In The Direction of Perfect Design of Self-Assembled Monolayers: Scanning Tunneling Microscopy Study of SAMs Made of Decanethiol on Au(111)

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Abstract

Self-assembled monolayers (SAMs) of decanethiol (C10) on Au(111) substrate, prepared at room and elevated temperatures, were studied using scanning tunneling microscopy (STM). Preparation at elevated temperature results in highly-ordered layers with large ordered domains spreading on gold surface with dimensions easily exceeding 25×25 nm². At room and 313 K of temperatures, the oblique (√3×√3)R30° structure was observed, whereas, at 333 K the superstructure (4√3×2√3)R30° was covering the gold substrate with four molecules per unit cell. The high-quality of STM results enables us to resolve four symmetry-inequivalent C10 molecules per 10 Å× 8.6Å unit cell. The dissimilarity in topographic heights of C10 molecules on Au(111) was attributed to the binding of sulfur headgroup moiety of C10 molecules with different adsorption sites on Au(111).

Keywords: SAM's; STM; Decanethiol; Monolayers; Ordered domains; Vacancy islands.

Introduction

Spontaneously chemisorbed monolayers of thiols and disulfides on gold, so-called self-assembled monolayers (SAM), have drawn substantial attention of many research groups [1-16]. They resemble a model system for fundamental studies in surface science due to their wide potential technical applications on the basis of their well-ordered structure and high stability [1-16]. In most cases, the preparation of SAMs leads to the formation of high-quality and well-defined organic surfaces with homogeneous composition, structure, and thickness. Therefore, SAM serves as an ideal model system in understanding various interfacial phenomena, such as wetting [17,18], adhesion [19,20], and catalysis[21]. Moreover, understanding and controlling the properties of organic monolayers on metal surfaces can offer strong promise for the development of molecular technologies [22,23].

During the last two decades, alkanethiols monolayers formed on gold are the most widely investigated SAMs in considerable details for understanding and clarifying the surface structures and for obtaining knowledge about the physical and chemical properties of the resulted thin organic films [12,24-36]. From previous studies, it becomes

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clear that upon adsorption, the thiols are converted into thiolates with the sulfur atoms bonded to the A(111) surface and the alkyl chains are tilted by about 35° with respect to the surface normal \cite{37,38}. The alkyl chains also exhibit a twist angle of about 52° defined by the zig-zag of the carbon atom structure of the chain \cite{23} and are tilted 14° away from the direction of nearest-neighbor (NN) \cite{27}. The distance between the adjacent sulfur atoms, S-S, was found to be 5 Å (\sqrt{3}a, a: the diameter of the gold atom)\cite{27}. As a result, the sulfur atoms of thiols form a (\sqrt{3}x\sqrt{3})R30° overlayer. For alkanethiolates, a commensurate c(4\sqrt{3}x2\sqrt{3}) R30° (short-hand notation, c(4 x 2)) superstructure with respect to the basic (\sqrt{3}x\sqrt{3})R30° lattice on Au(111) is generally observed \cite{25,29}. This structure exhibits a rectangular unit cell containing four molecules with an area of 21.6 Å² per molecule. In scanning tunneling microscopy (STM) images of these alkanethiolate films, the molecules in the c(4\sqrt{3}x2\sqrt{3}) R30° unit cell appear with two different topographical heights. The last observation indicates the presence of at least two classes of inequivalent molecules. Later and in another study, three different heights were observed for the adsorbed thiolates in the same c(4\sqrt{3}x2\sqrt{3}) R30° structure \cite{27}. In addition to the c(4\sqrt{3}x2\sqrt{3}) R30° structure, an interesting (6\times\sqrt{3}) structure of alkanethiolates overlayer was observed after long-time storage at room temperature \cite{27}. The STM results concerning the (6\times\sqrt{3}) phase show that the unit cell consisting of four molecules appears at three different topographic heights. Recently, SAMs generated from a homologue series of molecules which are characterized by biphenyl and terphenyl moieties attached to the thiol group via an alkane spacer of varying length CH3-(C6H4)2-(CH2)n-SH (BPn, n=1-6) and (C6H4)-(C6H4)2-(CH2)n-SH, (TPn, n=1-6) were studied \cite{4,6,39}. A pronounced odd-even change in the molecular arrangement and packing density was found. A (2\sqrt{3}x\sqrt{3}) structure was observed for BPn and TPn, n= odd with two molecules per the unit cell. In the unit cell the molecules appear with different heights. SAMs made from BPn and TPn, n= even exhibit a very different structure. A (5\sqrt{3}x3) rectangular unit cell containing eight molecules was found with a total of four different heights levels were observed.

