

Fabrication of silicon hierarchical nanopillar arrays based on nanosphere lithography

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Published in Micro & Nano Letters; Received on 15th May 2014; Revised on 15th August 2014; Accepted on 18th August 2014

A fabrication process of silicon hierarchical nanopillar arrays (NPAs) based on the self-assembled colloid particle monolayer is presented. Using colloid particles assembled by the evaporation-induced method as masks, well-ordered silicon NPAs were fabricated by assessing the deep reactive ion etching process. After the optimisation of the cycles of etching and passivation steps, double-layer hierarchical NPAs were achieved simultaneously. Systematic analysis and experiments were conducted to investigate the transition from well-ordered silicon NPAs to silicon hierarchical NPAs. An explanation of this transition is provided based on the collapsing phenomenon discovered in the experiments.

1. Introduction: Nowadays, the ordering and aggregation of colloidal particles in two dimensions are hot topics, which have attracted much interest, from both fundamental and applied aspects. Spheres made of silica or organic polymer have been applied to generate various functional nanostructures, from photonic bandgap materials [1, 2] to surface plasmon sensors [3]. There are three general categories of particle monolayer fabrication. The first is to spread a colloidal suspension on the solid substrate by spin coating [2, 4–6] and then allow the solvent to evaporate. Another approach is using field-enhanced [7] or molecular interaction-induced [8, 9] deposition from a colloidal suspension onto the solid substrate. The last method is spreading a colloidal suspension of hydrophobic particles on a water surface [10, 11], forming a monolayer on the surface and then transferring them to the solid substrate. These three categories are all broadly adopted to fabricate well-ordered nanoparticle monolayers, which are mainly utilised in nanosphere lithography. Different from the traditional lithography, nanoparticle arrays replace the photoresist as masks to fabricate numerous nanostructures, such as porous material, nanopillars, silicon and polymer nanocones [12–15]. In the work reported in this Letter, the aim was to obtain a well-ordered polystyrene (PS) particle monolayer using the evaporation-induced method.

There is growing interest in the fabrication of one-dimensional (1D) silicon structures since freestanding silicon pillars show high potential in areas such as DNA separation [16, 17], the construction of superhydrophobic surfaces [18, 19] and solar cells [20, 21]. Recently, besides these useful applications, the use of NPAs in the surface-enhanced Raman scattering (SERS) system has also been promoted [22]. However, in these works, the silicon nanopillars are uniform and always have the same height. In this Letter, we put forward a novel method to fabricate two-layer hierarchical NPAs based on nanosphere lithography.

This Letter presents the main processes (seen in Fig. 1) in the fabrication of silicon NPAs. We first introduce the colloidal particles assembly process (Fig. 1a). Afterwards, the modification process (Fig. 1b) to tailor the sizes of well-ordered PS particles is presented. We then explain the essential steps and proper parameters used to fabricate well-ordered silicon NPAs by deep reactive ion etching (DRIE) process (Figs. 1c and d). The silicon hierarchical NPAs are subsequently put forward. To discover the transition process of the two totally different NPAs, a set of experiments have been conducted. Based on these experiments, a reasonable explanation of the transition is provided.

2. Self-assembly: To obtain a well-ordered PS particles monolayer using the evaporation-induced method, we use a self-made evaporation system, shown in our previous paper [23].

To form a PS particle monolayer on a silicon wafer, a template to restrict suspension is necessary. In our experiments, a self-made polydimethylsiloxane (PDMS) template with cells of 10 mm diameter was used. To make the silicon wafer hydrophilic, the wafer was treated in a solution (a 1:1:5 mixture of 30% $\text{NH}_3 \cdot \text{H}_2\text{O}$, 30% H_2O_2 and Milli-Q water), then heated to 80°C for 25 min, rinsed with Milli-Q water and dried in a stream of nitrogen for use.

