

Growth and characterization of Au clusters on alkanethiol self-assembled monolayers

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We have prepared nanometer-sized gold clusters on alkanethiol $[\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$, abbreviated as C_n] self-assembled monolayers (SAMs) on Au(111) substrates by thermal evaporation. Typically, the Au clusters are one atomic layer thick and plate-like, with a diameter of $\sim 2-10$ nm. While most of the Au clusters are found at the SAM/Au(111) interface, a fraction of the clusters reside on top of the SAMs as evidenced by the existence of the Coulomb blockade and Coulomb staircase in the scanning tunneling spectroscopy. Using scanning tunneling microscopy under ambient conditions, we also investigated the stability of the gold clusters at the SAM/Au(111) interface. For a given nominal coverage of Au, the gold clusters on C_7 are larger and diffuse faster than those on C_{10} and C_{18} . © 2000 American Vacuum Society. [S0734-211X(00)00805-2]

I. INTRODUCTION

Nanometer-scale metal clusters play important roles in correlated single-electron tunneling (SET), which has been proposed as a basis for nano-electric digital circuits.¹ In the past, much effort has been devoted to the study of semiconductor clusters—quantum dots such as InAs on GaAs and Ge on Si^{2,3} as well as to nanosized metal clusters.⁴⁻⁹ One major problem in the application of metal clusters is to find a suitable insulation layer to separate the clusters from the conducting substrate, which can be either a semiconductor or a metal. It is generally difficult to form an atomically flat surface with a controlled thickness with an oxide insulation film. Self-assembled monolayers (SAMs) of thiol molecules constitute a potential candidate for application as ultrathin insulating layers because of their ease of preparation, atomic flatness, long-term stability, controllable surface chemical functionality, and adjustable thickness through the selection of various chain lengths of thiol molecules.¹⁰ Recently, using a double ended aryl dithiol (*p*-xylene- α , α' -dithiol) SAM as an insulation layer to support the nanometer-sized gold clusters deposited from a cluster beam, Andres *et al.* successfully showed evidence of SET behavior of a Au cluster at room temperature.¹¹ With a different thiol monolayer, HS(CH₂)₁₁OH, with a hydroxyl group termination, Anselmetti *et al.* used an evaporation method to form three-dimensional (3D) Au clusters with a height of $\sim 2-3$ nm.⁷ In their case, Coulomb blockade, a characteristic feature of SET, was also observed at room temperature as well as at low temperatures.

It is interesting to study Au clusters grown on alkanethiol SAMs with methyl termination. This is because the interaction between the gold atoms and the methyl terminated SAMs is small. When the gold atoms are deposited on this surface and form clusters, the clusters resemble free clusters

with only very weak interactions with the substrates. Inherent from the atomic flatness and the ordering of SAMs, these clusters can be easily characterized with scanning probe microscopy. However, it was often found that the weak interaction between the Au atoms and the methyl-ended SAMs would imply penetrations of the Au clusters to the SAM/Au(111) interface.

In previous work, the behavior of deposited metal films on SAMs has been studied with x-ray photoemission spectroscopy (XPS), ultraviolet photoelectron spectroscopy, and ion scattering spectroscopy (ISS).¹²⁻¹⁶ In these studies, metal films with different reactivity, such as Ag, Cu, Cr, and Ti, were deposited on SAMs with different functional end groups (e.g., CH₃, OH, COOCH₃, COOH, and CN). It was found that at room temperature, highly reactive metals remain on top of the SAMs by forming bonds with the SAMs' end groups, but the low reactive metals penetrate through the SAMs to the SAM/Au interface.^{14,15} It was suggested that the penetration rate depends on the extent of defects in the SAMs, e.g., the number of pinholes, the gauche defects along the chains, and the nature of the domain boundaries. These defects could provide diffusion paths for the metal atoms between the end group and the SAM/Au interface. The results of a scanning tunneling microscopy (STM) study of Au deposition on the octanethiol SAMs⁹ showed that all the gold clusters have monoatomic height, based on which the authors concluded that Au atoms penetrate to the SAM/Au interface. However, it remains unclear (i) if all the Au atoms penetrate into the interface; and (ii) if, for those that did penetrate to the interface, the deposited gold atoms first diffuse and form clusters on SAMs and then penetrate through the SAMs as clusters, or if the gold atoms first penetrate through the SAMs and diffuse at the SAM/Au interface to form clusters.

In this article, we report on the growth and characterization of Au clusters formed on alkanethiol SAMs by the evaporation method. Only one-layer-thick, two-dimensional (2D) plate-like Au clusters were observed up to a cluster size of 10 nm in diameter. Atomic resolution imaging revealed

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that most of the clusters were formed at the SAM/Au interface through penetration. However, a fraction of the clusters ($\sim 5\%$) were found on top of the SAMs even at room temperature. This was evidenced by scanning tunneling spectroscopy (STS) on those clusters on top of the SAMs, which displayed Coulomb blockade and Coulomb staircases (signatures of SET). When the growth temperature was lowered to 78 K, a significantly higher fraction of the clusters ($\sim 30\%$) showed the SET effect, further lending support to the notion that Au clusters can form on top of SAMs. Using ion scattering spectroscopy, Herdt and Czanderna¹⁵ showed that more deposited silver remain on top of octadecanethiol as the temperature is decreased from 220 to 113 K. The evolution of the penetrated clusters at the SAM/Au(111) interface as a function of time was measured using STM. After preparation, the size of these clusters slowly increased in the first few days and then stabilized. This indicates that diffusion of thiolated Au atoms at the SAM/Au interface is significant for clusters with sizes smaller than a critical value (~ 1 nm), and most of the clusters are likely to be formed after the penetration of Au atoms through the SAMs.

