

STM Study of 2-Mercaptoethanol Self-Assembled Monolayer on Au(111)

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Presented are the STM images of self-assembled monolayer of 2-mercaptoethanol on Au(111). Striped structures of $(6X\sqrt{3})$, $(5X\sqrt{3})$, $(4X\sqrt{3})$ and compact- $(5X\sqrt{3})$ were observed after annealing at 80 °C. Analysis of the ordered structures revealed that the basic fundamental units of the ordered structures were three crystallographically non-equivalent $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies, and that the way of combination of the assemblies produced the four different structures. The $(6X\sqrt{3})$ structure ($\theta = 0.33$) was composed of one $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly, while the $(5X\sqrt{3})$ ($\theta = 0.30$) and $(4X\sqrt{3})$ ($\theta = 0.38$) structures were consisted of two $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies, separated by 5a and 4a, respectively. Furthermore, the compact- $(5X\sqrt{3})$ structure ($\theta = 0.50$) was obtained by overlapping three $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. In spite of the diversity in the adsorption structures, all the adsorption sites of 2-mercaptoethanol were fundamentally identical. On the other hand, the unannealed primitive SAM of 2-mercaptoethanol was characterized by two observations: a short-range order keeping the adsorbed molecules at approximately $\sqrt{3}$ a and the small domains of the striped structures supporting that the observed surface structures on the annealed surface were the extension of the primitive layer of 2-mercaptoethanol. Comparing these observations with the already published structures of ethanthiol, it was concluded that the interaction between the hydroxyl groups of 2-mercaptoethanol might play a significant role in the adsorption step of 2-mercaptoethanol on Au(111) to organize the adsorption structures different from those of ethanthiol.

Keywords : Self-assembled monolayer (SAM), 2-Mercaptoethanol, Au(111), Scanning tunneling microscope (STM).

Introduction

Self-assembled monolayers (SAMs) of organic compounds have been investigated extensively in view of fundamental sciences as well as in the light of potential applications.¹ Among the fundamental researches, much of attention has been focused on structural information to understand the interactions of adsorbate-substrate and/or adsorbate-adsorbate.² One of the examples would be the SAMs of octanethiol and decanethiol on Au(111).³⁻⁷ In these particular SAMs, the sulfur atoms of the thiols adsorbed at hexagonally closed packed (hcp) sites aligned in a $(\sqrt{3} \times \sqrt{3})R30^\circ$. Although the sulfur atoms are in the $(\sqrt{3} \times \sqrt{3})R30^\circ$, the alkyl chain attached to the sulfur atoms are arranged to reduce the repulsive force between them. Due to the periodicity in the relative orientations of the alkyl chains, the real structures of the SAMs turned out to be a $c(4X2)$ superlattice of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. In parallel with such fundamental researches, tremendous efforts in technical aspect have been directed toward various SAMs, especially functionalized ones. The reason is that SAMs with functional end groups have various physicochemical properties enough to be employed as they are, or to be modified properly for further applications. One example is the control of hydrophilicity by varying compositions of mixed SAMs of alky thiol and hydroxy-functionalized thiol.^{8,9}

Generally, functional groups have influence on the equilibrium structures of various SAMs. For example, the pristine SAM of mercaptohexanol packs in an oblique lattice¹⁰ while the SAM of unfunctionalized hexanethiol organizes in a hexagonal $(5\sqrt{3} \times \sqrt{3})R30^\circ$ pattern.¹¹ These observed results have implied that the structure of a SAM depends on the chemical interactions between end-groups. Another example is the comparison of the images of dodecanethiol and of mercaptoundecanol.¹² A $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice was clearly observed from the hydrophobic SAM of dodecanethiol while a striped image structure was imaged on the hydrophilic SAM of mercaptoundecanol. Based on a molecular dynamic calculation, this structural difference was interpreted as directional hydrogen bonding in a linear fashion.

