

Fabrication of Sub-50-nm Solid-State Nanostructures on the Basis of Dip-Pen Nanolithography

Hua Zhang, Sung-Wook Chung, and Chad A. Mirkin*

*Department of Chemistry and Institute for Nanotechnology, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208*

Received October 15, 2002; Revised Manuscript Received November 15, 2002

ABSTRACT

The fabrication of arrays of sub-50-nm gold dots and line structures with deliberately designed 12–100-nm gaps is reported. These structures were made by initially using dip-pen nanolithography to pattern the etch resist, 16-mercaptohexadecanoic acid, on Au/Ti/SiO_x/Si substrates and then using wet-chemical etching to remove the exposed gold.

Many lithography methods such as electron-beam lithography,¹ photolithography,¹ microcontact printing,² nanoimprint lithography,³ and scanning probe lithography⁴ are being used to fabricate structures and patterns on substrates from the micro- to the nanoscale. Very few methods offer the ability to work routinely in the sub-50-nm regime with control over the feature size and interfeature distance, especially when such features are made of both hard and soft materials. Herein we use an experimental method that combines the high-resolution lithographic technique of dip-pen nanolithography (DPN)⁵ with wet-chemical etching⁶ to fabricate dot arrays of Au-coated, Ti-coated silicon oxide with features in the 25–50-nm range. In addition, this protocol can be used routinely to make nanogaps ranging from 12 to 100 nm. The novelty in the work presented herein does not lie in the general chemical procedure for using self-assembled monolayers (SAMs) as wet-chemical etch resists⁶ but rather in the scale and geometry (nanogaps) of the structures generated via this approach. Indeed, to the best of our knowledge, these are the smallest Au structures prepared by a wet-chemical etching strategy.

In a typical experiment, Au-coated (10 nm), Ti-coated (1 nm) silicon oxide (Au/Ti/SiO_x/Si)^{6a,b} was patterned via DPN with 16-mercaptohexadecanoic acid (MHA) using an Autoprobe CP AFM TMmicroscopes, Sunnyvale, CA) and commercial lithography software (DPNWrite, DPN System-1, NanoInk Inc., Chicago, IL).^{5,6a,b} All patterning experiments were carried out under ambient conditions (set point = 0.5 nN, 24–26 °C, 44–49% relative humidity) with a MHA-coated tip, which was prepared by immersing a Si₃N₄ tip (spring constant = 0.05 N/m, TMmicroscopes, Sunnyvale,

CA) in an acetonitrile solution saturated with MHA for ~5 s with subsequent drying with compressed difluoroethane (Dust-off, Ted Pella, Inc., Redding, CA). Each DPN dot feature was generated by holding an MHA-coated tip in contact with an Au surface for 0.01 s, and each line was generated by moving an MHA-coated tip on an Au surface at a constant rate (given below).

MHA-patterned Au substrates were treated with a ferri/ferrocyanide etchant—a 1:1:1:1 (v/v/v/v) aqueous mixture of 0.1 M Na₂S₂O₃, 1.0 M KOH, 0.01 M K₃Fe(CN)₆, and 0.001 M K₄Fe(CN)₆—for ~20 min under constant stirring to remove the Au completely from areas not modified with MHA.^{6a} After rinsing with Milli-Q H₂O and drying with N₂, the etched Au nanopattern was characterized by tapping-mode AFM (TMAFM) (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA). Figure 1A shows the TMAFM image of an etched Au dot array. In this type of array, the distance between dots is 100 nm, and the measured diameter of each etched Au dot is approximately 50 nm (see Supporting Information for section analysis). The uniformity of the nanostructures is quite good, demonstrating the ability to fabricate high-quality small-scale features via the DPN process. Indeed, a scanning electron microscopy (SEM) image of a portion of a 40 000 dot array shows the regularity of the feature size and the interfeature distance. The actual dot diameter as measured by SEM is ~45 nm (Figure 1B). The larger diameter value obtained from the AFM analysis of the nanopattern is due to tip convolution. Although we can use this strategy to fabricate even smaller features, at present our ability to control dot feature size deliberately becomes less reproducible below 45 nm. The smallest diameter structures made to date via this method are 25 ± 5 nm (Figure 1C) (see Supporting Information for section

* To whom correspondence should be addressed. E-mail: camirkin@chem.nwu.edu.

