Functional Group-Selective Adsorption Using Scanning Tunneling Microscopy

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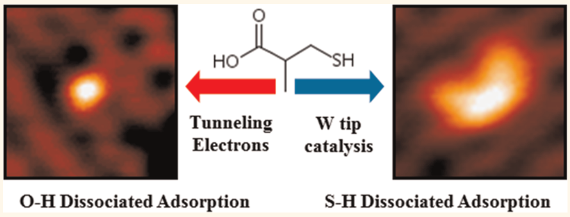
ABSTRACT



In this study, we selectively enhanced two types of adsorption of 3-mercaptoisobutyric acid on a Ge(100) surface by using the tunneling electrons from an STM and the catalytic effect of an STM tip. 3-Mercaptoisobutyric acid has two functional groups: a carboxylic acid group at one end of the molecule and a thiol group at the other end. It was found that the adsorption occurring through the carboxylic acid group was selectively enhanced by the application of electrons tunneling between an STM tip and the surface. Using this enhancement, it was possible to make thiol group-terminated surfaces at any desired location. In addition, *via* the use of a tungsten STM tip coated with a tungsten oxide (WO_3) layer, we selectively catalyzed the adsorption through the thiol group. Using this catalysis, it was possible to generate carboxylic acid group-terminated surfaces at any desired location. This functional group-selective adsorption using STM could be applied in positive lithographic methods to produce semiconductor substrates terminated by desired functional groups.

KEYWORDS: STM · bifunctional molecule · selective adsorption · tunneling electron · tungsten oxide · catalysis

The adsorption and termination of organic molecules on semiconductor surfaces has attracted much attention due to the potential uses of these modified surfaces in biosensor applications.[1−6] Organic molecules for biosensors are composed of at least two functional groups, one for anchoring to the surface and the other to give the desired biosensitivity. However, the two functional groups in the organic molecules adsorb on the surface competitively, leading in many cases to undesired termination and poor biosensitivity. Hence, to achieve the precise production of biosensors and to optimize the biosensitivity, the ability to anchor bifunctional molecules through selected functional groups is essential.

Recently, scanning tunneling microscopy (STM) has been widely applied to control surface reactions at the molecular scale. In most cases, the electrons tunneling between the STM tip and the surface are responsible for the STM-induced surface reactions. In these cases, the electronic or vibrational excitation of adsorbed molecules is induced by the tunneling electrons, and as a result, surface reactions only occur under the tip.[7−13] The electric field or mechanical force between the tip and the surface may also cause surface reactions in specific areas.[14,15] In rare cases, the STM tip acts as a chemical catalyst for surface reactions.[16,17] We previously reported that the WO_3 layer on a W STM tip catalyzed the S−H dissociated adsorption of thiol molecules (phenylthiol, 1-octanethiol) on a Ge(100) surface.[17] Although there are many factors controlling surface reactions such as these, most STM-induced surface reactions have been limited to simple reactions, and the control of complex surface reactions such as the functional group-selective adsorption of a bifunctional molecule has not yet been reported.

Considering the variety of factors that induce surface reactions, we developed a new idea to control the functional group-selective adsorption using STM. The idea concerns the fusion of the electrons tunneling between an STM tip and a surface and the catalytic effect produced by STM tip; specifically, (1) the tunneling electrons selectively enhance one of the two types of adsorption of a bifunctional molecule, and (2) the other type of adsorption is selectively catalyzed using the STM tip coated by the catalytic material, which enhances this adsorption process. If this concept were realized, the functional group-selective adsorption of bifunctional molecules could be controlled using an STM.