The goal of this work is to investigate the structural information of the 2-mercaptoethanol SAMs on Au(111), using STM. Since 2-mercaptoethanol has very short alkyl group, the van der Waals interaction between the alkyl chains would be minimal to enhance the effect of the hydrogen bond between the end groups on the structures of 2-mercaptoethanol. Then, one would anticipate the structure of 2-mercaptoethanol SAM to be influenced greatly by the interactions of substrate-adsorbate and end group-end group.

Experimental Section

The Au(111) single crystal used in this work was made with Clavilier method.¹³ An Au wire (99.999%, $\phi = 0.5$ mm, Aldrich) was melted in a H_2-O_2 flame to form a single crys-

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tal bead. The bead had eight planes of (111) and six ones of (100). The bead single crystal was spot-welded to a Pt foil (99.9%, 0.254 mm, Johnson Matthey) so that one of the (111) facets, identified with a He-Ne laser, was oriented upward. A well-defined surface of Au(111) was prepared by annealing the single crystal bead in H₂ flame and quenching in a H₂-saturated water.

The adsorption of 2-mercaptoethanol was produced by immersing a well-defined surface of Au(111) into an ethanol solution (99.8% Seccosolv, Merck) of 2-mercaptoethanol (10 mM) (99.8%, SIGMA) for 2 hours. The Au(111) crystal with adsorbed 2-mercaptoethanol was annealed at 80 °C in air for 1 hour to crystallize the adlayer.

STM images were obtained with a STM instrument (PSI, model CP) and a 5 nm scanner was used after calibration with a HOPG. The tips for STM were made by etching a W wire (0.25 mm in diameter) in 1 M KOH solution. The atomic images were obtained in constant-height mode.

Results and Discussions

Figure 1 shows four molecular-level images of 2-mercaptoethanol on Au(111). One of the major characteristics of the images is that all the images have striped structures. The different repeating periods of the stripes in each image, however, indicate that the 2-mercaptoethanol molecules are

arranged in different ways.

Figure 2(a), a zoomed and slightly filtered image of Figure 1(a), is consisted of three molecular rows aligned in the [112] direction: bright zigzag line, bright and dark rows of distinctive spots. These features repeat at period of 17.2 ± 0.33 Å (equivalent to 6 times of a Au-Au distance ($a = 2.88$ Å), *i.e.* $6a$) in the [110] direction. On the other hand, the repeating period along the molecular rows is 5.1 ± 0.39 Å, corresponding to $\sqrt{3}a$. Then, the unit cell of Figure 2(a) is obviously $(6 \times \sqrt{3})$. In addition, the distances between the nearest spots including the ones in the zigzag line are consistently 5.1 ± 0.21 Å, which reveals that all the 2-mercaptoethanol molecules in Figure 2(a) are separated by $\sqrt{3}a$. This particular distance of $\sqrt{3}a$ between the adsorbed 2-mercaptoethanol is coherent with the separations between alkane-thiols on Au(111), which is well-known as $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure.²

Figure 2(b) is a proposed model of the $(6 \times \sqrt{3})$ structure, assuming 2-mercaptoethanol molecules adsorb at hcp sites as in the case of alkane-thiols on Au(111).² The fundamental building unit of the proposed $(6 \times \sqrt{3})$ structure is a $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly, designated with a dotted mesh. What makes the proposed $(6 \times \sqrt{3})$ structure different from an ideal $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is the existence of the zigzag lines repeating at the period of $6a$. The appearance of the zigzag lines may be originated from a special interaction

