

Facile fabrication of 2-dimensional arrays of sub-10 nm single crystalline Si nanopillars using nanoparticle masks

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A simple procedure for the fabrication of sub-10 nm scale Si nanopillars in a 2-D array using reactive ion etching with 8 nm Co nanoparticles as etch masks is demonstrated. The obtained Si nanopillars are single crystalline tapered pillar structures of 5 nm (top) \times 8 nm (bottom) with a density of $\sim 4 \times 10^{10}$ pillars cm^{-2} on the substrate, similar to the density of Co nanoparticles distributed before the ion etching process. The uniform spatial distribution of the Si nanopillars can also be patterned into desired positions. Our fabrication method is straightforward and requires mild process conditions, which can be extended to patterned 2-D arrays of various Si nanostructures.

The assembly and patterning of functional nanostructures onto desired substrates with density control is of critical importance for the advancement of nanotechnology. Since many of the desired physical properties are interrupted or degraded due to the inhomogeneity of 0-D or 1-D nanomaterials, the fabrication and distribution of nanostructures with uniform size and shape are significant challenges to be overcome.

In particular, arrays of pillared structures of Si have potential applications in future Si-based electronic devices. They may serve as a base structure for Si nanowires and quantum dots in the fabrication of electroluminescent or field emitting devices.¹⁻² In addition, they can be beneficial for developing nanoscale Si structures that exhibit novel photoluminescence properties.³

In previous work, arrays of Si pillars have been fabricated using an electron-beam lithography directed method while Si nanocolumns have been produced by scanning tunneling microscopic techniques.⁴ Although these methods in principle provide Si nanostructures with high resolution and uniformity, throughput is low, sophisticated equipment is required and procedures are somewhat unwieldy. Self-assembly techniques for Si nanostructure fabrication have been demonstrated using polystyrene colloidal particles,⁵ but they too have drawbacks including poor size uniformity and comparably larger sizes *versus* those obtained by e-beam lithography. Slightly differently, interstices of self-assembled polystyrene templates have been successfully utilized as masks for sub-10 nm Si nanopillar formation.⁶ Although there has been significant progress in reducing the size of Si nanopillar structures utilizing colloidal gold nanoparticles as the etch mask followed by an ion etching procedure,⁷ additional procedures such as specific chemical treatment of the substrate surface [*e.g.* 3(2-aminoethyl)aminopropyltrimethoxysilane] are still required to attach the gold nanoparticles onto the substrate. In addition, obtaining Si nanopillars without a mask (*i.e.* colloidal gold nanoparticles) requires extremely harsh chemical conditions (*e.g.* aqua regia) which are in general incompatible with many key materials in electronic devices.

In this work, we report a facile fabrication method for sub-10 nm scale Si nanopillars arrayed uniformly over a wide area on a N-type Si(100) wafer using cobalt nanoparticles as the etch mask. Although various types of colloidal nanoparticles can be synthesized chemically with high qualities and narrow size distribution,⁸⁻¹¹ it is still a difficult task to position the nanoparticles regiospecifically onto the Si wafer with well defined particle densities while retaining the nanoparticles reliably under the harsh etching processes typical of modern mass production processes. Our method demonstrates that cobalt nanoparticles can be uniformly assembled onto a Si wafer by a spin coating method without the use of any chemical linkers. Single crystalline Si nanopillar arrays are then obtained after reactive ion etching (RIE) and mild chemical etching processes to remove nanoparticle masks.

Co nanoparticles with an average diameter of 8 nm ($\sigma = \sim 6\%$) were prepared by chemical synthesis and stabilized by AOT [bis(2-ethylhexyl) sulfosuccinate] in toluene.^{12,13} The Co nanoparticles were distributed on a large area of Si wafer using a spin coating method without employing a chemical linker on the surface of the substrate. The substrate was subsequently baked at 600 K for 20 min in air. At high temperatures the AOT surrounding the Co nanoparticles dissociate and leave a carbon containing sticky residue, leaving the Co nanoparticles strongly attached to the substrate. The attached Co nanoparticles are stable and do not wash off during a sonication period of more than 10 min. in water, ethanol, and acetone solution. No other chemical treatments were necessary.

