PHYSICAL REVIEW B **79**, 113412 (2009)

Uncovering the hidden gold atoms in a self-assembled monolayer of alkanethiol molecules on Au(111)

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(Received 18 February 2009; published 30 March 2009)

Self-assembled monolayers (SAMs) of alkanethiols on Au(111) contain adatoms of gold in the form of gold thiolate (Au-S-R). Using localized water dissociation underneath the tip of a scanning tunneling microscope, we are able to break the Au-S bond within a confined area of an octanethiol SAM to release the gold adatoms which subsequently coalesce into single atomic layer gold islands. By measuring the volume of the resultant gold islands, and considering the incorporation of gold atoms into the herringbone reconstructed surface, we found about 0.22 ML of gold atoms are released during the desorption of the octanethiol SAM.

DOI: 10.1103/PhysRevB.79.113412 PACS number(s): 81.16.Dn, 68.37.Ef, 68.43.−h

Self-assembled monolayers (SAMs) of alkanethiol molecules on Au(111) are model systems formed from a self-regulated surface organizational process.[1–3] The thiol molecule within the SAM is known to use the sulfur (S) atom to bind to the gold substrate with the hydrocarbon chain pointing away from the surface. The S-Au bond gives the chemisorption strength of the adsorbed molecule, while van der Waals interactions between the alkane chains provide an extra chain-length-dependent stabilization effect for the molecular layer. Although direct bonding between the S atom and gold atoms in a nearly perfect (1×1) Au(111) surface had been assumed for nearly 20 years, recent studies raised serious questions about the validity of the earlier structural models, and new bonding schemes involving gold adatoms are proposed.[4–7] The new structural models, albeit still not completely in agreement with each other, have one thing in common: the incorporation of a significant number of gold atoms into the SAM, either in the form of adatoms (Au-S-R) or as bridging atoms in the R-S-Au-S-R configuration. The incorporation of gold atoms into the SAM has been shown by theoretical calculations to be able to reduce the total energy of the SAM-substrate system.[7] A recent experimental study, using atomic hydrogen-induced desorption of vapor-deposited octanethiols, has revealed a 0.14 ML (monolayer) of gold in the form of monolayer islands on the gold substrate following the removal of the adsorbed molecules.[8]

Here we present findings from the experimental study of localized electrolysis-induced desorption of SAM molecules and the formation of gold islands as a direct consequence of gold atom release from the SAM layer. We remove the adsorbed octanethiol from the gold surface by localized electrolysis of water below the tip of the scanning tunneling microscope (STM). The products from electrolysis of water drift into the SAM-Au interface under the influence of the electric field, where they react with the adsorbed thiolate causing desorption of the thiol molecules and the appearance of single atomic layer gold islands. These gold islands are formed with gold atoms liberated from the SAM, and by measuring the total amount of gold atoms released in such processes, we found that the high coverage, $\sqrt{3}\times\sqrt{3}$ phase of octanethiol monolayer contains >0.22 ML of adatoms of gold. This is higher than the 0.14 ML obtained from a vapor phase deposited SAM treated with atomic hydrogen[8] and reasons for the discrepancies are discussed. Our findings are in reasonable agreement with recent models,[4,5,7] which predicted up to 0.33 ML of gold adatoms[4] associated with a saturation coverage of gold thiolate monolayer sitting on top of the (1×1) Au(111) substrate.

We conducted our experiments in air at room temperature using a Nanoscope III STM (Veeco, Santa Barbara, CA). The STM tip was made by mechanically cutting a Pt/Ir (80%/20%) wire, and only tips able to produce atomic resolution were used. The Au(111) sample was a thin film (~400 nm) prepared by thermal evaporation of gold onto mica in a BOC Edwards Auto 306 deposition system. The mica substrate was held at 360 °C during deposition and annealed at 360 °C for 30 min in vacuum afterward. The deposition rate was 0.5 ML/min as monitored with a quartz crystal microbalance. The freshly prepared Au(111) sample was then transferred into a 1 mM octanethiol solution in ethanol (99.5%) and left for 24 h at room temperature for the completion of the octanethiol monolayer. The sample with the SAM was then taken out of the solution and thoroughly rinsed with pure ethanol and dried in air. Octanethiol with a purity of 98.5% was purchased from Sigma-Aldrich and used without further purification. The as-prepared SAM consists of a high density of nanometer-sized etch pits as observed with the STM. We subsequently annealed the sample at 80 °C for 30 min in a vacuum of 10^{-6} mbar, leading to a dramatic reduction in the number of etch pits and the appearance of very large domains of an ordered SAM in the $\sqrt{3}\times\sqrt{3}$ structure, Fig. 1.

