Electric Field Effect on the Adsorption State of Methylthiolate on Au(111)

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We have studied the effect of the electric field on the adsorption structures of methylthiolate (MeS) on the Au(111) surface by using density functional theory. MeS has the bridge, fcc-hollow and atop adsorption configurations and the relative stability among those configurations can be changed by applying the electric field perpendicular to the surface. The energy difference between the bridge and fcc-hollow configurations can be well described by a simple dipole-field interaction model and the relative stability is reversed at an electric field of about 26 V/nm. As for the energy difference between the bridge and atop configurations, the effect of polarization becomes large at high electric field.

Keywords: Density functional calculations; Field effect; Gold; Nano-electronics and related devices

I. INTRODUCTION

As the integration of semiconductor devices increases, the device structure is decreasing quite rapidly. Molecular-scale electronics is one of promising technologies to overcome the device scale problem and conductance properties of single molecules have been intensively studied. Weiss and co-workers observed switching behavior of oligo (phenylene ethynylene) (OPE) molecules in alkanethiolate self-assembled monolayers (SAMs) on gold by using scanning tunneling microscopy (STM) [1–6]. They demonstrated that the switching behavior can be controlled by the polarity of the applied electric field between the STM tip and the substrate and the polarity dependence can be altered by changing the molecular dipole moment. From these results, they suggested that the conductance switching is due to changes in hybridization at the molecule-metal contact induced by tilting of the molecule. However, other mechanisms were also proposed to explain conductance changes. Seminario and co-workers carried out density functional theoretical calculations (DFT) and found that the character of the lowest unoccupied molecular orbital (LUMO) changes dramatically depending on the charged state of the molecule, leading to the changes in conduction [7]. Di Ventra and co-workers calculated the conductance of the benzene-1,4-dithiolate molecule with NO₂ group and found that the rotation of the NO₂ functional group affects the conduction of the molecule significantly [8]. On the other hand, Brédas and co-workers and Taylor and co-workers suggested that a twist of the central phenyl ring has strong effect on the localized nature of the HOMO and LUMO levels and affects the conductance of the molecule [9, 10]. Ramachandran and co-workers observed conductance switching behavior of simple n-alkane dithiols by using STM and suggested that the conductance switching is caused by bond-breaking at the molecule-metal contact [11]. Very recently, Zandvliet and co-workers suggested that the conductance switching is attributed to fluctuations of the number of molecules in the bundles due to diffusion and exchange of molecules [12]. Therefore, the origin of the conductance switching behavior of adsorbed molecules is still in debate. In the present study, we have investigated the effect of the electric field on the structure of the simplest thiolate molecule, methylthiolate (MeS) on the Au(111) surface.

II. THEORETICAL METHODS

All calculations are carried out using a first-principles program package STATE-Senri (Simulation Tool for Atom Technology) [13–15] which is based on the DFT [16, 17] with a generalized gradient approximation (GGA) [18]. Ultrasoft [19] and norm conserving [20] pseudopotentials are used to represent the interaction between electrons and ion cores. Wave functions are expanded by plane wave basis sets and the cut off energy is set to 25 Ry for wave functions and to 225 Ry for the charge density. Surfaces are modelled by a repeated slab model, in which one slab consists of four gold atomic layers separated by vacuum regions of about 1.4 nm thickness. MeS is adsorbed only on one side of a slab and MeS molecules and the top gold layer were relaxed while the bottom three gold layers were fixed at their ideal bulk positions during struc-
The calculated work function changes due to MeS adsorption ($\Delta \Phi$) are also summarized in Table I. The fcc-hollow configuration gives the largest decrease of the work function (−1.83 eV) and the bridge configuration follows and the ontop configuration gives the smallest change. The work function change correlates with the molecular tilting angle $\theta$. As $\theta$ becomes larger, the work function change becomes smaller. This suggests that the work function change is ascribed to the molecular permanent dipole. 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 electric field dependent total energy differences can be defined by

$$\Delta E_{\text{f-c}}(E) = E_{\text{f}}(E) - E_{\text{b}}(E),$$

$$\Delta E_{\text{o-c}}(E) = E_{\text{o}}(E) - E_{\text{b}}(E),$$

where, $E_{\text{b}}(E)$, $E_{\text{f}}(E)$, and $E_{\text{o}}(E)$ are total energies of the bridge, fcc-hollow and ontop configurations at electric field of $E$, respectively. If we assume that the polarization of adsorbates due to an applied electric field is negligible, the relative energies can be approximated by

$$\Delta E_{\text{f-c}}(E) = \Delta E_{\text{f-c}}(0) - (\mu_{\text{f}} - \mu_{\text{b}}) \times E,$$

$$\Delta E_{\text{o-c}}(E) = \Delta E_{\text{o-c}}(0) - (\mu_{\text{o}} - \mu_{\text{b}}) \times E,$$

where, $\Delta E_{\text{f-c}}(0)$ and $\Delta E_{\text{o-c}}(0)$ are total energy differences at zero electric field and $\mu_{\text{f}}$, $\mu_{\text{o}}$, and $\mu_{\text{b}}$ are induced dipole moments by adsorption of MeS in the bridge, fcc-hollow and ontop configurations, respectively. The induced dipole moments ($\mu$) can be estimated from the calculated work function change ($\Delta \Phi$) by

