Journal of the Korean Physical Society, Vol. 40, No. 4, April 2002, pp. 712∼715

Gold Nanoparticle Assemblies on a Functionalized Surface Patterned by AFM Lithography

Young Mee Jung, Sang Jung Ahn, Eung Ryul Kim and Haiwon Lee*
Department of Chemistry, Hanyang University, Seoul 133-791

(Received 11 February 2001)

We studied the fabrication of gold nanoparticles selectively deposited on the self-assembled monolayers (SAMs)/Si surface which had been already patterned with atomic force microscope (AFM) anodization lithography. In addition, dip-pen lithography was applied on the functionalized substrate surface. For this, a combination of nanolithography and the self-assembly process can be used to build the deposition of gold nonoparticles selectively on the patterned surface with AFM anodization lithography, which gives new insight into a the well-ordered patterned multilayer system.

PACS numbers: 85.40
Keywords: Gold nanoparticle assemblies, Self-assembled monolayers(SAMS), Atomic force microscope(AFM), AFM lithography, Anodization

I. INTRODUCTION

A number of recent studies have demonstrated the great utility of the atomic force microscope (AFM) owing to both its microscopic and lithographic capabilities [1–5]. In general, lithographic methods using an AFM consist of AFM tip-induced anodization of silicon surfaces and dip-pen lithography [1–6]. The former involves the application of an electrical bias to both the conducting probe and the sample substrate to locally oxidize selected regions of a sample surface to form groove patterns on a nanoscale. The latter uses the AFM tip as a nib, a solid-state substrate as paper, and molecules with a chemical affinity for the solid-state substrate as ink to directly write nanopatterns. There has also recently been another demonstration of nanodevices. Klein *et al.* [7, 8] reported that the fabrication of a single-electron transistor (SET) was conducted by using a hybrid scheme that combined fabrication of a metal electrode by electron beam lithography and positioning of nanocrystals by wet chemistry to bind nanocrystals in tunneling contact between two closely spaced metallic leads and that a single excess charge on a nanocrystal could markedly influence its properties; they also measured the electrical transport in a SET made from colloidal nanocrystals of cadmium selenide.

Since thin and uniform resist films are required for a well-ordered pattern in AFM lithography, a self-assembled method is a good candidate for this study. We have studied patterning of self-assembled monolayers (SAMs) on a nanometer-scale with AFM anodization lithography [9–13]. The recent achievements in AFM anodization lithography enabled us to engrave a nanoscale pattern on well-ordered monolayers adsorbed on a substrate. Furthermore, more advanced studies using these pre-patterned nanostructures have been accomplished to fabricate molecular devices.

The purpose of the present study is to fabricate a gold nanoparticle selectively on a funtionalized substrate surface and to explore the possibility that a combination of nanolithography and the self-assembly process can lead us to build SAMs selectively on surfaces pre-patterned with AFM anodization lithography. This contribution has two significant novelties. One is obtaining a high-resolution pattern of SAMs on a conducting substrate, a primary electrode, using AFM anodization lithography. The other is the selective attachment of a gold nanoparticle, a secondary electrode, on the SAMs. This proposed system was further designed for a SET.

II. EXPERIMENTAL

The trimethylsilyl (TMS)-derivatized hydrophobic surface of silicon was prepared by using the SAM technique with hexamethyldisilazane (HMDS) (Aldrich, USA) after acid-cleaning of p-type Si (100) wafers (LG Siltron, Korea) on which the native oxide provided a suitable density of reaction sites. A more detailed sample pre-paration procedure for SAMs was described previously [12]. In this study, the selective SAM of 3-aminopropylmethyldiethoxysilane (APS) (Aldrich,

*E-mail: haiwon@hanyang.ac.kr; Fax : +82-2-2296-0287

USA) was fabricated by immersing a prepattened TMS-derivatized silicon wafer substrate for 8 hours; then, successive gold nanoparticle layers were prepared by immersing the APS-derivatized substrate in a colloidal gold solution for 24 hours.