It was suggested that the two symmetry-different molecules per c(4\sqrt{3}x2\sqrt{3}) R30° unit cell originate from a different twist about the chain axis. Chains are either twisted clockwise or counterclockwise, resulting in a different orientation of the topmost C—C bond. Since the chains are tilted by 30° from the surface normal and occupy two different twist conformations, this results in geometrically different height levels for the terminal methyl group\cite{25}.

In the present work, SAMs made from decanethiol on Au(111) were studied at different temperatures. The very high-resolution scanning tunneling microscopy images acquired in this work facilitate the proposal of a model that explains the appearance of the decanethiol molecules on gold surface at different topographical heights.
Experimental

Chemicals

Decanethiol (Aldrich, 99.9%), Ethanol (Baker, absolute), acetone (Baker, HPLC grade), and chloroform (Baker, absolute) were used as received.

Sample preparation

For STM investigations a freshly cleaved sheet of mica has been heated up to 370 °C for about 48 h inside an evaporation apparatus (Leybold) to remove the residual water which could be enclosed between the mica sheets. 100 nm of Au (99.995 %, Chempur) were then evaporated at the same temperature of the substrate and a pressure of approximately 10^{-7} mbar. The thickness and the deposition rate (20 Å s^{-1}) was monitored using a crystal oscillator (Leybold Inficon). After deposition the substrates were cooled down and the vacuum chamber was filled with purified nitrogen. The substrates were stored under argon and flame-annealed in a butane/oxygen flame immediately before the adsorption experiments were carried out. This procedure yielded Au substrates with several 100 nm large terraces exhibiting a (111) surface orientation.

C10 monolayers on Au(111) substrates were prepared at an appropriate temperature (see the text) by soaking the gold substrates into dilute ethanolic solutions (1 mM) of C10. The substrate was removed from the solution and rinsed carefully with pure ethanol, Acetone, chloroform and again ethanol. Then the substrates were dried in a nitrogen stream.

Structural investigations

All STM measurements were carried out in air using a Digital Instrument (Nanoscope III) Multimode microscope equipped with a scanning tunneling microscope head. Tips were prepared mechanically by cutting a 0.25 mm Pt/Ir alloy (8:2, Chempur) wire. The data have been collected in constant-current mode using tunneling currents between 120 pA and 500 pA and a sample bias between 100 mV and 1 V (tip positive).

Results and Discussion

Figure 1(a)-(d) show constant current STM images recorded for an Au(111)-substrate, which has been immersed for 24 h in 1 mM solution of C10 in ethanol at room temperature. In (a)-(c), the STM micrographs show several Au terraces which are separated by monoatomic steps. Within the terraces numerous depressions appearing as dark islands in the STM images with diameter of 2-6 nm and a depth in proportion to that of monoatomic steps on Au(111) (2.4 Å) are observed. As described previously, these “pits” correspond to vacancy islands in the topmost layer of gold surface generated during the self-assembly process^{40,41}. 
Figure 1 Constant-current STM images showing the gold surface after being immersed into 1 mM ethanolic solution of C10 at 298 K for 24 h. Oblique box in (d) marks the (√3×√3)R30° unit cell. Tunneling parameters: (a) \( U_t = 820 \text{ mV}, I_t = 140 \text{ pA}; \) (b) \( U_t = 345 \text{ mV}, I_t = 210 \text{ pA}; \) (c) \( U_t = 384 \text{ mV}, I_t = 150 \text{ pA}; \) and (d) \( U_t = 580 \text{ mV}, I_t = 150 \text{ pA}. \)