II. EXPERIMENT

The preparation of the substrates, SAMs of alkanethiol [$\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$, $n=7, 10$, and 18 , abbreviated as C_7 , C_{10} , and C_{18}] on Au(111) involves two steps, namely the preparation of the gold substrates and the formation of the alkanethiol monolayers. First, we evaporated a ~ 160 -nm-thick gold film at a rate 0.05 nm/s [~ 0.2 monolayer (ML)/s] onto freshly cleaved mica sheets under a vacuum of $\sim 1.0 \times 10^{-7}$ Torr. For good quality gold films, the mica sheets were baked at 300 °C for 24 h in a vacuum of 6×10^{-8} Torr before evaporation and maintained at 300 °C during evaporation. The deposited gold films were quickly quenched in ethanol and then immersed in a 2 mM ethanol solution of C_7 , C_{10} , or a tetrahydrofuran (THF) solution of C_{18} . The SAMs were formed spontaneously by keeping the substrates in the alkanethiol solutions for about 48 h at room temperature. Final rinsing was carried out to clean any residual physically adsorbed molecules. In the preparation process, high purity, low-water-content ethanol and THF were used. The alkanethiols were purchased from Aldrich and used without further purification.

Thermal evaporation was used to fabricate the Au clusters. For samples prepared at room temperature, three $\sim 15 \times 15$ mm² substrates each with either C_7 , C_{10} , or C_{18} SAMs were placed on the same sample holder simultaneously in a vacuum chamber. After pumping to a pressure of 1×10^{-7} Torr, a submonolayer of gold was evaporated onto these substrates at a rate ~ 0.016 ML/s. By controlling the deposition time to either 15 or 25 s, two coverages of gold were prepared, $\theta=0.25$ ML and $\theta=0.40$ ML. For comparison, a piece of bare gold thin film without the SAMs was also placed on the same sample holder for the gold deposition. After the submonolayer of gold was deposited, the samples were quickly transferred to a STM under ambient conditions for morphology characterization, and then to a commercial

OMICRON low-temperature ultrahigh vacuum (UHV) STM for STS measurement. After each imaging, the samples were kept under dry nitrogen at room temperature. To study the growth-temperature effect, clusters were also prepared at 78 K in the OMICRON UHV STM system with similar conditions and then characterized in the same chamber at different temperatures without breaking the vacuum. Morphologically, no obvious difference was observed between the *in situ* and *ex situ* prepared clusters. The imaging resistance was typically 1–2 G Ω , which allowed nondisruptive imaging on C_7 and C_{10} but not on C_{18} .

The image analysis and statistics of clusters were performed by using the Q600 (Leica) software, which allows one to subtract the substrate contribution. Choosing a suitable height threshold for the clusters in the images, the coverage of clusters (fractional area occupied by clusters), the cluster size and its distribution, and the number density (number of clusters per area) could be calculated. In our analysis, the threshold used included only the areas of 2D cluster plateaus, which reduces the convolution effect of the STM tip. For better precision, the STM images were taken with a resolution of 512×512 pixels. Typically, at 0.25 ML initial coverage, 50×50 nm² size images were used for statistical analysis of the Au clusters on C_7 , C_{10} , and C_{18} . At an initial coverage of 0.4 ML, the image sizes used were 200×200 nm² on C_7 , and 100×100 nm² on C_{10} and C_{18} . In the case of Au clusters on bare Au(111), 500×500 nm² images were used for both initial coverages. The reason for choosing different sizes of images was to have enough Au clusters, ~ 50 clusters on gold substrate and ~ 200 clusters on SAMs substrates, to be included in each image for the analysis. All the data were averaged over ten images taken at different sample areas separated ~ 1 mm apart.

III. RESULTS AND DISCUSSION

A. On the location of the Au clusters

The samples were measured immediately after fabrication of clusters (time $t=0$ day). Figures 1(a)–1(d) show the typical images at an initial Au coverage of 0.25 ML, and Figs. 1(e)–1(h) show the cluster images at 0.40 ML on substrates of bare Au(111), C_7 , C_{10} , and C_{18} SAMs, respectively. Most of the observed clusters are 2D and plate-like and have a height of ~ 0.25 nm, about one atomic layer thick. For the same substrate, a higher Au coverage results in not only more clusters but also larger cluster size. The size of the clusters on bare Au(111) is the largest. Those on C_7 , C_{10} , and C_{18} are sequentially smaller. This indicates that the diffusion of the Au adatoms on Au (111) is much faster than that on SAMs. These 2D clusters are not observable on SAM samples without the postdeposition of Au. For those samples, the etched pinholes, which are also covered with alkanethiol molecules,¹⁷ are visible (see Fig. 2). Our observation of 2D clusters is similar to that reported in Ref. 9, but quite different from the case of gold deposited on SAMs with a terminal $-\text{OH}$ group, in which 3D clusters with a height ~ 2 – 3 nm were observed.⁷

