doi:10.1246/cl.2012.392

Nanotemplate Prepared by Means of Vacuum Ultraviolet Patterning of Alkylsilane Self-assembled Monolayer on ITO Using a Porous Alumina Mask: Application to the Fabrication of Gold Nanoparticle Arrays

Jeonghyeon Yang,[1] Takashi Ichii,[1] Kuniaki Murase,[1] Hiroyuki Sugimura,*[1] Toshiaki Kondo,[2] and Hideki Masuda[2,3]
[1]*Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501*
[2]*Kanagawa Academy of Science and Technology, 5-4-30 Nishihashimoto, Sagamihara, Kanagawa 229-1131*
[3]*Department of Urban Environmental Sciences, Tokyo Metropolitan University,*
1-1 Minamiosawa, Hachioji, Tokyo 192-0397

(Received November 25, 2011; CL-111133; E-mail: hiroyuki-sugimura@mtl.kyoto-u.ac.jp)

Gold nanoparticles (AuNPs) have been arranged on a nanotemplate prepared on indium tin oxide substrate. This template, consisting of circular areas of about 200 nm in diameter hexagonally assembled with an interval of 450 nm, was prepared by using an anodic porous alumina membrane mask and vacuum ultraviolet light at 172 nm. The site-selective immobilization of AuNPs was controlled with the electrostatic affinity difference of AuNPs toward functionalized surface characterized by self-assembled monolayer.

Procedures to arrange nanoparticles and functions of the arranged nanoparticles have been widely investigated due to their unique properties. In the application of nanoparticles, assembly of nanoparticles on desired areas with high regularity is essential.[1,2] Organosilane self-assembled monolayers (SAMs) have attracted considerable attention, because these readily alter surface properties which are needed to manipulate functional molecules on a predetermined area.[3] The use of vacuum ultraviolet (VUV) light of 172 nm in wavelength has been proven a powerful tool for patterning organic thin films by irradiating through a photomask.[4,5] This method completes patterning of the thin films only irradiating their surface through a photomask without complicated photoresist processes such as developing, etching, and removing, which are essentially needed in a conventional photolithography and other advanced lithographic methods such as nanoimprint lithography.[6] Thus, by VUV lithography, minute SAM patterns can be fabricated more simply. In particular, Khatri et al. have reported 500 nm patterning of SAM based on the VUV lithography.[5] Considering the short wavelength of the VUV light finer features down to 200 nm or smaller are expected to be printed on a sample surface, if a proper photomask is available. Highly ordered porous membranes, which are formed by anodizing Al in an acidic solution, have attracted tremendous interest as the mask, because those are good templates to fabricate fine structures of submicron to nanometer scale.[7,8] Thus, application of the porous alumina mask to VUV patterning is of special interest.

Here, we demonstrate VUV etching of a methyl-terminated SAM using an anodic porous alumina membrane mask and the fabrication of minute aminosilane SAM patterns on which gold nanoparticles (AuNPs) are arranged by the self-aligned deposition. Indium tin oxide (ITO) was selected as a substrate material due to its optical transparency and conductivity favorable for future applications with plasmonic functions of AuNPs.

A methyl-terminated SAM was prepared on ITO (Kuramoto Co., thickness: 150 nm, rms roughness: 0.4 nm, over 5 × 5 μm^2) surface by chemical vapor deposition (CVD).[9] The substrate was sonicated in ethanol and ultrapure water for 20 min, respectively. Furthermore, it was irradiated with VUV light at a wavelength of 172 nm in air for 20 min. We confirmed that the substrate surface became hydrophilic by measuring its water contact angle (near 0°). To prepare the octadecyltrimethoxysilane (ODS) monolayer, the substrate was placed in a cylindrical Teflon container with a glass vessel filled with ODS liquid under dry nitrogen atmosphere. The Teflon container sealed with a cap was placed in an electric oven maintained at 150 °C for 3 h. The sample was sonicated in ethanol for 10 min and blown dry with nitrogen gas. The ODS-terminated ITO substrate was further kept in the Teflon container for 1 h at 110 °C with trimethoxy(propyl)silane (TPS) liquid to heal defects of the ODS monolayer. Again, the sample was sonicated in ethanol for 10 min and blown with dry N_2. The water contact angle of the substrate was found to be 104 ± 1°.

