An HREELS Study of Alkanethiol Self-Assembled Monolayers on Au(111)

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The adsorption structures of alkanethiol self-assembled monolayers (SAMs) on Au were studied for various alkyl chain lengths [$CH_3(CH_2)_{n-1}SH$, where $n = 2, 4, 6, 8, 10, 11, 12, 14, 15, 16,$ and 18] in the frequency range from 150 to 3500 cm^{-1} by means of high-resolution electron-energy-loss spectroscopy (HREELS). In the spectra, we observed a clear odd–even effect depending on the alkyl carbon number, which confirms that the signals were obtained from well-ordered domains of alkanethiol SAMs. Thus, the multiple Au–S stretching modes observed for several alkanethiol SAMs correspond to multiple adsorption sites in the ordered alkanethiol SAMs on Au(111). The variety of the adsorption sites depending on the alkyl chain length implies that the adsorption sites in alkanethiol SAMs are not simple as generally believed, but instead are complicated.

Introduction

The interface structures between alkanethiol self-assembled monolayers (SAMs) and Au(111) surfaces remain controversial, even though much effort has been exerted in describing their adsorption configurations.[1–3] In the early studies, it was generally accepted that the stable adsorption site of the saturated alkanethiol SAMs on Au(111) at room temperature is unity, because a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° pattern was observed by helium atom diffraction[4,5] and low-energy electron diffraction (LEED).[6] The adsorption site was attributed to a hollow site on Au(111) by theoretical calculations.[7] Later, using scanning-tunneling microscopy (STM), the stable structure of alkanethiol SAMs on Au(111) was determined to be a $c(4 \times 2)$ structure consisting of different height protrusions on the ($\sqrt{3} \times \sqrt{3}$)-R30° lattice.[8–13] The $c(4 \times 2)$ diffraction was observed for various alkanethiol (C_n-thiol, $10 \leq n \leq 30$) SAMs on Au(111) by grazing incidence X-ray diffraction (GIXD),[14] where the authors commented that the single adsorption-site model is questionable.

Recently, theoretical investigations reexamined the adsorption site, and the most stable site was attributed to the bridge site rather than the hollow site.[15–18] Moreover, multiple adsorption-site models for alkanethiol SAMs on Au(111) have been suggested by several experimental studies using GIXD,[19] sum frequency generation (SFG),[20] X-ray standing wave (XSW) technique,[21] and high-resolution X-ray photoelectron spectroscopy (XPS).[22] For this controversy, vibrational spectroscopy at low-frequency regions will reveal the bonding features of sulfur headgroups.[15,23–25] In this study, we measured the vibration spectra of various alkanethiol SAMs [$CH_3(CH_2)_{n-1}SH$, where $n = 2, 4, 6, 8, 10, 11, 12, 14, 15, 16,$ and 18] on Au in the range from 150 to 3500 cm^{-1}, using high-resolution electron-energy-loss spectroscopy (HREELS). The spectra clearly showed low-frequency modes assigned to sulfur atom vibrations, in which multiple Au–S stretching modes for several alkanethiol SAMs were observed. On the basis of the clear vibration features, we discuss the interface structure between sulfur headgroups and Au surfaces.

Experimental Section

The saturated alkanethiol SAMs were formed on deposited gold films by immersion into 1 mM ethanolic solutions of alkanethiols for 1 day. The gold films (100 nm thick) were deposited onto freshly cleaved mica sheets that were prebaked at 320 °C under 10^{-5}–10^{-6} Pa before the deposition. After the deposition of gold, the substrates were annealed at 350 °C *in vacuo* for 2 h, by which large terraces exceeding 100–300 nm in diameter and a herringbone reconstruction characteristic of the clean Au(111) terraces were obtained. STM images of the alkanethiol SAM samples thus prepared showed well-ordered domains reflecting the symmetry of *fcc*(111), e.g., the $c(4 \times 2)$ domains at saturated coverage for $CH_3(CH_2)_5SH$ SAM[12] and $CH_3(CH_2)_7SH$ SAM.[13] In addition, little oxygen contamination was confirmed using conventional XPS.