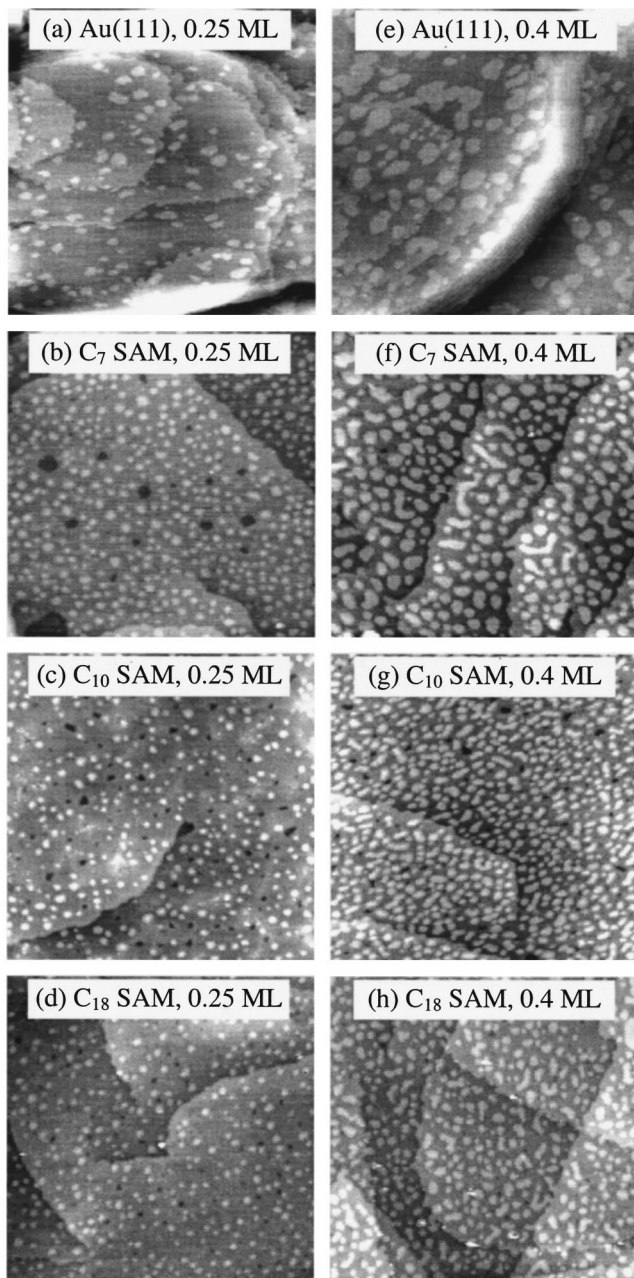


FIG. 1. Representative images of Au clusters on Au(111), C_7 , C_{10} , and C_{18} SAMs immediately after deposition ($t=0$ day). (a) and (e) $500 \times 500 \text{ nm}^2$, (b)–(d) and (f)–(h) $200 \times 200 \text{ nm}^2$. The images were taken at $-0.3 \text{ V}/1 \text{ nA}$ for Au(111), and $-1.0 \text{ V}/0.5 \text{ nA}$ for C_7 , C_{10} , and C_{18} .

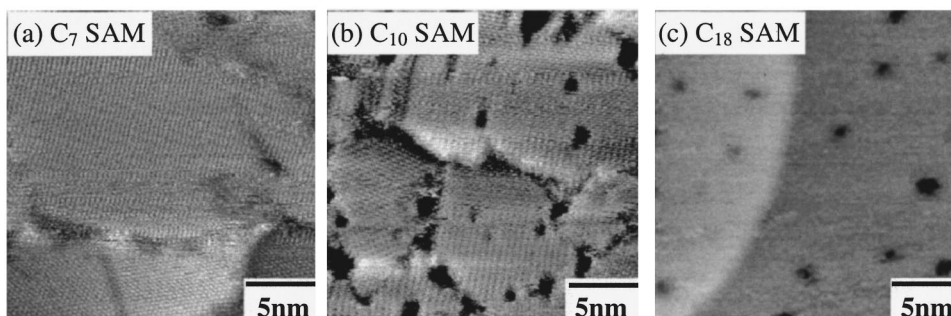


FIG. 2. Typical images of (a) C_7 , (b) C_{10} , and (c) C_{18} bare SAMs. The images were taken at $-1.0 \text{ V}/0.1 \text{ nA}$, at which monolayer lattices are resolved for C_7 , C_{10} , but not for C_{18} .

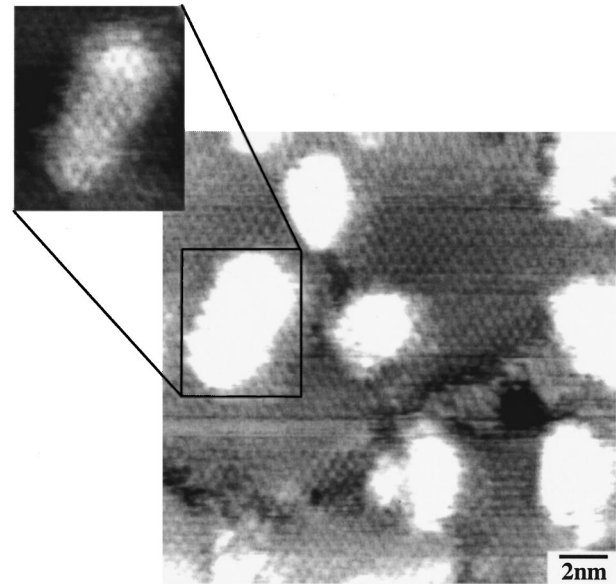


FIG. 3. High-resolution images of the clusters showing a periodicity identical to those of the SAMs. This lends support to the physical picture that the gold clusters in this case are buried at the SAM/Au(111) interface.