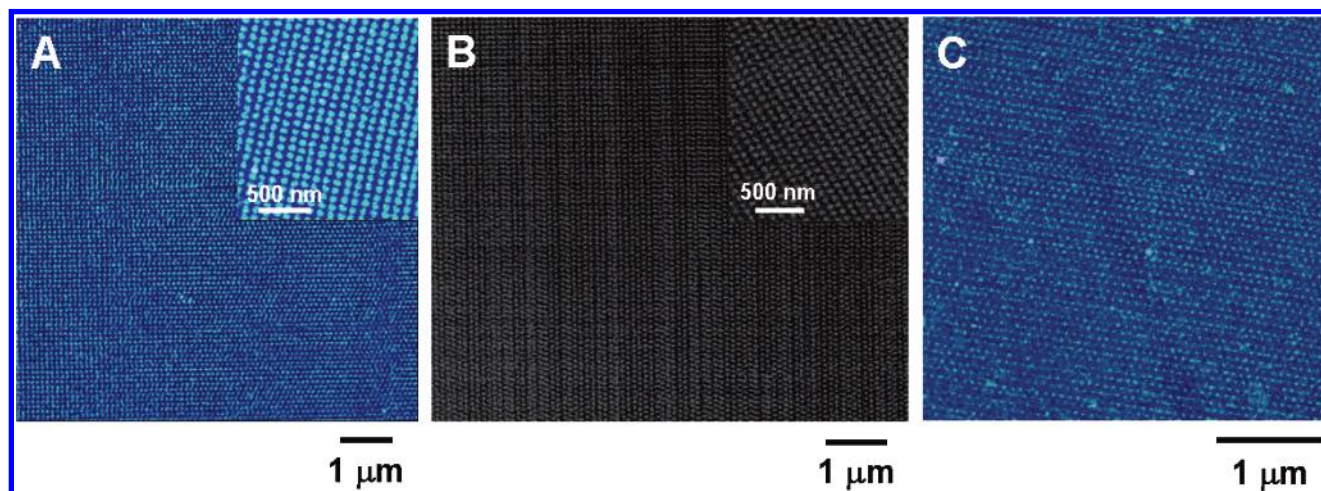


Figure 1. TMAFM topographic images (A, C) and SEM image (B) of an etched MHA/Au/Ti/SiO_x/Si dot nanoarray. The insets are high-resolution images.

