Analysis of Diamondoids on metallic surfaces with Scanning Probe Microscopy

Thesis

in Physics

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1 Introduction

In 1965, Gordon Moore published an article which stated that the number of transistors in an integrated circuit doubles every year (Moore [1965]). This statement with a slightly adapted time span between 18 and 24 months has since been known as Moore's law. For the last several decades it has proven to be highly accurate (L.S. [2015]). The methods applied today for keeping this speed of miniaturization have reached a level of complexity which at least puts a question mark to the future reliability of Moore's law (Courtland [2016]). The top-down approach to building these increasingly smaller circuits, although constantly improved, will soon reach its physical boundaries, and therefore the need for new ways of production is growing. One promising approach for the realization of future electronics is the construction via the application of self-assembled structures. The creation of these structures requires a sophisticated understanding of the way molecules assemble on surfaces and of how self-assembly can be directed into the desired state.

Beside the semiconductor industry, other sectors are facing similar challenges. The increasing numbers of patients diagnosed with cancer (Weir et al. [2015]) or Alzheimer's disease (Prince et al. [2015]) over the last years put pressure on pharmaceutical research to develop new drugs antagonizing this trend. The search for new, more effective, and less risky agents for the treatment of those diseases is pushing the pharmaceutical industry towards an extensive investigation on molecules in the nanoscopic regime.

The above mentioned examples are just a small fragment of a large field of research in which new developments depend on the success of the understanding and the precise controlling of processes on the nanoscopic scale. Newly discovered materials with outstanding physical and chemical properties like carbon nano tubes (Iijima [1991]), graphene (Lee et al. [2008]), or diamondoids (Schwertfeger et al. [2008]) belong to a group of materials scientists are focussing on to meet those challenges.

To solve these issues in semiconductor, pharmaceutical, and other industrial sectors, instruments are required which have the ability to operate in nanoscopic dimensions. Microscopic techniques like Scanning Tunnelling Microscopy (STM) or Atomic Force Microscopy (AFM) are important elements of this group. For the first time in history, they have opened the door to a new way of production (Desai et al. [2016]; Fuechsle et al. [2012]) because they have the ability to construct devices on the atomic scale. Although the direct assembly of circuits or new molecules with this technique, a bottom-up approach, is far too inefficient to reach application, other ways seem more promising. The combination of known methods with the new tools' power is a promising field of research. Self-assembled structures are a candidate for the construction of new "nano-devices" irrespective of their field of application. Scanning probe techniques allow to observe, manipulate, or initiate reactions on surfaces, directing the way to more complex nano-structures.

In this work, we based the determination of self-assembled monolayers on Scanning Probe Microscopy (SPM). We focused on two different aspects of SPM. The first aspect concerns the instrumentation applied in this research. With the development of new techniques and their ongoing application and improvement, all parameters needed for the exact deduction of results inevitably have to be determined. We carried out measurements and simulations which helped to clarify the spring constant for the common qPlus sensor. This sensor is the new standard tool for high-precision scanning probe techniques. The second focus in this work is the structure of self-assembled monolayers. With the application of high resolution, submolecular scanning probe techniques, we studied the island structure of two diamondoids (namely [121]Tetramantane] and [123]Tetramantane), as well as their exact orientations, with a never before seen distinction between similar molecules.

Closing the gap between science fiction and reality is the ultimate aim of fundamental research, and our ambition is to deliver one small piece towards closing this gap and to help solve some of the problems mentioned above.

2 Experimental Methods

In the following chapter, a short introduction to the theory of the experimental methods applied in this thesis is given. The chapter is based on the books of Adam Foster [2006], Chen [1993], Bhushan [2004], and Israelachvili [2011b], which can be recommended for further reading.

The Scanning Tunnelling Microscope (STM) and the Atomic Force Microscope (AFM) belong to the group of Scanning Probe Microscopes (SPM). This group is characterized by acquiring data line-by-line with a probe. The final image is created by stringing the single lines to a 2D image. Beside STM and AFM, other SPM techniques have been developed and successfully applied. They differ in the way the probe and sample interact and in how information is gathered. The interactions which have been utilized for SPM range from electrical, optical, mechanical to even chemical interactions. Since only STM and AFM were applied in this work, the theory in this chapter focuses on them.