Before discussing the evolution of the Au clusters, it is important to pinpoint where the Au clusters are located. As pointed out in the introduction, Au interacts weakly with the alkanethiol molecules and may penetrate through the SAMs to the SAM/Au(111) interface. Our high-resolution images in Fig. 3 show that the periodicity of the observed clusters, near a boundary or in the middle of a domain, is the same as that of the SAMs. By also considering the evidence from XPS and ISS for Ag/SAMs by Herdt and Czarderna,^{15(d)} which show convincingly that Ag penetrates to the SAM/Au(111) interface, it is reasonable for us to conclude that most of the Au clusters are located at the interface, and what we see in the high resolution images of the clusters are the SAM lattices. As will be discussed later, the failure to observe the Coulomb blockade in STS for most of the Au clusters lends further support to a Au penetration mechanism. Although most of the Au clusters observed are within the SAM domains, most of the Au penetration probably takes place near the defect sites such as pinholes and domain boundaries. The penetrated Au atoms then diffuse along the SAM/Au(111) interface to the middle of the domains where they nucleate into clusters. The observation of clusters on

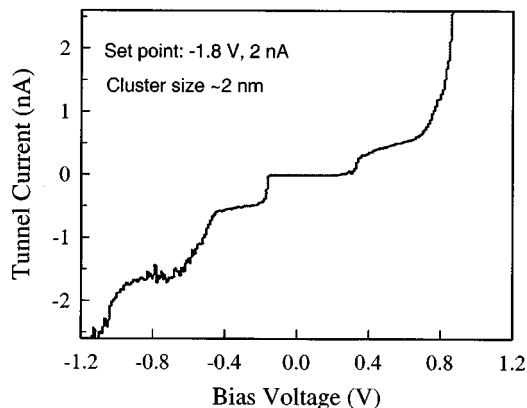


FIG. 4. A typical I - V curve showing Coulomb blockade and Coulomb staircases on a Au cluster with a diameter of 2 nm on C_{10} SAM. The measurement was taken at 5 K.

C_{18} is additional evidence that the clusters are at the SAM/Au(111) interface. This is because if the Au clusters were sitting on top of the C_{18} SAM, they would be damaged since the tip must penetrate and disrupt the C_{18} SAM for such a low imaging resistance (~ 2 G Ω).

Although most of the Au clusters are situated at the SAM/Au(111) interface via diffusion through the SAM layers, either through pinholes, domain boundaries, or even along alkyl chains with gauche defects within the domains, some 2D Au clusters still reside on top of the SAM layers. As shown in Fig. 4, the Coulomb blockade and Coulomb staircases are clearly seen for some Au clusters on the C_{10} SAM in the STS current-voltage (I - V) curves. Cooling the sample to a low temperature is important for clear resolution of the SET phenomenon since at room temperature thermal excitations smear out the characteristic features. However, the location of the Au clusters is believed not to be altered by cooling. In fact, about 5% of clusters prepared at room temperature possesses the SET effect when measured at 77 or 5 K. Since the SET phenomenon can only be seen for small metal clusters sandwiched in double barrier tunneling junctions, the Au clusters in electrical contact with the Au(111)

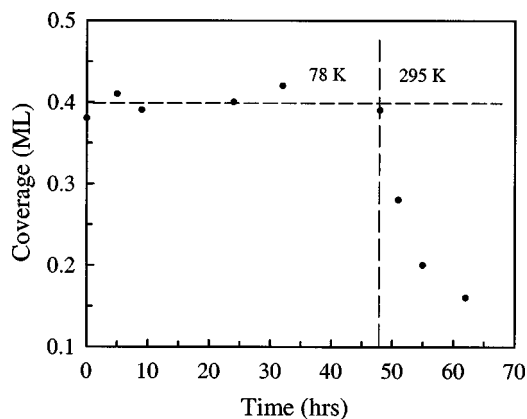


FIG. 5. The Au coverage of *in situ* deposited gold clusters on C_{10} SAM as a function of time. The sample was maintained at 78 K for 48 h, and then warmed up to 295 K.

surface, either by Au residing at the SAM/Au(111) interface or by connecting the Au cluster via a conduction path through pinholes or other defects to the Au(111) substrate, would not show the Coulomb blockade or Coulomb staircases in the I - V curves. Thus, we conclude that the clusters showing the SET phenomenon are isolated from the substrate and located on top of the defect-free areas of the SAM. The success rate of observing SET in our case is similar to those of Ag clusters on Sb-terminated Si(100),⁸ where only a small fraction of clusters show the SET behavior. In order to observe the clusters on top of the SAMs, we further found that the Au deposition rate to prepare clusters is very important at room temperature. Stable clusters cannot form at slow deposition rates because all the Au atoms penetrate to the interface before they can nucleate on top of the SAMs. A suitable and controllable deposition rate is about ~ 0.02 ML/s for the formation of stable clusters on top of the SAMs. This fact indicates that nucleation on top of SAMs and penetration through SAMs are two competing processes. Depending on the flux, one process may dominate the other.

