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Local Probe Investigation of Self-Assembled Monolayers

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ABSTRACT. Characteristic depressions with a diameter of 3 - 7 nm and a depth of 0.2 - 1.0 nm are found in scanning tunneling microscopy (STM) images of self-assembled monolayers (SAM) made from linear alkylmercaptanes on gold (111). High-resolution constant-current images and current response to vertical modulation of the probe (dI/dz) show periodic structures with a molecular spacing that can be correlated with the sulfur $\sqrt{3} \times \sqrt{3}$ addlattice. Deformation-free topographies of SAMs can be extracted with a deconvolution method when force and force gradient are measured on a constant-current STM contour. Results obtained with a combined STM/scanning force microscope on SAMs show that the characteristic depression pattern found with an STM is an electronic effect. The ratio of current versus the generated third harmonic signal in a scanning surface harmonic microscope changes little in the depressions, suggesting that there the electron transfer mechanism is the same as on the flat part of the monolayer. Depressions in STM images are due to a decrease in molecular density of the monolayer that causes a local reduction of the electron conductance.

1. Introduction

The modification of solid surfaces by spontaneously self-assembling monolayers is of theoretical importance since it provides a model system for the study of mechanical and electronic properties of molecules, and is of technical importance for the fabrication of biosensors, transducers and patternable materials [1]. Self-assembled monolayers (SAM) can be formed from linear alkylmercaptanes with different chain lengths or different surface functional groups [2]. This has triggered an increasing interest in the short-range order within these monolayers and led to several scanning tunneling microscopy (STM) studies [3-5]. These studies all revealed flat surfaces with randomly distributed depressions which were explained by holes in the monolayer [5], mismatch between substrate and molecular spacing [3], or gold erosion. The interpretation of STM images on soft materials with large vertical dimension in terms of a conduction mechanisms and elastic effects is not straightforward [6]. For a better understanding of these phenomena it is important to perform combinations of simultaneous measurements like STM and scanning force microscopy (SFM) [7], or STM and third-harmonic generation (scanning surface harmonic microscopy, SSHM) [8-10].

Molecular dynamic and Monte Carlo calculations have been carried out on monolayers chosen to represent SAMs formed by adsorption of 16-mercaptohexadecane ($HS(CH_2)_{15}CH_3$) [11] and SAMs formed by adsorption of 1,11-mercaptoundecanol [12] on gold (111). Monte Carlo calculations on monolayers with no functional groups at the surface revealed areas with

preferentially aligned and tilted molecules as well as regions with larger disorder due to gauche conformations [11]. Molecular dynamic calculations performed on monolayers with hydroxyl functional groups at the surface showed additional features due to hydrogen bonding [12]. Monte Carlo calculations of the mechanical relaxation of SAMs showed an elastic response when the monolayer is compressed by less than 25% of its original length. Compression led to substantial but reversible changes in the conformations of the molecules [11].

To provide a basis for the comparison of experimental data with Monte Carlo calculations we have carried out high-resolution STM studies on SAMs formed by adsorption of 1,11-mercaptoundecanol. Studies with STM [13], combined STM/SFM [14], and STM with higher harmonic generation at microwave frequency [15] allowed the separation of topographic, mechanic and electronic contributions in the respective datasets.

2. Results

SAMs assembled from a solution of 0.2 mM 1,11-mercaptoundecanol ($HS\text{-}(CH_2)_{11}\text{-}OH$) in ethanol on gold (111) [13] show a smooth surface with randomly distributed depressions with diameters and depths of 3 to 7 nm and 0.2 to 1 nm, respectively. Figure 1a shows a constant-current STM image with a size of 5×5 nm of the monolayer surface and a part of a depression to the lower right. The pattern detected on the SAM surface can be attributed to rows of molecules with all-trans conformation attached to sulfur atoms in the characteristic $\sqrt{3} \times \sqrt{3}$ addlattice. Lines are formed from molecules with the same tilt and azimuth angle, and have a separation of 0.43 nm (A), which corresponds to half of the next-nearest neighbor spacing on the sulfur addlattice [13]. On the simultaneously recorded dI/dz signal (Fig. 1b) the features of the topographic image are still faintly visible but lines with a separation of 1.1 nm (B) become predominant. The lines in Fig. 1b are rotated by 20° with respect to those in Fig. 1a. The black spots (*) visible along the lines form rhombohedral patterns with those from neighboring lines. In the depression, the periodic structures disappear, and there is no significant change in dI/dz signal level.

