

Real-Space Observation of Nanoscale Molecular Domains in Self-Assembled Monolayers

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Scanning tunneling microscopy with very high gap impedance reveals several stable molecular conformations of organic monolayers self-assembled from alkanethiols on gold. Thermal annealing of the preassembled films favored well-packed large molecular domains that were studied in real space with unprecedented detail and accuracy. At room temperature the system has several stable molecular conformations, which implies that chemisorption energies balance the energy of interaction between molecular chains. A similar probability of different conformations indicates almost equal total energies, which makes it an interesting—and challenging—object for molecular dynamics simulations. Our results contribute to a long-standing scientific debate on the structure of self-assembled monolayers and provide the basis for an improved understanding of organic interfaces.

Self-assembled monolayers (SAMs) are currently of considerable interest for basic research as well as for technological applications. A well-ordered and stable monomolecular film can serve as a model system for biomembranes and can be used for measurements of mechanical and electronic properties of single molecules.¹ The molecular self-assembly is governed by competing mechanisms, such as surface corrosion, chemisorption, molecule–solvent interaction as well as molecular attraction and repulsion. The technological interest stems from the ability of SAMs to tailor surface properties in order to optimize lubrication and wetting, to control corrosion, and to design biological sensor surfaces.² The present understanding of the molecular structure of SAMs made of alkanethiols ($\text{HS}-(\text{CH}_2)_{n-1}-\text{CH}_3$) on Au(111) is largely derived from averaging methods such as reflectance infrared spectroscopy,³ transmission electron diffraction,⁴ X-ray diffraction,^{5,6} and molecular dynamics simulations.^{7,8} The consensus is that a commensurate ($\sqrt{3} \times \sqrt{3}$)R30° overlay exists, the structure of which is a balance of the sulfur–gold chemisorption, an interaction between the sulfurs, and an interaction between the chains. The average conformation of a single chain of dodecanethiol ($n = 12$) adsorbed on Au(111) is depicted in Figure 1. The molecule, in an all-trans conformation, is tilted 33° from the surface normal (Θ_m), 14° away from the nearest-neighbor (NN) direction (χ),⁶ and is rotated

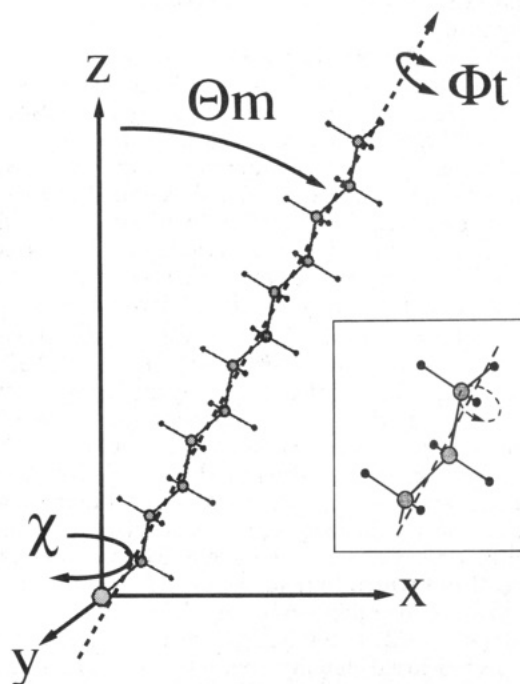


Figure 1. Representation of a dodecanethiol molecule in all-trans conformation. The orientation of the molecule is defined by the molecular tilt $\Theta_m = 32.5 \pm 1^\circ$, the angle of rotation (twist) of the C–C planes about the molecular axis $\Phi_t = 55^\circ$, and the angle of precession about the surface normal $\chi = 13.8 \pm 2^\circ$ away from the NN direction. The molecular twist changes the position of the terminal methyl group (path represented by a circle in the inset).

