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Site-Selective Assembly and Reorganization of Gold Nanoparticles along Aminosilane-Covered Nano lines Prepared on Indium-Tin Oxide

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Circular Arrays of Gold Nanoparticles of a Single Particle Line Thickness Formed on Indium Tin Oxide

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Highly controlled arrays of gold nanoparticles (AuNPs) were fabricated on optically transparent indium tin oxide (ITO) substrates by combining atomic force microscope (AFM) lithography and surface modification using self-assembled monolayers (SAMs). The nanopatterns of methyl and amino groups were fabricated on ITO substrates and AuNPs were assembled just on the amino-terminated nanopatterns, which is based on the different affinities of the AuNPs for the functional groups. The site selectivity was intensively improved by dehydration and repairing defects in a long alkylsilane SAM with short alkylsilane molecules. © 2012 The Japan Society of Applied Physics

The assembly of nanomaterials on a desired area has received increasing attention because of their unique electrical and optical properties in technological application, such as electronics, optics, and sensor devices.^{1–6} For exploiting the specific properties of nanomaterials, chemical patternings on the nanometer or micrometer scale have been identified as an efficient way to form arrays of nanomaterials.^{1,7,8} Self-assembled monolayers (SAMs) are useful for controlling the physical and chemical properties of a solid substrate with versatile molecular arrangements of molecular thickness.^{9,10} In addition, SAMs can be easily applied to various patterning processes, which leads to patterning of the chemical functionalities of the surface.^{11–14}

Conventional lithography techniques including the optical lithography and scanning beam lithography have some problems such as resolution limit, high cost and restricted applicability.^{15–17} However scanning probe-based lithography is possible to fabricate the nanostructure within nanometer size area under environment conditions with easy process. In particular, atomic force microscope (AFM) lithography that is the most promising probe-based lithography technique can be applied to patterning SAM on various surfaces by local chemical reaction and guide the site-selective surface modification by deposition of functionalized SAMs on patterned oxide domains.^{7,15–23}

In this work, we demonstrate the highly controlled arrays of AuNPs by combining AFM lithography and SAM modification on indium tin oxide (ITO) substrates. ITO has attracted extensive interest for application due to its optical transparency and conductivity. The template was fabricated by AFM lithography and subsequent SAM deposition on the ITO surface, for guiding the site-selective immobilization of AuNPs by using the electrostatic affinity difference of AuNPs towards functionalized surfaces.

Figure 1 depicts the experimental procedures for the site-selective assembly of citrate-capped AuNPs on an ITO substrate. First, an ITO substrate was covered by a SAM composed of methyl-terminated alkylsilanes by chemical vapor deposition (CVD). Then the SAM was locally degraded by AFM lithography where a bias voltage (−6 to −7 V) was applied to the tip against the substrate. A commercially available AFM (Asylum Technology MFP-3D-SA) was used in contact mode using rhodium-coated silicon cantilevers (tip radius < 30 nm, spring constant: 1.8 N/m). The scan rate was 1 μm/s at 60 to 70% relative

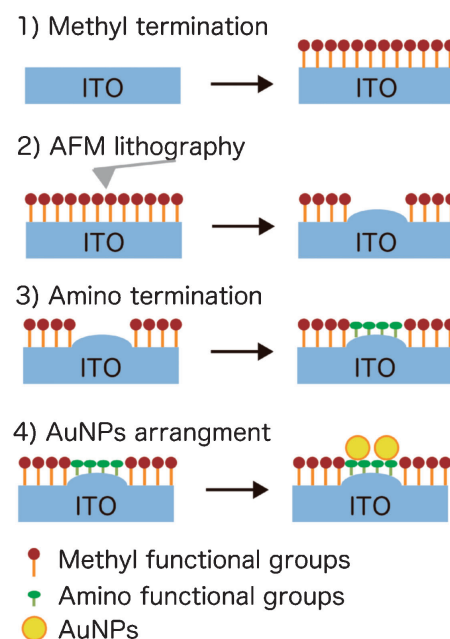


Fig. 1. Experiment procedure for fabrication of AuNPs on ITO substrate via site-selective self-assembly.

humidity and room temperature. Then the sample was kept on the vapor of aminopropyltriethoxysilane (APS) at 100 °C for 2 h in order to terminate the degraded area with amino groups. Finally, the locally amino-terminated sample was subsequently immersed in the suspension of citrate-stabilized AuNPs ($\phi = 20 \pm 3$ nm, Sigma-Aldrich) for site-selective assembly on the patterned template for 12 h.

