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Translational transitions at domain boundaries in octanethiol monolayers on Au(1 1 1)

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ABSTRACT

Systematic studies of domain boundaries of self-assembled monolayers of octanethiols on (1 1 1) oriented gold surfaces have been performed by ultrahigh vacuum scanning tunnelling microscopy (STM). The monolayers consist of domains that exhibit the $c(4\times2)$ superstructure of the hexagonal $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure of alkanethiols on gold. By high-resolution images domain boundaries are displayed with molecular resolution. These are used to deduce the exact relation between the adsorption sites of the molecules belonging to different domains on the gold substrate. A translational transition is shown here in detail and it is demonstrated that hexagonal close-packed (hcp), and face-centred cubic (fcc) triple hollow sites are occupied similarly by octanethiols.

1. Introduction

Close-packed monolayers of alkanethiols on Au(1 1 1) surfaces belong to the most studied self-assembled systems and are often used as reference system [1–6]. The close-packed monolayer structures consist of standing-up molecules with the sulphur atom bonded to the gold lattice. The self-assembled monolayers show a variety of surface textures, which can be described by different molecular superlattices caused by different twist angles of the molecules or by the occupation of different adsorption sides on the gold atoms. The $c(4\times2)$ superstructure of the alkanethiols is the most observed and best described structure so far for close-packed layers [7–10]. Five slightly different phases of the $c(4\times2)$ superstructure of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ hexagonal lattice structure with the same unit cell, but different height distributions of the molecules, were observed with STM [11–14] and AFM [10,15] for these close-packed monolayers.

Assuming the $c(4\times2)$ superstructure for the close-packed layer, a multiplicity of different domain boundaries exists, depending on the number of different possible occurrences of the unit cell. The $c(4\times2)$ superstructure has a 3-fold orientational degeneracy, a 12-fold positional degeneracy, and a 3-fold tilt degeneracy [16], so that the symmetry of the molecular lattice gives rise to translational boundaries, rotational boundaries, and antiphase boundaries. Rotational boundaries always exist, because of the 120° symmetry of the gold substrate. A rotational transition shows a very thin, almost invisible domain boundary, whereas transitions involving a translational difference form wider boundaries up to several tenths of a nanometer [17].

Even though there is a thorough understanding of the structural nature of ordered alkanethiol monolayers and a principle grasp about the domain boundaries, there is still a discussion about the energy differences of the diverse adsorption sites, especially of fcc and hcp adsorption sites. Here our studies of domain boundaries will give more insights.

2. Experimental

The octanethiol (=C8) monolayers presented here are grown on (1 1 1) oriented gold films, which are deposited on mica in a two-step process resulting in large terraces and low surface roughness [18]. A highly ordered, full-coverage monolayer of octanethiol (Aldrich, >97% purity, used as purchased) is formed by exposing the sample surface to a 1 mmol/l solution of octanethiol in ethanol for more than 24 h. Thereafter, the sample is transferred immediately to an ultrahigh vacuum scanning tunnelling microscope (JEOL JSPM 4600, base pressure 3×10^{-10} mbar). All images were obtained in constant-current mode using homemade electrochemically etched tungsten tips.

3. Results and discussion

High-resolution STM offers the opportunity to study molecular domains and their boundaries with molecular resolution. Fig. 1

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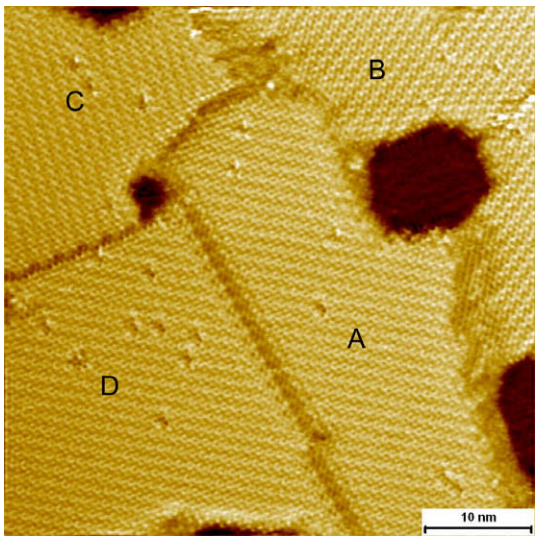

Fig. 1. $50 \times 50\,nm^2$ STM image of a C8 SAM. ($V_T = 1.5$ V, $I_T = 35$ pA). The image shows different domains of the $c(4 \times 2)$ structure (A–D) and domain boundaries.

shows a STM image with different domain structures and domain boundaries. Five different domains with the $c(4 \times 2)$ structure (marked with A–D in Fig. 1) and different types of domain boundaries in between can be verified in the following. There are rotational boundaries between the domains A and B, B and C, and C and D, and a translational boundary between domain A and D.

