

Chemisorption of ferrocene on Si(111)–Ag $\sqrt{3}$: Frustrated conformational flexibility

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ABSTRACT

The adsorption of ferrocene-dithiol on Si(111)–Ag $\sqrt{3} \times \sqrt{3}$ reconstruction has been studied by scanning tunneling microscopy. Preferred chemisorption was found at defect sites, e.g. grain boundaries, with characteristic distortions of the two dimensional electron gas. Occasionally, adsorption also occurs at perfect terrace sites, where submolecular resolution was achieved and the adsorption geometry was deduced. Due to the formation of Ag–S bonds, the conformational flexibility of the free ferrocene is restricted. Thus, the frozen rotation leaves only two different rotational configurations of ferrocene.

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1. Introduction

Molecular electronics has been discussed intensively in the last years as the ultimate realization of nano-scale systems [1,2]. Almost 30 years after the pioneering work by Aviram and Ratner [3], the proposed molecular rectifier was finally realized using donor and acceptor like molecular units [4]. However, it is clear and also evident from these experiments that the modular concept of molecular electronics, i.e. the intended functionality is solely determined by the molecule, is limited to the regime of weak coupling.

Weakly coupled molecular systems have been realized by physisorption of molecules on metallic substrates or between metallic contacts. These reveal indeed signatures known from mesoscopic quantum dot physics [5–7]. The regime of strong or at least intermediate coupling to contacts has to take the contacts explicitly into account. It is interesting not only because chemisorption is an alternative for immobilizing molecules and it allows intriguing adjustments of barriers and thus adjustment of electron transmission, but also because this approach opens pathways to study many body effects in molecular systems [8].

The electronic transmission of electrons through single molecules is closely related with the delocalization of π -electrons, e.g., oligo-phenyl-ethylene (OPEs) and corresponding thiophene-derivatives can be used as molecular wires showing a certain conductivity [1,9]. Similarly, metal-organic complexes like ferrocenes are promising molecules as well, because the conformational flexibility ensures a largely undistorted electronic system of the cyclopentadienyl (Cp) system even if the molecule is adsorbed [10,11]. In general, ferrocene is a model system for a class of three-dimensional molecules and first adsorption experiments of the ferrocene [12] and ferrocene derivatives [13] on Au(111) have

been performed recently. Ferrocenes have a rotational flexibility and the steric extension allows the spatial separation of certain functional groups from the surface. As we will show, the rotational flexibility is frozen upon adsorption and enantiomers are formed, which might be candidates for isomerization experiments similar to the cis–trans isomerization seen for planar azobenzene [14]. Ferrocene bond formation to the surface was realized in this study by thiol groups (ferrocene-1,1'-dithiol(FDT)).

As substrate the Ag $\sqrt{3} \times \sqrt{3}$ reconstructed Si(111) surface was used. This unconventional approach has several advantages over single crystalline surfaces. The reconstruction possesses a well defined metallic surface state, which is energetically well separated from bulk states. As our results show, the formation of a thiolate bond with Ag-atoms of the Ag $\sqrt{3} \times \sqrt{3}$ phase is comparable to those of Ag surfaces. Moreover, the strong corrugation of the reconstruction allows the determination of the adsorption geometry of the molecule even at room temperature. Finally, as the template provides a 2d electron gas, any charge redistribution around (local) chemical bonds can be imaged. In the past the Ag $\sqrt{3} \times \sqrt{3}$ structure was used for adsorption of C₆₀ molecules [15].

In this STM-study stable tunneling was achieved only in the high bias regime. The electronic tunneling transport was recently studied in detail by us for the Ag/Si(111) system [16]. This study shows an intriguing interplay between the Schottky barrier formed by the Ag/Si interface and lateral transport within the Ag film. While for the bare Ag $\sqrt{3} \times \sqrt{3}$ structure tunneling turns out to be dominated by the (vertical) Schottky barrier that effectively even widens the band gap experimentally seen, for dense islands grown on top of the Ag $\sqrt{3} \times \sqrt{3}$ structure the lateral conductance dominates and turns the overall conductance characteristic towards a metallic state.

The FDT/Ag system has been intensively investigated in the past by our group. The adsorption geometry and sites of FDT on Ag(111) have been studied in detail using the density functional theory [17]. Special focus was put on whether the FDT forms thiol or thiolate bonds to the Ag-atoms. Although the latter is energetically marginally more favorable,

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the process of dissociation is activated and imperfections, e.g. atomic steps, are preferred adsorption sites. Based on these results, the transmission for electron transport was calculated [18], which was in qualitative agreement with first transport experiments [19]. However, the calculations revealed also an anti-correlation between binding energy and transmission. Although the barrier for tunneling along the molecule is reduced by a stronger bond, the transmission is lowered by the shift of bonding states below the Fermi level and their complete filling. Hence, a detailed knowledge about the adsorption itself is very important in order to understand transport phenomena.

Here we present first results from tunneling microscopy of the adsorption of FDT on the $\text{Ag}\sqrt{3} \times \sqrt{3}$ -Si(111) system. Although it is obvious that this Ag monolayer on Si(111) is not equivalent to bulk Ag, it seems that still these calculations for FDT on Ag(111) facilitate the interpretation of our results as explained below.