After direct bonding between PDMS and the silicon wafer, a fixed amount of suspension was instilled into the centre of the cell. The hydrophilic wafer and the cell's special shape promote a slightly concave meniscus. After the injection of liquid into the template cell, there are generally three steps during the ordering procedure. First, the suspension quickly spreads around till it reaches the margin of the template. Several seconds later, about 20 μl of solution covers the template and forms a slightly concave meniscus. Secondly, the solution evaporates spontaneously at a moderate

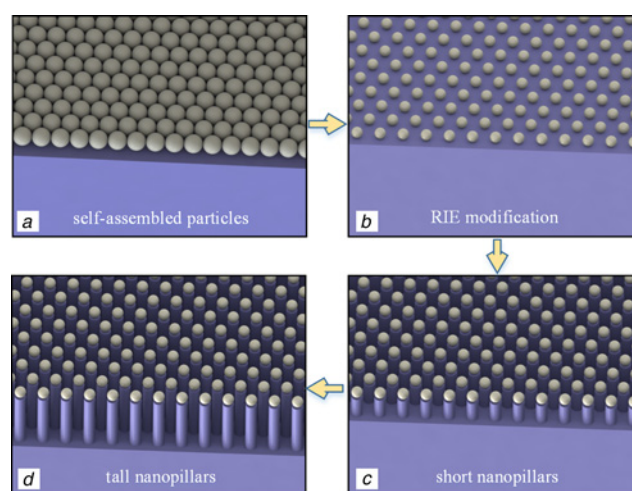


Figure 1 Experimental processes to fabricate silicon NPAs
a Self-assembled PS particles
b RIE modification of PS particles
c Short nanopillars after a few cycles of DRIE
d Tall nanopillars after long time of DRIE

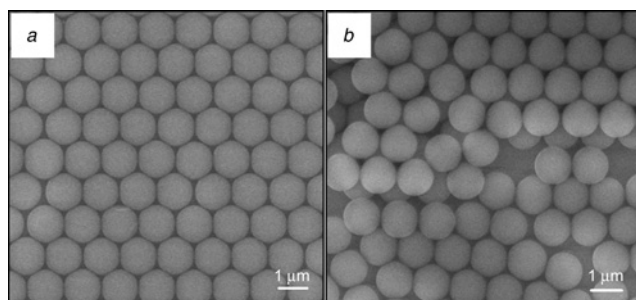


Figure 2 SEM images of the well-ordered PS particles
a 1250 nm PS particle monolayers
b PS particle bilayers

speed in the container. As we know, liquid in the centre of the meniscus is the thinnest and with the evaporation of water, the centre's thickness will certainly be the earliest to achieve a height comparative to the diameter of the colloid particles. The particles are then pressed onto the substrate firmly by the liquid's surface tension. Lastly, other unfixed particles are pushed to the ordered region by the liquid's capillary force, which impels the ordered region to grow larger till the region spreads to the whole cell. With the evaporation of water, the colloid particles are left to form a monolayer on the wafer in about 15 h. The evaporation time depends on the humidity and airflow of the environment. In the whole experiment, the temperature, humidity and other environmental elements can be strictly controlled in the container.

By controlling all factors in the evaporation-induced method, we obtained a well-ordered monolayer for PS sub-microparticles, shown in Fig. 2. The particles had a hexagonal order with little defects in Fig. 2*a*. The spherical particles assembled on the substrate next to another, leaving a little uncovered space between the spheres. That uncovered space can be used in nanosphere lithography to fabricate many nanostructures [12–14], while the spheres act as masks just like photoresist in traditional photolithography. As the tension cannot be strictly the same in the evaporation process, the spherical particle bilayers can always appear in some regions of the cell, shown in Fig. 2*b*. After the water's evaporation, the upper layer can be firmly trapped in the space on top of the under layer because of the Brownian movement and the surface tension. Applying the evaporation-induced method for the self-assembly process, two-dimensionally well-assembled PS particle monolayers can be observed on the silicon surface.

