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Self-assembled monolayers of decanethiol on Au(111)/mica

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Abstract. We report here a preparation for thin gold films on mica substrates. We have investigated the influence of the substrate temperature and the evaporation rate on the morphology of the films. After careful outgasing of the substrate, 100 nm of Au is evaporated onto the mica surface maintained at high temperature. After slow cooling, *ex situ* characterizations are performed using AFM and STM. For our purposes, the best compromise between roughness and grain size is found to occur for an evaporation rate of 2 Å s^{-1} onto a mica substrate maintained at 460 °C. We have used these substrates for STM and AFM study of decanethiol self-assembled monolayers (SAMs). We present results for gold samples immersed for a few seconds in decanethiol solutions, revealing an incomplete organization of the films. The organization process is discussed through comparison between AFM and STM data recorded on the SAMs. Then we present molecular resolution STM pictures of ordered SAMs for longer immersion times.

PACS. 61.16.Ch Scanning probe microscopy: scanning tunnelling, atomic force, scanning optical, magnetic force, etc. – 68.35.Bs Surface structure and topography

1 Introduction

Scanning tunnelling microscopy (STM), and atomic force microscopy (AFM), are considered as powerful analytical techniques for surface science. Scanning probe microscopy (SPM, as these techniques are collectively designated) is successfully applied to the studies of organic self-assembled monolayers, and more particularly to alkanethiol systems on gold [1]. Self-assembled monolayers (SAMs) are molecular assemblies chemically bonded to the substrate, spontaneously formed during immersion of a substrate in a solution of surfactant molecules. One of the SAMs' interests is that they allow chemical elaboration of ultra-thin films (around 10 Å) exhibiting crystalline order. Many systems lead to such SAMs [2], but alkanethiol on gold are the most studied ones, mainly by SPM [1]. The physical and chemical properties of the substrates are of prime importance for such studies. In addition, to be chemically well defined, the substrates must be atomically flat over wide areas. In the case of alkanethiol self-assembly, the flat areas must be larger than the organized domains of molecules on the surface (as we will see below, typically 20 nm). Because of its high affinity with organic thiols [3], gold is the most usual substrate used. Gold substrates can be prepared by various techniques [4–7], in particular by vapour deposition to form (111) oriented thin films on the (001) cleavage planes of mica. Numerous publications report about the elaboration of such substrates (*e.g.* [8,9]), however, the described experimental procedures are often difficult to reproduce and we have found it useful to give here guidelines detailing our approach. We then present a SPM study of decanethiol SAMs grafted onto such substrates. In this work, we focus on both the early stage of organization and fully ordered decanethiol films, using STM and AFM down to the molecular scale.

2 Experimental

2.1 Materials and instrumentation

Gold deposits are realized in an UHV chamber (base pressure 10^{-9} Torr), using an ATE60 electron gun (Riber, France). The film thickness is monitored using a quartz crystal micro-balance (TM200, Maxtech Inc., USA). We use 99.99% pure gold (Puratronic, Alfa, Germany), deposited on ruby muscovite mica (Rubis CLSS scratchless, Metafix, France). The mean roughness measured by AFM after heating was found to be below 0.1 nm on 20 μm^2 area. Atomic force microscopy and scanning tunnelling microscopy are carried out on a Nanoscope III (Digital Instruments Inc., USA), using mono-crystalline Si cantilevers with integrated Si tips for AFM experiments (NSCS12, NT-MDT, Russia and Nanoprobes, Digital Instruments Inc., USA), and home made Pt-Ir tips for STM. All chemicals and solvents used for the preparation of self-assembled monolayers of decanethiol on gold are commercial grades of highest purity.

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2.2 Preparation of gold films

Scratchless mica sheets (50 mm diameter) are cut into 1 cm^2 pieces with scissors, and are then cleaved using adhesive tape, prior to their introduction into the evaporation chamber. The mica sheets are heated from the rear through the sample holder. The temperature is controlled at the surface of the sample by an IR pyrometer. Before Au evaporation, the mica is heated overnight at deposit temperature (pressure of 10^{-7} Torr), in order to allow removal of adsorbed molecules from its surface.

