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# Adsorption state of diethyldisulfide on Au(111) studied with a combined system of HREELS and STM

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**Abstract**

The adsorption behavior of diethyldisulfide (DEDS), $CH_3CH_2S_2CH_2CH_3$, on Au(111) was investigated using a combined system of high-resolution electron energy-loss spectroscopy (HREELS) and scanning tunneling microscopy (STM). At low exposure (0.5 L), all vibration modes of ethylthiolate on Au(111) were observed by HREELS, and linear chains were recognized in STM images. At 100 L, some loss peaks decreased drastically in intensity and bright spots appeared in STM images. At low exposure, the ethylthiolate moiety tends to form a chain structure on Au(111) with the terminal sulfur bonded to gold. The ethyl group is randomly oriented. At an exposure of 100 L, the orientation of the molecules is fixed, with the C—C bond of the ethyl group parallel to the surface due to the interaction between neighboring molecules. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Adsorption; Diethyldisulfide; Gold; High resolution electron energy loss spectroscopy; Scanning tunneling microscopy

## 1. Introduction

Recently, studies of ultrathin organic films have been motivated by their technological applications in the fields of microelectronics, non-linear optics, biosensors, and so on [1,2]. Self-assembled monolayer (SAM) films of alkanethiol or disulfide on noble transition metals such as gold have attracted significant interest as a consequence of their stability and high ordering. Many studies about the adsorption of alkanethiol or disulfides on Au(111) have been conducted using scanning tunneling microscopy (STM) [3–5]. However, there are still many fundamental problems about SAM films to be resolved, such as their structures and adsorption processes. Using STM images alone, we cannot obtain detailed pictures of the adsorption state of molecules on the surface, such as the orientation of admolecules.

High-resolution electron energy-loss spectroscopy (HREELS) enables us to observe modes that are invisible in the infrared (IR) spectrum because of the impact scattering mechanism. In the specular scattering geometry, we can observe vibration modes that are normal to the surface; modes which are parallel to the surface are very weak due to the image charge effect [6,7]. In contrast, impact scattering results in a relatively homogeneous distribution of scattered electrons. By measuring the spatial distribution of electrons, we can distinguish vibration modes with components normal to the surface from others.

Studies of SAM films investigated by HREELS have been reported previously [8]. However, there has been no report about the structural variation

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of a SAM film measured with a combined system of HREELS and STM. We discuss the structural variation of diethyldisulfide (DEDS) according to its coverage and the geometries of DEDS on Au(111).

## 2. Experimental

Experiments were performed in an ultrahigh vacuum chamber equipped with facilities for HREELS and STM (JEOL, JSTM-4500XT), as well as ordinary tools of surface science such as low-energy electron diffraction (LEED) optics, an ion gun, an Auger electron spectrometer (AES) and a quadrupole mass spectrometer. The base pressure was kept below $1.5\times10^{-8}$ Pa. The HREEL spectrometer (Vacuum Science Instruments) consists of a fixed two-stage monochromater and a one-stage rotatable analyzer. The incident electron energy was fixed at 4 eV. HREEL spectra were recorded in both specular and off-specular scattering geometries. The typical resolution for the adsorbate-covered surface was 11–30 $cm^{-1}$ [full-width at half-maximum (FWHM)].

Au(111) used as the substrate was an evaporated film on mica (1000 Å thick). This sample was fixed on a ceramic heater, and its temperature was measured with a thermocouple. The sample was cleaned by argon-ion sputtering and annealing (at 670 K) procedures. Surface cleanliness was monitored by AES, and the Au(111)-$22\times\sqrt{3}$ reconstruction features were observed by STM. STM images were collected at room temperature in the constant current mode. The STM tip was made of polycrystalline tungsten. The gas exposures of DEDS are expressed in Langmuir [1 Langmuir (L) $=1.33\times10^{-4}$ Pa s], determined by the time of exposure and the pressure of DEDS. The DEDS pressure was measured by an ion gauge without normalizing the ion sensitivity factor for DEDS. DEDS was purified by degassing in several freeze–pump–thaw cycles prior to use. DEDS was introduced into the vacuum chamber through a variable-leak valve.