Figure 1(d) shows a high-resolution STM image of a C10 monolayer for samples prepared at RT. Examination of this image reveals the presence of periodic arrangement of protrusions adopting hexagonal arrangement. Each protrusion in the STM image is assigned to a sulfur atom and therefore, to an individual alkanethiolate molecule. The distance between adjacent sulfur atoms is found to be 5 Å. The latter value is larger than the bulk value for the distance between closely packed alkane chains (4.2-4.4 Å). As a result, the alkane chains tilt away from the surface normal in order to achieve a close-packed structure. The 5 Å distance between the neighboring molecules is compatible with (√3×√3)R30° structure. Since the hexagonal (√3×√3) \( R30^\circ \) unit cell consists of one molecule, the area occupied by a single molecule is 21.6 Å². The oblique unit cell is overlaid on the image in fig 1(d).
STM images for C10 layer prepared at 313 K are displayed in figure 2(a)-(e). Compared to that within the films prepared at RT, the size of the depressions within the film prepared at 333 K is slightly larger (5-15 nm) whereas their density is lower (see fig. 2(a) and (b)). The last observation is in agreement with previous published results for aromaticthiolate adlayers \(^{[4-6,39]}\). Additionally, the size of the ordered domains increases with preparation temperature see fig. 1(d) and 2(d). The attainment of high-resolution STM images of C10 SAMs prepared at room temperature turned out to be rather difficult, but noteworthy an increase, in contrast and resolution, was observed when using solution at elevated temperature such as 313 K. From figures 2(c) and 2(d), one can see that the same hexagonal \((\sqrt{3} \times \sqrt{3}) R30^\circ\) molecular arrangement is formed by C10 molecules at 313 K. In fig. 2(e), 3-D representation of STM image for samples prepared at 313 K was displayed to show the \((\sqrt{3} \times \sqrt{3}) R30^\circ\) structure more clearly.

Figure 3(a)-(c) show large-scale constant-current STM images of C10 prepared at 333 K. Comparison of SAMs prepared at room temperature and at 313 K with SAMs formed at 333 K reveals an increase in size and a corresponding decrease in density of the vacancy islands due to Ostwald ripening process. The size of the depressions increases to about 30 nm. It is worth noting that these depressions are not free of C10 molecules instead they are covered with C10 molecules having the same molecular arrangement as those in the vicinity (the figure is not shown). Although these depressions consist of ordered domains of C10 molecules, nevertheless and for some applications they are considered to be film-defects. As a consequence reduction of their density and enlargement of their sizes result in the formation of almost free-defect films. Such resulting films are highly required for several technical applications \(^{[22,23]}\).
Figure 2  Constant-current STM images showing the gold surface after being immersed into 1 mM ethanolic solution of C10 at 313 K for 24 h. (e) A 3-D representation of STM image showing (√3×√3) R30° structure of C10 SAM. Tunneling parameters: (a) $U_t= 800$ mV, $I_t= 500$ pA; (b) $U_t= 750$ mV, $I_t= 200$ pA; (c) $U_t= 510$ mV, $I_t= 180$ pA; (d) $U_t= 550$ mV, $I_t= 150$ pA; and (c) $U_t= 550$ mV, $I_t= 150$ pA.

At molecular level, three different ordered domains formed by C10 molecules rotated by 120° with respect to each other are recognized as can be seen in fig. 3(b)
and 3(c). The occurrence of three ordered domains reflects the perfect match of the molecular overlayer to the hexagonal symmetry Au(111) substrate.

