

Surface and Adsorption Structures of Dialkyl Sulfide Self-Assembled Monolayers on Au(111)

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Surface and adsorption structures of dioctadecyl sulfide (DOS) self-assembled monolayers (SAMs) on Au(111) were examined by scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS). In comparison with alkanethiol or dialkyl disulfide SAMs, the molecularly resolved STM images clearly showed that DOS SAMs have significant structural differences in the formation of depressions and ordered domains, and in the lattice structure, including the presence of conformational defects in the ordered domains. In addition, the clear red shift of the Au–S stretching mode and the existence of the C–S stretching mode were also observed for DOS SAMs by HREELS measurements. The unique surface structure and the existence of such characteristic features at the Au–S and C–S stretching modes for DOS SAMs strongly support the intact adsorption of DOS molecules on Au(111).

Introduction

The spontaneous adsorption of organosulfur compounds on metal surfaces serves as a simple method for achieving a variety of modifications of the metal surfaces, resulting in the formation of organic self-assembled monolayers (SAMs).¹ It has been demonstrated that the resulting SAMs can be used as molecular templates for various technical applications such as wetting,² corrosion inhibition,³ molecular sensors,^{4–6} and nanopatterning.^{7–10} In particular, to understand fundamental aspects such as structures and self-assembly processes, the SAMs prepared by alkanethiols or dialkyl disulfides on gold have been extensively studied by a variety of surface characterization techniques.^{11–21} As a result, it is generally believed that adsorption of dialkyl disulfides on gold occurs via S–S bond cleavage and alkanethiols adsorb via S–H bond cleavage. Therefore, both compounds on gold form identical SAMs consisting of gold-bound thioliates.^{15–21}

Dialkyl sulfides are very stable against oxidation and other chemical reactions compared to alkanethiols or dialkyl disulfides. The chemical structures of dialkyl sulfides, which have different alkyl chains and/or different terminal functional groups, can also be modified easily by a simple synthetic method.^{22–24} Hence the SAMs prepared using dialkyl sulfides of two alkyl groups with various modifications are very attractive for revealing structure–property relationships, such as charge transfer or nanotribological properties with respect to the resulting various SAM structures.^{23,24} Compared to alkanethiol or dialkyl disulfide SAMs on gold, dialkyl sulfide SAMs show significantly different characteristics in structural ordering, adsorption kinetics, and thickness.^{22,23,25} Such different SAM characteristics between dialkyl sulfides and alkanethiols or

dialkyl disulfides can be attributed to a difference in the adsorption mechanism. Because Zhong and Porter²⁶ proposed that the adsorption of dialkyl sulfides on gold undergoes C–S bond cleavage, resulting in the formation of a gold-bound thiolate monolayer as with alkanethiol or dialkyl disulfide SAMs, the adsorption process for dialkyl sulfides has become an interesting subject in this research field. However, their recent study that was performed using carefully purified dialkyl sulfides showed evidence for the intact adsorption of molecules, without C–S bond cleavage.²⁷ Actually, this result is consistent with many of the results obtained by others.^{18,25,28–30}

On the other hand, only a few studies for dialkyl sulfide SAMs have been performed to reveal surface structures. From atomic force microscopy (AFM) measurements, it has been revealed that didecyl or dihexadecyl sulfide SAMs³¹ have a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° structure with intermolecular distances of approximately 4.9 Å, whereas dioctadecyl sulfide SAMs³² have an incommensurate structure with intermolecular distances of approximately 4.6 Å. In comparison with AFM measurements, scanning tunneling microscopy (STM) measurements often provide more detailed SAM structures with high-resolution images. To date, however, there is no STM result revealing a closely packed structure of dialkyl sulfide SAMs, although our previous STM study showed the formation of striped phases at the initial stage of SAM growth.²⁹

In the present study, based on high-resolution STM observation, we report unique surface structures for dioctadecyl sulfide SAMs on gold, which are quite different from those observed from alkanethiol or dialkyl disulfide SAMs. In addition, using high-resolution electron energy loss spectroscopy (HREELS), which is a powerful technique for clarifying the interfacial structures of adsorbed molecules on metal surfaces,^{33,34} we reveal a clear difference in the bonding features of sulfur headgroups between dialkyl sulfide SAMs and alkanethiol or dialkyl disulfide SAMs.

