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Rich Coordination Chemistry of Au Adatoms in Gold Sulfide Monolayer on Au(111)

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The rich chemistry of Au nanoparticles and ions has attracted tremendous interest, in part because the surfaces of bulk Au have traditionally been considered to be chemically inert. On the other hand, large-scale mass transport and the formation of vacancy islands have been observed on the Au(111) surface following the deposition of adsorbates, such as sulfur and thiols, that can interact strongly with the Au surface. In this work, we revisit the structure and chemistry of an ordered incommensurate AuS adlayer that forms on Au(111) following the deposition of sulfur and annealing to 450 K. A structural model of this AuS surface phase has not yet been determined experimentally due to the complexity of the system. Here, we use state-of-the-art density functional theory to develop an atomic-scale model that is consistent with the previously reported Au−S stoichiometry. In particular, we introduce theoretical techniques to take into account the charge transfer in an incommensurate system. Our model reproduces convincingly STM images and is remarkably robust. Bonding analysis based on Wannier functions shows that the model exhibits rich coordination chemistry corresponding to different Au oxidation states. The extraordinary stability and rich chemistry of this structure have implications for related S−Au interfaces and previously reported surface features of this system.

Gold is widely considered to be an element with fascinating chemistry, in part because its chemical properties change dramatically depending on its structural phase and environment.[1] For example, Au has long been known as the noblest of all metals and has traditionally been associated with jewelry, an application that stems from the chemical inertness[2−4] of bulk Au. On the other hand, Au nanoparticles were recently discovered to have remarkable catalytic properties, in the oxidation of carbon monoxide at low temperatures, for instance.[5] Au atoms or ions can actually give rise to a rich variety of structures with interesting chemistry, as evidenced by the large number of Au compounds synthesized in solution and in the gas phase.[1,3]

The inertness of gold surfaces results from high reaction barriers to the dissociation of molecular reactants. This, however, does not imply that the surface cannot form strong bonds with under-coordinated adsorbates.[2] For example, sulfur is known to bind well to Au surfaces, forming the basis of self-assembled alkylthiol monolayers (SAMs) on Au(111).[6] The strong interaction of sulfur with Au can even lead to large-scale mass transport

of Au atoms on Au(111), resulting in pit and island formation.[6,7] Similar observations have been made for the Au/oxygen interaction, where mass transport induced by atomic oxygen results in facile O_2 dissociation on the otherwise inert Au(111) surface.[8] These observations bring into question the conventional picture of an inert Au(111) surface and call for a fundamental study of the chemistry of Au surface atoms involved in the interaction with adsorbates.

In this work, we revisit the Au(111)/sulfur interaction which was the subject of a previous scanning probe microscopy study.[7,12] In short, our experiments revealed that sulfur adsorption at 300 K lifts the surface reconstruction of Au(111) in the low-coverage regime (0.1 ML) and leads to the formation of a 2D AuS phase involving large-scale mass transport in the high-coverage regime (>0.3 ML). The reaction is completed once the S coverage reaches a value of approximately 0.6 ML. At this point, the surface is completely covered with a sponge-like AuS overlayer. Locally ordered regions of ring-like structures develop during annealing at 420 K. Similar features have been observed during electrochemical deposition[10,11] and have been attributed to strained S_8 molecules. Further annealing to 450 K decreases the sulfur coverage by approximately 20% (to 0.5 ML), and large vacancy islands of monatomic depth develop by Ostwald ripening of the original irregular etch pits. At this point, the Au(111) surface is uniformly covered (terrace areas as well as vacancy islands) with an ordered AuS film. The sulfur-induced formation of pits and vacancy islands can be explained by Au atoms which are etched from terrace sites
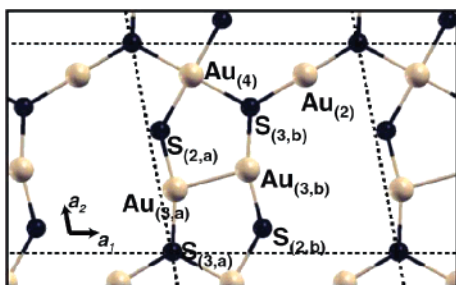
Figure 1. Atomic structure of *A*. The numerical subscripts correspond to the coordination of each atom. The AuS structure is planar.
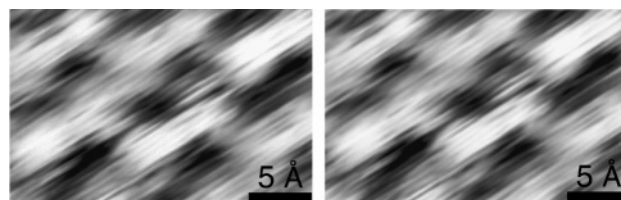