The SAM surface is hydrophobic and is thus free from water condensation at room temperature. The surface of the Pt/Ir tip, however, becomes covered by a thin layer of water almost instantaneously following mechanical cutting under ambient conditions. It is this thin water film on the STM tip that was used in our work to generate charged ions that drift toward the gold surface and initiate chemical reactions leading to the detachment of the thiol molecules. The existence of water on the STM tip and its effect on STM induced surface modification of alkanethiol SAMs have been known for a long time.[9,10] It was found in our experiments that when the bias voltage on the sample is in the range $-1.5\ \text{V} < V_b$

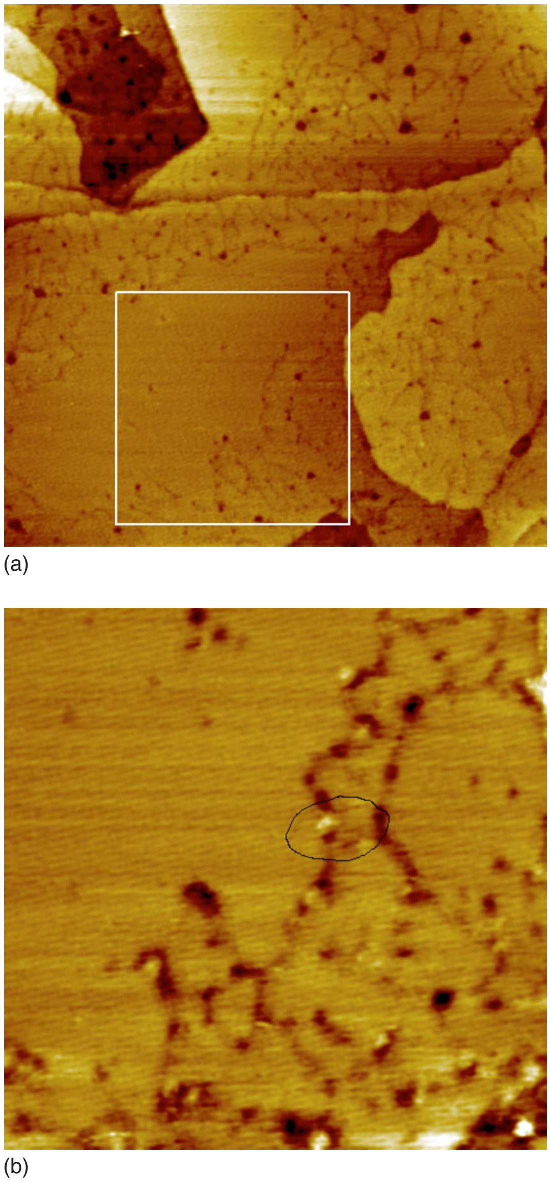

FIG. 1. (Color online) (a) STM image (280 nm×280 nm) of octanethiol monolayer on Au(111) following thermal annealing in vacuum at 80 °C for 30 min. Sample bias voltage: −0.8 V; Tunnel current: 40 pA. To the lower left part of the image, there is a large, almost defect-free, domain SAM. Other regions consist of smaller domains connected by domain boundaries, and the usual one-atomic deep vacancy islands. (b) This STM image (100 nm ×100 nm), from the region inside the white square in (a), shows the formation of small gold islands at locations of vacancy islands and domain boundaries after the area has been scanned with a sample bias of −1.5 V. One of the gold islands is highlighted with a black oval. The image was acquired using a sample bias −0.8 V and tunneling current 40 pA.