Gold evaporation is carried out at evaporation rates ranging from 0.5 up to 5 Å s^{-1} (pressure lower than 10^{-7} Torr), at substrate temperatures ranging from 410 up to 535 °C. The thickness of the film is controlled by a quartz micro-balance. After evaporation, the film is annealed for 45 minutes at deposit temperature, and then slowly cooled down to room temperature at a rate of 10 °C min^{-1}.

2.3 SPM measurements

AFM experiments on gold samples are performed in an ambient atmosphere, using the intermittent contact mode (also known as "Tapping Mode") on 20 micron × 20 micron areas at a scan frequency of 1 Hz. The contact mode is used for SAMs friction measurements. The probes are mono-crystalline Si cantilevers with integrated Si tips (nominal normal spring constant ranging from 0.2 to 16 Nm^{-1} for NSCS12, and from 17 to 64 Nm^{-1} for Nanoprobes). STM experiments are also performed in ambient conditions, in constant current and/or current image modes. For decanethiol studies, we use the low current option which allows imaging at tunnelling currents below the pA. All pictures shown in the following are raw data.

2.4 Preparation of decanethiols SAMs

Prior to use, all the vessels are cleaned in a hot solution (60 °C), containing 20% NH_3, 20% H_2O_2 in deionized water, for half an hour. They are then extensively rinsed with water, dried under nitrogen flow, and rinsed with dichloromethane. SAMs are elaborated by immersing fresh gold substrates in a 10^{-3} M solution of decanethiols in dichloromethane for at least two hours. Samples are then extensively rinsed with dichloromethane and then dried under nitrogen flow.

3 Results and discussion

3.1 Elaboration of gold films

Our first need is to elaborate thin gold films suitable to STM and AFM studies down to molecular resolution. It is thus necessary to prepare films with low roughness, exhibiting atomically flat Au terraces. Moreover, for STM studies, our thin films must also be conducting in the surface plane at the centimetre scale (from the tip to the electrical contact). This is achieved by realizing films of 100 nm thickness, and by paying a particular attention to the cooling rate to avoid the formation of fractures in the film.

Table 1. Summary of the RMS roughness data for the gold samples.

Temperature (°C)	Evaporation rate (Å s^{-1})	RMS (nm)
410	2	2.7
460	0.5	4.5
460	2	1.75
460	5	5
535	2	33.7

We have investigated the influence of evaporation parameters (substrate temperature and evaporation rate) on gold film morphology. The AFM characterizations have always been carried out on several areas of the samples. The reliability of our procedure and of our measurements has been carefully verified.

A heating of the substrate during evaporation is necessary to obtain epitaxial growth. At temperatures lower than 300 °C [8,10], films consist of small grains (typical size lower than 200 nm). As we require atomically flat gold terraces larger than the typical domain size of SAMs, such films are unsatisfactory for our purpose. For temperatures above 540 °C, films consist of large grains [4,11]. Their height fluctuations are of the order of magnitude of the film thickness.

We will show that intermediate temperatures are suitable. Therefore, we investigate the morphology of the films prepared in the 410–535 °C temperature range.

We present 100 nm thin gold films elaborated at three different temperatures: 410, 460 and 535 °C, for three evaporation rates: 0.5, 2 and 5 Å s^{-1}. It is noteworthy that 0.5 Å s^{-1} is the lowest stable evaporation rate we can obtain with our electron gun. Figure 1 shows typical 20 micron wide AFM pictures of such films. The influence of substrate temperature on the morphology can be summarized as follows: the higher the temperature, the larger the typical grain size. The evaporation rate has also an influence on the morphology, but it is not obvious to extract a general behaviour. Roughly, the higher the evaporation rate, the smaller the typical grain size. In addition, the mean roughness of the films is also an important parameter. In Table 1 we have summarized the RMS (root mean square in nm) found on the gold films described above.