3. Reactive iron etching (RIE) modification: As stated in Section 2, the whole sphere arrays occupied almost all the space on the substrate surface. Some modification steps should be taken to release some space for the silicon NPAs' fabrication. In our experiments, a RIE process was utilised employing oxygen as the etching gas. The size of the spheres can be diminished by oxygen plasma. Gaps between particles can be controlled, and the diameter of the nanopillars is adjusted at the same time. In this process, we can change gas flow, air pressure and etching power to obtain PS particles with suitable size, which were fixed at 100 sccm, 10 Pa and 120 W, respectively, in our experiments. By changing the etching time, PS particles can be shaped to different sizes.

After the RIE process, a thermal treatment was carried out to make PS particles cling to the substrate. The well-ordered substrate was placed on a hotplate of 110°C for 40 s to make the surface of the PS particles thaw slightly and stick to the substrate firmly when returning to room temperature.

In the RIE process, although their sizes become smaller with the increasing etching time, the positions of colloid particles are all settled. That is, the gap between the two particles becomes larger.

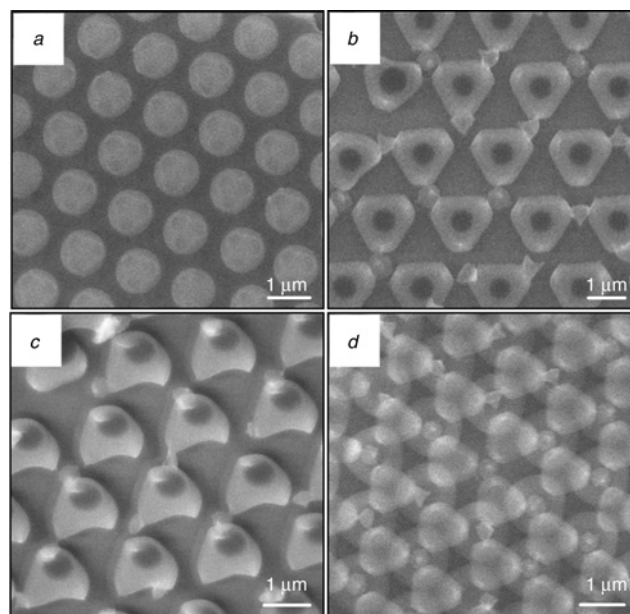


Figure 3 Colloid particles on silicon substrate after RIE by oxygen plasma
a Monolayer
b Top view of bilayers
c 30° tilt view of bilayers
d Top view of three layers
 Scale bars are shown in the images

After the RIE process, some interesting patterns were observed, which are shown in Fig. 3. Particles with a diameter of 970 nm, about 77% of the previous diameter, were left after 340 s etching process, shown in Fig. 3*a*, while the gap between the two particles is 560 nm. In our experiment, we chose a proper etching time of 340 s to make the gap proper for the fabrication of NPAs. Fig. 3*b* shows the etching results of the bilayers. The upper layer of this picture worked as the shelter mask, protecting the under layer from being etched. After the upper layer was almost etched, as the white dots shown in Fig. 3*b*, the under layer presented the triangle structures. With the same mechanism, the three layers can be etched as shown in Fig. 3*c*. The formation principle of this structure is appropriate for etching self-assembled nanoparticles of more than two layers.

4. Fabrication of well-ordered NPAs: By using the patterns formed in the RIE process as masks, the standard DRIE process was employed to obtain silicon NPAs. In this process, the tailored particles are regarded as masks, protecting the silicon beneath them from being etched, while the unprotected silicon disappears over time. The silicon nanopillars with PS nanoparticles on their top end stand straight. In this process, SF₆ and C₄F₈ were utilised as the etching and passivation gas, respectively. Specific parameters used in the DRIE process are shown in Table 1. As a result, silicon nanopillars with different aspect ratios can be obtained with a different reaction time.