Each layer fabricated on the substrate was characterized by ellipsometry, UV-Vis, AFM, and lateral force microscopy (LFM). The thickness of the films were measured by using a Rudolph AutoEl ellipsometer (Rudolph Technology, Inc., USA) at an angle of incidence ϕ=70°. UV-Vis spectra were obtained by using an HP 8452A diode-array spectrophotometer. All AFM experiments in this study were performed with an Autoprobe CP AFM (Park Scientific Instruments Co., USA) and Nanoscope IIIa (Digital Instruments, USA) using a biasing circuit for the applied potential control and conducted in air at room temperature. The relative humidity during the AFM lithography experiment was about 60 %.

Dip-pen lithography uses an AFM tip as a "nib", a substrate (in this paper, self-assembled APS monolayer) as "paper", and molecules (in this paper, gold nanoparticles) with a chemical affinity for the substrates as "ink". A scheme of the positioning of gold nanoparticles to a specific area is presented. First, an area of substrate was imaged by using a conventional contact AFM method. Then, the scanning area was reduced to a specific area for the position of the nanoparticle. Then, holding all the parameters constant, the tip was withdrawn from the substrate for wetting by the gold colloidal solution. Finally, the tip with gold nanoparticles was inserted near the substrate and was maintained under a constant force over a specified scan area. The duration of adsorption of a gold nanoparticle on a self-assembled APS monolayer was about 30 min.

The gold nanoparticles used in this study were prepared by using the method proposed by Frens [14]. The reduction of gold chloride acid (10^{-2} wt %) with sodium citrate (1 wt %) in an aqueous solution yields a series of monodisperse gold suspensions with widely different particle sizes, depending upon the relative amounts of gold chloride. The suspensions had a red-violet color, depending upon the particle size, and showed an absorption maximum near 530 nm.

III. RESULTS AND DISCUSSION

A technique for selective positioning of gold nanoparticles on a silicon surface patterned by AFM lithography has been proposed. A high-resolution pattern of SAMs on a silicon substrate was obtained by using AFM anodization with a negative DC voltage applied to the tip of AFM. The patterned self-assembled silicon surfaces were modified with an immobilized organosilane polymers, such as APS, to organize the gold nanoparticles. Self-assembled gold nanoparticles can be prepared by covalent attachment of colloidal gold to functional groups

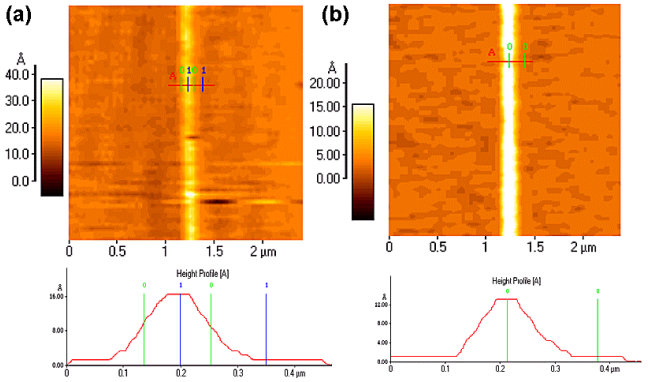

Fig. 1. AFM images of (a) the fabricated APS layer on the silicon surface patterned by AFM anodization lithography on an HMDS layer and (b) the silicon surface itself patterned by AFM anodization lithography on an HMDS layer.

on surface-confined organosilanes. To characterize the fabricated APS layer on the silicon surface patterned by AFM anodization lithography, we used AFM and LFM. Fig. 1 compares the AFM images of the fabricated APS layer on the silicon surface patterned by AFM anodization lithography with the silicon surface itself patterned by AFM anodization lithography. From comparing the AFM images of the fabricated APS layer on the silicon surface patterned by AFM anodization lithography with the silicon surface itself patterned by AFM anodization lithography, we found that the height of the protrude line by AFM anodization lithography on a HMDS layer was 12.0 Å while that on an APS layer was 15.4 Å. That suggests that APS was selectively deposited on the silicon surface patterned by AFM anodization lithography.

