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Formation of Self-Assembled Monolayers of *n*-Alkanethiols on Gold: A Scanning Tunneling Microscopy Study on the Modification of Substrate Morphology

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Single-crystal Au(111) surfaces covered with self-assembled monolayers of *n*-alkanethiols ($\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$) ($n = 6, 22$) are investigated with scanning tunneling microscopy. After adsorption new morphological features are observed which can be shown to originate from a removal of 30–50% of a monolayer of Au atoms from the surface into the solution. Only a very low concentration of defects within the films ("pinholes") was observed. In addition experimental evidence for two different tunneling mechanisms in short and long alkyl chains is provided.

The formation of self-organizing films of *n*-alkanethiols by immersing a gold surface in a saturated solution of thiols in ethanol has recently attracted considerable interest.¹ The spontaneous self-organization leads to a formation of well-ordered films of molecules, where the alkyl chains are inclined with respect to the surface normal by 35°, as determined with infrared spectroscopy² and NEXAFS (near edge X-ray absorption fine structure) spectroscopy.³ Diffraction experiments^{4,5} indicated the presence of lateral order with a $\sqrt{3} \times \sqrt{3}$ periodicity. The same periodicity is also visible in previous STM (scanning tunneling microscopy) and AFM (atomic force microscopy) data,^{6,7} which is most presumably due to an imaging of the S atoms bonding to the substrate as the methyl end groups of the alkyl chains, which form the film–air (or film–vacuum) interface, are thermally strongly disordered at room temperature.⁵

So far the main interest has been devoted to the structure and the temperature behavior of these films, whereas the process of self-assembly itself has been the subject of very few experiments. From results obtained by SAW (surface acoustic wave) devices,⁸ SHG (second harmonic generation), and XPS (X-ray photoelectron spectroscopy) analysis,⁹ it has been concluded that the adsorption process can be described by a Langmuir kinetics. Recent measurements using NEXAFS indicate, however, that the process of self-assembly involves additional time-dependent ordering processes.¹⁰

The purpose of the present study is the investigation of the surface morphology of the self-assembled films by STM in air with a special emphasis on the search for defects in these films ("pinholes"). Figure 1 shows a typical image of a gold single crystal (111)-surface with a self-assembled monolayer¹¹ of docosanethiol (MC22) on a scale of 1350

Å × 675 Å. We clearly observe typical substrate defects such as steps. The most prominent features are, however, depressions of circular shape of about 20–60 Å in diameter and a depth of ≈ 2.5 Å (equal to the step height of the substrate), which are not observed on the clean surface (see inset Figure 1). We never did observe periodic structures, which are not expected in the case of nondestructive imaging of the thiol film, since it is known that the ends of the alkyl chains are strongly disordered at room temperature.⁵

Before we proceed with an interpretation of the data shown in Figure 1, we have to address the question of the imaging mechanism for the long alkyl chains in the STM and whether a nondestructive imaging of these films is possible. Figure 2 shows an area of the Au(111)-surface covered with MC22 (imaged with 0.5 nA), part of which had been imaged before with a current of 7 nA. Clearly the first imaging process has created irregular-shaped defects with varying depths. By repeating this process on different places it was found that for the long alkyl chains (22 carbons) high currents ($I > 2$ nA) induced large defects and created deep depressions with depths up to the film thickness (25 Å for MC22). For tunneling conditions using small currents and voltages ($I < 0.5$ nA and $V < 200$ mV), defects caused by the imaging process could not be observed in subsequent images.

Images taken with roughly the same tunneling parameters as in Figure 1 but for a *n*-alkanethiol with six carbons (not shown) looked virtually identical to the image shown in Figure 1. In this case no tip-induced defects like the ones shown in Figure 2 were observed. This is in agreement with expectation since the conductivity of the short alkyl chain should be sufficiently high to allow for an undisturbed imaging process. Ethylidyne on Pt(111) (corresponding to a two-carbon atom chain) has been successfully imaged with STM.¹²

Although more systematic studies are needed to obtain a better understanding on the conduction mechanism in the long alkyl chains in STM, we can conclude that an imaging of the morphology of a gold-surface covered with a monolayer of *n*-alkanethiols with STM is possible, provided that the tunneling current is sufficiently small. We currently believe that the Poole–Frenkel effect¹³ (field enhanced thermal excitation of trapped electrons into the

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(11) The Au(111) single crystal was flame-annealed at 800 °C and immersed in a 1 mM solution of docosanethiol in ethanol for 24 h. Without further preparation the STM measurements were done in air with Pt/Ir tips.

