

Letters

Observation of *n*-Octadecanethiol Multilayer Formation from Solution onto Gold

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Formation of multilayers was observed when gold substrates were immersed in air-saturated, ethanolic solutions of *n*-octadecanethiol. The scanning tunneling microscope (STM) was used to image the multilayers and to etch the organic layers by using the interaction between the STM tip and the organic layers. In addition, *ex situ* measurements of the mass change using a quartz crystal microbalance (QCM) revealed formation of approximately 4 monolayers after 6 days of immersion of the gold substrate in the *n*-octadecanethiol ethanol solution.

Formation of self-assembled monolayers of *n*-alkanethiols from solution onto gold has provided a useful method for the fabrication of interfacial structures.¹ Such self-assembled films have been characterized by external reflectance Fourier transform infrared spectroscopy, ellipsometry, and X-ray photoelectron spectroscopy.² These studies revealed formation of well-ordered monoalayers of *n*-alkanethiols ($\text{CH}_3(\text{CH}_2)_x\text{SH}$, $x > 10$) on gold. Scanning tunneling microscopy (STM) has been employed to image organothiol self-assembled on gold and to determine the

packing structures and presence of defects in the layers.³ STM has also been used to etch alkanethiol layers on gold using the strong physical interaction between the STM tip and the organic layers.^{3d}

Here we report that, on extended immersion in 1 mM solution, *n*-octadecanethiol multilayers form on gold; these were studied by STM and the quartz crystal microbalance (QCM). These *n*-octadecanethiol multilayers could be etched by bringing the STM tip close to the film during scanning. When the etched film interface was imaged by STM, multiple layers could be seen. *Ex situ* QCM determination of the mass change of a gold electrode during immersion in an EtOH solution of *n*-octadecanethiol confirmed the formation of approximately 4 monolayers after 6 days.

Experimental Section

All STM experiments were performed with the specimen in air with a Nanoscope II (Digital Instruments, Santa Barbara, CA). The films were formed on clean gold films (approximately

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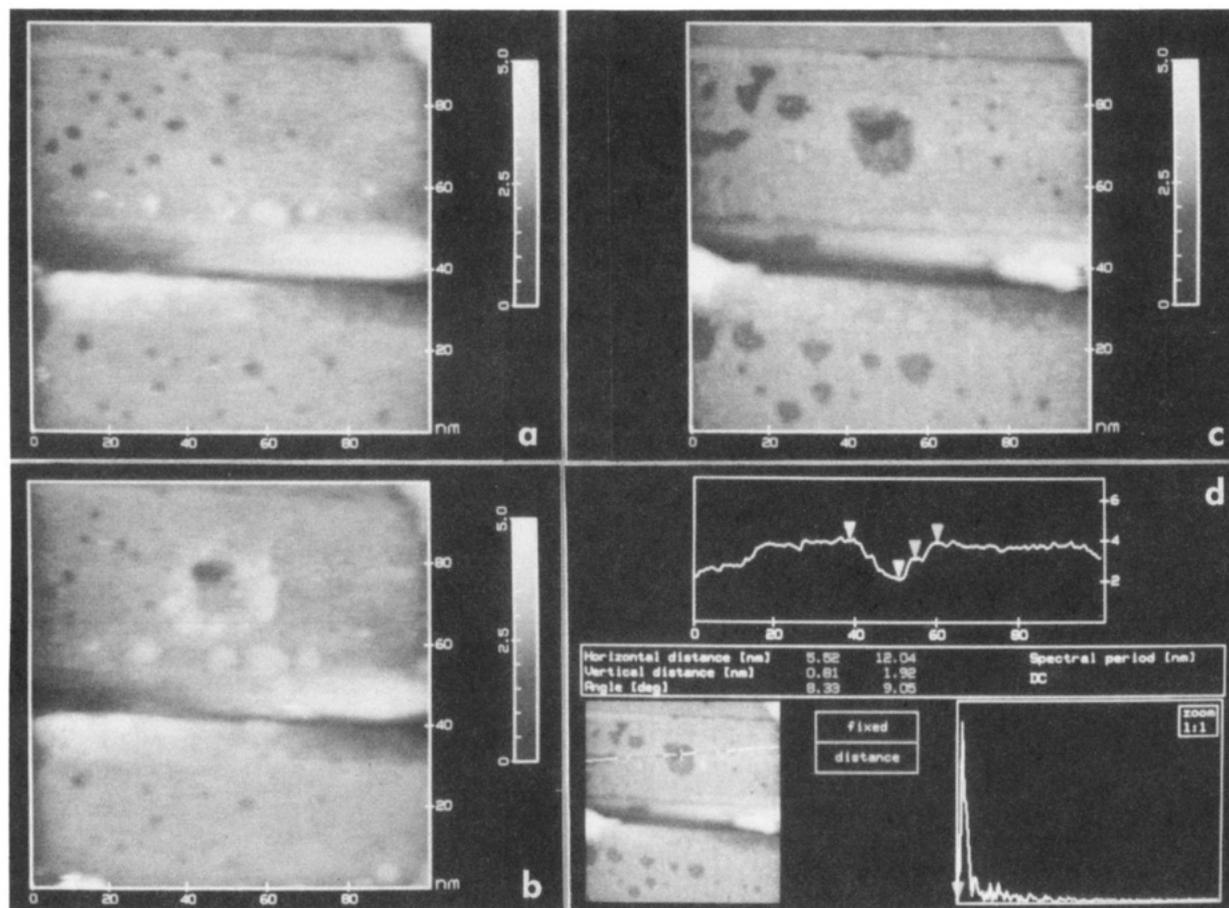