2.1 The Scanning Tunneling Microscope

The invention of the Scanning Tunneling Microscope (STM) in 1983 by Binnig and Rohrer (Binnig et al. [1982]; Binnig and Rohrer [1982]) marked the beginning of a new technological era. The STM was the first microscope that allowed direct atomic resolution combined with atomic manipulation (Crommie et al. [1995]) and opened the door to the often cited "room at the bottom" by Richard Feynman (Feynman [1992]). The two fundamental parts the microscope is constructed of are the sample and a sharp probe. The information is gathered through the measurement of a current, therefore probe and sample have to be electrically conductive. For the measurement, the probe is positioned closely to the surface without direct contact. In classical physics, the only possibility for measuring a current is via the application of high voltages to cause electrical field emission. In quantum mechanics a second path - the tunnelling effect - exists, which allows particles to travel between probe and sample even if only a small voltage is applied. In 1897, Robert Williams Wood discovered the tunnelling effect in electron field emission (Wood [1897]) but was not able

to explain his observations. The first explanation of this effect was achieved by Friedrich Hund in 1926/27 (Hund [1927a, b, c]) and delivered the theoretical background for the STM. The tunnelling effect describes the probability of a wave passing a barrier which is higher than the wave's amplitude. In classical physics, there is no possibility of waves passing a potential barrier higher than the amplitude of the wave. This rule loses its validity in quantum mechanics. The tunnelling effect allows the wave to be found in the space behind the barrier. Since every particle has a wave character, a non-vanishing probability exists which allows an electron, or any other particle, to pass a barrier higher than its own energy.

The probability of an electron with the mass m and the energy E to be found behind the barrier can be described in 1D with (Schiff [1968]):

$$T(E) = exp\left[-2\int_{0}^{s}\sqrt{\frac{2m}{\hbar^{2}}(V(z) - E)}\right]dz = exp\left[-2\sqrt{\frac{2m}{\hbar^{2}}(V_{0} - E)}d\right]$$
(2.1)

In this equation, V_0 is the potential barrier height and d its diameter. This equation is derived using the Wentzel-Kramers-Brillouin approximation and shows the exponential correlation between the tunnelling probability and the thickness of the tunnelling barrier. According to Chen [1993], the current between tip and sample can be approximated from the tunnelling probability, with ϕ as the work function for the electron leaving the tip:

$$I \propto \exp\left[-A\sqrt{\phi d}\right] \tag{2.2}$$

The STM utilizes this exponential relation between the tunnelling probability and the thickness of the barrier d. In the case of the microscope, the barrier is given by the distance between the sample and the tip. When the tip has approached the sample closely enough, the topography of the sample can be measured by applying a bias to the tip or the sample. The high sensitivity of the STM for any topographical change is a result of the tunnelling current's exponential dependency.

There are two basic modes in which the STM can be operated. In the first one, a constant bias is applied to the tip or the sample. The tip then scans line-wise over the surface and records the measured current. The topographical information in this mode is derived from the change in current. This mode is called "constant height mode" because the tip is moved over the sample without adjusting the distance to the sample. Although it has the advantage of being a very fast measuring mode as no feedback has to be given to the tip, it has the obvious disadvantage of neglecting larger topographical variations. A depression in the scan can cause the current to vanish, and a protrusion or tilt can result in a tip crash which in many cases destroys the tip. The constant height mode is hence only used if the sample surface is known to be very flat. These complications led to the development of the second mode called "constant current mode" which works with a feedback loop connected to the tunnelling current. The current is kept constant by retracting the tip from the surface and thus increasing the distance if the measured current increases, or approaching the surface if the current decreases. The topographic information is gathered via the voltage applied to the piezo element that controls the tip's z-movement. The integration of a feedback loop slows the measurement down, as the system needs time to adapt to the registered current. On the upside, if the scan speed is chosen properly, this feedback loop prevents the tip from being destroyed. It is certainly used in most cases if the sample system is unknown.