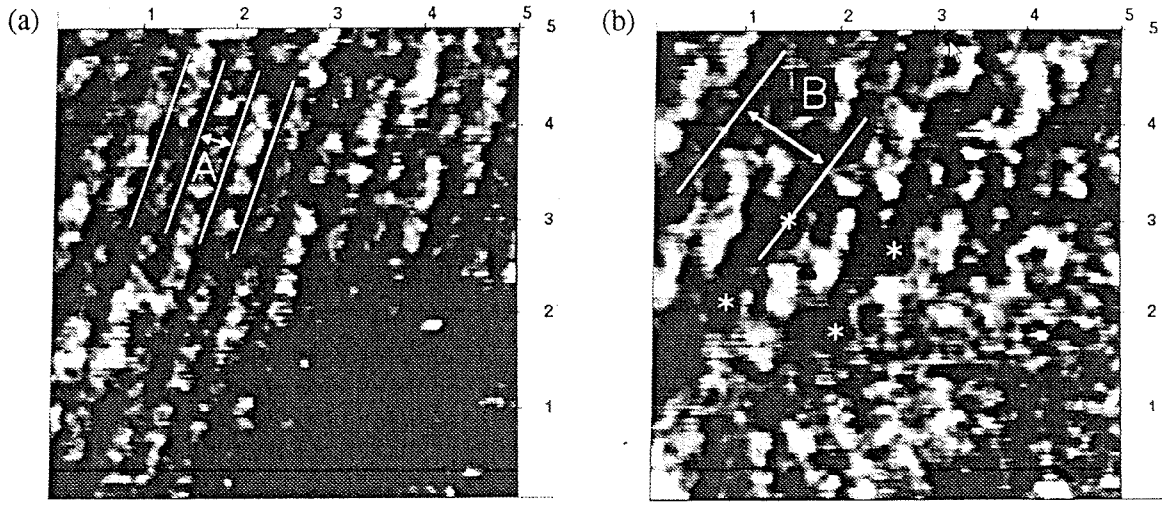

Fig. 1: Surface of a SAM of 1,11-mercaptoundecanol on gold (111). (a) Constant-current image with a vertical range of 1 nm showing lines (A) of molecules separated by 0.41 nm. Imaging conditions: $V_t = 300$ pA and $V_{dc} = 0.3$ V, tip positive. (b) Simultaneously recorded current response to gap width modulation (dI/dz); the line spacing (B) is 1.1 nm and the angle between A and B is 20°.

SAMs adsorbed from mixtures of alkyl molecules with perfluoro molecules have been found to separate into domains with different surface properties [13]. d*I*/d*z* signals on the alkyl domains showed striations with similar line separations (0.7 nm) as those on the surfaces of simulated monolayers of 16-mercaptohexadecane [11].

A microfabricated cantilever with integrated tip was coated with gold and used as a local probe that can measure forces (*f*) in constant-current mode. In addition, a gap modulation technique was used to measure compliance (d*f*/d*z*). By using a small tunneling current as feedback signal, it is possible to reduce the force without losing lateral resolution. Due to capillary forces, the measured force is attractive on the SAMs. Although this attractive force is not local, the lateral variation of the measured force is as local as the constant-current topography. Thus, we assume that the measured force is a sum of the nonlocal attractive force and smaller local repulsive force, and that the attractive force can be treated as a constant offset.

The constant-current contour image (Fig. 2a) shows several monoatomic terraces on the gold (111) surface which are visible through the monolayer of 1,11-mercaptoundecanol as well as depressions with an average size of 3 nm and a depth of 0.3 nm. The repulsive force is larger in the depressions, and in areas with increased depression density in the constant-

