Damping in Dynamic Force Microscopy: The Role of Functionalized Groups

Damping in Dynamic Force Microscopy: The Role of Functionalized Groups. As a relatively new scanning probe technique, Dynamic Force Microscopy [1] has proved to be a powerful tool, allowing for imaging the topography of a sample surface with true atomic resolution. Besides topographic imaging, the simultaneously recorded damping signal is related to non-conservative interaction between tip and sample. For a molecular system, we show the tip-induced switching of the functionalized groups of the organic molecule leading to an enhanced damping signal.

Dynamic Force Microscopy

Dynamic Force Microscopy (DFM) is a scanning probe technique using an oscillating tip to measure the interaction between this tip and a sample. By scanning the sample and applying a distance control maintaining a constant interaction, its topography is represented. In this way, true atomic resolution can be achieved [2]. In most experimental setups, the oscillation of the tip is realized by attaching it to a micro fabricated silicon cantilever beam which is excited by a dithering piezoelectric element. One type of DFM is frequency modulation atomic force microscopy; this technique is mostly used for measurements in ultra-high vacuum (UVH) and was used for the experiments reported in this article. In this mode of operation, the oscillation amplitude is kept constant by adjusting the excitation amplitude of the dither piezo. The forces between tip and sample cause a shift of the original resonance frequency of the cantilever beam. By adjusting the distance between tip and sample, a constant frequency shift is maintained while scanning the sample. On the other hand, the amplitude control loop reveals further information beyond topography: The energy that is necessary to keep the amplitude constant equals the energy that is dissipated by means of non-conservative interaction (‘damping’) between tip and sample. While the influence of forces on the frequency shift and hence the topographic imaging is well understood also in theory [3], damping mechanisms have been debated for quite a long time. Of those mechanisms, the so-called adhesion hysteresis is now the established theory.
A representation of this process is shown in fig.1: When the tip approaches the sample during an oscillation cycle, conformational changes within the tip-sample system, e.g., a chemical bonding between tip and sample, may occur at a critical tip-sample distance $z_1$. A breaking of this chemical bond at a different distance $z_2$ causes a hysteresis of the force between tip and sample, leading to an energy dissipation given by the area between the approach and retraction curves in the force-vs-distance graph [4]. In a recent experiment, the damping for a reconstructed Germanium surface was measured, a corresponding adhesion hysteresis could be confirmed by ab initio simulations of force-distance curves [5].

**Organic Molecules: PTCDA on Ag(111)**

Studies of structural and electronic properties of organic molecules on various surfaces are an important and still growing field in surface physics and chemistry, especially with respect to future applications in molecular electronics. Within this field, DFM studies allow for the imaging of molecules on all types of surfaces (the more common technique of scanning tunnelling microscopy (STM) is restricted to conducting surfaces); high resolution imaging is nowadays a standard technique [6]. The motivation of the experiments presented in this article was to reveal information beyond topographic imaging from the damping signal. It was presumed that the functionalized groups of organic molecules play an important role for the damping, as they should provide a channel for adhesion hysteresis processes as found on the atomic scale in experiment and theory [5].

As a model system for this study, DFM experiments have been performed for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on (111)-orientated silver single crystal surfaces. This system is very popular in basic research, a large number of general concepts in molecular electronics have been studied and analyzed for PTCDA on Ag(111) [7,8]. Figure 2 shows a sketch of the molecule and its ordered herringbone-like structure on Ag(111). Note that the molecule is flat in
the gas phase, exhibiting a D2h symmetry. However, when adsorbed on the Ag surface, a deformation of the functional groups occurs due to a chemical bonding of the carboxylic oxygen atoms to the surface [9].

All experiments have been performed in UHV, using a commercially available microscope (Omicron AFM/STM). Clean surfaces have been produced by several cycles of Ar+ sputtering and thermal annealing of a Ag(111) single crystal, PTCDA molecules have been evaporated onto the surface from a home-built crucible. For the measurements, PPP-NCL type cantilevers (Nanosensors) have been used with typical resonance frequencies of 160 kHz, spring constants of 40 N/m, quality factors of 40000 in UHV and amplitudes of 20 nm. For the frequency shift, various set points have been used for imaging.

**Experimental Results**

When evaporated onto a clean Ag(111) surface, PTCDA molecules form rather large, compact islands. Figure 3(a) shows such an island at a molecular coverage of about 0.3 monolayers. The edges of the islands are fuzzy due to mobile molecules; however, in the middle of an island, images with molecular resolution can easily be achieved, as shown in figure 3(b). Single molecules can be distinguished; one can see the rectangular unit cell as well as bright and dim rows of molecules due to the inequivalent binding sites of the two molecules within a unit cell.

The appearance of the molecules in DFM topography images depends very strongly on the microscopic shape of the tip apex. For different tips, a large variety of molecular appearances can occur. The tip shape also determines whether there is a non-conservative interaction between the tip and the molecules, i.e., whether or not there is a contrast in the damping channel. This influence of the tip has been studied in a recent publication [5]. In figure 4, two extreme cases are shown. Figure 4(a) shows brilliant topographic imaging; the orientation of the PTCDA molecules is represented very clearly, and even sub-molecular contrast is visible. On the other hand, for this image, the damping signal showed no contrast at all. For figure 4(b), the experimental findings were quite different: The image represents the damping signal, showing a clear contrast. In this case, the contrast in topography was very poor. The arrangement of the molecules was determined by taking several images for different set points of the frequency shift. The location and orientation of the molecules was found as indicated in figure 5. For the figure, the signal-to-noise ratio of the raw data has been improved by means of unit cell averaging. One can see two maxima per molecule in the damping signal which are located at the short ends of the molecule, i.e., at the functionalized groups. Two line profiles along the long axis of the molecules show the amount of dissipated energy per oscillation
cycle of the tip: At the maxima, 1.5 electron volts (eV) are dissipated, energy in the order of magnitude of a chemical bond.

**Discussion**

The contrast in the damping signal showing enhanced energy dissipation at the functional groups can be explained by an adhesion hysteresis mechanism. As mentioned above, the carboxylic oxygens of each PTCDA molecule are bent to the Ag(111) surface, forming chemical bonds in addition to the main π bonding of the perylene core. The bonds of the carboxylic oxygens being quite soft, they can easily be broken when a tip approaches. We assume that a temporary bond to the tip is formed which breaks when the tip is retracted again during an oscillation cycle (see fig. 5). This tip-induced switching of the functionalized groups is more probable when the lower turning point of the tip is above the short ends of the molecules, leading to an enhanced damping signal at these sites.

The proposed adhesion hysteresis mechanism is supported both by experimental and theoretical findings. A hysteresis as proposed here was found in recent low-temperature STM experiments [10]: When an STM tip is approached to a carboxylic oxygen atom of PTCDA on Ag(111) in a very controlled way, a sudden rise of the tunnelling conductance is observed: A chemical bond between tip and molecule is formed at a critical distance. When the tip is retracted, the conductance drops to the former value at a different distance. This hysteresis in tunnelling conductance is likely to appear as a similar hysteresis of the tip-sample force, causing energy dissipation as observed in our experiments.

Further evidence is found in ab initio simulations of a tip approach and retraction above two different sites on a PTCDA molecule adsorbed on Ag(111): Above the perylene core of the molecule, no adhesion hysteresis can be seen, above the functionalized groups, the hysteresis in the tip-sample force amounts to about 2 eV, which is in good agreement with the experimental results.

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**References**


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