We prepared three samples for this work. For sample 1, methyl termination was just carried out by octadecyltrimethoxysilane (ODS). To prepare the ODS-SAM, an ITO substrate was placed with a glass vessel with 150 μL of neat ODS in a cylinder Teflon container under dry nitrogen atmosphere. The Teflon container was sealed and placed in an electric oven at 150 °C for 3 h. The deposited sample was sonicated in ethanol for 10 min and was blown with nitrogen gas.

The root mean square roughness value of ODS-modified substrate was 0.4 ± 0.05 nm in the $5 \times 5 \mu\text{m}^2$ AFM image, which is similar to that of the bare ITO surface. The water contact angle of the sample was found to be $104 \pm 1^\circ$. These results suggest the formation of a conformationally ordered ODS-SAM.¹⁴

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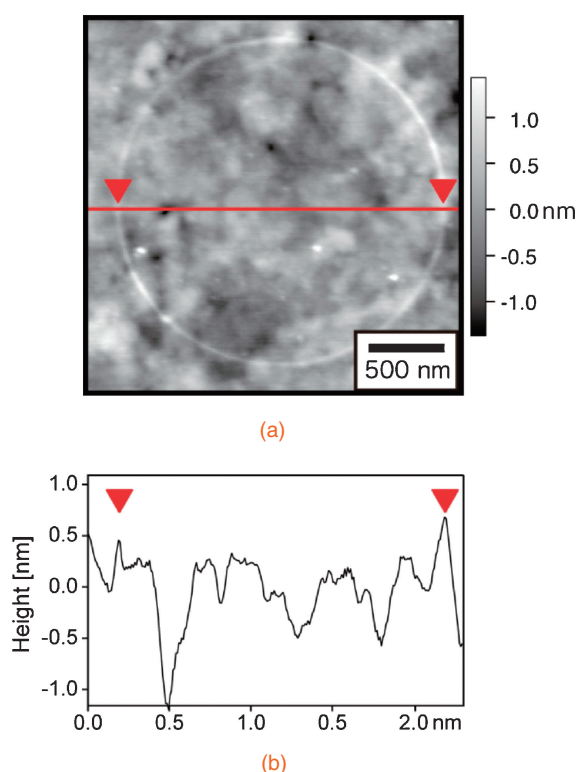


Fig. 2. AFM image of degraded ITO substrate by AFM lithography. (a) Gray-scale image and (b) cross-sectional line profile.

The ODS-SAM was locally degraded by AFM lithography. Figures 2(a) and 2(b) show an AFM image and line profile of sample 1 after the AFM lithography. The degraded area protruded approximately 0.7 nm. This is possible to control the size of degraded area by calibrating the bias voltage, scan speed and relative humidity.^{19,20} This protrusion is not proved by any experimental proof. We suggest a possible mechanism as follow; when given enough bias voltage on the tip, a nanometer-sized electrochemical cell is formed between the tip and the sample, and OH^- and O^{2-} ions are produced by electrolysis of the surface water, as suggested by Sugimura *et al.*²² The generated oxygen species react with the ITO substrate that has oxygen vacancies and then make up the indium oxide products. Then the indium oxide combined with water creates the hydroxyl products such as $\text{In}(\text{OH})_3$ and InOOH .²⁴ The hydroxylated surface would react with the silanol groups and form silane coupling.^{25,26}

Figure 3(a) shows an AFM image of sample 1 after immobilization of AuNPs. AuNPs were immobilized on the patterned area. This immobilization originates from the electrostatic interaction between the negatively charged AuNPs and the positively charged amino groups of the APS-SAM. This result proved the successful assembly of APS molecules to hydroxyl products on the degraded area. We also found that the AuNPs immobilized not only on the patterned area but also on the ODS-modified area. This result indicates that the APS molecules were adsorbed on the ODS-modified area as well as the degraded area.