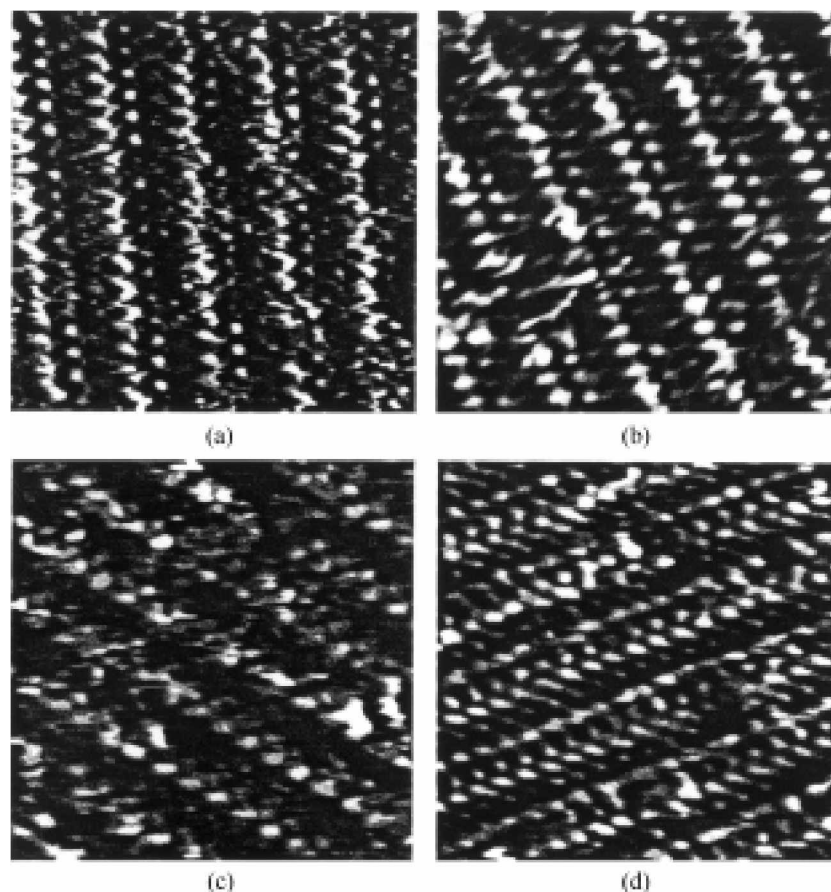


Figure 1. Four different STM images (80 Å x 80 Å) of 2-mercaptoethanol on Au(111).

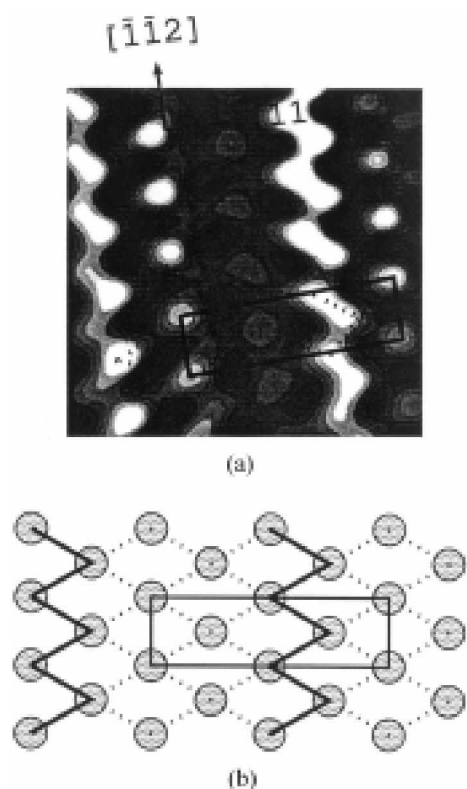


Figure 2. The $(6X\sqrt{3})$ structure of 2-mercaptoethanol on Au (111). (a) A zoomed and slightly filtered image ($27 \text{ \AA} \times 27 \text{ \AA}$) of Figure 1 (a) and (b) the proposed model.

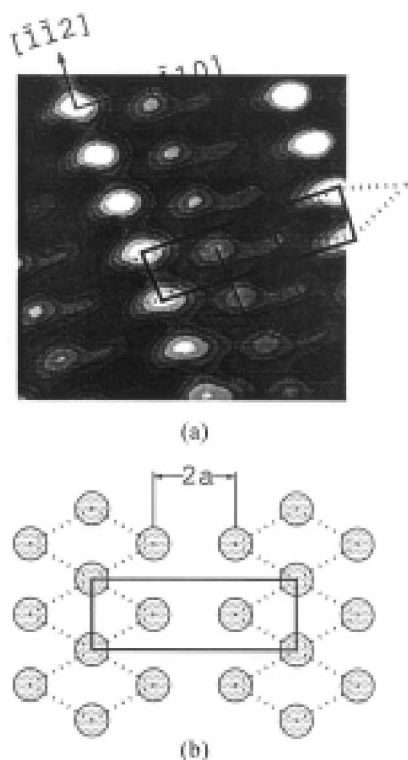


Figure 3. The $(5X\sqrt{3})$ structure of 2-mercaptoethanol on Au (111). (a) A zoomed and slightly filtered image ($27 \text{ \AA} \times 27 \text{ \AA}$) of Figure 1 (a) and (b) the proposed model.