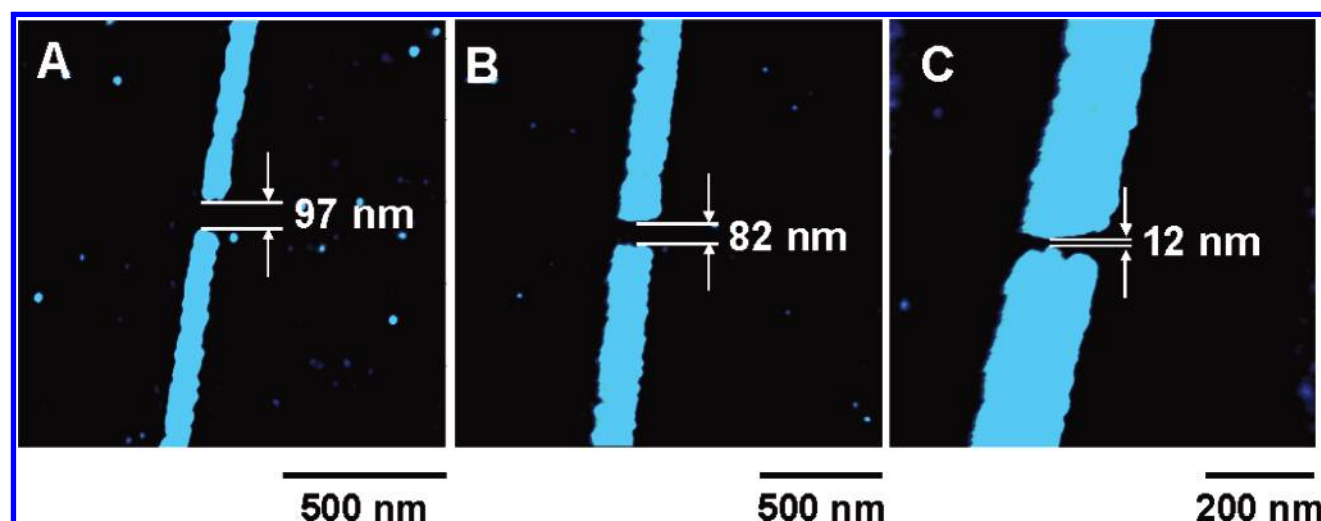


Figure 2. TMAFM topographic images of etched MHA/Au/Ti/SiO_x/Si nanogaps.

analysis), and the distance between them is 80 nm. Note that these structures often have irregular shapes, which is likely a consequence of nonuniform etching and the rough polycrystalline Au substrates, which reduces the packing density of the MHA SAM patterns formed by DPN.⁷ The resist features in this case (~ 25 -nm Au dots) are only approximately 50 MHA molecules in diameter. This estimate is based upon the known lattice parameters for an MHA SAM⁸ and the assumption that there is no loss of SAMs during the etching process. It is known that the monolayer resist remains on the solid features after the wet-chemical etching process.^{6a,c,9}

Importantly, because DPN can be used deliberately to make almost any sort of feature regardless of shape and size (up to many micrometers in length), the technique can be used to generate gaps as well as dot features. Sub-50-nm gaps are attainable via the more labor-intensive e-beam lithography, but sub-20-nm gaps are difficult to produce by any method. Indeed, a variety of labor-intensive e-beam-based techniques¹ as well as electrochemical methods have been worked out to produce such structures,¹⁰ but researchers could benefit from more straightforward methods of prepar-

ing such structures. At present, stamping methods do not provide the resolution or alignment registration capabilities necessary for fabricating such structures. DPN, however, allows one to pattern structures on this length scale, and herein we show how one can use this technique to prepare gaps in the range of 12 to 100 nm (Figure 2).

In a typical experiment, 20- μ m-long lines of MHA were generated by moving an MHA-coated tip on an Au surface at rates of 0.5 (Figure 2A), 0.25 (Figure 2B), and 0.25 (Figure 2C) μ m/s with designed gap distances of 100 (Figure 2A), 90 (Figure 2B), and 20 nm (Figure 2C). After etching the exposed areas of the Au film with a ferri/ferrocyanide etchant,^{6a} TMAFM images show that the measured sizes of the obtained nanogaps are ~ 97 (Figure 2A), 82 (Figure 2B), and 12 (Figure 2C) nm (see Supporting Information for section analysis). The obtained gap sizes are a little smaller than the designed gap sizes, a consequence of MHA diffusion that is not accounted for in the software or experimental protocol, which do not take into account differences in the ink diffusion as a function of tip coating. The widths of the etched lines are ~ 70 (Figure 2A), 170 (Figure 2B), and 165

(Figure 2C) nm. These data show that one can conveniently control both the line width and gap size using this protocol.

In summary, this work demonstrates how one can use DPN and wet-chemical etching to fabricate arrays of gold features with sub-50-nm dimensions. This type of methodology could open avenues for exploring quantum phenomena associated with deliberately designed arrays of inorganic materials such as Au, especially in the cases of surface enhancement in Raman spectroscopy,¹¹ plasmon optical coupling,¹² and nanoparticle-based biodiagnostics.¹³ In addition, nanogaps are widely used for making electrical measurements on nanoscale matter¹⁴ and even molecules.¹⁵ Although the electrical properties of the structures reported herein have not yet been explored, the ability to make metallic structures with sub-50-nm precision is a promising step toward a fast and convenient method for the fabrication of electrodes with nanogaps.

