

# Metastable-Atom-Induced Dissociation of Dodecanethiolate Self-Assembled Monolayers on Gold Substrates

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Received: September 17, 2002; In Final Form: February 19, 2003

Emission of  $H^+$  and  $CH_x^+$  is observed for dodecanethiolate SAMs on Au(111) surfaces under irradiation of the slow helium metastable atom beam at a thermal energy. Metastable atom deexcitation spectroscopy measurements show that impinging metastable helium atoms predominantly interact with  $\sigma_p$  orbitals constituted mainly of carbon 2p and hydrogen 1s atomic states of the methyl group at the top end of the alkane chain of the dodecanethiolate molecule. These results indicate that the hole created in the  $\sigma_p$  orbitals leads not only to C–H bond scission followed by  $H^+$  desorption but also to C–C bond scission between the methyl group and the neighboring carbon atom followed by  $CH_x^+$  desorption.

## Introduction

To continue lithographic scaling down to the nanometer-range, self-assembled monolayers (SAMs) of molecules has attracted attention because thinner resists attain finer spatial resolution. Metastable atom beams can realize the ultimate resolution of SAMs beyond the diffraction limit, proximity effect, or transmission of the conventional exposure radiations, i.e., ultraviolet light, electron beam, and soft X-ray.

Metastable atoms at a thermal energy region carrying fairly large excitation energy (20 eV) in their electronic system interact only with topmost atoms at surfaces because the kinetic energies of the atoms are so low (<1 eV) that they are reflected above surfaces. When metastable atoms deexcite at surfaces, the surface electrons are ejected, receiving the excitation energy released. This type of electron ejection has been utilized as metastable-atom deexcitation spectroscopy (MDS) for many years and is known to exhibit extreme surface sensitivity and nondestructive features without energetic collisions.<sup>1</sup> Extreme surface sensitivity is desirable for exposure radiation for thin resists such as SAMs. The opaqueness means no backscattering such as that occurring in electron beams, which limits the resolution of lithography. Furthermore, the masses of metastable atoms are large enough to keep de Broglie wavelengths, which are directly connected to the resolution limit, small. Thus, it is natural that the next step be to introduce metastable atom beams into lithography.

Pattern transfer employing metastable atom beams to damage self-assembled monolayer (SAM) resists followed by wet chemical etching has been demonstrated by several groups.<sup>2</sup> As to the phenomena in SAM resists caused by exposure to a metastable atom beam, however, it is merely speculated that the irradiation of metastable atom beams damages SAM molecules and damaged molecules lose their hydrophobicity and that an etchant then attacks the relatively hydrophilic area.<sup>3</sup> The fundamental processes of the damage are not known yet, except the change of electronic state reported by Yasufuku et al.<sup>4</sup>

Metastable-atom-stimulated desorption (MSD) has been newly discovered for water and alkali coadsorbed surfaces.<sup>5</sup>

During the irradiation of metastable helium atom beams,  $H^+$  ion desorption is observed for water and sodium coadsorbed Ni(110) surfaces. The energy distribution of desorbed ions is relatively narrow at around 1 to 5 eV, which is typically observed in desorption induced by electronic transition (DIET), such as photostimulated desorption (PSD) or electron-stimulated desorption (ESD). The mechanism of MSD is explained within the framework of the Menzel-Gomer-Readhead (MGR) model, according to which an electron hole is created in the valence band by the Auger deexcitation of a helium metastable atom followed by electronic transition to the repulsive interatomic potential between the surface and  $H^+$  ion. This mechanism has been confirmed by a spin-polarized MSD experiment for water and sodium-coadsorbed Fe (100) surfaces in a remanent state.<sup>6</sup> The spin dependency of the desorbed ion intensity is consistent with the spin polarization of surface electrons measured by spin-polarized MDS.

We report on the MSD of ions from dodecanethiolate SAMs under the irradiation of metastable helium atom beams. The MSD data provide direct evidence of the damage, namely, the dissociation of dodecanethiolate SAMs by the electron abstraction from bonding orbitals with extra excitation energy during the deexcitation process of metastable helium atoms without electron emission. In the following sections, we describe the experimental details and results; then, we discuss the mechanism of the dissociation and ion emission.

