Photoemission core-level shifts reveal the thiolate-Au(111) interface

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(Received 6 July 2010; published 11 August 2010)

The nature of the thiolate/Au(111) interface is a long-standing puzzle. It has been suggested that thiolates drive surface reconstruction, however, a consensus regarding the adsorption configuration is missing. Herein, the density-functional theory is used to evaluate surface core-level shifts (SCLSs) for methyl thiolates on Au(111) assuming a representative set of different surface reconstructions. The SCLSs are found to provide sensitive fingerprints of the anchoring configuration, and it is only thiolate adsorption in the form of MeS-Au-SMe complexes that can be reconciled with experimental data.

DOI: 10.1103/PhysRevB.82.085416 PACS number(s): 73.20.−r, 68.43.Bc, 82.80.Pv

I. INTRODUCTION

Structural knowledge at the atomic scale is a prerequisite for fundamental understanding of materials and surface properties. Complete structural determinations of surfaces are, however, generally challenging due to the lack of translational symmetry and the possibility of surface reconstructions. Efforts to resolve surface structures often employ a combination of electron or photon diffraction techniques, photoemission core-level spectroscopy and local probes such as scanning probe microscopy. Moreover, the interplay between experiments and theoretical first-principles electronic-structure calculations has proven to be essential. One recent example is the determination of the Pd(100) surface oxide where the atomic structure has been established via a combination of techniques, including low-energy electron diffraction, scanning tunneling microscopy (STM), core-level spectroscopy, and density-functional theory (DFT) calculations.[1]

A yet unresolved structural surface puzzle is the thiol(ate)/Au(111) interface. Self-assembled monolayers (SAMs) of alkylthiolates (*R*S-, where *R* is an alkyl chain) are readily formed from thiols (*R*SH) of disulfide (*R*SS*R*) and offer a convenient route to surfaces with tailored properties.[2,3] Despite considerable experimental and theoretical efforts, the nature of adsorption configuration is still controversial.[4] Early electron and helium diffraction measurements showed that RS groups form a hexagonal $(\sqrt{3}\times\sqrt{3})R30°(\sqrt{3})$ overlayer on Au(111) and it was assumed that *R*S occupies threefold hollow positions. Subsequent helium diffraction measurements indicated a rectangular $c(4\times2)$ superstructure with respect to the $\sqrt{3}$ lattice.[5] More recently, structures have been proposed that comprise Au adatoms. Based on x-ray standing wave (XSW) measurements, it was suggested that thiolates are bonded to the surface via atop adsorption on Au adatoms (*R*S-Au).[6] On the other hand, *R*S-Au-S*R* complexes bonded to Au(111) have been observed with STM.[7] Moreover, a combined grazing incident x-ray diffraction (GIXRD) and *ab initio* molecular-dynamics study proposed a model with different structural elements,[8] namely, one $(R\mathrm{SAu})_x$ polymer, and thiolates adsorbed at surface point defects.

On the theoretical side, it is established that *R*S is adsorbed in a bridge-fcc site (bridge with S slightly bent over fcc) on the unreconstructed Au(111) terrace.[9–14] This configuration is, however, predicted to be unstable with respect to surface reconstruction with *R*S adsorbed at defects[15,16] or adatoms.[17–21] Among the different suggestions, one that comprises two *R*S-Au-*R*S units in each $c(4\times2)$ supercell is predicted to be energetically favored.[22] Although there is an uncertainty concerning the ability of state-of-the-art DFT methods to predict small energy differences [in particular, for reconstructed *R*S/Au(111) systems, as the cohesive energy of gold is underestimated by ~15%] the structure based on *R*S-Au-*R*S units is consistent with the bulk of experimental data. *R*S-Au-S*R* complexes bonded to Au(111) has been observed at different coverages by STM,[23] calculations of the infrared (IR) vibrational signatures match the experimental data,[24] simulations of the GIXRD maps[25] are in agreement with experiments and calculations for the *R*S-Au-*R*S structure compare favorably with sulfur *K*-edge near-edge x-ray absorption fine-structure (NEXAFS) measurement.[26] It has also been suggested that the *R*S-Au-*R*S structure might be consistent with normal-incidence XSW data.[26] In most cases, however, the experimental assignments are not conclusive.