Although it often appears like a true topographical scan, the STM image contains more than the topographical information alone. It is a convolution between the real topography and the tunnelling current from the same "Local Density Of States" (LDOS) of the tip into the sample or vice versa. An analytical approach to calculating the tunnelling current between tip and sample is presented by Chen [1993]. Chen applied and modified Bardeen's perturbation approach for tunnelling currents to the microscopic set-up of the STM (Bardeen [1961]). The modifications take the influence of the sample's wave function on the tip's wave function into account and have been tested successfully on the quantum mechanical hydrogen molecule. The corrections to the wave functions can either be determined by experiments or calculated with other tools afterwards. The current is then given by:

$$I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} [f(E_F - eV + \epsilon) - f(E_f + \epsilon)] \times \rho_S(E_F - eV + \epsilon)\rho_T(E_F + \epsilon)|M|^2 d\epsilon \quad (2.3)$$

In this equation, f(E) is the Fermi distribution function, ρ_S and ρ_T are the DOS of the sample and tip, respectively. M as Bardeen's matrix element can be interpreted as the energy lowering between the tip and the sample due to the interaction between them. For the case of a low k_BT , the function can be simplified to:

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_S(E_F - eV + \epsilon) \rho_T(E_F + \epsilon) |M|^2 d\epsilon$$
(2.4)

This equation shows that, at temperatures at which our measurements were carried out, the tunnelling current is a convolution between the LDOS of the tip, and the sample, and the matrix element M.

2.2 The Atomic Force Microscope

The second Scanning Probe Microscopy method applied in this work is the Atomic Force Microscope (AFM). Developed in 1986 by Gert Binnig, who also invented the STM, Calvin Quate, and Christoph Gerber, the AFM was the next revolution in Scanning Probe Microscopy. It measures surface forces instead of the tunnelling current as in the STM (Binnig et al. [1986]). The need for the development of the AFM is the STM's limitation to electrically conducting surfaces. The break-through in overcoming this handicap was the AFM's utilization of surface forces characteristic of all matter, independent of their conductivity.

At the time of the invention of the AFM, it by far did not reach the resolution of the STM. It took until the year 1995 for the AFM to catch up by achieving atomic resolution (Giessibl [1995]; Kitamura and Iwatsuki [1995]). This marked a major step revealing the real potential AFM could deliver in studying non-conducting surfaces. The year 2009 marks the last resolution breakthrough when Gross et al. [2009] discovered the possibility of imaging bonds between atoms within organic molecules. In the following chapter, the theoretical background behind the AFM and the surface forces is summarized.

2.2.1 Surface Forces

As mentioned above, the AFM uses surface forces to image the sample. They can be roughly divided into long range forces and short range forces. Both forces together add up to a potential which can be described by a Lennard-Jones-Potential shown in Fig. 2.1. The Lennard-Jones Potential is characterized by a long attractive potential (highlighted in green), which increases up to a turning point. From this point on, the repulsive forces (highlighted in red) increase much faster than the attractive forces, compensating the attractive force at a certain point and finally rising up to infinity for zero distance.



Distance Tip - Sample

Fig. 2.1: Scheme of a Lennard-Jones Potential. The attractive force increases when the tip approaches the surface up to the turning point, at which the repulsive Pauli interaction takes over and leads to an overall repulsive interaction.

2.2.1.1 Long Range Forces

The longest ranging force which is of matter in the nanoscopic regime is the electrostatic force. It consists of two different aspects: electric charges and the work functions of the tip and the sample. The first part is caused by a difference in the electric charge between the surface and the probe. Depending on the charges, it can be either attractive or repulsive. The interaction can be described by assuming the probe and sample together form a capacitor with capacitance C(z), voltage ΔV , ϵ_0 as the vacuum permittivity, and z as the distance between tip and sample resulting in the force (Olsson et al. [1998]):

$$F_e st(z, \Delta V) = -\frac{1}{2} \frac{dC}{dz} \cdot \Delta V^2$$
(2.5)

If in the next step the tip is assumed to be spherical with radius R, the electrostatic force can be written according to Olsson et al. [1998] as:

$$F_e st \approx -\pi \epsilon_0 \frac{R}{z} \Delta V^2 \tag{2.6}$$

As this force is of significant size and interferes negatively with the measurement, it is necessary to reduce the electrostatic part as much as possible. But beside the influence of the charges on the tip and on the sample, the work functions of both also contribute to it. If the work function is taken into consideration, it is possible to reduce ΔV to zero and thus eliminate the electrostatic influence completely.

