Adsorption states of methylthiolate on the Au(111) surface

Adsorption states of methylthiolate on the Au(111) surface

Akihiro Nagoya[1,2] **and Yoshitada Morikawa**[1,2,3]

[1] The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan
[2] CREST, Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan
[3] Research Institute for Computational Sciences (RICS), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

E-mail: morikawa@sanken.osaka-u.ac.jp

Abstract

We have studied the adsorption structures of methylthiolate (MeS) on the Au(111) surface using density functional theory. The most stable adsorption structure of MeS is the MeS–Au–MeS configuration, which has been proposed by Maksymovych and co-workers (2006 *Phys. Rev. Lett.* **97** 146103), followed by the bridge configuration. The calculated work function change and vibrational mode analysis for the two configurations agree quite well with the experimental results. These results strongly support the conclusion that the MeS–Au–MeS and the bridge configurations coexist on the MeS adsorbed Au(111) surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As the integration of semiconductor devices increases, the device structure is decreasing quite rapidly. Molecular electronics is one of the promising technologies for overcoming the device scale problem and conducting properties of single molecules are now intensively studied. Self-assembled monolayers (SAMs) of thiol molecules on metal surfaces are used as the playground of molecular electronics. Among them, alkanethiolates adsorbed on the Au(111) surface are prototype SAMs and have been actively studied. Although the structure of the bonding between the S head group and Au substrate is quite important for the conducting properties of molecules sandwiched between two electrodes, the adsorption structure of thiolates on Au is still under debate. Nuzzo *et al* investigated dimethyl disulfide (CH_3S–SCH_3, denoted as DMDS hereafter) adsorption on the Au(111) surface by using high resolution electron energy loss spectroscopy

(HREELS), thermal desorption spectroscopy (TDS), and x-ray photoelectron spectroscopy (XPS) experiments, and concluded that the S–S bond is cleaved at room temperature and the molecule is adsorbed as thiolate with the S–C bond tilted from the surface normal [1]. In contrast, Fenter *et al* concluded that decanethiol is adsorbed as disulfide and that two S atoms are adsorbed at different adsorption sites, according to the results obtained by the x-ray standing wave and the grazing incidence x-ray diffraction techniques [2, 3]. Very recent x-ray photoelectron diffraction (XPD) and normal incidence x-ray standing wave (NIXSW) experiments concluded that S is located at the atop site [4–6]. Early theoretical studies concluded that methylthiolate (denoted as MeS hereafter) is adsorbed at the fcc hollow site with its S–C bond nearly perpendicular to the surface [7–10]. Recent first-principles studies on Au(111) reported that S is adsorbed on the bridge site slightly off center toward the fcc hollow site [11–16]. One of the present authors showed that MeS is adsorbed at the bridge site with its S–C bond tilted from the surface normal by about 50°. The calculated vibrational spectra agree very well with the experimental one, confirming the theoretical results [11, 12]. However, these theoretical results are not in accordance with the experimental x-ray diffraction, XPD and NIXSW results mentioned above. Recently, a possibility of substrate reconstruction has been discussed [17–21]. One of the present authors [17] and Molina and Hammer [18] showed that adsorbed MeS stabilizes vacancy formation on the Au(111) surface because Au atoms adjacent to the Au vacancy attract MeS more strongly than those on the flat Au(111) surface. Molina and Hammer also suggested a possibility of MeS adsorption on top of Au adatoms (denoted as the adatom configuration hereafter) and this was very recently supported by Yu and co-workers using x-ray standing wave experiments [20]. Maaksymovych and co-workers proposed another structural model in which one adatom Au is sandwiched by two MeS molecules, and MeS molecules are located on top of substrate Au atoms [19]. This model is denoted as the MeS–Au–MeS configuration hereafter. Mazzarello and co-workers carried out first-principles molecular dynamics simulations of four MeS adsorbed on the Au(111) $2\sqrt{3} \times 2\sqrt{3}$ surface and observed that two of the four MeS were adsorbed in the bridge configuration while the other two MeS extracted one substrate Au atom and formed the MeS–Au–MeS configuration [21]. It is not clear whether the structural models proposed so far can account for the available experimental results or not. In the present study, we have investigated adsorption states of MeS on Au(111) by using the density functional theory and calculated the work function change and the vibrational spectra to compare with experimental results.