Remarkable is the translational domain boundary in the centre region of Fig. 1 between domain A and D, which is shown in more detail in part a of Fig. 2. The superstructure of the octanethiols on Au(1 1 1) surfaces could be identified by linescans along the molecular rows (parts a and b in Fig. 3), two-dimensional FFT (Fast Fourier Transformation) spectra (part b of Fig. 2), and comparison with literature data [14]. Both domains, on the left and on the right side of the boundary, show the same phase of the $c(4 \times 2)$ superstructure with two different heights of the molecules. The 2D-FFT spectrum (part b of Fig. 2) shows the spots of the gold substrate, the ground structure of the alkanethiol monolayer, and additional spots of a superlattice, like those observed in F. Schreiber [19]. White circles denote surface diffraction peaks from the Au(1 1 1) surface ((2, 0), and so on). Blue circles denote peaks which correspond to the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of the SAM ((1, 1), (2, 2), and so on), whereas peaks marked with open squares are due to the $c(4 \times 2)$ superlattice ((0.5, 0), (0.5, 1), and so on). The systematic absence of superlattice peaks ((1, 0), (1, 2), and so on) implies that the molecules in the different zig–zag rows have to be symmetry-equivalent. So these domains show a $c(4 \times 2)$ superstructure with delta-phase characteristics, that is, a superlattice with two different heights per unit cell [11–13].

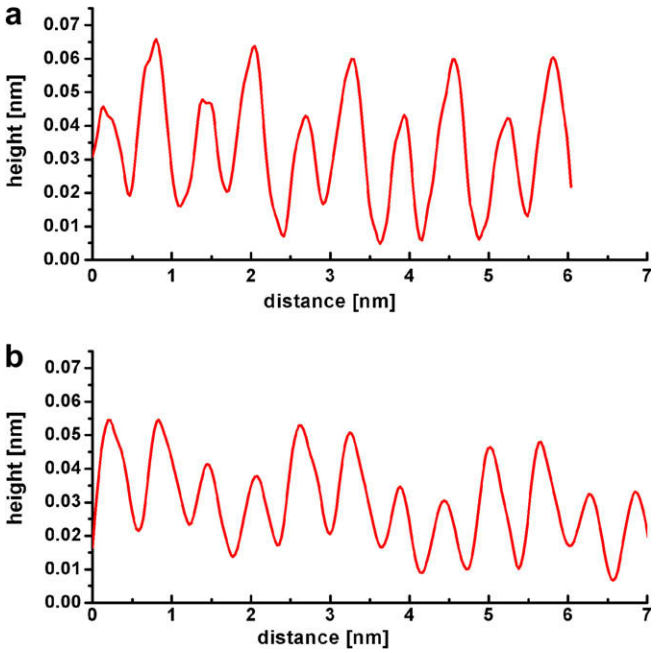

Fig. 3. (a,b) Linescans along the directions of nearest neighbour molecules to show the characteristic of the delta-phase with two different heights.

It is generally assumed that the different apparent heights of the molecules in the $c(4 \times 2)$ unit cell are caused by different twist angles of the molecules around their molecular axes. However the effect of the molecular twist alone, around 0.6–0.7 Å for a full rotation of the molecular chain [6,20], is not the only possibility to explain the amplitude of the height differences. Another effect under

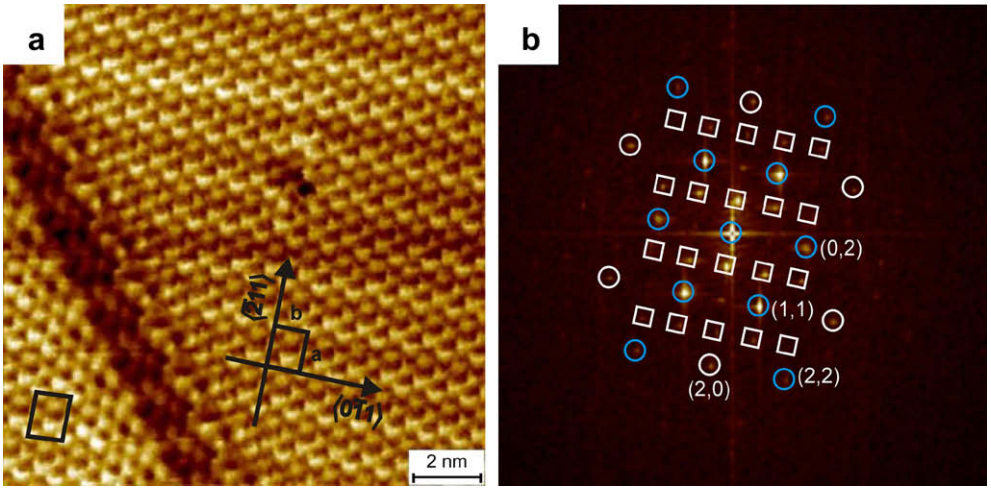

Fig. 2. (a) $14.1 \times 14.1\,nm^2$ STM Topography scan ($V_T = 1.8$ V, $I_T = 65$ pA) of the hcp/fcc translational domain boundary (dark area) with the surrounding delta-phase $c(4 \times 2)$ domains. The unit cells of the respective structures and the gold substrate-vectors are marked. (b) 2D-FFT Spectra showing the spots of the gold substrate (white circles), the $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal ground structure of the alkanethiol monolayer (blue circles), and additional spots of the delta-phase of the $c(4 \times 2)$ superlattice (open squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)