For our purpose, it is of prime importance to reach a good compromise between grain size (flat Au terraces of interest must be easy to find within a 1 micron frame) and roughness (to be able to perform STM experiments). By combining the results shown in Figure 1 and Table 1, this compromise occurs for an evaporation rate of 2 Å s^{-1} and a substrate temperature of 460 °C (centre image in Fig. 1).

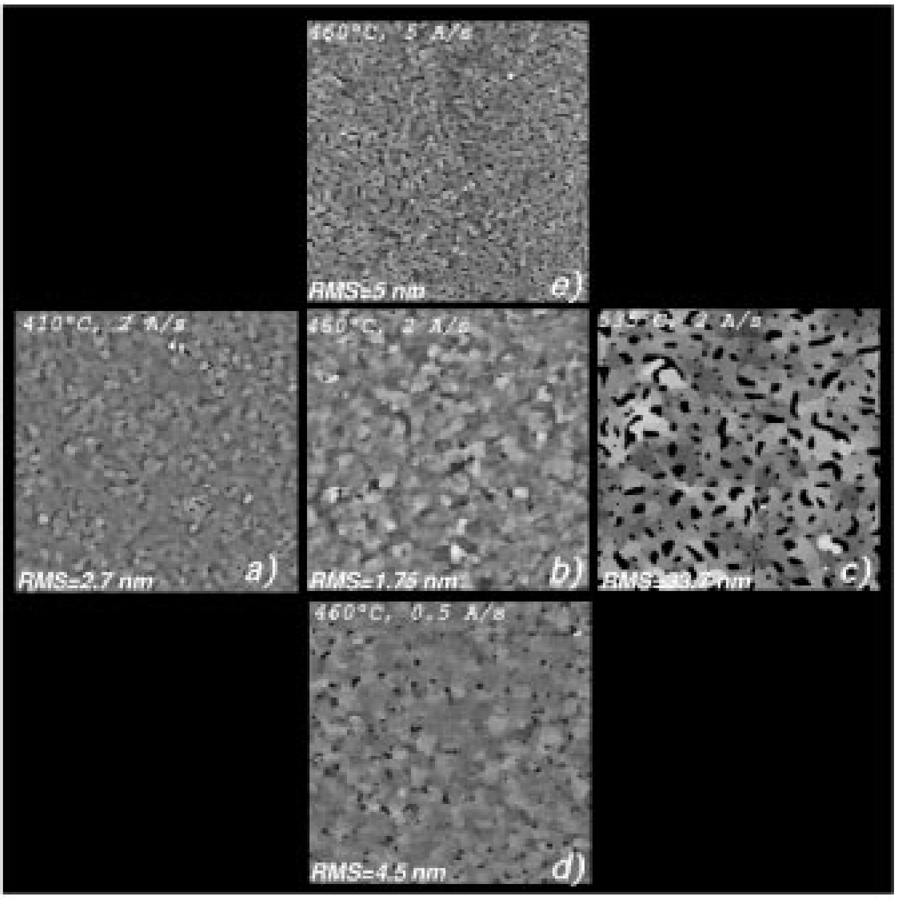

Fig. 1. AFM pictures (20.4 μm × 20.4 μm) of gold films elaborated at three different temperatures: 410 (a, z scale: 10 nm), 460 (b, z scale: 10 nm) and 535 (c, z scale: 75 nm) °C with an evaporation rate of 2 Å s^{-1}, and at three different evaporation rates: 0.5 (d, z scale: 20 nm), 2 (b) and 5 (e, z scale: 20 nm) Å s^{-1} at 460 °C. RMS roughness in nm are given for each sample.