The van-der-Waals force is the other significant long range force concerning AFM (Israelachvili [2011a]). It is an many body electron correlation which is caused by spontaneously introduced dipole-dipole interactions between probe atoms and sample atoms. The so-called London Dispersion Interaction represents the most important attractive part of the van-der-Waals force. If the non-polar atoms of the probe approach the nonpolar atoms of the sample, they are able to induce a dipole momentum into each other. Its origin is of quantum mechanical nature but can be explained using a half-classical approach for reasons of simplicity. The electrons surrounding the nucleus are constantly in motion which, if observed on a sufficiently large time scale, gives the impression of an electrically neutral atom. If now the time scale is narrowed down, it is plausible that the electron is located at a certain spot within the probability density of its wave function. This is quantum-mechanically correct, as the probability wave function tells that the electron's charge is not smeared out around the nucleus, but rather gives the probability of measuring it at a certain location. This inequality in charge distribution is sufficiently high, so that, if the distance between two atoms is low enough, this dipole can interact with the atoms close to it. If the probe is now close to the surface, a second dipole is induced as the positive charge attracts the electron of the sample atom. This interaction only exists for a very short time and is relatively weak compared to other interactions like ionic bonding. However, due to the amount of atoms within the probe and the sample, it results in a measurable effect. The potential of the van-der-Waals force is given by:

$$V_{vdW} = \frac{C}{z^6} \tag{2.7}$$

C is the coefficient in the atomic exchange potential in this equation. The interacting force between probe and surface can be calculated by integrating over the probe and the sample volume, this results in:

$$F_{vdW}(z) = -\frac{A \cdot r}{6z^2} \tag{2.8}$$

In this case, r is the probe radius and z the probe sample distance. A in this equation is called the Hamaker constant. This constant depends on the material and the density of

the two spheres and represents the strength of the van-der-Waals force.

As the exact solution for the Schrödinger equation for a system of this extent is far too complex, Hamaker [1937] derived an approximation for the interaction between two spheres with radii R_1 and R_2 and the distance z:

$$F_{vdW}(z) = -\frac{AR_1R_2}{(R_1 + R_2)6r^2}$$
(2.9)

Beside London dispersion, the van-der-Waals force can have two other causes. If both probe and sample have permanent dipoles, the electromagnetic interaction between them is called Keesom force (Israelachvili [2011a]). The other stems from a permanent dipole within the probe or the sample which induces a dipole in the sample or the probe, respectively. This force is called Debye-force. The Keesom and Debye forces only have relevance if the system already contains a dipole and can therefore be ignored in many cases.

2.2.1.2 Short Range Forces

In addition to the long range forces, short range forces are of significant influence in AFM measurements. The most important of those are the Pauli repulsion and chemical interactions or capillary forces (Pavliček et al. [2013]). The latter aren't elaborated in the following. The Pauli repulsion is the result of the quantum-mechanical Pauli exclusion principle. This principle states that a fermion, in the case of the AFM the electron, is not allowed to occupy the same quantum state as another fermion in the same local region. To fulfil the Pauli exclusion principle, the electron orbitals are bent or the electrons are lifted into a higher unoccupied state which results in a strong repulsive force. The Pauli repulsion has a distance dependence of the r^{-12} magnitude.

