DPN-Generated Nanostructures Made of Gold, Silver, and Palladium

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Dip-pen nanolithography (DPN) has been used to generate resist layers on Au, Ag, and Pd that when combined with wet-chemical etching can lead to nanostructures with deliberately designed shapes and sizes. Monolayers of mercaptohexadecanoic acid (MHA) or octadecanethiol (ODT), patterned by DPN, were explored as etch resists. They work comparably well on Au and Ag, but ODT is the superior material for Pd. MHA seems to attract the $FeCl_3$ etchant and results in nonuniform etching of the underlying Pd substrate. Dots, lines, triangles, and circles, ranging in size from sub-100 to several hundred nanometers have been fabricated on Si/SiO_x substrates. These results show how one can use DPN as an alternative to more complex and costly procedures such as electron beam lithography to generate nanostructures from inorganic materials.

Introduction

In the emerging field of nanoscience and technology, functionalized inorganic metallic nanostructures and nanoarrays have been widely studied because of their potential applications in electronics,[1] optics,[2] biodiagnostics,[3] and catalysis.[4] There are a variety of methods for fabricating such structures, all of which possess certain attributes and shortcomings. For example, high-resolution lithographic methods, such as electron-beam lithography[5] and nanoimprint lithography,[6] can be used to fabricate metallic nanostructures/nanoarrays, but these methods do not allow one to pattern surfaces with soft materials. Microcontact printing (μCP)[7] allows one to directly deposit molecules onto a surface in massively parallel fashion, but it is a relatively low resolution technique when compared with e-beam lithography and nanoimprinting. Moreover, none of these methods allow one to make structures out of many materials (or inks) with nanoscale registration capabilities.

Scanning-probe-based lithographies[8] allow one to generate sub-100 nm structures on surfaces but often only in serial fashion. Dip-pen nanolithography (DPN),[9] a new scanning-probe-based tool for fabricating sub-100 nm to many micrometer structures on surfaces, is unique in this regard since it is a direct-write method with high registration capabilities that has been transitioned from a serial to parallel writing tool through the use of cantilever arrays.[9c,10] Importantly, because it is a direct-write method, one can fabricate not only single-component nanostructures but also multicomponent ones made from different inks. Thus far, capabilities have been demonstrated for small organic molecules[9a−c,11] dendrimers,[12] conducting polymers,[13] biological molecules (DNA,[14] proteins,[15] and peptides,[15d,16]), nanoparticles,[17] sol gels,[18] and metal ions.[19] These combined capabilities make DPN a powerful tool for

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fabricating both hard and multicomponent soft nanostructures with nanoscale precision.

In a previous manuscript,[20] we developed a method for fabricating arrays of Au nanostructures on a Si/SiO$_X$ surface based on DPN with subsequent wet-chemical etching.[21] We have successfully made sub-50 nm Au nanodot arrays and 12 nm Au nanogaps using this approach.[22] The Au nanoarrays generated via this procedure also can be used as templates to assemble other structures on top of them, including oligonucleotides,[20] proteins,[23] and Au nanoparticles.[20,23] In addition, by using the Au features as a resist, high-quality sub-100 nm Si structures could be generated.[24] In this paper, we explore the generality of this approach and how it can be used to fabricate structures made from Ag and Pd, two metals that are of interest for a variety of optical[25] and catalytic[26] applications. In addition, we explore the prospect of preparing structures other than lines and dots in square and hexagonal lattices, including circles and triangles. Such capabilities are important for fabricating many types of structures that have applications in optics and electronics. Some of these applications include substrates for surface-enhanced Raman spectroscopy,[27] plasmon wires,[28] biodiagnostics,[3] and electrical measurements on nanoscale matter and even molecules.[29]

Experimental Section

Chemicals. Ammonium hydroxide and hydrogen peroxide (30%) were purchased from Fisher Scientific. The FeCl$_3$-based etchant, TFP, was purchased from Transene, Inc. (Danvers, MA). All other chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. Milli-Q water (>18 MΩ cm) was used for all aqueous experiments.

