

## STM INVESTIGATIONS OF SELF-ORDERED *n*-OCTANE ACID FILMS ON Au(111) SURFACE

**A.A. MARCHENKO, A.G. NAUMOVETS, D.T. TARASCHENKO,  
V.V. CHEREPANOV**

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**Institute of Physics, Nat. Acad. of Sci. of Ukraine**

(46, Nauky Ave., Kyiv 03680, Ukraine; e-mail: amarch@voliacable.com)

It has been shown that highly ordered monolayer films of *n*-octane acid  $\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$  can be obtained by the deposition from its solutions in methanol  $\text{CH}_3\text{OH}$  or *n*-tetradecane  $n\text{-C}_{14}\text{H}_{30}$ . Using the scanning tunneling microscopy (STM), it has been found that the ordered monolayers have a brush-like structure on a reconstructed Au(111) surface. In this structure, the main molecular axes are tilted with respect to the surface, and the packing of alkyl chains corresponds to the  $c(4 \times 2)$ -structure. The bonding between the molecules and the surface is implemented through the interaction between COOH groups and Au atoms. The stability of *n*-octane acid films and a relatively low concentration of defects in the lateral direction allow the homologous series of saturated organic acids to be considered as a promising class of adsorbates for the surface functionalization, in particular, for the creation of dielectric buffer layers.

### 1. Introduction

Superthin organic films on crystal surfaces are a subject of intensive experimental and theoretical researches. This is related to their wide use in molecular electronics [1], information displays [2], solar batteries [3], pyroelectric detectors and other sensor controls [4]. The physical properties of such films depend on the degree of their ordering. To a great extent, these properties are determined by the first layer of a film. Therefore, a special attention is paid to studying both the factors that affect the monolayer structure and the interaction between the monolayer and the substrate. After the STM method had been discovered, the monitoring of molecular structures with a spatial resolution that sometimes could reach 0.001 nm became possible. The overwhelming majority of STM researches dealt with physically adsorbed organic films, in particular, films on the basis of chemically passive aliphatic compounds [5], liquid crystals [6], fullerenes [7], and many others. At the same time, chemically active adsorbates were given a much less attention. Meanwhile, one of the most important problems related to the creation of the element base of nanoelectronics on the basis of organic molecules is the problem of fabrication of ordered dielectric buffer layers, for instance, at

developing the organic transistors on atomically smooth surfaces [8].

To achieve this purpose, amphiphilic molecules with chemically active end groups are used. Traditionally,  $-\text{SH}$  groups (thiols) [9] or groups with a silicon atom, such as  $-\text{SiH}_3$  or  $-\text{Si}(\text{CH}_3)_3$  (silanes) [10], play this role. However, the monolayers of corresponding substances are multiphase, and, as a consequence, they possess numerous defects of the types of interfaces and domain walls.

Below, we demonstrate that the molecules of octane acid  $n\text{-CH}_3-(\text{CH}_2)_6-\text{COOH}$  form stable monolayers on a reconstructed Au (111) surface. The concentration of defects in those monolayers is substantially lower. For the sake of comparison, we report the results of STM researches of *n*-dodecanethiol  $\text{C}_{12}\text{H}_{25}\text{SH}$  films deposited under the same conditions. This result testifies to a high potential of using organic acids as alternative substances to thiols and silanes for the purposes concerned.

### 2. Experimental Part

To prepare Au(111) substrates, single-crystalline mica plates,  $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$ ,  $10 \times 20 \times 0.2 \text{ mm}^3$  in dimension (produced at United Mineral & Chemical Corp.) were used. Films of gold (99.99%, "Metron") about  $150 \pm 50 \text{ nm}$  in thickness were sputtered onto fresh cleavages of mica plates. Sputtering was carried on in vacuum at a rate of about  $0.2 - 0.3 \text{ nm/s}$  at a residual gas pressure of no more than about  $10^{-8} \text{ Pa}$ . The temperature of substrates was maintained within the interval  $500 \pm 20 \text{ K}$ , and it was measured making use of a thermocouple. The thickness of gold films was monitored by means of a quartz balance.