HREELS measurements were performed in an ultrahigh-vacuum (UHV) system ($<2 \times 10^{-8}$ Pa) equipped with a sample entry system and a set of a monochromator and an electron energy analyzer (Specs GmbH: DELTA 0.5) for HREELS.[26] All spectra were measured at room temperature using a primary beam energy of 3.5 eV and an incidence angle of 60° from the surface normal. For the specular spectra, an intense elastic peak was obtained with a full width at half-maximum of about 3.5 meV. The typical elastic-peak current was 0.5 pA. The frequency accuracy for all spectra exhibited in the present report was about ±10 cm^{-1} (= 1.2 meV).

In the specular spectra of HREELS, the signals contain both dipole- and impact-scattering components. The selection rule for dipole-scattering is the same as that in the infrared reflection absorption spectroscopy (IRAS),[27] 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°, and were plotted with the specular spectra in the presented figures after the intensity correction for the detection angle difference assuming an isotropic distribution, i.e., the factor of cos60°/cos42°. We confirmed that all of the results presented in this paper were reproducible between different samples thus prepared.

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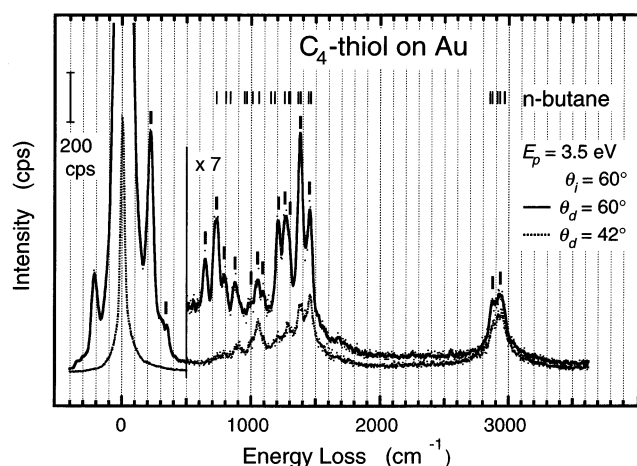‡ Local Spatio-Temporal Functions Laboratory, Frontier Research System.

Figure 1. HREEL spectra of butanethiol (C_4-thiol) SAM on Au. The specular spectrum (solid line) and the off-specular spectrum (dotted line) were measured at the detection angles of 60° and 42° with respect to the surface normal, respectively. Vibration frequencies corresponding to the kinds of C−H stretching, C−H bending, and C−C stretching modes of gaseous *n*-butane (C_{2h}) are indicated by thin solid bars.

Results and Discussion

Figure 1 shows the specular and off-specular HREEL spectra of butanethiol (C_4-thiol) SAM on Au. The enhanced components in the specular spectrum with respect to those in the off-specular spectrum are the dipole active vibrations that reflect its adsorption configuration. The large signals of these dipole active modes indicate the existence of well-ordered domains of the alkanethiol SAMs prepared in this study, because the dipole-scattering process is enhanced at the ordered domains as electron diffraction.

The observed vibrations at frequencies higher than 700 cm^{-1} correspond well to C−H stretching, C−H bending, and C−C stretching modes of gaseous *n*-butane,[28] as shown in Figure 1. Hence, these vibrations are assigned to those of the alkyl group, as listed in Table 1. These assignments agree with those of previous vibrational studies.[15,23−25,29−32] The other lower frequency vibrations are expected to be CCC deformation modes of the alkyl group and/or the modes of sulfur atom vibrations, i.e., S−C stretching, Au−S stretching, and SCC deformation.[15,23−25,31] The loss peak at 645 cm^{-1} is assigned to the C−S

stretching mode. The highest loss peak at 220 cm^{-1} is assigned to the Au−S stretching mode, because its transition dipole is parallel to the surface normal and the excitation cross-section is considered to be high in the specular spectra. The lack of the S−H stretching mode at about 2600 cm^{-1} is also consistent with this assignment of the Au−S stretching mode in C_4-thiol SAM on Au. A broad shoulder at about 340 cm^{-1} can be assigned to SCC and/or CCC deformation modes.

