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Self-assembled monolayers of methylselenolate on the Au(111) surface: A combined STM and DFT study

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ABSTRACT

In this study scanning tunneling microscopy (STM) and density functional theory (DFT) were used to investigate the structural formation of methylselenolate (CH_3Se) self-assembled monolayers (SAMs) on the Au(111) surface. SAMs were prepared by two different methods, from solution and by exposing the Au(111) surface to gaseous dimethyldiselenide (DMDSe). For methylselenolate (MSe) on the Au(111) surface, our STM measurements revealed the presence of $(4 \times \sqrt{3})$ and $(3 \times 2\sqrt{3})$ rectangular striped phases. These structures were verified by DFT calculations. For both phases, the DFT calculations clearly found a bridge adsorption geometry for MSe on Au(111). Furthermore, they provide information about the electronic structure of the MSe–SAMs.

1. Introduction

In the last two decades self-assembled monolayers (SAMs) have attracted considerable attention in modern science and technology due to their large potential in applications, such as molecular electronics [1,2], chemical and biological sensors [3], and modifying surfaces, e.g. corrosion, friction, adhesion, and wetting properties [4,5].

The chemisorbed SAM constituents consist of three parts: An anchor providing a strong bonding to the substrate, a tail group defining surface properties, and a spacer, that separates anchor and tail group. In recent years many studies on sulphur based SAMs, especially alkanethiols have been performed [6–9]. Alkanthiols are chainlike molecules with a sulphur anchor, a linear hydrocarbon chain, and an optional functional tail group. The sulphur atom forms a chemical bond on metallic surfaces and therefore thiolate SAMs provide a stable bonding to the substrate.

The surface-molecule bonding itself considerably influences the self assembly process, the SAM structures, and their electronic properties. Therefore, it is very important to understand the bonding in detail. In this context the simplest alkanethiolate, methylthiolate (CH_3S: MS), is very often discussed [10–17]. Due to its structure it is a good model system for investigating the molecule–substrate interaction. Despite several experimental and theoretical studies in recent years the adsorption geometry of MS on the Au(111) surface is still not clear yet [18]. Presently, various different geometries are discussed in literature: For single MS molecules bridge-sites [12,13], hollow-sites [14], and on-top sites [15] are proposed. Another possible configuration assumes a building block consisting of two MS molecules with one gold ad-atom in between (CH_3S–Au–CH_3S) [16,17]. Therefore they are not suitable for technical applications since a distinct bonding should be guaranteed. Additionally, an application of thiolates in air or even harsher environments is impossible due to their instability towards oxidation. Since the chemical properties of sulphur and selenium are rather similar the substitution of sulphur by selenium was proposed in order to avoid some of the previously mentioned problems observed for sulfur based SAMs. The first selenium based SAM was reported by Samant *et al.* [19]. In the following years several studies [20–23] were able to report on well-ordered selenium based SAMs on noble metal substrates similar to thiol SAMs. In this study the dialkyl diselenide dimethyldiselenide (CH3Se–SeCh$_3$: DMDSe) has been used for preparing methylselenolate (CH_3Se: MSe) SAMs on the Au(111) surface. MSe consists — like MS — of a methyl group with the sulphur atom being replaced by a selenium atom. Analogous to MS it is a good model system for the investigation of the molecule–substrate interaction.

To the best of our knowledge we present the first microscopic results of the structural formation of MSe SAMs on the Au(111) surface by scanning tunneling microscopy. Our results, obtained by preparation from immersion, show the formation of a striped MSe structure with $(4 \times \sqrt{3})$rect. (rectangular) symmetry. A subsequent annealing step induces a phase transition to a $(3 \times 2\sqrt{3})$rect. striped phase. A preparation by vapour deposition initially leads to an unordered surface. Annealing reveals the $(4 \times \sqrt{3})$rect. striped phase as observed by immersion preparation, but in contrast to it with very high structural quality. The results of the DFT calculations are in excellent agreement with the experimental observed structures. For the adsorption geometry a bridge-site of a single MSe-molecule on Au(111) is clearly favoured. Also, the calculation provides detailed information on the adsorption

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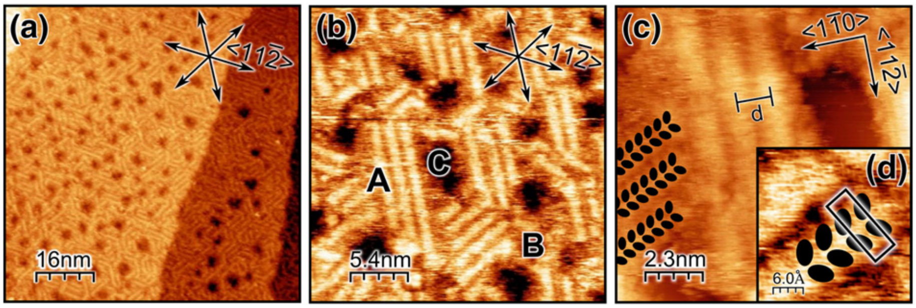

Fig. 1. STM images of MSe SAMs formed in a 1 mM ethanolic solution with 1 h immersion time. Panel (a) shows the MSe covered surface with two step edges originating from the Au(111) substrate. Due to chemisorption the herringbone reconstruction has been lifted all over the surface. Panel (b) displays ordered domains with different orientations (A), disordered regions (B), and with 20–25% vacancy islands (C). Panel (b) shows the double row structure of the (4 × √3)rect. phase, the unit cell is marked by the black rectangle in the inset (d). The topographic images were obtained for $I_{set} = 10$ pA and $U_{set} = -1.2$ V.

angle and the strength of the chemical bond to the surface. Finally, the calculation indicates a metallic behaviour of the MSe SAM due to the electronic features of the selenium atom at the surface.

