal lithography, periodic colloidal arrays are formed as a result of the self-organization process. These periodic colloidal arrays not only can be used as the building blocks for various nanostructures but also have been shown to have great potential in many applications such as photonic crystals,20,21 data storage,21,22 and biosensors.23 Because the formation of periodic colloidal arrays relies on the physical contact of colloidal particles, the size and the shape of the templates formed by colloidal lithography cannot be easily changed. Several approaches have been explored to control the geometry of the colloidal arrays including self-assembly in patterned areas,24,25 electrostatic assembly,26 electrophoretic deposition,27,28 and chemically functionalized surfaces.29 However, the colloidal arrays produced by these meth-

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ods are difficult for use as templates for the construction of nanostructures. To construct nanostructures with independent size and shape control, we propose to utilize colloidal lithography to create two-dimensional periodic nanostructures, which are then transferred into silicon substrates by reactive ion etching, forming periodic nanopillar arrays. When various etching recipes are used for silicon, silicon nanopillars with different size and shape can be obtained. The silicon nanopillar arrays fabricated by this method can be further used as stamps to print various materials on substrate surfaces using techniques such as nanoimprinting, microcontact, and nanocontact printing.

In this article, we report the detailed fabrication procedure for producing large-area (up to cm²), well-ordered periodic silicon nanopillar arrays. Our approach is to prepare the etching masks on silicon substrates using the close-packed structures formed by monodisperse polystyrene beads. After metal deposition, lift-off, and etching processes, large-area periodic silicon nanopillar arrays have been obtained. Our results indicate that with variation of the etching parameters, such as mask materials and etching recipes, the size and the shape of silicon nanopillars, indeed, can be modified, therefore achieving size and shape control of nanostructures.

**Experimental Section**

A typical fabrication procedure for periodic silicon nanopillars is to transfer the periodic patterns, which can be produced via various lithographic techniques, into silicon substrates by reactive ion etching. In our experiment, we have utilized nanosphere lithography to create large-area periodic metal patterns. The detailed procedure of nanosphere lithography can be found in the literature. In short, N-doped silicon (100) wafers (Gredmann) were cut into several cm² pieces. These silicon substrates were first cleaned in piranha solution (3:1 concentrated H₂SO₄:30% H₂O₂; CAUTION: Explosive!) for 30 min and then rinsed repeatedly with ultrapure water (18.2 MΩ, Millipore Simplicity). These substrates were further cleaned with acetone and methanol before use. Monodisperse polystyrene beads of various diameters purchased from Bangs Laboratories, Inc. (Fishers, IN) were diluted in a solution of surfactant Triton X-100 (Aldrich) and methanol (1:400 by volume). Polystyrene solution was then spin-cast onto silicon substrates (~1 cm², Gredmann) to form hexagonally closed-packed two-dimensional colloidal crystals. By adjusting the speed of the spin-coater (800–3600 rpm) and the surfactant concentration, both single-layer (SL) and double-layer (DL) large-area (up to 1 cm²) close-packed structures have been obtained similar to those reported previously. These two-dimensional periodic nanosphere arrays were then used as the deposition templates. Two different metals were deposited on the polystyrene templates as etching masks. The aluminum masks were fabricated by depositing a 50-nm-thick Al film on the top of the polystyrene wafers at a rate of 10 Å/min in an ULVAC sputter deposition system at a pressure of 10⁻³ Pa, while the chromium masks were prepared by reactive ion etching.

In this experiment, both single-layer (SL) and double-layer (DL) polystyrene templates have been used to produce metal masks. As observed from previous experiments, these two types of templates formed triangular metal particles into two different lattice arrangements, hexagonal and triangular. Therefore, the nanopillar arrays fabricated by these metal masks possess the same lattice arrangement as shown in Figure 1a,b. These nanopillar arrays were fabricated using the

**Figure 1.** SEM images (45°) of nanopillar arrays using 100-nm-thick Al masks formed by (a) a SL 440-nm-diameter polystyrene template and (b) a DL 440-nm-diameter polystyrene template. Etching conditions: CHF₃ (20 sccm), O₂ (2 sccm), total pressure 100 mTorr, and 80-W rf power.
aluminum masks formed by depositing a layer of 100-nm-thick aluminum on the template formed by 440-nm-diameter polystyrene beads. The height of the nanopillars was measured to be 440 nm after 60 min of etching using a gas mixture of CHF₃ (20 sccm) and O₂ (2 sccm) at a total pressure of 100 mTorr. Because the metal masks were formed by depositing metals into the interstices of the close-packed polystyrene beads, the lateral dimension of metal mask is determined by the diameters of polystyrene beads. For 400-nm-diameter polystyrene beads, the lateral dimension of the triangular metal nanoparticles (the base of triangles) would be around 118 nm for a single-layer template, while the double-layer template would produce 79-nm metal nanoparticles. However, due to the undercut in the etching process, the lateral dimensions of these nanopillars were measured to be 70 and 55 nm, respectively. The aspect ratios for nanopillar arrays using SL and DL templates were about 6:1 and 7:1, respectively.