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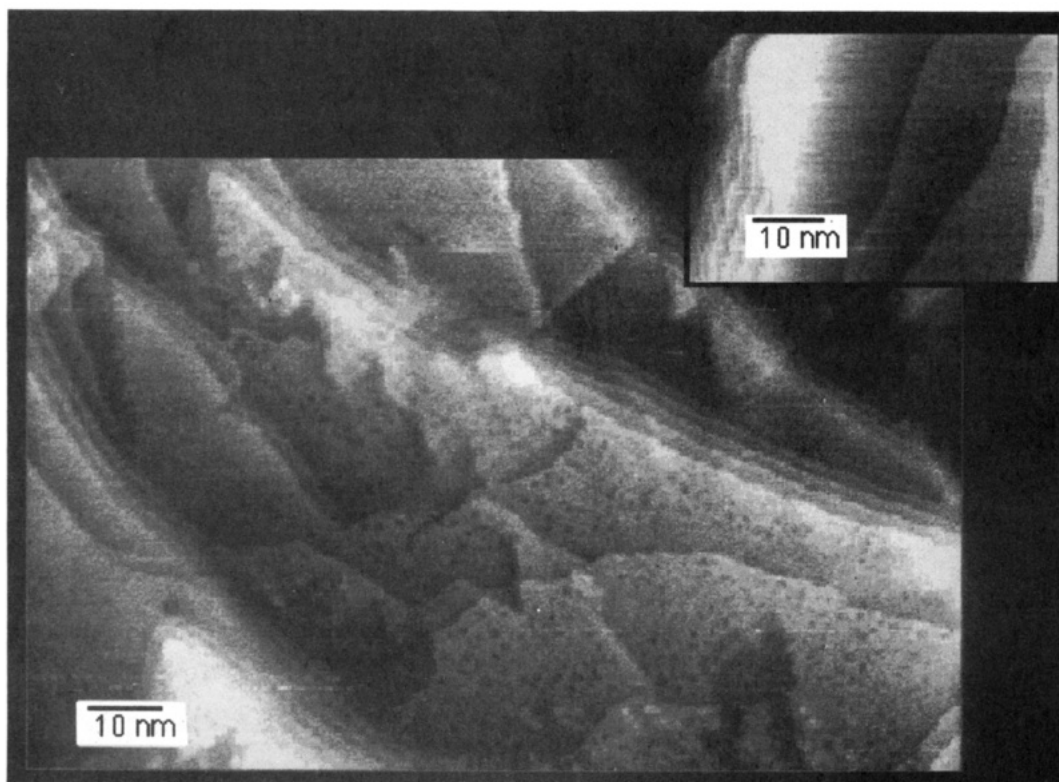


Figure 1. STM image of an Au(111) single crystal surface with a self-assembled monolayer of docosanethiol: tunneling parameters, $1350 \text{ \AA} \times 675 \text{ \AA}$; current, 0.2 nA; tip voltage, 200 mV. The inset shows an area of the clean Au(111) surface before adsorption.