2. Experimental details

All measurements and preparations were performed at room temperature in an ultra-high vacuum chamber with a base pressure of 2×20^{-10} mbar. The experimental set-up consists of a preparation chamber connected to a main chamber with a room-temperature STM. All STM tips were prepared by electrochemical etching in 20% NaOH. The tip material is polycrystalline tungsten with 0.125 mm in diameter. The Au(111) single crystal substrate was prepared by standardized sputter/annealing cycles. The clean surface was checked by STM and LEED in order to verify the cleanness and surface reconstruction.

For solution preparation the Au(111) surface was immersed into a 1 mM ethanolic solution of DMDSe (98% purity) for 1 h. Prior studies reported on dissociative adsorption of dialkyl diselenides at room temperature [24,25,22]. Subsequently, the sample was rinsed with pure ethanol in order to remove weakly bond molecules. Eventually, the sample was dried under a flow of pure nitrogen and then mounted to the UHV chamber. For gas-phase preparation the sample was moved into the preparation chamber where the surface was exposed to gaseous DMDSe at a pressure of 4×10^{-4} mbar for 12 h.

3. Theoretical details

Our first-principles calculations have been performed by employing the density functional theory (DFT) [26] in its Kohn–Sham formulation [27]. In this study, the electron-ion interactions are described by the projector augmented wave method (PAW) [28] as implemented in the VASP code [29,30]. Furthermore, the exchange-correlation energy functional was approximated by the Perdew–Burke–Ernzerhof (PBE) [31] functional while the cutoff kinetic energy which controls the number of plane-waves in the basis set was set to 500 eV. The Au(111) substrate with (4 × √3) and (3 × 2√3) in-plane surface unit cells has been modelled by a six layer slab separated from its periodically repeated images by ≈ 24 Å of vacuum, using the theoretical lattice constant of 4.173 Å. The upper two atomic layers and the adsorbed molecules were fully relaxed until the calculated forces were smaller than 0.01 eV/Å. These structural relaxations have been carried out with a 4 × 4 × 1 Monkhorst–Pack [32] *k*-mesh to sample the surface Brillouin zone.

4. Results and discussion

4.1. Immersion preparation

Fig. 1 shows the structural formation of CH_3Se on the Au(111) surface prepared by immersion. The herringbone reconstruction of the clean Au(111) surface has been lifted completely, as can be seen in Fig. 1(a), which is a clear evidence of MSe being chemisorbed to the surface. In panel (b) domains of a striped phase (A), unordered areas (B), and ≈ 20–25% vacancy islands (C) are marked. Since the appearance of vacancy islands is a well known phenomena for the adsorption of thiols on the Au(111) surface [33], the chemical features of thiols and selenides are similar even in the adsorbed phase. The orientation of stripes along all three equivalent <11$\bar{2}$> directions indicates the 3-fold symmetry of the underlying hexagonal gold substrate. The ordered domains between vacancy islands are rather small-sized with about ~50 nm^2. Each domain consists of 2–5 stripes with stripe lengths up to 15 nm. Fig. 1(c) shows each stripe being composed of two rows of MSe molecules. The distance between two stripes is d ≈ 1.3 nm, as indicated in Fig. 1(c). The unit cell of the striped phase forms a (4 × √3) rect. structure, as displayed by the rectangle in Fig. 1(d).

An annealing step at $T = 360$ K for 15 min induces a phase transition. Fig. 2(a) shows the surface directly after annealing. The striped (4 × √3)rect. phase and the vacancy islands disappeared due to the annealing step and the surface shows unordered (A) and ordered areas (B). Again, ordered areas consist of a striped sub-structure with orientations along all three equivalent <11$\bar{2}$> directions. Furthermore, the stripe lengths and the domain sizes increased up to 40–80 nm and ~3000–4000 nm^2, respectively. In Fig. 2(b) the structure is shown in high resolution. In contrast to the double rows for the (4 × √3)rect. phase, as displayed in Fig. 2(b), each stripe is composed by only one row of MSe molecules now. The MSe surface density is reduced and the structure exhibits missing molecules and entire missing rows randomly located on the surface. The unit cell forms a (3 × 2√3)rect. structure, as shown by the rectangle in Fig. 2(c).

4.2. Gas-phase preparation

The gas-phase preparation leads to an unordered surface initially. Fig. 3(a) shows the surface after annealing at $T = 360$ K for 15 min.

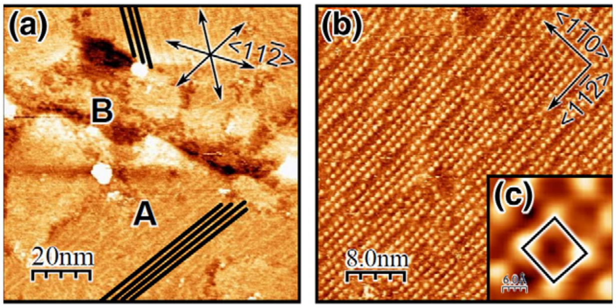

Fig. 2. The experimental STM images of MSe SAMs formed by immersion after an annealing step. As indicated in panel (a) the surface exhibits ordered (A) and disordered areas (B). Panel (b) shows the single row structure of the (3 × 2√3)rect. phase, the unit cell is marked by the black rectangle in the close-up view (c). The topographic images were obtained for $I_{set} = 10$ pA and $U_{set} = -1.15$ V.