The SEM images of well-ordered NPAs are shown in Fig. 4. Fig. 4*a* shows the top view of the nanopillars, Figs. 4*b* and *c*

Table 1 Parameters used in the DRIE process

	Gas flow, sccm		Upper electrode power, W	Bottom electrode power, W	Time, s
	SF ₆	C ₄ F ₈			
etching cycle	100	0	400	50	0–1200
passivation cycle	0	85	100	0	

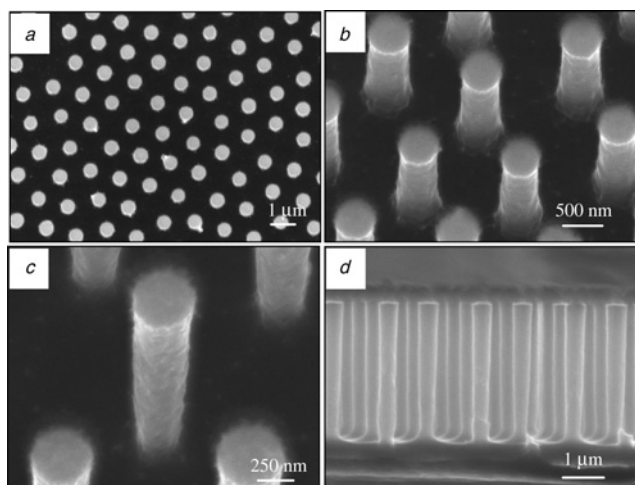


Figure 4 Well-ordered silicon NPs fabricated by DRIE process
a Top view of the NPs
b and *c* 20° tilt view of the NPs with heights of 2.08 and 2.72 μm , respectively
d Cross-section of the NPs
 Scale bars are shown in the images

show the 20° tilt view of pillars with a height of 2.08 and 2.72 μm , respectively, Fig. 4*d* shows the cross-section of the nanopillar arrays. The nanoparticles in Fig. 4*d* exhibit a diameter of 420 nm, about one-third of the original particle. The size of the PS particle masks was fixed according to this diameter in all DRIE processes.

Regarding the different etching cycles, we obtained NPs with various aspect ratios. Fig. 4*b* shows the aspect ratio of 4.95 by 18 etching cycles, while Fig. 4*c* shows 6.48 by 27 cycles. By employing the fixed etching parameters, silicon nanopillars with an aspect ratio of 9, and density of 10^8 per cm^2 , can be fabricated.

5. Fabrication of hierarchical NPs: With the increased etching cycles, an interesting hierarchical structure was observed by SEM, shown in Fig. 5. Figs. 5*a* and *c* and the magnified images Figs. 5*b* and *d* show the hierarchical silicon NPs with PS particles on the top end of short NPs.

It is observed that NPs have mainly two different heights. The tall nanopillars and the short pillars stand straight on the silicon ground in a disorderly manner. It is easily found that many tall NPs lost their PS particle heads, while most short pillars keep theirs. As to the PS heads, shown in Fig. 5*b*, they become oblate because of the thermal treatment and seem more likely to fall down from the top. Compared with the well-ordered NPs shown in Fig. 4*d*, the hierarchical ones are disordered and with poor quality for tall or short ones. However, the prominent features of hierarchical NPs are that they have nanopillars of double heights and possess a huge altitude difference, which may lead to a wider range of applications.

For the well-ordered NPs, when we extend the etching time (including the etching and passivation process), the only change for the NPs is their aspect ratio. That is, it is impossible for the formation of the hierarchical NPs to take place. Hence, something different must happen during the transition process.