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To realize this concept, the present study investigated the adsorption of 3-mercaptoisobutyric acid on a Ge(100) surface using an STM. 3-Mercaptoisobutyric acid is a bifunctional molecule that has a carboxylic acid group at one end and a thiol group at the other, as shown in Figure 1A. At room temperature, 3-mercaptoisobutyric acid molecules adsorbed on the surface through the carboxylic acid groups; the thiol groups did not participate in the adsorption. When electrons tunneling between an STM tip and the surface were applied in the presence of the molecules, the adsorption of the carboxylic acid groups was enhanced in this area. A thiol group-terminated area could therefore be obtained wherever desired. Conversely, by scanning the surface with an STM tip coated with a WO_3 layer, we were able to selectively catalyze the adsorption *via* the thiol groups. It was found that this catalysis only acted to cause the adsorption *via* the thiol groups, and the carboxylic acid groups did not participate in the adsorption. Thus, using this catalysis, a carboxylic acid group-terminated surface could be obtained wherever desired. To our knowledge, the present work here constitutes the first report of functional group-selective adsorption using this concept, that is, the fusion of the electrons tunneling between an STM tip and a surface and the catalytic effect produced by an STM tip.

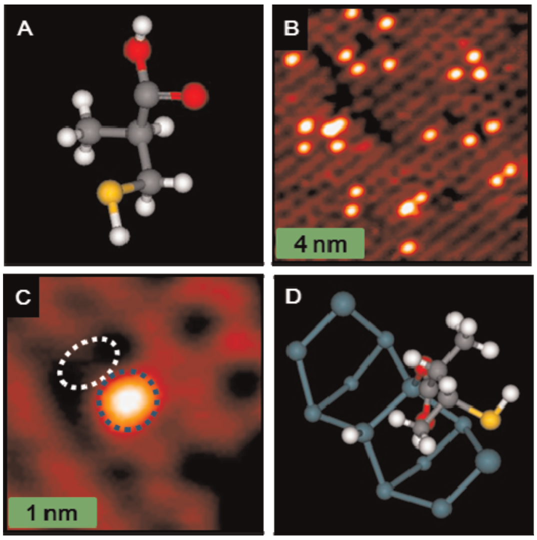

Figure 1. **(A) Schematic illustration of 3-mercaptoisobutyric acid. red, O; yellow, S; gray, C; white, H. (B) Filled-state STM image (12.00 nm × 12.00 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of the Ge(100) surface at low 3-mercaptoisobutyric acid coverage ($\theta = 0.05$ ML). One major adsorption structure (feature α) was observed. (C) Enlarged filled-state STM image (3.00 nm × 3.00 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of feature α. (D) Schematic illustration of feature α (top view). red, O; yellow, S; gray, C; white, H; green, Ge. All schematic illustrations are results of DFT geometry optimization.**

RESULTS AND DISCUSSION

Adsorption Structure of 3-Mercaptoisobutyric Acid. After the exposure of the Ge(100) surface to 3-mercaptoisobutyric acid at room temperature, one major adsorption structure was observed. Figure 1B shows an STM image (sample bias voltage (V_s) = −2.0 V, tunneling current (I_t) = 0.1 nA) of the Ge(100) surface exposed to 3-mercaptoisobutyric acid, at a low coverage ($\theta = 0.05$ ML). In the STM image, one kind of adsorption structure (indicated as feature α) was observed; the feature α is shown enlarged in Figure 1C. In Figure 1C, one dark Ge dimer (dotted white circle) and a bright protrusion (dotted blue circle), which appeared brighter than the top Ge atoms, are shown. Because one Ge dimer appeared as a dark protrusion, it is likely that two dangling bonds of the Ge dimer were saturated by chemical bonding with the 3-mercaptoisobutyric acid. There are two possible causes for the saturation of the two dangling bonds of a Ge dimer: (i) O–H dissociated adsorption (adsorption through a carboxylic acid group) or (ii) S–H dissociated adsorption (adsorption through a thiol group). In both cases, one dangling bond can be saturated by chemical bonding with the hydrogen atom originating from the O–H or S–H dissociation of the datively bonded 3-mercaptoisobutyric acid, and the other dangling bond can be saturated by chemical bonding with the O–H dissociated oxygen atom or the S–H dissociated sulfur atom. Previously, we reported the S–H dissociated adsorption structures of phenylthiol and 1-octanethiol[17] and the O–H dissociated adsorption structures of methanol[18] and water[19] on a Ge(100) surface. In the case of the thiol molecules, the sulfur atoms appeared as protrusions that were brighter than the up Ge atoms at $V_s = -2.0$ V, $I_t = 0.1$ nA. On the other hand, in the case of the alcohol molecules, the oxygen atoms appeared as protrusions that were darker than the top Ge atoms at $V_s = -2.0$ V, $I_t = 0.1$ nA. From these results, we concluded that the dark Ge dimer in Figure 1C was due to the O–H dissociated adsorption of 3-mercaptoisobutyric acid.