between the OH groups of the adsorbates. The coverage (defined as the ratio of the number of the adsorbed 2-mercaptoethanol molecules to that of the surface Au atoms) of the $(6X\sqrt{3})$ structure is 0.33 ($= 4/12$).

Figure 3(a) is a zoomed and slightly filtered image of Figure 1(b). A major difference between this image and the image of the $(6X\sqrt{3})$ structure is the absence of the zigzag line. Three molecular rows, composed of distinctive spots, are discernible along the $[\bar{1}\bar{1}2]$ direction and their repeating periods in the $[\bar{1}\bar{1}0]$ direction are $15.2 \pm 0.35 \text{ \AA}$, equivalent to $5a$. The spots in the rows are located consecutively at the distance of $\sqrt{3}a$ ($5.0 \pm 0.22 \text{ \AA}$). These values lead us to a conclusion that the unit cell of Figure 3(a) is $(5X\sqrt{3})$. In addition, it is very important to recognize that there are two parallelograms in the $(5X\sqrt{3})$ structure, as designated with dashed lines. The length of the sides of the parallelograms is sufficiently equivalent to $\sqrt{3}a$ so that the fundamental building unit of the $(5X\sqrt{3})$ structure is an $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly as well as that of the $(6X\sqrt{3})$ structure. However, the distances of the closest vertices of two adjacent assemblies in the $[\bar{1}\bar{1}0]$ direction is $5.9 \pm 0.12 \text{ \AA}$, close enough to $2a$. Based on these observations, a model in Figure 3(b) is proposed for the $(5X\sqrt{3})$ structure.

In understanding the proposed $(5X\sqrt{3})$ structure, it is instrumental to notice that there are three different $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies of an adsorbate on the (111) surface of a face-centered cubic crystal like Au, as shown Figure 4(a).

The non-equivalency of the assemblies comes basically

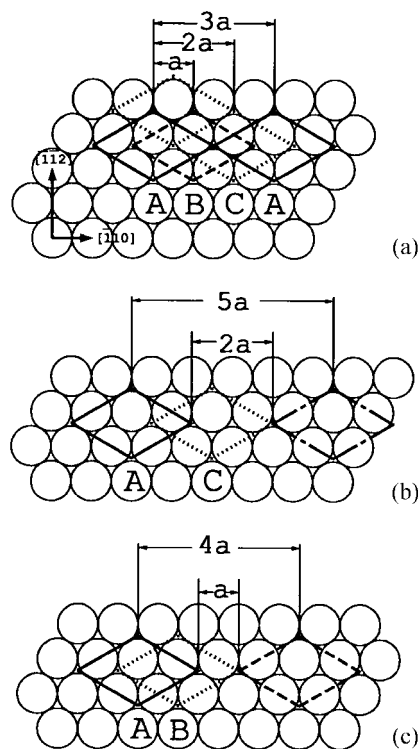


Figure 4. Crystallographically different $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. (a) Three different $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies, associated with one surface Au atom, (b) combination of two $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies for the $(5X\sqrt{3})$ structure and (c) the $(4X\sqrt{3})$ structure.

