n*-Alkane Monolayer on a Au(111) Template for Metal GrowthOsamu Endo[†] and Hiroyuki Ozaki*Department of Organic and Polymer Materials Chemistry, Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

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The growth of gold on top of a *n*-alkane monolayer, which consists of lamellar assemblies with close-packed flat-lying chains, is observed by using scanning tunneling microscopy. The *n*-alkane monolayer sustains gold atoms, and penetration of the atoms into the monolayer is inhibited. The molecular conformation is unaffected and the arrangement is only slightly changed upon deposition of the gold atoms. Two-dimensional clusters are grown and a smooth monolayer is finally obtained. [DOI: 10.1380/ejssnt.2015.209]

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I. INTRODUCTION

A self-assembled monolayer (SAM) of organic molecules on a solid surface is an intriguing system for studying molecular properties and metal-organic contact, which is essential for molecule-based nano-devices. Metal atoms deposited on top of SAMs, which are electronically isolated from the substrate, exhibit a peculiar low dimensional electronic behavior, including Coulomb blockade [1] and a reduced density of states at the Fermi level [2–4]. Upon metal deposition, molecules comprising a SAM are sandwiched with the substrate and deposited metal atoms and confined within a nano-space. Although the molecular arrangement and electronic properties in such an environment may differ from those in an exposed monolayer, thus far they have been examined in only a few studies. In this aspect, metal-molecule-metal systems are important, and constructing atomically well-defined structures as a model system is required.

Normal alkane (*n*-alkane) molecules physisorbed on a Au(111) surface form close-packed lamellar structures: extended chains with an all-trans conformation are flat-lying and assembled by the van der Waals interactions, as shown in Fig. 1(a) [5–9]. Flat-lying alkyl chains are in contact with the substrate with the entire molecule. Moreover, molecular movement is restricted within close-packed lamellae. Therefore, a monolayer of flat-lying *n*-alkane molecules is considered relatively rigid and capable of sustaining deposited metal atoms, in spite of the flexibility of the alkyl chain. The interaction between metal atoms and *n*-alkane molecules is considered weak, which may lead to three-dimensional (3D) island formation [10]. In fact, gold atoms deposited on an alkanethiol SAM formed on a Au(111) surface, in which the molecules stand upright, and on a SAM of alkyl diacetylene, which is flat-

FIG. 1. (a) Schematic drawing of the lamellar structure of *n*-alkane molecules. (b) Schematic drawings of layer-by-layer growth of metal and *n*-alkane molecules.

lying on a MoS₂(0001) surface, form 3D clusters [1, 11]. The top surface of these SAMs is, however, not necessarily smooth on the atomic scale, because of terminal methyl groups and the diacetylene moiety. In contrast, a *n*-alkane, which has no functional group and is flat-lying on a Au(111) surface, provides a smooth wide area for metal deposition, and therefore, 2D metal growth is expected. An atomically smooth metal layer constructed on a monolayer of chain molecules provides a “second floor” for SAM formation, as shown in Fig. 1(b) left. A periodic organic-metal layered material is obtained by repeating these deposition cycles (Fig. 1(b) right).

In this study, the growth of gold on a Au(111) surface covered with a *n*-alkane monolayer is observed by using scanning tunneling microscopy (STM). 2D clusters are grown isotropically on top of the *n*-alkane monolayer, without the molecular arrangement being penetrated or destroyed.

II. EXPERIMENTAL METHOD

A single crystal of Au(111) (MaTecK, Inc., Germany) was cleaned by flame annealing and cooled for several minutes in an inert atmosphere (Ar or N₂) and for sev-

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eral seconds in *n*-hexane (96%, Kokusan Chemical Co. Ltd., Japan). A *n*-alkane monolayer was obtained by dipping the cleaned Au(111) surface into *n*-C₃₆H₇₄ (98%, Wako Pure Chemical Industries, Ltd., Japan) or *n*-C₄₄H₉₀ (>97%, Tokyo Chemical Industry Co., Ltd., Japan) *n*-hexane solution, and rinsed with pure *n*-hexane to eliminate multilayers. The Au(111) covered with the *n*-alkane monolayer was transferred to a vacuum chamber for STM measurements. Gold was deposited on the sample surface at room temperature through resistive heating of a tungsten wire wrapped with a gold wire. The deposition amount was controlled via the heating time of the tungsten wire; the deposition rate was typically set at 0.025 monolayer (ML) per minute. STM measurements were performed at room temperature in ultrahigh vacuum (ca. 1×10^{-8} Pa). The coverage was estimated by measuring the cluster area obtained for each STM image.

