Observation of Au deposited self-assembled monolayers of octanethiol by scanning tunneling microscopy

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Abstract

Au deposited self-assembled monolayers (SAMs) of octanethiol molecules have been studied by scanning tunneling microscopy. We have observed ordered structures of the molecules on both the original terraces and subsequently grown Au islands after the Au deposition. These results indicate that Au atoms penetrate through and form islands underneath the SAMs. At the initial stage of Au deposition, islands with a monatomic height grow and become larger as more Au atoms are evaporated onto the surface. The number of islands remains constant as the Au coverage increases up to approximately 0.5 ML. Above this coverage, the islands on each terrace abruptly coalesce into one network structure. The second layer starts to form after coalescence, before the first layer fully covers the surface. This unique island growth is not seen in the normal homoepitaxial growth of Au on Au(111), and is presumably attributed to both the high nucleation density of deposited atoms caused by SAMs and the relatively high diffusion of adatoms along island step edges. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-assembled monolayers (SAMs) have been extensively studied [1] and shown to have potential applications in molecular based devices. Since the SAMs of thiol molecules on the Au(111) surface have an ordered structure over a large area and a thickness that can be precisely controlled by the length of the alkyl chain, one could expect these SAMs to be used as an insulating layer or a tunneling barrier. The design of tunneling barriers is a very important factor in the performance of, for example, single electron tunneling devices, which are characterized by the Coulomb blockade

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and Coulomb staircase [2,3]. Metal/SAMs/metal heterostructures have been fabricated for studying electrical transport properties of this kind of monolayers [4–7], and the structural characterization of such deposited metal surfaces of SAMs has been reported [8–10]. The study of the interaction between SAMs and deposited metal atoms is important not only for this kind of application, but also for fundamental interests such as the kinetics of atoms or molecules in their interacting system. To our knowledge, it is still not clear what happens after metal deposition on SAMs at the molecular scale, or more specifically, how deposited atoms interact with the molecules of SAMs. In this paper, we show the results of Au deposition on the SAMs of octanethiol ($CH_3(CH_2)_7SH$) molecules. The surfaces are studied by scanning tunneling microscopy (STM) in air. Deposited Au atoms

are found to penetrate through the SAMs and to form monatomic height islands underneath them. The SAMs act to disturb the diffusion of the deposited Au atoms on the Au(111) surface, leading to growth characteristics different from the normal metal-on-metal epitaxial growth [11–14].

2. Experiment

The Au(111) substrates, ∼100 nm in thickness, were made on freshly cleaved mica by using electron beam (EB) evaporation. The substrate temperature was kept at about 350°C during the Au evaporation, with a base pressure of about 6×10^{-5} Pa at a rate of 1 Å/s. An atomically flat Au(111) surface with a terrace size of around 100 nm was obtained after this procedure. These substrates, after exposure to air for less than 5 min, were dipped into the 1 mM octanethiol solution diluted by ethanol, and then incubated at 55°C for more than 12 h, and finally rinsed by ethanol. After checking the SAMs surfaces by STM (JEOL, JSTM-4200S) in air, gold (99.99%) was deposited on the SAMs at room temperature by an EB evaporator at a rate of about 0.01 ML/s. The amount of gold deposited was strictly controlled by a shutter and a quartz thickness monitor. Surface observations by STM were started within 20 min after Au deposition. All images were taken in the constant current mode, typically with +1.0 V bias voltage (sample biased) and 40 pA tunneling current. STM tips were made by mechanically cutting a PtIr (10% Ir) wire. Since heat radiation from the evaporation source could affect the ordered structure of SAMs, care was taken not to expose them under radiation for a long time; in other words, higher coverage deposition with a low deposition rate was not attempted.