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Experimental Section

Octadecanethiol ($C_{18}H_{37}SH$, ODT) and dioctadecyl sulfide ($(C_{18}H_{37})_2S$, DOS) were purchased from Tokyo Chemical Industry (Tokyo, Japan). The ODT and DOS compounds were carefully purified by recrystallization several times from diethyl ether. Dioctadecyl disulfide ($(C_{18}H_{37})_2S_2$, DODS) was synthesized by a previously described method.³⁵ The purity of these compounds was confirmed by mass spectrometry. The Au(111) substrates on mica were prepared by vacuum deposition as reported in a previous paper.¹⁴ Organosulfur SAMs were prepared by dipping the gold substrates into a freshly prepared 1 mM diethyl ether solution of the corresponding compounds for 1 day. After the SAM samples were removed from the solutions, the SAM samples were rinsed thoroughly with pure diethyl ether to remove physisorbed molecules from the surface.

STM measurements were performed with a NanoScope E (Digital Instruments, Santa Barbara, CA) and a commercially available Pt/Ir tip (80:20). All STM images were obtained in air in the constant current mode, and the imaging conditions were a bias voltage of 0.8 V and a tunneling current of 0.12 nA.

HREELS measurements were carried out using an HREELS system equipped with a sample entry system under an ultrahigh-vacuum (UHV) of $\sim 2 \times 10^{-10}$ Torr (Specs GmbH: DELTA 0.5).^{36,37} All HREEL spectra were recorded at an incident angle of 60° from the surface normal. In the specular spectra of HREELS, the signals involve both dipole- and impact-scattering components. For the dipole-scattering components, the selection rule at observation is the same as that in infrared reflection adsorption spectroscopy³⁸ and is useful for characterizing the adsorption structures. To clarify the dipole-scattering components, off-specular spectra consisting of impact-scattering components were measured at the detection angle of 42° .

Results and Discussion

STM images in Figure 1 show surface structures of DOS SAMs on Au(111) formed after a 1-day immersion of the gold substrates in a 1 mM diethyl ether solution. As shown in Figure 1a, the SAMs consist of three different features: depressions (A region), closely packed and highly ordered phases (region B), and less ordered phases (region C). Actually, the surface structures of the monolayer are significantly different from those observed from alkanethiol or dialkyl disulfide SAMs. In particular, dialkyl sulfide SAMs on Au(111) show significant differences in the number, size, and distribution of depressions. A small number of large size depressions were observed in DOS SAMs, whereas it was found that alkanethiol or dialkyl disulfide SAMs are composed of a large number of small size depressions with a uniform distribution on the gold surface.^{13,14,21,39–41} In addition, the fraction of the areas of the depressions to the total surface area was measured to be approximately 1.4–2.0%, which is significantly less than the observed value of 6–8% from alkanethiol SAMs.^{40,41} Such noticeable differences in the formation of depressions for DOS SAMs can be ascribed to the weaker interaction between the sulfur headgroups of DOS molecules and gold compared to alkanethiols or dialkyl disulfides. It has been reported that adsorption of dialkyl sulfides occurs through physisorption.^{27,42,43} Due to this weaker interaction, it is expected that the gold atoms in the first gold layer during the self-assembly of dialkyl sulfides become highly mobile, resulting in the formation of a small number of large size depressions driven by edge tension.⁴⁴ For alkanethiol or dialkyl disulfide SAMs chemisorbed on gold, however, it was

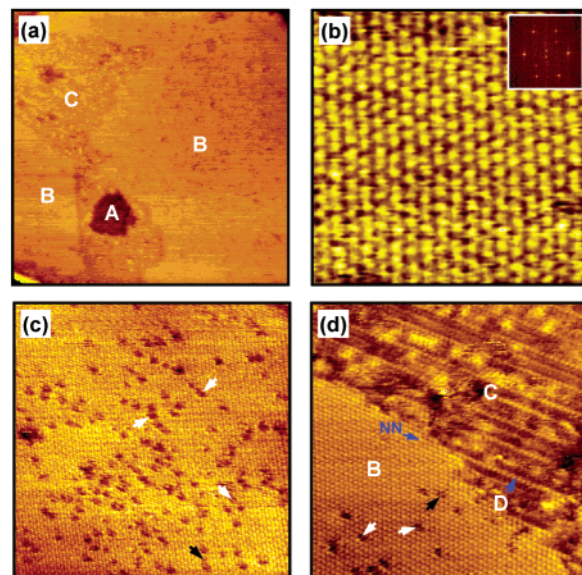


Figure 1. STM images of DOS SAMs on Au(111) formed after a 1-day immersion of the gold substrates in a 1 mM diethyl ether solution: (a) 80 nm \times 80 nm STM image showing three different features, i.e., less and highly ordered domains and one large depression; (b) 7 nm \times 7 nm high-resolution STM image showing a hexagonal packing structure (inset shows 2D fast Fourier transform); (c) 30 nm \times 30 nm STM image showing conformational defects in the highly ordered monolayer; (d) 22 nm \times 22 nm STM image exhibiting two domain structures consisting of less and highly ordered phases. Note that the white and black arrows indicate conformational defects in ordered domains. All STM images were obtained with a bias voltage of 0.8 V, and a tunneling current of 0.12 nA using the constant current mode.