To verify this suggestion, we obtained the detailed reaction pathways for the two possible adsorption structures (O–H dissociated adsorption, S–H dissociated adsorption) using the NEB method. These two reaction pathways are shown in Figure 2. As shown in Figure 2A, the activation barrier to the conversion of the COOH datively bonded structure to the O–H dissociated adsorption structure was 0.274 eV/molecule, which was easy to overcome at room temperature. In contrast, as shown in Figure 2B, the activation barrier to the conversion of the S datively bonded structure to the S–H dissociated adsorption structure was 0.523 eV/molecule, which was much harder to overcome at room temperature than the barrier to the O–H dissociated adsorption. Although the S–H dissociated adsorption structure was thermodynamically more stable than the O–H dissociated adsorption structure (0.271 eV/molecule), it is important to note that 3-mercaptoisobutyric acid molecules kinetically selected to adsorb with the O–H dissociated adsorption structure.

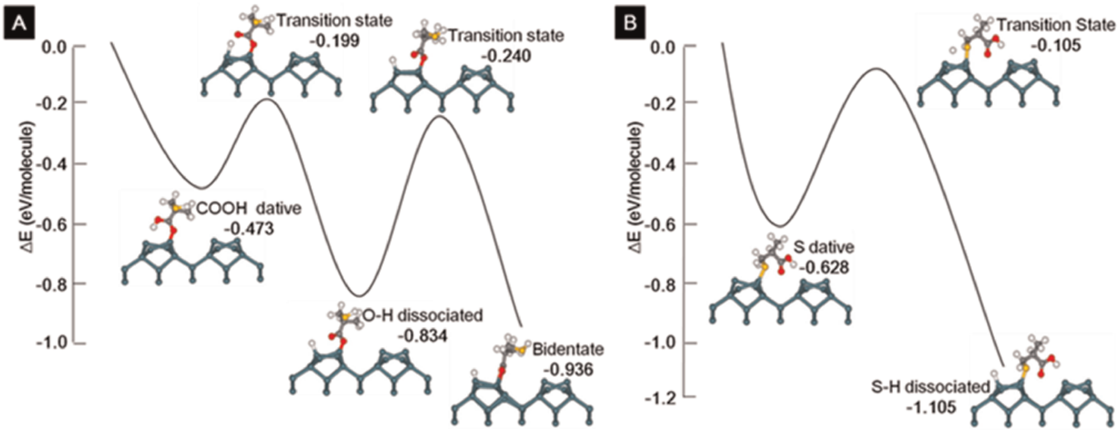

Figure 2. (A) Reaction pathway to the O—H dissociated adsorption structure. The activation barrier from the COOH datively bonded structure to the O—H dissociated structure is 0.274 eV/molecule. The activation barrier from the O—H dissociated structure to the end-bridged bidentate structure is 0.594 eV/molecule. (B) Reaction pathway to the S—H dissociated adsorption structure. The activation barrier from the S datively bonded structure to the S—H dissociated structure is 0.523 eV/molecule. At room temperature, 3-mercaptoisobutyric acid kinetically selects to adsorb with O—H dissociated adsorption structure on Ge(100), even though it is not the thermodynamically most stable configuration.