To further prove that some Au clusters indeed reside on top of the SAMs, we deposited about 0.4 ML Au on C_{10}

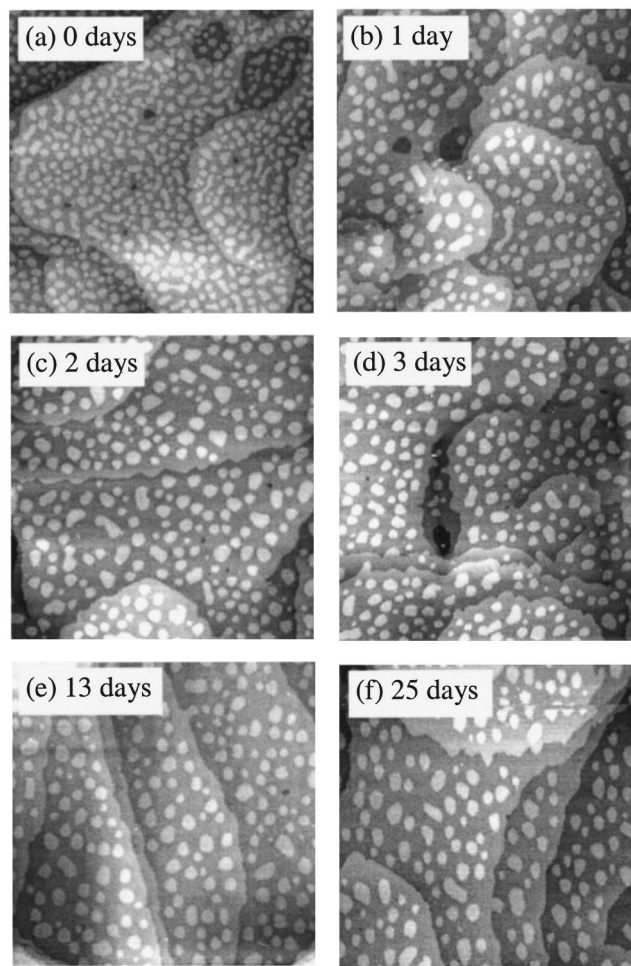


FIG. 6. Typical images of clusters on C_7 at different times after deposition. The areas of all the images are 300×300 nm². The images were taken at -1.0 V/1 nA.

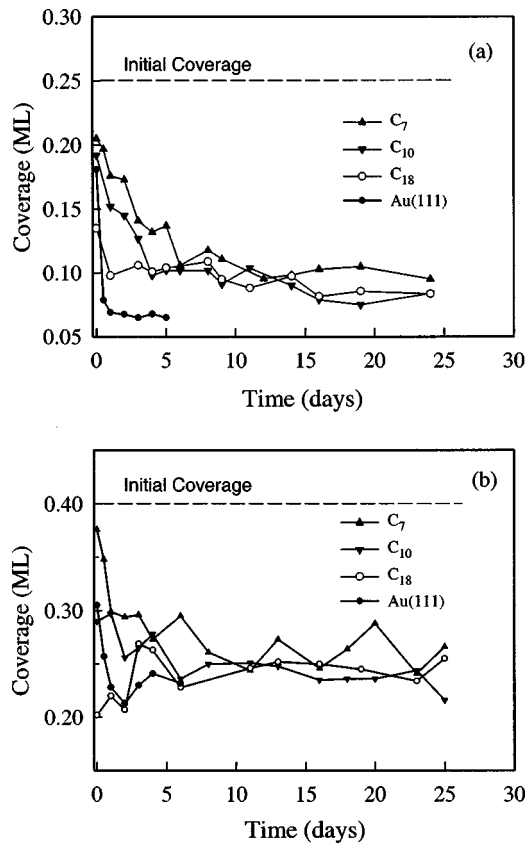


FIG. 7. Au coverage of clusters as a function of time on different SAMs at, (a) initial coverage $\theta=0.25$ ML, (b) initial coverage $\theta=0.4$ ML. The dashed lines give the initial coverage values.

SAM at 78 K in the OMICRON UHV STM system. Within 2 min, the sample was transferred to the low temperature STM (precooled down to 78 K) sample holder without breaking the vacuum. The coverage, which is plotted in Fig. 5 as a function of time, stays constant for 48 h by maintaining the temperature at 78 K. This is consistent with Tarlov's result that Ag films are stable and reside on methyl end group when deposited at 90 K.¹² Moreover, when we measured the I - V spectra on these Au clusters, a much higher percentage ($\sim 30\%$) of the clusters shows the Coulomb blockade and Coulomb staircases. This is because the low temperature significantly reduces the penetration rate of Au atoms and thus a larger fraction of Au clusters nucleate on top of the SAMs. When the temperature is raised to room temperature (in vacuum), the Au cluster coverage is observed to decrease quickly in the first several hours as shown in Fig. 5. The decrease of Au coverage results from Au penetration to the SAM/Au(111) interface, followed by incorporation to the step edges of Au(111) via diffusion. The penetration of the Au clusters can happen via two potential channels: either the clusters diffuse through the SAMs as a whole, or the clusters dissociate first and then diffuse through the SAMs. It is likely that the former works for small clusters and the latter works for large ones. Nevertheless, a smaller fraction of the Au clusters is still found resid-

