Nanografting of Silanes on Silicon Dioxide with Applications to DNA Localization and Copper Electroless Deposition

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Nanoshaving and nanografting were first introduced in 1995 and 1997.[1,2] These nanoscale patterning methods have been used in a variety of applications. For example, nanoshaving, which uses an atomic force microscopy (AFM) tip to mechanically remove a molecular monolayer, has been shown to remove sexithiophene crystals physisorbed between electrical contact pads on silicon dioxide,[3] to pattern streptavidin on gold surfaces for DNA binding,[4] and to remove covalently attached alkyl monolayers from a silicon surface.[5] Nanografting is physisorption or chemisorption of a species of interest concurrent with nanoshaving. Nanografting has been used to pattern various thiols on gold,[6] including thiolated DNA[7] and bifunctional compounds that bind proteins,[8] as well as alkene, alcohol, and alkyl halide monolayers on silicon.[9−10] From a materials science perspective, it is advantageous to be able to nanograft on an insulating surface as shown in this work, in addition to nanografting on metal and semiconductor surfaces, which has already been demonstrated. Silicon dioxide is a desirable substrate for nanografting; because it is available as an atomically flat substrate, it can form strong covalent bonds, especially to silanes, and it is inexpensive.

Other scanning probe microscopy (SPM) methods, besides AFM nanografting, have been used to pattern silicon dioxide with certain limitations. For example, SPM electrochemical oxidation of silane layers allows silver and gold metallization, as well as the localization of DNA on silicon dioxide.[11−13] Dip-pen nanolithography has been used to deposit aminosilanes which bind gold particles[14] or, alternatively, to deposit proteins.[15]

Two other published reports relate specifically to nanoshaving of silanes and to this work. One indicated that even with an AFM tip forces of 3 μN, octadecyltrichlorosilane monolayers could not be removed from silicon dioxide.[5] The other, an AFM tribology study of silanes on mica, reported that the strength of silane films is heavily dependent on their cross-linking networks.[2] Elimination of this cross-linking should facilitate nanoshaving of silanes on silicon dioxide. Accordingly, and although previous attempts have been unsuccessful,[5] in this paper we demonstrate at least partial nanoshaving and also nanografting as shown in Scheme 1, of silanes on silicon dioxide. The viability of biological and nanocircuitry applications is also demonstrated.

Even though others could not nanoshave trifunctional, highly cross-linked octadecyltrichlorosilane monolayers, we have found that we can partially nanoshave the monochloro analogue, octadecyldimethylmonochlorosilane (C_{18}DMS),[16,17] as shown in Figure 1.[18] Such monofunctional silanes should be tethered to the surface by only a single Si−O bond. Typically, we removed 2−4 Å of the layer with a single nanografting pass of an AFM tip and more with additional passes. As measured by spectroscopic ellipsometry, the thickness of the C_{18}DMS layers was 9−10 Å, which is comparable to published values for layers of C_{18}DMS deposited by the same method.[16] By comparison, a densely packed monolayer of C_{18} alkyl chains should be approximately 20 Å thick, assuming a tilt angle of approximately 30°.[19] This suggests a large number of gauche defects in our films and that the exposed surface is principally composed of methylene ($-CH_2-$) units. Removal of a few of these chains from the monolayer would not fundamentally alter this surface chemistry at the monolayer−air interface.