After the formation of the O—H dissociated adsorption structure, further attack of the adjacent Ge atom by the unreacted oxygen atom of the carbonyl group could have occurred, as shown in Figure 2A; this led to the formation of an end-bridged bidentate structure. In the case of formic acid and acetic acid on a Ge(100) surface, the presence of a bidentate structure at 310 K was reported by Bent *et al.*[20] However, the amount of bidentate structures was very small, and such structures could hardly be detected. Moreover, as shown in Figure 2A, the activation barrier of 3-mercaptoisobutyric acid molecules to the conversion of the O—H dissociated adsorption structure to the bidentate structure (0.594 eV/molecule) was much larger than the reported activation barrier of acetic acid molecules (0.28 eV/molecule).[21] We could therefore exclude the further reaction converting the O—H dissociated adsorption structure to the bidentate structure at room temperature. On the basis of the experimental observations and the energetic calculations, we concluded that, at room temperature, 3-mercaptoisobutyric acid molecules adsorbed through the carboxylic acid groups (O—H dissociated adsorption structure), and the thiol groups did not participate in the adsorption. A schematic illustration of the feature α is shown in Figure 1D.

Effect of Tunneling Electrons on the Adsorption. To study the effects of the electronic properties of an STM on the adsorption of 3-mercaptoisobutyric acid, a clean Ge(100) surface was exposed to 3-mercaptoisobutyric acid molecules during the scanning of the Pt—Ir tip, under feedback conditions of $V_s = -2.0$ V and $I_t = 0.1$ nA. After ceasing exposure, an STM image was recorded for a sample area larger than the area scanned during exposure. This STM image is displayed in Figure 3A, and the area scanned during exposure is indicated by a white dotted square. In the white dotted square, the surface was densely covered with α features. However, outside the white dotted square, few adsorption features were observed. This result indicated that the O—H dissociated adsorption was enhanced by the scanning of the Pt—Ir tip. To further clarify which factor caused the enhancement, the relationship between the number of the adsorbed features and the number of the tunneling electrons applied at $V_s = -2.0$ V was investigated at a constant rate of the molecular dose. We did the experiment as in the following. First, we divided the scanning area into three equal sections widthwise. Over constant rate of the molecular dose, we started scanning a Pt—Ir tip under the feedback conditions of $V_s = -2.0$ V and $I_t = 0.1$ nA from the bottom. We changed I_t to 0.3 nA the moment that the tip reached the second section, and changed it to 0.5 nA the moment that the tip reached the third section. The moment that the tip reached the top of the scanning area, the molecular dose was stopped. The rate of the molecular dose, V_s, and the scanning speed (100 s/frame) were kept constant during the scanning. Therefore, we could confirm the effect of the tunneling electrons to the O—H dissociated adsorption by counting the number of adsorbed structures at each section. Because few adsorbed structures were observed outside the scanning area, we could neglect the number of naturally adsorbed structures inside the area. At the first section ($I_t = 0.1$ nA), the number of adsorbed structures is 19, and at the second section ($I_t = 0.3$ nA), the number of adsorbed structures is 55 (Supporting Information, Figure S1). At the third section ($I_t = 0.5$ nA), the number of adsorbed structures is 108. The number of the electrons tunneling between the tip and each section is 0.1 nA × 33.33 s = 2.08×10^{10} (section 1), 0.3 nA × 33.33 s = 6.24×10^{10} (section 2), and 0.5 nA × 33.33 s = 1.04×10^{11} (section 3). We drew the graph of these results (*x* axis, the number of applied tunneling electrons; *y* axis, the number of