The typical grain size is one micron, with Au(111) terraces larger than 100 nm, as can be seen on the STM picture in Figure 2. Although the film obtained at 535 °C consists of larger grains (typical grain size > 1 micron), they are however separated by holes whose depth corresponds to the film thickness. This is in good agreement with a previous study in the same temperature range [11]. This is incompatible with molecular resolution STM experiments. Therefore, films prepared with an evaporation rate of 2 Å s^{-1} onto a mica substrate maintained at 460 °C are selected for the SPM study of decanethiol self-assembled monolayers.

3.2 SPM studies of decanethiol SAMs on Au(111)

SAMs of alcanethiols have been widely studied using various techniques [12], but their observation in direct space is unrivaled for obtaining information on the quality of the films. For this, STM is the most powerful technique, which allows observation of such systems down to molecular resolution [1,13–16].

The main difficulty is the insulating nature of the decanethiol molecules which are composed of saturated carbon chains [14]. Indeed, the STM technique images the gold substrate through an insulator of about 1 nm thickness. The tunnel resistance must be then chosen

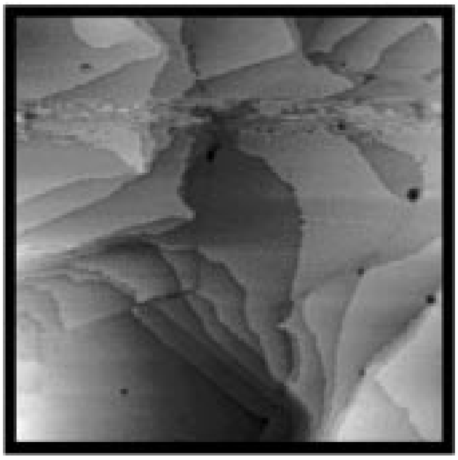

Fig. 2. STM picture (500 nm × 500 nm, bias −1 V, tunnelling current 30 pA, z scale: 5 nm) of a bare gold film elaborated at 460 °C, with an evaporation rate of 2 Å s^{-1}.

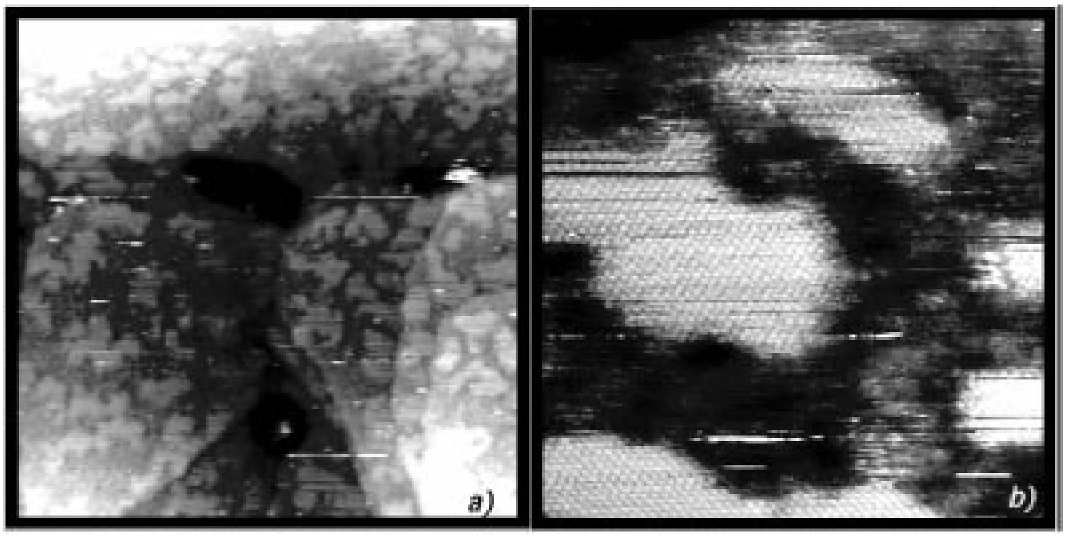

Fig. 3. (a) STM topographic picture (256 nm × 256 nm, bias −1 V, tunnelling current 2 pA, z scale: 2.5 nm) of a decanethiol film grafted on gold, after 1 s of immersion. The surface is fully covered by the molecules, but exhibit lighter areas which can be attributed in picture b (25 nm × 25 nm, bias −1 V, tunnelling current 2 pA, z scale: 1 nm) to ordered domains of molecules separated by unordered areas.