3. Results and discussion

Fig. 1 shows the STM image of the octanethiol SAMs on Au(111) with a molecular resolution. As reported in many other papers [15–17], there exist many holes of a monatomic depth and many domains with a typical size of about 10 nm. Thiol
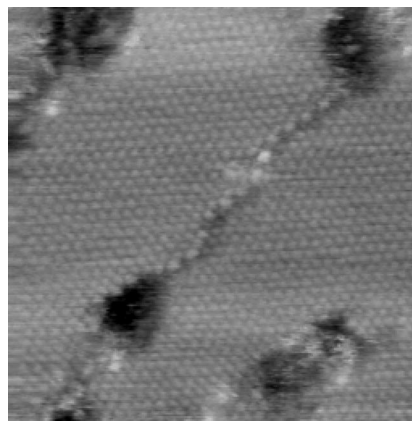

Fig. 1. STM image of self-assembled monolayers (SAMs) of octanethiol molecules on Au(111) in constant current mode [bias (V_b) = 1.2 V, tunneling current (I_t) = 100 pA]. The area size is 17 nm × 17 nm.

molecules are considered to make chemical bonding with the gold substrate (−S−Au), stand on the Au(111) surface with a tilt angle of ∼30° with respect to the surface normal, and form a $(\sqrt{3} \times \sqrt{3})R30°$ overlayer structure [1]. The density and occupation percentage of holes in our samples are ∼9.5×10^{11}/cm² and ∼7%, respectively. Most of the surface is covered with closely packed molecules and there are few defects in the SAMs except at domain boundaries, as shown in Fig. 1. Most boundaries are straight and have three directions originating from the Au(111) surface symmetry. The boundaries are terminated by either the Au(111) step edges or monatomic-depth holes, or other boundaries. The origin of the monatomic-depth holes is not well understood yet, but is probably related to clustering of the Au defects during dipping in the solution and stabilization of these structures by closely packed SAMs (below).

Fig. 2 shows images after the vapor deposition of Au onto these substrates. An ordered structure of molecules was observable on both the original Au(111) terraces and the subsequently grown islands at the initial stage of deposition. This indicates that the deposited gold atoms penetrate through the SAMs and form islands at the interface between the Au(111) substrate and SAMs. At low coverages, all islands are of monatomic height and densely distributed on the surface
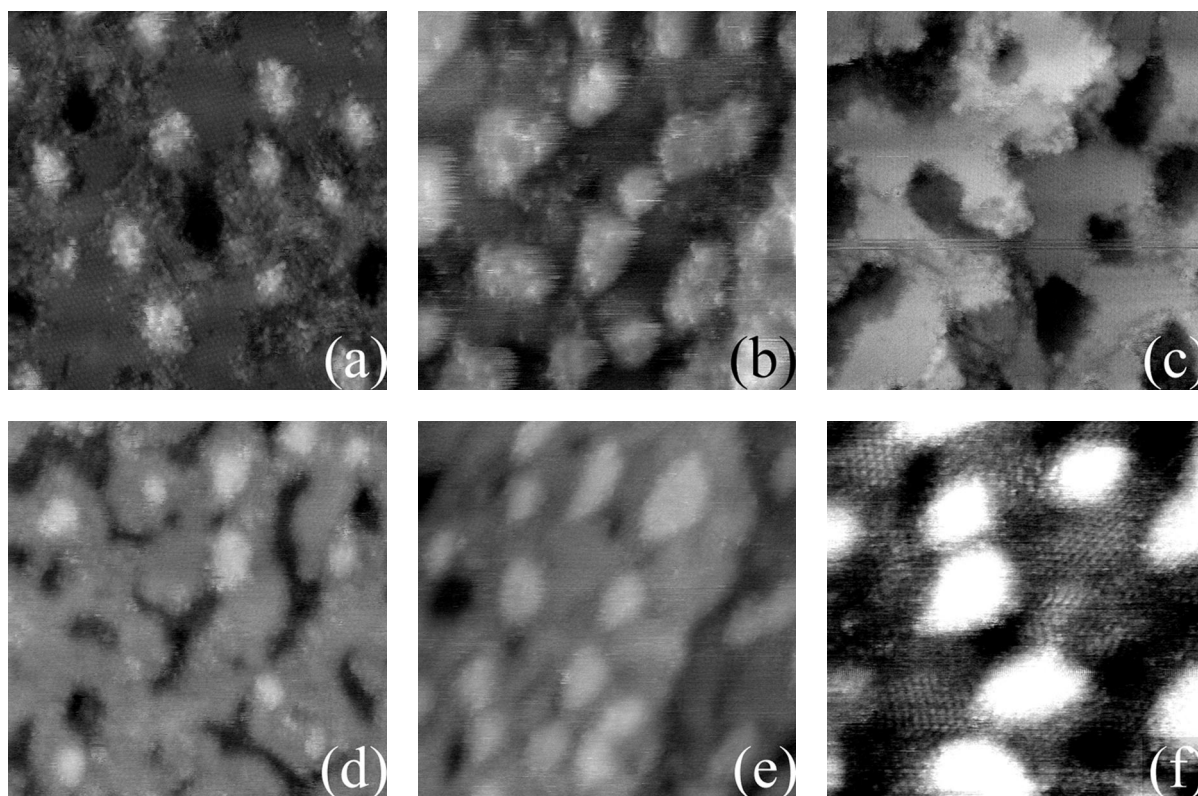
Fig. 2. STM images of octanethiol SAMs after (a) 1/8 ML, (b) 2/8 ML, (c) 5/8 ML, (d) 7/8 ML and (e, f) 10/8 ML Au deposition ($V_b = 0.9$–1 V; $I_t = 30$–70 pA). The area size is 33.7 nm × 33.7 nm in (a–e) and 21.1 nm × 21.1 nm in (f). In (f), contrast adjustment has been applied to obtain better resolution of molecules on the first layer.