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(17) Piranha cleaned silicon (*use proper protective gear and caution when using Piranha solution*) with native or thermal oxide was heated at 80 °C for 20 min in the presence of neat silane (used as received from Gelest, Morrisville, PA). The samples were then sonicated in anhydrous methanol to remove excess silane. See Supporting Information for more detailed experimental information.
(18) Nanoshaving and nanografting were performed with a Dimension 3100 atomic force microscope with a fluid cell (Digital Instruments, Santa Barbara, CA) using high-k Si_3N_4-coated silicon cantilevers (NSC11/Si3N4/AlBS, Mikromasch, Estonia). See Supporting Information for more detailed experimental information.
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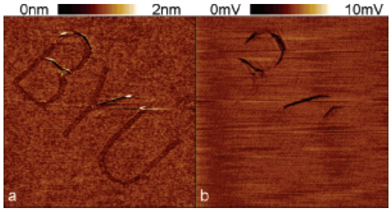
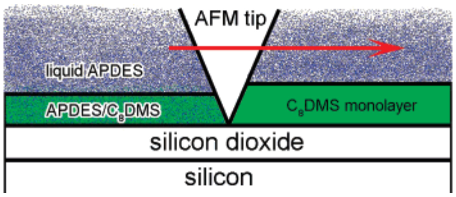


Figure 1. AFM height (a) and lateral force (b) images of the letters "BYU" nanoshaved in a surface of C_{18}DMS on silicon dioxide. The imaged area is 5 μm on a side. The letters are indented approximately 2−4 Å, except for the deep regions on the top and middle of the "B" and the right arm of the "Y", which show a depth of 1−2 nm. A force of approximately 30 μN was applied to nanoshave these letters.

Scheme 1. Nanografting Process on Silicon Dioxide



The letters in Figure 1a show an average depth of 2 Å by AFM, except for the regions at the top and middle of the "B" and on the right arm of the "Y". These points of elevated pressure on the surface during nanoshaving (mostly at curved features) led to gouging into the underlying oxide, which demonstrates that although partial nanoshaving is routine, complete nanoshaving should also be possible. It is significant that the partially nanoshaved portions of the "BYU" are nearly invisible in the friction image. The implication of this similarity in lateral force is that the chemistry for the letters remains essentially identical to that of the background, that is, composed of methylene ($-CH_2-$) units. This retention of surface chemistry, together with previous unsuccessful attempts to nanoshave trifunctional silane molecules,[5] suggests that the movement of the tip across the monolayer at high pressure pulls individual molecules out of the monolayer by breaking Si−O bonds rather than fracturing the molecules by breaking C−C or Si−C bonds.

While the forces used in these experiments are higher than those reported previously,[5] the tips were observed to dull quickly during nanoshaving and nanografting, reducing the effective pressure applied to the monolayer, where the key parameter for nanografting is pressure, not force. Tip dulling was reported previously in a study of chemomechanical nanografting on hydrogen-terminated silicon.[9] Although only a portion of the silane layer is typically removed in this study with a single pass of the AFM tip, it will be shown herein that this removal of silane molecules and the apparent exposure of surface silanol groups for reaction effectively enables nanografting on silicon dioxide.

Even with only partial removal and replacement of the alkylsilane monolayer by nanografting, the surface chemistry is significantly altered. We were able to nanograft both perfluorinated silanes[20] and an aminosilane (APDES)[21] in both C_{18}DMS and octyldimethylmonochlorosilane (C_8DMS) monolayers. Accordingly, we present perfluorinated silane lines nanografted in a C_{18}DMS monolayer (Figure 2) and APDES lines nanografted in a C_8DMS monolayer (Figure 3).

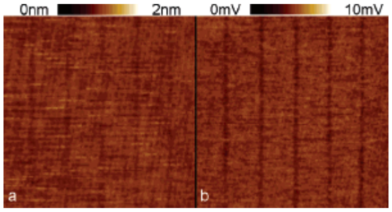


Figure 2. Lines of perfluorinated silane nanografted to silicon dioxide through C_{18}DMS. Panel a is AFM height, while panel b is the corresponding lateral force image. Panels a and b are 2.5 μm on a side. A force of ca. 12 μN was applied to the tip during nanografting. The depth of the lines is 0.5−1 Å. The linewidths are 100−150 nm.

