

Interfacial Ordering of Self-Assembled Thiol Monolayers on Au(111)

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1. Introduction

Self-assembled monolayers formed by the spontaneous chemisorption of alkyl-disulphides on gold surfaces¹ have attracted an increasing interest both because of their ease in preparation and their prospects as model systems for technological applications such as corrosion inhibition or molecular lithography. Though various surface analytical techniques have been exploited, the actual molecular order in these films is still not clear. To a first approximation the molecular order is determined by the delicate balance between the interfacial sulphur-gold bonding and the van der Waals forces between neighbouring alkyl chains.

The general belief has been that the molecules reside in hollow sites of the Au(111) substrate, adopting a commensurate $\sqrt{3}\times\sqrt{3}R30^\circ$ superstructure. This has been shown by electron diffraction as well as scanning tunnelling microscopy studies.^{2,3} Infrared spectroscopy (IR)⁴ and thermal helium diffraction⁵ described the ordering of the molecular chains in similarity to bulk alkanes. At temperatures below 70 K the hydrocarbon chains are in all-trans conformation with an approximate tilt from the surface normal of about 30° and an additional supermolecular ordering associated with a periodic $(c(4\times 2))$ twist-angle arrangement of the carbon planes. As the temperature is raised to more than 200 K the molecular superordering of the chains is destroyed by an increasing number of gauche defects as revealed by IR spectroscopy.

Latest photoelectron spectroscopy measurements⁶ suggest that the description of the gold-sulphur interface by a simple $\sqrt{3}\times\sqrt{3}R30^\circ$ overlay of equivalent thiolates cannot be complete. From the observed splitting of the 2p sulphur core level the authors conclude that two types of inequivalent sulphur species have to be present in the monolayer. Since the $c(4\times 2)$ superstructure has been observed by STM and recently also by x-ray diffraction⁷ even at room temperature, we believe that such complex interfacial sulphur properties could be at the origin of the hydrocarbon chain ordering observed only at low temperatures.

In this paper we report on STM studies of the self-assembly of alkanethiols on Au(111) and the molecular ordering in the monolayer. Previous measurements showed that the self-assembly of the molecules is accompanied by the formation of a high density of one gold monolayer deep depressions with an average diameter of some nm. They are probably due to a chemical erosion processes during the adsorption. Annihilation of the defects at substrate steps upon at elevated temperature has proven this theory. To follow the kinetics of the mass transport in detail we performed isothermal measurements between 320 and 350 K. The growth kinetics of the average vacancy island radius can be described by an Ostwald ripening mechanism governed by the desorption/readsorption of monovacancies at step edges.

Molecular resolution images show that the molecules assemble after annealing to 350 K in well ordered domains (~10-30nm) consisting of two different $c(4 \times 2)$ molecular superstructures with four molecules per unit cell. Short-chain molecules (hexanethiol) show in addition uniaxial superstructures with domain sizes which are often only limited by substrate defects like step edges. The difference between long- and short-chain molecules illustrates the importance of the balance between interchain and adlayer-substrate interactions for the resulting order of the molecules in a self-assembled monolayer.

2. Experimental details

Hexanethiol ($\text{CH}_3(\text{CH}_2)_5\text{SH}$) and decanethiol ($\text{CH}_3(\text{CH}_2)_9\text{SH}$) monolayers on Au(111) substrates were prepared by spontaneous adsorption of the molecules from an ethanol solution. The substrates were prepared by vacuum deposition of a 1000 Å thick gold film on a mica sheet heated to 550 K during deposition, followed by a flame annealing in a butane-oxygen flame and an ethanol quench. STM inspections of the gold surface showed the presence of 100-300 nm wide (111) terraces, separated mostly by monoatomic steps. After a second flame annealing and ethanol quenching, the substrates, while still covered with an ethanol droplet, were immersed in a 1 mM thiol solution and kept therein for periods of time ranging from 15 to 40 hours. The as-prepared samples were thoroughly rinsed with ethanol and then dried in a dry nitrogen flow.

STM measurements were performed with a beetle-type scanning tunnelling microscope whose sample holder has been coupled to a Peltier element to allow imaging temperatures from 260 to 400 K. Because of its thermal self-compensation, this STM is well suited for variable temperature studies. Isothermal high temperature measurements have been performed while flushing the STM compartment with dry nitrogen gas.