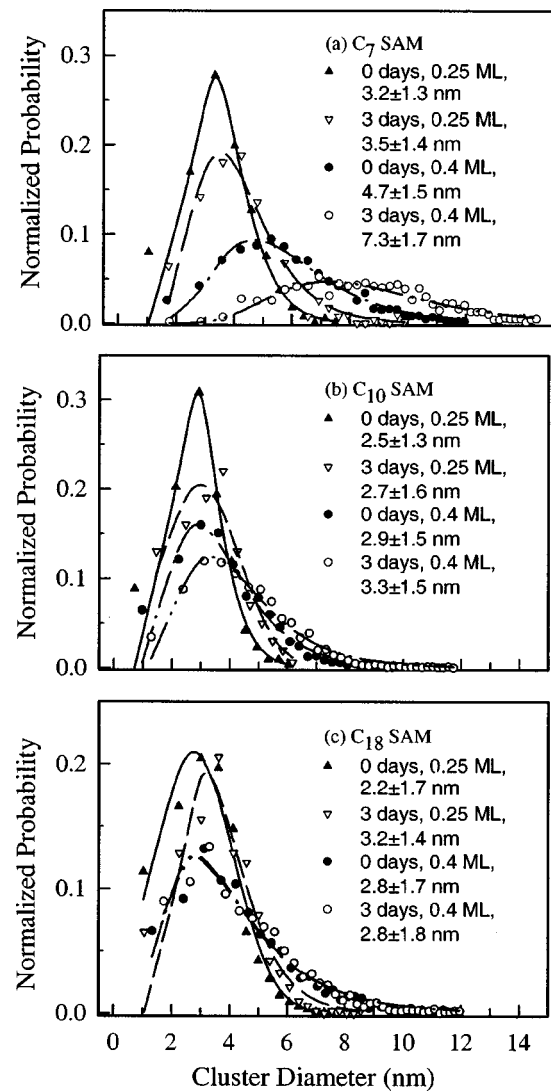


FIG. 8. Cluster size distribution with the statistical probability vs cluster diameter on C₇, C₁₀, and C₁₈ SAMs after 0 or 3 days after deposition and at initial coverages of 0.25 and 0.4 ML. The curves are fitted by $f(x) = 1/[(2\pi)^{1/2} \ln \sigma] \exp[-(\ln x - \ln \bar{x})^2 / (2 \ln^2 \sigma)]$, with x , \bar{x} , and σ as the diameter, the mean and the standard deviation of the clusters. The fitting parameters are included in the legends correspondingly.

ing on top of the methyl end group of the SAMs after warming the sample to room temperature.

B. On the stability of the Au clusters

At room temperature, while the Au clusters on the Au(111) surface disappear quickly by diffusion to the step edges, the Au clusters at the SAM/Au(111) interface are stabilized. Here, we present our results on the evolution of these clusters at room temperature in air. We have imaged the clusters at different times and then analyzed them using the Q600 (Leica) software.

The coverage of the Au clusters depends on time and decreases in the first few days after deposition. In Fig. 6, we show a series of images taken for Au clusters on C₇ as a function of time. The loss of Au in the clusters is clearly seen. It appears to the naked eye that the loss of coverage

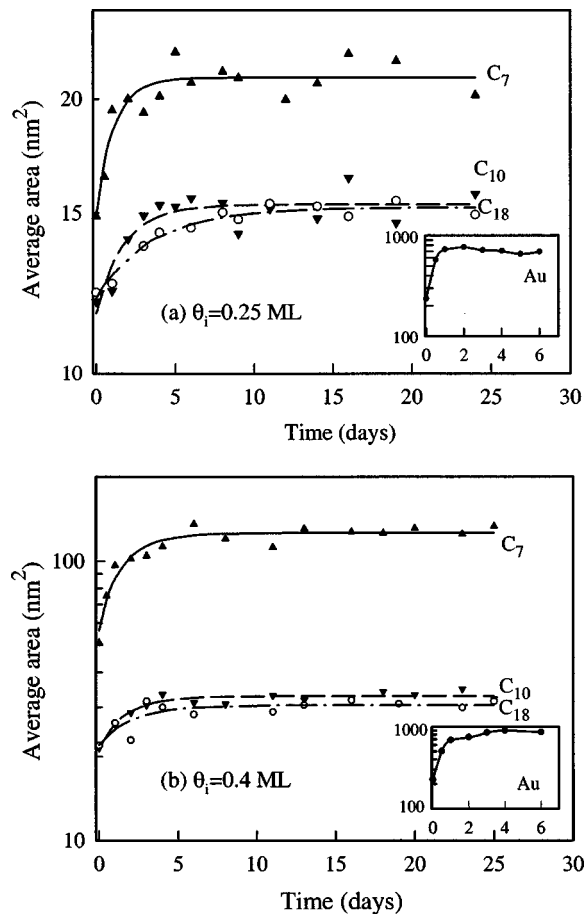


FIG. 9. Average size (area) of clusters measured as a function of time on C_7 , C_{10} , and C_{18} SAMs at initial coverages θ_i of 0.25 or 0.40 ML. The fitting curves by Eq. (1) are also plotted for C_7 (solid line), for C_{10} (dashed line), and for C_{18} (dash-dotted line), respectively. The error for each data point is about $\pm 2 \text{ nm}^2$. The insets in (a) and (b) are measured for clusters on Au(111), where the solid lines are only a guide for the eye.

only one day after deposition is already significant. The Au coverage in the clusters is plotted in Fig. 7 as a function of time. In all cases, the measured Au coverage of clusters is smaller than the expected value (dashed lines in Fig. 7), even immediately after Au deposition. This is in contrast to the low temperature deposition case for which no decrease of coverage was observed at 78 K. The decrease of coverage terminates after the first 3–5 days (Fig. 7).