## Experimental Section

The experiments described in the following sections were performed with a spin-polarized MDS device that consists of a pulsed metastable helium atom beam source<sup>7</sup> and a sample chamber with a Stern-Gerlach analyzer, a cylindrical mirror analyzer (PHI 590), and a sputtering ion gun. Two turbomolecular pumps in tandem evacuate the sample chamber. Throughout the experiments, the base pressure of the sample chamber was in the range of  $10^{-9}$  Torr without baking, although the apparatus is completely bakable so that it can reach an ultimate pressure of  $10^{-11}$  Torr. The metastable helium atom beam source is operated in the pulsed discharge mode so that photons created simultaneously during the discharge can be clearly distinguishable from slow metastable atoms at thermal

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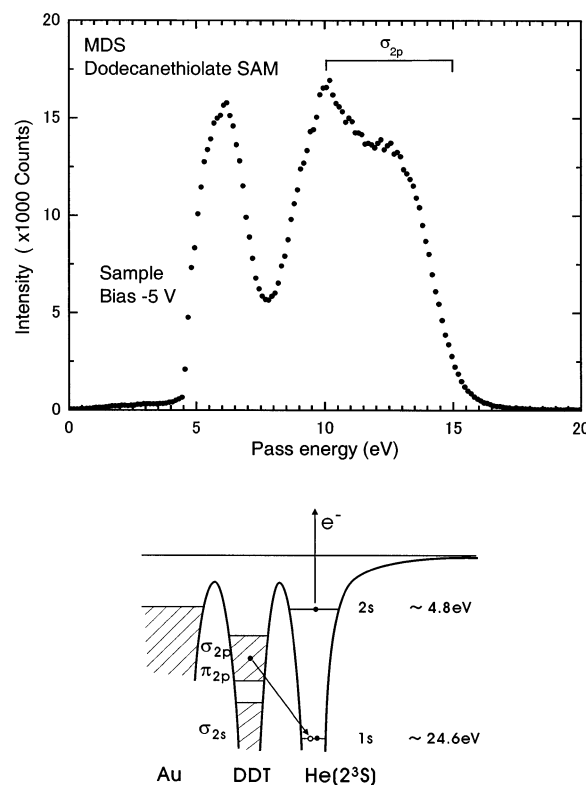
energy by their different arrival time at a sample surface.<sup>7</sup> In our experimental arrangement, the arrival time of metastable atoms was delayed 100–200  $\mu$ s from that of photons and fast neutral atoms. Charged particles ejected from a sample are energy-analyzed by the CMA, and a multichannel scaler (MCS) records the output pulses of the channel electron multiplier for the selected particles. The MCS is operated in the time-of-flight mode by keeping the pass energy of the CMA constant, and it can also be used in the energy scan mode by sweeping the pass energy of the CMA. Thus, this setup enabled us to obtain TOF spectra and energy spectra of both desorbed positive ions and ejected electrons.

**Preparation of SAM.** The standard procedure was adopted to prepare dodecanethiolate SAM/Au samples.<sup>8</sup> Au films are formed on optical flat mica sheets (ASTM-VI) at a temperature of 350  $^{\circ}$ C by vapor deposition of gold using a tungsten basket evaporator after several hours of outgassing at the same temperature. This is the typical procedure to obtain an atomically flat surface of Au (111). A turbo-molecular pump evacuates the physical vapor deposition chamber to attain a hydrocarbon-free vacuum. The base pressure is better than  $1 \times 10^{-6}$  Torr, and the vacuum pressure during vapor deposition is at around  $1 \times 10^{-5}$  Torr. After cooling to room temperature, Au films on mica sheets are taken out from the chamber and immediately immersed in a millimolar ethanolic solution of 1-dodecanethiol,  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ , for more than 24 h at room temperature. The dodecanethiolate SAM/Au samples are rinsed with clean ethanol and quickly introduced into the sample chamber. The cleanliness of the SAM samples is checked by Auger electron spectroscopy using the CMA and the electron gun equipped in it. The SAM samples contained carbon, sulfur, and gold, as expected from the composition, but no trace of oxygen due to water adsorption or to oxidation of SAM was detected even at a vacuum pressure of  $10^{-9}$  Torr without baking or surface cleaning.