($\sim 2.1 \times 10^{12}$/cm^2), in contrast to a low density for the normal metal-on-metal growth. The islands are distributed randomly on the surface, as shown in Fig. 2a, and nucleate not necessarily on defects or domain boundaries of SAMs, although some domain boundaries cross over the network structure (Fig. 2c). The monatomic islands become larger as the Au coverage increases. But the island density remains almost constant for coverages up to ~ 0.5 ML. Above this coverage, the islands on each terrace abruptly coalesce into one single network structure, as shown in Figs. 2c and 3a. The second Au layer starts to form after coalescence before fully covering the first layer, and also lies beneath the ordered structure of molecules. Fig. 4 plots the density and average size of islands versus the Au coverage. The growth of the second layer is slower than that of the first layer because

part of Au atoms are used to fill out the first layer, 5–10% of which are still not covered perfectly even after 1.2 ML deposition.

The density of islands at the initial stage is at least twice as high as the density for the normal metal-on-metal epitaxial growth [11–14] or for systems with surfactants [18]. In the case of a normal homoepitaxial growth of Au on Au(111), the density of islands, which nucleate at certain parts of the elbow sites on the reconstructed Au(111) surface, is much lower [11,13], less than a few per cent of the elbow density ($\sim 1 \times 10^{12}$/cm^2), because most atoms stick at the step edges due to their high diffusion coefficient on the terrace. In our case, SAMs act as an obstacle for the Au diffusion on the Au(111) surface, resulting in the high nucleation density.

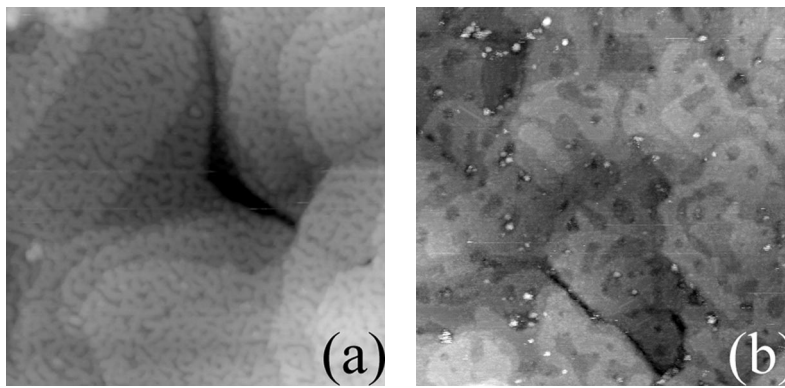The density and occupation percentage of origi-