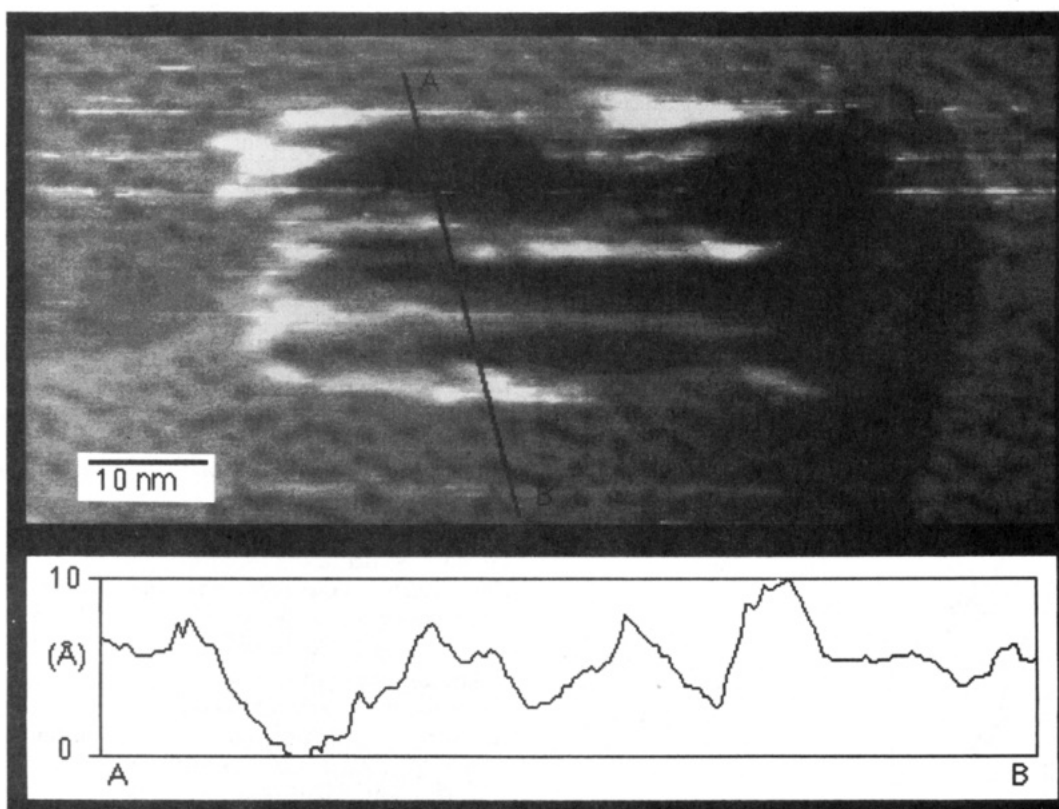


Figure 2. Region of the self-assembled monolayer which had been imaged before with 7 nA (see text): tunneling parameters, $900 \text{ \AA} \times 450 \text{ \AA}$; current, 0.5 nA; tip voltage, 100 mV.

conduction band) may provide a possible explanation for this observation. At higher currents we observe the creation of defects in a monolayer of long (22 carbon) thiols with a maximum depth corresponding to the total thickness of the film in agreement with the results of Kim and Bard.¹⁴ The absence of this sensitivity for short alkyl

chains (six carbon) indicates the presence of two different tunneling (or conduction) mechanisms for different chain lengths.

These observations also lead us to interpret the previously published STM⁶ and probably also AFM⁷ images of periodic structures on substrates covered with