Figure 2 shows the HREEL spectra of the alkanethiol SAMs with even carbon numbers (C_{even}-thiol SAMs) on Au. There are no significant frequency shifts of the vibrations at the alkyl group, whereas relative peak intensities differ depending on the alkyl chain length. Hence, it is concluded that the assignment for C_4-thiol SAM is applicable to other alkanethiol SAMs on Au, as summarized in Table 1.

For the specular spectra of even-carbon-number thiol SAMs, one typical feature observed at alkyl group vibrations is the increase in intensity of the three peaks ascribed to the CH_2 rocking mode at 720 cm^{-1}, the CH_3 s-deformation mode at 1380 cm^{-1}, and the overlapping peak of the CH_3 d-deformation and CH_2 scissoring modes at 1460 cm^{-1}. According to the selection rule of dipole-scattering,[33] the increase in intensity implies that the alkyl chain axis is tilted from the surface normal and the alkyl carbon plane has both the surface perpendicular and parallel components. This is consistent with previous studies, in which it has been proposed that the alkyl chain axis is tilted 30−45° from the surface normal[7,14,29,30,34] with the alkyl carbon plane rotated by an angle around the alkyl chain axis.[30]

Figure 3 shows another set of HREEL spectra that include those of odd-carbon-number thiol SAMs, i.e., C_{11}- and C_{15}-thiol SAMs, on Au. In the specular spectra, the signal intensities of the CH_3 s-deformation mode at 1380 cm^{-1} clearly alternate depending on odd and even numbers of alkyl carbons, i.e., the odd−even effect.[30,32] This has been understood because the −CH_3 end group tends to the surface normal or the surface parallel depending on the alkyl carbon number, as shown in the inset of Figure 3. A weak odd−even effect consistently appears in the CH_3 rocking mode at 895 cm^{-1}; there is a signal intensity increase of the CH_3 rocking mode for the odd-number-carbon thiol SAMs, as shown in Figure 3. So far, the odd−even effect has been clearly observed for the CH_3 stretching modes using IRAS with a good resolution (typically 2−4

TABLE 1: Assignment of the Observed Vibrations of Alkanethiol SAMs on Au by HREELS[a]

mode		C_2	C_4	C_6	C_8	C_{10}	C_{11}	C_{12}	C_{15}	C_{16}	C_{18}
C−H stretch	{	2925	2935	2930	2925	2925	2920	2920	2920	2920	2920
		2850	2875	2865	2860	2855	2855	2860	2855	2855	2855
CH_3 d-deform CH_2 scissors	}	1460	1450	1455	1455	1460	1460	1460	1465	1460	1460
CH_3 s-deform		1380	1380	1380	1380	1380	1375	1380	1375	1380	1380
CH_2 wag		1300	1300	1300		1315	1305	1300	1295	1285	1300
CH_2 twist		1240	1260	1250	1265	1250	1255	1230	1240		
CH_3 rock			1210	1195	1190						
			1090								
C−C stretch	{	1050	1050	1050	1050	1055	1065	1055	1060	1060	1060
			1000								
CH_3 rock		900	875		915	895	895	895	890		900
CH_2 rock	{	720	790	810	715	715	815	725	720	720	720
			730	720			715				
S−C stretch			645	650							
SCC deform CCC deform	}	≈410	≈340	≈390	385	≈310	≈330	≈400	≈360	≈350	≈320
				≈290				≈320			
Au−S stretch	{	320			255			250	≈280	265	245
		250	220	220	225	230	225	215	≈210	230	170
		210								180	

[a] Vibration frequencies are given in wavenumbers [cm^{-1}]. The accuracy is about ±10 cm^{-1}.