Sample 2 was appropriately pretreated by rinsing with ethanol and sonicating in toluene for 10 min to dehydrate the ODS-modified ITO substrate, before the APS assembly.

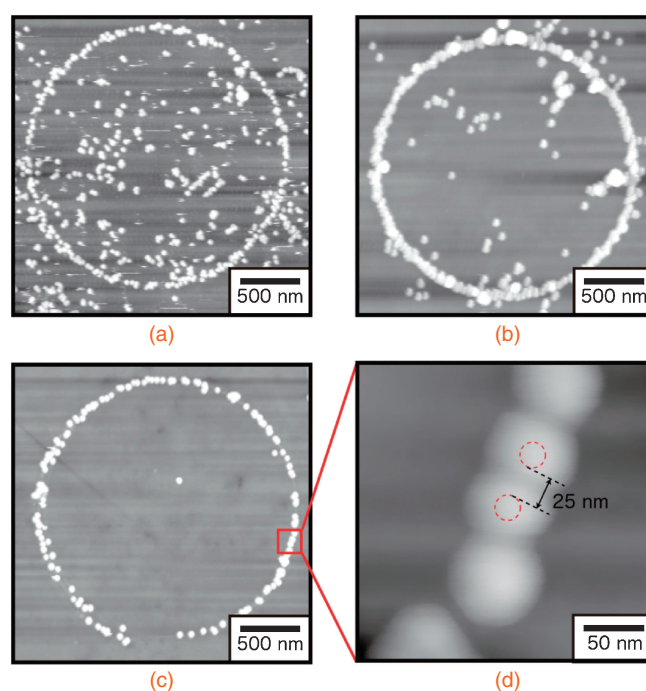


Fig. 3. AFM images of (a) sample 1, (b) sample 2, and (c) sample 3. (d) Magnified image of homogeneously distributed AuNPs in sample 3 (dashed line: real size of AuNPs).

Figure 3(b) shows an AFM image of sample 2 after the immobilization of AuNPs. AuNPs were also immobilized on the APS-modified area. In addition, the amount of immobilized AuNPs on the ODS-modified area was decreased. This result strongly suggests that the APS adsorption on the ODS-modified surface was reduced by the dehydration process. The silane-coupling reaction is known to be very sensitive to the adsorbed water on the surface. When surface water exists on the ODS monolayer, the APS molecule adsorbs on the wet surface through hydrogen bonds, such as $-\text{H}_2\text{N}\cdots\text{HOH}$ or $-\text{Si}-\text{OH}\cdots\text{HOH}$.²⁵ The dehydration process on the ODS-modified ITO sample improved the selectivity of AuNP immobilization as shown in Figs. 2(a) and 2(b).

For sample 3, the methyl termination on the ITO substrate was carried out by using both ODS and trimethoxy(propyl)silane (TPS). First, an ITO substrate was covered with ODS-SAM. After that, the ODS-terminated ITO substrate was kept in the teflon container for 1 h at 110 °C with TPS molecules and subsequently sonicated in ethanol for 10 min and blown with dry N_2 in order to reduce the number of defects on the ODS-SAM. Because the size of TPS is much smaller than that of ODS and is slightly smaller than that of APS, TPS should be suitable for filling defects in ODS-SAM. Then, the dehydration process using ethanol and toluene was also carried out prior to the APS deposition. Figure 3(c) shows an AFM image of sample 3 after the AuNP assembly. We found the precise distribution of AuNPs in a circular pattern on a predefined site, and the methyl-terminated surface was almost unexposed to the AuNPs, that is, the site-selective assembly of AuNPs was improved by preventing defects and dehydration.

Figure 3(d) shows an AFM image of the homogeneously distributed AuNPs on the patterned area as indicated in

Fig. 3(c). The apparent diameter of the AuNPs was about 75 nm, while the real diameter was 20 nm. This is because of the convolution of the AuNPs and the AFM tip. The interparticle distance between the AuNPs can be measured as 25 nm from Fig. 3(d), i.e., the AuNPs were not closely packed. This was expected because of the electrostatic repulsion among the citrate-coated AuNPs.

