

LETTERS

Low-Temperature Ordered Phase of Methylthiolate Monolayers on Au(111)

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Low-temperature phases of methylthiolate (CH_3S) monolayers on Au(111) have been investigated by using cryogenic scanning tunneling microscopy. The methylthiolate monolayers have a structure with a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ lattice at room temperature, while at 110 K it is transformed into a one-dimensional "chain structure" near step edges and a two-dimensionally ordered structure with an anisotropic lattice on terraces. The latter structure has an oblique commensurate (3×4) unit cell ($8.6 \times 11.5 \text{ \AA}$) in which four methylthiolates are located as a "tetramer". This temperature-dependent phase transition is reversible. The formation of tetramers is interpreted as evidence of an important role of a clustering of sulfur species in forming the ordered structure of the thiolate monolayers.

Alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$) adsorbed on Au(111) have been extensively studied from the viewpoints of the fundamental understanding of self-assembling phenomena because of their simplicity, highly ordered structures, and chemical stability.¹ Nuzzo et al. have found in their early work² that alkanethiols are bound to gold substrates through a strong Au–S bond. Later, He atom diffraction,³ grazing incidence X-ray diffraction,⁴ and scanning tunneling microscopy (STM)⁵ studies have revealed that the *n*-alkylthiolate monolayers on Au(111) with a saturated coverage primarily adopt a $c(4 \times 2)$ superlattice of a commensurate $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ lattice with their molecular axes being tilted by $30\text{--}34^\circ$ from surface normal. The $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ lattice is one of the most popular arrangements of sulfur adatoms on (111) surfaces of fcc metals. The $c(4 \times 2)$ superlattice was associated with the hydrocarbon packing within the layer because it resembles the packing found in the bulk *n*-alkanes. Thus, the observed structures of the *n*-alkylthiolate monolayers on Au(111) seem to fulfill structural requirements from both intralayer and monolayer–substrate interactions.

In the case of monolayers of functionalized alkanethiols ($\text{X}(\text{CH}_2)_n\text{SH}$; $\text{X} \neq \text{CH}_3$), fundamentally different arrangements

of the thiolates have been observed on Au(111),^{6–9} which depend on the end group X. The end-group-dependent structural changes were attributed to relatively strong intralayer interactions induced by the end groups.^{6–8} The structures of this sort of system are believed to be significantly influenced by a balance between the intralayer and the monolayer–substrate interactions. If we go to the other limit, that is, the weakest intralayer interactions, the lattice should be dominated by the monolayer–substrate interactions. In this sense, a methylthiolate (CH_3S) monolayer is one of the most appropriate systems to study a dominant factor to determining the molecular arrangement in a weak intralayer-interaction system. So far, low-energy electron diffraction (LEED) for methylthiolate monolayers on Au(111) showed a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ pattern at room temperature.¹⁰ However, a recent STM study of this system indicated that the surface methylthiolates exhibit considerably fast motions compared to a typical STM-tip scan rate, resulting in no methylthiolate-associated features imaged at room temperature.¹¹

In this work, we have studied structures of methylthiolates adsorbed on Au(111) at low temperature by using cryogenic STM. We were able to observe molecular arrangements of the methylthiolates at 110 K probably due to freezing of the fast

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motions. From low-temperature STM observations, we found that the room-temperature structure exhibiting the $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is transformed into a structure with an anisotropic lattice at 110 K. Furthermore, clustering of the surface methylthiolates was observed, which is similar to an adsorption system of atomic sulfurs on a hexagonal close-packed metal surface.¹² This structure is fundamentally different from the common structure observed for monolayers of thiolates with longer alkyl chains on Au(111).

The experiments were performed using an ultrahigh-vacuum (UHV) cryogenic STM system (JEOL, JSTM-4500XT). The STM chamber is linked to a second chamber for preparing and characterizing samples using LEED, Auger electron spectroscopy (AES), and thermal desorption spectroscopy (TDS).