Substrate Preparation. An oxidized silicon wafer (~500 nm of oxide) was cut into 1 × 1 cm^2 squares. After being ultrasonicated with acetone for 10 min and rinsed with Milli-Q water, the Si substrates were immersed into a boiling solution of ammonium hydroxide and hydrogen peroxide ($V(NH_4OH)$:$V(H_2O_2)$:$V(H_2O) = 1:1:5$) for 1 h. The cleaned substrates were rinsed with Milli-Q water, dried with N$_2$, and then put into a thermal evaporator chamber. Under vacuum conditions (pressure $< 1 \times 10^{-7}$ Mbar), the substrates were coated with a 1 nm Ti adhesion layer via thermal evaporation and subsequently coated with Au (10 nm), Ag (30 nm), and Pd (20 nm), respectively, to make Au, Ag, and Pd thin films. These substrates were used immediately for DPN experiments.

Dip-Pen Nanolithography (DPN) and Wet-Chemical Etching. The metal substrates were patterned with 16-mercaptohexadecanoic acid (MHA) or 1-octadecanethiol (ODT) by DPN,[9,20,22−24] and all DPN experiments were carried out under ambient conditions (set point = 0.5 nN, 22−24 °C, 30−36% relative humidity) by using an AutoProbe CP AFM (TM Microscopes, Sunnyvale, CA) and commercial lithography software (DPNWrite, DPN System-1, NanoInk Inc., Chicago, IL) with MHA- or ODT-coated tips. MHA-coated tips were prepared by immersing Si$_3$N$_4$ cantilevers ($k = 0.05$ N/m, TM Microscopes, Sunnyvale, CA) in an acetonitrile solution saturated with MHA for ~5 s. They were subsequently dried with compressed difluoroethane (Dust-off, Ted Pella, Inc., Redding, CA). ODT-coated tips were prepared by thermal evaporation of ODT onto Si$_3$N$_4$ tips at 65 °C for 30 min.

The Au substrates, patterned with MHA or ODT, were immersed in a ferri-/ferrocyanide etching solution (a 1:1:1:1 (v:v:v:v) aqueous mixture of 0.1 M Na$_2$S$_2$O$_3$, 1.0 M KOH, 0.01 M K$_3$Fe(CN)$_6$, and 0.001 M K$_4$Fe(CN)$_6$) for ~20 min under constant stirring to remove the Au layer from the exposed regions of the Au substrate.[20,22,23] The Ag substrates, patterned with MHA, were treated with a ferri-/ferrocyanide etching solution[30] (a 1:1:1 (v:v:v) aqueous mixture of 30 mM Na$_2$S$_2$O$_3$, 3 mM K$_3$Fe(CN)$_6$, and 0.3 mM K$_4$Fe(CN)$_6$) for 1−2 min to remove the exposed Ag layer. The Pd substrates, patterned with MHA or ODT, were immersed in a TFP etchant, which was diluted to a 5:1 ratio of H$_2$O:etchant for 10−30 s to remove the unprotected palladium.[31] (Note: The etching time is dependent on the type of metal, the thickness of the metal films, and how fresh the metal films are. When the unprotected metal is completely etched, the substrate's color changes from the color of a coated metal film to the color of bare Si/SiO$_X$.) After being rinsed with Milli-Q H$_2$O, the etched substrates were immersed into a 0.5% (v/v) aqueous HF solution for 10−15 s to remove the 1 nm Ti layer. Then the substrates were rinsed with Milli-Q H$_2$O and dried with N$_2$.

Tapping Mode AFM (TMAFM) Images. All etched metal nanostructures were imaged under ambient conditions in tapping mode using a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA).

Results and Discussion

1. Au, Ag, and Pd Nanostructures of Almost Any Shape and Size.

Dip-pen nanolithography (DPN) can be used to generate nanostructures of arbitrary size and shape consisting of a monolayer of organic molecules adsorbed to an underlying substrate (e.g., alkanethiols on gold).[9] The as-deposited nanostructures can be used as resists to prevent the underlying Au from being etched when the substrate is immersed into a ferri-/ferrocyanide-based Au etchant. In our previous work, using monolayers of mercaptohexadecanoic acid (MHA) generated by DPN as etch resists, we were able to generate sub-50 nm Au dot arrays,[22] 12-nm gaps between Au lines,[22] and arrays of sub-100 nm Au lines[20,23] on a Si/SiO$_X$ substrate. Herein, we describe the