2. Method

All calculations are carried out using a first-principles program package STATE-Senri (Simulation Tool for Atom TEchnology) which is based on the density functional theory (DFT) [22, 23] with a generalized gradient approximation (GGA) [24]. Ultrasoft [25] and norm conserving [26] pseudopotentials are used to represent the interaction between electrons and ion cores. Wavefunctions are expanded in plane wave basis sets and the cut-off energy is set to 25 Ryd for wavefunctions and to 225 Ryd for the charge density for structural optimization. For vibration mode analysis, we increased the cut-off energies of wavefunctions and the charge density to 36 Ryd and 400 Ryd, respectively. Surfaces are modelled by a repeated slab model, in which one slab consists of six gold atomic layers separated by vacuum regions of about 1 nm thickness. MeS is adsorbed only on one side of a slab and for geometry optimization, MeS molecules and the top two gold layers were relaxed and the bottom four gold layers were fixed at their ideal bulk positions. To compensate for the work function difference between the two sides of a slab, we inserted a potential gap in the middle of the vacuum region as proposed by Neugebauer and Scheffler [27]. The Brillouin zone integration was sampled with an $8 \times 8 \times 1$
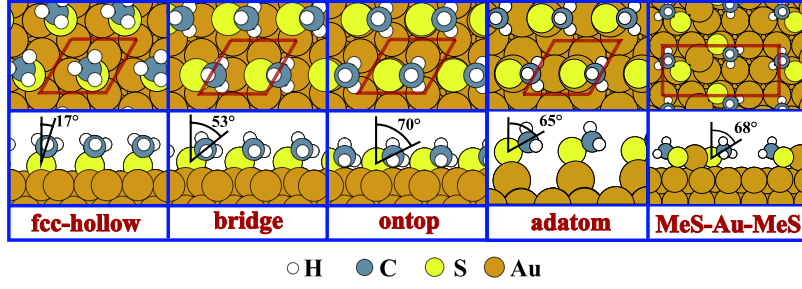
Figure 1. Top and side views of methylthiolate (MeS) adsorbed on the Au(111) surface in the fcc hollow, bridge, on top, adatom, and MeS–Au–MeS configurations. The angle between the S–C bond and the surface normal is shown in the figure.

uniform k-point mesh for the $\sqrt{3} \times \sqrt{3}$ surface unit cell and similar mesh points were used for other surface unit cells. The peak intensity of the high resolution electron energy loss (HREEL) spectra from the dipole scattering mechanism is calculated using [11, 28]

$$\frac{I_{\text{loss}}}{I_{\text{elastic}}} = \frac{\hbar(1 - 2\theta_E)^{1/2}}{8a_0\epsilon_0 E_I \cos\theta_I} \left(\frac{\mathrm{d}\mu}{\mathrm{d}Q}\right)^2 \frac{1}{\omega_s} F_s(\hat{\theta})n_s, \tag{1}$$

where a_0 is the Bohr radius, ϵ_0 is the vacuum permittivity, ω_s is the normal frequency, $\mathrm{d}\mu/\mathrm{d}Q$ is the dynamic dipole moment, E_I is the primary energy of the electron beam, and θ_I is the incident angle of electron beam. $\theta_E = h\omega_s/2E_I$ and $\hat{\theta}_c = \theta_c/\theta_E$, where θ_c is the acceptance angle of the spectrometer. $F_s(\hat{\theta})$ is given by

$$F_s(\hat{\theta}_c) = (\sin^2\theta_I - 2\cos^2\theta_I)\frac{\hat{\theta}_c^2}{1 + \hat{\theta}_c^2}$$
$$+ (1 + \cos^2\theta_I)\ln(1 + \hat{\theta}_c^2). \tag{2}$$

In the present study, $\mathrm{d}\mu/\mathrm{d}Q$ and ω_s are obtained from self-consistent GGA calculations and other parameters are taken from experimental conditions.