Figure 2. STM images collected at room temperature (left, 118 mV; right, 520 mV).
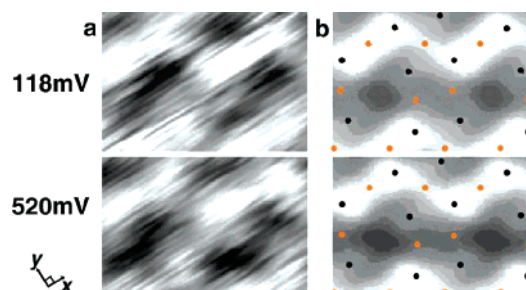

Figure 3. (a) Constant height STM images collected at room temperature. (b) STM simulations. The orange and black dots mark the positions of Au and S.

and incorporated into the growing gold sulfide phase. On the basis of the area covered by vacancy islands, it was estimated that approximately 0.5 ML of Au are incorporated into the ordered AuS layer, suggesting a 1:1 stoichiometry.[7] High-magnification scanning tunneling microscopy (STM) images and low-energy electron diffraction (LEED) patterns[7] collected from the ordered 2D AuS phase are consistent with an incommensurate quasi-rectangular unit cell with lattice parameters of $(8.8 \pm 0.4) \times (8.2 \pm 0.4)$ Å^2 and an angle of $(82 \pm 4)°$ between lattice vectors. Although these observations unequivocally demonstrate the formation of a 2D AuS phase via sulfur-induced Au mobilization, the complexity of the AuS phase prevented us from developing a structural model.

Here, we go one step further and develop an atomistic model using state-of-the-art density functional theory. The structure we obtain is remarkably robust, reflects the rich coordination chemistry of Au, and reproduces the experimental observations. The basic idea of our approach is the following. Since an incommensurate layer interacts only weakly with the substrate, we first consider an isolated AuS layer. We explored several models with different numbers of atoms in the ratio Au:S = 1:1, in a unit cell consistent with experiment, and found only one stable structure, *A* (Figure 1). The corresponding S coverage is reasonably close to the experimental estimate. We next fully optimize the unit cell parameters. This did not change the atomic geometry of *A* but resulted in an almost uniform shrinking of the unit cell by ∼7−8%, indicating a robust atomic structure and cell *shape* for model *A*. The shrinking of the unit cell is consistent with the fact that bonds in *A* are ∼8−11% longer than those in bulk Au$_2$S[13] and other compounds with Au−S bonds.[4]

To analyze the effect of the substrate, we first note that a natural choice of unit cell alignment is given by the black box in Supporting Information Figure S1, which is within experimental error bars for the AuS unit cell, given the experimental Au lattice constant $c_{expt} = 2.884$ Å. In this arrangement, the AuS lattice matches with the substrate in direction a_1 but not a_2. Although it is impossible to simulate the incommensurate system, we obtain a good approximation by considering a unit cell commensurate with the substrate, which also fits within experimental error bars for the AuS unit cell, provided we use instead the theoretical bulk Au lattice constant $c_{theory} = 2.948$ Å (shown in Supporting Information Figure S1). We can now simulate a AuS layer on top of a six-layered Au(111) slab in this unit cell. These calculations provide two key insights into the stability of the AuS structure in the presence of the substrate: First, the most stable structure, which we call *B*, is remarkably robust. In *B*, the 2-fold coordinated Au$_{(2)}$ and 4-fold coordinated Au$_{(4)}$ are at distinct bridge sites on Au(111), which we call **X** and **O**, respectively (Supporting Information Figure S1). If instead Au$_{(4)}$ is placed initially at **X** and Au$_{(2)}$ at **O**, each of these Au atoms remains at its initial site during relaxation,

while the remaining atoms completely rearrange to yield *B* again, interchanging the coordination of Au atoms at **X** and **O**. Thus, the AuS structure obtained is favored even in the presence of the Au substrate.

Second, the substrate-induced stretch in bond lengths described above is stabilized by charge transfer from the substrate. We model charge transfer effects between the metallic AuS layer and substrate by calculating the change in Fermi level, ΔE_f, of the layer due to interaction with the substrate (see the Supporting Information). To capture the incommensurate nature of the interaction, we average this value over several different configurations, varying the relative position of the planar layer on Au(111) in the incommensurate direction a_2. Our calculations indicate charge transfer from the substrate with $\Delta E_f = (0.85 \pm 0.03)$ eV. From the estimated ΔE_f value, we determine the charge transferred to the layer and optimize its structure to obtain lattice constants of 8.4 Å and 7.9 Å and an angle of 76°, all reasonably close to experimental values.

We can now simulate STM images to compare with high-magnification STM images collected at room temperature (Figure 2), by using *A* with E_f shifted by $\Delta E_f = 0.85$ eV. We use the Tersoff−Hamann approximation with Gaussian broadening to take into account the effects of convolution with tip wavefunctions,[14] as well as the small amount of spot-broadening in the scan direction *x*. The results, shown for standard deviations of $s_x = 1.2$ Å and $s_y = 0.8$ Å (both less than half of the bond lengths in the structure), reproduce convincingly the experimental images at two different bias voltages (Figure 3).