(or “twisted”) about the chain axis by 55° (Φ_t).⁹ More recently, helium diffraction measurements on SAMs consisting of octadecanethiol showed evidence of a rectangular primitive unit mesh with dimensions of 0.868 nm

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$\times 1.002$ nm containing four hydrocarbon chains, equivalent to a $c(4 \times 2)$ superlattice.¹⁰

Scanning tunneling microscopy (STM) offers the possibility to locally study SAMs of alkanethiols on Au(111) in real space.^{11,12} Typical results showed depressions of variable lateral size and a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice on parts of the surface.¹³ By use of low currents and large tip-sample voltages, $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattices could be reliably resolved on large areas.¹⁴ In this Letter, high-resolution STM studies on SAMs formed by chemisorption of dodecanethiol on Au(111) are presented, revealing domain-like film growth and several molecular superlattice structures. The effect of thermal annealing on domain formation and order during molecular self-assembly is discussed.

STM data were recorded in constant-current mode under ambient conditions. Au(111) surfaces formed by epitaxial growth on freshly cleaved mica exhibit terraces of up to several hundred nanometers¹⁵ with hexagonal atomic structure and $(\sqrt{3} \times \sqrt{3})$ surface reconstruction. Freshly evaporated Au(111) surfaces were immersed in a 1 mM solution of dodecanethiol (Fluka) in ethanol for 2 h at room temperature under argon and annealed at 50 °C in the same solution for at least 48 h. Predominant changes of the surfaces upon annealing were an increase of the average domain area by at least a factor of 3, an alignment of domain boundaries along the next-nearest-neighbor (NNN) direction of the sulfur lattice, and abundant superstructures superimposed on the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice.

Figure 2 is an STM image of dodecanethiol chemisorbed on Au(111) and annealed as described above. At the molecular level, the predominant feature of the SAMs is the $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice with an intermolecular distance of 5.0 Å and angles of 60° (domain A in Figure 3). A superlattice of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ hexagonal lattice was observed (domains B, C, and D in Figure 3) in which individual chains are either protruded or depressed by 0.7 Å. All these structures are consistent with a $c(4 \times 2)$ superlattice containing four molecules with a rectangular unit cell of $|\bar{a}| = 3a_h = 8.5$ Å, $|\bar{b}| = 2\sqrt{3}a_h = 10.1$ Å, where $a_h = 2.88$ Å denotes the interatomic spacing of Au(111). In domains B and C, molecules occupying the corner sites of the unit cell (Figure 4a, dashed lines) are either protruded (domain B and Figure 4c) or depressed (domain C), and can be understood using the model of Figure 4a. In addition, another superstructure is identified in domain D and Figure 4d. The zigzag pattern, oriented along the NNN direction, can be explained by a closely related model (Figure 4b) in which four molecules of the unit cell are either protruded or depressed. All four domains show an areal density of 21.5 ± 0.5 Å²/molecule, consistent with the expected areal density required for a close-packed arrangement of the chains. Camillone *et al.*¹⁰ suggested that analogous to bulk alkanes, the $c(4 \times 2)$ superlattice originated from a twist about the chain axis. The structure of bulk alkanes (n even) is monoclinic with the c -axis parallel to the alkyl chains. Half of the chains are either twisted clockwise or counterclockwise, resulting in a different orientation of the topmost C—C bond. Since the

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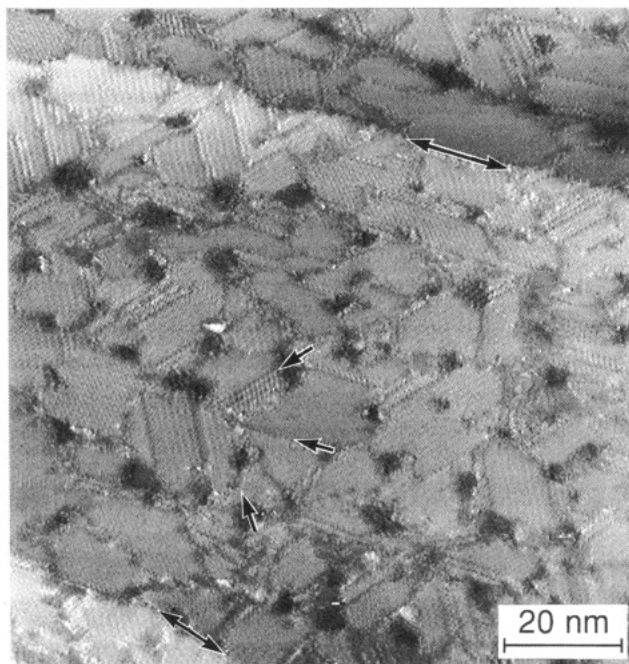