Gold single-crystal thin films with (111) orientation were prepared on cleaved mica in another chamber using the vacuum deposition method. The Au(111) substrate was introduced into the UHV system and cleaned by Ar^+ bombardment and annealing. Cleanliness and ordering were confirmed by AES, LEED, and STM. The "herringbone" structure due to $23 \times \sqrt{3}$ reconstruction of clean Au(111) was clearly observed by STM. The clean Au(111) surfaces were exposed to gaseous dimethyl disulfide at room temperature, which is known to dissociate spontaneously into methylthiolates on Au(111) resulting in formation of methylthiolate monolayers.² Dimethyl disulfide was purified by a number of freeze-pump-thaw cycles before being used, and mass spectrometry confirmed that no significant impurities were present. The vapor of dimethyl disulfide was introduced onto Au(111) surfaces via a variable leak valve with a nozzle (hole diameter, 0.5 mm; nozzle length, 200 mm; distance from sample, 10 mm). Here, since the local pressure at the sample position during the exposure could not be precisely calibrated, we use readings of an ion gauge located 200 mm underneath the sample as apparent gas pressures. Saturated monolayers of methylthiolate were formed with exposures of more than 2 langmuirs ($1 \text{ langmuir} = 1 \times 10^{-6} \text{ Torr s}$; $1 \text{ Torr} = 133 \text{ Pa}$) in our vacuum system.

STM observations were carried out with the constant current mode using electrochemically prepared tungsten tips. Tunneling conditions used here were typically bias voltages ranging from 1 to 2 V and tunneling currents of around 50 pA. For low-temperature observations, the sample was cooled by liquid nitrogen stored in a coolant reservoir which is connected to the sample through highly flexible copper braids. Sample temperatures were measured with an alumel-chromel thermocouple directly attached to the sample. LEED observations for methylthiolate-covered Au(111) surfaces showed a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure at room temperature as reported before.^{10,11} Figure 1 shows a STM image of a methylthiolate-saturated Au(111) surface taken at room temperature. Although a monoatomic-height step of gold is imaged (top right), no methylthiolate-associated features are observed. This invisibility of the methylthiolates is probably due to a fast motion of the methylthiolates (surface diffusion and/or fluctuation of conformation) of which the time scale is shorter than the image acquisition time of our STM (typically 10 ms/line).¹³ Since thiolates with longer alkyl chains ($\text{CH}_3(\text{CH}_2)_n\text{S}$; $n \geq 1$) on Au(111) are visible with STM even at room temperature,^{5,14,15} the fast motion of methylthiolate may be caused by relatively weak methyl-methyl intermolecular interactions. It is interesting to note that a "chainlike" ordered structure of the surface thiolates is sometimes observed at regions near kinked steps along the substrate $\langle 121 \rangle$ direction (within fairly narrow regions of 30–50 Å width from the step edges) even at room temperature.¹⁶

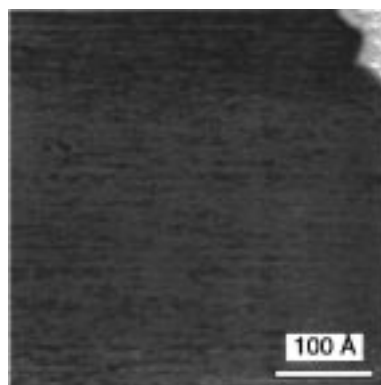


Figure 1. STM image of a methylthiolate-saturated Au(111) surface at room temperature. No molecular features are observed due to fast motions of the surface methylthiolates.

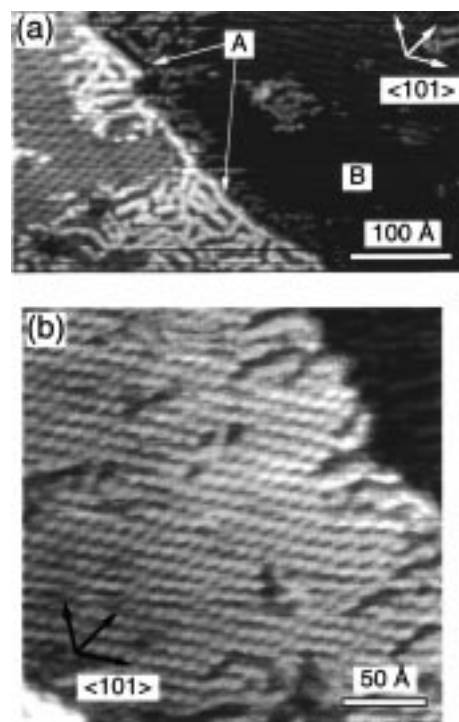


Figure 2. STM images of a methylthiolate-covered Au(111) surface at 110 K. (a) Two distinct types of structures are seen, i.e., a chainlike structure near a step edge (A) and a two-dimensionally (2D) ordered structure on terraces (B). (b) Close-up image of the 2D-ordered structure. Bright protrusions are aligned in rows along substrate $\langle 101 \rangle$ directions and arranged in a distorted hexagonal lattice.