Figs. 2(a) and (b) show the LFM images of APS/Si and the Si wafer itself patterned by AFM anodization lithography on a HMDS layer, respectively. In Fig. 2, the LFM image of the silicon surface itself patterned by AFM anodization lithography on a self-assembled APS layer is also shown for comparison (Fig. 2 (c)). Because

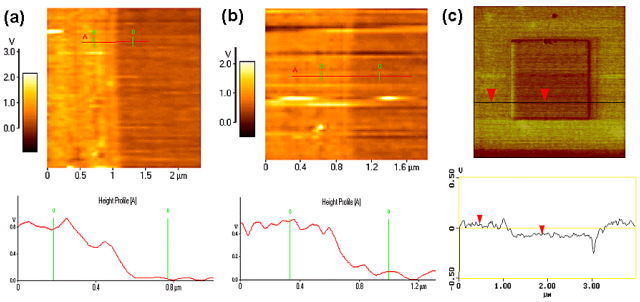

Fig. 2. LFM images of (a) the fabricated APS layer on the silicon surface patterned by AFM anodization lithography on an HMDS layer, (b) the silicon surface itself patterned by AFM anodization lithography on HMDS layer, and (c) the silicon surface itself patterned by AFM anodization lithography on self-assembled APS layer.

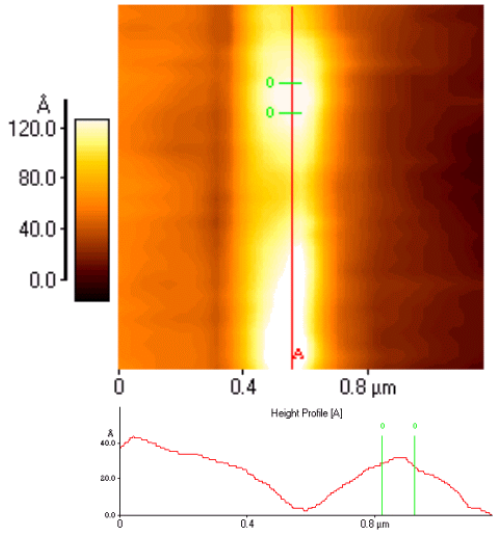

Fig. 3. AFM image of gold nanoparticles on the APS/patterned HMDS/Si surface.

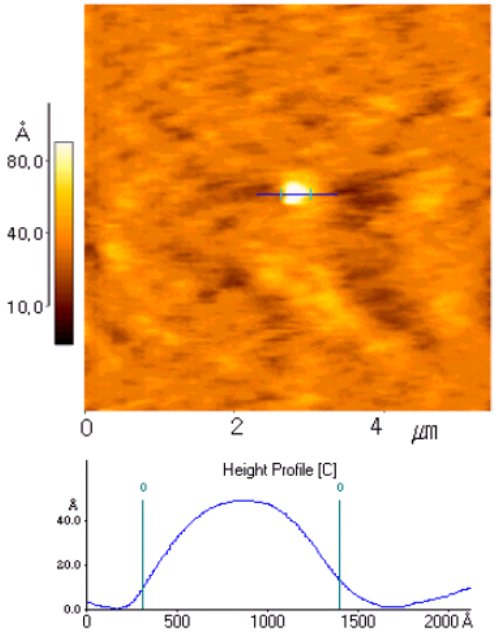

Fig. 4. AFM image of gold nanoparticles on the APS/Si surface by using dip-pen lithography.

LFM measures lateral deflections of the cantilevers that arise from the change in the surface friction which can arise from inhomogeneity in surface material, as well as from the change in slope, even in the same material, we compare the LFM images for a large area patterned by AFM anodization lithography, as shown in Figs. 2(a) and (b). Particularly striking in the comparison of Figs. 2(a) and (b) is that the average height differences were 0.757 V and 0.45 V, respectively. Furthermore, in order to directly elucidate the frictional differences between the APS surface and the patterned silicon oxide, we also patterned self-assembled APS surfaces. The obtained friction difference is 0.103 V, as shown in Fig. 2(c). That again confirmed that APS was selectively deposited on the HMDS/Si surface patterned by AFM anodization lithography. Thus, it is possible to fabricate gold nanoparticle assemblies on the APS layer selectively. Based upon these results, we found that this combination of nanolithography and the self-assembly process can be used to build SAMs, which result in surface modification of selected areas on various substrates.