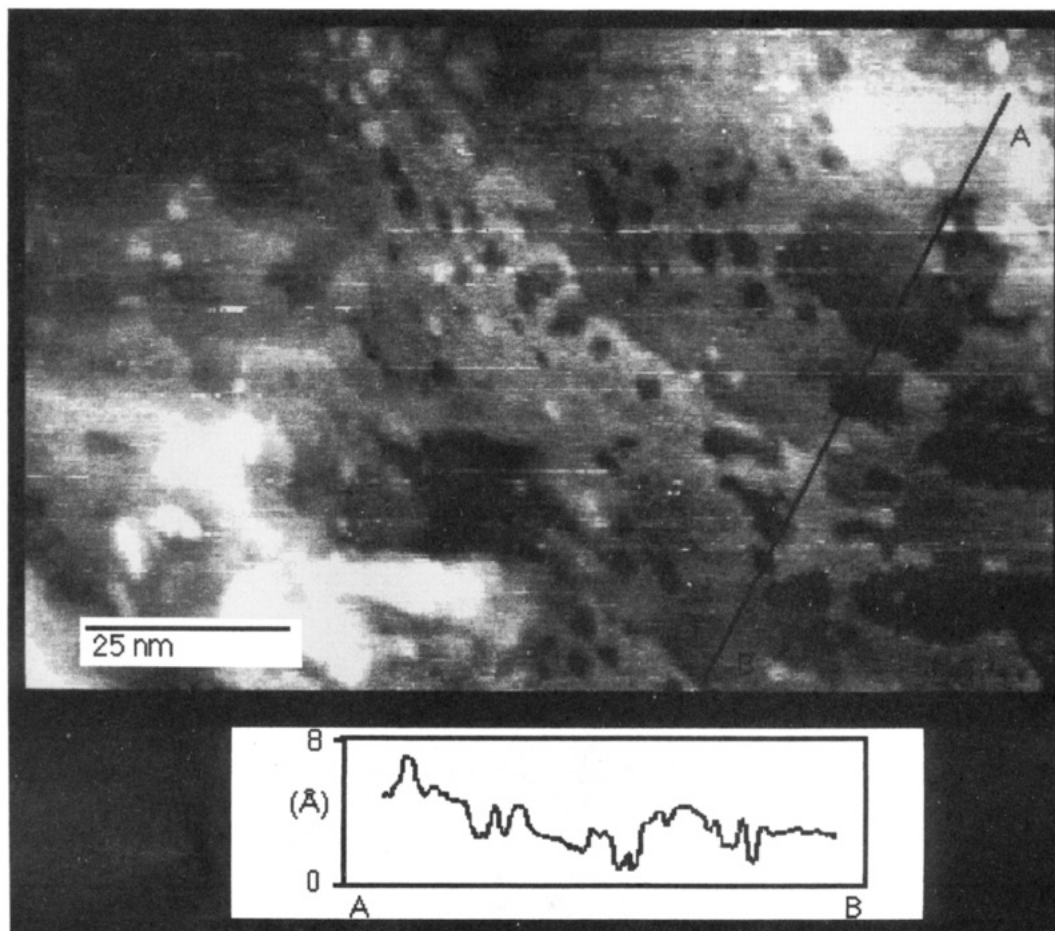


Figure 3. STM image of an Au(111) single crystal surface with a self-assembled monolayer of docosanethiol: tunneling parameters, $1200 \text{ \AA} \times 600 \text{ \AA}$; current, 4 nA; tip voltage, 800 mV.

thiol films as a result of imaging the periodic overlayer of the S atoms. This requires a deep penetration of the STM (or AFM) tip into the film which almost certainly (at least for the long alkyl chains) will be destructive.

For tunneling conditions like those given for Figure 1 we estimate from the height difference to the bottom of artificially created defects that the tunneling tip penetrates less than about 5 \AA into the thiol film.

After this short consideration of the conduction mechanism for imaging organic films containing alkyl chains with varying lengths, we now turn back to a discussion of the prominent morphological features shown in Figure 1. Firstly, the step edges are not quite as straight as for the clean Au(111) single crystal surface (see inset Figure 1). This is an observation which has been made also for other chemisorbed molecules such as naphthalene on Pt(111).¹⁵

In addition we observe a high concentration of depressions with a diameter of $20\text{--}60 \text{ \AA}$ and a depth corresponding to the height of a substrate step ($\approx 2.5 \text{ \AA}$) for both MC22 and MC6. The observation of these structures has been reported before by Häussling et al.¹⁶ and Kim and Bard¹⁴ and was in both cases attributed to defects within the self-assembled film. In the latter case a depth of the depressions of 8 \AA for MC18 was reported, which was found to decrease to 5 \AA for shorter chains (MC10).¹⁴

We have, however, strong evidence that the depressions originate from holes within the top layer of Au atoms.

Whereas these irregular structural features appear as depression of circular shape with closed borderlines inside terraces, their borderline is open when they are located close to step edges. For all of these particular structures, we observe that the bottom of the depressions is indistinguishable from the lower terrace (see Figure 3). As the shape and the depth of these depressions with nonclosed borderlines at step edges is otherwise identical to that of the holes inside terraces, we conclude that these features are due to holes in the top substrate layer.

With regard to a determination of the depth of these depressions, detailed investigations close to well-known defects like steps and screw dislocations are considered to be more accurate than a measurement via calibration of the z -piezo. We do not, however, fully understand the discrepancy to the work of Kim and Bard¹⁴ concerning the depth of the depressions at the present time.¹⁷

The density of these holes on the surface is not uniform. For example areas with a small terrace length, corresponding to a high step density, almost have no holes at all (see Figure 1). Also the region above and below a step edge is inequivalent (see Figure 4). Multiple imaging of the same region (at proper tunneling conditions, see above) usually resulted in the same morphology, only in some cases we observed a modification of subtle features, such as removal of a thin border between two holes.

