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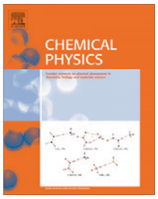

Two-photon photoemission from ex-situ prepared butanethiol SAMs on Au (111)

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ABSTRACT

Self-assembled monolayers (SAMs) of butanethiol on a Au (111) single crystalline surface in the $p \times \sqrt{3}$ lying-down phase prepared by deposition from solution were studied with two-photon photoemission (2PPE) spectroscopy. The spectra reveal clear signatures of two unoccupied resonance states at energies $E - E_F = 3.7$ eV and 3.9 eV. The low-energy state is assigned to the characteristic σ^*-resonance associated with the Au-S bond of the thiolate. The energy of the other resonance state agrees well with an interface state reported before for different alkanethiol SAMs on Au (111) in a standing-up phase. Furthermore the 2PPE data provide indications that the high quality of the ex-situ prepared SAMs support the formation of image potential states.

1. Introduction

Alkanethiol-based SAMs on surfaces have been intensively studied in the past motivated by their potential regarding technological applications in different fields of nanotechnology [1]. One example is the use of alkanethiols in self-assembled monolayers of photo-switchable azobenzene derivates on metal surfaces. The alkanethiols are attached by a suitable linker to the azobenzene moiety and, after adsorption, act as a decoupling spacer to the metallic substrate, which otherwise can efficiently quench the switching capability of the azobenzene subunit [2–4]. Furthermore, pure, short-chain alkanethiol molecules can be used to increase the free volume of individual azobenzene containing molecules in mixed (diluted) monolayers [5,6]. The goal is to reduce a steric hindering of the switching process induced by the interaction with neighbors and to improve the photoisomerization behavior of the SAMs.

2PPE is a unique experimental tool to study the unoccupied electronic structure of clean and adsorbate covered surfaces [7,8]. Recently, it was shown that this technique is also capable of distinguishing between the different isomerization states of adsorbed photoactive switching molecules. It was successfully applied to monitor a reversible switching of tetra-*tert*-butyl-azobenzene adsorbed on a gold single crystal surface [9,10].

In this work we present 2PPE data of SAMs of the short-chain alkanethiolate butanethiolate [CH_3–$(CH_2)_{n-1}$–S–, $n = 4$] on Au (111)—in the following referred to as C4/Au (111)—representing a precursor for a diluted monolayer containing azobenzene derivates. 2PPE data of alkanethiolate SAMs on Au (111) prepared by in situ (UHV) thermal evaporation have been published before [11]. The motivation for this work is to clarify, to what extent alkanethiolate SAMs prepared by liquid phase deposition can be used for 2PPE experiments in a reasonable manner, particularly as 2PPE studies of ex-situ prepared SAMs have barely been reported, yet [12–14]. For diluted switchable monolayers this preparation method is advantageous, as it provides a defined means of concentration control and as it bypasses problems arising from the thermally activated dissociation of large molecules such as the molecules containing the switching moiety. In this context the present experiment is considered a reference for future 2PPE studies of such diluted monolayers in two regards: First, we address the question to what extent a liquid phase preparation of SAMs can provide a sample quality suitable for a defined 2PPE study. For instance, can ex-situ prepared SAMs support image potential states, which are mainly located in front of the surface in the vacuum and which have been used in the past to probe the photoisomerization of the switching molecules [9,10]. Second, 2PPE reference data of the pure alkanethiol SAM are required for an unambiguous assignment of spectral signatures characteristic for the switching molecules in the diluted monolayer.

We like to point out that 2PPE studies of ex-situ prepared SAMs have been published before. For 4,4′-bis(phenyl-ethylnyl)

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benzenethiol on gold two excited electron states associated with the SAM were identified and the observed energies were compared to corresponding inverse photoemission data [12,13]. In another work, SAMs of [121]tetramantane-6-thiol on Ag (111) and Au (111) were investigated with the focus on the negative electron affinity (NEA) level of the molecule located right at the low energy cutoff of the 2PPE spectrum [14]. It was concluded, that the strong 2PPE emission from the NEA level triggered by a pulsed femtosecond laser source can routinely be used as an efficient source for ultrashort electron pulses.

In the present work we present 2PPE data of the $p \times \sqrt{3}$ lying-down phase of C4/Au (111). Recent STM data have shown that mixed SAMs of C4 and the molecular switch 3-(4-(4-hexyl-phenylazo)-phenoxy)-propane-1-thiolate exhibit a similar superstructure [15]. Our experimental results are in qualitative agreement with 2PPE spectra of in situ prepared hexanethiolate [CH_3–$(CH_2)_{n-1}$–S–, $n = 6$] SAMs on Au (111)—in the following referred to as C6/Au (111) [11]. An unoccupied σ^*-resonance, previously associated with the gold-sulfur bond of the thiolate can be clearly resolved. Furthermore, we identify another unoccupied adsorbate induced state at slightly higher intermediate state energies and an occupied state at a binding energy of 3 eV. Both states were not observed before for this type of alkanethiolate SAM. Finally, we have indications that the ex-situ prepared SAMs support image potential resonances/states which are known to be highly sensitive to the surface quality.