One step to resolve the issue was taken recently by the study of methyl thiolates (MeS) on Au(111) with Au($4f_{7/2}$) photoemission core-level spectroscopy.[27,28] For the clean Au(111) surface, deconvolution of the emission signal shows a surface component at −0.34 eV with respect to the bulk component. After MeS adsorption, a good fit was achieved by deconvolution into three components. In addition to the bulk signature, emissions at both higher (T=+0.34 eV) and lower (S=−0.22 eV) energies were deduced. On the basis of the relative $S:T$ intensities (3:1), it was put forth that the experiments support the *R*SAu model;[6] there are one adatom for every three atoms in the first unreconstructed surface layer. Whereas the use of intensities for conclusions regarding surface composition is ambiguous,[29,30] the energies of the surface core-level shifts (SCLSs) could provide fingerprints. In fact, SCLSs have been used extensively to resolve complex structures, see, e.g., Ref. 1. Herein, we use DFT calculations to demonstrate that the SCLSs indeed provide unique information and can be used to uncover the thiolate/Au(111) interface.

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II. COMPUTATIONAL METHOD

DFT is employed in the implementation with plane waves and pseudopotentials.[31,32] The spin-polarized Perdew-Burke-Ernzerhof approximation is used for the exchange and correlation functional[33] and ultrasoft scalar-relativistic pseudopotentials are used to describe the interaction between the valence electrons and the core.[34] The number of electrons treated variationally for each element are: Au(11), S(6), C(4), and H(1). A plane-wave kinetic-energy cutoff of 25 (30 when evaluating SCLSs) Ry is used to expand the Kohn-Sham orbitals.

Adsorption is investigated in a $(3\times 2\sqrt{3})$ surface cell [which corresponds to the $c(4\times 2)$ overlayer]. The surface is represented by five atomic layers. Repeated slabs are separated by 15 Å. To study saturation coverage, four MeS units are considered in each cell. Reciprocal space integration over the Brillouin zone is approximated with a finite sampling of eight special k points. Structural optimization is performed without any constraints. The bond lengths around Au in the center layer are within 0.1% of the bulk value. The SCLSs are evaluated by the use of a pseudopotential that is generated with an electron hole in the Au(4f) shell.[35] To describe the electronic relaxation in better detail, this potential include the 5s5p semicore in the valence. An Au(4f) core hole in the center of the slab is used to model the bulk reference. The approach assumes complete screening of the core hole. This is justified for the present systems by the favorable comparison to experiments for the clean Au(111) surface, see below.

III. RESULTS AND DISCUSSION

Atomic models of the considered structures are given in Fig. 1. The structure in Fig. 1(a) represents the traditional model with MeS adsorbed on the unreconstructed (111) terrace in a bridge-fcc position. The geometry in Fig. 1(b) is a MeSAu monomer adsorbed in fcc configurations as originally proposed in Ref. 6. The model in Fig. 1(c) is a recently proposed configuration based on *ab initio* molecular dynamics and GIXRD measurements.[8] The model has one stoichiometric gold-thiolate polymer and two monoatomic vacancies on which MeS is adsorbed. The configuration in Fig. 1(d) comprises two MeS-Au-MeS complexes with the carbon chains arranged in *cis*-configurations.[20]

The relative energies are reported with respect to the structure in Fig. 1(a) using Au in the bulk phase as a reservoir of adatoms. The monomer structure is unfavored (+1.44 eV) with respect to the traditional model. The geometry with surface vacancies is also higher in energy than the unreconstructed case (+0.24 eV). In contrast, the model based on MeS-Au-MeS complexes is clearly favored with respect to the traditional structure. The methyl groups are in this model arranged in a *cis*-configuration. Previous calculations[22] have shown that the *trans* version is ~0.1 eV higher in energy. The relative stabilities suggest that the interface consists of MeS-Au-MeS complexes. Several alternative structures have been proposed during recent years[15–19] of which some are preferred over the traditional model but not over the structure with methyl thiolate complexes [Fig. 1(d)].[22] The considered geometries in Fig. 1 include proposed bond motifs, namely, vacancies, polymers, and adatoms.