Figure 3 Constant-current STM images showing the gold surface after immersing into 1 mM ethanolic solution of C10 at 333 K for 24 h. Three different rotational domains corresponding to the Au(111) substrate symmetry are indicated by arrows in (b) and (c). Tunneling parameters: (a) \( U_t = 1000 \text{ mV}, I_t = 500 \text{ pA} \); (b) \( U_t = 580 \text{ mV}, I_t = 150 \text{ pA} \); and (c) \( U_t = 541 \text{ mV}, I_t = 150 \text{ pA} \).
The size of the ordered domains under these preparation conditions extends up to 45 nm. A close inspection within one of these domains reveals the existence of a new structural phase that was not seen for samples prepared at temperatures lower than 333 K.

In fig. 4(a) a very high-resolution STM image taken for one ordered domain is displayed with cross-sectional height profiles along the lines A, B, and C labeled in the STM image. The periodicity along the lines A amounts to 8.6 Å (see fig. 4(b)), which is three times the diameter of an Au atom. Therefore, the molecular array along the lines A ran in the [110], i.e., nearest-neighbor (NN), direction of the Au(111) surface. Along the line B, the distance between the neighbor bright spots is 10 Å, which is two times the \( a_h \) distance. Therefore, the molecular array along the line B ran in the [121], i.e., the next-nearest-neighbor (NNN), direction of the gold surface. The unit cell of the superstructure is therefore described as \( (2\sqrt{3} \times 3)R30^\circ \) structure. The superlattice contains four molecules with rectangular unit cell of \( |a| = 2\sqrt{3} a_h = 10 \) Å, \( |b| = 3 a_h = 8.6 \) Å (\( a_h = 2.886 \) Å). The area occupied by a single molecule amounts to 21.6 Å². In fact, the \( (2\sqrt{3} \times 3)R30^\circ \) or \( c(2 \times 4) \) structure has been previously observed for C10 molecules on Au(111) (25, 29).

Based on the results that emerged from this work, the suitable preparation conditions for the formation of \( (2\sqrt{3} \times 3)R30^\circ \) structure can be determined. It is obvious from our findings that at preparation temperature lower than 333 K, the \( (2\sqrt{3} \times 3)R30^\circ \) structure is either not formed or acquisition of STM images showing this structure turn out to be tricky as a result of the high density of the pits. As a summary, one can deduce that preparation of C10 SAMs in diluted ethanolic solution at about 333 K is the ideal course of action method for the formation of the full-coverage \( (2\sqrt{3} \times 3)R30^\circ \) phase.

Another interesting result obtained from this work as a result of the high-quality of our STM images is the resolution of four distinguishable and inequivalent C10 molecules appearing on Au(111) with different topographical heights per unit cell within the \( (2\sqrt{3} \times 3)R30^\circ \) phase. To the best of our knowledge, it seems that this is the first study in which four symmetry-inequivalent molecules per unit cell is microscopically determined. Along each of the lines A and B (labeled in the STM image fig. 4(a)), the topographical height repeats itself every two molecules. Whereas, along the line C every third molecule has the same topographical height (see fig. 4(b)-(d)). Figure 5 is 3-D STM image which is a subsection of figure 4(a) showing the protrusions in a unit cell together with the numeric labels. A comprehensive analysis of this and other unit cells in different STM images reveal that the heights of the protrusions are thoroughly different; the values referred to the height of protrusion H1 are shown in figure 5. A total of four different height levels are observed: height reference (in Å) H1, 0.35 H2, 0.42 H3, and 0.65 H4.
Figure 4 Constant-current STM image ($U_t = 541$ mV, $I_t = 150$ pA) for a Au(111) substrate, which has been immersed for 24 h into a 1 mM solution of C10 at 333 K (a). The rectangular box marks the unit cell of $(2\sqrt{3}\times3)$R30° structure. Cross-sectional height profiles taken along lines A, B, and C are presented in panels b, c, and d, respectively.
As a result, the data concerning \((2\sqrt{3} \times 3)R30^\circ\) phase demonstrate unambiguously that the unit cell contains four molecules appearing at different heights. Before further discussing the origin of the variation in the molecular topographic heights seen for \((2\sqrt{3} \times 3)R30^\circ\), we would like to point out that in our STM data the interpretation is based on the postulation that during scanning the tip is not buried through the SAM (the tip was above the layer). Therefore, the topmost methyl group unit of the C10 molecule was imaged. This conclusion was confirmed via the following experimental observations. First, changing the tunneling parameters (voltage and current) does not result in significant changes in the variation of contrast. Moreover, under different scanning conditions no tip-induced changes were seen even after scanning the same area on the sample several times. Therefore, it is rather safe to assume that during the STM scanning the methyl termini is mapped rather then the tip penetrates the layer and based on this conclusion, the probability that the tip might induce variation in the height of the protrusions is excluded.

