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A new striped-phase of decanethiol self-assembled monolayers on Au(1 1 1) formed at a high solution temperature

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ABSTRACT

Self-assembled monolayers (SAMs) of decanethiol (C10) on Au(1 1 1) prepared at room temperature (RT), 60 °C, and 70 °C have been investigated using high resolution scanning tunneling microscopy (STM). For SAMs prepared at RT, the $c(4 \times 2)$ superlattice of the basic $(\sqrt{3} \times \sqrt{3})$R30° structure was hardly observed in small-scale STM images. Increasing the solution temperature to 60 °C results in formation of SAMs having large ordered domains of the $c(4 \times 2)$ superlattice. In contrast to the previous studies, our results indicate the presence of four different topographical heights for the C10 molecules per $c(4 \times 2)$ unit cell. Preparation of C10 SAMs from 70 °C of solution temperature leads to the formation of new striped phase with $(4\sqrt{3} \times 2\sqrt{3})$R30° unit cell. The area of a single molecule in the $(4\sqrt{3} \times 2\sqrt{3})$R30° striped structure amounts to 57.73 Å^2, which is about 167% larger than that (21.6 Å^2) for a molecule in the $c(4 \times 2)$ structure.

1. Introduction

In the last 20 years, self-assembled monolayers (SAMs) derived from the spontaneous adsorption of organic thiols on metal surfaces have drawn considerable attention because of their scientific importance and technological applications in nano- and bio-technologies [1–9]. In particular, the formation and structure of *n*-alkanethiol SAMs on gold surfaces have been extensively studied due to their ability to form ordered organic films with well-defined composition and thickness [10–12]. Different techniques have been employed to investigate the structure and formation of alkanethiol SAMs. Some of these techniques are scanning probe microscopy (SPM), helium diffraction [13], contact angle measurement [14,15], ellipsometry [16–18], second harmonic generation (SHG) [19], surface plasmon resonance (SPR), X-ray photoelectron spectroscopy (XPS) [20–22], electrochemistry [16], and thermal desorption spectroscopy (TDS). It is known that the S—H bond cleaves and the molecule chemisorbs to the surface through a covalent Au—S bond while the hydrocarbon chains interact laterally through van der Waals attraction [23]. As a result, there was a general agreement that the SAMs formed from $CH_3(CH_2)_nSH$ with $n > 5$ form densely packed monolayers, with a chain tilt of ~30° respect to the surface normal that maximize the van der Waals interactions between alkyl chains, and a structure with a $(\sqrt{3} \times \sqrt{3})$R30° lattice. The helium diffraction [13] and STM [24] studies demonstrated the presence of a $c(4 \times 2)$ superlattice of the basic $(\sqrt{3} \times \sqrt{3})$R30° structure. The $(\sqrt{3} \times \sqrt{3})$R30° structure corresponds to a molecule–molecule spacing of ~5 Å and an area per molecule of 21.6 Å^2. While the structure of decanethiol SAMs on Au(1 1 1) are extensively studied and well-known. New structures and complex phase behavior have been progressively discovered when coverage of these layers falls below saturation. The unsaturated SAMs are usually prepared via annealing of densely packed decanethiolate films at high temperatures in UHV [24,25,26,27] and in air [28,29], or via varying the exposure in the gas phase deposition [30,31]. At low coverage of decanethiol on Au(1 1 1), frequently a so-called "striped-phases" have been observed [25,26,32–35]. They are characterized by the molecular backbones lying flat on the surface. The stripe phase is often denoted as $(p \times \sqrt{3})$ (p being integer or half-integer), where p is the stripe spacing and $\sqrt{3}$ the periodicity within the stripe in units of the Au(1 1 1) lattice spacing [35]. Poirier et al. reported the formation of six different phases of decanethiol on Au(1 1 1): four stable and two metastable phases were observed after gas phase deposition with increasing exposures [35]. The four stable structures are a 2-D gas phase (α phase), the $(11.5 \times \sqrt{3})$ stripe phase (β phase), a $(7.5 \times \sqrt{3})$ stripe phase (δ phase) and the densely packed $c(4 \times 2)$ overlayer structure (ϕ phase). The two metastable phases are a stripe phase with alternating $(7.5 \times \sqrt{3})$ and $(11.5 \times \sqrt{3})$ stripe segments (χ phase) and a non-periodic

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dynamic two dimensional liquid phase (ε phase). The β and δ stripe phases have been also observed both in the annealed densely packed decanethiol SAMs [25,27,34,36] and in situ in pure decanethiol liquid [37,38]. In addition to these phases, two new phases with $p = 9$ and 11 were reported for the decanethiol SAMs that annealed at temperature range of 345–400 K [39].

For aromatic thiols [2,4–7] and adamantanethiols [40] systems on Au(1 1 1), it has been reported that solution temperature is one of the crucial factors in determining the final SAM structures. The micrographs of the resulting SAMs on Au(1 1 1) that were prepared at higher temperatures than 298 K revealed a pronounced and progressive increase in the size of the well known etch-pits at the expense of their density. Also, the average domain size of the formed phases was found to increase significantly with increasing preparation temperature. In addition, different phases from those observed at room temperature were formed in SAMs prepared from hot solutions [2,40].

In an extension of the previous works on decanethiol SAMs on Au(1 1 1), in the present study we report the results of a rather extensive STM study on decanethiol SAMs prepared from solution at RT, 60 °C, and 70 °C. The high resolution STM images obtained in the present study enabled us to determine precisely a new structure, that have not been observed previously for decanethiol system on Au(1 1 1).