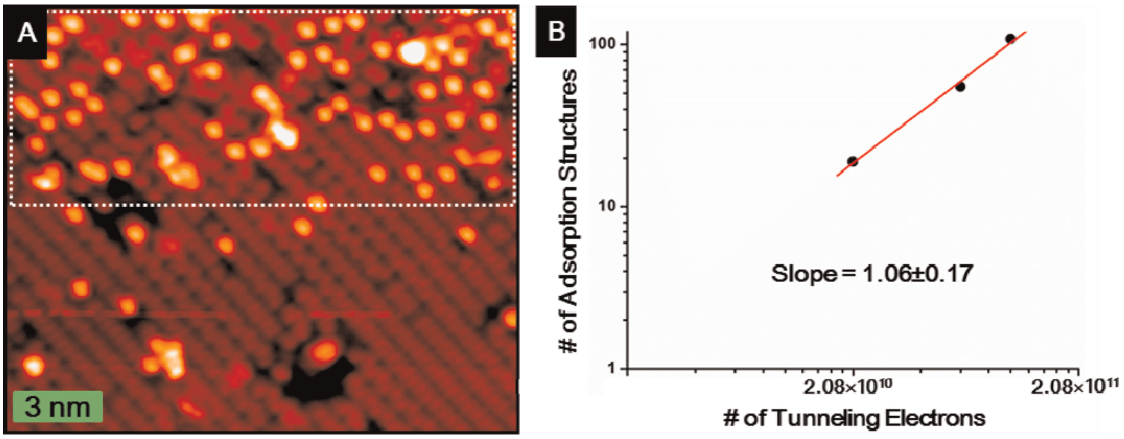

Figure 3. (A) Filled-state STM image (17.86 nm × 14.81 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of 3-mercaptoisobutyric acid on a Ge(100) surface using a Pt–Ir tip. White dotted square: Pt–Ir tip scanning ($V_s = -2.0$ V, $I_t = 0.1$ nA) area during exposure of 3-mercaptoisobutyric acid molecules. (B) Double-logarithmic plot of the number of adsorption structures *versus* the number of tunneling electrons at $V_s = -2.0$ V. The red line is least-squares fit to the data and corresponds to power law, number of adsorption structures ~ number of tunneling electrons^N, where $N = 1.06 \pm 0.17$. Therefore, the STM tip effect can be described as a one-electron process.

adsorbed structures) in Figure 3B on a logarithmic scale. The slope of the double-logarithmic plot was 1.06 ± 0.17. This indicated that the factor which caused the enhancement was the tunneling electrons, and that the enhancement was a single-electron process at $V_s = -2.0$ V.[13,22,23]

As seen in Figure 2A, there was one energy barrier for the transition from the COOH datively bonded adsorption structure to the O–H dissociated adsorption structure; this energy barrier was attributed to the O–H bond breaking of the COOH datively bonded adsorption structure (consult the schematic illustration of the transition state). Hence, it is reasonable to assume that the enhancement was due to the activation of the O–H bond breaking, which was induced by the energy of the tunneling electrons. The energy barrier for the O–H bond breaking was 0.274 eV, and thus a bias voltage of −2.0 V provided electrons with sufficient energy to overcome the dissociation barrier in a one-electron step. Because the tunneling electrons selectively enhanced the adsorption through the carboxylic acid groups (the adsorption through the thiol groups was not induced by the tunneling electrons), we were able to make thiol group-terminated areas wherever we desired using the electronic properties of an STM.

Effect of STM Tip Catalysis on Adsorption. As previously mentioned, at room temperature, 3-mercaptoisobutyric acid adsorbed on a Ge(100) surface through the carboxylic acid groups, and this adsorption was enhanced by the electrons tunneling between an STM tip and the surface. The thiol groups did not participate in the adsorption. However, the possibility that an STM tip coated with a WO_3 layer—which can catalyze the S–H dissociated adsorption of thiol moelcules[17]—could selectively catalyze the adsorption through the thiol groups was proposed. To realize this, we performed experiments using W tips coated with a WO_3 layer instead of Pt–Ir tips.