<1.0 V, scanning of the STM tip does not cause any change to the SAM. Outside this voltage range, electrolysis of water takes place and the products from the electrolysis react with the adsorbed molecules causing detachment of the molecules from the surface according to the following scheme:

$$H_2O \rightarrow OH^- + H^+, \tag{1}$$

$$H^+ + H_2O \rightarrow (H_3O)^+. \tag{2}$$

Under positive sample bias, OH^- drifts to the Au surface where

$$\begin{aligned} OH^- - e &\rightarrow \frac{1}{2}O_2 + H, \\ H + AuSR &\rightarrow Au + HSR. \end{aligned} \tag{3}$$

Under negative sample bias, $(H_3O)^+$ drifts to the Au surface where

$$(H_3O)^+ + e + AuSR \rightarrow H_2O + Au + HSR. \tag{4}$$

In both cases, electrolysis of water molecules leads to the breaking of Au-S bonds and the release of gold atoms. According to the recent models,[4–7] there are adatoms of gold above the (111) surface, and therefore reactions (3) and (4) are expected to create free gold atoms which should pack into gold islands via the standard nucleation and growth process. Electrolysis of water has a threshold voltage of 1.23 V.[11] The two "electrodes" in our experiments, Pt/Ir and Au, have different work functions of 5.7 and 5.4 eV, respectively.[12] Thus the threshold for water electrolysis at negative bias is shifted to −1.53 V (−1.23 −0.3 V =−1.53 V) and at positive bias it shifts to 0.93 V (1.23 −0.3 V=0.93 V), in good agreement with our experimental observation. (The work function of a material varies from one crystal plane to another; the Pt/Ir tip exposes more than one crystal plane, so the onset of electrolysis is expected to shift by a small amount from the predicted values.)

Figure 1(b) shows an STM image where the growth of gold islands (bright dots in the image) at domain boundaries of the SAM has taken place after the imaged region was scanned with a bias of −1.5 V. The lack of gold islands inside the well-ordered domains suggests that the drift of $(H_3O)^+$ to the Au(111) surface takes place only at the domain boundaries, and the well-ordered domains present a large barrier preventing the $(H_3O)^+$ ions passing through. For positive bias voltages, island growth was observed to occur almost uniformly inside the ordered SAM domains when the voltage is above 1.0 V, Fig. 2. The image in Fig. 2(a) was obtained by scanning an area [region inside the white square in Fig. 2(a)] with 1.5 V once, and then imaged with −0.8 V. It can be seen that the surface, following scanning with 1.5 V, is covered by a high density of raised islands. Figure 2(b) shows a slightly magnified view of the same surface. A height profile plot across the line A-B in Fig. 2(b) is shown in Fig. 2(c). The dark spots in Fig. 2(b) are the original one-atomic-layer-deep "etch pits" which conveniently serve as calibration standard for height measurements. The height profile of Fig. 2(c) clearly shows that all the bright features in the STM images have a uniform height of 0.24 nm which is exactly the dimension of a single layer of gold. Under suitable conditions, we have also found that Ostwald ripening of the islands can be induced leading to the formation of large islands at the expense of the smaller ones and the merging of some isolated islands with existing steps on Au(111).

Because the process described by Eq. (3) for positive sample bias involves the electrolysis of water, the area which