3. Results and discussion

After the preparation of a thiol monolayer on Au(111) at room temperature one observes depressions of 1 - 3 nm in diameter which cover about 20 % of the total surface (fig.1a). The nature of these holes has been subject of controversial discussions. Substrate as well as molecular defects have been taken into consideration. Bucher et al. showed by tunnelling microscopy that the depth of the depressions is independent of the carbon chain length of the adsorbed thiol and that it coincides with the height of one substrate monolayer. Furthermore the defects can be healed out by annealing at temperatures above 350 K.⁸ This, for substrate defects typical behaviour, is shown in fig.1b where an hexanethiol/Au(111) sample has been annealed at 350 K for 45 minutes. The number of holes and the total area of defects has been reduced remarkably. The healing process is driven by coalescence of smaller holes to bigger ones and the following annihilation of the defects at pre-existing substrate steps. The latter process has clearly proven the substrate origin of the defects. In a further step Cavalleri et al. showed that the early stage of the annealing kinetics can be understood as an Ostwald ripening process.⁹

We turn now to the molecular resolution images obtained by STM. In fig.2 we show a high resolution STM image characterising a decanethiol monolayer adsorbed on Au(111). Prior to imaging the sample has been annealed for 30 minutes at 350 K. The STM image reveals molecular domains with an average diameter of the order of 10 - 20 nm. Two different molecular domains (A and B) occupying almost the same fraction of the total surface area can be distinguished. The domain boundaries - here imaged as depressions - run preferentially along the high symmetry direction of the trigonal substrate. If we zoom more into the details of domains like A and B (right hand side of

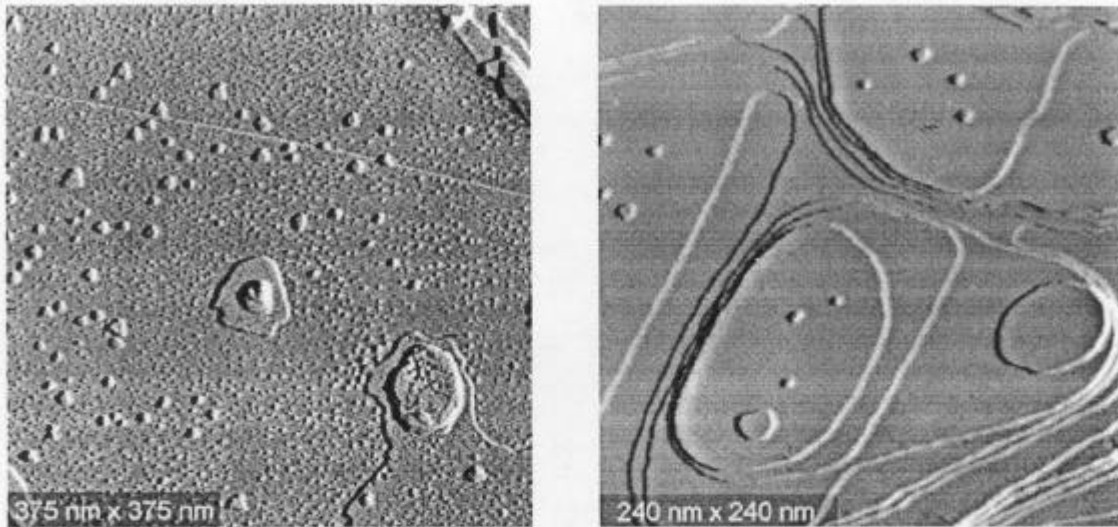


Fig. 1 : Morphology of the hexanethiol covered Au(111) surface after self-assembly at room temperature (a) and after careful annealing at 350 K for 45 min (b).

