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Influence of reconstruction on the structure of self-assembled normal-alkane monolayers on Au(111) surfaces

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Ordered normal-alkane monolayers of lamellar structures are found to form in the interface between alkane solutions and the reconstructed Au (111) surfaces. The boundaries of the lamellae may exhibit a zigzag shape. In the alkane monolayers, two kinds of packing of the alkane molecules are observed. The packing patterns are correlated to the structure of the gold surface and the molecular lengths of the alkanes. The orientation of alkane molecules is gently disturbed by the reconstructed gold ridges. Furthermore, the lamellar boundaries are located on the elbow positions of the reconstructed gold surfaces for long-chain alkanes. These results demonstrate that the structures of self-assembled monolayers of normal alkanes are sensitive to the structures of the Au (111) surfaces.

Introduction

Interfaces between a metal and an organic solution have been intensively investigated during the last decades because they play an important role in many technologically important fields, such as lubrication, adhesion, biocompatibility and chemical reactions. Models of these interfaces are provided by monolayers on a well-characterized surface.[1] Among these models, normal-alkane molecules in contact with the graphite surfaces have been studied in great detail.[2–7] At room temperature, n-alkanes with more than 17 carbon atoms form monolayers that consist of parallel lamellae separated by narrow troughs on the graphite basal plane. Each lamella which results from a close-packed arrangement of alkane molecules lying flat on the surface shows a width equal to the molecular length. Although there are a number of results on monolayers of organic molecules physisorbed on the solid surfaces being reported, the role of the substrate lattice parameters, the substrate structures, and defects in the formation of the highly ordered monolayers have not previously been well studied. Furthermore, for solids other than highly oriented pyrolytic graphite (HOPG), studies of the interfaces between an alkane solution and a surface remain scarce. On the $MoSe_2$ and MoS_2[8,9] surfaces, incommensurate ordered monolayers were found to form on the atomic flat terraces. Energy minimizations using a molecular mechanics approach were employed to explain the observed structure of the alkane monolayers on the MoS_2 surfaces.[10] On the metal surfaces, short-chain alkanes deposited on Pt (111) and Ag(111) surfaces in UHV were studied by low energy electron diffraction (LEED).[11,12] The interface between $C_{16}H_{34}$ and gold was studied by molecular dynamic simulation.[13,14] Recently, self-assemblies of n-alkanes on Au(111) surfaces have been studied by using scanning tunneling microscopy (STM).[15–19] Commensurate monolayers were found to form.[19] An odd–even effect on the molecular packing was observed for alkanes with short-chains.[15,16] Furthermore, it was found that a re-entrant self-organization of alkanes on Au(111) surfaces could be induced by the molecular length of the alkanes, showing that the structure of the gold surface strongly influences the formation of the alkane monolayers. However, the effect of the gold reconstruction was somewhat less considered. In this paper, we present an STM study of the effects of the gold reconstruction on the structures of the alkane monolayers. The roles of the surface geometry and defects in the formation of the alkane monolayers are discussed.

Experimental

Reconstructed Au (111) surfaces were prepared from gold films on mica surfaces or a massive gold single crystal, followed by careful annealing in a hydrogen flame. A saturated solution of hexatriacontane molecules (n-$C_{36}H_{74}$) in dodecane (n-$C_{12}H_{26}$) was prepared at room temperature from solid n-$C_{36}H_{74}$ and pure n-$C_{12}H_{26}$. Neat liquid hexadecane (n-$C_{16}H_{34}$) and tetradecane (n-$C_{14}H_{30}$) were used. Samples for STM observations (Nanoscope IIIa, Digital Instrument) were prepared by putting one droplet of the solution or liquid on the freshly annealed Au (111) surfaces. Pt/Ir tips were mechanically cut and immersed into the liquid solution to probe the interfacial structure.