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(17) We would like to note that using an Au single crystal as substrate enabled us to calibrate our z -piezo in situ by the height of monoatomic steps on the Au(111) surface. Kim and Bard¹⁴ have used evaporated Au films on mica, which are considerably more inhomogeneous. They have calibrated their z -piezo at defects on graphite.¹⁴

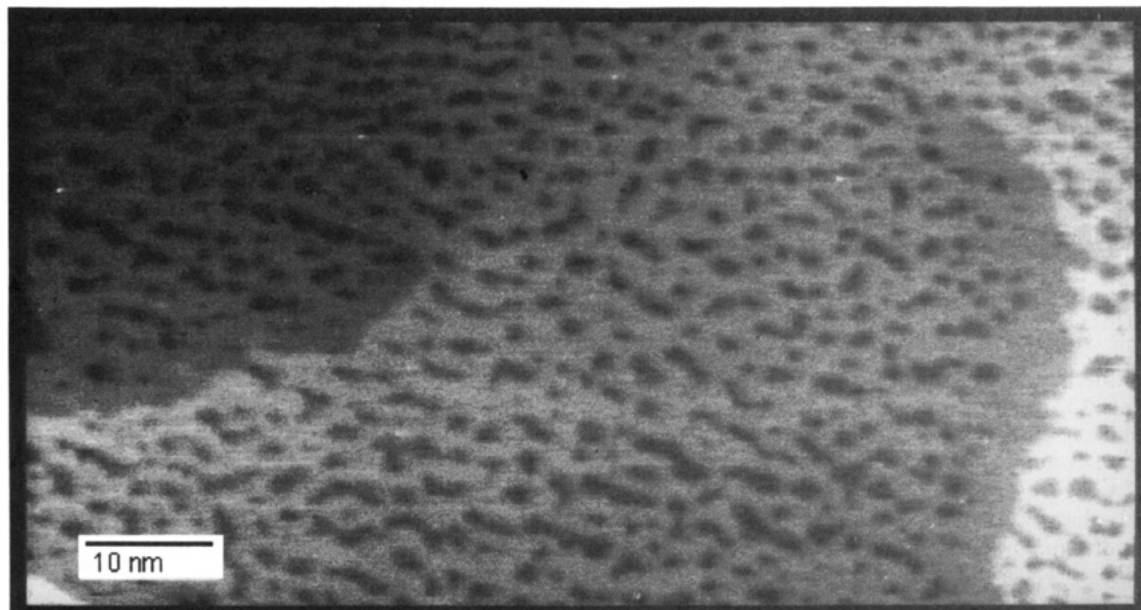


Figure 4. Region around a screw dislocation on an Au(111) single crystal surface with a self-assembled monolayer of docosanethiol: tunneling parameters, $900 \text{ \AA} \times 450 \text{ \AA}$; current, 0.5 nA; tip voltage, 100 mV.