We can understand the loss of Au coverage as follows. During deposition and sample transfer (~ 30 min) at room temperature, the Au atoms can penetrate to the SAM/Au(111) interface. Some of them diffuse to the Au(111) step edges to incorporate with the Au(111) substrate and get excluded from the coverage. Thus, they are “lost” from the measured Au coverage of the clusters. This accounts for the apparent coverage loss even for the $t=0$ day images. Because the small clusters are not as stable as large clusters, they diffuse and coalesce with other clusters. Part of the coalescence occurs with the step edges, which accounts for the further coverage “loss” for Au clusters on C_7 and C_{10} in the following days. Because the step densities of the Au(111) samples used are similar, the probability of meeting a step in

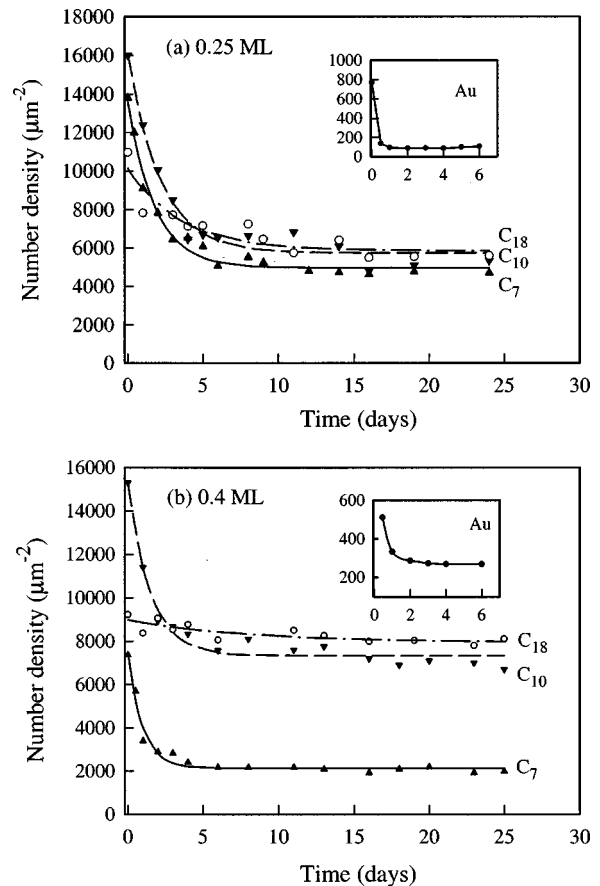


FIG. 10. Au cluster number density measured as a function of time on C_7 , C_{10} , and C_{18} SAMs at initial coverages θ_i of 0.25 or 0.40 ML. The curves fitted by Eq. (2) are also plotted for C_7 (solid line), for C_{10} (dashed line), and for C_{18} (dash-dotted line), respectively. The measurement error for each data point is about $\pm 500 \mu\text{m}^{-2}$. The insets in (a) and (b) are measured for clusters on Au(111), where the solid lines are only a guide for the eye.

all the cases is more or less the same. Thus, the final coverages are similar on different SAM substrates at a given initial coverage, i.e., $\theta_f \sim 0.1$ ML for initial coverage of 0.25 ML and $\theta_f \sim 0.25$ ML for initial coverage of 0.4 ML. On the other hand, one would expect that the loss of Au coverage depends on the diffusivity and the stable size of clusters and thus on the chain length of the SAMs. This appears to be the case, as seen in the time evolution of the coverages. For Au clusters on C_7 and C_{10} , the diffusion is sufficiently fast so that initially ($t=0$ day) all the Au atoms are either in clusters or incorporated at the steps. The subsequent decrease of coverage results from further incorporation of small clusters with the steps. For Au clusters on C_{18} , the diffusion of Au atoms or clusters at the interface of C_{18} /Au(111) is slow, due to the heavy mass of C_{18} carried by the diffusion atoms. Thus, only those Au atoms arriving near the steps during evaporation can join with the step edges immediately and appear as the coverage loss at $t=0$ day. Unlike Au clusters on C_7 and C_{10} , there could be a significant number of clusters on C_{18} consisting of only one or a few Au atoms that are too small to be recognized in the large area images. These invisible small clusters also contribute to the initial coverage loss. At a later

TABLE I. Initial $[(1-a)S_0]$ and saturation average cluster size (S_0) as well as the time constant τ_1 fitted by Eq. (1) for Au clusters on SAM/Au(111) interfaces with different chain lengths. Two initial Au coverages were included.

	0.25 ML			0.4 ML		
	S_0 (nm ²)	a	τ_1 (days)	S_0 (nm ²)	a	τ_1 (days)
C ₇ SAM	21.1±0.3	0.29±0.04	1.2±0.4	126.1±2.6	0.55±0.05	1.8±0.4
C ₁₀ SAM	15.3±0.3	0.24±0.04	1.9±0.7	32.9±0.3	0.35±0.04	1.8±0.3
C ₁₈ SAM	15.2±0.1	0.21±0.01	3.8±0.7	30.5±0.8	0.28±0.06	2.3±1.1

time, they can coalesce to form large clusters, and thus reappear in the Au coverage. This in effect compensates for the loss at the step edges and makes the time evolution of coverage for Au on C₁₈ weaker. In fact, an increase, instead of a decrease, of Au cluster coverage is observed for the case of 0.4 ML.

To further understand how the clusters evolve, we show in Fig. 8 the distributions of cluster size for the two initial Au coverages at $t=0$ day and $t=3$ days. A number of conclusions can be drawn from these statistics: (i) The clusters have a wider distribution with a larger average size on C₇ than on C₁₀ and C₁₈. (ii) The evolution of the clusters is quite different for clusters on SAMs with different chain lengths. The distribution peaks, for both initial coverages, shift relatively strongly to large sizes on short chain C₇ SAMs as compared to those on medium chain C₁₀ and long chain C₁₈ SAMs. (iii) Saturation of the cluster evolution is reached in about 3 days. The peak positions change only a little after that, although the width of the distribution continues to increase to some degree (not shown).