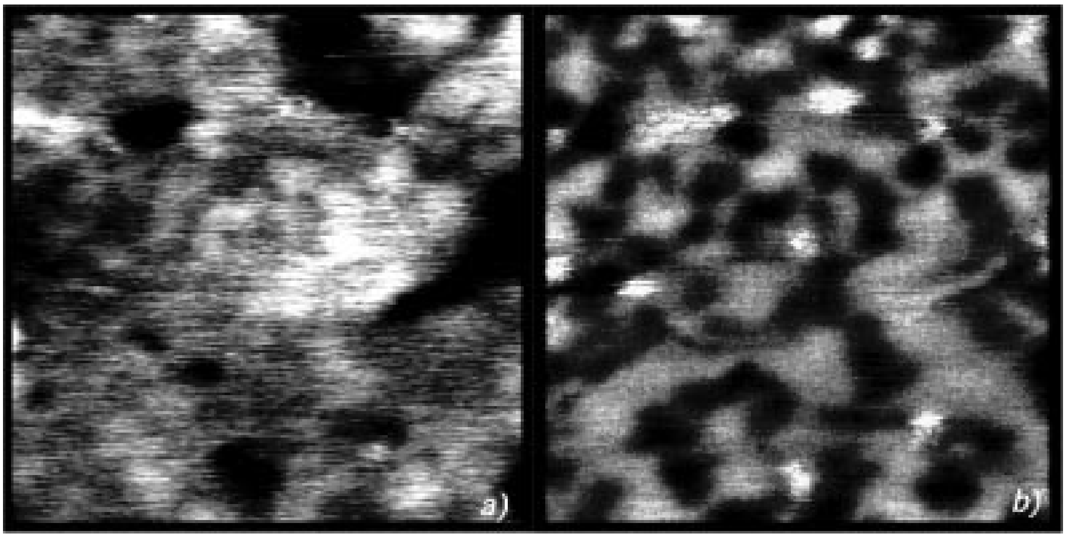

Fig. 4. (a) AFM topographic picture (256 nm × 256 nm, contact mode, z scale: 2.5 nm) of the sample of Figure 3. (b) AFM friction picture (256 nm × 256 nm, contact mode, z scale 0.1 V) recorded at the same time. Ordered domains are lightly contrasted in the topographic picture, but appear as low friction areas in the friction picture.

high enough (typically in the $T\Omega$ range [1]) to keep the tip farther from the Au surface than the length of the decanethiol chains. When working in air, the tip maximum bias cannot exceed 1 V, and therefore the regulation tunnel current has to be set in the range of a few pA.

3.2.1 First stages of the organization process

We first present results for gold samples immersed for a few seconds in the decanethiol solutions. Such films reveal an incomplete structure, as seen in Figure 3. The 256 nm wide STM picture (a), shows a surface fully covered by the molecules, but exhibiting some brighter areas. On the 25 nm wide STM picture (b), these brighter areas correspond to ordered domains. In such domains, a Fourier-transform analysis gives a typical distance between the molecules of 0.5 nm, in good agreement with the literature [1]. Darker areas are attributed to unordered molecules grafted to the substrate, indeed both bright and dark areas exhibit $I(V)$ (tunnel current *vs.* bias voltage) spectra drastically different from a bare gold surface (data not shown). These data are confirmed by AFM pictures recorded in contact mode on the same sample. Figure 4 shows 256 nm wide topographic (a) and friction (b) pictures recorded simultaneously. The friction picture shown here is the result of the subtraction of two friction pictures recorded on two opposite scan directions, in order