Figure 1. (a) STM image of a 100 nm \times 100 nm *n*-octadecanethiol film coated on Au/mica. (b) Same area after 15 s of etching ($V_b = 10$ mV, $I_t = 10$ nA) over a 10 nm \times 10 nm area. (c) Same area after 14 min of continuous scanning ($V_b = 1$ V, $I_t = 1$ nA). (d) Cross sectional view of the pit formed by etching the *n*-octadecanethiol layers.

1500 Å thick) vacuum-evaporated (pressure less than 5×10^{-7} Torr) on mica (heated to 310 °C) at a deposition rate of 2 Å/s.⁴ This procedure produces an atomically flat single crystal (111) surface with crystal grain sizes as large as 100–200 nm in diameter.^{3d,4} After preparation, the Au/mica substrate was immediately placed in an air-saturated 1 mM *n*-octadecanethiol solution in absolute ethanol for approximately 3–7 days at room temperature. Note that these exposure times are much longer than those usually used to produce monolayers (normally 3–24 h).^{1,2} The sample was then removed, rinsed with absolute EtOH, and dried with N₂ gas 3 times immediately before the STM imaging. Pt/Ir (80:20) tips mechanically cut with a wire clipper were used. STM images of large areas were obtained in the constant-current (topographic) mode.

The quartz crystal microbalance apparatus consisted of a frequency counter (Simpson 7026), oscillator power supply (home-built), oscillator (Leybold-Inficon, East Syracuse, NY), and 6-MHz Au-coated quartz crystal (Leybold-Inficon). The measurements were performed ex situ, i.e., the crystal was removed from the solution and the frequency change measured, then the crystal was reimmersed in the solution until the next reading. The Au-coated crystal was cleaned with 1:3 H₂O₂:H₂SO₄ just before the experiment. Details of the cell construction and its configuration can be found elsewhere.^{3f}

Results and Discussion

STM Imaging and Etching of *n*-Octadecanethiol Films on Gold. Figure 1a is a typical STM image of a 100 nm \times 100 nm area of *n*-octadecanethiol adsorbed on Au-(111)/mica scanned with the tip far from the surface, i.e.,

high bias ($V_b = 1$ V) and low current ($I_t = 1$ nA). As previously reported, the surface was characterized by some defects and bumps.^{3b-d} Pits were produced on the surface by the following procedures. First, a 10 nm \times 10 nm area was imaged on the surface. Then, the STM tip was brought very close to the surface using tunneling parameters of $V_b = 10$ mV, $I_t = 10$ nA. Under these tunneling conditions, the area was scanned for 15 s at a 78-Hz data acquisition speed. Finally, the imaging area was increased to a 100 nm \times 100 nm area for inspection of the pit with tunneling parameters of $V_b = 1$ V, $I_t = 1$ nA. Figure 1b is an STM image of *n*-octadecanethiol on a gold surface after the above procedure. A new pit (about 10 nm \times 10 nm) can be easily identified when compared with Figure 1a. Apparently, the *n*-octadecanethiol removed during the scan collected around the perimeter of the etched area. Continuous scanning with $V_b = 1$ V, $I_t = 1$ nA caused removal of the loosely-bound material, as seen in Figure 1c; this type of interaction was previously noticed.^{3d} After continuous scanning for about 14 min, most of the aggregates were removed and increased pit sizes were evident. Here we observe at least two layers of *n*-octadecanethiol by examining the depth profile of the pit as seen in Figure 1d. As discussed elsewhere^{3d} the heights found by STM for the *n*-octadecanethiol monolayers on gold are only apparent ones which do not agree with previously reported thicknesses of the layers. We attribute this to the different tunneling probabilities between the bare gold surface (at the bottom of a pit) and the adsorbed *n*-octadecanethiol layer. However, it is clear the depth profile of the pit shows two layers of the *n*-octadecanethiol (apparent heights of about 8.1 and 19.2 Å).

