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A Mild Etch for the Fabrication of Three-Dimensional Nanostructures in Gold

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Self-assembled monolayers (SAMs) formed by the adsorption of alkylthiols onto gold surfaces[1,2] have attracted widespread interest for applications in micro- and nanotechnology. A variety of methods have been developed for patterning SAMs on length scales from the macroscopic to the nanoscopic. Microcontact printing (μCP) has been used extensively.[3] On nanometer length scales, electron beam lithography[4] and scanning probe lithography techniques,[5] such as dip-pen nanolithography (DPN)[6] and nanografting/nanoshaving,[7] have attracted significant interest. Recently, we reported a new approach, termed scanning near-field photolithography (SNP), in which a scanning near-field optical microscope, coupled to a UV laser, is used to selectively photooxidize adsorbates, enabling the fabrication of structures significantly smaller than the conventional diffraction limit.[8]

Early on it was demonstrated that SAMs could be valuable as resist materials for the fabrication of metallic structures, presenting the possibility of novel, simple, low-cost fabrication processes capable of yielding gold micro- and nanostructures with high edge definition. Whitesides and co-workers used μCP to pattern SAMs onto a gold substrate, which was then etched using an aqueous solution of cyanide ions saturated with oxygen[9,10] and ferri/ferrocyanide etch solutions.[11,12] The latter approach has been previously used to create nanostructures when used in conjunction with DPN[13] and with SNP.[14] Here we report a new, very mild etch solution, consisting only of a solution of mercaptoethylamine (MEA) and dilute ammonia in ethanol, that yields, in conjunction with photopatterned monolayers, excellent edge resolution and low defect densities. The potential benefits of this approach for nanofabrication are illustrated by the fabrication of nanoscale trenches in gold films through nanopatterns created by SNP.

SAMs were prepared on polycrystalline gold substrates using well-established methods. Micron-scale patterns were fabricated by exposing samples to light from a frequency-doubled argon ion laser (emitting at 244 nm) through an electron microscope grid, and nanometer scale patterns were fabricated by SNP. In both cases, the chemistry is the same. In exposed areas, the adsorbate molecules are converted to alkylsulfonates:

$$\mathrm{AuSR} + {}^{3}/_{2}\mathrm{O_2} + \mathrm{e}^- \rightarrow \mathrm{Au} + \mathrm{RSO_3}^-$$

The reaction is thought to be initiated by the formation of "hot" electrons at the gold surface, which tunnel into antibonding states of the adsorbate molecule and initiate photooxidation.[15] The alkylsulfonates are, in contrast to the alkylthiolates, only weakly bound at the surface and may readily be displaced by a contrasting thiol, or, as in the present case, by a solution-phase etchant, MEA. Figure 1 shows qualitatively that three-dimensional structures may be etched into gold with good edge definition using MEA at a concentration of 0.1 mol dm^{-3}. Representative images are shown of samples etched using photopatterned monolayers of $HS(CH_2)COOH$, hereafter C_2COOH, and $HS(CH_2)_{11}CH_3$, hereafter $C_{11}CH_3$. In both cases, the resulting structures are clearly free of defects. Cross-sections demonstrate the sharpness of the edges and confirm that the height difference between the tops of the features and the surrounding regions after etching, Δh, is equal to the thickness of the gold film, in this case 14 nm.

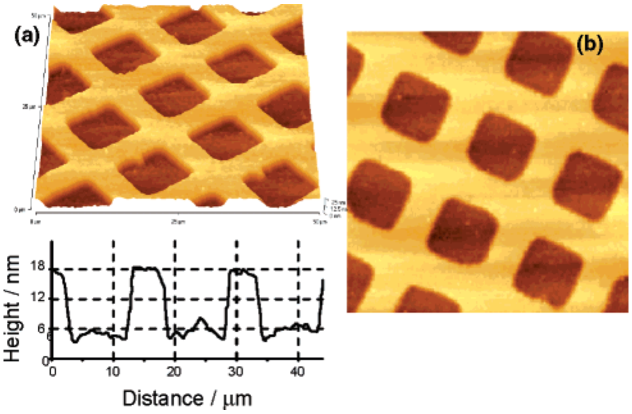

Figure 1. Typical 50 × 50 μm AFM images of structures etched into gold through photopatterned SAMs. (a) Monolayer of C_2COOH, together with line section through representative region. (b) Monolayer of $C_{11}CH_3$.

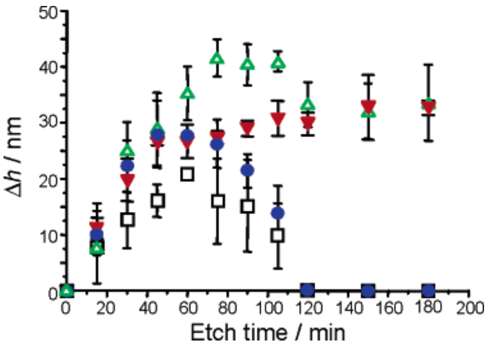

Figure 2. Etch behavior as a function of chain length and terminal group. Data shown are for C_2COOH (□), $C_{11}CH_3$ (●), $C_{10}COOH$ (△), and $C_{17}CH_3$ (▼) The thickness of the gold film was 30 nm.