$$\mu = -e_{0}A\Delta \Phi,$$

where, $A$ is the area per one molecule and $e_{0}$ is the permittivity in the vacuum. The induced dipole moments by adsorption of MeS are summarized in Table I. Figure 2 shows the electric field dependence of the total energy differences among the three configurations along with those estimated by a simple dipole-field interaction model. At zero electric field, the bridge configuration is the most stable state, followed by the fcc-hollow and ontop configurations. A positive electric field, which is directed from the substrate to the vacuum, stabilizes the fcc-hollow configuration more than the bridge configuration because the former configuration has larger positive dipole moment than the latter one. Therefore, the energy difference between the fcc-hollow and bridge configurations becomes smaller as the electric field becomes stronger and the fcc-hollow configuration becomes more stable than the bridge configuration at the electric field of about 26 V/nm. The energy difference between the fcc-hollow and the bridge configuration agrees with that estimated from a simple dipole-field interaction model. As for the energy difference between the ontop and bridge configurations, the electric field dependence is reversed because the ontop configuration has smaller dipole moment than the bridge configuration. Furthermore, the simple dipole-field interaction model is not valid for the ontop configuration, indicating that the polarization of the ontop configuration is large.

The adsorption energy $E_{\text{ad}}$ is defined by

$$E_{\text{ad}} = (E(\text{MeS}/\text{Au}(111)) - E(\text{Au}(111)) - E(\text{MeS})),$$

where, $E(\text{MeS}/\text{Au}(111))$, $E(\text{Au}(111))$, and $E(\text{MeS})$ are total energies of MeS adsorbed on Au(111), isolated Au(111) slab, and isolated MeS molecule, respectively. The adsorption energies of MeS on Au(111) are summarized in Table I. The present results for the bridge and the fcc-hollow configurations agree well with previous DFT results. The most stable configuration is the bridge configuration and the ontop configuration is the least stable one among the three configurations.

III. RESULTS AND DISCUSSION

We have examined three adsorption structures as shown in Fig. 1. Figure 1 shows optimized geometries of MeS on the Au(111) surface in the fcc-hollow, bridge, and ontop configurations. In the fcc-hollow configuration, S is located at the three-fold hollow site with molecular S-C bond nearly perpendicular to the surface. In the bridge configuration, S is located at the bridge site slightly off-centered towards a hollow site and the S-C bond is tilted from the surface normal by 53 degrees. In the ontop configuration, S is bound to a Au atom and the S-C bond is inclined from the surface normal by 70 degrees. The bridge configuration is the most stable adsorption configuration for MeS adsorbed on the unreconstructed Au(111) surface [22, 23]. Recently, it was reported that there are multiple adsorption states of MeS on Au(111) and bridge configuration and the MeS-Au-MeS configuration, in which one Au adatom is sandwiched between two MeS molecules and S atoms are located ontop of substrate Au atoms, co-exist [23–25]. For simplicity, we examined the bridge, fcc-hollow and ontop configurations and we did not considered substrate reconstruction as assumed in the MeS-Au-MeS configuration.

The adsorption energy $E_{\text{ad}}$ is defined by

$$E_{\text{ad}} = (E(\text{MeS}/\text{Au}(111)) - E(\text{Au}(111)) - E(\text{MeS})),$$

where, $E(\text{MeS}/\text{Au}(111))$, $E(\text{Au}(111))$, and $E(\text{MeS})$ are total energies of MeS adsorbed on Au(111), isolated Au(111) slab, and isolated MeS molecule, respectively. The adsorption energies of MeS on Au(111) are summarized in Table I. The present results for the bridge and the fcc-hollow configurations agree well with previous DFT results. The most stable configuration is the bridge configuration and the ontop configuration is the least stable one among the three configurations.
TABLE I: The adsorption energies ($E_{ad}$), tilting angles of the S-C bond from the surface normal ($\theta$), the Au-S bond distances ($r_{Au-S}$), the work function changes ($\Delta \Phi$) of MeS molecules adsorbed on Au(111), and the induced dipole moment by MeS adsorption ($\mu$).

| Geometry       | $E_{ad}$ / kJ/mol | $\theta$ / degree | $r_{Au-S}$ / nm | $\Delta \Phi$ / eV | $\mu$ / 10^{-30} Cm |
|----------------|-------------------|-------------------|----------------|-------------------|-------------------|
| bridge         | $-$164.7          | 52.8              | 2.49           | $-$1.21           | 2.39              |
| fcc-hollow     | $-$140.3          | 16.6              | 2.51           | $-$1.83           | 3.62              |
| ontop          | $-$129.3          | 70.1              | 2.37           | $-$0.31           | 0.61              |
| Exp.           | $-$188.3°, $-$167.4° |

$^a$Distance between S and a Au adatom.

$^b$Distance between S and a substrate Au.

$^c$Ref. [26].

$^d$Ref. [27].

$^e$Ref. [28].

FIG. 2: The total energy difference between the fcc-hollow and bridge configurations $\Delta E_{f-b}$ and that between the ontop and bridge configurations $\Delta E_{o-b}$ obtained from DFT-GGA-ESM calculations (Eqs. (2) and (3)) along with those estimated from the dipole-field interaction, $\Delta E_{t-b, dip}$ and $\Delta E_{o-b, dip}$ defined by Eqs. (4) and (5).

IV. CONCLUSION

In conclusion, we have investigated the effect of the electric field on the adsorption states of methylthiolate (MeS) on the Au(111) surface by using density functional theory. The relative stability between the fcc-hollow and bridge configurations can be well approximated by a simple dipole-electric field model and the relative stability is changed by applying a strong electric field of 26 V/nm. The polarization effect is large for the ontop configuration and the relative energy between the ontop and the bridge configuration deviates from a simple dipole-electric field model.

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