To see how the metal masks affect the formation of nanopillars, the 100-nm-thick aluminum masks were replaced by 50-nm-thick chromium masks. Nanopillar arrays with slightly different shapes have been obtained as shown in Figure 2. In this fabrication process, the etching gas mixture was the same as the previous one but the total pressure was decreased to 25 mTorr and the etching time was also reduced to 16 min. From Figure 2 it can be seen that the aluminum masks produced nanopillars with round tips whereas the tips of nanopillars fabricated by chromium masks were much sharper. The shape of nanopillars can also be altered by using different etching recipes. Figure 3 displays the nanopillar arrays fabricated using a gas mixture of CHF₃ (20 sccm) and O₂ (2 sccm), 30 mTorr, 9 min, and 100-W rf power. Wet etching conditions: oxidation at 800 °C for 2 h, and 30 s in BOE solution.

To further explore the possibility of controlling the shape of nanopillars using various etching schemes, we have utilized combinations of dry and wet etching. Figure 4a shows triangular-shaped nanopillars with
very straight sidewalls. These nanopillars were obtained by first depositing 50-nm thick chromium on a DL 440-nm-diameter polystyrene template and etching in a mixture of CHF3 (20 sccm) and O2 (2 sccm) for 15 min. After this procedure, the chromium mask was removed by dipping the substrate in a CR7 (Transene) solution for 4 min. The remaining silicon nanopillars were then oxidized in an oven purged with oxygen at 800 °C for 40 min. The silicon oxide on the outside wall of the nanopillars was then removed by etching in a BOE solution (J.T. Baker) for 10 s. If the chromium masks were not removed before the oxidation process, silicon nanopillars with very sharp tips (aspect ratio 7:1) can be obtained as shown in Figure 4b. To fabricate silicon nanopillars with such high aspect ratio, a SL 280-nm template has been employed, and the metal used was a 40-nm-thick chromium layer. After etching in a mixture of CHF3 (20 sccm) and O2 (2 sccm) for 9 min, the substrate was oxidized at 800 °C for 2 h. The remaining oxide was removed by dipping the substrate in a BOE solution for 30 s.

In addition to the shape of the nanopillar, the size and the height (the aspect ratio) of nanopillars are also other important features of nanopillars. To control the size and height of nanopillars, we have systematically investigated SL polystyrene templates with different sizes. The etching recipe used in this test was a mixture of CHF3 (20 sccm) and O2 (2 sccm) at a total pressure of 25 mTorr, and the rf power was 80 W. The results are depicted in Figure 5. Figure 5a shows the relationship between the etching and height of nanopillars for various sizes of polystyrene templates. It can be clearly seen that there exists a linear relationship between the etching time and the height of nanopillars. Since the size of the nanopillar reduces as the etching time increases, we have also measured the lateral dimensions of the nanopillar as a function of etching time (shown in Figure 5b). However, as the etching time increases, the undercut of the nanopillar also increases, which prevents the formation of nanopillars with very high aspect ratio.

It is remarkable to see that our fabrication procedure can control the size of nanopillars as suggested from Figure 5b. This is a great improvement from the colloidal lithography in which the size of nanoparticles cannot be altered because they are formed in the interstices of colloidal particles. Our approach offers an easy way to adjust the size and shape of nanopillars. To construct more versatile nanostructures, the periodic nanopillar arrays fabricated by this method can be used as stamps to “print” various materials. Nanoimprint lithography is one good candidate where the nanopillar arrays are pressed against silicon substrates coated with PMMA. Nanoparticles with desired size and shape could be obtained after deposition of materials into the imprinted holes and subsequent lift-off process. Other techniques such as microcontact printing and nanocontact printing can also be used to print molecules onto substrate surfaces. Our preliminary results suggested that the quality of nanopillar arrays is good enough to replicate nanostructures with sub-50-nm resolution by nanoimprinting lithography.

**Conclusions**

In conclusion, we have fabricated large-area well-ordered periodic nanopillar arrays using metal masks produced by nanosphere lithography. By adjustment of the etching recipes, the size and shape of nanopillars can be modified independently. The smallest nanopillars obtained by the method is around 40 nm and the highest aspect ratio of nanopillars is around 7:1. Our results indicate that it is possible to control the size, shape, and height of nanopillar arrays using various etching recipes. The periodic nanopillar arrays fabricated by this method can be used to produce more complicated nanostructures via printing lithography such as nanoimprinting lithography and microcontact printing.

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