Fabrication and Nonlinear Optical Characterization of Well-Ordered Nanopillar Arrays

Chun-Wen Kuo, Shuo-Wen Wu and Peilin Chen*
Institute of Applied Science and Engineering Research, Academia Sinica, 128, Section 2,
Academia Road, Nankang, Taipei 115, Taiwan

Abstract

Size-controllable nanostructure fabrication has drawn much of research attention lately, because it may allow the tuning of optical, magnetic, catalytic and electric transport properties of materials. To achieve this goal, we need to investigate the size dependent behavior of materials. The most popular method for size-controlled nanostructure fabrication is e-beam lithography. However, e-beam lithography is not an efficient process for large area fabrication. We report here a novel method to produce large area, well-ordered, size-controlled nanopillar arrays. Nanopillar arrays are among the most studied nanostructures because of their potential applications in photonic crystals, data storage, and sensors. To fabricate nanopillar arrays, we have employed both single layer and double layer nanosphere lithography. Nanosphere lithography, which uses the close packed structure formed by monodispersed colloidal particles as template, is known to produce large area, well-ordered nanostructures on substrate surfaces. These nanostructures have been utilized as the masks in the reactive ion etching process. By carefully controlling the gas composition and etching time, various sizes of nanopillar arrays have been produced. To characterize the optical properties of these nanopillar arrays, surface nonlinear spectroscopy has been used to investigate the size dependent response of nanopillar arrays.

Introduction

It has drawn lots of research attention in the development of size-controllable nanostructure fabrication, because size-controlled nanofabrication may enable us to modify the optical[1], magnetic[2], catalytic[3] and electric transport [4] properties of materials. To realize such application potential, it requires systematic investigation of the size dependent properties of nanostructured materials. Therefore, it is very important to develop inexpensive, large-scale nanofabrication techniques for the study of size dependent behavior. To produce nanostructures with satisfactory size control in the sub-100nm region, e-beam lithography is the most popular method. However, it is not practical to employ e-beam lithography for large-scale fabrication. Self-organization process, on the other hand, provides an alternative approach to fabricate large-area nanostructures with sufficient size control [5]. It has been demonstrate that both two-dimensional [6-11] and three-dimensional [12-14] crystalline structures can be obtained on the substrate surfaces using monodispersed colloid solutions. These crystalline structures can then serve as the templates for nanostructure manufacture [15-16].

In this article, we report the development of a novel fabrication technique that can produce various sizes of well-ordered periodic nanopillar arrays. Periodic nanopillar arrays are one of the most studied nanostructures, because of their applications in the photonic crystals[17], data storage[18-19] and optoelectronic[20]. In our laboratory we have fabricated two types of triangle shaped nanopillar arrays, hexagonal and rhombic, using etching mask produced by nanosphere lithography. By controlling the reactive gas mixture and etching time, nanopillars with different aspect ratios have been obtained. To investigate the size-dependent optical properties of nanopillar arrays, we have utilized sum frequency generation (SFG) to measure the surface enhancement factors of various size nanopillar arrays.

EXPERIMENT

Fabrication of nanopillar array

To fabricate silicon nanopillars, 1 x 1 cm^2 substrates cut from N-doped silicon (100) wafers (Gredmann) were used. These silicon substrates were cleaned by immersion in piranha solution (3:1 concentrated H_2SO_4:30% H_2O_2) and sonicated for 30 min. After sonication the substrates were rinsed repeatedly with ultrapure water (18.2 M-cm, Millipore Simplicity), acetone, and methanol and used immediately. To produce metal masks for the nanopillar array, nanosphere lithography has been employed. The detail procedure of nanosphere lithography can be found in the literatures[21]. In short, monodispersed 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). This solution was then spin-cast on to substrates to form hexagonally closed-packed 2D colloidal crystals. Depending on the experimental requirements (single or double layer), the speed of spin-coater varied from 800-3600 RPM, and the dilution ratios of polystyrene solutions have also been changed. It was found that the formation of self-assembled 2D colloidal crystal strongly depended on the speed of spin-coater as suggested by the evaporation rate studies [22]. These 2D colloidal crystals were then used as the deposition templates. A 100 nm thick aluminum film was deposited over the polystyrene masks at a rate of 15 nm/min in an ULVAC vapor deposition system at pressure of $1\text{x}10^{-3}$ Pa. After the aluminum deposition, the polystyrene beads were removed by sonicating the substrates in CH_2Cl_2 solution for 1-4 min. To fabricate silicon nanopillar arrays, substrates with metallic masks were placed in a reactive ion etcher (Oxford Plasmalab 80 Plus) with a gas mixture of CHF_3 (20 sccm) and O_2 (2sccm).