Results and discussion

A reconstructed Au(111) surface may exhibit straight and parallel ridges or a herringbone arrangement of ridges.[20–22] The different arrangement of the reconstructed ridges is due to the slightly different annealing conditions. In air, the reconstruction of gold is found to lift quickly during the STM tip scanning. However, when a droplet of n-alkane solution (*e.g.* n-$C_{36}H_{74}$) is put on such a reconstructed surface, the reconstructed structures of gold become very stable. Furthermore, a superimposed structure of zigzag rows with dark troughs is found on the typical reconstruction ridges of Au(111).The reconstruction ridges are marked by arrows or white lines on the images, and the zigzag rows are marked by dark lines, as shown in Fig. 1(a) and (b). The zigzag rows are identified as alkane monolayers, which are different from the straight lamellae observed for long-chain alkanes physisorbed on the graphite surfaces.[4–6] On the surfaces with straight reconstructed
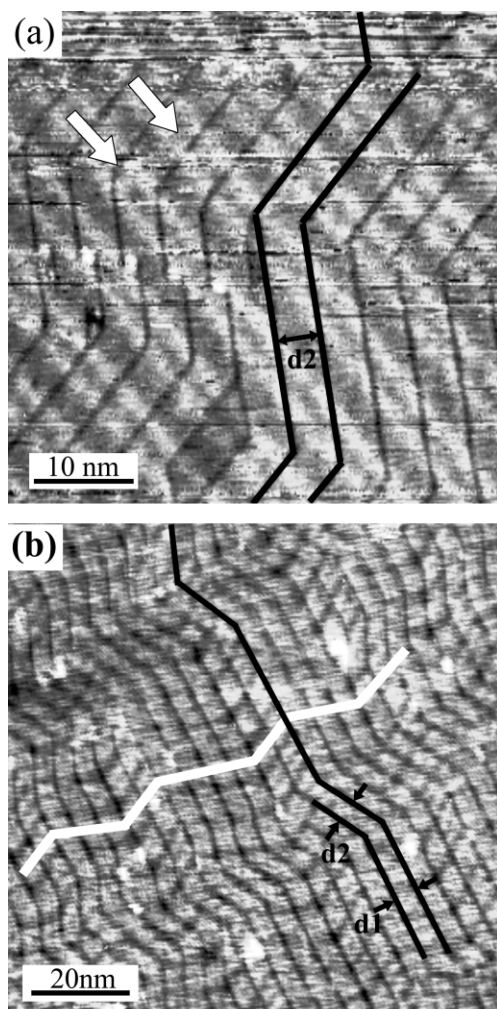
Fig. 1 Large-scale STM images of the n-$C_{36}H_{74}$ monolayers on the typically reconstructed Au(111) surfaces with (a) uni-axial reconstructed ridges (50 nm × 50 nm), (b) herringbone ridges (100 nm × 100 nm). Zigzag rows in the alkane monolayers are marked by dark lines. The two different widths of the rows are indicated by d1 and d2. The main directions of the reconstructed ridges are labelled by arrows or white lines. Tunneling condition: $V_b = -400$ mV, $I_t = 1.2$ nA.

Fig. 2 High-resolution STM images of n-$C_{36}H_{74}$ monolayers on the typically reconstructed gold surfaces with (a) straight and parallel ridges and (b) a herringbone arrangement of ridges. The long axes of the alkane molecules are tilted to the lamellar boundary at the narrow rows (4.3 ± 0.1 nm) and are perpendicular to the lamellar boundary at the wide rows (4.8 ± 0.1 nm). Arrows show the direction of the gold reconstructed ridges. Tunneling condition: $V_b = -400$ mV, $I_t = 1.2$ nA. Scanning area: 25 nm × 25 nm.

ridges shown in Fig. 1(a), the width of the rows is 4.3 ± 0.1 nm (marked as d2 on the image). However, on the surfaces with herringbone-like ridges, there are two kinds of rows observed, whose widths are 4.8 ± 0.1 nm and 4.3 ± 0.1 nm (marked by d1 and d2 in Fig. 1(b)), respectively. At a molecular resolution, as shown in Fig. 2(a) and (b), a lamellar structure is observed in the zigzag rows, where the lamellae are separated by dark troughs. Within a lamella, thin stripes form a close-packed arrangement, where each stripe is identified as an alkane molecule. Fig. 2(a) and (b) show the lamellar structures on the surfaces with straight reconstructed ridges and herringbone ridges, respectively. Remarkably, in the narrow rows (4.3 nm in width), the alkane molecules are tilted to the lamellar boundary, while the alkane molecules are perpendicular to the lamellar boundary in the wide rows (4.8 nm in width). Regardless of the orientation of the lamellar boundary, every strip is parallel and possesses the same length of 4.8 nm, which corresponds well to the length of the n-$C_{36}H_{74}$ molecule. In the tilted lamella, the alkane molecules are at an angle of about 62° with respect to the lamellar boundary, due to the fact that every neighbouring alkane molecule is shifted by one repeat unit of methylene groups ($-CH_2CH_2-$). The separations between the alkane molecules within a lamella are the same: 0.48 ± 0.02 nm. Furthermore, an angle of 30° is measured