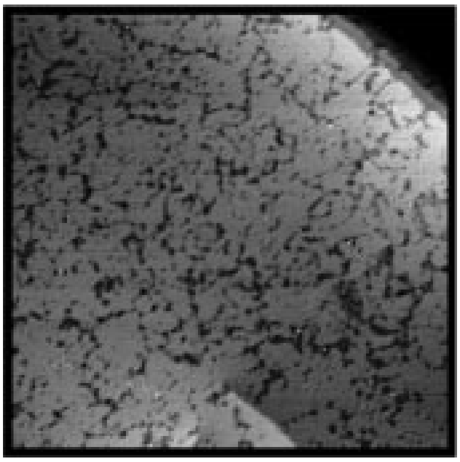

Fig. 5. STM picture (256 nm × 256 nm, bias −1 V, tunnelling current 2 pA, z scale: 5 nm) of a decanethiol film grafted on gold.

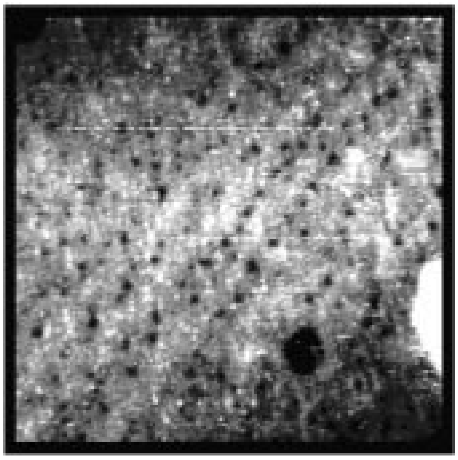

Fig. 6. STM picture (128 nm × 128 nm, bias −1 V, tunnelling current 2 pA, z scale: 5 nm) of a decanethiol film elaborated on gold.

to show information only related to friction [17]. Indeed, friction force and consequently the friction signal depends on the sliding direction. Therefore, by subtracting two friction pictures recorded in two opposite scan directions, the friction signal is emphasized, while the topographic signal is minimized. On the topographic picture the ordered domains are lightly contrasted, but appear as low friction areas on the friction picture. This observation is consistent with the dissipative origin of the friction force. Molecules in ordered domains are densely packed, and have fewer degrees of freedom than in unordered areas, leading to a lower friction signal [18]. It is noteworthy that such contrast is not observed on samples immersed for longer duration (for instance two hours). These results are consistent with previous STM studies of the first stage of alcanethiol deposited in UHV [19] or in liquid [20]. An *in situ* AFM study of octadecanethiol in 2-butanol led to the same conclusions, and to a kinetic model of the SAMs formation [21]. In this earlier study, the authors observed the formation of isolated ordered domains after ten minutes of immersion, compared to a few seconds in our case. This difference can be partially accounted for by the nature of the solvents used. In our case, we use dichloromethane in contrast to the 2-butanol used by the authors of reference [21]. Since dichloromethane is less polar than butanol, the interaction of the thiol group with the solvent is lower. Therefore a higher absorption rate can be expected using dichloromethane [12].

3.2.2 Structure of decanethiol films

The results presented hereafter correspond to gold films immersed in decanethiol solutions for two hours or more. Such films do not exhibit any friction contrast unlike the previous case. Figure 5 shows a 256 nm wide STM topographic picture of a decanethiol film on gold. The black depressions, which are one gold layer deep (2.35 Å), are attributed to chemical etching of gold by decanethiols [22]. STM studies have attributed these lacunar gold areas to the ejection of gold atoms during relaxation of the surface due to thiol absorption [1,19]. These gold vacancies are expected to preferentially grow on the elbow of the "herringbones" of the $23 \times \sqrt{3}$ native reconstruction of Au(111), because gold atoms are more reactive in those sites. Indeed, preferential absorption in those sites is already reported during metal deposition on gold [23,24].