Figure 2. STM topview with gray-scale encoding (5 Å from black to white) of dodecanethiol self-assembled on Au(111). Imaging conditions: Pt/Ir tip, 1.2 V (sample positive), 3 pA. The surface exhibits terraces separated by two Au steps of 2.4 Å (double arrows), statistically distributed depressions surrounded by several domains and interconnected by domain boundaries as well as various superstructures within individual domains. Domains are delimited by straight and well-oriented boundaries (arrows).

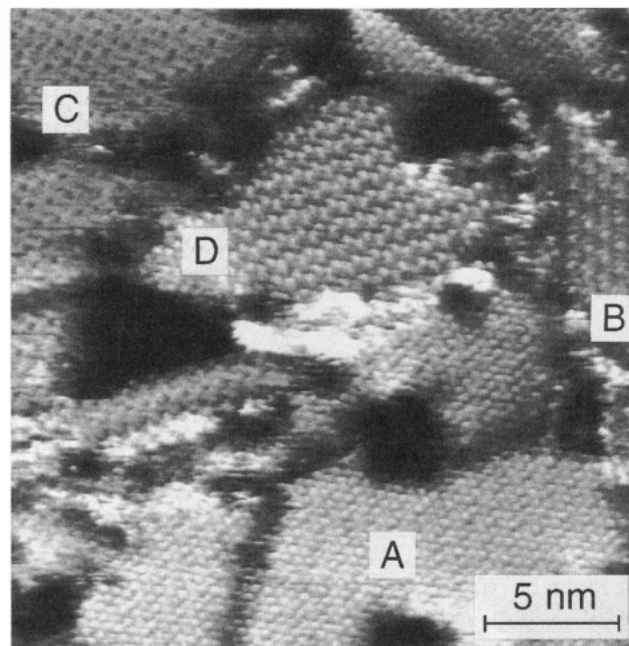


Figure 3. STM image taken at identical experimental conditions as in Figure 2. Depressions have an average diameter and depth of 5 and 0.25 nm, respectively. Some depressions have triangular shapes with edges parallel to the three equivalent Au(111) lattice directions. This identifies their origin as missing patches created by thiol-mediated corrosion during the self-assembly process.²⁰ Domain A shows the hexagonal $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice. In domains B, C, and D, variations of the $c(4 \times 2)$ superlattice can be clearly recognized (see text for explanation of superlattice).

chains are tilted by 33° from the surface normal and occupy two different twist conformations, this results geometrically in different height levels for the terminal methyl group (inset Figure 1). However, determination of the