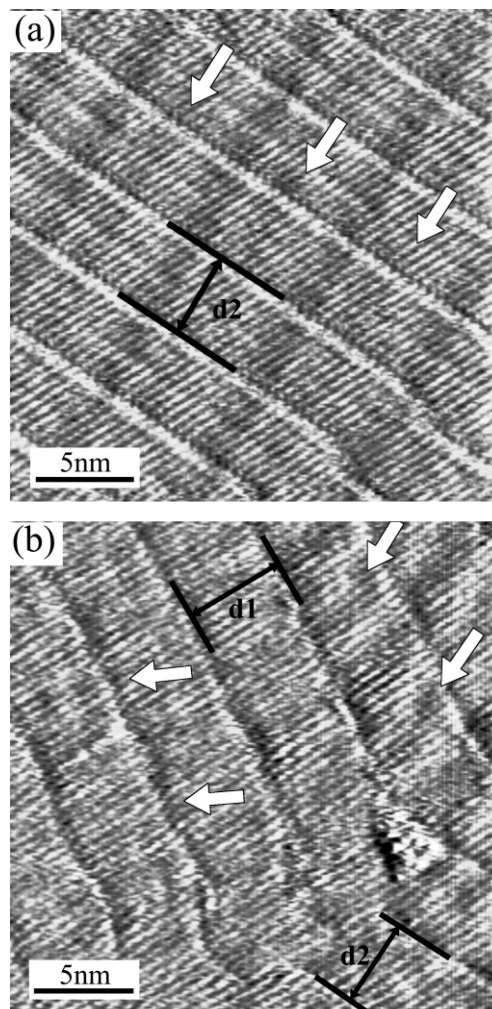between the molecular long axes of the alkanes and the Au (111) reconstructed ridges, such that the alkane molecules are found to locate along the approximate $[01\bar{1}]$ azimuth. In contrast to the monolayers of the long-chain alkanes, only lamellae with alkane molecules tilted to the lamellar boundary are found in alkane monolayers with even carbon number and carbon number less than 18, as shown in Fig. 3(a). This was also observed by Uosaki *et al.*[16]

In order to get a deeper insight into the molecular arrangement in the lamella, high-resolution images of alkane monolayers are shown in Fig. 3. It is clearly seen that the structure of the alkane monolayers is perturbed by the herringbone reconstruction ridges underneath them on the surface. There is a slight difference in the orientation of alkane molecules on the different sides of the elbow position of the herringbone reconstruction ridges, as marked on the figures with dashed and solid lines. The angle differences are measured as about 1°–4°. Furthermore, for alkanes with long carbon chain, such as n-$C_{36}H_{74}$, we find a strong correlation between the defects in the molecule packing and the relief of the reconstruction. The presence of meandering lamella of n-$C_{36}H_{74}$ is clearly related to the irregular herringbone ridges of the Au (111) reconstruction, where troughs between lamellae are always located on top of elbows of ridges, as marked by arrows in
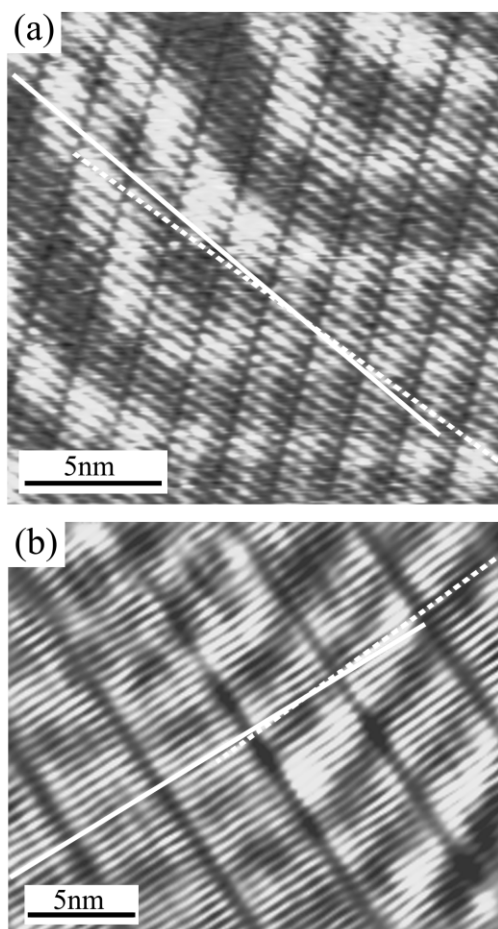
Fig. 3 STM images of the alkane monolayers on the herringbone-like Au(111) surfaces, showing a slightly different orientation of alkane molecules on the different sides of the elbow position as marked with solid and dashed lines. (a) n-$C_{14}H_{30}$ monolayer (18 nm × 18 nm) and (b) n-$C_{36}H_{74}$ monolayer (23 nm × 19 nm).