## Results

To characterize the SAM samples, an MDS measurement was carried out. The spectrum shown in Figure 1 well reproduces the specific features of dodecanethiolate SAM/Au reported.<sup>9</sup> Metastable helium atoms are known to eject electrons from an insulator surface with a band gap at the energy level of He 2s through an Auger deexcitation (AD) process, which is an electron process similar to UPS. As depicted in the energy diagram (Figure 1b), the electron at He 2s is ejected by receiving the energy corresponding to the difference between the level of a valence electron of the substrate and He 1s. Electron emission mainly comes from  $\sigma_{2p}$  molecular orbitals of the methyl groups at the top surface that are accessible to impinging metastable atoms rather than the methylene groups. Previous studies on the structures of long-chain alkanethiol SAMs reported that the carbon axes of alkanethiols on Au (111) are upright and tilted by  $30^{\circ}$  with respect to the surface normal.<sup>8</sup> Morgner<sup>10</sup> attempted to identify the characteristic MDS spectra of alkanes with the specific chain orientation by simulating the spectra on the basis of the *ab initio* calculation of hexadecane or within the semiempirical fitting from the angle-resolved ultraviolet spectroscopy data for polyethylene. The peak at 11 eV accompanied by a large shoulder to 15 eV was assigned to the electron density in front of the three hydrogen atoms of the methyl group. The work function is about 1 eV lower than that of the CMA and is in accordance with the work function change reported for the hexadecanethiolate SAM on a clean Au surface.<sup>9</sup>

Results of the TOF measurement for the SAM surfaces are displayed in Figure 2. Larger peaks distributed from 0 to 200

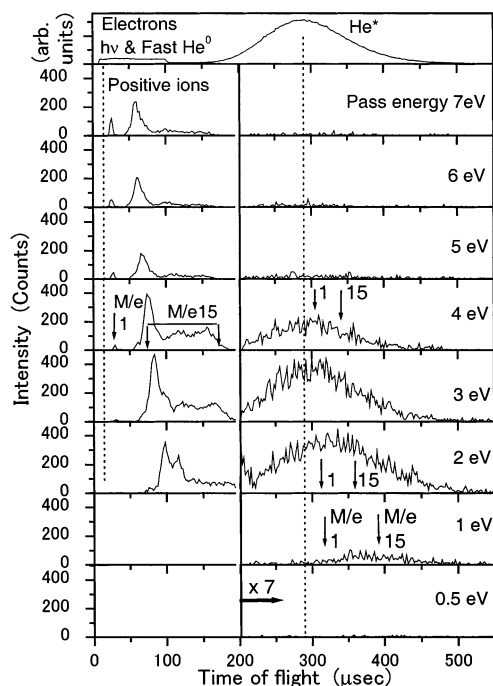


**Figure 1.** (upper panel) MD spectrum for dodecanethiolate SAM adsorbed on Au(111); (lower panel) schematics of the Auger deexcitation process of metastable helium atoms at this surface. The band identification in the upper panel is taken from ref 10.

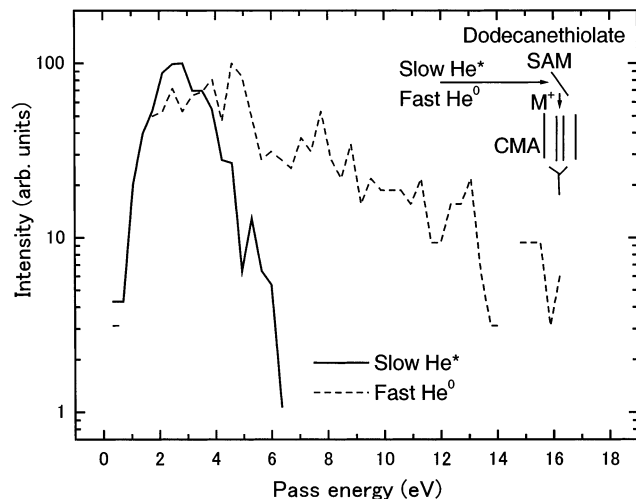
$\mu$ s in the TOF spectra of positive ions (the second to the seventh panel from the top) correspond to secondary ions of  $\text{H}^+$  and  $\text{CH}_x^+$  sputtered by fast helium neutral atoms contained in the primary beam. It has been reported that the fast neutrals spread over the pulse width of 100  $\mu$ s that has a large peak at its leading edge.<sup>11</sup> The sharp peaks at 30  $\mu$ s are assigned to the  $\text{H}^+$  created within the peak at the leading edge, and the wide peaks at 50–200  $\mu$ s are assigned to the  $\text{CH}_x^+$  created over the whole pulse width of fast neutrals.