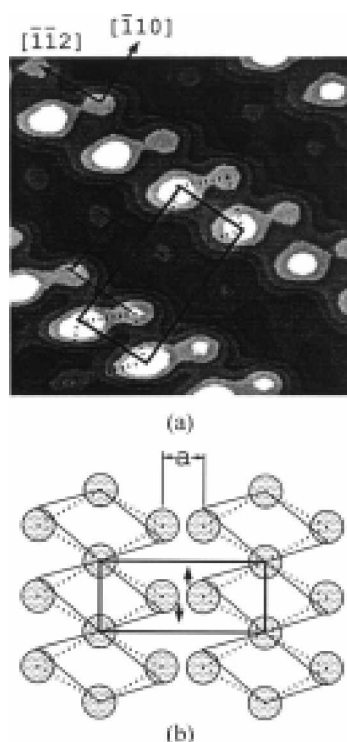


Figure 5. The $(4X\sqrt{3})$ structure of 2-mercaptoethanol on Au(111). (a) A zoomed and slightly filtered image ($27 \text{ \AA} \times 27 \text{ \AA}$) of Figure 1 (a) and (b) the proposed model.

from the fact that three hcp sites are associated around a surface metal atom. If one of the assemblies, let say the assembly A in Figure 4(a), is shifted by $\sqrt{3}a$ and $3a$ in the $[\Pi 2]$ and $[\Pi 0]$ directions respectively, the whole surface is filled in $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. However, only $1/3$ of all the hcp sites are occupied. Another $1/3$ of all the hcp sites is occupied by the assembly B and the other is by the assembly C. In this particular point of view, the three $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies are not equivalent to each other. The three assemblies are separated by one Au-Au distance in the $[\Pi 10]$ direction.

The proposed $(5X\sqrt{3})$ structure is formed by combination of the assemblies A and C in Figure 4(a). By shifting the assembly C as much as $3a$ in the $[\Pi 10]$ direction as shown in Figure 4(b), the distance between the vertexes of the assemblies becomes $2a$, which is identical to the experimentally observed value in Figure 3(a). Then, the $(5X\sqrt{3})$ structure is produced by repeating two non-equivalent $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies separated by $5a$ in the $[\Pi 10]$ direction, at the period of $\sqrt{3}a$ in the $[\Pi 2]$ direction. Another way to understand the $(5X\sqrt{3})$ structure is as follows: repeating a $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly at the period of $\sqrt{3}a$ in the $[\Pi 2]$ direction to form three molecular rows of different brightness and then the three rows at the period of $5a$ in the $[\Pi 10]$ direction. The coverage of the $(5X\sqrt{3})$ structure is 0.30 ($=3/10$).

There is another structure of 2-mercaptoethanol, which is composed of two non-equivalent $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. Figure 5(a) is a zoomed and slightly filtered image of

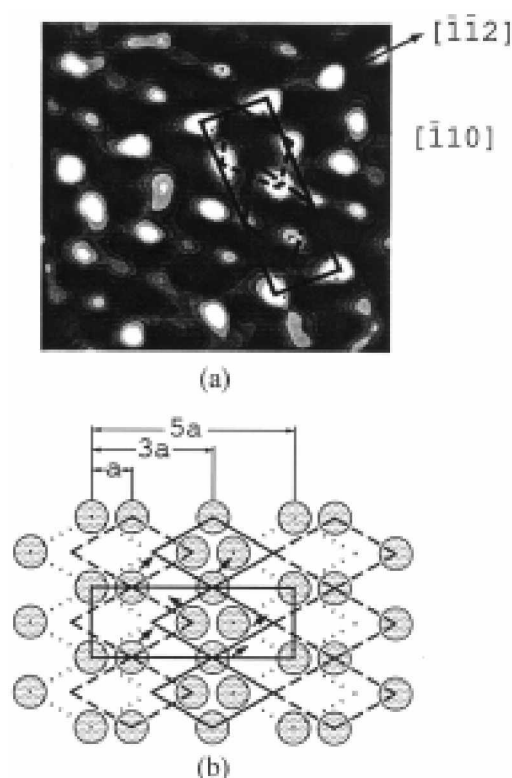


Figure 6. The compact- $(5X\sqrt{3})$ structure of 2-mercaptoethanol on Au(111). (a) A zoomed and slightly filtered image ($27 \text{ \AA} \times 27 \text{ \AA}$) of Figure 1 (a) and (b) the proposed model.