2. Experimental setup

The experiments were performed in ultra high vacuum ($<1 \times 10^{-8}$ Pa). The variable temperature scanning tunneling microscope system (STM, Fa. RHK) was upgraded by a preparation chamber hosting LEED (low energy electron diffraction) and XPS (X-ray photoelectron spectroscopy) in order to check the overall chemical and structural quality of the samples. The ferrocene-1,1'-dithiol molecules (FDT, Fig. 1a) were synthesized and purified by the Butenschön group (organic chemistry) of our university [10]. In a further step, the hygroscopic powder was purified in-situ by degassing the Knudsen cell extensively for at least 100 h around 400 K. The process was monitored by quadrupole mass spectrometry (QMS, 200 amu). Fig. 1b shows a QMA spectrum of ferrocene during evaporation. The molecular adsorption rate for FDT was extremely low (<0.01 ML/min, 500 K), possibly due to thermal defragmentation, as evident from the mass spectrum in which apart from the ferrocene molecule, other hydrocarbon species (C_6H_6 , CH_4 , C_2H_6 ,...) were seen. However, no indication of these

species was seen on our samples. The Si(111) samples were carefully degassed at 770 K for 12 h and finally shortly heated to 1400 K in order to remove the oxide. Slow cooling allows the surface to form a long-range ordered (7×7) reconstruction, as checked by LEED and STM (cf. Fig. 1c). $\text{Ag}\sqrt{3} \times \sqrt{3}$ reconstructions have been obtained by e-beam evaporation of Ag at 800 K substrate temperature. This process is self limiting, i.e. excess coverage desorbs. Thus well-ordered $\text{Ag}\sqrt{3} \times \sqrt{3}$ structures were obtained (Fig. 1d).

3. Results and discussion

3.1. Ferrocene bonding to defects

Fig. 1d shows a tunneling image out of the occupied Ag states taken at -2 V bias voltage. The characteristic honeycomb chained trimer reconstruction (for the structural model, which is shown in context with the ferrocene adsorption model, see Fig. 3a), valid at temperatures above 150 K [20,21], is not resolvable here due to strong fluctuations at room temperature. Upon adsorption of FDT, the $\text{Ag}\sqrt{3} \times \sqrt{3}$ structure undergoes characteristic changes, as visible in the sequence of Fig. 2, which shows an identical part of the surface during evaporation of FDT at room temperature.

Upon FDT adsorption, the most significant changes appear at defect structures. For the clean surface (Fig. 2a) we can identify steps, bright chain structures (marked by a rectangle) running along the $[11\bar{2}]$ direction, and a point defect (marked by a circle) in the center of the upper terrace. The latter two appear brighter than the terraces at these tunneling conditions. The apparent height is around 120 pm. The chain structures can be identified as grain boundaries of the HCT structure. Similar features were found for $\text{Ag}\sqrt{3} \times \sqrt{3}$ at low temperatures [21]. However, here the HCT phase itself separates into two IET (inequivalent triangle) domains.

The adsorption process is seen by modifications of the electronic contours at these defects, but also, with much slower adsorption

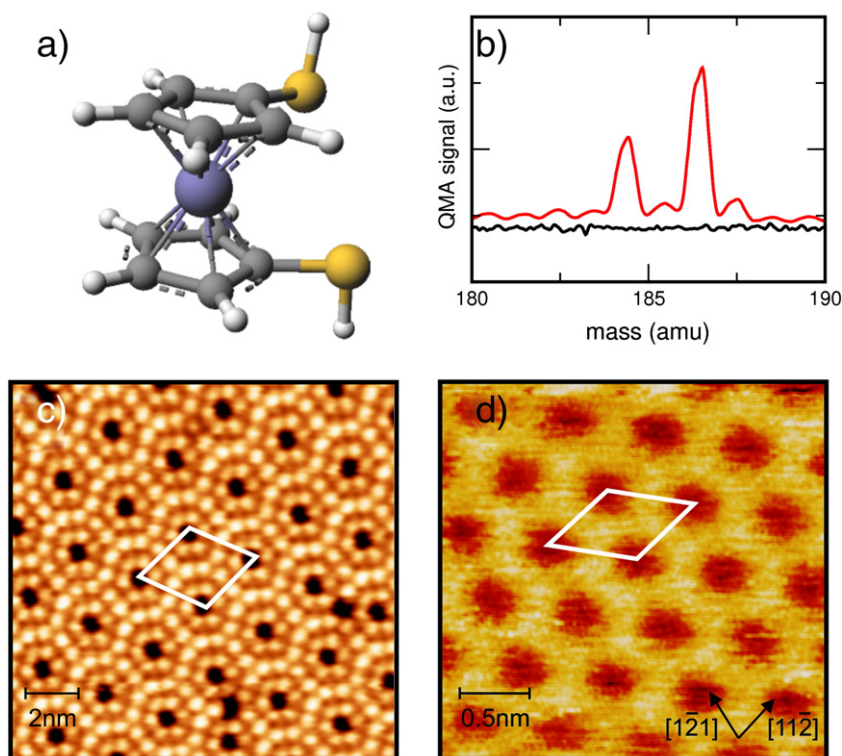


Fig. 1. a) The ferrocene-1,1'-dithiol (FDT, $\text{FeC}_{10}\text{H}_{10}\text{S}_2$) molecule. The H-atoms of the thiol groups dissociate thus Ag–thiolate bonds are formed between the molecule and the Ag surface. The distance of the two cyclopentadienyl rings can be varied between 3.7 and 4.1 Å due to rotation of the Cp-rings. The barrier for rotation is only 40 meV responsible for the configurational flexibility of these compounds [10,17]. b) QMA spectrum during evaporation of ferrocenes (186 amu) and fragmentation products due to partial dehydrogenation. c) Unoccupied state image of Si(111)– 7×7 ($+2$ V, 0.1 nA, 40 K). d) Occupied states of the $\text{Ag}\sqrt{3} \times \sqrt{3}$ reconstruction on Si(111) (-2 V, 0.25 nA, 300 K). The $\sqrt{3}$ unit cell is marked.

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