Smaller and broader peaks after 200  $\mu$ s in the TOF spectra of the positive ion (the fifth to the eighth panel of Figure 2) correspond to MSD ions of  $\text{H}^+$  and  $\text{CH}_x^+$  induced by slow metastable helium atoms. From the comparison of these peaks and the arrows, each of which indicates the calculated arrival time for the mass charge ratios ( $M/e$ ) of 1 (H) or 15 ( $\text{CH}_3$ ), it is clearly seen that the species of  $M/e = 15$  or so is dominant at a pass energy of 1 eV. As the pass energy increases, the peak of MSD intensity shifts from  $M/e = 15$  to 1. At a pass energy of 4 eV,  $\text{H}^+$  is apparently dominant. The energy distribution of  $\text{CH}_x^+$  is about 1 eV lower than that of  $\text{H}^+$ .

Another trend is observed in the TOF spectra, namely, that the energy dependence of the intensity of secondary ions sputtered by fast neutrals is wider than that of MSD ions. To clarify this trend, energy distributions were measured for both ions separately by gating the counting signal (Figure 3). MDS ions distribute sharply within a narrow energy width of about 5 eV, while secondary ions sputtered by fast helium atoms distribute exponentially over a wide range of 20 eV or more. The narrow distribution of MSD ions is inherent to the DIET, in contrast with the exponential distribution of sputtered ions, which is the common feature due to collision cascades induced by energetic projectiles.



**Figure 2.** TOF spectra of ejected positive ions (lower eight panels) and electrons (top panel) from dodecanethiolate SAM/Au for various pass energies of CMA. The TOF spectrum of ejected electrons shown in the top panel corresponds roughly to the profile of the primary beam, which consists of the fast component containing mostly ultraviolet photons and a few fast neutral helium atoms and the slow component corresponding to thermal metastable helium atoms.<sup>11</sup> The dashed line at the center is a guide for the eye, indicating the center of the arrival time of metastable atoms. The arrows indicate the time delays from the central line calculated at each pass energy for mass charge ratios of 1 (H) and 15 (CH<sub>3</sub>). The other dashed line at the left-hand side is also a guide for the eye, indicating the arrival time of the largest peak of fast neutral atoms at the leading edge of pulses.



**Figure 3.** Energy distribution of ejected positive ions from dodecanethiolate SAM/Au.

## Discussion

We will first clarify the insignificant contribution of ESD by secondary electrons to an MSD signal before proceeding to a discussion of the DIET process directly induced by the Auger deexcitation of metastable helium atoms. Secondary electrons are generated not only by metastable atoms but also by ultraviolet photons, as seen in the TOF spectrum of electrons (top panel of Figure 2), which shows a plateau at 0–100 μs.

On the other hand, the plateau, which is indicative of the effect of ultraviolet photons, is not visible at 0–200 μs in the TOF spectra of ions (lower panels of Figure 2), but, instead, the sharp peaks of H<sup>+</sup> due to the sputtering by fast neutrals are seen.<sup>11</sup> Thus, the ion intensity due to either the PSD or the ESD of photoinduced secondary electrons is negligible. The energy range of the photoelectrons (21.2 eV) is almost the same as or even higher than those of metastable atoms (19.8 or 20.6 eV). As the PSD is not accompanied by any appreciable ESD of photoinduced secondary electrons, the MSD should also be accompanied by negligible ESD.

The result of the MDS measurement mentioned earlier suggests that DIET starts from an abstraction of an electron in  $\sigma_p$  orbitals of dodecanethiol by Auger deexcitation of metastable helium atoms. H<sup>+</sup> desorption is most likely expected because  $\sigma_p$  orbitals are constituted mainly of C 2p and H 1s atomic states, and this abstraction may be directly connected to the scission of the C–H bond. On the contrary, CH<sub>x</sub><sup>+</sup> desorption needs the scission of the C–C bond that corresponds to  $\sigma_s$  orbitals constituted mainly of the C 2s atomic state, which are deeper than  $\sigma_{2p}$ . In Figure 1, however, the peak at a pass energy of around 6 eV corresponding to a kinetic energy of 2 eV cannot be attributed to  $\sigma_{2s}$  but to the secondary electrons, because  $\sigma_{2p}$  is much more accessible to impinging metastable atoms than  $\sigma_{2s}$  and a substantial amount of metastable atoms decay before interacting with  $\sigma_{2s}$ . This implies that the scission of the C–C bond is not triggered by the electron abstraction from  $\sigma_{2s}$  but by that from  $\sigma_{2p}$ .