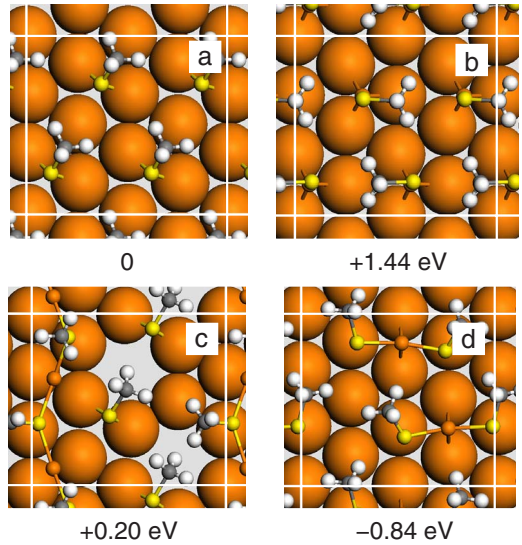

FIG. 1. (Color online) Optimized structures for MeS on Au(111). The relative energies with respect to the structure in (a) are reported in eV. Atomic color codes: orange (Au), yellow (S), gray (C), and white (H). The adatoms are represented by small spheres. The surface cells are indicated by white lines.

As the considered structures include adatoms and vacancies, we consider first the SCLSs signatures for the clean Au(111) terrace, adatoms, and monoatomic vacancies, see Table I. Energetically, the fcc site is preferred by 0.02 eV over the hcp site. The bridge site is not a minima on the potential-energy surface.[36] The SCLSs for clean Au(111) has been measured to be −0.31 eV in a high-resolution study[37] and lately to be −0.34 eV.[27] The calculated value is close to the measurements and demonstrates the accuracy of the applied methodology. The shifts for the adatoms are about −1 eV. The lower binding energy indicates a larger ability of the adatom to screen the core hole as a consequence of the low coordination. (The total energy is lower for the system with the core hole in the adatom as compared with the total energy with the core hole in the bulk.) The differences between the various adsorption sites are small. Surface atoms that are bonded to the adatom experience a reduced SCLSs. This could be attributed to increased coordination. Au atoms close to a vacancy are undercoordinated and have a larger negative shift than do the surface atoms on the defect-free Au(111) terrace.

The calculated SCLSs for the different thiolate/Au(111) interfaces are reported in Fig. 2. In addition to the shifts, the Au(4f) binding energies are shown together with the experimental result of Ref. 28. The theoretical binding energies are obtained by aligning the bulk component to the experimental binding energy for Au in the bulk (84.00 eV).[28]

The traditional model in Fig. 1(a) shows two main shifts with respect to the bulk component; one at −0.23 eV and one at −0.07 eV. The small shift (experienced by eight atoms in the cell) corresponds to gold atoms bridged by a thiolate. The four atoms in the cell not bonded to MeS have

TABLE I. Au(4*f*) SCLSs (eV) for Au(111), adatoms on Au(111), and a monoatomic vacancy. fcc, hcp, and bridge denote adatom adsorption sites. S1, S2, and S3 indicate adatom, atom bonded to adatom, and terrace atom, respectively. S4 denotes an atom in surface layer close to the vacancy.