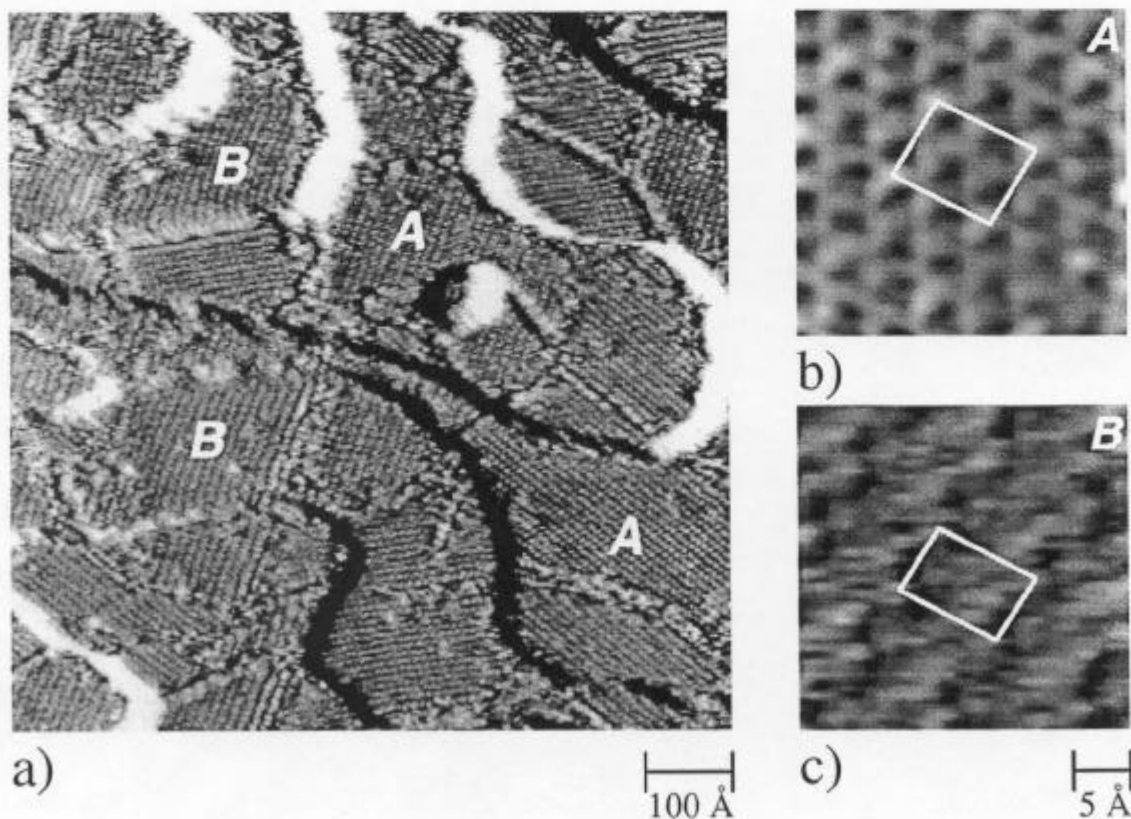


Fig. 2 : Multidomain molecular ordering of a decanethiol monolayer on Au(111) (a). The high resolution images (b) and (c) show details of the pin-wheel structure (domain A) and of the zig-zag structure (domain B), respectively.

fig.2), we recognise the from electron diffraction well-known $\sqrt{3}\times\sqrt{3}R30^\circ$ adsorption geometry. Additionally these figures -representing domain A and B respectively- own a further superordering feature. Domain A is a pinwheel-like pattern where one light appearing molecule is surrounded by 6 darker ones while domain B can be described as a zig-zag-like pattern. These superstructures are in complete accordance with previous helium scattering-⁵, infrared spectroscopy-⁴ and STM-¹⁰ measurements. They can be described as two types of a $c(4\times 2)$ -superstructure with respect to the $\sqrt{3}\times\sqrt{3}R30^\circ$ adsorption sites of the molecules. In domain A three out of four molecules in the unit cell are symmetry equivalent whereas in B the molecules are equivalent in pairs. From He scattering the idea has been evolved that the superstructures results from a patterned arrangement of different twist angles of the molecular carbon planes. We must notice, however, that our observations are made at room temperature or even higher (up to 350 K). This is the crucial point, because according to He scattering and IR spectroscopy the supermolecular $c(4\times 2)$ ordering of the methyl groups and the polymethylene chains is destroyed at already above 70 K and 200 K respectively. Note that the employed quiet ordinary tunnelling parameters (tunneling resistance of $\sim 1G\Omega$) could lead to a mechanical contact between the tunnelling tip and the molecules¹¹ which might also destroy any hypothetical twist-angle ordering of the chains. It is thus natural to conclude that the molecular superstructure-ordering has its origin at the gold-sulphur interface and that consequently the ordering of the chains results from the interfacial properties. In summary, the observation of the $\sqrt{3}$ sulphur-lattice and the superimposed $c(4\times 2)$ structure at room temperature under ordinary tunneling conditions support the $\sqrt{3}\times\sqrt{3}R30^\circ$ adsorption geometry where the superstructures may be due to chemically different sulphur species or different sulphur-gold bonding configurations. We mention that this model is not in accordance with a disulphide adsorption model inferred recently from x-ray diffraction measurements.⁷ However, the disulphide model cannot explain with the multidomain ordering observed in the STM (see fig.2). Moreover, the lack of Q_z modulation in the x-ray diffraction measurements of the superstructure would find a natural explanation in the above described picture. Nonetheless the chemical nature of the two sulphur species remains an open question.

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