3. Results and discussion

We have examined five adsorption structures as shown in figure 1. Figure 1 shows optimized geometries of MeS on the Au(111) surface in the fcc hollow, bridge, on top, adatom, and MeS–Au–MeS configurations. In the fcc hollow configuration, S is located at the threefold hollow site with the molecular S–C bond nearly perpendicular to the surface. In the bridge configuration, S is located at the bridge site slightly off-center towards a hollow site and the S–C bond is tilted from the surface normal by 53°. In the on top configuration, S is bound to a Au atom and the S–C bond is inclined from the surface normal by 70°. In the adatom configuration, S is located on top of an Au adatom and the S–C bond is inclined from the surface normal by 65°. In the MeS–Au–MeS configuration, one Au adatom is sandwiched by two MeS molecules and S atoms are located on top of substrate Au atoms.

The adsorption energy E_{ad} is defined by

$$E_{\text{ad}} = \frac{1}{n_{\text{MeS}}}(E(\text{MeS/Au(111)}) - E(\text{Au(111)}) - E(\text{MeS}) \times n_{\text{MeS}} - E(\text{Aubulk}) \times n_{\text{ad}}), \tag{3}$$

where $E(\text{MeS/Au(111)})$, $E(\text{Au(111)})$, and $E(\text{MeS})$ are total energies of MeS adsorbed on Au(111), the isolated Au(111) slab, and the isolated MeS molecule, respectively. n_{MeS} and

3

Table 1. The adsorption energies (E_{ad}), the angles of tilt of the S–C bond from the surface normal (θ), the Au–S bond distances ($r_{Au–S}$), and the work function changes ($\Delta\Phi$) of MeS molecules adsorbed on Au(111), and the work function change due to isolated MeS monolayers ($\Delta\Phi_0$).

Geometry	E_{ad} (kJ mol^{-1})	θ (deg)	$r_{Au–S}$ (nm)	$\Delta\Phi$ (eV)	$\Delta\Phi_0$ (eV)
Bridge	−164.7	52.8	2.49	−1.21	−1.14
fcc hollow	−140.3	16.6	2.51	−1.83	−1.81
On top	−129.3	70.1	2.37	−0.31	−0.65
Adatom	−129.8	64.9	2.28	−0.20	−0.80
MeS–Au–MeS	−187.7	68.7, 68.2	2.33[a], 2.51[b]	−1.07	−1.06
Exp.	−188.3[c], −167.4[d]			−1.2[e]	

[a] Distance between S and a Au adatom.
[b] Distance between S and a substrate Au.
[c] Reference [1].
[d] Reference [29].
[e] Reference [30].

n_{ad} are the number of molecules and the number of Au adatoms in a unit cell, respectively. n_{MeS} is 2 in the case of the MeS–Au–MeS configuration and 1 in other cases, while n_{ad} is 1 in the cases of adatoms and the MeS–Au–MeS configurations and 0 in other cases. The adsorption energies of MeS on Au(111) are summarized in table 1. The present results for the bridge and the fcc hollow configurations agree well with previous DFT results. The most stable configuration is the MeS–Au–MeS configuration followed by the bridge configuration, and the on top configuration turns out to be the least stable configuration. Although it is energetically less favorable to form adatoms from the flat Au(111) surface, the MeS–adatom bond becomes stronger and the MeS–Au–MeS configuration is stabilized significantly. In the case of the adatom configuration, the bonding between the MeS and the adatom is also strong, but just one MeS–adatom bond per adatom is not enough to make the adatom configuration more stable than the bridge or fcc hollow configurations. The calculated adsorption energies for the MeS–Au–MeS and bridge configurations agree reasonably well with the experimental results.