found that similar depressions were formed as a result of the migration of the gold–adsorbate complex after annealing at high temperature.^{44,45} In both cases, van der Waals interactions between alkyl chains can be maximized via the coalescence of depressions.

In comparison with previous AFM observations,^{31,32} the STM image in Figure 1b clearly shows a molecularly resolved hexagonal packing structure of DOS SAMs on Au(111). The lattice constant observed from DOS SAMs is 4.5 ± 0.2 Å, which is nearly equal to that of 4.6 ± 0.2 Å, obtained from the same SAMs observed in a recent AFM study.³² From these results, it is considered that the lattice constant of dialkyl sulfide SAMs is relatively smaller than that of 5.0 ± 0.1 Å, obtained from alkanethiol SAMs.^{12,14,32,39–41} This difference in lattice structure may be due to different adsorption mechanisms between dialkyl sulfides and alkanethiols or dialkyl disulfides, as revealed in previous studies.^{18,25,27–30,32} Because two alkyl chains positioned at one sulfur atom are structurally confined due to the intact adsorption of dialkyl sulfides on gold, a change in the tilt and twist angles of alkyl chains in the packing structure of the monolayer would be expected as a result of the spatial rearrangement of alkyl chains in two-dimensional ordering process, resulting in the different lattice structures.

On the other hand, we should note that the observed structure for DOS SAMs on Au(111) is the result of the optimization of the SAM preparation procedures. It has been pointed out that the results on dialkyl sulfide SAMs show poor reproducibility because of uncontrollable experimental conditions such as degree of surface contamination, purity of the substance, and small fluctuations of temperature, which are of crucial importance for the quality of physisorbed dialkyl sulfide SAMs.^{22,27,32} This is the major reason for very different results by different groups. It can be also considered that such a poor reproducibility

is regarded as one of the intrinsic characteristics of dialkyl sulfide SAMs, which is related to the low reactivity of the monosulfide group with gold. As a matter of fact, similar problems in experimental reproducibility were found in this study. Even if SAM samples were prepared by the same experimental procedure, striped phases with a low surface coverage were occasionally observed for those SAM samples.

On the basis of the lattice structure of DOS SAMs on Au(111) obtained by STM, it is interesting to discuss the STM imaging mechanism for organic SAM films by comparing XPS and AFM results. Recently, XPS measurements have demonstrated that DOS SAMs form by the intact adsorption of molecules, suggesting a double-chain conformation of molecules on the gold surface, by comparing the relative peak intensities of S(2p)/Au(4f), C(1s)/Au(4f), and C(1s)/S(2p) for ODT and DOS SAMs, which were prepared by 1-day immersion of the gold substrates in 1 mM CH₂Cl₂ solutions at room temperature.³² Our XPS measurements have also shown that the relative peak intensity of C(1s)/S(2p) for DOS SAMs is measured to be roughly twice as large as that of ODT SAMs, reflecting the adsorption of DOS molecules without C–S bond cleavage (data not shown here). In addition, as described above, the lattice structure of DOS SAMs revealed by their AFM study³² is almost the same as that obtained by our STM study and is similar to that of ODT SAMs. From these results, we assume that the STM imaging mechanism is strongly related to the electronic states of the terminal methyl groups of DOS SAMs rather than those of sulfur headgroups adsorbed on the surface, whereas the STM imaging mechanism of SAMs is still hard to understand clearly and under discussion.⁴⁶