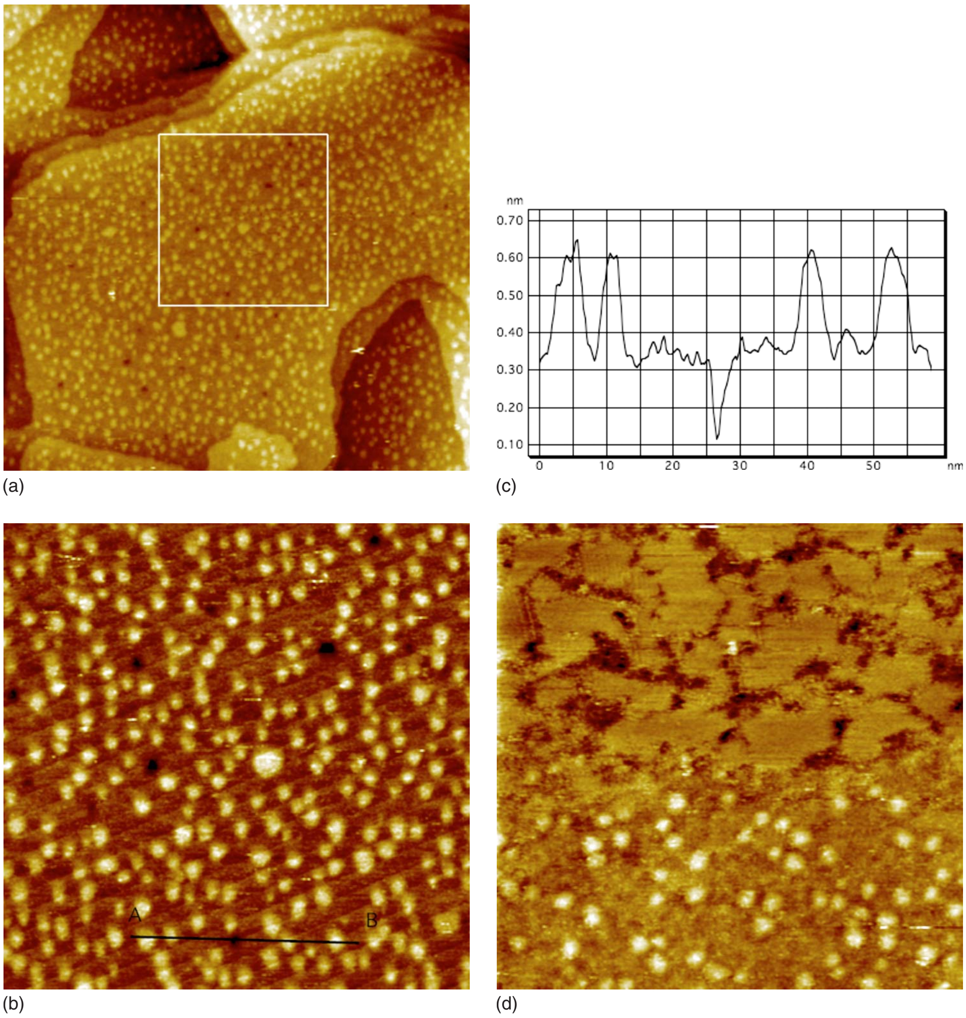

FIG. 2. (Color online) STM images showing the single atomic layer gold islands formed on the Au(111) substrate after the surface was scanned with 1.5 V. (a) This image, 300 nm × 300 nm, was obtained using −0.8 V and 40 pA. The region inside the white square was scanned by the STM tip with a 1.5 V bias before the image was taken. Gold islands are found well beyond the scanned area because the water meniscus on the tip is much larger than the scanned region. (b) A higher magnification image (120 nm × 120 nm) of the gold islands. (c) Height profile measured across the black line A-B. (d) STM image (100 nm × 100 nm) taken from a region containing the boundary of the water meniscus.

shows tip induced formation of gold islands is not determined by the scan size, but by the size of the water film on the STM tip. The size of the water film is much larger than all scan sizes used in our experiments. By laterally translating the sample, we were able to find the contact line of the water film, Fig. 2(d). The contact line clearly forms the boundary between the intact SAM [upper half in Fig. 2(d)] and the region of modification.

Using images like shown in Fig. 2(b), the total area of all the gold islands within the frame can be calculated. Since the islands are all one atom high, we can therefore calculate the number of atoms contained in these islands. From this, we find that the coverage of gold islands in Fig. 2(b) is 0.15 ML. We must point it out that as the SAM is removed, the Au(111) surface resumes its normal herringbone reconstruction. Because the reconstructed surface consists ~4.5% more gold atoms than the (1×1) surface, a 0.045 ML of gold atoms is thus incorporated into the reconstructed surface. This gives a lower limit of the adatom coverage in the SAM as 0.2 ML. Furthermore, the annealed SAM layer also consists of some vacancy islands which disappeared once gold islands were formed on the surface. Thus, some gold atoms are also used to fill the vacancy islands, and an estimated 0.02 ML of gold atoms is consumed this way. Considering that the annealed SAM is actually less than 1/3 ML in global coverage because of the existence of domain boundaries,[13] our findings are therefore in reasonable agreement with the model where each thiol molecule is associated with one gold adatom in the SAM.[4] The experiments performed by Kautz and Kandel[8] on a vapor deposited octanethiol prepared in vacuum gave a lower value of the adatom coverage of 0.14 ML, although it was added in the supporting information[14] that the coverage measured varied from 0.1 to 0.19 ML. Moreover, the extra gold atoms (0.045 ML) needed for the herringbone reconstruction were not taken into consideration by Kautz and Kandel. We have demonstrated previously that whenever a clean Au(111) surface is created at room temperature, the surface always takes the reconstructed form.[15,16] Thus, the adatom coverage could have been underestimated by Kautz and Kandel. In addition to the factors already discussed above that can influence the coverage determination of adatoms in the SAM, one also needs to consider that surface step edges can capture a number of diffusing atoms as well. This is clearly demonstrated by the existence of narrow denuded regions in the vicinity of all steps, Fig. 2(a). In our calculation, we used data from regions well away from surface steps, thus the effect of surface steps can be ignored.