We evidence the preferential growth of the vacancies on the elbows of the herringbones in Figure 6. Indeed we clearly see that gold vacancies are aligned with a typical distance between them of 7 nm, in good agreement with the distance between the elbows of the herringbones in the $23 \times \sqrt{3}$ native reconstruction of Au(111).

Figure 7 shows a 50 nm wide (a, current mode) and a 25 nm wide (b, topographic mode) STM picture of decanethiol SAM on gold at a molecular resolution. In Figure 7, we observe that the film is composed of ordered domains, separated by lines of defects or unordered areas. On this picture we also see that the typical domain size is in the 10 to 20 nm range, *i.e.* much smaller than the gold terraces size. The topographic picture (Fig. 7b) is recorded on one ordered domain and shows that the molecules are packed on the gold surface following a hexagonal compact lattice. We measure a periodicity of 0.5 nm, in good agreement with the literature [1], which corresponds to the $\sqrt{3} \times \sqrt{3}$ reconstruction of the Au(111) surface.

4 Conclusion

We have proposed a detailed and reliable procedure for obtaining gold films suitable for SPM studies by evaporation of gold on mica substrates. We have studied the influence of some evaporation parameters on the morphology of the gold films, by means of a large-scale AFM characterization.

These substrates have been used for the study of decanethiol self-assembled monolayers on gold. Low current

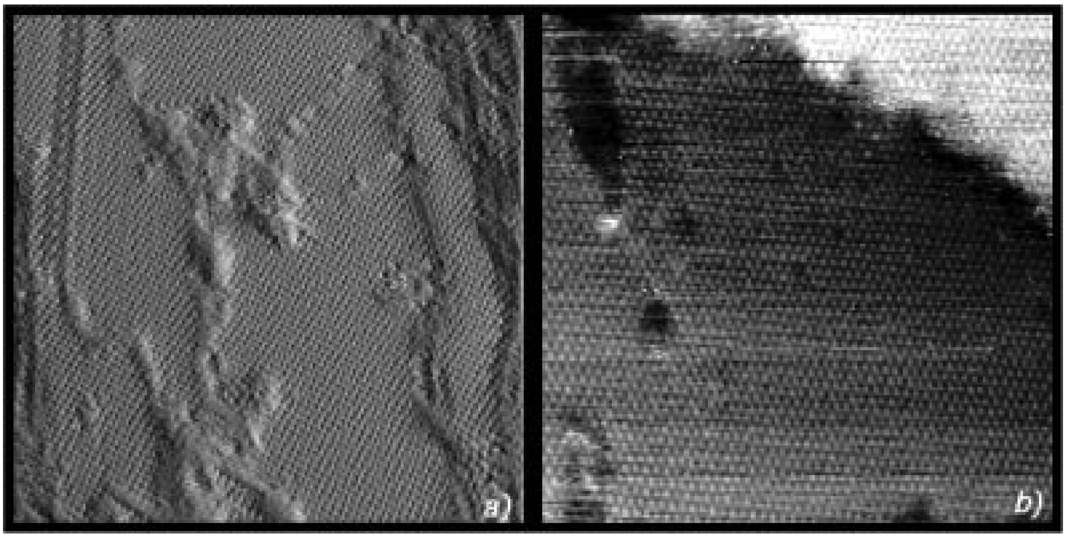

Fig. 7. (a) Current STM picture (50 nm × 50 nm, bias −1 V, tunnelling current 2 pA, z scale: 2 pa) of a decanethiol film grafted on gold. (b) Topographic STM picture (25 nm × 25 nm, bias −1 V, tunnelling current 2 pA, z scale: 1 nm) showing the hexagonal compact packing of decanethiol on gold.

STM in air allows the observation of such films down to molecular resolution. The molecules are ordered following the $\sqrt{3} \times \sqrt{3}$ reconstruction of the Au(111) surface.

We have also studied the first stages of the organization process. In this case, the surface is covered by ordered domains of decanethiol molecules, separated by unordered areas. Both STM and friction AFM allow the different areas on the surface to be distinguished.

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