## 3. Results

Fig. 1 shows the energy-loss spectra at different exposures (0.5 L, 10 L and 100 L at room temperature), recorded in the specular scattering geometry (angle of incidence $\theta_i=55^\circ$ and angle of scattering $\theta_s=55^\circ$ with respect to the surface normal).

The assignment of each loss peak is shown in Table 1. We calculated the value of each frequency for an ethylmercaptan molecule using GAUSSIAN 94. The basis set for this calculation was 6-31G(d). The frequencies calculated at the Hartree–Fock level contain known systematic errors due to the lack of electron correlation, resulting in 10% to 12% higher frequencies. Accordingly, the calculated frequencies were scaled by an empirical factor of 0.89 [9].

After exposure of 0.5 L, we could recognize all vibration modes of the molecule except vibration relating to an S—H bond as shown in Fig. 1. Since the reflectivity from the surface was too low at this exposure, we degraded the resolution to 30 $cm^{-1}$ in order to achieve a better signal-to-noise ratio. After exposure of 10 L, the reflectivity recovered, and the elastic peak was apparently more intense than that for 0.5 L. In addition, the peak for the Au—S stretching mode became sharp

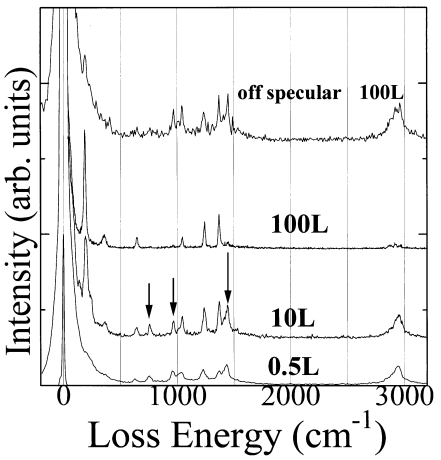


Fig. 1. HREEL spectra of DEDS measured in the specular scattering geometry at different exposures (0.5 L, 10 L and 100 L) and the 11.5° off-specular spectrum at 100 L ($\theta_i=55^\circ$, $\theta_s=65.5^\circ$).

Table 1
Assignment of the vibration peaks (in $cm^{-1}$). The calculated values for the vibration modes of an ethylmercaptan molecule, $CH_3CH_2SH$, in the gas phase were obtained by using GAUSSIAN 94 (restricted Hartree–Fock level), with an empirical correction factor of 0.89 [9]

| | Observed in spectra | Gaseous $CH_3CH_2SH$ (calculated) |
|---|---|---|
| Au−S | 187 | – |
| C−C−S deform | 361 | 293 |
| C−S stretch | 648 | 651 |
| $CH_2$ rock | 756 | 765 |
| C−C stretch | 966 | 951 |
| $CH_3$ rock | 1043 | 1031 |
| $CH_2$ twist | 1237 | 1243 |
| $CH_2$ wag | 1370 | 1295 |
| $CH_3$ s-deform | 1450 | 1398 |
| $CH_3$ d-deform | not resolved | 1463 |
| $CH_2$ scis | | 1464 |
| S−H stretch | – | 2595 |
| $CH_3$ d-stretch | 2950 | 2926 |
| $CH_3$ s-stretch | not resolved | 2868 |
| $CH_2$ d-stretch | | 2926 |
| $CH_2$ a-stretch | | 2950 |

and strong. At an exposure of 100 L, each peak was substantially sharpened and the intensities of some peaks decreased drastically ($CH_2$ rocking, C−C stretching, $CH_3$ s-deformation, $CH_3$ d-deformation, $CH_2$ scissors and series of C−H stretching). The background signal became much lower than those of the other spectra.

An off-specular spectrum ($\theta_i = 55°$, $\theta_s = 66.5°$) at 100 L exposure is shown in Fig. 1. This spectrum contains some peaks that are not involved in the specular spectrum; these peaks correspond to the peaks that decreased in intensity in the specular spectrum at 100 L.

Fig. 2 shows STM images of DEDS on Au(111) at different exposures. As shown in Fig. 2a, the molecules on the surface seem to form linear chains. In this STM image, molecular chains are not well ordered at an exposure of 0.5 L. Distances between the chains vary from 0.9 nm to 1.7 nm. Fig. 2b shows an STM image at an exposure of 10 L. In this image, the distance between each pair of neighboring lines is 1.08 nm, but the line is sporadically incomplete. Fig. 2c, measured at an exposure of 100 L, shows a perfect stripe pattern. The distance between the stripes is 1.08 nm. We can recognize bright spots in the stripes. The distance between the spots along the stripe is 0.6 nm. It was impossible to observe clear, bright spots at exposures below 100 L.