2. Experimental

The substrate used for the preparation of the C4 SAM is a commercial Au (111) single crystal that was routinely cleaned under ultrahigh vacuum (UHV) conditions (base pressure $< 1 \times 10^{-10}$ mbar) by repeated cycles of argon ion sputtering and annealing (500 V, 970 K) prior to each deposition process. The quality of the pristine surface was checked by low energy electron diffraction (LEED) (with emphasis on the appearance of the Au (111) $22 \times \sqrt{3}$ herringbone reconstruction [16], see Fig. 1(a)), and the 2PPE characteristics (energy and spectral width) of the Shockley surface state and the $n = 1$ image potential resonance of the Au (111) surface (see Fig. 2(a)). For the liquid phase deposition of the C4 molecules, the pristine Au (111) crystal was transferred under vacuum conditions into an argon filled glove box. There, the crystal was immersed for 6 h into 1 mmol solution of butanethiol (Merck, synthesis grade, purity > 98%) in dichlormethane (Merck, spectroscopy grade, purity > 99.9%) and subsequently rinsed with the pure solvent, dried and transferred under argon atmosphere back into the UHV chamber. Such samples already allowed the observation of ordered LEED patterns from the thiolate adsorbate characteristic for a $p \times \sqrt{3}$ lying-down phase. A value of $p \approx 9$ was found. The appearance of the superstructure is accompanied by the characteristic lifting of the Au (111) herringbone reconstruction. A brief annealing of the sample to $T = 350$ K further improved the data quality and a LEED pattern of a post-annealed sample recorded at $T = 130$ K is shown in Fig. 1(b). The electron diffraction results agree well with STM data reported by Poirier et al. [17], where a very similar preparation procedure was applied. The main difference in the latter case was the lack of the post-annealing step and a short overall exposure of the sample to air for some minutes.

For the 2PPE experiments we used the frequency tripled output of a tunable femtosecond Ti:sapphire laser providing pulses with photon energies tunable from 4.3 eV to 4.6 eV at a repetition rate of 80 MHz. The laser light is focused onto the sample using a fused silica lense (focal length 0.2 m) at an angle of incidence of 45° with respect to the surface normal. A zero-order half wave plate is used to change the laser light polarization from p- to s-polarization. The photoemitted electrons are analyzed by a commercial cylindrical sector analyzer (Focus CSA 150) at an instrumental resolution of 50 meV ($E_{\text{pass}} = 2$ eV). The sample surface is oriented at 45° with respect to the laser beam, and electrons are detected in the normal emission geometry. All 2PPE spectra were recorded at a sample temperature of 130 K.

3. Experimental results and discussion

Fig. 2(a) compares 2PPE spectra of the clean Au (111) surface and the C4 covered surface, both recorded with p-polarized light at a photon energy of 4.5 eV. The inset shows a close-up of the high energy part of the 2PPE spectra. Four main features can be identified in the spectra of the pristine Au (111) surface: (i) the characteristic 5*d* valence bands of gold at final state energies below 7 eV superimposed by a strong secondary electron background, (ii) a signature arising from the Au (111) upper *sp* band edge (UBE), (iii) the Au (111) Shockley surface state (SS) and (iv) a peak at the high energy cutoff of the spectrum which we assign to the off-resonant population of the $n = 1$ image potential resonance (IR1) of the Au (111) surface. From the low energy onset of the

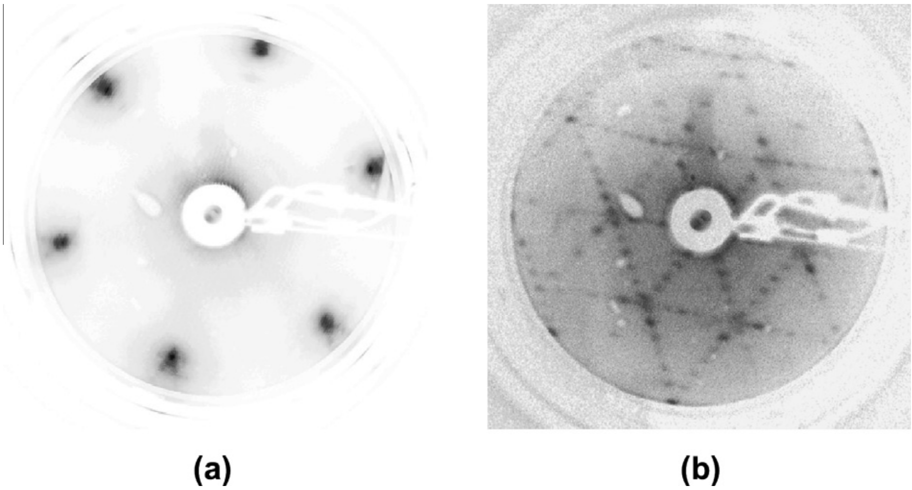

Fig. 1. (a) LEED pattern obtained for the pristine Au (111) surface exhibiting the characteristic pattern of the $22 \times \sqrt{3}$ herringbone reconstruction. (b) LEED pattern of the C4 coated gold sample after a short annealing to 350 K. The pattern is characteristic for the $p \times \sqrt{3}$ lying-down phase of the SAM. For the experiments an incident electron energy of 44 eV was used. The sample temperature was 130 K.