The calculated work function changes due to MeS adsorption $\Delta\Phi$ are also summarized in table 1. The fcc hollow configuration gives the largest decrease of the work function (−1.83 eV) and the bridge and the MeS–Au–MeS configurations follow, and the adatom and the on top configurations give the smallest change. The work function change correlates with the molecular tilting angle θ. As θ becomes larger, the work function change becomes smaller. This suggests that the work function change is ascribable to the molecular permanent dipole. To clearly show the contribution of the molecular permanent dipole to the work function change, we calculated that the work function change induced by an isolated MeS monolayer with its molecular axis aligned perpendicular to the surface is −1.89 eV. Then the work function changes due to isolated MeS monolayers with their molecular axis inclined from the surface normal by θ are given by $\Delta\Phi_0 = -1.89 \times \cos\theta$. As seen in table 1, $\Delta\Phi_0$ is close to $\Delta\Phi$, especially for the bridge, fcc hollow and the MeS–Au–MeS configurations, confirming that the work function change comes mainly from the molecular permanent dipole. In the cases of on top and adatom configurations, the discrepancy between $\Delta\Phi_0$ and $\Delta\Phi$ is not small and, therefore, the contribution from the charge redistribution between Au and MeS should be large. Experimentally, the work function change due to one-monolayer MeS adsorption on Au(111) is estimated to be −1.2 eV and this agrees very well with the bridge configuration. The work function change for the MeS–Au–MeS configuration is also close to the experimental value. Therefore, it is quite reasonable to conclude that the bridge and the MeS–Au–MeS configurations coexist on the Au(111) surface.
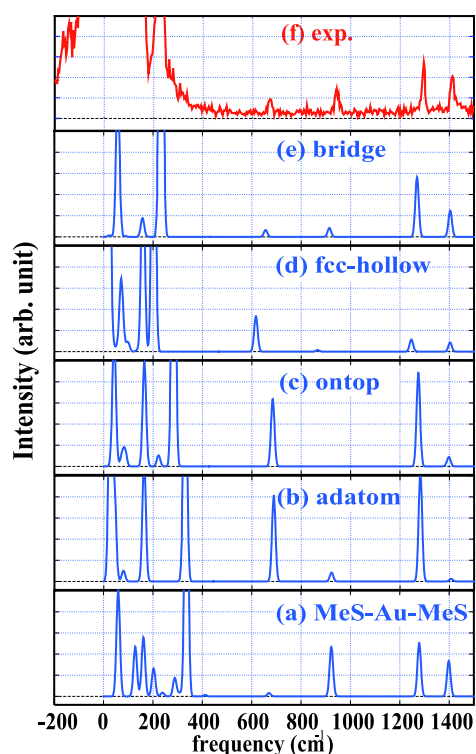
Figure 2. High resolution electron energy loss (HREEL) spectra of MeS/Au(111). (a)–(e) are calculated spectra while (f) is the experimental one from [11].

Figure 2 shows calculated and experimental HREEL spectra. Figures 2(a)–(e) are calculated spectra while (f) is the experimental one given in [11]. Experimentally observed peaks at 230 cm^{-1}, 680 cm^{-1}, 949 cm^{-1}, 1298 cm^{-1}, and 1415 cm^{-1} are assigned to the Au–S stretching (ν(Au–S)), the S–C stretching (ν(S–C)), the CH$_3$ rocking (ρ(CH$_3$)), the CH$_3$ symmetric deformation (δ_s(CH$_3$)), and the CH$_3$ asymmetric deformation (δ_a(CH$_3$)) modes, respectively. As seen clearly from figure 2, the spectrum calculated from the bridge configuration gives the best agreement with the experimental one. The spectrum calculated from the MeS–Au–MeS configuration also agrees with the experimental one reasonably well but it seems that the frequency of the ν(Au–S) mode is too high and the peak intensity of the ν(S–C) is too weak as compared with other peaks. In the cases of the fcc hollow, on top, and adatom configurations, the peak intensity of the ν(S–C) mode is too strong as compared with other peaks. These results are also consistent with the conclusion that both the bridge and the MeS–Au–MeS configurations coexist on the Au(111).

It is interesting to compare the peak intensity among different configurations. The peak intensity of HREELS from the dipole scattering mechanism is proportional to the square of the surface normal component of the dynamic dipole moment. In the case of isolated MeS molecules, the dynamic dipole moments of the ν(S–C) mode and δ_s(CH$_3$) are parallel to the molecular axis. Therefore, if we assume that the dynamic dipole moments of adsorbates are similar to those of isolated molecules, the peak intensities of the ν(S–C) and the δ_s(CH$_3$) modes should be proportional to the square of cos θ, where θ is the angle of tilt of the S–C bond from the surface normal. In reality, the peak intensity calculated from the on top and the adatom

configurations is stronger than that from the bridge and the fcc hollow configurations, being inconsistent with the simple model. This is in strong contradiction to the static dipole moment, which can be estimated quite well from the permanent dipole moment of an isolated molecule.