It is also found that DOS SAMs have a large single-ordered domain of more than 40 nm without depressions or domain boundaries (see region B in Figure 1a). More interestingly, many conformational defects in the ordered monolayer were clearly observed in STM images of Figure 1c,d (see white and black arrows). The height differences between the ordered monolayer and the defects were measured to be in the range from 0.5 to 1 Å. This result implies that the defects are not due to the removal of gold atoms in the first gold layer, i.e., depressions. Actually, individual molecules were also observed in the defect areas, as indicated by the black arrows. In general, such defects have never been observed in thiol SAM systems chemisorbed on gold. Therefore, we suggest that the origin of defects is related to weak association of dialkyl sulfide molecules on gold during the self-assembly process. A weakly adsorbed monosulfide group with two alkyl chains on gold has a much higher degree of freedom in spatial movement compared to the sulfur headgroup chemisorbed on gold. This allows two alkyl chains attached to the monosulfide group to have a more flexible motion in two-dimensional ordering process. In addition, although alkanethiols, in an all-trans conformation, are arranged with a tilt angle of about 30° from the surface normal, alkyl chains in dialkyl sulfide SAMs are hard to arrange in the form of the unidirectional molecular orientations with a certain tilt angle because of a double-chain conformation of the molecule. This results in no sharp domain boundaries in DOS SAMs, as shown in Figure 1a. It is also expected that alkyl chains would be two-dimensionally entangled with each other toward the optimization of van der Waals interaction between alkyl chains. Considering this adsorption configuration of alkyl chains for dialkyl sulfide SAMs on Au(111), the defect in ordered domains can easily be formed compared to alkanethiol or dialkyl disulfide SAMs. Conclusively, it is suggested that the defects observed from DOS SAMs are the result of a double-chain conformation

due to the weak association of molecules. From this STM observation, the formation of such defects can be considered as one of essential characteristics of dialkyl sulfide SAMs. However, it is hard to directly get the detailed information on the defect structure observed in nanometer-scale ordered domains by any other characterization techniques.

Figure 1d shows a high-resolution STM image revealing two domain structures with a highly ordered domain (region B) and a less ordered domain (region C). We should note that alkanethiol SAMs with high structural order can be formed within 10 min in a 1 mM solution.⁴⁷ Thus the conditions of our SAM preparation, i.e., a 1 mM concentration and a 1-day deposition time, seem to be sufficient for producing closely packed and well-ordered DOS SAMs on Au(111). However, the less ordered phase was still observed. This result probably reflects a complex in the adsorption behavior and ordering process of dialkyl sulfides during self-assembly. The existence of such structural inhomogeneity including the ordered and less ordered phases may be due to the local difference in surface contamination, as mentioned above. Several ordered molecular rows with intermolecular spacing of 4.5 Å were also found in the region C, and these rows tend to form along the nearest-neighbor (NN) direction of the hexagonal packing lattice. Moreover, the molecular row, indicated as D, is connected to ordered domains. Here we consider that the well-ordered DOS SAMs are formed via the formation of such molecular rows and the less ordered phase can be regarded as an intermediate phase that may appear during self-assembly. On the other hand, contact angle measurements revealed that dialkyl sulfide SAMs have lower water contact angles compared to alkanethiol or dialkyl disulfide SAMs.^{22,23,31,32} Therefore, we assume that the presence of conformational defects in ordered domains and structural inhomogeneity for dialkyl sulfide SAMs, found in this STM study, can be the main reasons for the observation of lower water contact angles.

Compared to alkanethiol or dialkyl disulfide SAMs on Au(111), DOS SAMs show considerably different characteristics in the formation of depressions and ordered domains, and in lattice structure, including the presence of conformational defects in the ordered domains. As mentioned above, these peculiar structural behaviors for DOS SAMs are attributed to the difference in the adsorption mechanism.

To compare adsorption structures of sulfur headgroups between dialkyl sulfides and alkanethiols or dialkyl disulfides on gold, we examined three different compounds with the same alkyl chain lengths, i.e., DOS, ODT, and DODS molecules. Figure 2 shows the specular and off-specular HREEL spectra of organosulfur SAMs on Au(111). On the basis of previous vibrational studies^{11,15,33,34,48–50} and our recent HREELS study of various alkanethiol SAMs on Au(111),³⁶ the peaks observed above 700 cm^{−1} are assigned to alkyl group vibrations and the peaks below 700 cm^{−1} are assigned to vibrations related to S atom motions, as listed in Table 1. The enhanced components in specular spectra with respect to those in off-specular spectra are dipole active vibrations reflecting the adsorption configuration.