Fabrication of the Si nanopillars using the attached Co nanoparticles as the etch mask was carried out using reactive ion etching (RIE). RIE was performed for 80 s at 10 mTorr with 4 sccm of SF₆ and 8 sccm of O₂ gas. Any portions of the Co nanoparticle mask remaining on top of the Si were subsequently removed by dipping the substrate into HCl solution for 20 s.

The Si nanopillars obtained are shown in Fig. 1. A scanning electron microscope (SEM) image showing the top view of pure Si nanopillars fabricated by using 8 nm Co nanoparticles as the etch mask is shown in Fig. 1a and array of Si pillars in a row is shown in Fig. 1b. A cross sectional transmission electron microscope (TEM) image of the Si nanopillars indicates lattice distance of 3.14 Å consistent with (111) direction of known value, which indicates the fabrication of single crystalline Si pillars is successful (Fig. 1c). The Si nanopillars have height of about 8 nm and the diameters at the top and the middle parts of about 5 and 8 nm, respectively. The top surfaces of the etched Si nanopillars are flat with a diameter of 5 nm which is smaller than the 8 nm diameter of the Co nanoparticles mask due to the undercut effect that occurs during the RIE process.

The density of the nanopillars in Fig. 1a is about 4×10^{10} pillars cm^{-2} , nearly the same as that of the Co nanoparticle density observed after spin coating before the RIE process.

Therefore, in principle, it is possible that the density of Si nanopillars can be controlled approximately between 1×10^9 and 9×10^{11} particles cm^{-2} by changing the molar concentrations of the Co nanoparticle containing colloids used in the spin coating process.¹²

Simple fabrication of discrete patterns of Si nanopillars is also possible. After spin coating the Si with Co nanoparticles, the polymethylmethacrylate (PMMA) layer is further developed into specific patterns and the exposed Co nanoparticles are etched away by HCl (Figs. 2a,b). The remaining PMMA pattern leaves the Co nanoparticles located only within the specific regions. After the removal of PMMA, the RIE process and chemical etching of the mask provide the Si nanopillars in specific patterns (Fig. 2c–e). The distribution of the fabricated Si nanopillars is uniform within the patterns and does not show boundary effects such as agglomeration of Si nanopillars near the edges of the pattern typically associated with μm -scale patterning (Fig. 2f).

This method using Co nanoparticles as the etch mask can also be useful in the formation of various Si-containing nanostructures including quantum wells and dots. Since Co nanoparticles of various sizes can be synthesized separately with narrow distribution and the density of nanoparticles on the substrate is reproducibly controllable by spin coating method,¹² both the size and density of Si-based quantum dots can be controlled separately and reproducibly by this method.

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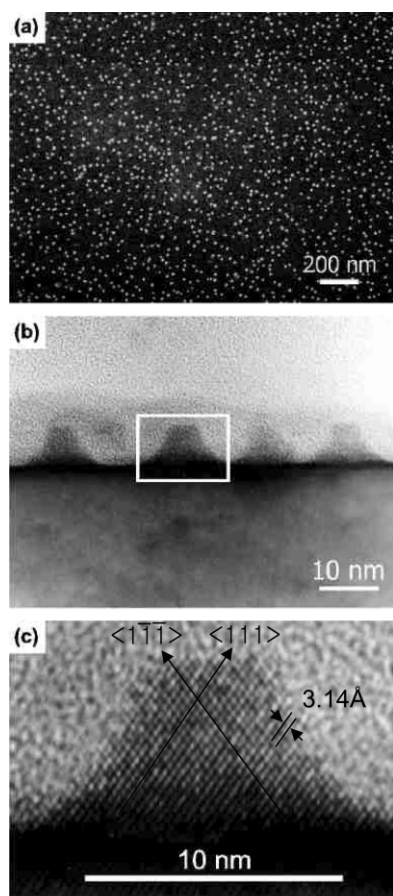


Fig. 1 (a) SEM top-view image of Si nanopillars fabricated using 8 nm Co nanoparticles. The density of Si nanopillars is about 4×10^{10} pillars cm^{-2} . (b) The cross sectional TEM image of the Si nanopillars. The top surface of each nanopillar is flat and about 5 nm in diameter, slightly smaller than the 8 nm diameter of the Co nanoparticle mask due to the effect of the SF_6 gas. (c) The magnified image of a Si nanopillar enclosed by the white rectangle in (b).