## 4. Discussion

At exposures of DEDS on Au(111) below 100 L, all the vibration modes of ethylmercaptan except vibrations relating to the S−H bond were observed. The vibrational peak assignable to the S−S stretching mode was not observed in the specular spectra nor in the off-specular spectra. (The off-specular spectra are not shown.) These facts mean that the S−S bond of DEDS splits spontaneously on Au(111), and DEDS adsorbs on Au(111) as ethylthiolate.

At an exposure of 0.5 L, one-dimensional chains were seen in STM images as shown in Fig. 2a. Judging from the AES intensities for sulfur, the coverage of ethylthiolate at 0.5 L is far less than that at 100 L. However, the domains of the chain-like features prevail in area even at 0.5 L. This means that the density of ethylthiolate along the chain is less than that at 100 L. The location and orientation of ethylthiolate are considered to fluctuate along the chain. This speculation about the adsorption state of ethylthiolate at 0.5 L contrasts with experimental findings such as the rather diffuse shape and the large width of the each chain, the low intensity of the elastic peak in HREELS and the low intensity of the Au−S stretching mode.

With increasing exposure of DEDS, the average distance between the chains decreases, and the chains become longer. After 10 L exposure, distances between chains reached an almost constant value of 1.08 nm, although the coverage of ethylthiolate continued to increase as the exposure exceeded 10 L. This means that the density of the chains on the surface is almost uniform above 10 L. Since the coverage of ethylthiolate at 10 L is substantially lower than that at 100 L, the density