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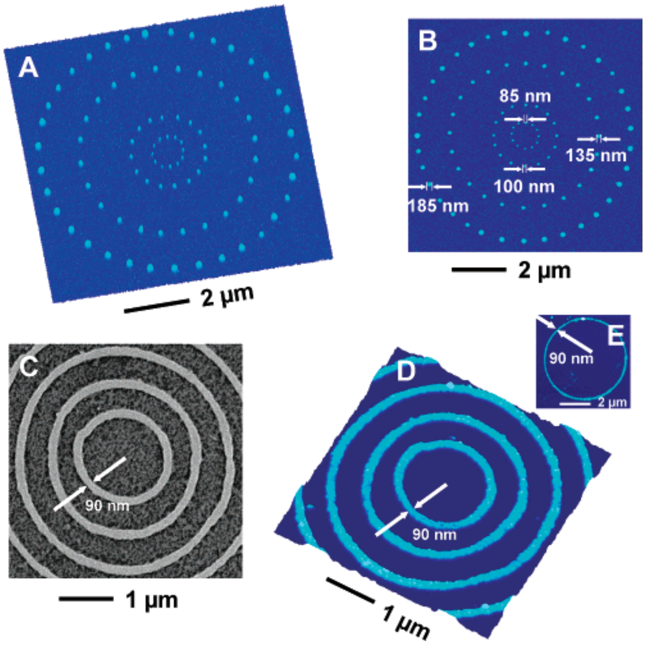

Figure 1. TMAFM images (A, B, D, E) and SEM image (C) of etched Au nanostructures on a Si/SiO$_X$ substrate. A and B and C and D are the same nanopatterns, respectively. *Z* scale bar: (A, B) 50 nm; (D) 70 nm; (E) 60 nm.

extension of this work to include Ag and Pd and show that nanostructures of almost any shape can be easily fabricated with DPN using related approaches.

As proof-of-concept, corral structures made of successively increasing diameter dots (85−185 nm) were fabricated on Au-coated Si/SiO$_X$ with a Ti adhesion layer (Figure 1A,B). The diameter of each resulting gold nanostructure was controlled by adjusting the tip−substrate contact time (3.2 s:185 nm, 1.6 s:135 nm, 0.8 s:100 nm, and 0.4 s:85 nm, respectively) during the deposition of the MHA resist layers. Circular structures with sub-100 nm line widths also could be generated, by drawing a circular structure made of MHA (writing speed = 0.31 μm/s) with subsequent wet etching (see Experimental Section) (Figure 1C−E). In general, the MHA features are typically a little larger than the resulting metal structures. The magnitude of the difference depends on how small the desired features are. Typically, small structures (sub-100 nm) lead to relatively larger differences between the size of the MHA resist structure and the metallic nanostructure that is generated in the wet-chemical etching process. The reason for this is that edge-etching effects become more important for the smaller structures which have larger edge-to-bulk ratios. Similar effects have been observed with respect to adsorbate exchange; exchange occurs considerably faster at feature edges as compared with their interiors.[32] Finally, it is worth noting that according to the literature,[33] MHA is not an optimum resist layer for etching structures generated by microcontact printing (μCP). The reason for this is that DPN-generated structures are more like bulk-solution deposited SAMs[9] whereas μCP structures are often less dense and nonuniform. Therefore, it is preferential to use hydrophobic resist layers such as octadecanethiol (ODT) in the case of resist layers fabricated by μCP.

Triangular structures also can be fabricated using the DPN-generated resist layers combined with wet-chemical etching. However, if one wants open triangular

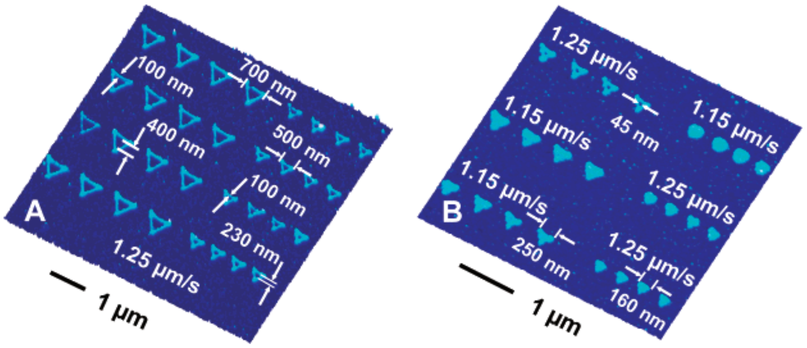

Figure 2. TMAFM images of etched Au nanostructures of triangles on a Si/SiO$_X$ substrate. (A) 700 nm (left) and 500 nm (right) edge length hollow triangles generated at a writing speed of 1.25 μm/s. Etched line width = 100 nm. (B) 250 nm (left) and 160 nm (right) edge length triangle generated at a writing speed of 1.25 (top left and low right corners) and 1.15 μm/s (the other part), respectively. *Z* scale bar: (A) 75 nm; (B) 70 nm.