	S1	S2	S3	S4
Bare			−0.36	
fcc	−0.95	−0.29	−0.36	
hcp	−0.99	−0.28	−0.36	
Bridge	−1.01	−0.21	−0.36	
Vacancy			−0.37	−0.47

a shift of −0.23 eV, thus the presence of MeS on the surface affects also atoms not directly involved in the bonding. Also the monomer structure in Fig. 1(b) have two main features; one at −0.60 eV and one at −0.27 eV. The −0.60 eV shifts are calculated for the atoms in the MeSAu monomer. All atoms in the unreconstructed surface have a common shift of −0.27 eV. The reduced shifts as compared to the clean terrace can be attributed to the increased coordination. The model with different structural motifs in Fig. 1(c) show shifts that range from −0.42 to +0.23 eV. The four shifts at −0.42, −0.28, −0.24, and −0.17 eV originate from surface atoms that do not connect to MeS (see Fig. 1). Surface atoms that are bound to MeS have shifts close to −0.10 eV. The two Au atoms in the polymer experience positive SCLSs, namely, +0.19 eV and +0.23 eV, respectively. The model with MeS-Au-MeS complexes is calculated to have three main shifts. One with a double feature at −0.25 eV, one close to 0.0 eV, and one centered at +0.27 eV. The SCLSs at −0.25 eV arise from surface atoms not bonded to the complex (with the lower component for the atoms that are bridged by the adatoms). The zero shift is calculated for the four surface atoms that are bonded to the complex. The two adatoms in the complexes have positive shifts.

In Ref. 20, an alternative MeS-Au-MeS structure (also *cis*-orientation of the methyl groups) was investigated with the axis of the complexes aligned along the short side of the surface cell. This structure is only 0.06 eV higher in energy than the geometry in Fig. 1(d). We have evaluated the SCLSs also for this structure and the results are similar to those of Fig. 2(d); it has a double feature centered at −0.27 eV, one at 0.0 eV, and one at +0.29 eV.

The results in Fig. 2 demonstrate that the SCLSs are sensitive fingerprints of the thiolate/Au(111) interface; the different models have unique signatures. In the recent experiments,[27,28] the photoemission spectrum was deconvoluted into three features (indicated in Fig. 2); two surface components at −0.22 eV and +0.34 eV, respectively, and one component assigned to bulk contributions. Among the considered models, it is only the MeS-Au-MeS structure that can be reconciled with this result; it has two clear features at positive and negative SCLSs, respectively, and one at zero that experimentally is masked by the bulk component. Positive SCLSs generally indicate oxidized metal atoms. One example is the surface oxide on Pd(100). This structure consists of one monolayer of PdO(101) that adhere to Pd(100).

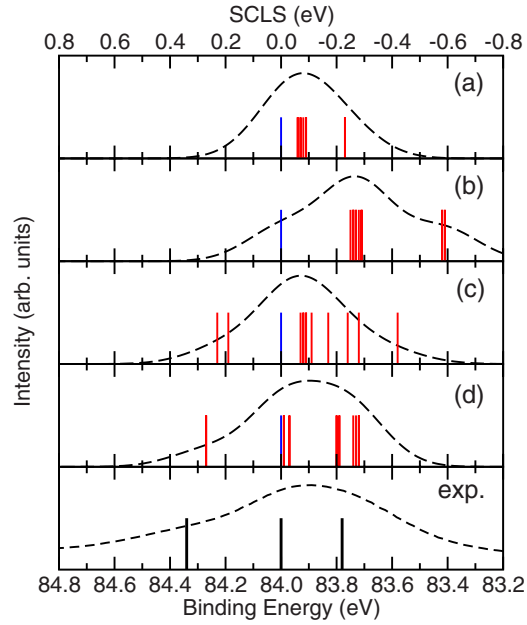

FIG. 2. (Color online) Au(4*f*) surface core-level shifts and binding energies for the optimized structures of MeS on Au(111). The structures are labeled as in Fig. 1. Red bars denote calculated surface shifts. Blue bars are the bulk components. To facilitate comparisons with experimental data, a convolution of the SCLSs with a 0.3 eV Gaussian is shown. A bulk contribution is added to the convoluted results to yield similar intensities for the bulk and surface contributions for (d). This choice is based on the unconstrained experimental fit in Ref. 28. The experimental data are reproduced from Ref. 28.