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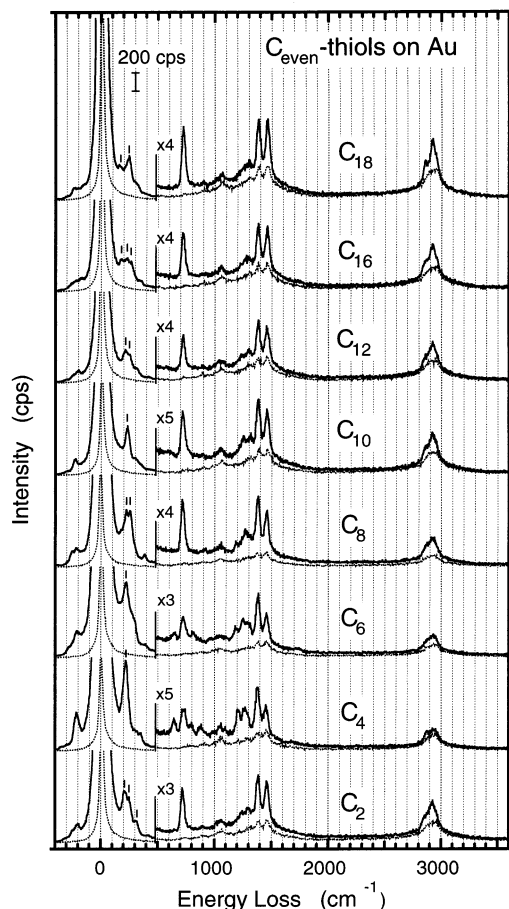*J. Phys. Chem. B, Vol. 106, No. 37, 2002* **9657**

Figure 2. HREEL spectra of even-carbon-number alkanethiol SAMs (C_{even}-thiol SAMs) on Au. The specular spectra detected at 60° and the off-specular spectra detected at 42° were plotted as solid and dotted lines, respectively. The measurement conditions were the same as those of Figure 1.

Figure 3. Odd-even effect on HREEL spectra of various alkanethiol (C_n-thiol) SAMs on Au. The specular spectra detected at 60° and the off-specular spectra detected at 42° were plotted as solid and dotted lines, respectively. The measurement conditions were the same as those of Figure 1. Inset shows the schematic models of odd- and even-carbon-number thiols on Au.

cm^{-1}).[30,32] At our HREELS measurements, the odd−even effect unfortunately was not confirmed for the observed C−H stretching modes, because the resolution (≈ 30 cm^{-1}) was not enough and the overlapped impact-scattering components made difficulty for deconvolution of each dipole-scattering component, in contrast to a significant advantage in intensity at the low-frequency region.

Note that the dipole-scattering components of the CH_3 s-deformation mode almost disappear in the specular spectra of the odd-carbon-number thiol SAMs after the impact-scattering components are subtracted. If signals were evenly obtained from the ordered and disordered SAMs, the odd−even effect would not appear. Therefore, the clear odd−even effect for strong dipole active modes is the certain evidence that the dipole-scattering components are *preferentially* obtained from the well-ordered domains on Au(111) terraces, although there are grain boundaries on our evaporated Au films. Such preferential detection is adequate for the dipole active mode measurement in the specular spectra, because the signal intensity increase in dipole scattering at the specular position, i.e., the (00) spot for LEED, is the same as that of electron diffraction.