<table>
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<th>Difference in height (Å)</th>
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<td>H_{1,2}</td>
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<tr>
<td>H_{1,3}</td>
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<td>H_{1,4}</td>
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**Figure 5** A 3-D STM image \((U_t = 570 \text{ mV}, I_t = 150 \text{ pA})\) where four different heights observed in the unit cell are marked with numbers.

In the previous studies, it was demonstrated that in the \((2\sqrt{3} \times 3)R30^\circ\) superstructure the two inequivalent molecules was ascribed to the difference in the twist angle of the molecules which result in two different topographical heights\(^{[25]}\). This model is clearly unable to account for the appearance of four variations in molecular height seen for the C10 molecules. Herein, we propose that the differences in molecular height could be originated from the adoption of the sulfur headgroups different adsorption sites on the Au(111) surface alone or together with the electronic
effect resulted from different conductivities of C10 molecules on account of having different conformational geometries. Recently published theoretical studies have demonstrated that the energy difference between different adsorption sites for thiolate on Au(111) may be quite small \cite{42-45}. It is accordingly plausible that the S-atoms adopt different adsorption sites. The different adsorption site model was proposed for the molecular arrangement structures formed by C_6H_5(C_6H_4)_2(CH_2)_nSH (TPn, n= 1-6) and CH_3(C_6H_4)_2(CH_2)_nSH (BPn, n=1-6) molecules. In the case of TP2, TP4, BP2, BP4, and BP6 the (5\sqrt{3} \times 3) structure was observed with four variations of molecular heights. Whereas, both the (5\sqrt{3} \times 3) and (6\sqrt{3} \times 2\sqrt{3}) structures were observed for TP6 molecules with the same number of molecular topographical heights \cite{4,6,39}.

Fig. 6 shows the simplest structural model of the (2\sqrt{3} \times 3)R30° structure. In this model the unit cell consists of four inequivalent molecules with an area of 21.6 Å² per molecule. The sulfur atoms are proposed to bind to several adsorption sites such as 3-fold hollow, on top, and on bridge adsorption sites. The sulfur atoms are proposed to form (\sqrt{3} \times \sqrt{3}) lattice with slight deviations due to the different adsorption sites.

**Figure 6.** A model of commensuration condition between C10 monolayer and bulk terminated Au surface. A diagonal slash represents azimuthal orientation of plane defined by all-trans hydrocarbon chain. The rectangular unit cell show the (2\sqrt{3} \times 3)R30° superstructure, while the large and small oblique unit cells show the (\sqrt{3} \times \sqrt{3})R30° structure and the primitive unit cell of the Au(111) surface, respectively.

**Conclusion**

In this work, we have studied the self-assembled monolayers of C10 on Au(111) using STM at different preparation temperatures. Our results show the formation of highly-ordered monolayer for the temperature range investigated in this work. The rotational ordered domains and the depressions increase in size with temperature. At RT and 313 K, the hexagonal (\sqrt{3} \times \sqrt{3}) structure was observed. At 333 K the surface was almost covered with C10 molecules exhibiting the (2\sqrt{3} \times 3)R30° superstructure.
For the first time, four different molecular heights of C10 on Au(111) were identified. The variation in topographic heights was attributed to the preference of the sulfur headgroup to bind with different adsorption sites on Au(111).

References