The ITO substrate covered with a methyl-terminated SAM was exposed to VUV light through with contacting an anodic porous alumina mask on its surface to replicate the alumina hole pattern through photoetching of the methyl-terminated SAM. Figure 1 shows an FE-SEM image of the uniformly ordered anodic porous alumina mask formed by Al anodizing in an acidic electrolyte. The diameter and interval of the holes were about 120 and 450 nm, respectively. The alumina membrane thickness, that is, the depth of the holes, was about 200 nm. Figure 2a shows the scheme for the VUV lithography of methyl-terminated monolayer. The VUV lithography of the methyl-terminated substrate was performed by using an excimer lamp ($\lambda = 172$ nm). The distance from the lamp window to the surface was maintained at 10 mm during VUV patterning. The sample located in a vacuum chamber of which pressure was regulated at 10^3 Pa was exposed to VUV light for 200 s.

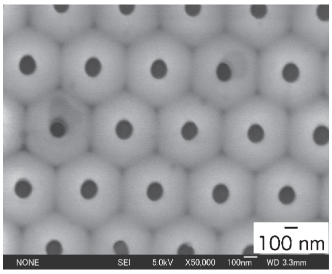

Figure 1. FE-SEM image of anodic porous alumina mask.

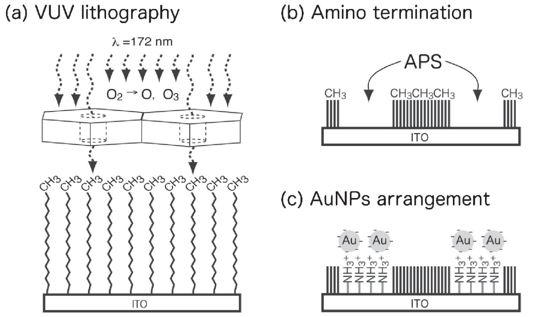

Figure 2. Schematic illustration for the site-selective assembly of AuNPs (a) VUV etching of the methyl-terminated SAM through the anodic porous alumina mask, (b) the VUV-etched area is covered with APS, and (c) assembly of AuNPs on the APS-modified area.

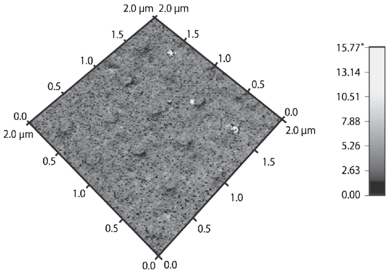

Figure 3. Phase image of tapping mode AFM on methyl-terminated surface after the VUV irradiation.

After the patterning, the sample was sonicated with ethanol to remove the alumina mask and pretreated by absolute toluene for dehydration of its surface. Figures 2b and 2c illustrated the AuNP assembly process. For depositing aminopropyltriethoxysilane (APS) on the etched area with VUV-generated active oxygen, the dehydrated sample was exposed to vapor of APS at 100 °C for 2 h. Subsequently the sample was sonicated in toluene, ethanol, and ultrapure water for 5 min each. The locally amino-terminated sample was immersed in a Au colloidal suspension (Sigma-Aldrich) which contains citrate-capped AuNPs ($\phi = 20 \pm 3$ nm) for 2 h.