The $\sqrt{3}\times\sqrt{3}$ SAM is associated with a 1/3 ML of adsorbed species. The 0.22 ML of gold found in our experiments suggests that there is about one gold adatom for every adsorbed unit, as proposed in the model of Yu *et al.*[4] However, the 0.22 ML is still someway below the expected 0.33 ML predicted by the model, and it is not possible at this stage to reject other models based on our findings. Our measurement of the area of the gold islands is accurate to 0.01 ML. However, a major source of error is the unknown numbers of atoms that are captured by existing surface steps. For this reason, we concluded that 0.22 ML is the lower limit of the amount of gold released by the SAM. More detailed studies, perhaps at lower temperature to suppress atomic diffusion, will shed some more light onto this important issue.

One of the major difficulties of the simple thiol-on-Au(111) (no adatom) model has been to explain the nature of the etch pits and indeed to identify the destination of the gold atoms that come out of the pits. Dissolution of gold atoms into the liquid is not sufficient to explain the formation of etch pits since vapor deposition in vacuum gives rise to the same structure.[17] The models involving the Au-SR units on the Au(111) surface can thus explain both the formation of etch pits during SAM formation and the appearance of gold islands after the removal of the molecules. Therefore, during the formation of the SAM at room temperature, about 0.22 ML of gold atoms must be provided by the substrate. A small fraction (4.5%) of the adatoms comes from the process when the herringbone reconstruction is lifted upon exposure to the thiol molecule. The majority of the gold adatoms are more likely extracted from the Au(111) surface during the formation of the etch pits. It is interesting to note that upon the formation of a layer of SAM on Au(111), a large number of single layer deep pits are observed. The area covered by the pits is 11% in our experiments, and a value of 15% was reported by Delamarche *et al.*[18] If we take the value of 11%, and add 4.5% from the contribution from the flat terrace during the transformation from the herringbone reconstruction to the (1×1) structure, 15.5% of adatoms can be counted. However, extraction of atoms from surface steps by adsorbed thiol molecules is expected to be quite effective at room temperature as demonstrated by an STM experiment conducted in liquid.[19] This suggests that the 15.5% estimated may well be below the real coverage of adatoms.

The results presented here are consistent with our previous findings from dodecanethiol monolayers.[20,21] In particular, it was shown that thermal desorption of dodecanethiol from Au(111) in vacuum causes a sudden release of a significant number of gold atoms which merge with existing step edges.[20] In that case, the mobility of the gold atoms is very high at the SAM desorption temperature and most of the atoms released are captured by surface steps.

In conclusion, using electrolysis of water assisted by the STM tip, we have successfully removed the octanethiol molecules and observed the adatoms of gold liberated from the SAM. The number of adatoms of gold within the high coverage phase of the octanethiol monolayer has been evaluated and a lower limit of 0.22 ML is obtained. Our findings provide further experimental evidence supporting the recent structural models.[4,5,7] These new structural models do not alter the surface chemical properties of the SAM as reported in the past,[1,2,22] but the stability of the SAM against thermal activation and the atomic scale structure of the SAM-Au(111) interface warrant fresh investigations.

We thank the EPSRC-GB for financial support and F.L. thanks the Chinese Scholarship Council for providing a studentship.

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