Nanoscale Molecular Patterns Fabricated by Using Scanning Near-Field Optical Lithography

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Self-assembled monolayers (SAMs) formed by the adsorption of alkanethiols onto gold surfaces have extraordinary utility for fundamental studies of interfacial phenomena such as cellular attachment,[1] protein adsorption,[2] and adhesion,[3] and for use in biological analysis, including array-based high-throughput screening and diagnostic applications.[4,5] There has been extensive research into methods for patterning SAMs, including microcontact printing,[6] dip-pen nanolithography,[7] and others.[8] Photopatterning has previously been used to create patterned SAMs[9,10] with chemically well-defined structures,[11] capable of exploitation as templates for the fabrication of molecular and biomolecular microstructures,[12] but has been regarded as a tool only for use in the creation of micron-scale features. Here we show for the first time that photolithographic processes may be used to create nanometer scale patterns in SAMs, by utilizing a UV laser coupled to a scanning near-field optical microscope (SNOM)[13] as the light source.

The process underlying photopatterning of SAMs on gold and silver is well-known at the phenomenological level.[9,10,14] Alkane-thiolates formed by the adsorption of alkanethiols are oxidized on exposure to UV light in the presence of air to alkylsulfonates:

$$Au-SR(CH_2)_nX + {}^3/_2O_2 \rightarrow Au^+ + X(CH_2)_nSO_3^-$$
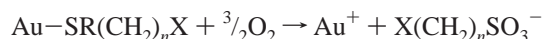
The mechanism of this reaction has been the subject of some debate. Several authors have suggested that the active agent is ozone, and that irradiation by light of wavelength less than 200 nm is necessary to cause SAM photooxidation.[15,16] Recently, however, we showed conclusively that oxidation could occur in the absence of ozone with use of a UV source emitting principally at 254 nm.[17] The reaction involved a specific photochemical oxidation of the sulfur headgroup to a sulfonate species. In the present work, a frequency-doubled argon ion laser has been used that emits light with a wavelength of 244 nm. It is expected that the photochemistry excited with such a source is likely to be qualitatively the same as that reported in our earlier investigation with a mercury lamp.[17] In previously published studies of SAM photopatterning, the sample has been masked during exposure to UV light, with oxidation occurring only at exposed regions of the surface. The process is limited in its applicability by the diffraction effects that would occur for small mask features. In the second stage of the process, the resulting photopatterned material is immersed in a dilute ethanolic solution of a contrasting thiol, which displaces the oxidation products and adsorbs onto the surface in exposed areas. In the present study, the important modification is made of replacing the mask/lamp combination in stage one by a SNOM. Coupling the UV laser to the SNOM enables delivery of UV light selectively to regions exposed underneath a SNOM fiber as it is traced across the surface. The oxidized regions may be substantially smaller than the wavelength of the light used by virtue
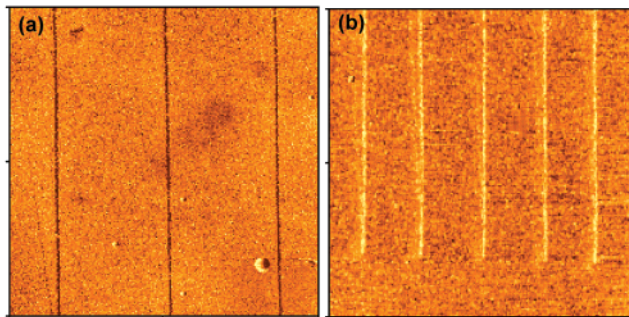

Figure 1. Friction force microscopy images (6 × 6 μm) showing lines of dodecanethiol written into a SAM of mercaptoundecanoic acid (a) and lines of mercaptoundecanoic acid written into dodecanethiol (b) by SNP.

of operating in the optical near field. This modification to the photolithographic process, termed scanning near-field photolithography (SNP), renders it into a powerful tool for creating chemically well-defined patterns with nanoscale dimensions.

Figure 1a shows a monolayer of mercaptoundecanoic acid (HS-$(CH_2)_{10}COOH$) that has been patterned with SNP.[18] Three lines have been drawn down the region shown in the image by using the SNOM. In these regions the adsorbate has been oxidized to its sulfonate. The sample has then been immersed in a solution of the contrasting adsorbate dodecanethiol (HS$(CH_2)_{11}CH_3$), leading to displacement of the oxidized mercaptoundecanoic acid molecules. The sample has been imaged by atomic force microscopy (AFM). The contrasting adsorbate terminal groups give rise to strong contrast differences in the friction force microscopy image. The carboxylic acid terminated regions exhibit brighter contrast than the methyl terminated regions, because they have a higher coefficient of friction due to adhesion to the polar surface of the silicon nitride tip employed to conduct AFM.[19] In contrast, the tip interacts more weakly with the methyl-terminated regions leading to darker contrast there. The contrast difference between areas with the different chemistries in Figure 1a is substantial, indicating that the lithographic process has proceeded with high efficiency and has yielded clean, well-defined nanoscale chemical patterns. When the process was carried out in the reverse order, beginning with a monolayer of dodecanethiol (Figure 1b), the contrast was reversed.