III. RESULTS AND DISCUSSION

Figure 2 shows STM images of the growth of gold on the Au(111) surface covered with the *n*-C₃₆H₇₄ monolayer for coverages: (a) and (b), 0.04 ML; (c) and (d), 0.14 ML; (e) and (f), 0.3 ML; (g) and (h), 0.55 ML; and (i) and (j), 1 ML. The left images (a,c,e,g,i) and the right images (b,d,f,h,j) show the growth of gold in a large scale and in a small scale, respectively. The lamellar structure, having a width of ca. 5 nm, which corresponds to the chain length of *n*-C₃₆H₇₄ molecules, is formed as indicated by the black arrows in Fig. 2(b). A schematic model is shown in the form of a white molecular drawing on Fig. 2(b), which shows that the lamellar axis is directed perpendicularly to the chain axis. Randomly dispersed small clusters with an average diameter of approximately 5 nm are observed at the initial stage of the growth, as shown in Fig. 2(a). The close-up image of one of the clusters in Fig. 2(b) shows an isotropic shape centered at the lamellar boundary of the *n*-C₃₆H₇₄ molecules. The height of the cluster, approximately 0.3 nm, is comparable to twice the atomic radius (0.14 nm) and corresponds to the monoatomic thickness. The isotropic cluster shape makes a striking contrast with the growth of palladium on the Au(111) surface covered with the *n*-alkane monolayer, which shows a nano-rod aligned along the alkyl chain with its length regulated by the lamellar boundaries [12]. The lamellar structure is continuous even for the two lamellae located at the center of the image with the gold cluster. Because an edge of the cluster, as indicated by the white arrow, does not reach the end of the molecule, parts of the molecules would be floating if gold atoms and *n*-alkane molecules exchanged places. This possibility is inconsistent with our observation, in which the lamellar boundary is the same with or without the gold cluster. Therefore, the gold cluster is considered formed on top of the *n*-alkene monolayer. As the coverage increases, the size of the gold clusters increases monotonically. The lamellar structure is seen after the coverage increases to at least 0.55 ML (Fig. 2(h)). A similar growth was observed on the Au(111) surface covered with the *n*-C₄₄H₉₀ monolayer.

Figure 3(a) shows the cross section of the gold clusters along the black line indicated in Fig. 2(j). The apparent height differences of 0.3 nm correspond to the monoatomic

FIG. 2. STM images for gold cluster growth on the Au(111) surface covered with the *n*-C₃₆H₇₄ monolayer. (a) and (b) 0.04 monolayer (ML), (c) and (d) 0.14 ML, (e) and (f) 0.3 ML, (g) and (h) 0.55 ML, and (i) and (j) 1 ML. Sample bias voltage *V*, tunneling current *I*, and image size are: (a) -1.5 V, 30 pA, and $110 \text{ nm} \times 110 \text{ nm}$; (b) -1.5 V, 30 pA, and $27.5 \text{ nm} \times 27.5 \text{ nm}$; (c) -1.5 V, 30 pA, and $138 \text{ nm} \times 138 \text{ nm}$; (d) -1.5 V, 30 pA, and $55 \text{ nm} \times 55 \text{ nm}$; (e) -1.5 V, 30 pA, and $138 \text{ nm} \times 138 \text{ nm}$; (f) -1.5 V, 30 pA, and $55 \text{ nm} \times 55 \text{ nm}$; (g) -1.5 V, 30 pA, and $138 \text{ nm} \times 138 \text{ nm}$; (h) -1.0 V, 1 nA, and $55 \text{ nm} \times 55 \text{ nm}$; (i) -1.5 V, 30 pA, and $138 \text{ nm} \times 138 \text{ nm}$; (j) -1.5 V, 30 pA, and $55 \text{ nm} \times 55 \text{ nm}$.

thickness. Therefore, the clusters with a bright contrast in Figs. 2(i) and 2(j) are attributed to the second layer of the deposited gold. Upon heating at 400 K, the clusters at the second layer disappear and a smooth monolayer is obtained. Figure 3(b) shows the size distribution of the gold clusters at the initial stage of the growth at the coverage of 0.04 ML. The average cluster size S/nm^2 estimated from the distribution in the STM images of each coverage of gold on the Au(111) surface covered with either *n*-C₃₆H₇₄ (red dots) or *n*-C₄₄H₉₀ (black dots) monolayer is plotted as a function of the coverage θ in a double loga-

FIG. 3. (a) Cross-section of gold clusters along the black line indicated in Fig. 2(j). (b) Size distribution of gold clusters at the initial stage of the growth at 0.04 ML. (c) Average cluster size S/nm^2 as a function of the coverage θ . (d) Cluster numbers per $100 \times 100 \text{ nm}^2$ N as a function of the coverage θ . Black and red dots represent the results for the $n\text{-C}_{44}\text{H}_{90}$ and $n\text{-C}_{36}\text{H}_{74}$ monolayer, respectively.

arithmic scale, as shown in Fig. 3(c). The cluster numbers per $100 \times 100 \text{ nm}^2$ N are plotted in Fig. 3(d) in the same manner. It should be noted that the coverage θ corresponds to the product $N \cdot S$. Both N and S are fitted with lines, with an abrupt change in the slope at the coverage of 0.45 ML. Before this coverage, S increases in proportion to the coverage θ , and N is almost constant. This means that the gold atoms are aggregated into the nuclei formed at the initial stage as a result of rapid diffusion. As the coverage exceeds 0.45 ML, the clusters begin to coalesce; S increases more rapidly in the form of $\sim \theta^5$ and N decreases with $\sim \theta^{-4}$. Because the average cluster number is ca. 30 per $100 \times 100 \text{ nm}^2$ at 0.45 ML, at which the coalescence begins, the average distance between the clusters is $\sim \sqrt{(100 \times 100)/30} \text{ nm} = 18 \text{ nm}$. This value is slightly larger than the average cluster size at the same coverage (ca. $12.5 \times 12.5 \text{ nm}^2$), and hence, a considerable number of clusters are separated by a smaller distance than the average value and preferentially connected.