Fig. 3. STM images of (a) densely packed SAMs and (b) incomplete SAMs after 5/8 ML Au deposition. The images were taken 1 day after deposition. The area size is 215 nm × 215 nm.
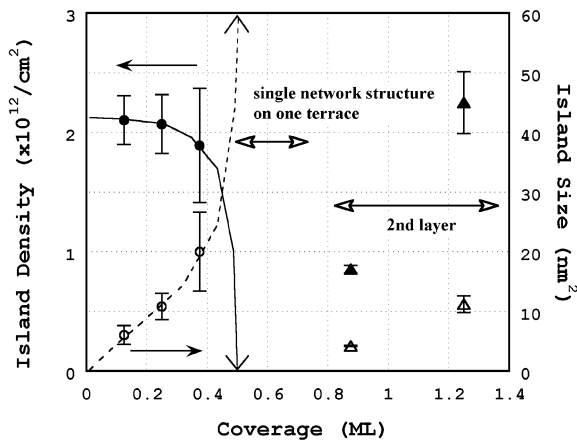

Fig. 4. Island density and size as a function of Au coverage. Filled and open symbols (both circles and triangles) denote the island density and the size, respectively. Circles and triangles denote first layer and second layer growth, respectively. Measurements were performed on 1/8, 1/4, 3/8, 1/2, 5/8, 7/8 and 5/4 ML. No symbols are shown at 1/2 and 5/8 ML coverage, because each Au(111) terrace is covered by only one network island structure.

nal monatomic-depth holes becomes lower with the increase of coverage during the initial stage of deposition. For example, the density of holes at 1/8 ML becomes less than 70% of that before deposition (i.e., the as-grown surface) and the ratio of holes to the whole surface is reduced to $\sim 5\%$, indicating that some of the deposited Au atoms are trapped inside the holes. The average distance between nearest-neighbor islands, $\langle L_{ii}\rangle$ is 6.0 ± 0.2 nm, while the distance from holes to their

nearest-neighbor islands, $\langle L_{hi}\rangle$, is 5.4 ± 0.3 nm. If we count holes as trapping sites for $\langle L_{ii}\rangle$, and also include those that disappeared due to the filling-in of deposited Au atoms, $\langle L_{ii}\rangle$ should become smaller. As a result, $\langle L_{ii}\rangle \approx \langle L_{hi}\rangle$. $\langle L \rangle$ can be considered as the 'mean free diffusion length' of deposited atoms. The fact that there exist depletion areas around both islands and holes, $\pi \langle L \rangle^2/4$ in size, suggests that holes also trap diffusing Au atoms, and that the real nucleation density could be much higher (more than $3 \times 10^{12}/\text{cm}^2$) than the value of $\sim 2.1 \times 10^{12}/\text{cm}^2$ calculated based on the images in Fig. 2.

The second Au layer starts to grow above $\sim 7/8$ ML where the local width size of the network structure becomes close to this 'mean free diffusion length' $\langle L \rangle$. This shows that there exists no special barrier for Au atoms deposited on islands to descend the island edges, and the diffusion coefficient of deposited Au atoms on the first layer is the same as on the original surface, that is, the growth of the second layer is also affected by SAMs.

In comparison with other metal-on-metal growths, coalescence of Au islands occurs more abruptly above a critical coverage in the present system, as shown in Fig. 4. Above ~ 0.5 ML (Figs. 2c and 3a), the coalescence leads to the evolution of originally isolated islands into one network structure on each Au(111) terrace. In the case of a normal metal-on-metal growth, even after coalescence the waist-narrowing feature is still

visible at the contact point of islands, from which one can distinguish each island growth center. In contrast, the present system poses difficulties in identifying the growth center for each island, since the width of the network structure is very homogeneous and waist-narrowing is not obvious. This means that the diffusion of Au atoms along the island edge is high enough to smooth the edge structure or, in other words, to minimize local line tension or local 'boundary free energy' [19] of the network structure. This is because, first, at the Au step edge SAMs also have a step structure, which lowers the interaction of molecules between the upper and lower terraces as the molecular interaction strongly depends on the overlap between molecules (1.4–1.8 kcal/mol per CH_2) [1]; second, it is difficult to make densely packed SAMs around a step edge because Au atoms on the upper terrace exist on the hollow sites of the lower terrace, which causes a mismatch in the positioning of molecules between the upper and lower terraces, and thus prevents dense packing at the step edge. It is noteworthy that molecules appear to hinder the diffusion of Au atoms more on terraces than along island edges, resulting in a high nucleation density in the former and a smooth structure for the latter. After coalescence, isolated holes which are surrounded by grown islands appear. Modification of these holes is accompanied by the movement of molecules, which could stabilize the area of holes. This situation is totally different from normal metal-on-metal growth [11], where islands can grow more freely. Unique network structure and abrupt change to it at around ~ 0.5 ML can be ascribed to these effects.