The $\langle 121 \rangle$ step edges may provide the surface thiolates with a higher-binding-energy site, which results in formation of one-dimensional chains of the thiolates along the edges with the motion being locked. These chains may be incentive for formation of another one or two chains on the terraces through a suppression of the fast motion near step edges.

In Figure 2 are shown STM images of a methylthiolate-covered surface after cooling the sample down to 110 K. Two types of surface structures are seen in Figure 2a: a "short-chain" structure which is observed near a step (A) and a two-dimensionally (2D) ordered structure (B). Further STM observations for the short-chain structure at several different regions of the sample indicated that the chains lie mainly along $\langle 121 \rangle$ directions and tend to have an interchain spacing of ~ 15 Å. It should be noted that the direction and the interchain spacing of this chain structure is the same as those of the chain structure

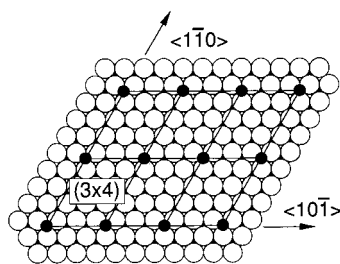


Figure 3. Schematic illustration of the distorted hexagonal lattice observed in Figure 2. The lattice points are assumed to be located at 3-fold hollow sites. This lattice has an oblique unit cell (8.64×11.52 Å), which corresponds to a commensurate (3×4) unit mesh of Au(111).

observed near step edges at room temperature. These facts suggest that the chain structure observed at low temperature originates from the step-induced chain structure formed at room temperature, though a few number of small clusters of the chain structure are seen on the terraces. These clusters might be induced by defects on the terraces. Continuous STM observations showed no evidence of time-dependent fluctuation of the structures, which indicates that no surface diffusion takes place inside the domains nor between the chain and the 2D-ordered domains at 110 K. The temperature-dependent structure transformation from the room-temperature structure to the “short-chain” and the 2D-ordered structures was found to be reversible. The possibility that these low-temperature structures are attributed to some other species, e.g., water molecules coming from a residual gas, can be excluded. Water can adsorb on the monolayers when the surface is cooled to 110 K since water molecules adsorbed on an alkylthiolate monolayer have been reported to desorb at 130–155 K.¹⁷ However, annealing of the sample at 180 K, which desorbs water molecules if present, gave rise to no change in the structure.

Figure 2b shows a close-up image of the 2D-ordered structure of methylthiolates formed at 110 K. A 2D-ordered arrangement of bright protrusions is seen on a terrace. This arrangement has a quasi-hexagonal lattice of which unit vectors are parallel to the $\langle 101 \rangle$ directions but have different lengths: 8.6 and 11.5 Å. The $\langle 101 \rangle$ directions are parallel to the substrate close-packed rows, and the unit-vector lengths are 3 and 4 times as long as the Au–Au interatomic distance (2.88 Å). Figure 3 shows a schematic of the 2D lattice for surface methylthiolates adsorbed on Au(111) at low temperature. The 2D lattice has an oblique unit cell with a commensurate (3×4) periodicity. The structure of the methylthiolate monolayer transforms from the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure to the (3×4) structure when cooled from room temperature to 110 K. A STM image of the (3×4) structure with higher resolution is shown in Figure 4. It is seen that one bright protrusion consists of four individual spots. If one individual spot corresponds to a single methylthiolate, the surface methylthiolates are considered to form tetramers at low temperature. The tetramers are observed to be slightly rotated from the $\langle 101 \rangle$ substrate directions. The apparent thiolate–thiolate distance within the tetramer is deduced from STM images to be 3.3 Å on average, which is rather smaller than that of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure (4.99 Å). According to the molecular dynamics calculations,¹⁸ alkylthiolate monolayers on facets of Au nanocrystals are “bundled” into groups of molecules with a contracted mean nearest-neighbor S–S distance by about 12% compared to that on a flat Au(111) surface. The present finding is not explained by this type of “bundling” of adsorbates, because the average area of the terraces on which the tetramers are observed is much larger

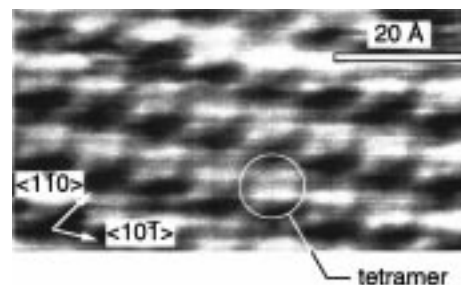


Figure 4. STM image with molecular resolution of the (3×4) structure. It is observed in this image that surface methylthiolates form tetramers. One (3×4) unit cell contains one tetramer, resulting in a molecular density of $1/3$ relative to the surface atom density of Au(111).