To examine the validity of the ion emission process, here we consider the thermodynamic energy balance. The dissociation energies of C<sub>2</sub>H<sub>6</sub> → C<sub>2</sub>H<sub>5</sub> + H and C<sub>2</sub>H<sub>6</sub> → 2CH<sub>3</sub> are known to be 4.2 and 3.8 eV, respectively. Since these values are smaller than the ionization energy of  $\sigma_{2p}$  (12–15 eV), the neutral species of H and CH<sub>3</sub> can be triggered by the creation of a hole in the  $\sigma_{2p}$  bonding orbital. Taking into account the ionization and the maximum kinetic energy of H (13.6, 5 eV) and CH<sub>3</sub> (9.8, 2 eV) and the work function (4 eV), the roughly estimated thermodynamic thresholds for the dissociation of dodecanethiol to C<sub>12</sub>H<sub>24</sub>S + H<sup>+</sup> and C<sub>11</sub>H<sub>22</sub>S + CH<sub>3</sub><sup>+</sup> are about 18.8 and 11.6 eV, respectively (dissociation energy + ionization energy + kinetic energy – work function). The threshold (11.6 eV) for CH<sub>3</sub><sup>+</sup> desorption is smaller than the ionization energy of  $\sigma_{2p}$ . The threshold (18.8 eV) for H<sup>+</sup> desorption is, however, larger than that of  $\sigma_{2p}$  even though it is still smaller than the excitation energy of metastable helium (19.8, 20.6 eV). This excludes the possibility that the ion desorption of H<sup>+</sup> is completely initiated by the creation of a hole in the  $\sigma_{2p}$  bonding orbital. Therefore, an electronic transition path might exist, along which the energy released by the electron transfer from the  $\sigma_{2p}$  orbital to the He-(2s) 1s hole does not yield any electron emission but, rather, an additional excitation in the dodecanethiol cation, instead.

We explain the ion emission starting from this highly excited state of dodecanethiol cation. The creation of a hole in the  $\sigma_{2p}$  orbital with the extra energy may be directly connected to the scission of the C–H bond and then to H<sup>+</sup> desorption. The hole in  $\sigma_{2p}$  with the extra energy can migrate<sup>12</sup> to  $\sigma_{2s}$  and may then cause the scission of the C–C bond and desorption of CH<sub>x</sub><sup>+</sup>. This itinerancy of the electron hole in the methyl group at the top end of the dodecanethiol molecule has to partially dissipate the excitation energy during the electronic transition so that CH<sub>x</sub><sup>+</sup> may desorb with less (excess) kinetic energy than H<sup>+</sup>. A detailed theoretical study on the electronic transitions of excited positive ions of long alkanes is needed to gain insight into the mechanism of CH<sub>x</sub><sup>+</sup> desorption.

As to the contribution from the abstraction of  $\sigma_{2s}$  electrons, the discussion above may also be examined by use of other metastable atoms having lower ionization energy. When the ionization energy of metastable atoms is smaller than the binding energy of  $\sigma_{2s}$  ( $>19$  eV), the electron abstraction from  $\sigma_{2s}$  is impossible. By changing the species of rare gas, the ionization energy can be reduced from 24 eV (He) down to 12 eV (Xe).

## Conclusions

Metastable-atom-induced dissociation of dodecanethiolate SAMs on a Au substrate is studied by means of the time-of-flight measurement of ejected ions with the combination of a pulsed metastable helium atom beam and the aid of metastable atom deexcitation spectroscopy. Two kinds of desorbed ions are observed and assigned to  $H^+$  and  $CH_x^+$ . It is also confirmed that metastable helium atoms primarily interact with the topmost methyl groups of dodecanethiolate SAMs through the Auger deexcitation process. The resultant electron abstraction from the topmost methyl groups with an extra excitation energy instead of an electron emission leads not only to direct C–H bond scission but also to indirect C–C bond scission, and, finally, the indirect electron transition leading to the  $CH_x^+$  desorption dissipates about 1 eV more energy than the  $H^+$  desorption. To understand the dissociation mechanism further, experimental

data on the excitation energy dependence using other rare gas species are required as well as the theoretical treatment of excited hydrocarbon cations. It is demonstrated that the enormous surface sensitivity of slow metastable atoms has the new capability to attack specified points on large molecules aligned on a surface.

## References and Notes

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