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The structure of methylthiolate and ethylthiolate monolayers on Au(111): Absence of the $(\sqrt{3}\times\sqrt{3})R30°$ phase

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ABSTRACT

Surface structures of self-assembled methylthiolate and ethylthiolate monolayers on Au(111) have been imaged with STM. For saturation coverage of 0.33 ML at room temperature, the well-known $(\sqrt{3}\times\sqrt{3})R30°$ phase routinely observed for longer chain alkanethiolates does not appear under any conditions for adsorbed methylthiolate and ethylthiolate. Instead, both thiolate species organize themselves into a well-ordered 3×4 structure. We thus conclude that the stable structure for saturation coverage of methylthiolate/ethylthiolate on Au(111) at RT is 3×4, not $(\sqrt{3}\times\sqrt{3})R30°$ as generally believed. For coverage less than 0.33 ML, a striped-phase with short-range order is observed for methylthiolate. Fourier transform of the STM image from the striped-phase produces a clear $(\sqrt{3}\times\sqrt{3})R30°$ "diffraction" pattern. This strongly indicates that the $(\sqrt{3}\times\sqrt{3})R30°$ diffraction pattern for methylthiolate monolayers reported in literature is likely from the striped-phase, rather than from a true $(\sqrt{3}\times\sqrt{3})R30°$ lattice in real space. Consequently, theoretical modeling that reproduces the $(\sqrt{3}\times\sqrt{3})R30°$ structure for methylthiolate monolayers should be re-examined.

1. Introduction

Self-assembled monolayers (SAMs) on solid substrates represent a classical system where properties of materials are modified by the addition of a single molecular layer [1–3]. Among the various types of SAMs, alkanethiol molecular layers supported on the Au(111) substrate have been most extensively studied over the last two decades. Yet, the structure of these molecular layers including the nature of the chemical bonding between the adsorbed molecule and the substrate remain highly controversial [4–7]. For long-chain alkanethiols consisting of more than two carbon atoms, three major structures of the adsorbed layer have been found [3,5,8]. Corresponding to saturation coverage, there is the well-known $(\sqrt{3}\times\sqrt{3})R30°$ structure [3,4], and the associated $(3\times2\sqrt{3})$-rect. variations [5]. For lower surface coverages, there is a third structure generally known as the striped phase with the inter-stripe period depending on the surface coverage [3–5].

When it comes to SAMs of methanethiol and ethanethiol, there is yet another, (3×4) [9–11], structure which does not exist for SAMs of the longer chain molecules. Using low temperature scanning tunneling microscopic (STM) imaging, Kondoh et al. observed a (3×4) structure after dosing dimethyl disulfide onto Au(111) [9]. The same structure has been reported later by others, using STM [10,11], low energy electron diffraction (LEED) [12–14] and helium atom scattering (HAS) [12,13,15]. This (3×4) structure has never been observed for SAMs of long-chain alkanethiols [16,17]. STM imaging at RT of a Au(111) surface exposed to methanethiol vapor shows the presence of the (3×4) phase co-existing with a striped phase [18].[1] Hagenstrom et al. [19], using STM imaging of ethanethiolate in an electrochemical cell, observed the (3×4) structure coexisting with a $p(7.5\times\sqrt{3})$ striped phase at RT.

Diffraction studies of methylthiolate monolayers have provided some evidence pointing to the possible existence of the well-known $(\sqrt{3}\times\sqrt{3})R30°$ phase, often reported to be co-existing with the (3×4) phase. However, real space imaging with the STM has so far not given any indication of a $(\sqrt{3}\times\sqrt{3})R30°$ phase for methylthiolate monolayers. There is one previous report on the observation of a $(\sqrt{3}\times\sqrt{3})R30°$ phase for ethylthiolate based on STM imaging in air [20], but this could not be verified in subsequent studies [19,21,22]. The key question to be answered is: are (3×4) and $(\sqrt{3}\times\sqrt{3})R30°$ both stable phases for methylthiolate/ethylthiolate monolayers, and if so what is the relationship between the two phases? To answer the above question, we performed experiments by imaging methylthiolate and ethylthiolate monolayers in ultra-high-vacuum (UHV) using high resolution STM. The methylthiolate monolayer was prepared by exposing a gold single crystal in vacuum to ~10^{-8} mbar of dimethyl disulfide (DMDS) vapor at RT until saturation coverage is reached. It is

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[1] In their original paper, the (3×4) phase was assigned to a $(3\times2\sqrt{3})$.

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known that DMDS adsorb dissociatively on Au(111) at RT by forming methylthiolate [10]. Ethylthiolate monolayer was prepared by exposing a (111) oriented gold film to 5×10^{-5} mbar of ethanethiol vapor at room RT for 2 h. The much higher exposure required for ethanethiol is due to the very low dissociation probability of this molecule. The sample temperature is measured with a thermocouple attached to the heating stage, and the quoted temperature is estimated to be lower than the real sample temperature by ~10 K.