The surfaces of Au substrates sputtered in such a way had a granular structure. To form atomically smooth Au(111) terraces, we annealed the films with the help of a gas torch under atmospheric conditions. Annealing had been carried out about 1 to 2 min before solutions of the studied substances were deposited. Propane, butane,

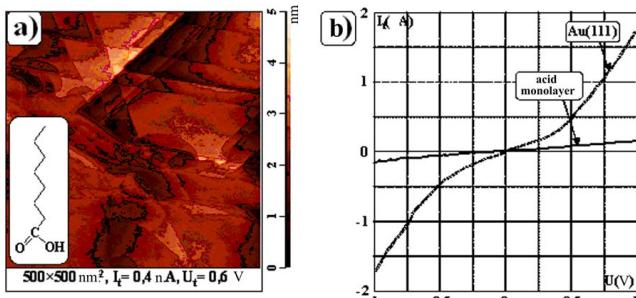


Fig. 1. (a) STM image of an *n*-octane acid  $\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$  monolayer on a Au(111) surface (submicronic scale). The inset illustrates the structural formula of *n*-octane acid. (b) Local current-voltage characteristics (CVCs) of both a clean Au(111) substrate and the same substrate covered with an *n*-octane acid monolayer. The distance between the tip and the surface during the CVC registration corresponded to the scanning parameters  $U_t = 0.6$  V and  $I_t = 0.4$  nA

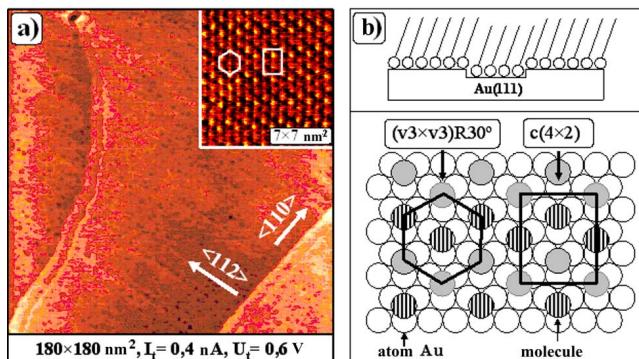


Fig. 2. (a) STM image of an *n*-octane acid monolayer on a Au(111) surface (nanometer scale). The presence of etched sites on the substrate (dark spots) testifies to a chemical activity of COON groups. The inset illustrates the molecular resolution of the film ( $a 7 \times 7 \text{ nm}^2$  section). The hexagon and the rectangle denote the unit packing cells for COOH groups and alkyl chains. (b) (top) Schematic model of “brush-like” structure. (bottom) Schematic models of packing for COOH groups (structure  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ ) and alkyl chains (superstructure  $c(4 \times 2)$ ). Grey and hatched circles denote alkyl chains with different environments (according to different STM contrasts)

or their mixture with a random content was used as a working gas. The annealing procedure included a short-term (for 4–5 s) insertion of the substrate into the flame region, where the temperature was about  $650 \pm 50$  K. After annealing, extended single-crystalline Au blocks with atomically smooth terraces, separated by mono- or multiautomic steps, were formed on the substrate. The terrace lengths reached several hundreds

of nanometers. Within the first 5 to 10 min after annealing, STM images revealed the characteristic lines of a  $23 \times \sqrt{3}$  reconstruction [11], which testified that the plane terraces were densely packed Au(111) faces.

Methanol  $\text{CH}_3\text{OH}$  and *n*-tetradecane  $n\text{-C}_{14}\text{H}_{30}$  were used as solvents for the film deposition. The corresponding concentrations and volumes of the solutions (per area unit of the substrate) had been so selected experimentally that a single monolayer was formed after the substance had been completely deposited onto the Au(111) surface. The coating thickness was monitored making use of STM images with subnanometer resolution.

STM measurements were carried out on a scanning tunnel microscope (NT MDT, Russia), which was adapted by us for operating with liquid media. The tips were prepared of a Pt-Ir wire 0.25 mm in diameter by sharpening the wire mechanically. Both STM measurements and the film deposition were performed at room temperature. STM images were obtained in the dc mode, without any application of filtration procedures, except for the subtraction of the average slope of the scan plane in order to improve the visualization of STM images. Local CVCs were registered in the absence of a feedback and at a distance between the tip and the surface that corresponded to scanning parameters.

### 3. Results and Discussion

An *n*-octane acid molecule (the inset in Fig. 1,*a*) consists of a linear hydrocarbonic chain of about 0.9 nm in length and an end group –COOH. In 10 min after the solution deposition, the STM images made on the submicronic scale revealed plane terraces of the Au(111) substrate several hundreds of nanometers in length. The terraces were separated from one another by monoatomic steps (Fig. 1,*a*). On the STM images, the characteristic lines of the  $23 \times \sqrt{3}$  reconstruction of the Au(111) surface were reproduced before the solution was put, but they were not observed after the film was deposited. The local CVCs that were registered before and after the solution was put (Fig. 1,*b*) evidence for a film presence on the substrate. One can see that the electric resistance of the film is about  $8 \text{ G}\Omega$  in comparison with about  $0.6 \text{ G}\Omega$  for a clean Au(111) substrate (the calculations were carried out for the linear CVC section).