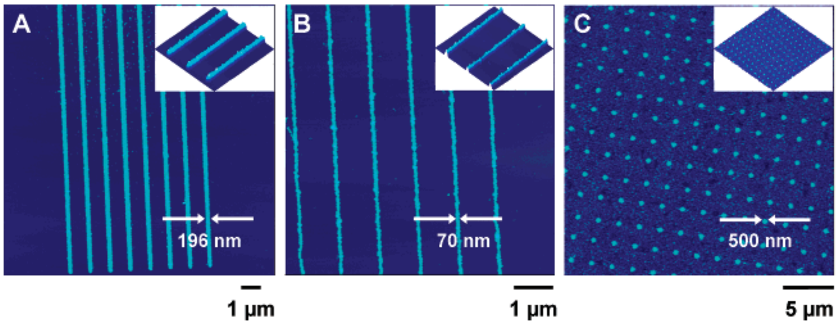

Figure 3. TMAFM images of etched Ag nanostructures on a Si/SiO$_X$ substrate. (A, B) Line arrays, insert: high-resolution 3D image. The writing speed of the MHA-coated tip on the Ag substrate was 0.10 (A) and 0.20 μm/s (B). (C) Dot array, insert: 3D image. The contact time between the MHA-coated tip and the Ag substrate was 5 s. *Z* scale bar: (A, B, C) 200 nm.

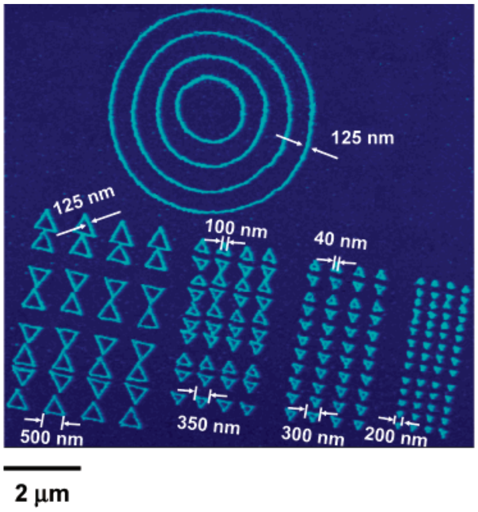

Figure 4. TMAFM images of etched Ag nanostructures of triangles and circles on a Si/SiO$_X$ substrate. With a writing speed of a MHA-coated tip on a Ag substrate = 0.13 μm/s, four Ag nanocircles and four kinds of Ag nanotriangles with 125 nm line width were obtained after etching the exposed Ti/Ag films. The edge lengths of Ag triangles are 500, 350, 300, and 200 nm, respectively. When the edge length of Ag triangles decreased to 200 nm, the shape of the triangle was irregular due to MHA diffusion. The interior hollow was decreased with decreasing edge length. *Z* scale bar: 200 nm.

structures, writing speed is critical and must be relatively fast to avoid MHA diffusion into the interior of the structure (Figure 2). For example, open structures with a fixed 100 nm line width but with variable edge lengths (250−700 nm) could be generated by moving the tip at a rate of 1.25 μm/s during the DPN experiment. However, if slower writing speeds were used, the resulting triangles often would be filled structures, presumably because the MHA diffuses too quickly under these conditions and fills the triangle etch resist structure [Figure 2B (top right and lower left corners)]. In some cases, rounded structures were observed as well, again presumably because of rapid diffusion of the MHA resist under the conditions employed to generate the nanostructures. Also, for particularly small triangular structures, even the 1.25 μm/s writing rate resulted in the formation of filled rather than open triangles [Figure 2B (lower right corner)].

A related strategy can be used to generate nanostructures of Ag and Pd. Alkanethiols can form SAMs on Ag[34] and Pd[35] substrates. These SAMs patterned by μCP also can be used as etch resists, and they have been used by others to generate micrometer-scale structures made of such metals[30,31,36] (170 nm Pd nanowires have been generated by μCP-patterned with an eicosanethiol SAM as an etch resist for Pd).[37] By using the DPN-based approach to draw line and dot arrays of MHA structures on silver, we were able to utilize wet-chemical etching to generate high-quality sub-100 nm to 500 nm structures (Figure 3). Feature size correlates well with writing speed when 196 and 70 nm wide lines were generated at writing speeds of 0.10 and 0.20 μm/s, respectively (Figure 3A,B). In general, the sub-100 nm lines generated on Ag are less uniform than on Au,[20,23] primarily because the gold grains on the substrates studied are smaller (25−45 nm, RMS = 0.895 nm for 3 × 3 μm^2) and more uniform than the silver grains (40−140 nm, RMS = 1.413 nm for 3 × 3 μm^2). As with Ag dot arrays (500 nm diameter and 2 μm interfeature distance (Figure 3C), Ag triangles, and circles (Figure 4) all could be fabricated using similar procedures and the appropriate resist structures drawn by DPN.