After minimization of local 'boundary free energy' by forming circular islands or the unique network structure shown in Figs. 2 and 3a, morphological changes of these structure were not visible at least within a few days in the case of densely packed SAMs, suggesting no obvious diffusion of Au atoms. In contrast, it was reported that the metal–molecule complex diffuses on terraces and reforms the step structure in a few hours [20]. Indeed, in the case of disordered SAMs structures on Au(111) due to, for example, a short dipping time, we observed the change to a simpler network structure within a day (Fig. 3b): small

monatomic depth holes combine with each other and the step edges become smoother. In this kind of surface, an ordered structure of densely packed molecules, shown in Fig. 2f, was not observed on the whole surface. In some parts of the surface, an ordered structure was observed with molecules lying (not standing) on the surface, showing low density of molecules. The diffusion in the previous report [20] might be similar to this case. Our results suggest that closely packed SAMs, in which molecules have strong interaction with each other, stabilize the structure underneath.

It is still not clear whether deposited gold atoms diffuse first and form clusters on SAMs and then penetrate through, or whether they penetrate through SAMs first and then diffuse at the interface and form clusters. Ion scattering spectroscopy (ISS) studies of Ag deposited SAMs showed that Ag atoms rapidly penetrate through octadecanethiol ($HS(CH_2)_{17}CH_3$) SAMs, within 5 min at most [8,10], which is the minimum time-interval between the end of deposition and the start of ISS measurements. If the penetration process occurs within minutes, the island parameters such as size and density would be strongly affected by the rate of evaporation. However, no significant differences were observed over 0.005–0.1 ML/s for the present system, an implication of penetration occurring at the very early stage of deposition followed by clustering. In addition, an ISS study of metal overlayers on SAMs of thiol with COOH end-groups ($HS(CH_3)_nCOOH$) also shows that the penetration time strongly depends on the molecular length; deposited metal overlayers on the SAMs of $n=15$ penetrate through SAMs at least 50 times more slowly than that on the SAMs of $n=11$ [10]. Since the length of the octanethiol molecule is about half that of octadecanethiol, penetration should occur more rapidly. Therefore, we believe that the observed island structure is formed after the penetration of deposited atoms through SAMs. Moreover, the ordered structure of molecules appears not to be destroyed during the penetration, or recovered readily after the penetration in densely packed SAMs, probably due to that the number of molecules is conserved even after Au deposition and the interaction between molecules is still strong.

There exist some discrepancies with the ISS studies. Previous results showed that penetrated Ag atoms form clusters under SAMs, and even after more than 10 Å deposition, some of the original Au surface remains uncovered [8,10]. An island growth mode is implied, in contrast to our result which shows a layer-by-layer growth. Considering similar island growth of Au and Ag on bare Au(111) surface and the interaction between thiolate and Ag, it is difficult to ascribe this Ag clustering to a unique Ag property. We believe that the sample roughness, which comes from the different procedure for sample preparation, might cause the insufficient Ag coverage on Au.

In the case of normal metal on metal epitaxial growth, it is known that the important factor for the density of grown islands is deposition rate and substrate temperature. By tuning these parameters, one could gain insight into the kinetics of adatoms, e.g., diffusion coefficient. This technique may also apply to the present system for working out how molecules affect growth and structure. To achieve this target, a systematic study is desirable, in addition to solving the technical difficulties such as keeping the quality of SAMs under higher temperatures, which are heated up not only by the substrate but also by the heat radiation from the deposition source.

4. Conclusion

We have studied Au deposited SAMs of octanethiol molecules ($CH_3(CH_2)_7SH$) by scanning tunneling microscopy in air, and found that deposited Au atoms penetrate through SAMs and form monatomic height islands under SAMs at the initial stage. An ordered structure of molecules was observed not only on the original surface, but also on the subsequently grown Au surface of both the first and second layers, assuring the penetration phenomenon. The interactions among deposited Au atoms and octanethiol molecules of monolayers are responsible for the high density nucleation and unique growth properties

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