6. Explanations of the transition: When the cycles were increased to 32 (etching time of 700 s), an interesting phenomenon was discovered in the DRIE process in that the silicon NPs began to collapse. The aspect ratio was 9 at that time. As shown in Fig. 6, the NPs became thinner and thinner from the PS heads to the bottom, and the bottom of the nanopillars broke. As a consequence, the pillars fell down to the substrate. As there was no force that could control the orientation of the collapse, the nanopillars would fall in different directions at random. Owing to

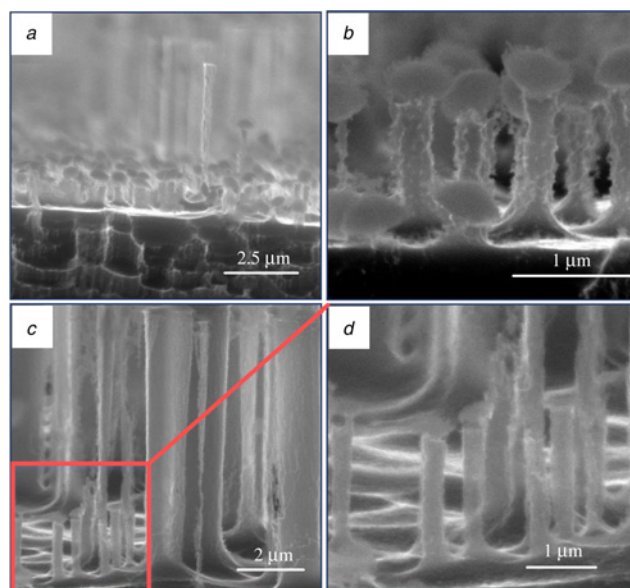


Figure 5 Cross-section of silicon hierarchical NPs fabricated by DRIE process
a Hierarchical arrays
b Short NPs
c Hierarchical NPs
d High magnification of (Fig. 5*c*)
 Scale bars are shown in the images

the passivation process, there were still a few nanopillars that were vertical to the wafer, as shown in Fig. 6*b*.

It is obvious from the SEM images that the nanopillars had big PS heads and small bottoms standing on the ground. If the etching time increased, the bottom would become thinner and could never hold the pillar. This phenomenon is shown in Figs. 6*a* and *b*. After the collapse, the lying nanopillars would be etched by SF_6 because of the absence of PS masks. A short silicon pillar remains unetched in Figs. 6*c* and *d* as a result of insufficient etching time. At this time, the fallen PS particles spread around the wafer in a disordered manner. As there is no restriction

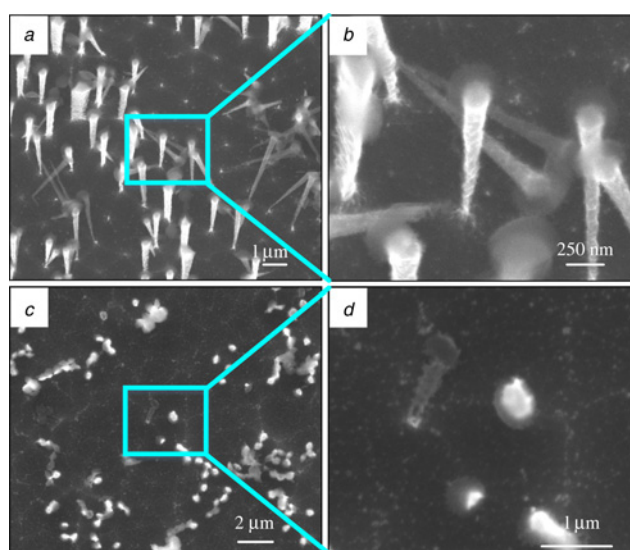


Figure 6 Collapsing process of well-ordered NPs at 700 s
a 20° tilt view of the collapsing NPs
b High magnification of (Fig. 5*a*)
c Collapsed NPs etched by SF_6
d High magnification of Fig. 5*c*

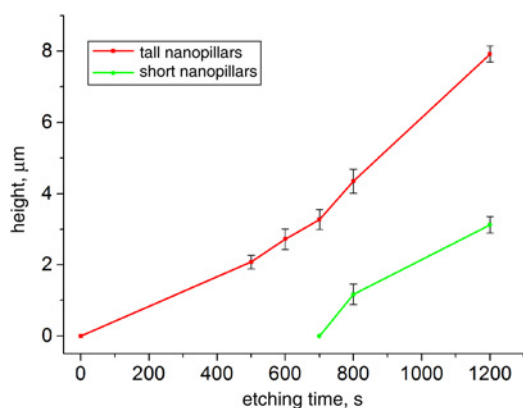


Figure 7 Line chart showing the height of NPs changing with etching time. Red points represent the tall NPs. Green points represent the short NPs. Error bars are shown in the image.

of the fallen PS particles, any air flow or vibration may be responsible for their displacement.

