# COMMENTS

## Comment on "Formation of Holes in Alkanethiol Monolayers on Gold"

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We comment on conclusions by Sondag-Huethorst, Schönenberger, and Fokkink (hereafter referred to as SSF) published in an earlier volume of this journal.[1] While the experiments upon which these conclusions were based were quite sound, we suggest an alternative interpretation of the data based upon both previously published material and experimental evidence obtained within our laboratory (*vide infra*).

In scanning tunneling microscopy (STM) images of alkanethiolate monolayers on gold, one type of defect appears which does not appear on bare gold. This defect, which has been noted and discussed previously,[1-7] looks like holes in the thiolate monolayer as shown in Figure 1. SSF have concluded that these holes result from an as yet uncharacterized "(electro)chemical etching process".[1] We believe instead that experimental evidence supports the conclusion that these defects are primarily due to a nonequilibrium surface arrangement produced by the highly exothermic adsorption process.

Several pieces of convincing evidence have been amassed indicating that these holes are actually holes in the underlying gold surface,[1,2] and we will not enumerate these here. However, several facts which have been previously reported about these defects should be noted here. First, these holes appear everywhere on the surface and are distributed fairly evenly. Second, in most cases, these holes are quite small (3−6 nm in diameter), they are generally circular, and they exhibit a rather narrow size distribution. Third, in most cases, the holes do not seem to appear very near step defects in the gold surface (self-assembled monolayers deposited from concentrated solutions represent an exception to this rule). Fourth, the area covered by these holes is greatest when deposition is carried out at high thiol concentration.[1] Fifth, the evolution of the holes appears to cease once the self-assembled monolayer (SAM) has formed. Finally, there seems to be at least some correlation between the amount of gold that dissolves into the supernatant liquid during deposition and the spatial extent of these holes, though the amount of dissolved gold is always insufficient to account for the entire area of the holes.[1]

SSF[1,2] have concluded that these holes are due to some "(electro)chemical etching process." We give several reasons below why we think this explanation is insufficient.

Chemical etching processes generally occur preferentially at surface defects rather than in the middle of crystal facets, since the atoms present at defects have a higher free energy and are thus more weakly bound to the surface. In contrast, these holes are distributed uniformly over the surface. They are not usually found very near existing step defects, and time-resolved STM images collected in this lab show that the general shape of step defects do not change during the adsorption/self-assembly process. Furthermore, these holes do not seem to grow as deposition proceeds; that is, once a hole is formed, etching does not continue at that defect site—instead, other holes are initiated very nearby.
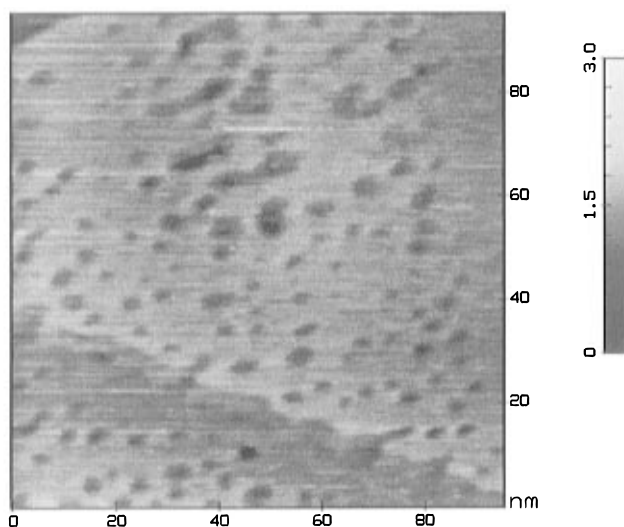


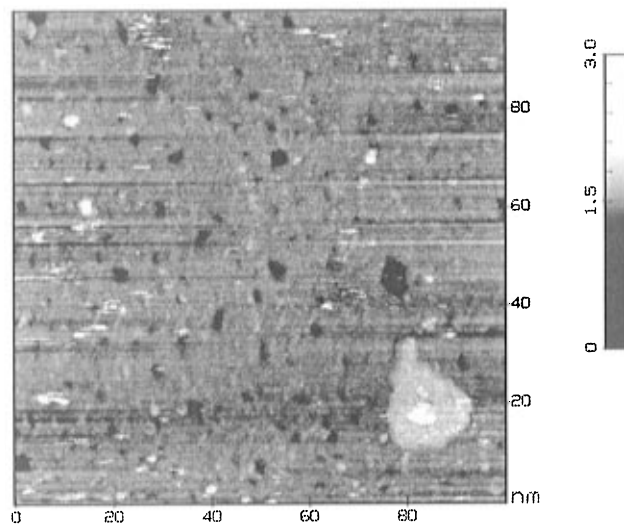**Figure 1.** Octadecanethiol monolayer on Au[111].



**Figure 2.** Monolayer of 2-mercaptoethanol deposited in air. The holes still pervade the surface, in spite of the fact that no solvent is present to solvate and carry away the gold−thiolate complex.

Since alkanethiols can be deposited from a wide range of solvents to form very stable alkanethiolate films on Au, it seems likely that the gold dissolved in the supernatant liquid after adsorption exists as the alkanethiolate. No evidence for side reactions between RSH and gold is known. If the etching process required reagents other than RSH (such as $O_2$), the rate should vary greatly from solvent to solvent. We have observed the formation of these holes in 1 mM solutions of ethanol, hexane, 2-propanol, and even in vapor-deposited thiols, as shown in Figure 2. Thus, a physical rather than (electro)chemical process seems most likely.