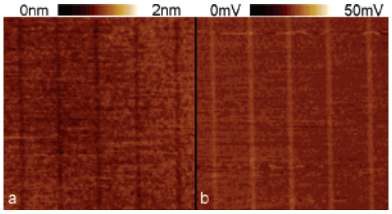


Figure 3. Lines of aminosilane nanografted to silicon dioxide through C_8-DMS. Panel a is the AFM height, while panel b is the corresponding lateral force image. Panels a and b are 5 μm on a side. A force on the order of 60 μN was applied to the tip to nanograft the lines. The depth of the lines is 1−1.5 Å. The linewidths are 150−200 nm. The contrast in this lateral force image is opposite that in Figures 1 and 2.

The presence of another silane should solvate and facilitate displacement of the alkylsilane molecules that are removed during nanoshaving. The depressions where nanografting was performed are consistent with partial removal of the monolayer and nanografting of molecules. Because of insertion of the nanografted molecules, the lines are shallower than those seen in Figure 1b. However, the change in the lateral force is unmistakable for the perfluorinated silane (Figure 2b) and even greater with the APDES nanografted lines (Figure 3b). These images differ substantially from the nearly complete absence of contrast in the lateral force image (Figure 1b) for nanoshaving alone. Thus, even though only a portion of the monolayer appears to have been replaced, the surface chemistry still appears to have been transformed. As a further confirmation of the significance of this change, APDES patterns nanografted in a C_8DMS monolayer were used to pattern DNA and also metal.

To create a pattern for localization of DNA, a layer of C_8DMS was nanografted with APDES. The resulting lines showed the characteristic indentation seen before in the AFM height image and the distinct chemical change observed previously by lateral force microscopy. This surface was then exposed to a solution of λ-DNA.[22] The negatively charged DNA molecules associate with positively charged amine groups, but not with the uncharged alkyl layer or with any exposed, negatively charged oxide. Prior to DNA exposure, the patterned areas were lower in height than the surrounding C_8DMS layer, but afterward, the areas are raised, where ropes of DNA molecules (Figure 4) and individual DNA strands are apparent on and around the lines that were imaged at high lateral resolution (Figure 4, inset). In summary, DNA localization on the patterns illustrates that even if a single

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(20) Perfluoroalkylethyltriethoxysilane (predominantly perfluorohexylethyl and perfluorooctylethyl homologues), 90%+, Gelest.

(21) 3-Aminopropylmethyldiethoxysilane, 95%+, Gelest.

(22) Nanografted samples were incubated in a 10 ng/μL solution of λ-DNA in TE buffer adjusted to pH 7.2. See Supporting Information for more detailed experimental information.

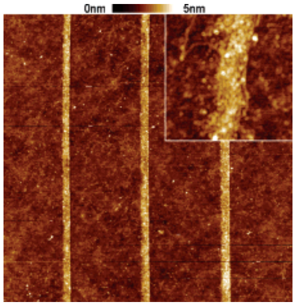

Figure 4. AFM height images of DNA self-aligned on APDES lines nanografted on a C_8DMS monolayer on silicon dioxide. Prior to DNA exposure the lines were depressed, but after exposure, they are ca. 3 nm tall. The negatively charged DNA ropes deposited preferentially on the positively charged amine-functionalized lines (bright regions). The lines are approximately 100 nm wide. The image is 3 μm on a side. The inset shows a close up image revealing individual DNA strands; the inset is 300 nm on a side.

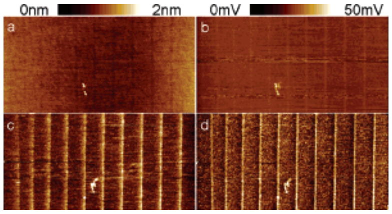

Figure 5. Lines of APDES nanografted through a C_8DMS monochlorosilane monolayer on silicon dioxide. Panels a and c are AFM topography images; panels b and d are lateral force images. Each panel shows a 10 μm × 5 μm region. Panels a and b were obtained in situ, immediately after patterning with APDES. The height image shows an average depression of 0.2−0.9 Å for each line, respectively, from left to right, that correlates well with the force used in nanografting, increasing from 9 μN up to 30 μN. The lines show a definite chemical change in panel b. (The contrast in these lateral force images is opposite to that found in Figures 1 and 2.) The linewidths are ca. 200 nm. Panels c and d were imaged in air subsequent to copper plating. After plating the lines are raised with heights of 2−8 Å, from left to right.

nanografting pass does not completely replace the alkyl monolayer with an amine-terminated layer, the exchange of molecules by partial nanografting still results in a significant and useful change in surface chemistry.