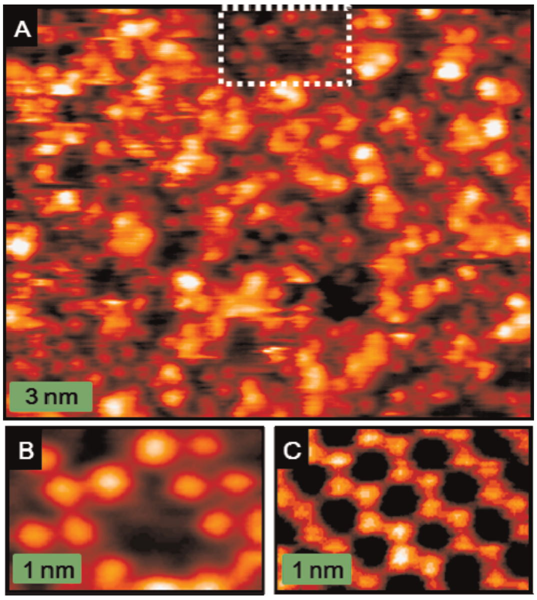

Figure 4. (A) Filled-state STM image (20.00 nm × 15.50 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of 3-mercaptoisobutyric acid on a Ge(100) surface using a WO_3 tip during exposure to 3-mercaptoisobutyric acid molecules. The area showing only α features is indicated by a white dotted square. (B) Enlarged filled-state STM image (4.20 nm × 2.68 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of the white dotted square in Figure 3A. (C) Filled-state STM images (4.20 nm × 2.68 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of a clean Ge(100) surface with the same size as Figure 3B.

To investigate the catalytic effect of the W tip on the adsorption of 3-mercaptoisobutyric acid, a clean Ge(100) surface was exposed to 3-mercaptoisobutyric acid molecules during scanning of the W tip, under feedback conditions of $V_s = -2.0$ V, and $I_t = 0.1$ nA. After ceasing exposure, continuous STM images were recorded for the same area until the base pressure of the STM chamber was recovered. One STM image from the series of continuous STM images is displayed in Figure 4A. As shown in Figure 4A, the scanned area was

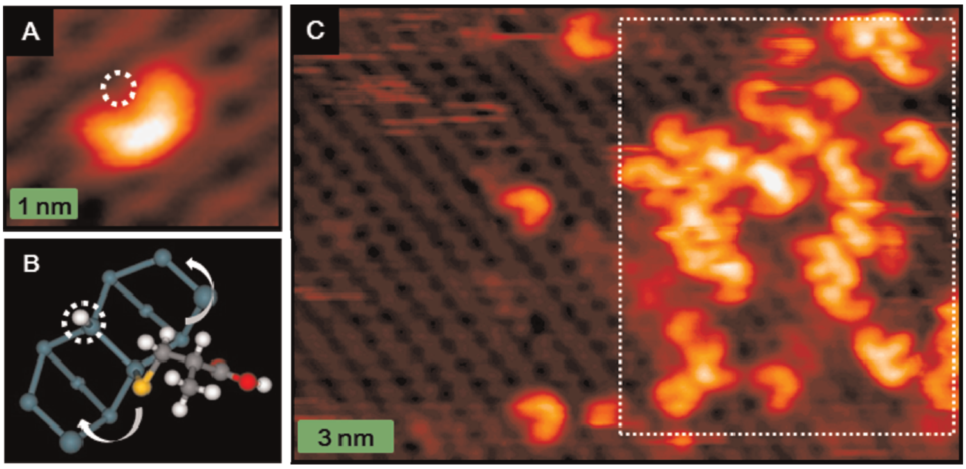

Figure 5. (A) Filled-state STM image (4.26 nm × 3.42 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of feature β. The dark protrusion (a top Ge atom saturated by the S−H dissociated hydrogen) is indicated by a white dotted circle. This adsorption structure was only observed in the presence of the WO_3 tip. (B) Schematic image of feature β (top view). red, O; yellow, S; gray, C; white, H; green, Ge. The top Ge atom saturated by the S−H dissociated hydrogen is indicated by white dotted circle. The directions of the rotation of the $-SCH_2CH(CH_3COOH)$ fragment is shown by white arrows. (C) Filled-state STM image (20.00 nm × 13.52 nm, $V_s = -2.0$ V, $I_t = 0.1$ nA) of 3-mercaptoisobutyric acid on a Ge(100) surface using a WO_3 tip. White dotted square: W tip scanning ($V_s = -2.0$ V, $I_t = 0.1$ nA) area after exposure to 3-mercaptoisobutyric acid molecules.