In conclusion, we performed the site-selective immobilization of AuNPs on an ITO substrate by using AFM lithography and self-assembly techniques. The site selectivity was improved by combining the following two methods; 1) dehydration on the methyl-terminated surface and 2) reduction of the number of defects on the methyl-terminated surface. It is expected that these techniques will have broad applications to the nanofabrication on electronics, biological and chemical sensors, etc.

- 1) W. M. Wang, R. M. Stoltenberg, S. Liu, and Z. Bao: *ACS Nano* **2** (2008) 2135.
- 2) J. Sung, E. M. Hicks, R. P. V. Duyne, and K. G. Spears: *J. Phys. Chem. C* **111** (2007) 10368.
- 3) Y. Sun and Y. Xia: *Science* **298** (2002) 2176.
- 4) S. Liu, J. B. H. Tok, and Z. Bao: *Nano Lett.* **5** (2005) 1071.
- 5) Y. Seol, A. E. Carpenter, and T. T. Perkins: *Opt. Lett.* **31** (2006) 2429.
- 6) N. Nath and A. Chilkoti: *Anal. Chem.* **74** (2002) 504.
- 7) L. Ressier, B. Viallet, A. Beduer, D. Fabre, L. Fabie, E. Palleau, and E. Dague: *Langmuir* **24** (2008) 13254.
- 8) Q. Li, J. Zheng, and Z. Liu: *Langmuir* **19** (2003) 166.
- 9) H. Sugimura, K. Ushiyama, A. Hozumi, and O. Takai: *Langmuir* **16** (2000) 885.
- 10) R. B. A. Sharpe, D. Burdinski, C. van der Marel, J. A. J. Jansen, J. Huskens, H. J. W. Zandvliet, D. N. Reinhoudt, and B. Poelsema: *Langmuir* **22** (2006) 5945.
- 11) H. Sugimura and N. Nakagiri: *Jpn. J. Appl. Phys.* **34** (1995) 3406.
- 12) Y. Xia and G. M. Whitesides: *Angew. Chem., Int. Ed.* **37** (1998) 550.
- 13) Y. Xia, J. A. Rogers, K. E. Paul, and G. M. Whitesides: *Chem. Rev.* **99** (1999) 1823.
- 14) O. P. Khatri, K. Murase, and H. Sugimura: *Jpn. J. Appl. Phys.* **47** (2008) 5048.
- 15) B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson, and G. M. Whitesides: *Chem. Rev.* **105** (2005) 1171.
- 16) M. Peter, X. M. Li, J. Huskens, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **126** (2004) 11684.
- 17) D. Wouters and U. S. Schubert: *Angew. Chem., Int. Ed.* **43** (2004) 2480.
- 18) H. Sugimura, K. Okiguchi, N. Nakagiri, and M. Miyashita: *J. Vac. Sci. Technol. B* **14** (1996) 4140.
- 19) J. Han, D. Kasahara, T. Ichii, K. Murase, and H. Sugimura: *J. Vac. Sci. Technol. B* **27** (2009) 928.
- 20) B. Garipcan, J. Winters, J. S. Atchison, M. D. Cathell, J. D. Schiffman, O. D. Leaffer, S. S. Nonnenmann, C. L. Schauer, E. Piskin, B. Nabet, and J. E. Spanier: *Langmuir* **24** (2008) 8944.
- 21) S. Krämer, R. R. Fuierer, and C. B. Gorman: *Chem. Rev.* **103** (2003) 4367.
- 22) H. Sugimura and N. Nakagiri: *Langmuir* **11** (1995) 3623.
- 23) B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson, and G. M. Whitesides: *Chem. Rev.* **105** (2005) 1171.
- 24) A. J. Bard, M. Stratmann, I. Rubinstein, M. Fujihira, and J. F. Rusling: *Encyclopedia of Electrochemistry* (Wiley-VCH, Weinheim, 2007) Vol. 10, p. 18.
- 25) X. Ling, X. Zhu, J. Zhang, T. Zhu, M. Liu, L. Tong, and Z. Liu: *J. Phys. Chem. B* **109** (2005) 2657.
- 26) A. Ulman: *Chem. Rev.* **96** (1996) 1533.