Fig. 4(a). However, for alkanes with a short carbon chain, such as n-$C_{16}H_{34}$ and n-$C_{14}H_{30}$, the boundary of the lamella is usually straight and is not always rigidly restricted to the elbow position of the reconstructed gold surface, as shown in Fig. 3(a) and 4(b).

Reconstruction ridges are known to correspond to the higher gold atoms resting in the saddle positions located between surface areas of the fcc and the hcp packings with respect to the (111) planes underneath.[20–22] For the reconstruction with the herringbone ridges, the reconstruction is similar to that of the uni-axial one. However, the troughs of gold atoms along the approximate [01$\bar{1}$] azimuth differ a little from the exact [01$\bar{1}$] direction, as shown in the schematic model given in Fig. 5.[20,21] The deviation of the [01$\bar{1}$] row corresponding to positions of surface atoms from hcp to fcc is equal to $\sqrt{3}/3\ d$ (0.16nm) while that from fcc to hcp is $\sqrt{3}/6\ d$ (0.08nm), where d is the diameter of the gold atom. On the reconstructed gold surface, a well commensurate overlayer is formed. This has been reported in our previous paper.[19] It is reasonable to suppose that alkane molecules adsorb along the gold troughs, where each alkane molecule interacts with two neighbouring rows of gold atoms along the [01$\bar{1}$] azimuth. In the case where a lamella lies across a ridge, the packing of alkane molecules should be perturbed since the gold trough suffers from a small in-plane deviation with respect to the [01$\bar{1}$] close-packed rows of the bulk. Otherwise, some alkane molecules would have to cross some gold atoms, which would decrease the adsorbed energy. As a consequence, the alkane molecules on different sides of the "V" shape ridge gently
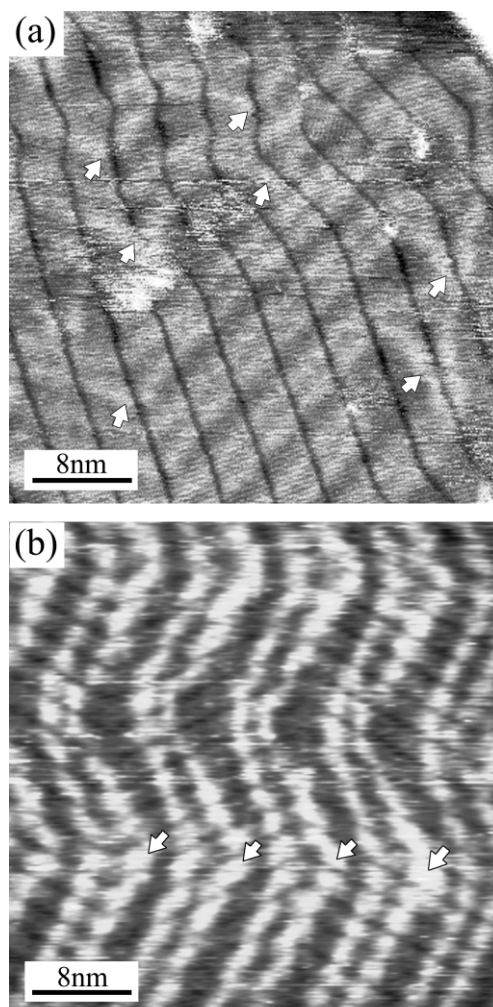

Fig. 4 STM images of the alkane monolayers on the herringbone-like Au(111) surfaces. (a) The dark troughs of a lamella locate on the elbow position of the reconstructed ridges for long-chain alkanes (e.g. n-$C_{36}H_{74}$). (b) The boundaries do not rigidly fit the elbow position for short-chain alkanes (e.g. n-$C_{16}H_{34}$). Arrows show the elbow positions of the gold reconstruction. Scanning area: 40 nm × 40 nm.

re-orientate a little in order to accommodate the deviations caused by the transition from fcc to hcp packing on the reconstructed surface.