On the STM image of the nanometer scale (Fig. 2,*a*), one can see that the presence of the acid film provokes the Au(111) terrace to lose their atomic smoothness and to get covered with a net of hollows, which look

like dark spots and occupy, on the average, about 10% of the scanned area (the so-called “leopard” structure [12]). The cross-sections of STM images reveal that all the spots are almost identical by depth, and this depth is equal to the height of a monoatomic gold step (of about 2.4 Å). Therefore, the hollows are, in essence, two-dimensional pores in the first layer of the Au(111) substrate and in the “leopard” structures of *n*-alkanethiols [12]. By analogy with thiols, the formation of “leopard” structures in *n*-octane acid films testifies to a chemical activity of its molecules with respect to the reconstructed Au(111) surface.

The STM image with a molecular resolution (the inset in Fig. 2,*a*) reveals a regular arrangement of spots with different brightnesses. The distance between the neighbor spots is  $0.5 \pm 0.02$  nm, which agrees well with the diameter of the main COOH group. Therefore, the spots registered by STM correspond to individual acid molecules. It is worth noting that the monolayer packing is characterized by a superposition of two unit cells with different symmetries—a hexagonal one irrespective of the spot brightness, and a rectangular cell which corresponds to the arrangement of spots with enhanced brightness (the inset in Fig. 2,*a*). We admit that the molecules are adsorbed in linear conformations so that their main axes are either perpendicular or inclined to the Au(111) surface (the upper part of Fig. 2,*b*). In this case, the end —COOH groups are in contact with the substrate, and the alkyl chains are directed to the liquid depth (the so-called “brush-like” structure with the vertical geometry of adsorption). The distance between neighbor molecules ( $0.5 \pm 0.02$  nm) measured from the STM image (Fig. 2,*a*) is close to  $a\sqrt{3} = 0.498$  nm, where  $a = 0.288$  nm is the period of the lattice on the Au(111) surface. This distance coincides with that between other,  $\langle 110 \rangle$ , neighbor rows of gold atoms. Taking the measured distances into account and based on the fact that long-period modulations of the STM contrast were never observed when plane monolayer sections were scanned, we may assert that the film is commensurate with the Au(111) substrate along three equivalent directions:  $\langle 112 \rangle$ ,  $\langle 121 \rangle$ , and  $\langle 211 \rangle$ .

The coexistence of two superstructures in the film lattice can be explained by a difference between the packing of molecular head groups —COOH and alkyl chains. We suppose that, in the monolayer, the COOH groups of all molecules occupy equivalent adsorption places and form a hexagonal ( $\sqrt{3} \times \sqrt{3}$ )R30°-structure with the basic vectors  $a = b = 0.5 \pm 0.02$  nm. The packing of alkyl chains corresponds to a rectangular

structure  $c(4 \times 2)$ . Within a unit  $c(4 \times 2)$  cell, alkyl chains have a nonequivalent environment, which is responsible for the difference between their STM contrasts. A schematic model of the *n*-octane acid molecule packing is illustrated in Fig. 2,*b*. However, it should be noted that molecules can occupy adsorption places of three types on the Au(111) surface: these are 1) hollows between three nearest atoms (“three-fold hollow” sites), 2) tops of gold atoms (“top” sites), and 3) bridge positions (“bridge” sites) [12]. It is evident that the same basic vectors of the crystal lattice determine the packing structure in each of those three cases. In a model proposed in Fig. 2,*b*, molecules occupy bridge positions. Unfortunately, the visualization of the substrate’s atomic structure was not possible; therefore, we did not manage to determine the type of adsorption sites.

It is known that the type of a solvent can substantially affect the structure and the properties of the films obtained, if the deposition is carried out from a liquid [13]. To elucidate the influence of this factor, we experimented with two solvents characterized by different polarities, namely, a polar solvent methanol (CH<sub>3</sub>OH) and a nonpolar solvent *n*-tetradecane (*n*-C<sub>14</sub>H<sub>30</sub>). In this case, the structure of *n*-octane acid monolayers turned out independent of the solvent type. Moreover, the structure of the films described above was observed both in a liquid environment and after the complete evaporation of a solvent. Therefore, the deposition technique used in this work can be used as a basis for the fabrication technology of “dry” monolayers made up of saturated organic acid molecules.