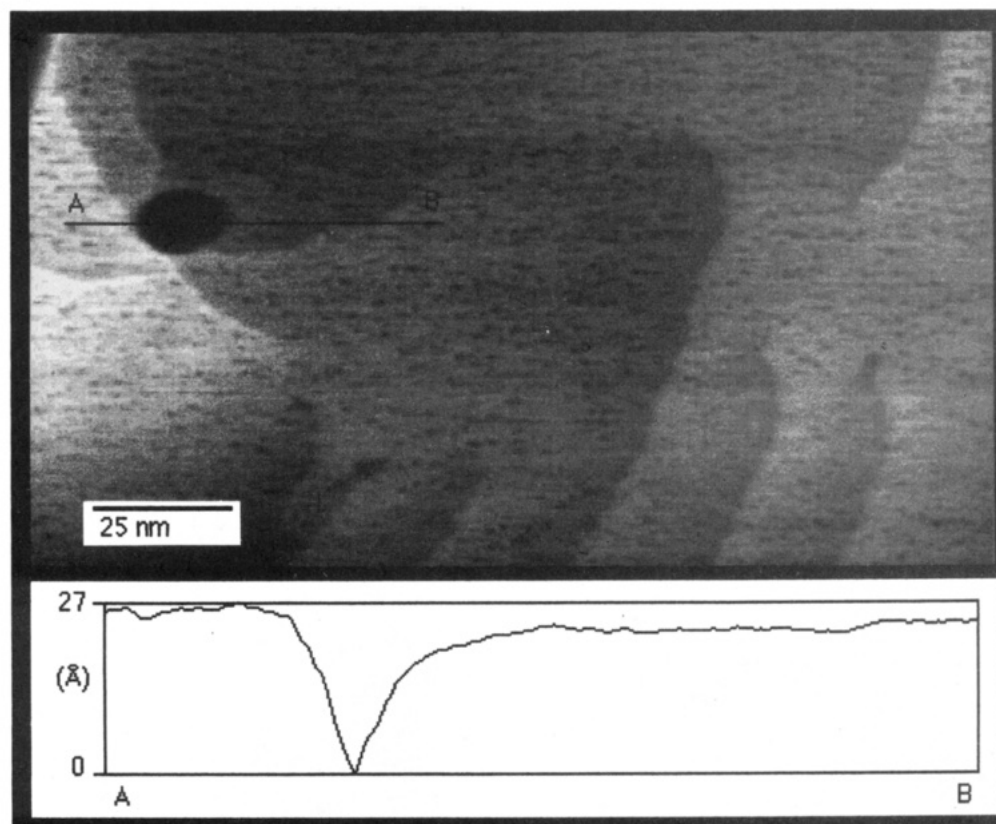


Figure 5. Image of an intrinsic defect in a film of docosanethiol: tunneling parameters, $1800 \text{ \AA} \times 900 \text{ \AA}$; current, 1 nA; tip voltage, 30 mV.

Defects within the self-assembled films which are not caused by the imaging process like the ones shown in Figure 2, were only observed in very few instances. An example of such a pinhole is shown in Figure 5. The depth is roughly equal to the film thickness (25 Å). The small concentration of these defects indicates a very high structural quality of the thiol films, limited only by the structural quality of the substrate.

We also did not observe any structures within the films which could be related to domain boundaries between regions of the film where the molecular axes are tilted in

different directions. These domain boundaries should be present at least for the docosanethiols where both IRS and NEXAFS indicate a high degree of molecular order. For the hexanethiol film we do not expect domain boundaries at room temperature, as measurements with infrared spectroscopy as well as with NEXAFS have shown that the short alkyl chains are not well ordered.³ Our present explanation for our inability to observe domain boundaries is that during imaging the STM tip is in a region of the film which is thermally rough¹⁸ and the domain boundaries should be obscured accordingly. For

lower temperatures the thickness of this region is expected to decrease and the domain boundaries should become visible.

The presence of holes within the top layer of the Au substrate indicates mass transport phenomena upon adsorption of the alkanethiols. The rather uniform distribution of holes within single, large terraces suggests a corrosion process, possibly originating from dissolving of gold atoms or small gold clusters via complex formation with thiols to the ethanol. This hypothesis has been validated by immersing a 10-cm² Au film (evaporated on a Si wafer) into a 1 mM solution of docosanethiol in ethanol for 24 h. The amount of Au dissolved in the thiol solution was determined by atom absorption spectroscopy (AAS).¹⁹ It amounts to 150 ng, corresponding to approximately 50% of a monolayer. This is in reasonable agreement with an area of $\approx 1/3$ of a monolayer estimated from the STM images as shown in Figure 1.

From this observation it can be concluded that the holes are a result of removing material from the surface into the solution. The precise chemistry of these gold thiolates as well as the detailed adsorption geometry of the terminal

S atom of the thiol molecule are not known at present, but there is evidence (see ref 20 for the case of methanethiol CH₃SH on Cu(111)) that the adsorption occurs via an adsorbate-induced reconstruction where a substrate Au atom is replaced. This displacement of Au atoms may be an intermediate step for the formation of an Au-containing complex which is dissolved afterward.

Note, that the low concentration of holes at the down-side of step edges as shown in Figure 4 indicates inequivalence of the two sides of a step-edge, which is consistent with an retraction of step edges as expected for a removal of atoms from the surface.

In conclusion we have shown that the morphology of Au(111) surfaces is drastically changed upon the self-assembly of alkanethiol monolayers by removal of about 30–50% of a monolayer. This and other observations by NEXAFS¹⁰ indicate that the process of self-assembly may be considerably more complicated than presently assumed. Aside from the holes, which are defects in the substrate rather than defects in the thiol film, the thiol monolayers are found to have a very dense, uniform structure with very few intrinsic defects ("pinholes").

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