With Pd, two different resist layers were studied, MHA and ODT. When MHA was used as a resist, Pd nanostructures could be generated, but all of the features were nonuniform and discontinuous in structure (Figure 5A−D). The reason for this may be that the carboxylic acid terminal groups attract the FeCl$_3$-based etchant, resulting in partial etching of the resist-coated areas. For example, if one looks at the high-resolution image of the array of 500 nm dots, one can see that each dot is made up of a series of discontinuous smaller structures (Figure 5A,B). The same is true for ~600 nm wide lines (Figure 5C,D). Consistent with this hypothesis, when ODT, which results in hydrophobic monolayers, is used as the resist layer, more uniform structures are formed (Figure 5E,F). With ODT as a

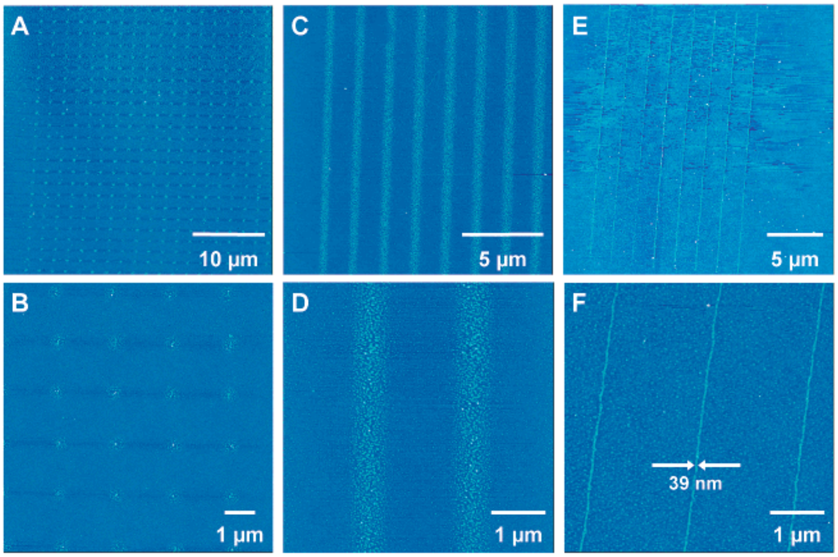

Figure 5. TMAFM images of etched Pd nanostructures on a Si/SiO$_X$ substrate. (A, B) Dot arrays with MHA as a resist (2-s holding time of a MHA-coated tip on a Pd surface) and (C, D) line arrays with MHA as a resist (writing speed = 0.13 μm/s). (E, F) Line arrays with ODT as a resist (writing speed = 0.13 μm/s). *Z* scale bar: (A−D) 30 nm; (E) 10 nm; (F) 20 nm.

resist layer, relatively uniform lines as narrow as 39 nm could be generated via wet-chemical etching (Figure 5E,F). Note that because the alkanethiol monolayers formed on Pd are less stable in air[35] than those formed on Au and Ag, one must work quickly with these materials and minimize air exposure. Finally, because we use a negatively charged etchant in the case of Ag and Au (ferri/ferrocyanide), we do not see a similar effect with MHA as the resist.

Conclusions

This paper shows how one can use DPN to fabricate metallic (Au, Ag, and Pd) nanopatterns on a Si/SiO_X surface with control over feature size, interfeature distance, and shape. Sub-100 to 500 nm structures can be easily generated on all of the substrates studied. Both mercaptohexadecanoic acid (MHA) and octadecanethiol (ODT) can be used as resist layers. In the case of Pd, ODT is the superior resist layer because it is more efficient at inhibiting access of the $FeCl_3$ etchant to the underlying metal surface. Control at the nanometer length scale with these materials potentially will allow researchers to construct all sorts of optically and electrically interesting nanostructures that rely on feature size and interfeature distance. This is especially true in the case of Au and Ag for those interested in studying surface-plasmon coupling and the concept of plasmon wires.[28]

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