Consider also some basic differences between the structures of the *n*-octane acid and *n*-alkanethiol monolayer films. For the sake of comparison and using the technology described above, we deposited a monolayer of *n*-dodecanethiol C<sub>12</sub>H<sub>25</sub>SH onto an Au(111) surface and carried out structural STM researches under the same conditions (Fig. 3). Figure 3 demonstrates that the *n*-dodecanethiol film is a two-dimensional biphasic polycrystal, in which two phases—( $\sqrt{3} \times \sqrt{3}$ )R30° and  $c(4 \times 2)$  ones—coexist. The ordered domains in the monolayer are oriented along three equivalent crystallographic directions of the Au(111) surface. Note that the longitudinal domain sizes do not exceed 5–10 nm. At the same time, in *n*-octane acid monolayers, the dimensions of single-crystalline domains reach several hundreds of nanometers. For instance, we did not reveal domain walls within the area of STM rasters that are shown in Figs. 1,*a* and 2,*a*. All raster sections demonstrated an ordered structure, as is observed in the inset in Fig. 2,*a*.

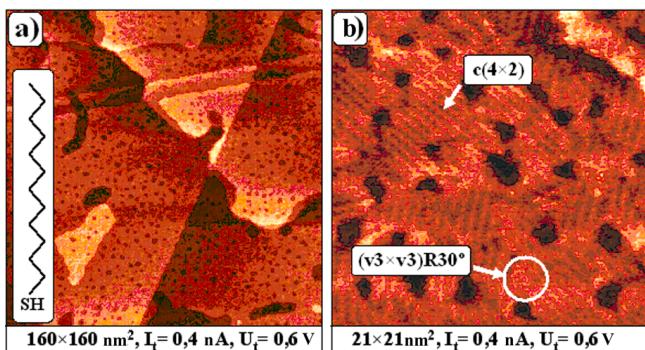


Fig. 3. (a) “Leopard” structure of an *n*-dodecanethiol  $C_{12}H_{25}SH$  monolayer on the Au(111) surface. The inset illustrates the structural formula of *n*-dodecanethiol. (b) Molecular resolution of the *n*-dodecanethiol monolayer. Structures  $(\sqrt{3} \times \sqrt{3})R30^\circ$  and  $c(4 \times 2)$  coexist

Another basic difference consists in the “leopard” structures of the films. As is seen in Fig. 2,*a*, in the case of an *n*-octane acid monolayer, the etched sites of the substrate (dark spots) are grouped strictly along the crystallographic direction  $\langle 112 \rangle$ , which the direction of Au(111) surface reconstruction lines coincides with. In contrast to the *n*-octane acid case, if a monolayer of *n*-dodecanethiol is deposited, the etched sites are arranged stochastically (Fig. 3).

#### 4. Conclusions

In this work, making use of the STM method, we have shown that highly ordered monolayer films of *n*-octane acid  $CH_3-(CH_2)_6-COOH$  can be obtained by depositing them from the solution in either methanol  $CH_3OH$  or *n*-tetradecane  $n-C_{14}H_{30}$ . It is found that, on the reconstructed Au(111) surface, the ordered monolayers have a brush-like structure, in which COOH-groups of molecules form a hexagonal structure  $(\sqrt{3} \times \sqrt{3})R30^\circ$ , while the packing of alkyl chains corresponds to the  $c(4 \times 2)$  structure. The molecule–substrate coupling occurs due to the interaction between –COOH groups and Au atoms. The stability of *n*-octane acid films and a rather low concentration of defects in the longitudinal direction allow the homologous series of saturated organic acids to be considered as a promising class of adsorbates for the surface functionalization. The effect of the COOH-group sensitivity with respect to the reconstruction lines on the Au(111) surface, which has been revealed in this work, can be used as a model one in the theoretical

studies of the chemical reactions of organic acids and their derivatives with a metal surface.

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СТМ-ДОСЛІДЖЕННЯ САМОВПОРЯДКОВАНИХ ПЛІВОК *n*-ОКТАНОВОЇ КИСЛОТИ НА ПОВЕРХНІ Au(111)

*O.A. Марченко, А.Г. Наумовець, Д.Т. Таращенко, В.В. Черепанов*

Р е з ю м е

Показано, що високовпорядковані моношарові плівки *n*-октанової кислоти  $CH_3-(CH_2)_6-COOH$  можуть бути отримані осадженням з розчину в метанолі  $CH_3OH$ , або *n*-тетрадекані  $n-C_{14}H_{30}$ . Методом сканувальної тунельної мікроскопії встановлено, що на реконструйованій поверхні Au(111) упорядковані моношари мають щіткоподібну структуру, в якій головні осі молекул нахилені до поверхні підкладки, а пакування алкильних ланцюгів відповідає структурі  $c(4 \times 2)$ . Зв’язок молекул з підкладкою здійснюється взаємодією –COOH-груп з атомами Au. Стабільність плівок *n*-октанової кислоти і порівняно низька концентрація дефектів у латеральному напрямку дозволяє розглядати гомологічний ряд насичених органічних кислот як перспективний клас адсорбатів для функціоналізації поверхні, зокрема, при отриманні буферних діелектричних моношарів.