Figure 1(c). The distances between the brightest molecular rows and the spots in the row are $11.8 \pm 0.25 \text{ \AA}$ and $5.0 \pm 0.41 \text{ \AA}$, respectively. These values are equivalent to $4a$ and $\sqrt{3}a$, so that the unit cell is definitely $(4X\sqrt{3})$. A corresponding model of the $(4X\sqrt{3})$ structure is shown in Figure 5(b). As in the case of the $(5X\sqrt{3})$ structure, there are two $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. However, the distance between the vertexes is one Au-Au distance, which means that the proposed $(4X\sqrt{3})$ structure is the one composed of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly A and B (in Figure 4(a)) after shifting the B assembly by $3a$ in the $[\Pi 10]$ direction as shown in Figure 4(c). Due to the relatively short distance between the vertexes of the adjacent assemblies in the $(4X\sqrt{3})$ structure, a strong repulsion is expected so that a distortion of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies is anticipated. Indeed, a distorted $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit is observed in Figure 5(a). Therefore, we conclude that in the $(4X\sqrt{3})$ structure, a distorted $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly is repeating at the period of $\sqrt{3}a$ in the $[\Pi 2]$ direction and $4a$ in the $[\Pi 10]$ direction. The coverage of the $(4X\sqrt{3})$ structure is 0.38 ($=3/8$).

Figure 6 shows crystalline structures of 2-mercaptoethanol, which is proposed to be formed by overlapping $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. Figure 6(a) is a zoomed and slightly filtered image of Figure 1(d). The distance between the spots is $5.1 \pm 0.43 \text{ \AA}$ in the $[\Pi 2]$ direction, while the repeating period is $14.9 \pm 0.18 \text{ \AA}$ in the $[\Pi 10]$ direction. Then, the unit cell shown in Figure 6(a) is definitely $(5X\sqrt{3})$, in which

three $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies are recognizable. Figure 6(b) is a proposed model structure of Figure 6(a). A major difference of this particular structure from the previous ones is that a few 2-mercaptoethanol molecules in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies are missing. Such a missing is quite reasonable, since otherwise, there would be tremendous repulsions. In addition, this particular structure has a remarkably high coverage of 0.5 ($=5/10$), compared to those of other structures. Therefore, we name this particular $(5X\sqrt{3})$ structure as compact- $(5X\sqrt{3})$. Although a few molecules are missed, still there would be repulsive forces among the adsorbed molecules in the unit cell due to the high compactness of the compact- $(5X\sqrt{3})$. The repulsion may be reduced to some extent by lateral movements, as designated with arrows in Figure 6(b), based on the observation that the distances between the spots in the unit cell are within the range of 3.2 Å and 4.7 Å.

From the structures discussed so far, two common characteristics in the 2-dimensional structures of the 2-mercaptoethanol on Au(111) are extracted. One is that the basic building assembly to form the SAMs of 2-mercaptoethanol on Au(111) is three non-equivalent $(\sqrt{3} \times \sqrt{3})R30^\circ$ units whose vertexes are at hcp sites. The way of repeating the assemblies produces four different crystalline structures: $(6X\sqrt{3})$, $(5X\sqrt{3})$, $(4X\sqrt{3})$ and compact- $(5X\sqrt{3})$. The other is that in spite of the variety in the ways to repeat the building unit, all the adsorption sites of 2-mercaptoethanol molecules on Au(111) are identical. It is remarkable, however, that a few molecules are shifted to reduce repulsive forces in the $(4X\sqrt{3})$ and compact- $(5X\sqrt{3})$ structures.