The time variation of size distribution results from the diffusion of Au atoms or Au clusters at the SAM/Au(111) interface. This diffusion is dependent on the chain length of the SAMs. The average cluster size and the cluster number density are plotted as a function of time in Figs. 9 and 10, respectively. Because of the irregular cluster shape, we use area rather than a characteristic length to characterize the cluster size. From both figures, it is clear that large changes in the average sizes and cluster density occur mainly in the first few days (3–5 days) after Au deposition. After that, both the size and density of the Au clusters stabilize.

The data in Fig. 9 are well described by the formula

$$S = S_0[1 - a \exp(-t/\tau_1)], \quad (1)$$

where S_0 is the average saturation size, $(1-a)S_0$ is the initial cluster size, and the characteristic time τ_1 is related to the diffusion rate. The fitted parameters are given in Table I. It is obvious that, for both coverages, the value of S_0 on short chain C₇ is significantly larger than that on C₁₀ and C₁₈. While the values of S_0 on C₁₀ and C₁₈ are similar and increase only by a factor of 2 when the initial Au coverage is increased from 0.25 to 0.4 ML, the S_0 value on C₇ increases by about sixfold. Furthermore, the time constant τ_1 is observed to increase as the chain length of the SAMs increases. The results are consistent with the following physical picture of Au cluster formation at the SAM/Au(111) interface. When the cluster size is below the stable size, which is larger on C₇ than on C₁₀ and C₁₈, dissociation as well as cluster diffusion can occur. The diffusion of the dissociated Au atoms or small clusters enables the coalescence into larger clusters. The diffusing unit is probably a single Au atom, rather than the thiolated Au because breaking a bond with the alkanethiol molecule and diffusing on the Au(111) substrate should be easier than pushing its way through a densely packed SAM layer with an alkanethiol molecule on top. By comparing the rate of diffusion of Au atoms and clusters on Au(111) without the SAMs, it is clear that the alkanethiol molecule not only slows down the diffusion significantly, but also stabilizes the Au clusters. For short chain molecules, the effect is weaker and that means faster diffusion and a larger S_0 . For long chain molecules, the effect of the alkanethiol molecule is stronger, which translates into slower diffusion and smaller values of S_0 .

Both processes of coalescence of small clusters into larger ones and the incorporation to the step edges reduce the number density of clusters. The data in Fig. 10 can be fitted with an equation similar to Eq. (1):

TABLE II. Initial $[(1+b)\rho_0]$ and saturation number densities (ρ_0) as well as the time constant τ_2 fitted by Eq. (2) for Au clusters on SAM/Au(111) interfaces with different chain lengths. Two initial Au coverages were included.

	0.25 ML			0.4 ML		
	ρ_0 ($\times 10^3 \mu\text{m}^{-2}$)	b	τ_2 (days)	ρ_0 ($\times 10^3 \mu\text{m}^{-2}$)	b	τ_2 (days)
C ₇ SAM	4.9±0.2	1.7±0.1	1.8±0.2	2.2±0.1	2.5±0.2	1.0±0.1
C ₁₀ SAM	5.7±0.3	1.8±0.1	2.2±0.3	7.3±0.2	1.1±0.1	1.5±0.2
C ₁₈ SAM	5.8±0.4	0.72±0.2	3.6±1.2	7.9±0.3	1.0±0.3	7.9±6.7

$$\rho = \rho_0 [1 + b \exp(-t/\tau_2)], \quad (2)$$

where ρ_0 is the saturation cluster density, $(1+b)\rho_0$ is the initial cluster density, and τ_2 is a time scale again related to the diffusion rate of the Au atoms or clusters. The fitting parameters are summarized in Table II. To compensate for the larger saturation cluster size on C_7 , a lower saturation cluster density is observed correspondingly. This is particularly true for the case of 0.4 ML initial Au coverage on C_7 . As with the time constant τ_1 , the time constant τ_2 is a measure of the mobility of Au atoms or Au clusters at the SAM/Au(111) interface. In most cases, the two values of τ_1 and τ_2 on a given SAM are practically identical because they originate from the same diffusion mechanism. For Au clusters on C_{18} with an initial coverage of 0.4 ML, there is a large difference between τ_1 and τ_2 . In that case, it is a result of the initial undercounting of the number density because of the invisible Au atoms (or smaller clusters) in large area images as discussed before. Thus, the time constant τ_1 should be a better measure of the diffusion at the C_{18} /Au(111) interface.

IV. SUMMARY

We have performed STM measurements on Au clusters on Au (111) and SAMs with different chain lengths (C_7 , C_{10} , and C_{18}). Although most of the clusters penetrate to the SAM/Au(111) interface, a small fraction of Au clusters reside on top of the methyl end group. The observed Coulomb blockade and Coulomb staircases lend strong support to the existence of 2D isolated Au clusters. In the future, these may provide a good template for studying the SET phenomenon of nearly isolated 2D metal clusters on insulating films with low dielectric constant even though the SAMs cannot be regarded as a good insulation layer for most of the clusters. For the Au clusters formed at the SAM/Au(111) interface, our evidence shows that they are stabilized by the attached SAMs. By characterizing the time evolution of these clusters through coverage, size, and the number density, it is shown that gold atoms and gold clusters diffuse faster with short chain SAMs than with long chain SAMs. It follows that larger Au clusters can be formed at the short chain C_7 SAM/Au(111) interface than that at longer chain C_{10} and C_{18} SAM/Au(111) interfaces.

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