fully covered by α features and some bright protrusions. The area showing only α features (indicated by a white dotted square) is enlarged in Figure 4B, and an STM image of a clean Ge(100) surface of the same size as Figure 4B is shown in Figure 4C to clarify the packing density (one α feature per two Ge dimers). After the base pressure was recovered, an STM image for a sample area larger than the scanned area during exposure was recorded. This STM image is displayed in Supporting Information, Figure S2. Outside the scanned area during exposure, few α features were observed. This result indicated that the W tip also enhanced the O−H dissociated adsorption of 3-mercaptoisobutyric acid, due to the electrons tunneling between the tip and the surface.

Surprisingly, we also found a new adsorption structure outside the scanned area during exposure (Figure S2). An enlarged STM image of the new adsorption structure (indicated by feature β) is shown in Figure 5A. In Figure 5A ($V_s = -2.0$ V, $I_t = 0.1$ nA), a bright half-moon-shaped protrusion and a dark protrusion (white dotted circle) are shown. This STM image was very similar to the previously reported STM image of the S−H dissociated adsorption structures of 1-octanethiol on a Ge(100) surface (Supporting Information, Figure S3).[17] In the case of 1-octanethiol, the dark protrusion was due to the saturation of the dangling bond of a top Ge atom, which occurred *via* chemical bonding with an S−H dissociated hydrogen atom, and the bright half-moon-shaped protrusion was due to the S−H dissociated $-SCH_2(CH_3)_7$ fragment bonding to a bottom Ge atom. Because the Ge−S bond is a single bond, the $-SCH_2(CH_3)_7$ fragment could rotate freely (excluding the position of the Ge−H bond) at room temperature, and this rotation made the $-SCH_2(CH_3)_7$ resemble a half-moon-shaped protrusion. The S−H dissociated adsorption of 1-octanethiol was chemically catalyzed by the WO_3-covered W tip. Because feature β was only observed in the presence of the W tip, it is likely that the half-moon-shaped adsorption structure in Figure 5A did not originate from the electronic properties of the STM, but originated from the W tip-catalyzed, S−H dissociated adsorption of 3-mercaptoisobutyric acid. A schematic illustration of feature β is shown in Figure 5B. The top Ge atom saturated by the S−H dissociated hydrogen is marked by a white dotted circle, and the rotation directions of the $-SCH_2CH(CH_3COOH)$ fragment are indicated by white arrows.

To further clarify this catalysis, we performed additional experiments. First, we exposed the W tip to 3-mercaptoisobutyric acid molecules. After the exposure was stopped and the base pressure was recovered, the tip was moved close to the clean Ge(100) surface, and we then repeatedly scanned a certain area, under feedback conditions of $V_s = -2.0$ V and $I_t = 0.1$ nA. An STM image was then recorded for a sample area larger than the repeatedly scanned area. This STM image is displayed in Figure 5C, and the repeatedly scanned area is indicated by a white dotted square. Surprisingly, in the white dotted square, the surface was densely covered with β features, and few β features were observed outside the white dotted square. Because we scanned the surface after the base pressure was recovered, the adsorption of the residual molecules in the STM chamber could be neglected. Thus, it was confirmed that the adsorbed β features originated from the 3-mercaptoisobutyric acid molecules already adsorbed on the W tip. When the clean area was scanned with the W tip, the 3-mercaptoisobutyric acid molecules were easily transferred from the WO_3 layer to the Ge(100) surface, and they adsorbed on the Ge(100) surface *via* the thiol groups. We therefore concluded that the W tip catalyzed the S−H dissociated adsorption of the 3-mercaptoisobutyric acid molecules already adsorbed on the W tip. When a Pt−Ir tip was used, neither this phenomenon nor β features were observed. This result directly supported the notion that the W tip acted as a catalyst for the S−H dissociative adsorption of the 3-mercaptoisobutyric acid molecules. Moreover, in Figure 5C, feature α was not observed, which meant that the W tip selectively catalyzed the S−H dissociative adsorption of the 3-mercaptoisobutyric acid molecules already adsorbed on the W tip (the carboxylic acid groups did not participate in the adsorption). As previously mentioned, adsorption through the thiol groups (S−H dissociated adsorption) on a Ge(100) surface was kinetically prohibited at room temperature. However, we suggest that the activation barrier decreased as the molecules passed through the additional step consisting of the adsorption of the molecules on the WO_3 layer. Because the carboxylic acid groups remained in an unreacted state in feature β, we were able to make carboxylic acid group-terminated areas wherever we desired using this catalysis.