than that of the facets (5 atoms wide) of the calculated nanocrystals. Since one (3×4) unit cell contains one tetramer, the methylthiolate density is estimated to be $1/3$ of the surface atom density of Au(111), which is in agreement with a density at room temperature deduced from the observation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. This surface density has been widely accepted for various thiolates on Au(111).^{4,5,10,14,15}

It is somewhat surprising that the methylthiolate monolayer adopts the anisotropic lattice despite the simple hexagonal lattice of the Au(111)– (1×1) surface. In the case of (111) substrates of other noble metals, diffraction and STM studies showed that methylthiolate monolayers pack in a $(\sqrt{7} \times \sqrt{7})R10.9^\circ$ lattice on Ag(111)^{19,20} and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice on Cu(111),²¹ both of which are hexagonal. In the case of Au(111), thiolate monolayers with longer alkyl chains ($\text{CH}_3(\text{CH}_2)_n\text{S}$; $n \geq 5$) have been known to form an anisotropic $c(4 \times 2)$ superlattice of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice,^{3–5} which is interpreted in terms of the result of a patterned arrangement of rotations of the carbon-backbone planes about their molecular axes. For methylthiolate monolayers, however, this explanation is not the case since it has no carbon-backbone plane. Longer-alkyl-chain thiolates on Au(111) show another type of anisotropic lattice at low coverages, where the surface thiolates adopt a flat-lying configuration forming one-dimensional rows along the $\langle 121 \rangle$ direction.^{22,23} These lattices can be described with respect to the Au(111) lattice as a $p \times \sqrt{3}$ rectangular unit mesh, where p is the periodicity of the rows and almost equal to the length of the corresponding fully stretched dialkyl disulfide. The periodicity p is decreased as the chain length is shortened. In the case of methylthiolate, p should be close to the length of dimethyl disulfide, which is estimated to be 8.2 Å including the van der Waals radius of hydrogen. Although this value is comparable to one of the observed lattice constants (8.6 Å), neither the direction nor the length of another lattice vector ($\langle 101 \rangle$ direction, 11.5 Å) are in disagreement with those of the $p \times \sqrt{3}$ lattice ($\langle 121 \rangle$ direction, 5.0 Å). This indicates that the anisotropy of the methylthiolate lattice cannot be explained in terms of the $p \times \sqrt{3}$ lattice with the flat-lying adsorption geometry.

Very interestingly, the same oblique unit mesh has been observed for hydroxy-functionalized hexanethiol ($\text{HO}(\text{CH}_2)_6\text{SH}$) monolayers on Au(111) by Poirier et al.⁸ Furthermore, formation of “tetramers” was also found for this system, though the averaged intermolecular distance is about 20% larger than that in the present system. They attributed the anisotropic arrangement of hydroxyhexanethiol to strong end-group chemical interactions and also suggested that the formation of molecular tetramers is induced by the mutual hydrogen bonding

which has the directional nature. However, the observation of the similar packing for methylthiolate monolayers suggests a possibility that the driving force to form the packing is not associated with the terminal-group interaction but associated with Au–S interactions, since it is common for the both systems to have Au–S bonding. In fact, formation of sulfur clusters (S_n) has been observed on hexagonal close-packed metal surfaces such as Re(0001) ($n = 3, 4, 6$)¹² and Au(111) ($n = 8$).²⁴ In these sulfur clusters, the S–S distances are much larger than covalent S–S bond lengths (1.9–2.2 Å). The formation of sulfur clusters has been interpreted as evidence of substrate-mediated many-body forces.¹² The many-body forces may play an important role to form the thiolate tetramers on Au(111), though theoretical investigations are needed to elucidate their origin.

In conclusion, we have shown that methylthiolate monolayers on Au(111) have a two-dimensionally ordered structure with a commensurate (3×4) unit mesh on terraces and a chainlike structure mostly running along the $\langle 121 \rangle$ direction near step edges at 110 K. In the (3×4) structure, surface methylthiolates were observed to form tetramers. We emphasize that the methylthiolate monolayers adopt a significantly different two-dimensional structure compared to other thiolates with longer alkyl chains, probably due to weak methyl–methyl interactions. In such a case, Au–S interactions could be dominant in determining the molecular arrangement of monolayers.

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