Fig. 1 shows STM images, obtained at 77 K, of a methylthiolate covered Au(111) surface. By exposing Au(111) to a saturation amount of DMDS at RT, a very well ordered 3×4 phase as shown in Fig. 1a is observed all over the surface. Further exposure to DMDS at RT does not lead to any new structure. Fig. 1b shows a high-resolution image of the 3×4 phase. The dashed line in Fig. 1b separates two rotational equivalent domains. The bright spots in Fig. 1b are seen in groups of six. The origin of these bright spots will be discussed later. The sample with the 3×4 phase is then annealed at gradually higher temperatures in order to see what other structures may evolve. Fig. 1c shows an image after the monolayer has been annealed at 330 K. In this image, the 3×4 structure is retained at the right hand side. A disordered

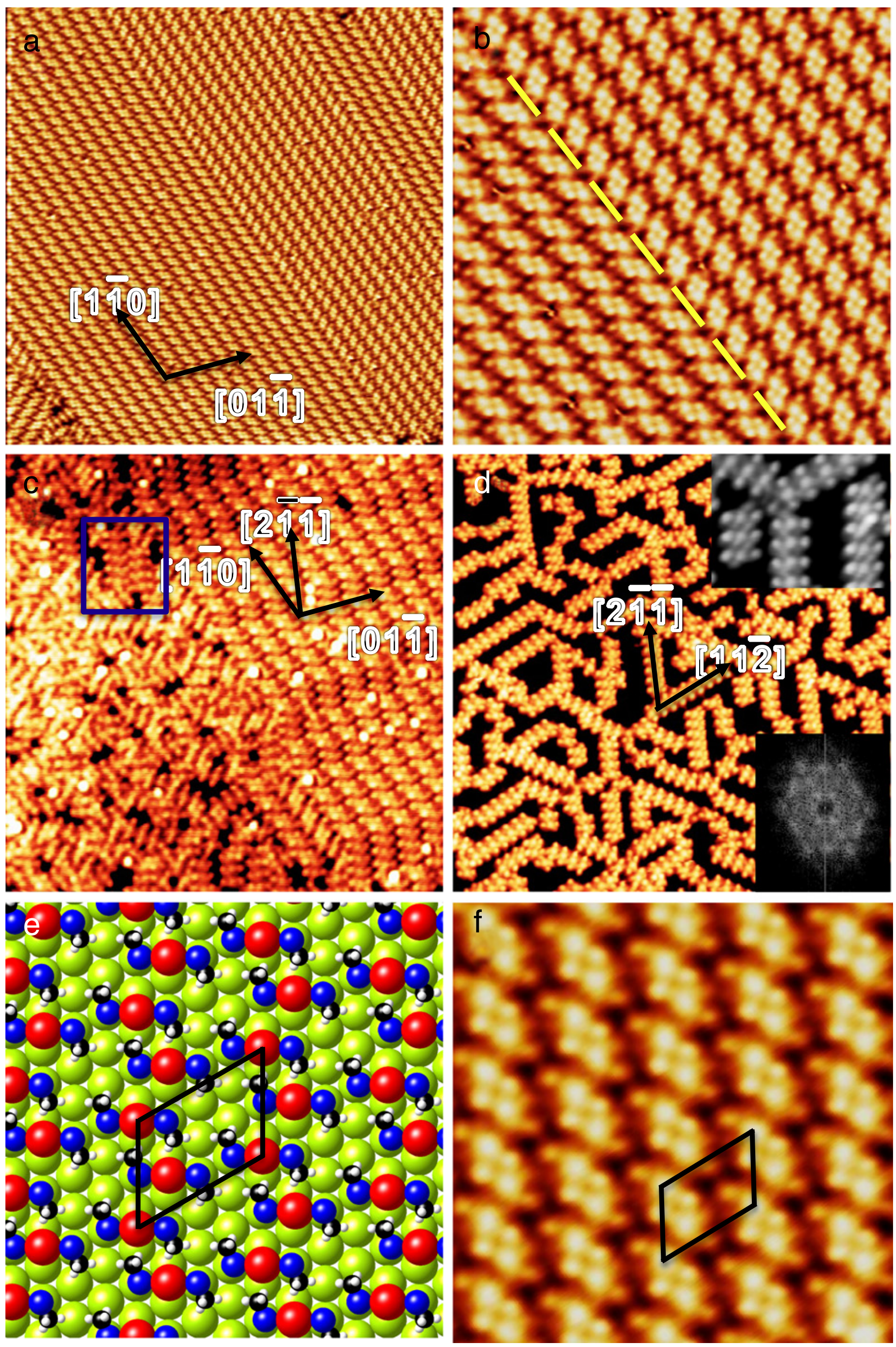

Fig. 1. STM images of methylthiolate monolayer on Au(111). All images are collected at 77 K using −0.09 V sample bias voltage and 1 nA tunnel current. (a). 3×4 structure corresponding to a saturation coverage at RT. Image size is 30 nm × 30 nm. (b) Magnified view, 11 nm × 11 nm, of the 3×4 structure where bright spots appear in groups of six. (c) Thermal annealing at 330 K causes local disorder of the monolayer and the appearance of the striped phase. Image size is 17 nm × 17 nm. (d) Further annealing to 350 K leads to the complete disappearance of the 3×4 structure. The surface is covered by a single phase consisting rows of thiolate. Image size is 20 nm × 20 nm. Inset at the upper right corner shows detailed structure of the building block of the rows, while inset at the lower right hand corner is a Fourier transform of the STM image. (e) Structural model based on the Au-adatom-dithiolate scheme proposed by Voznyy et al. The 3×4 unit cell is highlighted and compared directly with that in the STM image of Fig. 1f.