2. Experimental

2.1. Chemicals

Decanethiol, C10 (Aldrich, 99.9%), Ethanol (Baker, absolute), acetone (Baker, HPLC (grade)), and chloroform (Baker, absolute) were used as received.

2.2. Sample preparation

2.2.1. Substrates

At first a freshly cleaved sheet of mica was heated to 370 °C for about 72 h inside the evaporation apparatus to remove residual water contained between the mica sheets. Subsequently, 100 nm of Au were deposited at a substrate temperature of 370 °C and a pressure of approximately 10^{-7} mbar. After deposition, the substrates were allowed to cool, and the vacuum chamber was vented with purified nitrogen. Between substrate preparation and SAM formation, the substrates were stored in an argon atmosphere. Immediately before the SAM formation, the substrates were flame-annealed using a butane-oxygen flame. This procedure yielded Au substrates with well-defined terraces exhibiting a (1 1 1)-oriented surface. The terraces are separated by steps of monatomic height and have sizes in excess of 100 nm.

2.2.2. Preparation of the C10 SAMs

C10 monolayers on Au(1 1 1) substrates were prepared by immersing the gold substrates into dilute ethanolic solutions (2 μM) of the C10 thiol for 18 h at 343 K. The substrate was removed from the solution and rinsed carefully with pure ethanol, acetone, chloroform and again ethanol. Finally the substrates were dried in a stream of dry nitrogen.

2.2.3. Structural investigations

STM data were obtained using a JOEL STM 4210 instrument. The tips were mechanically prepared by cutting a 0.25 mm $Pt_{0.8}Ir_{0.2}$ (Goodfellow). The data were collected in constant current mode using tunneling currents between 120 pA and 300 pA and a sample bias of between 500 mV and 700 mV. No tip-induced changes were observed.

3. Results and discussion

Due to the technological applications of organic SAMs, the control of their adsorption configuration on Au(1 1 1) is an extremely important issue because the surface properties of SAMs can be simply altered by the molecular orientation of adsorbed molecules. To elucidate the effect of the solution temperature on the adsorption structure of the C10 SAMs on Au(1 1 1), SAM samples prepared from C10 solutions at RT, 60 and 70 °C were studied.

In Fig. 1, we present STM images of C10 monolayer prepared at RT for 24 h of immersion time. In Fig. 1(a), the image exhibits high density of etch-pits. The etch-pits are randomly distributed on the surface. As discussed in previous studies [2,4,10], the etch-pits are actually depressions in Au surface originating from an etching process during the adsorption and organization process of the molecules. Fig. 1(b) shows that the solution-grown C10 SAMs exhibit the close-packed $c(4 \times 2)$ superstructure of the basic $(\sqrt{3} \times \sqrt{3})R30^\circ$ commensurate structures. This structure has been previously reported for C10 on Au(1 1 1) [10,33]. The typical domain size of the crystalline SAM lattice is about 20 nm (see Fig. 1(b)). In low magnification images (such as Fig. 1(b)), the $c(4 \times 2)$ superstructure can be easily observed. By zooming into the same surface area of the image in Fig. 1(b), the periodic height modulation of the C10 molecules within the $c(4 \times 2)$ superstructure cannot be seen anymore (see Fig. 1(c) and (d)). The images show the C10 adsorbates of an equivalent topographical height i.e. the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Even though the tunneling parameters were changed to extreme values such as that of the image in Fig. 1(c), achieving an obvious molecular contrast variation within the ordered domains showing the $c(4 \times 2)$ structure was still not possible. One of the reasons that lead to this difficulty in the STM probing may be the small size of the ordered domains that prevents the resolving of the periodic height modulation of the C10 molecules.

In Fig. 2(a), the images show the topography of the C10 SAMs prepared at 60 °C for immersion time of 24 h. Obviously, the number of etch-pits is significantly reduced, at the expense of an increased size for the residual pits. Preparation of SAMs from hot solutions can heal the etch-pits to a great extent by Au and/or thiolate diffusion and can also enhance the domain size [2,4,10,40]. The image displayed in Fig. 2(b) shows that the SAM surface is decorated by the presence of elevated patches (see areas surrounded by dotted loops). The height of these patches compared to their surrounding areas was determined from the cross-sectional height profile displayed in Fig. 2(d) to be 1 ± 0.3 Å. On these patches, the $c(4 \times 2)$ superstructure was frequently resolved. Also, each patch was found to carry a unidirectional ordered domain as evidenced by the image displayed in Fig. 2(c). The size of the ordered domains was restricted by the size of the underneath patch that is about 50 nm. The STM images in Fig. 2(a)–(c) exhibit that the elevated patches are separated by grooves and elevated stripes (see the white and black arrows in Fig. 2(b) and (c)). In Fig. 2(d), a cross-sectional height profile for the line B marked in Fig. 2(c) is displayed. The line B was assigned to pass over two neighboring patches that are separating by grooves and elevated stripes. Accordingly, the depth of the grooves was determined to be about 1 Å compared with the patches. This value is different from the depth of the etch-pits i.e. 2.4 Å. Therefore, we rule out the possibility that the grooves are etch-pits on gold surface. From the STM image displayed in Fig. 2(c), the grooves were found to accommodate C10 molecules. The nature of these grooves seems to be related to a lower C10 coverage, at which the molecules do not stand normal to the surface. The elevated stripes are molecular rows of height approximately 0.5 Å higher than the neighboring patches. The C10 molecules in these stripes are expected to bind with the underneath gold surface adopting high adsorption sites such as on-top sites.