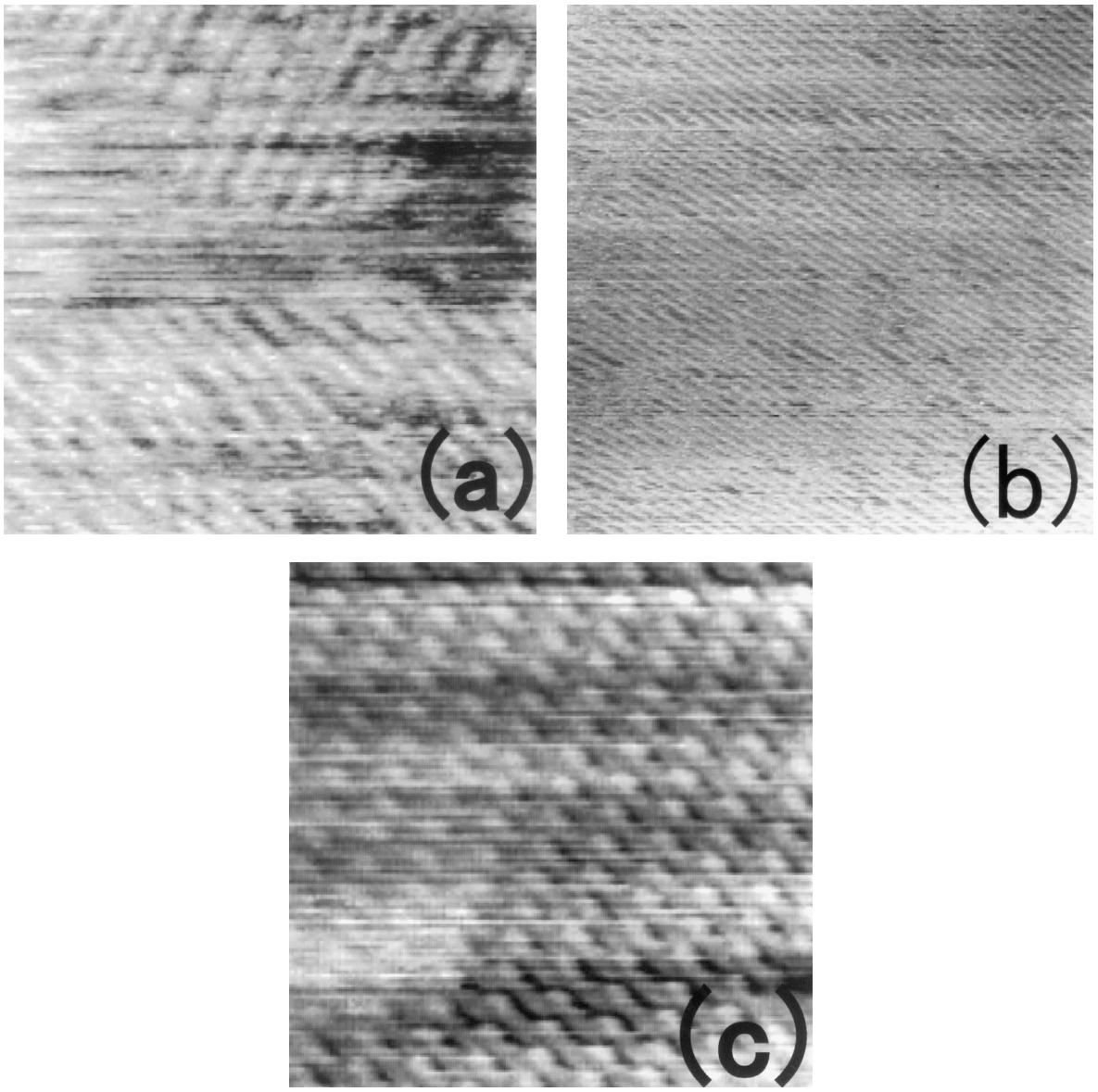


Fig. 2. STM images of DEDS monolayers on Au(111) at various DEDS exposures [(a) 0.5 L, (b) 10 L and (c) 100 L]. (a) Tunneling current $I=0.1$ nA, sample bias $V_s=2.0$ V, image size $=30.5$ nm $\times 30.5$ nm; (b) $I=0.2$ nA, $V_s=2.0$ V, image size $=65$ nm $\times 65$ nm; (c) $I=0.2$ nA, $V_s=2.0$ V, image size $=9.5$ nm $\times 9.5$ nm.

of ethylthiolate along the chain is lower than that at 100 L. Since the intensity of the Au—S stretching mode in the specular spectrum of HREELS is strong at DEDS exposures above 10 L, the location of sulfur is considered to be the same as for the above 10 L, although all possible sites are not occupied below 100 L. Since we cannot observe clear bright spots along the chain in STM images and all the vibration modes are observed in the specular HREEL spectrum at 10 L, ethylthiolates were changing their position between the adsorption sites faster than the scanning speed of the tip

of the STM with random orientation of ethylthiolate moieties.

At 100 L exposure, bright spots are observed along the chain in STM images along with a decrease of some of the peaks in the HREEL spectrum. Ethylthiolate seems to be locked in a rigid, two-dimensional crystal. The appearance of a well-ordered structure contrasts with the recovery of reflectivity of the HREELS electron beam. The decrease of some of the peaks in the HREEL spectrum provides us information about the geometry of the molecules on the surface, as mentioned in the Introduction.

In the specular scattering geometry, only the modes that have a transition dipole moment perpendicular to the surface should appear. The intensities of the peaks corresponding to $CH_2$ rocking ($756\,cm^{-1}$), C—C stretching ($966\,cm^{-1}$), $CH_3$ s-deformation ($1450\,cm^{-1}$), $CH_3$ d-deformation ($1450\,cm^{-1}$), $CH_2$ scissors ($1450\,cm^{-1}$) and a series of C—H stretching modes (around $2950\,cm^{-1}$) decreased in the specular HREEL spectrum at 100 L. Their weak intensities in the specular geometry indicate that these losses were manifested by the impact scattering mechanism. The peaks that were weak in the specular geometry became stronger in the off-specular geometry than the other modes. We can conclude that the transition dipoles of the vibrational modes described above are parallel to the surface. As shown in Fig. 1, the Au—S stretching mode is intense in the specular spectra above 10 L, but it decreased drastically in the off-specular scattering geometry. This indicates that the Au—S stretching mode has a strong dipole moment perpendicular to the surface.

The sulfur atom of ethylthiolate is believed to be located at a hollow site of Au(111). However, further study is necessary to establish the position of the sulfur atom exactly. It should be stressed that a combined system of HREELS and STM is very useful for following the structural evolution of organic molecules on single-crystal metal surfaces.

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