The Pd atoms in the surface-oxide layer have positive SCLSs with respect to Pd bulk.[1]

Given that the experimental spectrum for MeS/Au(111) can be deconvoluted with only three features implies that the interface has a limited number of different atom types. Assuming two types of atoms would fit the traditional thiolate [Fig. 1(a)] or the monomer [Fig. 1(b)] model. However, our results show that these conformations can be ruled out; none of them have positive SCLSs with respect to the bulk component. The model proposed by Cossaro *et al.*[8] [Fig. 1(c)] have Au atoms in several arrangements. This does not account for the experimental situation where a good fit is achieved with only three components. The MeS-Au-MeS model includes three types of Au atoms. An agreement with experimental data[27–29] is obtained as one set of the atoms have a zero SCLSs. It should be noted that the ratio of the intensity between surface and bulk components ($S+T:B$) in the photoemission signal has been measured to decrease upon monolayer formation,[29] which indicates that Au atoms at the surface exist with negligible surface core-level shifts.

The differences in the Au(4*f*) SCLSs for the structure with MeS-Au-MeS complexes is a measure of differences in the ability to screen the core hole. The Au atoms that are linearly coordinated between the thiolates in the complexes show the weakest screening. This property is consistent with the calculated[38] excess charges after electronic relaxation around the core hole. We calculate excess charges of 0.59, 0.65, and 0.75 electrons for atoms with SCLSs of +0.27 eV,

0.0 eV, and −0.25 eV, respectively. The excess charge for the reference core hole in the bulk is calculated to be 0.64 electrons, thus in perfect agreement with the 0.0 eV component.

High-resolution photoemission studies of SAMs formed from hexanethiolate and dodecanethiolate on Au(111) was recently reported.[39] In agreement with the methylthiolate case, the experiments indicate a branching of the Au(111) surface signal into two components upon RS adsorption. With respect to the bulk component, the two features were found at −0.16 and +0.40 eV. This is in qualitative agreement with the experimental results for methylthiolate[27] as well as the present calculations and an indication that the same adsorption configuration apply irrespective of carbon-chain length.

IV. CONCLUSIONS

The nature of the thiolate/gold interface has been a long-standing puzzle ever since the original SAMS proposal. Herein it has been demonstrated that shifts in the Au(4*f*) core levels provide a sensitive fingerprint of the *R*S-Au bond configuration. In particular, it has been shown that it is only an interface that comprises MeS-Au-SMe complexes that can account for the measured data. Thanks to the match between the calculated shifts and the experiments, the character of the interface appears to be solved. We note that the results from the core-level spectroscopy conform to the energetic argument in the preference for the MeS-Au-SMe structure over alternative adsorption models.[22] It is also consistent with experimental STM,[23] IR,[24] GIXRD,[25] and NEXAFS (Ref. 26) data.

The structure for the extended surface incorporates similar motifs as experimentally completely resolved structures of thiolate-protected nanoclusters, see, e.g., Refs. 40–42. These systems are characterized by metal cores that are capped by gold-thiolate complexes. Moreover, $Au_{144}(RS)_{60}$ (for which a structure with *R*S-Au-*R*S complexes has been proposed[43]) has Au(4*f*) core levels in similarity with thiolates on Au(111).[44] Thus, the present results provide a consistent picture of the thiolate/gold interface from extended macroscopic surfaces to gold at the nanoscale.

ACKNOWLEDGMENTS

We thank D. P. Woodruff for valuable comments. Support from the Swedish Research Council is acknowledged (H.G.). The calculations have been performed at C3SE (Göteborg).

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