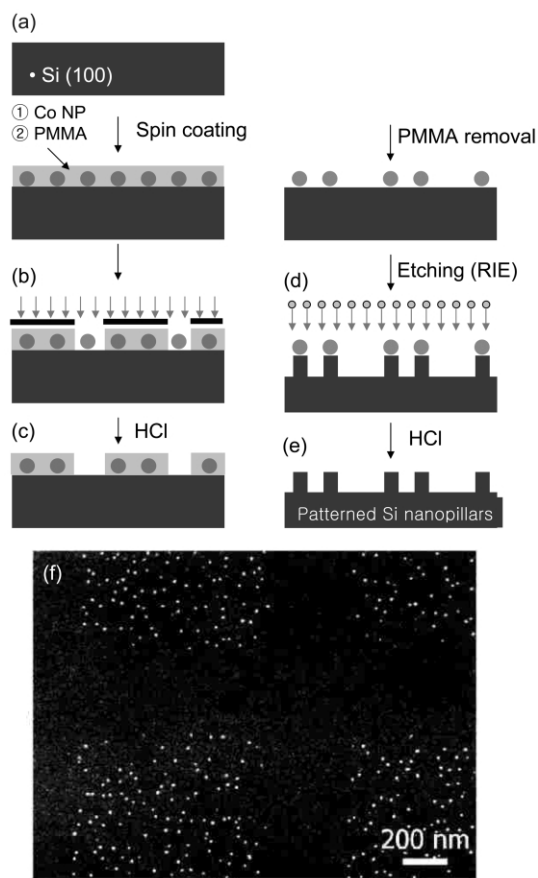


Fig. 2 A schematic for producing specific patterns of Si nanopillars. (a) 8 nm Co nanoparticles are distributed by a spin coating method and associated to the substrate by a brief baking period. (b) Patterns of PMMA resists are made via electron beam lithography. (c) Unnecessary Co nanoparticles are etched away by HCl. (d) After removal of PMMA, Si nanopillars are then fabricated by RIE. (e) The remaining Co nanoparticles used as the etch mask are finally removed by HCl. (f) The SEM image of finally obtained Si nanopillars filling specific patterns.

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Notes and references

- H. I. Liu, D. K. Biegelsen, F. A. Ponce, N. M. Johnson and R. F. W. Pease, *Appl. Phys. Lett.*, 1994, **64**, 1383.
- A. G. Nassiopoulou, S. Grigoropoulos and D. Papadimitriou, *Appl. Phys. Lett.*, 1996, **69**, 2267; D. M. Pooley, H. Ahmed, H. Mizuta and K. Nakazato, *Appl. Phys. Lett.*, 1999, **69**, 2191.
- C. A. Canaria, M. Huang, Y. Cho, J. L. Heinrich, L. I. Lee, M. J. Shane, R. C. Smith, G. M. Miskelly and M. J. Sailor, *Adv. Funct. Mater.*, 2002, **12**, 495.
- W. Chen and T. Ahmed, *Appl. Phys. Lett.*, 1993, **63**, 1116; T. Tada, A. Hamoudi, T. Kanayama and K. Koga, *Appl. Phys. Lett.*, 1997, **70**, 2538.
- C. Haginoya, M. Ishibashi and K. Koike, *Appl. Phys. Lett.*, 1997, **71**, 2934.
- C.-W. Kuo, J.-Y. Shiu, P. Chen and G. A. Somorjai, *J. Phys. Chem. B*, 2003, **107**, 9950.
- P. A. Lewis, H. Ahmed and T. Sato, *J. Vac. Sci. Technol. B*, 1998, **16**, 2938; P. A. Lewis and H. Ahmed, *J. Vac. Sci. Technol. B*, 1999, **17**, 3239.
- C. B. Murray, D. B. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
- X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343.
- S.-M. Lee, S.-N. Cho and J. Cheon, *Adv. Mater.*, 2003, **15**, 441.
- S. Sun and C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325.
- Y.-K. Hong, H. Kim, G. Lee, W. Kim, J.-I. Park, J. Cheon and J.-Y. Koo, *Appl. Phys. Lett.*, 2002, **80**, 844.
- J.-I. Park, N.-J. Kang, Y.-W. Jun, S. J. Oh, H.-C. Ri and J. Cheon, *ChemPhysChem*, 2002, **3**, 543.