Acknowledgment. C.A.M. acknowledges the AFOSR, DARPA, and NSF for support of this research.

Supporting Information Available: Section analyses of the TMAFM images of the etched Au nanodot arrays and nanogaps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) See a review: Wallraff, G. M.; Hinsberg, W. D. *Chem. Rev.* **1999**, 99, 1801. and references therein.
- (2) (a) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 550. (b) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, 99, 1823.
- (3) Chou, S. Y. *MRS Bull.* **2001**, 26, 512.

- (4) Liu, G. Y.; Xu, S.; Qian, Y. *Acc. Chem. Res.* **2000**, 33, 457. and references therein.
- (5) (a) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, 283, 661. (b) Hong, S.; Zhu, J.; Mirkin, C. A. *Science* **1999**, 286, 523.
- (6) (a) Zhang, H.; Li, Z.; Mirkin, C. A. *Adv. Mater.* **2002**, 14, 1472. (b) Weinberger, D. A.; Hong, S.; Mirkin, C. A.; Wessels, B. W.; Higgins, T. B. *Adv. Mater.* **2000**, 12, 1600. (c) Xia, Y.; Zhao, X. M.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, 7, 2332.
- (7) (a) Ivanisevic, A.; McCumber, K. V.; Mirkin, C. A. *J. Am. Chem. Soc.* **2002**, 124, 11997. (b) Zhang, Y.; Salaita, K.; Lim, J. H.; Mirkin, C. A. *Nano Lett.* in press.
- (8) Hong, S.; Zhu, J.; Mirkin, C. A. *Langmuir*, **1999**, 15, 7897.
- (9) (a) Geissler, M.; Schmid, H.; Bietsch, A.; Michel, B.; Delamarche, E. *Langmuir* **2002**, 18, 2374. (b) Carvalho, A.; Geissler, M.; Schmid, H.; Michel, B.; Delamarche, E. *Langmuir* **2002**, 18, 2406.
- (10) (a) He, H. X.; Boussaad, S.; Xu, B. Q.; Li, C. Z.; Tao, N. J. *J. Electroanal. Chem.* **2002**, 522, 167. (b) Morpurgo, A. F.; Marcus, C. M.; Robinson, D. B. *Appl. Phys. Lett.* **1999**, 74, 2084.
- (11) (a) Felidj, N.; Aubard, J.; Levi, G.; Krenn, J. R.; Salerno, M.; Schider, G.; Lamprecht, B.; Leitner, A.; Aussenegg, F. R. *Phys. Rev. B* **2002**, 65, 075419. (b) Gearheart, L. A.; Ploehn, H. J.; Murphy, C. J. *J. Phys. Chem. B* **2001**, 105, 12609.
- (12) (a) Krenn, J. R.; Dereux, A.; Weeber, J. C.; Bourillot, E.; Lacroute, Y.; Goudonnet, J. P.; Schider, G.; Gotschy, W.; Leitner, A.; Aussenegg, F. R.; Girard, C. *Phys. Rev. Lett.* **1999**, 82, 2590. (b) Malinsky, M. D.; Kelly, K. L.; Schatz, R. G. C.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2001**, 123, 1471.
- (13) Bogunia-Kubik, K.; Sugisaka, M. *Biosystems* **2002**, 65, 123.
- (14) (a) He, H. X.; Zhu, J. S.; Tao, N. J.; Nagahara, L. A.; Amlani, I.; Tsui, R. *J. Am. Chem. Soc.* **2001**, 123, 7730. (b) Bogozi, A.; Lam, O.; He, H. X.; Li, C. Z.; Tao, N. J.; Nagahara, L. A.; Amlani, I.; Tsui, R. *J. Am. Chem. Soc.* **2001**, 123, 4585.
- (15) (a) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, 292, 2303. (b) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, 286, 1550.

NL0258473