The rate of etching was found to be independent of the concentration of ammonia. Typically, etching was carried out using 4% v/v of 88% ammonia in ethanol. Increasing the concentration led to no increase in the rate of etching, and equally, only a few microliters of ammonia per 25 mL of ethanol was adequate to ensure etching still occurred. Most likely, it has a catalytic effect, with the MEA acting as a bidentate ligand as it dissolves the gold (coordination of MEA to gold was confirmed by mass-spectrometric analysis of the MEA solution after etching and extraction of the solvent), coordinating to gold atoms through both the thiol and amine ends of the molecule.

The rate of etching varied significantly with the terminal group and alkyl chain length of the adsorbate. Figure 2 shows data acquired using a 0.1 M solution of etchant. Samples on 30 nm thick

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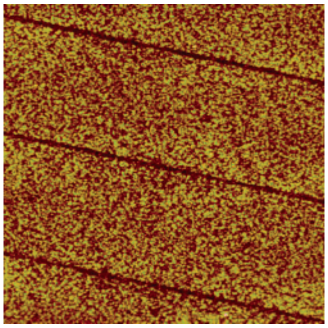

Figure 3. A 6 × 6 μm AFM image showing three nanotrenches etched into a gold substrate using a combination of SNP and the MEA etch solution.

gold were exposed to the etchant for a range of times, and Δh was measured from AFM images. For the short-chain carboxylic acid-terminated monolayer, C_2COOH, and the methyl-terminated monolayer, $C_{11}CH_3$, Δh increased with exposure to the etchant, reaching a maximum after ca. 45 min. For both SAMs, however, the magnitude of Δh decreases after longer exposures, due to attack of the etchant on unoxidized regions of the sample. Eventually, after longer times (ca. 120 min), all the gold is eroded.

Although this is very similar to the behavior reported by Xia et al. for microcontact-printed SAMs of $C_{15}CH_3$,[19] different behavior was observed using the MEA etch for the longer adsorbate, octadecanethiol ($C_{17}CH_3$) and mercaptoundecanoic acid ($C_{10}COOH$). For $C_{17}CH_3$, the maximum value of Δh was reached after 40 min, corresponding to complete removal of the gold from the oxidized areas of the sample, but at longer exposure times, there was no evidence for further removal from unoxidized areas; the value of Δh remained unchanged after several hours' exposure. This may be attributed to the superior order of the $C_{17}CH_3$ SAM compared to that of the $C_{11}CH_3$ SAM. The superior performance compared to that reported by Xia et al. may be attributed to a lower density of defects in the unoxidized regions of the photopatterned SAMs.

For $C_{10}COOH$ SAMs, the performance was also better than for $C_{11}CH_3$ monolayers, with SAM-protected regions remaining intact after several hours. This may be attributed to the influence of additional stabilization from the formation of hydrogen bonds between adsorbate terminal groups, impeding the progress of MEA molecules to the metal surface and thus inhibiting the dissolution process. In earlier studies of the kinetics of photooxidation of SAMs, we reported a similar effect.[16]

To explore the utility of this method in nanofabrication, samples were patterned by SNP and etched. In SNP, UV light is delivered to the sample surface via an aperture-based near-field scanning optical microscope.[15,16] Exposure of the adsorbates to UV light from the near-field probes leads to their conversion to weakly bound sulfonates, which we have previously shown may be displaced by solution-phase thiol molecules to yield structures as small as $\lambda/12$,[8] or by a solution-phase etchant, such as MEA. Figure 3 shows the result. Three lines have been written into a SAM of C_2COOH, which has been subsequently immersed in a solution of MEA, leading to etching of the gold underlying the oxidized regions. The lines have sharply defined edges. Figure 4 shows an AFM image of a single line etched in this way at higher magnification. Analysis of a line section taken through the trench indicates that the full width at half-maximum depth (fwhm) is 30 nm, although subsequent analyses by electron microscopy suggest that the dimensions determined by AFM may be over-estimated by ca. 20% because of the convolution of the tip with the surface. A narrow feature is also observed in Figure 4, identified by asterisks placed at either end. This feature resulted from a rapid sweep of the tip across the sample between writing operations. This trench is only 9 nm wide, an unexpectedly high level of resolution. The observation of structures such as this suggests that significant optimization of the process is feasible by control of the scan rate and careful selection of the chemistry excited during SNP.

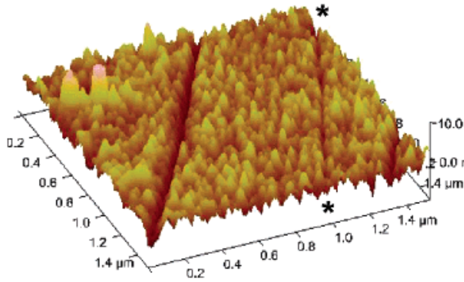

Figure 4. AFM image of a single trench, fwhm = 30 nm, etched into gold using a combination of SNP and the MEA etch. A 9 nm wide structure runs between the asterisks.

In conclusion, we have demonstrated that mercaptoethylamine may be utilized as a novel, mild etchant for gold, yielding sharply defined structures with good edge definition on length scales from tens of microns down to a few nanometers. When photopatterned long-chain thiols are used as the resist, degradation of the masked areas of the sample is minimal. The smallest features fabricated to date reflect a resolution of approximately $\lambda/30$.

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Supporting Information Available: Experimental information describing sample preparation and etching methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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