We now analyze the bonding characteristics of the stable structure *A* in Figure 1, using a recently developed scheme that provides an excellent description of bonding in metallic and covalent systems.[15] The analysis relies on the construction of atom-centered orbitals (AOs) and bond-centered orbitals (BOs) (see the Supporting Information). The AOs for Au 6*s*, S 3*s*, and S 3*p* electrons are spatially extended (Supporting Information Figure S2), indicating substantial bond covalency. Each Au (S) atom contributes 0.3−0.4 *e* (0.8−0.9 *e*) per bond. The Au−S bonds are partially polar, as indicated by their asymmetric BOs (Figure 4a,b). This is consistent with excess charge in S 3*p* AOs and a shortage of charge in Au 6*s* (and some 5*d*) AOs. Figure 4c indicates that the Au$_{(3,a)}$−Au$_{(3,b)}$ bond is multicentered

Letters

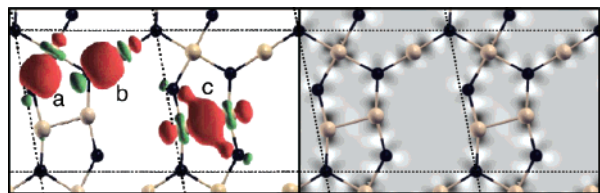*J. Phys. Chem. B, Vol. 110, No. 32, 2006* **15665**

Figure 4. Left: BOs for (a) $Au_{(4)}$–S, (b) $Au_{(2)}$–S, and (c) $Au_{(3,a)}$–$Au_{(3,b)}$. Colors represent isocontours of the same absolute value (red, positive; green, negative). Right: Charge density difference between structure *A* and the superposition of atomic densities, in the plane of the structure; the scale runs from $-0.0005e$ (black) to $+0.0002e$ (white).

and stabilized by delocalization over $S_{(2,a)}$ and $S_{(2,b)}$. The amount of electron charge in Au AOs is largest for $Au_{(2)}$ and smallest for $Au_{(4)}$, consistent with formal oxidation states expected from the literature: Au^+ and Au^{3+} have linear and square planar coordination, respectively, while the $5d^9$ configuration in Au^{2+} is typically accompanied by a Au–Au bond.[3] Indeed, the ring, $Au_{(4)}$–$S_{(3,b)}$–$Au_{(3,b)}$–$S_{(2,b)}$–$Au_{(4)}$–$S_{(3,a)}$–$Au_{(3,a)}$–$S_{(2,a)}$, is a motif found in Au^{2+} compounds.[3,4] S is known to form bonds with Au in all three oxidation states;[4] the 2- and 3-fold coordination for S is similar to that for O in Au_2O_3[16] (the structure of Au_2S_3 is unknown). The 1:1 stoichiometry in *A* thus arises from having one Au^{3+} ($Au_{(4)}$), one Au^+ ($Au_{(2)}$), and two Au^{2+} ($Au_{(3,a)}$ and $Au_{(3,b)}$) atoms per unit cell. This is distinct from bulk gold sulfides (Au_2S and Au_2S_3),[17] which contain purely Au^+ or Au^{3+}.

To understand the effects of the substrate, we perform a similar analysis on structure *B*. Again, the amount of electron charge in Au AOs is largest for $Au_{(2)}$ and smallest for $Au_{(4)}$. Compared to the isolated layer, the electronic charge in each BO increases by 54% on average, except for the multicentered BO, where the increase is only 15%. In contrast, the contribution of each AO to bonding does not change significantly. The BOs are slightly extended toward the substrate atoms but remain largely confined within the AuS plane. This implies that bonds within the AuS layer are strengthened at the expense of substrate electrons, which may explain the robustness of the AuS structure.

In conclusion, we have proposed an atomic-scale model for an ordered, incommensurate adlayer formed on the Au(111) surface following sulfur deposition and annealing at 450 K. This adlayer has been observed to completely cover the Au surface in STM images, which span hundreds of nanometers. We investigated the stability and nature of bonding in this model and found it to be remarkably robust, with rich coordination chemistry corresponding to different Au oxidation states. Our model also reproduces convincingly STM images, indicating that the large-scale mass transport on Au(111), commonly observed in SAM formation,[6] and other instances involving strong interaction with adsorbates,[8] is likely to involve etching

of Au(111) atoms which changes the chemistry of Au on the surface. While we are not able to prove that this model exactly corresponds to that experimentally studied because of possible uncertainty in the experimental stoichiometry, the extraordinary stability of the model, even in the presence of the Au substrate, strongly suggests that it is favored, and is at least an important precursor state. This structure and its chemistry have implications for related S–Au interfaces and previously reported surface features of this system.

Supporting Information Available: Figures showing unit cell alignment and the AOs for structure *A* and the Methods section. This material is available free of charge via the Internet at http://pubs.acs.org.

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