Nonlinear optical measurement

To investigate the size dependent optical properties of nanopillar arrays, we have utilized SFG to monitor the nonlinear optical response of gold coated nanopillar arrays. The light source used in this experiment was generated by an optical parametric generator (Eksma PG401/DFG2-10), which was pumped by a YAG laser (Eksma, PL2143). To measure the SFG from nanopillar arrays, a tunable IR beam and the second harmonic of YAG laser (532 nm) were directed to the substrate surface at an incident angle of 50^0 and 55^0 respectively. The SFG signal was recorded by a PMT (Hamamatsu R3896) and a reflected IR beam was used for normalization.

RESULTS

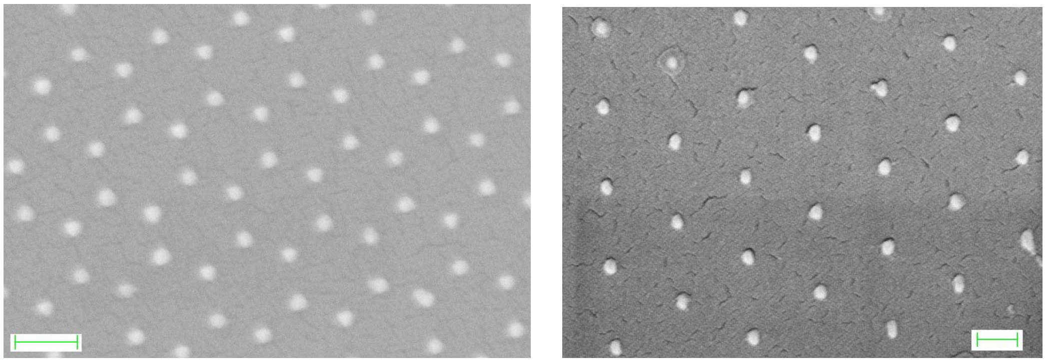

Figure 1. Representative SEM images of metallic masks produced by nanosphere lithography. Left: mask formed by single layer 280 nm polystyrene beads. Right: mask generated using a double layer 400nm polystyrene beads. Bar: 200 nm.

The basic idea for nanopillar fabrication is to employ reactive ion etching on silicon substrates with metal masks produced by nanosphere lithography, which utilizes monodispersed polystyrene beads to form two-dimensional closed packed structure on substrate surfaces. Most of nanopillar arrays fabricated so far have utilized e-beam lithography, which is limited by its low throughput. With our new fabrication procedure, it is very easy to manufacture various sizes of nanopillar arrays in large scale. Figure 1 shows the SEM images (taken by a LEO 1154 scanning electron microscope, 5 KV) of metallic masks produced by single layer and double layer nanosphere lithography using 280 and 400 nm polystyrene beads. The size and the separation distance of metallic islands were governed by the geometry of the interstices formed by the close packed nanosphere. In some occasion, nanoring formation was observed, which was consisted of undissolved polystyrene as observed by other group [11]. To remove the residual of polystyrene, all samples were cleaned by oxygen plasma.

To fabricate the nanopillar arrays, 100 nm thick aluminum films were used as the masks for the reactive ion etching. Figure 2 shows the nanopillar arrays fabricated using both single layer and double layer nanosphere lithography. It can be clearly seen that single layer nanosphere lithography produced nanopillar array in a hexagonal arrangement while double layer nanosphere lithography fabricated rhombic nanopillar arrays with periodicity equal to the diameter of polystyrene beads (400 nm in this case). We have constructed nanopillar arrays with size ranging from 40 nm to 140 nm. Using different combination of gas mixtures and etching time, silicon nanopillars with aspect ratio as high as 7:1 have been obtained.

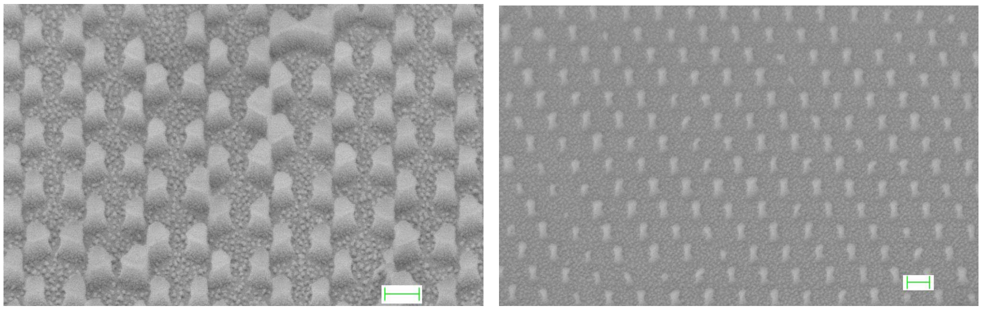

Figure 2. SEM images of etched silicon samples (tilt angle 45^0) using masks produced by single layer (left) and double layer (right) nanosphere lithography (350 nm polystyrene beads). Bar: 200nm

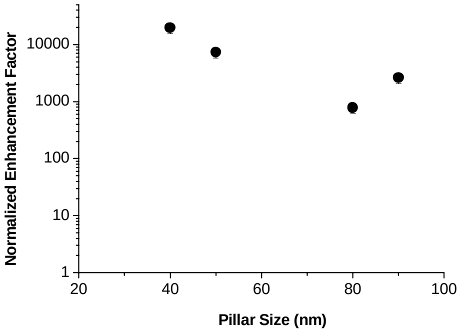

Figure 3. Normalized SFG enhancement factors as a function of pillar dimension.