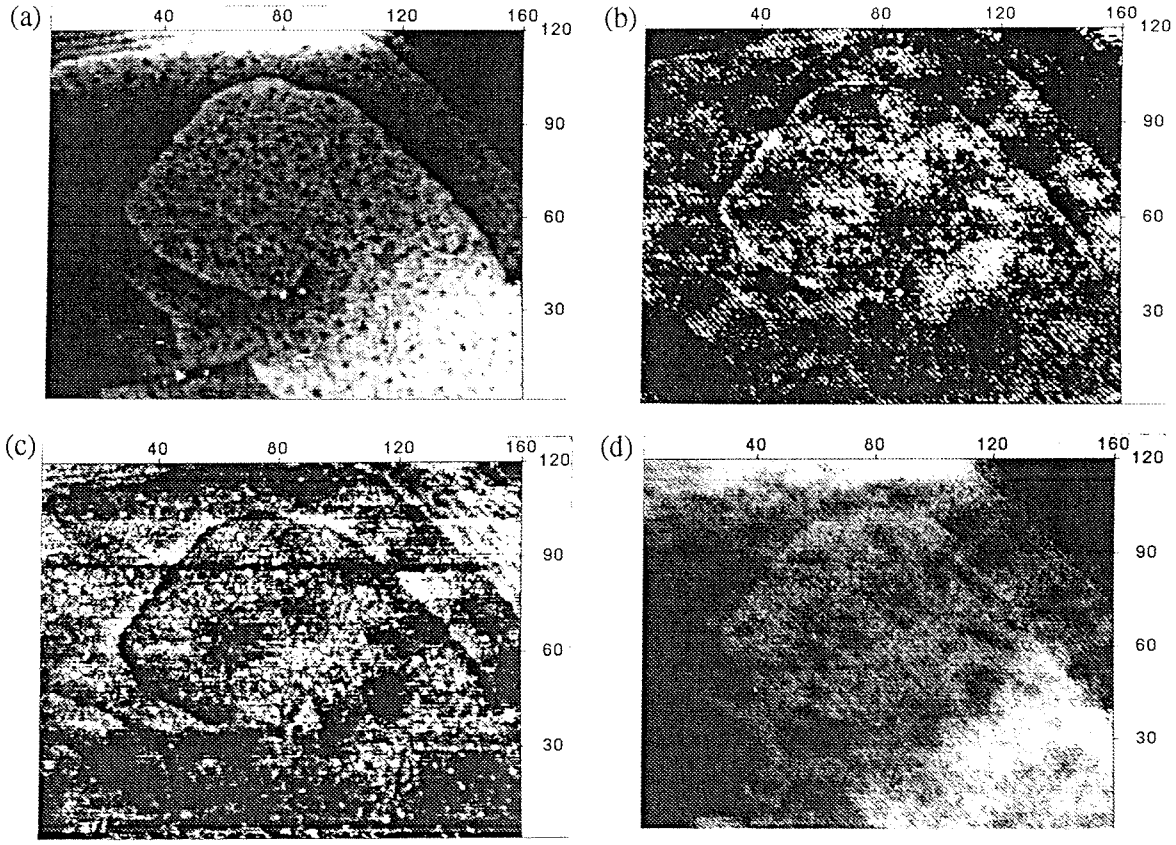

Fig. 2: Surface of the same SAM as in Fig. 1 imaged with the combined STM/SFM. (a) Constant-current contour with a vertical range of 2 nm. Imaging conditions: $I_t = 100$ pA and $V_{dc} = 0.5$ V, sample positive. (b) Force map with a range from 2.9×10^{-7} n to 3.2×10^{-7} N. (c) Compliance with a range from 5 to 20 N/m. (d) Deformation-free topography with a range of 2 nm calculated using simultaneously measured force and compliance.

current contour the repulsive force is smaller than on the rest of the surface (Fig. 2b). A similar contrast is found in the compliance image, where the compliance is larger on the depressions and on the areas with an increased depression density compared to the areas with low depression density (Fig. 2c). The compliance image is proportional to the elasticity of the SAM and hence can be used together with the repulsive force to calculate the deformation-free topography of the monolayer [14]. Applying the deconvolution method to this dataset results in the deformation-free topography (Fig. 2d) where the depressions have disappeared. The resulting surface shows gold terraces with the same height as those in Fig. 1. Within the terraces, the surface shows features with dimensions of about 20 nm which can be correlated with areas of higher and lower depression density.

Microwave fields applied between an STM tip and the sample generate higher harmonics due to the nonlinearities of the gap and/or molecules in the gap. Third harmonic (TH) signals could be detected or used as a feedback signal by including the tip and sample of an STM in a microwave resonant cavity [15]. Since the pure gold surfaces show a very weak TH signal when investigated with a gold tip [8], we can attribute the measured TH signal on the SAM-covered surface to the adsorbed layer and/or the interface.

Figure 3a is a constant TH image of the same SAM as in Fig. 1. Despite the large average dc current of 20 nA, the depressions are well resolved and have a similar size (3 nm) and depth (1 nm) as those obtained in constant-current mode. On the depressions the simultaneously measured dc current changes little (Fig. 3b). The close relation between tunneling current and TH generation on the SAM suggests that the higher harmonic current component originates from nonlinear *I-V* characteristics and that the tip radiates the generated higher harmonic signal into the cavity. Protrusions on SAMs cause large changes in local nonlinearity and thus give rise to changes in the ratio between current and TH signal generation. Gap resistance modulations due to dipole moment-induced oscillations of molecules in domain walls cause an enhancement of the TH signal on mixed SAMs with perfluoro molecules [15].