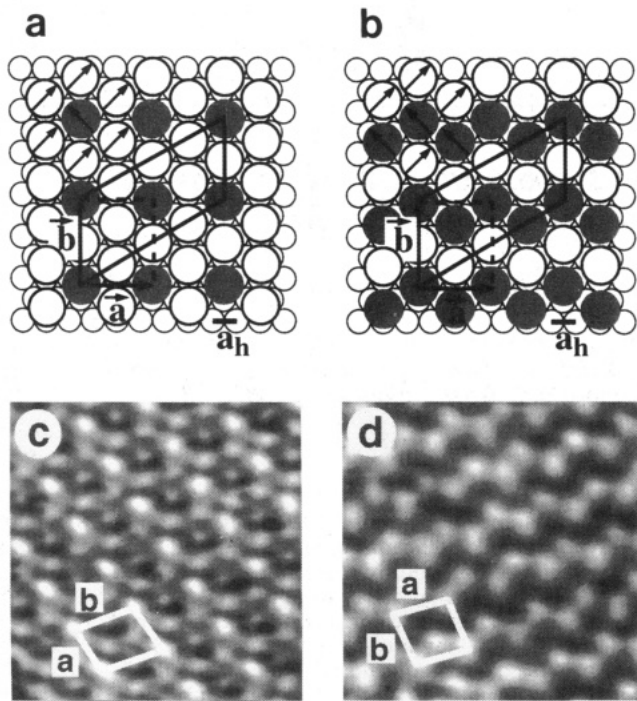


Figure 4. Proposed $c(4 \times 2)$ superlattice models describing the observed superstructures in Figure 3 where sulfurs are depicted by large circles and arrows represent the projection of the topmost C—C bond. The lattice vectors of the rectangular unit cell are $|\vec{a}| = 3a_h = 8.5 \text{ \AA}$ and $|\vec{b}| = 2\sqrt{3}a_h = 10.1 \text{ \AA}$, where $a_h = 2.88 \text{ \AA}$ denotes the interatomic spacing of Au(111)). (a) Model of domains B and C where two chains are twisted counterclockwise and six clockwise. (b) Model of domain D. Four chains are either twisted clockwise or counterclockwise. (c) Enlarged view of domain B with one superlattice cell outlined. (d) Enlarged view of domain D with one superlattice cell outlined.

exact height difference is difficult since additional electronic effects cannot be excluded.¹⁶ The maximal effective height difference for a full rotation around the twist axis is 0.6–0.7 Å, which is close to the level difference measured on the superlattice structures. Given a vertical orientation for the first twist state, the measured height difference of 0.7 Å would result in a twist angle difference of roughly 90°.

The use of a very high tunneling resistance precludes tip penetration into the monolayer and allows the observation of the $c(4 \times 2)$ superlattice in real space. The mechanisms for adsorption and growth of the monolayer can be explained by an initial, fast nucleation on the gold surface, followed by slow completion.¹⁷ Each domain grows with the same sulfur adlattice and the same chain tilt

orientation. The independent origin of the domains (nucleation site) leads to mismatches of the sulfur lattice as well as of the chain tilt orientation. The observation of larger molecular domains in annealed samples can be explained by a fixed tilt mismatch at room temperature which heals out at elevated temperature as suggested by Sellers *et al.*,¹⁸ while the sulfur lattice mismatches remain fixed, which limits domains to finite size. To date, domain sizes were estimated on the basis of diffraction peak widths.¹⁹ Depending on the experiments, different domain size values exist in the literature and are subject to intense discussion. Our results allow domain sizes to be measured directly and independently of domain boundary effects. For dodecanethiol on Au(111), average domain sizes of $6.5 \pm 1 \text{ nm}$ and $12 \pm 1 \text{ nm}$ were found for the as-prepared and annealed samples, respectively.

Our results show for the first time that several molecular conformations coexist in SAMs at room temperature. Some conformations are similar to bulk alkanes; others confirm the model provided based on He-scattering and X-ray diffraction experiments.^{6,10} The exact determination of the surface corrugation allowed the identification of new variants of the $c(4 \times 2)$ superlattice and their explanation with specific molecular models. Thermal annealing of preassembled SAMs improves molecular packing, so that these films can be studied with better accuracy. Moreover, annealing favors the formation of large domains by healing of chain-tilt mismatches. It is striking that SAMs made from dodecanethiol have several stable conformations at room temperature. A similar probability of these conformations indicates almost equal total energies, which makes it an interesting—and challenging—object for molecular dynamics simulations.⁷ Application of this method to SAMs with surface functional groups will provide the basis for a better understanding of organic interfaces and the use of such systems in nano-engineering.

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