Furthermore, we developed a technique for selective positioning gold nanoparticles on a patterned silicon wafer. Using this technique, we selectively deposited gold nanoparticles on APS/patterned HMDS/Si. Fig. 3 shows an AFM image of gold nanoparticles selectively deposited on the APS/patterned HMDS/Si surface. This suggests that this multilayered system might be used as a hybrid system for the fabrication of SETs.

In order to position the gold nanoparticle on the specified functionalized silicon surface, we have also studied dip-pen lithography with AFM. Fig. 4 shows the AFM image of a gold nanoparticle on a self-assembled APS layer obtained by using dip-pen lithography. As shown in Fig. 4, the size of the gold nanoparticle was about 100 nm with a 30-minute dip-pen time. In case of longer dip-pen times, doughnut-shaped clusters are formed by aggregation of several particles and in case of shorter dip-pen times, there is no evidence of the dip-pen process. This suggests that dip-pen lithography might be useful to fabricate an SET using metal or semiconductor nanoparticles.

IV. CONCLUSION

We have investigated several fabrication technologies for gold nanoparticle with AFM lithography. The selective deposition of gold nanoparticles on a silicon surface patterned by AFM anodization lithography was efficiently accomplished using the AFM, and the nanoparticle assembly was characterized by using AFM and LFM. Furthermore, it was found that this combination of nanolithography and the self-assembly process can be used to build SAMs selectively on patterned surfaces with AFM anodization lithography, which gives new insight into a well-ordered patterned multiplayer system.

ACKNOWLEDGMENTS

This study was supported by the Brain Korea 21 Project and by a program of the National Research Laboratory, the Ministry of Science and Technology (Grant Number: 99-N-NL-01-C-103).

REFERENCES

[1] C. R. K. Marrian, F. K. Perkins, S. L. Brandow, T. S. Koloski, E. A. Dobisz and J. M. Calvert, Appl. Phys. Lett. **64**, 390 (1994).

[2] W. T. Muller, D. L. Klein, T. Lee, J. Clarke, P. L. McEuen and P. G. Schultz, Science **268**, 272 (1995).

[3] H. Sugimura and N. Nakagiri, J. Vac. Sci. Technol. A **14**, 1223 (1996).

[4] E. Dubois and J.-L. Bubbendorff, Solid-State Electronics **43**, 1085 (1999).

[5] C. Huh and S. J. Park, J. Vac. Sci. Technol. B **18**, 55 (2000).

[6] R. D. Piner, J. Zhu, F. Xu, S. Hong and C. A. Mirkin, Science **283**, 661 (1999).

[7] D. L. Klein, P. L. McEuen, J. E. B. Katari, R. Roth and A. P. Alivisatos, Appl. Phys. Lett. **68**, 2574 (1996).

[8] D. L. Klein, R. Roth, A. K. L. Lim, A. P. Alivisatos and P. L. McEuen, Nature **389**, 699 (1997).

[9] J. C. Kim, Y. Oh, Y. W. Shin, S. W. Park and H. Lee, Japan J. Appl. Phys. **37**, 324 (1998).

[10] J. C. Kim, Y. Oh, H. Lee, Y. W. Shin and S. W. Park, J. Korean Phys. Soc. **33**, S84 (1998).

[11] Y. Oh, J. C. Kim and H. Lee, Mol. Cryst. Liq. Cryst. **337**, 7 (1999).

[12] E. J. Bae, E. R. Kim and H. Lee, J. Korean Phys. Soc. **37**, 1026 (2000).

[13] Y. M. Jung, S. J. Ahn, H. J. Chai, E. R. Kim and H. Lee, Mol. Cryst. Liq. Cryst. **370**, 231 (2001).

[14] G. Frens, Nature Phys. Sci. **241**, 201 (1973).