The peaks related to the vibrations of alkyl groups observed above 700 cm^{−1} for DOS SAMs are nearly the same as those observed from ODT or DODS SAMs. This result means that DOS SAMs have a packing structure similar to ODT or DODS SAMs, as revealed by our STM study. In addition, the HREEL spectra for ODT and DODS SAMs are indistinguishable in the entire frequency region, reflecting the formation of identical monolayers via S–H bond cleavage in ODT and via S–S bond

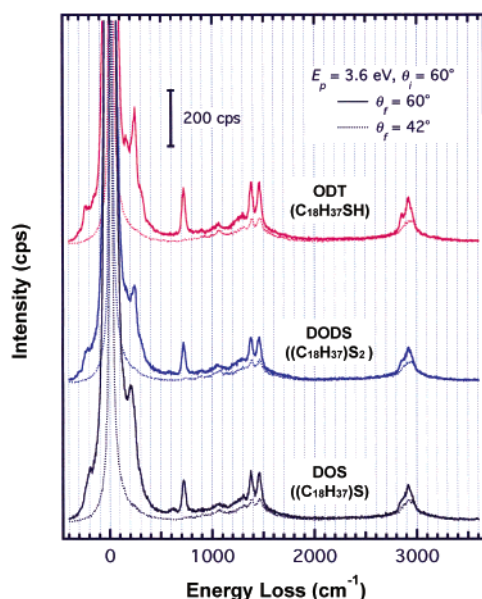


Figure 2. HREEL spectra of organosulfur SAMs on Au(111). The specular spectra detected at 60° and the off-specular spectra detected at 42° were plotted as solid and dotted lines, respectively.

TABLE 1: Assignment of the Observed Vibrations of Organosulfur SAMs on Au(111)^a

| mode/SAMs | ODT SAMs | DODS SAMs | DOS SAMs |
|--------------------------|----------|-----------|----------|
| C–H stretch | 2290 | 2920 | 2915 |
| | 2855 | 2855 | 2855 |
| CH ₃ d-deform | 1460 | 1460 | 1460 |
| CH ₂ scissors | | | |
| CH ₃ s-deform | 1380 | 1380 | 1380 |
| CH ₂ wag | 1300 | 1300 | 1300 |
| C–C stretch | 1050 | 1050 | 1050 |
| CH ₃ rock | 900 | 900 | 900 |
| CH ₂ rock | 720 | 720 | 720 |
| S–C stretch | | | 620 |
| SCC deform | 320 | 320 | |
| CCC deform | | | |
| Au–S stretch | 245 | 240 | 205 |
| | 170 | 165 | |

^a Vibration frequencies are given as wavenumber (cm^{−1}). The accuracy is approximately ±10 cm^{−1}.

cleavage in DODS. This HREELS result shows good agreement with the results obtained by many other techniques.^{15–21}

The most important feature of DOS SAMs on Au(111) was observed in the Au–S stretching mode. Although the intense peak of the Au–S stretching mode for ODT and DODS SAMs was observed at approximately 245 cm^{−1}, that of the Au–S stretching mode for DOS SAMs was observed at 205 cm^{−1}, as shown in Figure 2. The observation of such a clear red shift can be attributed to the weakness of the Au–S bond as well as the presence of two alkyl chains attached to one sulfur atom in DOS SAMs. In addition, the presence of the C–S stretching mode at 620 cm^{−1} for DOS SAMs also reflects the difference of adsorption structure between DOS and ODT or DODS. Therefore, it is reasonable to consider that the C–S–C bond of DOS remains in the SAMs. As described above, our HREELS measurements strongly support the intact adsorption of DOS molecules unlike the adsorption of ODT or DODS molecules on gold that occurs via S–H or S–S bond cleavages, respectively.

Conclusion

From STM and HREELS measurements, we clearly revealed that there are significant differences in the surface structure and

the adsorption structure of sulfur headgroups for DOS SAMs on Au(111) as compared with ODT and DODS SAMs. High-resolution STM images showed that DOS SAMs have different structural characteristics in the formation of depressions and ordered domains, and in the lattice structure, including the presence of peculiar defects in the closely packed and well-ordered domains. On the basis of STM, XPS, and previous AFM results for DOS SAMs, it is reasonable to consider that the STM imaging mechanism is strongly related to the electronic states of the terminal methyl groups of DOS SAMs rather than those of sulfur headgroups adsorbed on the surface. In addition, the clear red shift of the Au–S stretching mode and the existence of the C–S stretching mode in DOS SAMs were found by HREELS measurements. The significant differences in the surface structure and the adsorption structure of sulfur headgroups between DOS SAMs and ODT or DODS SAMs can be attributed to the intact adsorption of DOS molecules on Au(111), as revealed by other surface characterization techniques.

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