To investigate the size dependent surface enhancement effect, 200 nm tall nanopillars were coated with 20nm gold, and SFG signal was recorded as a function of pillar size. In this measurement all three beams: SFG, IR and green were P-polarized. To calculate the enhancement factor, the non-resonance SFG signal with infrared wavelength in the region of 3300-3400 nm were averaged. Figure 3 shows the normalized enhancement SFG enhancement factors. The detail normalization procedure can be found elsewhere [23]. Our result exhibits similar behavior as previous SFG enhancement measurement [23].

CONCLUSIONS

In conclusion, we have fabricated well-ordered nanopillar arrays using metal masks from nanosphere lithography. The pillar size as small as 40 nm and the aspect ratio as high as 7:1 have been achieved by proper selection of etching gas mixture and etching time. The hexagonal nanopillar arrays were obtained by single layer nanosphere lithography, while double layer nanosphere lithography produced rhombic nanopillar arrays. Nonlinear optical study has shown that the surface enhancement factors do depend on the size of nanopillars.

ACKNOWLEDGMENTS

This research was supported in part by National Science Council under contract 91-2113-M-001-021.

REFERENCES

1. M.J. Feldstein, C.D. Keating, Y.-H. Liau, M.J. Natan, N.F. Scherer, *J. Am. Chem. Soc.* **119**, 6338 (1997).
2. M. Hehn, K. Ounadjela, J.-P. Bucher, F. Rousseauz, D. Decanni, B. Bartenlian, *Science*, **272**, 1782 (1996).
3. U. Heiz, F. Vanolli, A.Sanchez, W.-D. Schneider, *J. Am. Chem. Soc.* **120**, 9668 (1998).
4. R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney, R.G. Osifchin, *Science,* **273**, 1690 (1996).
5. C.L. Haynes, R.P. Van Duyne, *J. Phys. Chem. B*, **105**, 5599 (2001).
6. U.C. Fischer, H.P. Zingsheim, *J. Vac. Sci. Technol.,* **19**, 881 (1981).

7. H.W. Deckman, J.H. Dunsmuir, *J. Vac. Sci. Technol. B*, **1**,1109 (1983).
8. J.C. Hulteen, R.P. Van Duyne, *J. Vac. Sci. Technol. A*, **13**,1553 (1995).
9. R. Micheletto, H. Fukuda, M. Ohtsu, *Langmuir,* **11**, 3333 (1995).
10. F. Lenzman, K. Li, A.H. Kitai, H.D.H. Stover, *Chem. Mater.,* **6**, 156 (1994).
11. J. Boneberg, F. Burmeister, C. Schafle, R. Leiderer, D. Reim, A. Frey, S. Herminghaus, *Langmuir*, **13**, 7080 (1997).
12. Y.A. Vlasov, X.Z. Bo, J.C. Sturm, D.J. Norris, *Nature*, **414**, 289 (2001).
13. P.V. Braun, P. Wiltzius, *Nature*, **402**, 603 (1999).
14. A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John; S.W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J.P. Mondia, G.A. Ozin, O. Toader, H.M. Van Driel, *Nature*, **405**, 437 (2000).
15. P. Jiang, J.F. Bertone, V.L. Colvin, V.L., *Science*, **291**, 453 (2001).
16. S. Han, X. Shi, F. Zhou, Nano Lett. **2**, 97 (2002).
17. V.V. Poborchii, T. Tada, T. Kanayama, *J. Appl. Phys.*, **91**, 3299 (2002).
18. P.R. Krauss, S.Y. Chou, *Appl. Phys. Lett.* **71**, 3174 (1997).
19. A. Born, R. Wiesendanger, *Appl. Phys. A*, **68,** 131 (1999).
20. A.G. Nassiopoulos, S. Grigoropoulos, D. Papadimitriou, *Appl. Phys. Lett.* **69**, 2267 (1996).
21. J.C. Hulteen, D.A. Treichel, M. T. Smith, M.L. Duval, T.R. Jensen, R.P. Van Duyne, *J. Phys. Chem. B,* **103**, 3854 (1999).
22. S. Rakers, L.F.Chi, H. Fuchs, *Langmuir,* **13**, 7121 (1997).
23. S. Baldelli, A.S. Eppler, E. Anderson, Y.R. Shen, G.A. Somorjai, *J. Chem. Phys.*, **113,** 5432 (2000).