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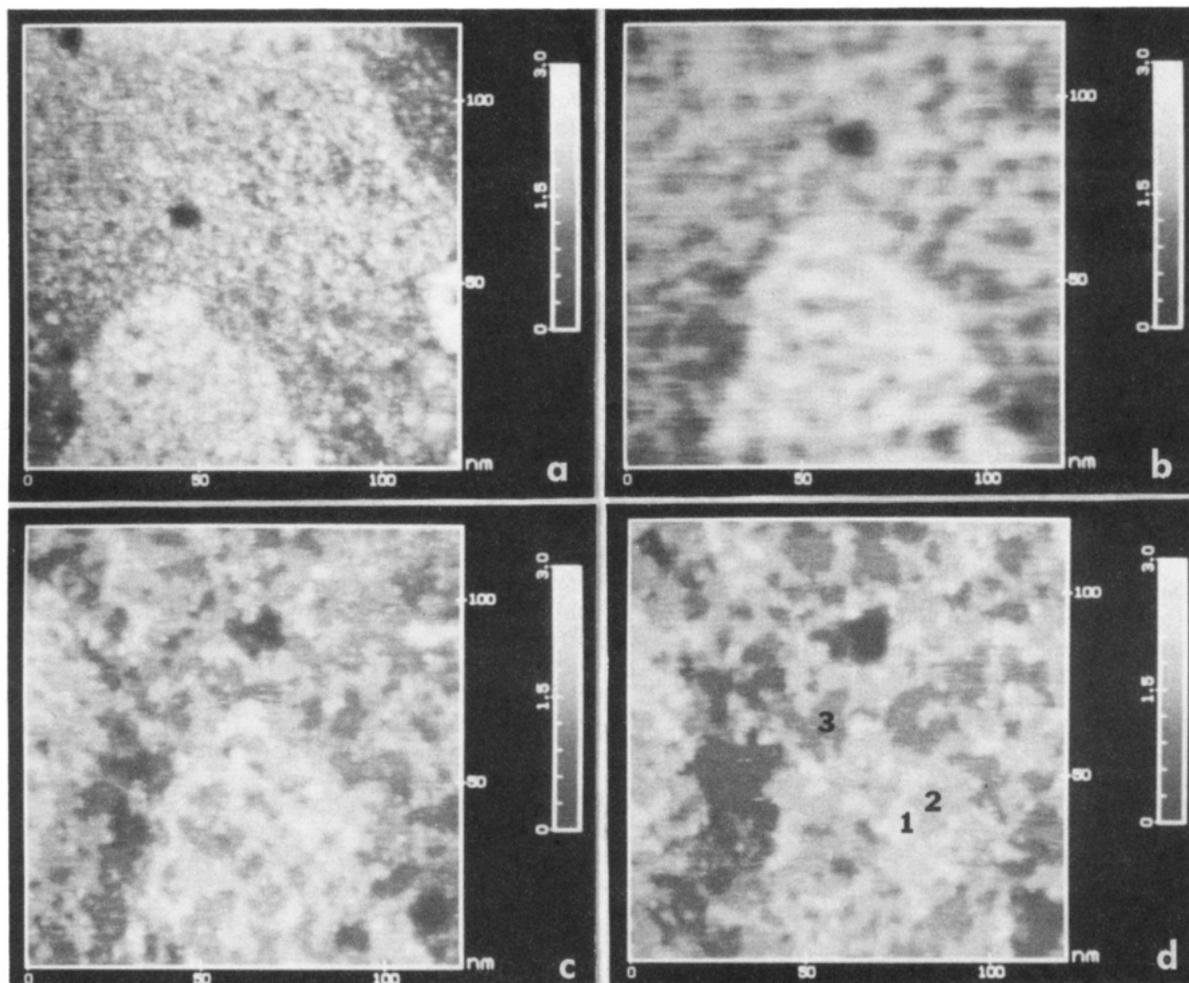


Figure 2. Four sequential STM images (a-d) of a 100 nm \times 100 nm area. Time interval between each image is 20 s. $V_b = 1$ V; $I_t = 1$ nA.

Further evidence of multilayer formation can be seen in Figure 2, a time-dependent STM image of *n*-octadecanethiol covered Au(111)/mica. The same 100 nm \times 100 nm area was scanned with tunneling parameters of $V_b = 1$ V, $I_t = 1$ nA, which results in slow etching of the organic layers. When Figure 2d is compared with Figure 2a, at least three layers of *n*-octadecanethiol on gold, marked 1 to 3 in Figure 2d, can be seen.