It is noteworthy that the images observed in this work were obtained after annealing the primitive SAM of 2-mercaptoethanol at 80 °C. The unannealed layer of 2-mercaptoethanol showed an image (not shown), whose Fourier transformed pattern was a diffuse circle of a radius corresponding to $1/\sqrt{3}$ a. This particular observation implies that although a 2-dimensional long-range order was not developed, the distance between the 2-mercaptoethanol molecules was kept at approximately $\sqrt{3}$ a. Such a lack in long-range order would be due to the randomness in the direction of the hydrogen bonds between the OH terminal groups. On the other hand, small domains (~ 500 Å²) of the striped structures as discussed previously were observed frequently in the large not-annealed domains ordered in a short-range. These small domains strongly support that the annealing process resulted in ordering the domains in a short-range order to the crystalline domains of the striped structures as shown in this work. Therefore, the observed images of the annealed layers of 2-mercaptoethanol were concluded to be the extension of the primitive structures on the unannealed surface of Au(111).

At this point, it would be interesting to compare the ordered structures of 2-mercaptoethanol observed in this work with those of ethanthiol on Au(111). Kolb *et al.*¹⁴ have reported three ordered structures in 0.1 M H₂SO₄: two pin-striped structures of $(pX\sqrt{3})$ ($p=4.5$ and 7.5) and an oblique structure of $(4X3)$. In the $(4.5X\sqrt{3})$ and $(7.5X\sqrt{3})$ structures, all the adsorbed molecules are in the registry of

$(\sqrt{3} \times \sqrt{3})R30^\circ$, but every third and fifth rows are missing, respectively. The $(4X3)$ structure is a closely packed structure having four resolved spots at the corner points of the unit cell, which indicates that the adsorbed molecules are not in $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern. On the other hand, only $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of ethanthiol on Au(111) has been observed by Porter *et al.*¹⁵ In our results, all the 2-mercaptoethanol molecules were in the registry of $(\sqrt{3} \times \sqrt{3})R30^\circ$ although non-equivalent assemblies are combined, and any missing row was not observed. Since the self-assembled monolayers of 2-mercaptoethanol and ethanthiol were prepared from ethanolic solution, the observed structural differences exclusively were resulted from the presence of the hydroxyl end group. Concerning the role of terminal group in the formation of thiol monolayer, Poirier *et al.*¹⁰ suggested that the contribution of an end group to a final equilibrium structure depend on the alkyl chain length: the shorter the alkyl chain length, the more contribution of the terminal hydroxyl group. The alkyl chain length of 2-mercaptoethanol is very short so that a great contribution of the hydroxyl end group is expected. The interaction between the hydroxyl groups of 2-mercaptoethanol may play a significant role in the adsorption step of 2-mercaptoethanol on Au(111) to organize the adsorption structures different from those of ethanthiol.

Summary

Several ordered self-assembled monolayers of 2-mercaptoethanol molecules were observed on Au(111) after annealing at 80 °C. The basic fundamental units of the ordered structures were three crystallographically non-equivalent $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies, and the way of combination of the assemblies produces four different monolayers of $(6X\sqrt{3})$, $(5X\sqrt{3})$, $(4X\sqrt{3})$ and compact- $(5X\sqrt{3})$. The $(6X\sqrt{3})$ structure ($\theta=0.33$) was composed of one $(\sqrt{3} \times \sqrt{3})R30^\circ$ assembly, while the $(5X\sqrt{3})$ ($\theta=0.30$) and $(4X\sqrt{3})$ ($\theta=0.38$) structures were consisted of two $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies, separated by 5a and 4a, respectively. Furthermore, the compact- $(5X\sqrt{3})$ structure ($\theta=0.50$) was formed by overlapping three $(\sqrt{3} \times \sqrt{3})R30^\circ$ assemblies. In spite of the diversity in the adsorption structures, all the adsorption sites of 2-mercaptoethanol were fundamentally identical. On the other hand, the unannealed primitive SAM of 2-mercaptoethanol was characterized by two observations: a short-range order keeping the adsorbed molecules at approximately $\sqrt{3}$ a and the small domains of the striped structures supporting that the observed surface structures on the annealed surface were the extension of the primitive layer of 2-mercaptoethanol. Comparing these observations with the already published structures of ethanthiol, it was concluded that the interaction between the hydroxyl groups of 2-mercaptoethanol might play a significant role in the adsorption step of 2-mercaptoethanol on Au(111) to organize the adsorption structures different from those of ethanthiol.

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