4. Conclusion

In the present study, we have investigated five possible adsorption structures of methylthiolate (MeS) on the Au(111) surface by using density functional theoretical calculations. The MeS–Au–MeS structure recently proposed by Maksymovych and co-workers [19] is the most stable among the five configurations and the bridge is the second most stable. The work function change and the high resolution electron energy loss spectra calculated from the MeS–Au–MeS and the bridge configurations agree rather well with the experimental results, strongly supporting the conclusion that the MeS–Au–MeS and the bridge configurations coexist on the Au(111) surface.

Acknowledgments

References

[1] Nuzzo R G, Zegarski B R and Dubois L H 1987 *J. Am. Chem. Soc.* **109** 733
[2] Fenter P, Eberhardt A and Eisenberger P 1994 *Science* **266** 1216
[3] Fenter P, Schreiber F, Berman L, Scoles G, Eisenberger P and Bedzyk M J 1998 *Surf. Sci.* **412/413** 213
[4] Kondoh H, Iwasaki M, Shimada T, Amemiya K, Yokoyama T, Ohta T, Shimomura M and Kono S 2003 *Phys. Rev. Lett.* **90** 066102
[5] Roper M G, Skegg M P, Fisher C J, Lee J J, Dhanak V R, Woodruff D P and Jones R G 2004 *Chem. Phys. Lett.* **389** 87
[6] Shimada T, Kondoh H, Nakai I, Nagasaka M, Yokota R, Amemiya K and Ohta T 2005 *Chem. Phys. Lett.* **406** 232
[7] Sellers H, Ulman A, Shnidman Y and Eilers J E 1993 *J. Am. Chem. Soc.* **115** 9389
[8] Beardmore K M, Kress J D, Grønbech-Jensen N and Bishop A R 1998 *Chem. Phys. Lett.* **286** 40
[9] Grönbeck H, Curioni A and Andreoni W 2000 *J. Am. Chem. Soc.* **122** 3839
[10] Yourdshahyan Y, Zhang H K and Rappe M A 2001 *Phys. Rev.* B **63** 081405(R)
[11] Hayashi T, Morikawa Y and Nozoye H 2001 *J. Chem. Phys.* **114** 7615
[12] Morikawa Y, Hayashi T, Liew C C and Nozoye H 2002 *Surf. Sci.* **507–510** 46
[13] Akinaga Y, Nakajima T and Hirao K 2001 *J. Chem. Phys.* **114** 8555
[14] Vargas M C, Giannozzi P, Selloni A and Scoles G 2001 *J. Phys. Chem.* B **105** 9509
[15] Gottschalck J and Hammer B 2002 *J. Chem. Phys.* **116** 784
[16] Yourdshahyan Y and Rappe A M 2002 *J. Chem. Phys.* **117** 825
[17] Morikawa Y, Liew C C and Nozoye H 2002 *Surf. Sci.* **514** 389
[18] Molina L M and Hammer B 2002 *Chem. Phys. Lett.* **360** 264
[19] Maksymovych P, Sorescu D C and Yates J T Jr 2006 *Phys. Rev. Lett.* **97** 146103
[20] Yu M, Bovet N, Satterley C J, Bengió S, Lovelock K R J, Milligan P K, Jones R G, Woodruff D P and Dhanak V 2006 *Phys. Rev. Lett.* **97** 166102
[21] Mazzarello R, Cossaro A, Verdini A, Rousseau R, Casalis L, Danisman M F, Floreano L, Scandolo S, Morgante A and Scoles G 2007 *Phys. Rev. Lett.* **98** 016102

[22] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[23] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[24] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[25] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[26] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[27] Neugebauer J and Scheffler M 1992 *Phys. Rev.* B **46** 16067
[28] Ibach H and Mills D L 1982 *Electron Energy Loss Spectroscopy and Surface Vibrations* (New York: Academic)
[29] Kondoh H, Kodama C, Sumida H and Nozoye H 1999 *J. Chem. Phys.* **111** 1175
[30] De Renzi V, Rousseau R, Marchetto D, Biagi R, Scandolo S and del Pennino U 2005 *Phys. Rev. Lett.* **95** 046804