CONCLUSION

We studied the adsorption structures and adsorption behaviors of 3-mercaptoisobutyric acid at Ge(100) surfaces. At room temperature, 3-mercaptoisobutyric acid molecules adsorbed *via* carboxylic acid groups, and this adsorption was enhanced by tunneling electrons. Using this phenomenon, we could make thiol group-terminated areas wherever we desired. In addition, by exploiting the catalytic properties of the WO_3 tip, we were able to selectively catalyze the S−H dissociative adsorption of 3-mercaptoisobutyric acid. Because the carboxylic acid groups remained in an unreacted state, we could make carboxylic acid group-terminated surfaces in any desired location. This STM-controlled functional group-selective adsorption of bifunctional molecules could be applied to make selective terminations on semiconductor surfaces.

METHODS

STM Investigation. All experiments were performed at room temperature in a UHV chamber equipped with an OMICRON VT-STM. The base pressure of the chamber was maintained at below 1.0×10^{-10} Torr. A Ge(100) sample (n-type, Sb-doped, $\rho = 0.10-0.39\ \Omega$) was cleaved to a size of $2 \times 10\ \text{mm}^2$ and mounted between two tantalum foil clips in the holder for STM measurements. The Ge(100) surface was cleaned by several cycles of sputtering with 500 eV Ar^+ ions for 20 min at 700 K followed by annealing at 900 K for 10 min. An infrared optical pyrometer was used to measure the Ge(100) sample temperature. 3-Mercaptoisobutyric acid ($C_4H_8O_2S$, >98.0% purity) was purchased from Tokyo Chemical Industry and was inserted into the UHV chamber through a doser with a seven-capillary array controlled by a variable leak valve. All STM images were recorded with a sample bias voltage between -2.0 and $+2.0$ V and a tunneling current between 0.1 and 1.00 nA, using electrochemically etched tungsten tips and mechanically cut platinum−iridium tips. The W tips and Pt−Ir tips were washed using deionized water and ethanol and then used for the STM imaging without additional cleaning procedures.

Theoretical Calculations. To investigate the adsorption configurations of 3-mercaptoisobutyric acid on the Ge(100) surface, DFT calculations within the generalized gradient approximation (GGA) using the Vienna ab initio simulation package (VASP)[24] were performed. The ionic pseudopotentials were described *via* the projector-augmented wave (PAW) method. The transition states for adsorptions were investigated by using the nudged elastic band (NEB) method. The 3-mercaptoisobutyric acid adsorbed Ge(100) surface was modeled as a slab composed of six Ge atomic layers and adsorbed 3-mercaptoisobutyric acid molecules. The Ge bottom layer was passivated with two H atoms per Ge atom. We used a $p(4 \times 2)$ supercell with a $c(4 \times 2)$ surface symmetry. The topmost four layers of the slab and the adsorbed molecules were allowed to relax with respect to the calculated Hellmann−Feynman forces, and the two remaining Ge layers were kept frozen during the structure optimization. The surface structure was relaxed until the Hellman−Feynman forces were smaller than 20 meV/Å. A Gaussian broadening with a width of 0.02 eV was used to accelerate the convergence in the *k*-point sum.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: The relationship between the number of α adsorption features and the tunneling current is shown in Figure S1. When we scanned the surface using a WO_3 tip during exposure to the molecules, a new adsorption structure, feature β, was observed (Figure S2). An STM image and a schematic image of the S−H dissociated adsorption structure of 1-octanethiol are shown in Figure S3. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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