A principal advantage of using silicon dioxide as a substrate is its dielectric character, which can isolate metal traces on its surface. Because nanografting can create patterns next to objects already on a surface, nanografting on an insulator should be optimal for drawing wires from microscale electrodes to nanoscale objects that cannot be precisely positioned. Feasibility is demonstrated by plating nanografted APDES with an electroless plating scheme: seeding with Pd^{2+}, reduction, and electroless plating with copper.[23,24] The resulting patterns are shown in Figure 5 and again attest to a change in surface chemistry by nanografting. Panels a and b in Figure 5, height and lateral force images, respectively, again show the characteristic depression and change in lateral force due to amine nanografting prior to plating. Panels c and d show raised copper deposition only on the lines, as well as a chemical change on the surface that is much greater than that seen in panel b. Although the copper as shown is only approximately 1 nm thick and likely oxidized, a longer plating time or a more inert metal could produce conductive, metallic wires.

In addition to showing the feasibility of nanografting on monochlorosilane monolayers, we were also interested in the possibility of nanoshaving in the air and then backfilling the exposed region with a silane, analogous to that demonstrated with thiols on gold.[25] To achieve this, we nanshaved two boxes (labeled NS in Figure 6) with multiple passes of the tip and then wetted this surface with the perfluorosilane. Two additional boxes were then nanografted with a single pass of the tip (labeled NG, in Figure 6). As the tip moves over the surface to functionalize the area within the box by drawing closely spaced lines, the overlap between successive lines is a likely source of the apparent increased contrast compared to that seen in Figure 2b, which is approximately an order of magnitude lower. The similarity between the surfaces with both backfilling and nanografting suggests that individual silane molecules from the initial surface are indeed removed, and replaced by the second silane.

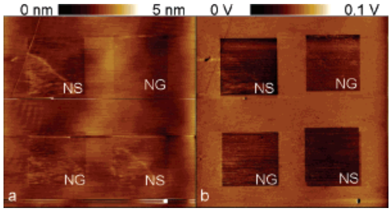

Figure 6. AFM Nanoshaving and backfilling compared to nanografting. Panel a is the AFM height, while panel b is the corresponding lateral force image. Panels a and b are 70 μm on a side. The initial surface layer was C_{18}DMS. Two boxes, labeled “NS”, were nanoshaved into the C_{18}DMS with multiple passes at about 23 μN. Then perfluorinated silane was added, and the other two boxes were nanografted, labeled “NG”, with a force of 26 μN. The images were then taken with a low-k AFM tip. All four boxes show a small decrease in height of the layer and a similar contrast change. The image was taken in air after removal of the perfluorinated silane and cleaning and drying the surface.

We have demonstrated at least partial nanoshaving as well as nanografting of various silanes on silicon dioxide. This method is compatible with patterning on both thin and thick oxide layers. Both octadecyl- and octyl-dimethylmonochlorosilane monolayers were removed, and patterns were made by nanografting both perfluorinated silanes and aminosilanes. DNA was localized on aminosilanes, and individual strands were imaged. Pd^{2+} was also allowed to associate with aminosilane lines, and electroless plating was demonstrated. This method should allow conductive wires to be drawn to test electrical properties of nanoscale objects on surfaces.

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Supporting Information Available: Experimental details and characterization of planar surfaces by XPS, ellipsometry, and wetting (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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