If we keep increasing the etching and passivation cycles, the disordered PS particles will act as masks again, which may promote the formation of the second generation NPAs. Fig. 5b shows the second generation of silicon NPAs with slightly different heights because of the minor difference of the first generation's collapse time. During the etching process, the PS particles can hardly keep their spherical structure because of the etching itself and the heat produced by etching. Therefore they become oblate, as shown in Fig. 4b. Many chapped PS particles could be observed at the same time. PS particles are not stable enough to be firmly fixed on the head of nanopillars because of the lack of contact area and the PS particles' surface deformation. That is the reason why some particles escaped from the nanopillars' heads to the ground.

Figs. 5a and c show the first and second generation of nanopillars on the same sample. They have two different heights and diameters. In the collapsing process, some pillars of the first generation did not fall down because of the passivation treatment and became much taller as time went on. The second generation nanopillars were shorter than the first generation as they experienced less etching time. As discussed above, some PS particles might deform to pieces, resulting in the loss of mask area, which can explain the second generation's shorter diameter.

Concerning the relationship between the etching time and the height of NPAs, Fig. 7 shows that the height of NPAs changes with etching time. The red points show the tall nanopillars, whereas the green ones represent the short ones. As observed in the SEM images, 700 s represents the transition time from well-ordered arrays to hierarchical ones. This important time saw the end of first generation arrays and the beginning of the second generation. At the transition time, the second generation just begins to appear, so the height is zero. While the tall ones still experience the etching process, the height is 3.27 μm at that time. After discovering the collapse phenomenon, we put the coordinates of (700, 3.27), (700, 0) into the chart. As a result, we can obtain the etching tendency for both generations of arrays, nearly linear, as shown in Fig. 7.

With this simple DRIE process, silicon NPAs of two generations with different heights and diameters can be fabricated. Theoretically, NPAs of more than two generations can be obtained by employing self-assembled PS particles as masks. However, PS particles are not stable enough to undergo the SF₆ etching and withstand the heat produced in the etching process. That is to say, generation above two is difficult to prepare, while ordered NPAs can only be obtained in the first generation. After the first collapse of pillars, the particles will be chaotic, that is, no controllable operation can be taken afterwards.

7. Conclusions: This Letter demonstrates the formation of well-ordered, large area, 2D nanoparticle monolayers using the evaporation-induced method. After the plasma treatment, PS particles are tailored to small sizes. Well-ordered silicon NPAs have been fabricated by the DRIE process. Parameters of the RIE process and the DRIE process are systematically investigated, and the optimised recipes are obtained. To explain the transition from well-ordered silicon NPAs to hierarchical NPAs, an interesting collapsing phenomenon is explored in the experiments. This Letter presents a DRIE-based method to fabricate hierarchical NPAs. This method is mainly based on the two dimensionally self-assembled PS particles. The well-ordered and the hierarchical NPAs show attractive potential applications in SERS, superhydrophobic surfaces, photovoltaic devices and other fields.

8. Acknowledgments: The authors thank H. Li at the Institute of Microelectronics of Peking University for advice on PDMS template fabrication. They also thank J. Xiao at the Chemistry School of Peking University for assisting with the wafer pretreatment. This work is supported by the National Natural Science Foundation of China (grant nos 61176103, 91023045 and 91323304), the National Hi-Tech Research and Development Program of China ('863' Project) (grant no. 2013AA041102) and the National Ph.D. Foundation Project (grant no. 20110001110103) and the Beijing Natural Science Foundation of China (grant no. 4141002).

9 References

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