Figure 2 shows a high magnification image of a single line created in this fashion. Analysis of line profiles drawn across the feature revealed that the width of the oxidized line was only a few tens of nanometers. Figure 2 shows a representative cross-section through one of the wider parts of the line, from which its width was determined to be 39 nm. In places, the feature is even narrower. Using this method we have on occasion achieved line widths as small as 25 nm, although routinely 40 nm was obtained. These are
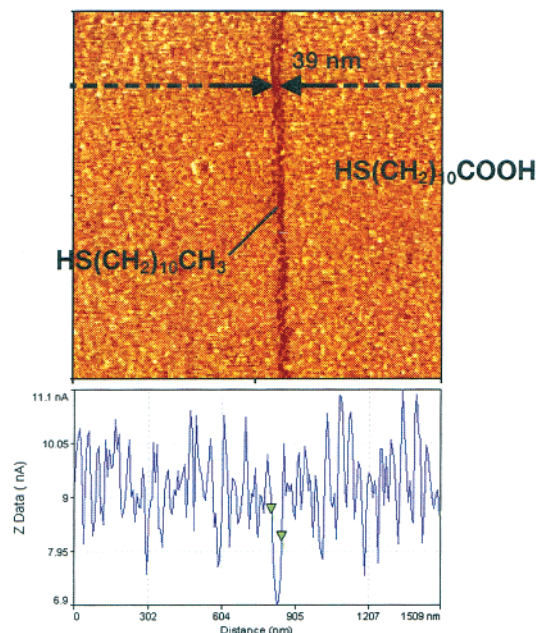
Figure 2. A 1509 × 1509 nm high magnification lateral force image of a single line (top) and section through it (bottom).
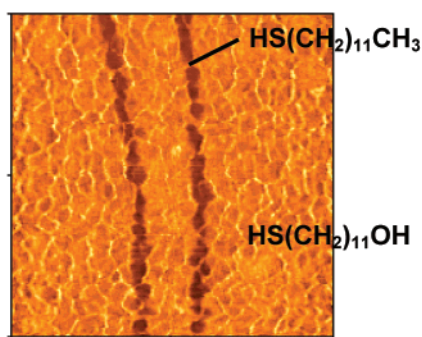

Figure 3. A high magnification lateral force microscopy image of two lines created by SNP. Image size = 973 × 973 nm.

exceptionally small features for a photolithographic process, indicating the effectiveness of SNP.

Scanning electron microscopy (SEM) of representative SNOM fibers (see Supporting Information) revealed that the aperture had a diameter of 40 nm, suggesting that this plays a large part in determining the feature resolution. However, high-resolution AFM images of features created by SNP suggest that the morphology of the underlying substrate also plays a role in determining the lower limit on feature size.

Figure 3 shows high-resolution images of lines created in monolayers of mercaptoundecanol (HS(CH$_2$)$_{11}$OH) by SNP and subsequent immersion in a solution of dodecanethiol. Again, clear contrast is observed between the dark, methyl-terminated regions of the surface and the bright, hydroxyl-terminated ones, indicating effective replacement of oxidized adsorbates by those in solution. The line widths clearly vary as the morphology of the underlying polycrystalline gold varies. The lines of dodecanethiol may be seen to be composed of a series of conjoined oxidized regions, some of which cover an entire grain. In some places, the line is slightly wider as it spans two adjacent grains, while in other places it is slightly narrower as it crosses a small grain. The variations in line width were nevertheless small in all cases and features were typically not wider than 40 nm.

There have been previous attempts to use SNOM to perform photolithography.[20,21] However, layers of organic materials (such as photoresists) were employed in these studies that were typically thicker than the monolayers used in the present work and line widths were wider due to thermal migration within the film. The essential basis of our approach, and the superior line width realized, is the photochemical excitation of specific reactions in a particular functional group (in this case a thiolate sulfur atom) distributed with monolayer coverage on a solid surface. There is a wide range of systems that satisfies this general description, and it seems very likely that the application of SNP may be extended to materials that are not SAMs. For example, there are many photoactivated coupling agents and reactions that may be utilized to attach biological molecules to solid phases;[22,23] these may potentially be adapted for creating biological nanostructures by combination with SNP. Given the ability of SNOM to function under ambient conditions, and even under liquid, this suggests that SNP may offer a convenient and rapid method for the fabrication of biological nanostructures for a wide range of applications.

Supporting Information Available: SEM micrograph of a typical SNOM fiber used in this work; topographical image acquired simultaneously with Figure 1a (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Scanning near field optical lithography was carried out with use of a ThermoMicroscopes Aurora Near-field Scanning Optical Microscope coupled to a Coherent Innova 300C Frequency-Doubled Argon Ion Laser. Fused silica probes attached to tuning forks were used to deliver UV light. In lithographic mode the laser power was typically 25 mW (but was varied between 10 and 50 mW) and the scan rate was 1 μm s^{-1}. After photooxidation, samples were immersed in a 10 mmol dm^{-3} solution of a contrasting thiol for 10 min to displace the oxidized material and create a pattern. Resulting patterns were imaged in contact mode with use of a ThermoMicroscopes Explorer AFM, using silicon nitride probes (Nanoprobes, Veeco, Cambridge UK) with a spring constant of 0.12 N m^{-1}.
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