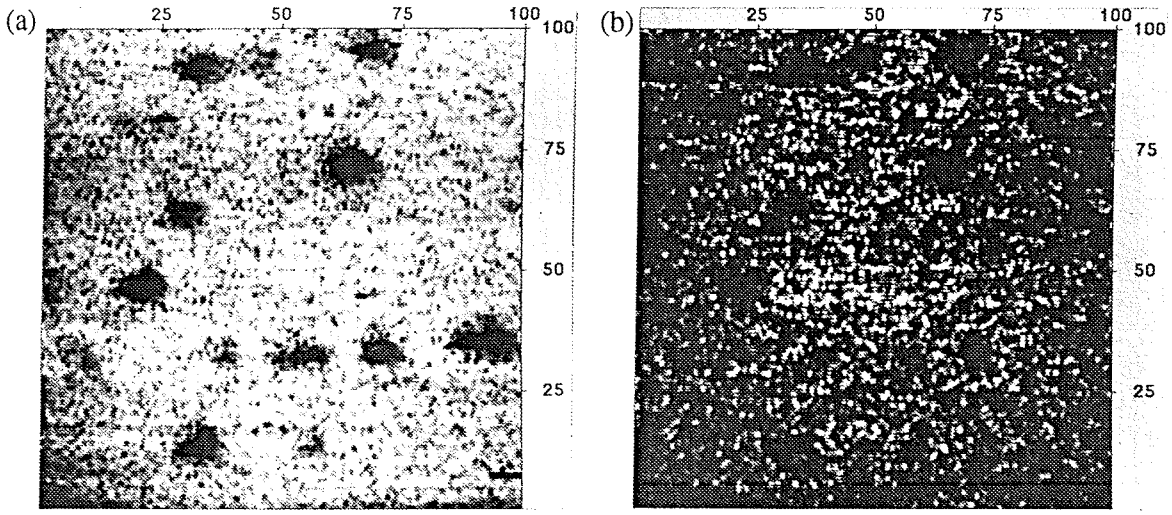

Fig. 3: Surface of the same SAM as in Fig. 1 imaged with the combined STM/SSHM. Imaging conditions: $V_{ac} = 1.3$ V, TH = − 134 dBm (4×10^{-17} W), $V_{dc} = 0.1$ V, sample positive. (a) Constant TH image showing depressions with a depth of 0.5 to 1 nm. (b) Simultaneously recorded current image with an average current of 20 nA and a range of 20 nA.

3. Discussion and Conclusion

High-resolution images on the surface of SAMs made from 1,11-mercaptoundecanol are readily achieved with STM in contrast to images on SAMs made from unfunctionalized alkylmercaptanes. We attribute this finding to the increased stability of the surface due to hydrogen bonding between adjacent molecules. The different spacing of the pattern found in the d*I*/d*z* image may represent a reconstruction of the molecules via hydrogen bonds, which connect several molecules and make them rigid. This reconstruction seems to change only the elastic properties and not the electronic conduction, and hence it is apparent in the d*I*/d*z* image and not in the topography. The surface of SAMs made from unfunctionalized alkylmercaptanes are more stable when they are adsorbed from mixtures with perfluorinated mercaptanes. The increased stability in these monolayers seems to be due to the compensation of the mismatch between the spacing of the sulfurs and the area requirement of the molecular tails. Domains of alkylmercaptanes in mixed SAMs show surface periodicities as expected from Monte Carlo calculations.

The lack of surface reconstruction in the depressions indicates that the molecular packing is not tight in these areas. In fact, force and system compliance are higher in the depressions of constant-current contours. In the force-free topographies the depressions have disappeared which proves that they are due to electronic effects that reduce the conductivity and cause the local probe to press onto the surface. The force seems to be small enough so that the film is not destroyed in this area which is in accordance with Monte Carlo calculations of mechanical relaxation of SAMs.

The STM/TH generation shows that the nonlinearity does not change on the depressions, which strongly suggests that the electron transport is essentially the same as on the flat part of the SAM. Assuming that the electronic conductivity depends on the density of the molecules in the monolayer, and also that the electron transport mechanism does not depend on a small change in the density, the depression observed by STM can be explained by a decrease in molecular density.

Combinations of STM with gap modulation, SFM, and TH generation were used to separate local electronic and elastic properties of the SAMs from the topography. Our results show that depressions are caused by a decrease in the molecular density of the monolayer, which locally reduces the electron conductance. Patterns in constant-current contours and additional features in the d*I*/d*z* response can be correlated with the sulfur reconstruction, as expected for chains in all-trans conformation. Hydrogen bonding between functional groups affects both elastic properties and surface reconstruction of the monolayer.

Acknowledgments

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