Figure 4(a) shows the STM image of a gold cluster formed on the Au(111) surface covered with the $n\text{-C}_{36}\text{H}_{74}$ monolayer at a coverage of 0.55 ML. This image shows both the cluster and the underlying $n\text{-C}_{36}\text{H}_{74}$ molecules. All the alkyl chains indicated by the black lines on the right side of the image appear straight and intact. Even the molecular chains crossing a cluster edge are observed to be straight, as indicated by the black arrow. Moreover, the molecules are aligned parallel on both sides of a cluster edge, as indicated by the white arrow. This image suggests that the parts of the molecules observed with the gold cluster exist at the same height as other parts (or molecules) and stabilized by the neighboring molecules. Therefore, the gold atoms are believed to be adsorbed on top of the $n\text{-C}_{36}\text{H}_{74}$ molecules without penetrating the

FIG. 4. (a) STM image of a gold cluster formed on the Au(111) surface covered with the $n\text{-C}_{36}\text{H}_{74}$ monolayer at the coverage of 0.55 ML. $V = -1.0 \text{ V}$, $I = 30 \text{ pA}$, $27.5 \text{ nm} \times 27.5 \text{ nm}$. (b) Schematic drawing of the structure of the gold cluster and the underlying $n\text{-C}_{36}\text{H}_{74}$ monolayer.

FIG. 5. (a) STM image of gold clusters formed on the Au(111) surface covered with the $n\text{-C}_{36}\text{H}_{74}$ monolayer at the coverage of 0.2 ML. $V = -1.5 \text{ V}$, $I = 30 \text{ pA}$, $55 \text{ nm} \times 55 \text{ nm}$. (b) STM image of gold clusters formed on the Au(111) surface covered with the $n\text{-C}_{36}\text{H}_{74}$ monolayer at the coverage of 0.2 ML. $V = 0.1 \text{ V}$, $I = 1 \text{ nA}$, $55 \text{ nm} \times 55 \text{ nm}$.

monolayer. The lamellar assembly is, however, slightly altered as a result of the deposition of the gold atoms. A schematic drawing of the cluster and the lamellae of the $n\text{-C}_{36}\text{H}_{74}$ molecules is shown in Fig. 4(b). The direction of the lamellar axis is slightly changed from that observed before the gold deposition (Fig. 2(b)) and makes an angle of 60° to the alkyl chains. This arrangement is observed for several n -alkane molecules on the Au(111) surface, in particular, for a shorter molecule (carbon number 22–36) [9]. The interaction between molecules that dominates the interaction between the molecule and substrate is considered the cause of the tilted arrangement [9]. The interaction between gold and n -alkane molecules will be discussed in the near future according to the results of X-ray absorption fine structure spectroscopy at the near carbon K-edge.

Figure 5(a) shows the STM image of gold clusters formed on the Au(111) surface covered with the $n\text{-C}_{36}\text{H}_{74}$ monolayer at a coverage of 0.2 ML. The sample bias voltage and tunneling current are $V = -1.5 \text{ V}$ and $I = 30 \text{ pA}$, respectively. Figure 5(b) shows almost the same area observed in Fig. 5(a) but with $V = 0.1 \text{ V}$ and $I = 1 \text{ nA}$. The clusters observed with a near-zero bias voltage, as shown in Fig. 5(b), exhibit a different contrast compared

with those observed with an ordinary bias voltage, as shown in Fig. 5(a). The inner area of each cluster appears darker than the surrounding area, which indicates that the tunneling current hardly flows through the cluster. This phenomenon is characteristic of clusters electronically isolated from a metal substrate. Because of the low dimensionality of a cluster, electrons are localized within the cluster. Hence, the electrostatic energy of a cluster changes dramatically upon the charge transfer. Without the application of a sufficient bias voltage, electron transfer is suppressed (Coulomb blockade) [13]. This effect is predominantly observed with a near-zero bias voltage.

These STM images strongly suggest that the clusters are grown on top of the *n*-alkane monolayer and electronically isolated from the Au(111) substrate.

IV. CONCLUSION

Gold atoms deposited on a Au(111) surface covered with a *n*-alkane monolayer with lamellar structures exhibit 2D cluster growth. A slight change in the lamellar direction is observed, although the arrangement of the underlying *n*-alkane molecules is not destroyed upon the deposition.

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