That these holes are defects resulting from a disordering (localized fusion) event on the surface is consistent with the fact that deposition from concentrated solutions leads to abundant holes. The rapid deposition which occurs in concentrated solutions is accompanied by a rapid release of thermal energy. This energy is released faster than it can be dissipated, increasing temperature and stress within the film. The resulting surface structure does not represent a thermodynamically favored

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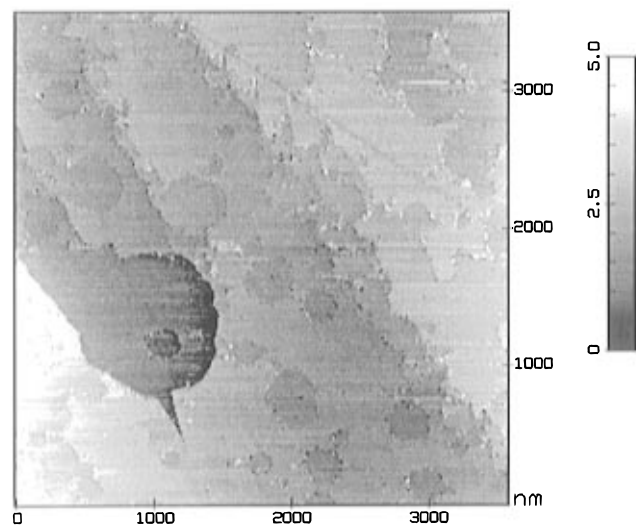


**Figure 3.** Highly oriented pyrolytic graphite surface showing effects of oxidative etching in air. Note: etch pits remain circular throughout growth, they grow together in places, and new pits form inside of other, larger pits.

state; rather, this structure is "frozen in" when the deposition is complete. As deposition proceeds, the reduction in the number of exposed Au sites causes a decrease in the adsorption rate (reducing the rate of heat evolution) and also causes a decrease in the mobility of the surface-bound thiolates. The combination of these effects leads to a surface locked into an energetically unfavorable arrangement, much like a crystalline solid which has been melted and quickly refrozen.

The SAM interface can be thought of as a two-dimensional liquid in terms of the lattice theory.[11,12] The holes are the entropic manifestation of the melting of the crystal as a result of the free energy released during adsorption. As described above, relaxation to a perfect crystal is prevented by the rapid cooling of the surface which freezes in the defects (semi)-permanently.

This hypothesis is concordant with the fact that the holes are distributed relatively evenly across the surface and that holes may form in the middle of large, defect-free basal planes. Thermal energy evolved during the adsorption process desta-bilizes the adsorbed thiolate relative to the solvated phase, resulting in the expulsion of some of the gold−thiolate complexes. This expulsion may result in part from the building of lateral stresses within the monolayer as thermal energy is released. Unlike an etching process, the phenomenon described above is expected to occur far from ledge defects, since ledges would provide stress relief through reduced steric confinement of the adsorbate.

The dissolution of gold (most likely as gold thiolate) in the supernatant liquid probably results from the reduced stability of the bound thiolates associated with local temperature increases and stress. In other words, the thiolates "evaporate" into the supernatant fluid. Data in ref 1 (see Figure 6b in that reference) seem to support these conclusions, as the concentration of dissolved gold reaches a maximum shortly after self-assembly is complete, apparently reincorporating itself into the surface within an hour or so after self-assembly. The products of a spontaneous electrochemical etching reaction as has been suggested by SSF would be thermodynamically favored over the adsorbed gold−thiolate complexes and should not revert

back to the same. The evidence for reincorporation suggests that the dissolved gold is not the thermodynamically favored product of an etching reaction. Once the surface nears equi-librium (room temperature in these experiments), some of the expelled gold thiolate reincorporates itself into the layer. Reincorporation accounts for both the decline in the dissolved gold concentration after monolayer formation and the fact that the amount of gold in solution is never sufficient to account for all of the holes on the surface.

The etching hypothesis is perhaps most strongly impugned by images of thiol surfaces after deposition from neat liquid.[1] In these cases, the holes become highly convoluted in shape and appear very near gold ledges. Some of the holes even join with gold steps. The convoluted hole shapes and the absence of etching beyond the first rank of Au atoms indicate that the pertinent measurable variable in these images is probably not hole area but rather ledge defect density, which can be measured in length of ledge or hole boundary per unit area of surface. This ledge density, $D$, would thus have units of inverse length $(m^{-1})$.

At low to moderate defect densities, the holes are uniform and circular, an arrangment which minimizes the ledge-to-area ratio. It can be shown by simple geometry that the maximum achievable ledge density for circular holes is

$$D = \frac{2\pi\sqrt{3}}{3S} \qquad (1)$$

where $S$ is the distance between hole centers. If hole area merely increased while retaining circularity (as would be expected in a chemical etching process), the holes would begin to grow together, eventually eliminating the ledge defects in the top layer. One would then expect the etching to begin affecting successive layers of gold. This is what happens when graphite surfaces are etched by $O_2$ at high temperature, as shown in Figure 3; however, this is not what happens in the gold−thiolate SAM. Instead of merely increasing hole diameter, the holes become quite convoluted in shape. Convolution is necessary to achieve a high ledge defect density. Thus, convolution of the holes and the absence of etching beyond the first layer of gold seem more consistent with an internal disordering mech-anism than with a chemical etching process.

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