Self-assemblies of alkanes on MoS_2 surfaces have been studied previously. It was reported that normal alkanes (with even carbon number) tend to form monolayers with alkane long axes tilted to the lamellar boundary.[8,10] The tilted alkane
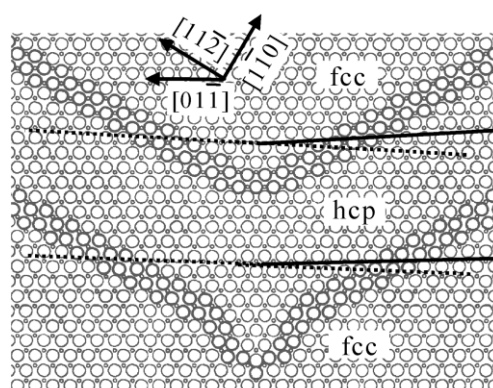

Fig. 5 Schematic model of the reconstructed Au(111) surfaces with the herringbone ridges.

lamella corresponds to the case where every neighbouring alkane molecule shifts by one repeat unit of methylene groups. The intermolecular distance was measured to be 0.48 nm, which is similar to our findings for the alkane monolayers on the reconstructed Au(111) surfaces. Therefore, it is reasonable to compare the structures of the alkane monolayers on gold with that on MoS$_2$ surfaces. Molecular mechanics calculations showed that the tilted lamella for alkanes with even carbon number has energetic preference on MoS$_2$ surfaces.[10] However, the calculated energy difference between a tilted and a non-tilted alkane overlayer is very small. Based on the geometric similarity between the alkane overlayers on both surfaces, we assume that the tilted one could be slightly more stable and the perpendicular one would be a metastable structure. Tilted lamellae were also considered to be more stable for alkanes with even carbon number by qualitatively analysing the interaction between the terminal methyl groups.[16] Molecular mechanics calculations of alkanes on the Au(111) surfaces also showed that the tilted lamella is energetically preferred, disregarding the molecule–gold interaction along the molecular long axes.[23] As a result, the tilted lamellae form on the reconstructed gold surfaces with straight reconstructed ridges, where the surface structures are very uniform.

Let us now focus on the molecular packing in the elbow area of the reconstructed ridges on the herringbone-like Au(111) surfaces. There are two possibilities for an alkane molecule to adsorb on the surface of the elbow area: either it crosses over some gold atoms if the molecule is rigid or it gently bends to follow the surface corrugations. In any case, an energy increase for the adsorbate/substrate system is expected. Such an energy increase in the molecule/gold interface is important in the vicinity of the elbow area of the gold reconstruction structure. The structure of the lamella should be determined by the competition between the following two factors: the energy increase owing to the change of direction of the lamellar boundaries and the energy increase due to the molecule crossing at the elbow position of the reconstructed gold ridges. Apparently, for a long-chain alkane, molecule crossing over the elbow area is non-profitable. On the herringbone-like reconstructed surfaces, the elbow positions usually locate in a line which is perpendicular to the [01$\bar{1}$] direction. When the lamellar boundaries are across the elbow positions of the reconstructed ridges, the alkane molecules are perpendicular to the lamellar boundaries. Considering the mismatching of a long-chain alkane with the substrate gold at the elbow position, a metastable structure with the alkane molecules perpendicular to the boundaries would become the most stable structure. This hypothesis is supported by the fact that the lamellar boundaries turn irregularly in order to fit into the irregular arrangement of the reconstructed ridges at the elbow position (see Fig. 4(a)). However, for a short-chain alkane with $n < 18$, the energy increase would be smaller if the alkane molecule lies across the elbow position, because the mismatching between a short alkane molecule and the substrate lattice is smaller. The lamellar troughs in the alkane monolayers could pass the elbow positions of the reconstructed ridges. As a consequence, short-chain alkanes adopt the type of tilted lamellae that are energetically preferable. It could be expected that alkanes with short carbon chain might take the structure of the perpendicular lamellar boundary on the herringbone-like reconstructed surfaces at certain low temperatures when the interaction between the adsorbate and the substrate is increased.

Summary

Molecular structures of alkane monolayers formed at the interface between an alkane-containing solution and an Au(111) surface have been investigated with STM. Two kinds of packing of alkane molecules in the self-assembled monolayers are found, which are correlated to the structures of the gold surface and the molecular lengths. The reconstruction of the Au(111) surfaces locally disturbs both the orientation and the arrangement of the alkane molecules in the monolayers. The defects of the monolayers are strongly related to the surface structures.

Acknowledgement

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