The most important feature in the spectra is the variety of Au−S stretching modes observed at about 220 cm^{-1}, as marked in Figures 2 and 3. The strong signals in the specular spectra imply that the signals come from the well-ordered domains, as mentioned above. In addition, the multiple Au−S stretching modes in the specular spectra of several alkanethiol SAMs on Au were observed. The frequency difference exceeds 30 cm^{-1}.
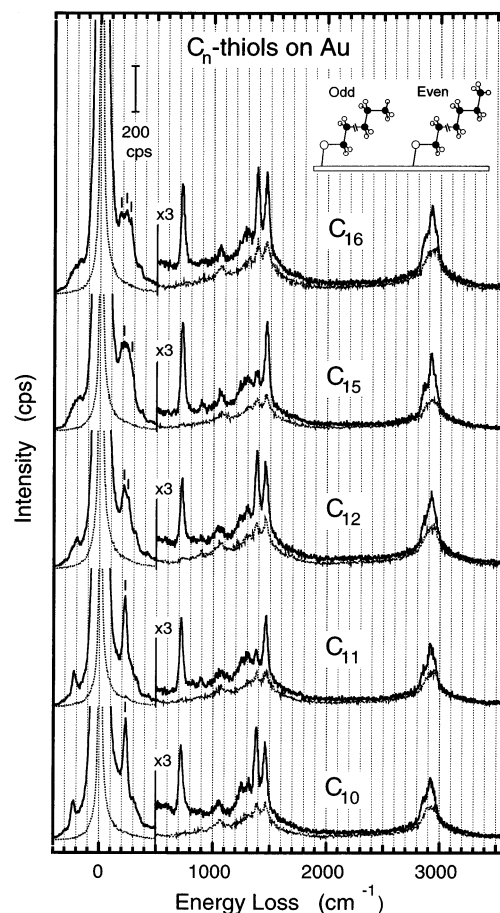
The large frequency difference in the Au−S stretching modes can be attributed to the difference in adsorption site. According to the nearest-neighbor force-constant model,[35] the frequency of the stretching mode between substrate and adsorbates sensitively decreases with increasing ligancy at the adsorption sites. Hence, we propose that the observed multiple Au−S stretching modes reflect the presence of multiple adsorption sites in ordered alkanethiol SAM on Au(111). Moreover, the adsorption sites strongly depended on the alkyl chain length, whereas the $c(4 \times 2)$ diffraction was observed for various alkanethiol (C_n-thiol, $10 \leq n \leq 30$) SAMs on Au(111).[14] In particular, longer alkanethiol SAMs show more intricate Au−S stretching modes. These imply that the interface structure between alkanethiol SAM and Au(111) is a result of competitive interactions not only between the sulfur headgroup and the Au substrate but also between alkyl groups.

The presence of multiple adsorption sites in stable alkanethiol SAMs on Au(111) has also been pointed out by recent experimental studies.[19−22] Fenter et al. proposed a disulfide model for C_{10}-thiol SAMs on Au(111),[19,21] in which sulfur atoms form bonds with each other and occupy different adsorption sites. The observed $(\sqrt{3} \times \sqrt{3})R30°$ lattice has been considered to be a result of the spatial relaxation of the alkyl groups. The model explains well the coverage dependence of the structures generally observed, i.e., the $c(4 \times 2)$ structure for the saturated SAM and the $p(m \times \sqrt{3})$ structures for unsaturated SAMs.[21] However, we did not observe an S−S stretching mode in

any spectra of the alkanethiol SAMs. The S−S stretching mode at about 575 cm^{-1} was observed only after heating the samples, as reported by Kluth et al.[24] If Fenter's disulfide model holds, the S−S stretching mode will most likely to be detected in the specular spectra, because the paired sulfur atoms occupy different positions in height on the substrate.[19,21] In addition, the dissociative adsorption of dialkyl disulfide on Au has been confirmed using experimental and theoretical techniques.[15,17,36,37] These clearly show that the S−S bond is not stable on Au surfaces. It is considered that sulfur atoms in alkanethiol SAMs are adsorbed as gold-bound monomers, and not as the dimerized form of sulfur headgroups at room temperature. We suggest that the pairing structure proposed by Fenter et al. may be formed by an indirect interaction through the Au substrate rather than the direct S−S chemical bond. The indirect interaction can be expected because the alkanethiol adsorption causes the torsion of the surrounding Au atoms[15,17] and a part of the torsion is possibly released by additional adsorptions.

Conclusion

The adsorption structures of alkanethiol SAMs on Au were studied using HREELS. Here, we compared the vibration spectra for various alkanethiol SAMs in the range from 150 to 3500 cm^{-1}. Because a clear odd−even effect was observed in the specular spectra, it was confirmed that the detected signals were mostly obtained from the well-ordered domains on Au(111) terraces. In addition, the multiple Au−S stretching modes for several alkanethiol SAMs on Au were observed simultaneously, on the basis of which we propose the existence of multiple adsorption sites in ordered alkanethiol SAMs on Au(111). Moreover, the observation of various adsorption sites depending on the alkyl chain length reflects the complexity of the interface structures. The interface structure is a result of the competitive interactions not only between the sulfur headgroup and the Au substrate but also between alkyl groups, whereas the alkyl groups are stabilized in closely packed structures such as $c(4 \times 2)$ based on the $(\sqrt{3} \times \sqrt{3})R30°$ lattice.

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