Quartz Crystal Microbalance Studies of *n*-Octadecanethiol Self-Assembly on Gold. Mass changes due to long-term exposure of gold substrates to an EtOH solution of *n*-octadecanethiol were measured using a QCM. The frequency change, Δf , for an oscillating quartz crystal can be related to the change in mass (Δm) by the Sauerbrey equation.⁵ Here, monolayer formation of *n*-octadecanethiol on gold on our crystal would correspond to a 28 Hz/cm² decrease, assuming a gold surface roughness factor of 1.5^{3f} and a packing structure of $(\sqrt{3} \times \sqrt{3})R30^\circ$ (i.e., surface coverage of 1/3). After exposure of the crystal to a 1 mM EtOH solution of *n*-octadecanethiol for 40 min, a frequency decrease of 23 Hz was observed; this corresponds to approximately 1 monolayer. Longer exposure times in the solution (up to 3 h) did not cause further decreases in the frequency, which indicates complete monolayer formation. Monolayer formation of *n*-octadecanethiol on gold has been reported to be complete within a half hour and

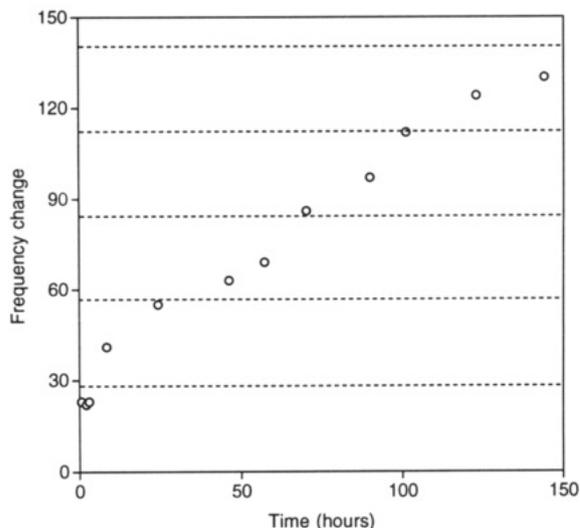


Figure 3. Frequency changes of the crystal during the adsorption of *n*-octadecanethiols on gold. Dashed lines correspond to the calculated frequency changes for each monolayer formation (up to 4 monolayers) of *n*-octadecanethiol on gold.

self-annealing follows.^{1b,2i} However, further exposure of the crystal to the *n*-octadecanethiol solution revealed a continuous decrease with four small discontinuities in the Δf vs time plot (increase in the mass) as seen in Figure 3. The frequency change reached a value corresponding to a mass equivalent to approximately 4 monolayers at the

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end of the sixth day of the experiment. (The frequency change corresponding to the formation of each monolayer is marked with dashed lines in Figure 3.) The multilayers are not expected to form a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure and may be more dense, leading to deviations in the plateaus of Figure 3. Moreover, the shear wave may propagate differently in the loosely bound multilayer and give rise to variations in the Δf for each layer. The formation of multilayers can account for the previously unexplained positive deviation in the ellipsometrically-determined thickness of alkanethiols adsorbed on gold.²ⁱ Recently, Crooks and co-workers also reported multilayer formation of *n*-alkanethiols on gold by gas phase adsorption.⁷

One possible model of formation of *n*-octadecanethiol multilayers on Au as determined by STM and QCM is via the formation of disulfides. Thiols oxidize to disulfides in the presence of oxygen and the solubility of disulfides in EtOH is much less than that of thiols.⁸ If solutions of *n*-octadecanethiol in EtOH exposed to oxygen oxidize and form *n*-octadecane disulfide, this could precipitate onto the *n*-octadecanethiol/Au surface. The interactions between the terminal methyl groups of the *n*-octadecanethiol/Au and the disulfide should enhance formation of the disulfide deposit. Growth of additional layers may also

be affected by interactions between the sulfur groups of disulfides with other disulfides or thiols. Upon rinsing a Au/QCM surface which had shown a frequency change corresponding to approximately 4 monolayers of *n*-octadecanethiol with chloroform (a better solvent for disulfides), a mass decrease (14 Hz) was observed, although this decrease is less than that expected for a monolayer. A more fully oxidized form of *n*-octadecanethiol (a sulfonate) has been reported by mass spectral analysis of *n*-octadecanethiol/Au surfaces.⁹ Formation of multilayers due to *n*-octadecanesulfonate may also be possible.

In conclusion, STM and quartz crystal microbalance studies of the formation of *n*-octadecanethiol layers on gold revealed multilayer formation. Thus, if one desires a single monolayer of *n*-octadecanethiol on gold, the substrate should not be immersed more than 4–5 h in an air-saturated *n*-alkanethiol ethanol solution. Conventional schemes using a 24-h immersion may produce more than one layer.

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