The change of the methyl-terminated surface after VUV exposure was analyzed by phase imaging in the intermittent contact mode atomic force microscopy as shown in Figure 3. Circular areas with a slightly large phase lag can be recognized in this phase image. The circular areas are hexagonally arranged with an interval of about 450 nm identical to the interval of the hole array of the alumina mask. This result indicates that some chemical changes are induced on the methyl-terminated monolayer under the holes of the alumina mask due to VUV irradiation. We assume this chemical conversion process as follows: First, VUV light dissociatively excite atmospheric oxygen molecules to form atomic oxygen. Ozone molecules are formed as well through collision of oxygen atoms and oxygen molecules. Second, these active oxygen species diffuse into the alumina holes so that the methyl-terminated SAM surface is oxidized. As reported previously, hydrophilic functional groups such as –OH and –COOH are formed on the monolayer surface and finally the SAM is etched away.[10,11]

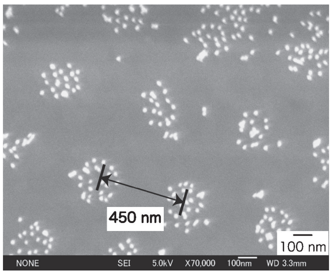

Figure 4. FE-SEM image of immobilized AuNPs on predefined area.

Figure 4 shows an FE-SEM image of a AuNPs array fabricated on the ITO substrate. We confirmed that AuNPs were anchored on the predefined circular areas with precise positioning, while the remaining surface was almost unexposed to the AuNPs. The distance of the AuNPs islands was about 450 nm, which agrees well with the interval of the alumina mask holes. This may be attributed well that APS molecules modified the area etched with VUV-generated active oxygen. Namely, the area was covered with an APS monolayer. The immobilization of AuNPs originated from electrostatic interactions between citrate-stabilized AuNPs and amino groups of the APS monolayer. In addition, the area of immobilized AuNPs was broader than the hole diameter of porous alumina mask (120 nm). This result indicated the diffusion of VUV-generated oxidants under the masked area.

In conclusion, we have succeeded in the near-wavelength patterning of the amino/methyl-terminated SAM on ITO by VUV lithography using the anodic porous alumina mask. The methyl-terminated SAM could be etched through the holes smaller than the VUV wavelength. Moreover, the site-selective immobilization of AuNPs on the etched areas was attained. Since this photoetching as shown in Figure 2a was successfully conducted through holes smaller than the VUV wavelength, finer features in nanometer scales are expected to be fabricated with the strong oxidants generated by VUV irradiation, regardless of the optical limit.

This work was supported by KAKENHI (Grant-in-Aid for scientific research) No. 19049010 on Priority Area “Strong Photon–Molecule Coupling Fields (470)” from the Ministry of Education, Culture, Sports, Science and Technology of Japan, an international cooperative program of the Japan Science and Technology Agency (JST).

References

1 M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
2 Y. Wang, C. A. Mirkin, S.-J. Park, *ACS Nano* **2009**, *3*, 1049.
3 K. Hayashi, A. Hozumi, N. Saito, H. Sugimura, O. Takai, *Surf. Sci.* **2003**, *532–535*, 1072.
4 H. Sugimura, K. Ushiyama, A. Hozumi, O. Takai, *Langmuir* **2000**, *16*, 885.
5 O. P. Khatri, H. Sano, K. Murase, H. Sugimura, *Langmuir* **2008**, *24*, 12077.
6 S. Gilles, C. Kaulen, M. Pabst, U. Simon, A. Offenhäusser, D. Mayer, *Nanotechnology* **2011**, *22*, 295301.
7 H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.
8 M. Harada, S. Murata, T. Yanagishita, H. Sugimura, K. Nishio, H. Masuda, *Chem. Lett.* **2007**, *36*, 1266.
9 H. Sugimura, A. Hozumi, T. Kameyama, O. Takai, *Surf. Interface Anal.* **2002**, *34*, 550.
10 L. Hong, H. Sugimura, T. Furukawa, O. Takai, *Langmuir* **2003**, *19*, 1966.
11 Y.-J. Kim, K.-H. Lee, H. Sano, J. Han, T. Ichii, K. Murase, H. Sugimura, *Jpn. J. Appl. Phys.* **2008**, *47*, 307.