2.3 AFM Sensors

With the fundamental knowledge of the surface forces, the working principle of the AFM can now be understood better. The probe of the AFM is an ideally atomic sharp tip, which is similar to the STM. In most cases, this tip is a silicon tip attached to a silicon beam. This tip configuration has the advantage of a very precise, simple, and reliable signal detection mechanism. While a potential current or voltage can be detected by attaching the tip electrically conductive, a possible influence of the surface forces results in

a deflection of the silicon beam. Due to this effect, these probes are called "cantilever". The deflection can be detected via the light pointer principle. A laser beam is directed onto the back side of the cantilever and, every time the cantilever is moved out of its resting position, the beam gets deflected under a different angle, which is then detected by a position-sensitive photo diode. The surface force, to which the cantilever is exposed, can be calculated by Hooke's law $F = k \cdot \Delta z$.

Beside the cantilever, which is the most common sensor type, some alternative designs have been developed. One of them is the qPlus Sensor (Giessibl [1997]). It consists of a quartz single crystal tuning fork, which is glued to a macor holder. A commercially available tuning fork, designed for the use in quartz watches, has two different vacuumdeposited gold electrodes on each prong. One of these gold electrodes can be used to measure the deflection of the prong; the piezoelectric effect of the quartz single crystal causes a small voltage if the prong is bent. The other gold electrode is used to measure and/or apply voltages to the tip, which is achieved by glueing the tip to the side on one prong with an electrical conducting epoxy. A very common material for the tip is tungsten, as it offers the possibility of simultaneously measuring the tunnelling signal and the deflection signal. The other advantage lies in the preparation. A very sharp tip for AFM and STM measurements can be created if a tungsten wire is attached to the prong and afterwards cut to the desired length via electrochemical etching (Falter et al. [2013]). This allows the tip preparation to happen the moment it is needed, and thereby prevents the tip from becoming blunt by prolonged oxidation in the atmosphere. The qPlus sensor will be explained in detail in chapter 3.

2.3.1 Static Operation Mode

The first developed AFM mode of operation is the simplest one - the static operation mode without any feedback loop. Static, in this case, means that the tip is moved along the surface with no oscillation applied to the cantilever. This mode can either be applied if the cantilever is above or in contact with the surface. In both cases, the deflection is caused by the surface forces. If the cantilever is above the surface, it is attracted, if it is in contact with the sample, it is repulsed. These variations have in common that they allow a very fast surface scan, but they also have significant disadvantages.

If the cantilever is brought into contact with the sample and "scratches" over it during the measurement, the tip wears off instantaneously. This results in an increasingly larger tip



Fig. 2.2: Area of highest resolution can not be reached in the static mode. The cantilever jumps into contact as soon as the attractive forces become too strong. When retracting the cantilever, it snaps off because the attractive forces decrease and the retractive force of the lever exceeds them.

interacting with the sample, which makes high resolution images impossible. The larger contact area of the tip does not allow to detect the smaller changes in the sample topography. To avoid the wear, the tip can be moved above the surface without any contact. With a sufficiently large distance, the tip only experiences long range forces. The drawback in this case is - again - a low resolution. It is caused by the larger number of atoms participating in the long range interactions. Smaller changes in topography can not be resolved any more, as the interacting force between the tip and the sample is summed over a large volume. Within this large volume, minor topographical changes have no effect at all.

The obvious solution to this issue would be the approach of the tip to a distance at which the short range forces become dominant. However, this mode of operation can not be applied. The reason is found in the unequal growth of the attractive force and the cantilever's antagonizing elastic force. The result of this imbalance is that, at a certain point, the attractive force pulls the cantilever directly into contact. The "snap to contact" is the reason why the second static mode does not allow to retrieve scans with atomic resolution. This can be understood by taking a look at the Lennard-Jones potential in Fig. 2.2. The area suited best for high resolution scans is that of the highest slope in the attractive potential, as with a minimal change in distance the resulting force increases the most. But due to the "snap to contact", this area is excluded from the static operation mode. Due to the same effect, retracting the cantilever to reach the desired position is not possible. The snap off causes the cantilever to jump from the point of the strongest attractive force into the area of only small attractive interaction. This dilemma required the development of other modes of operation for the AFM.

2.3.2 Dynamic Operation Mode

The large disadvantage of the static mode, the non-accessibility of the regime with the highest resolution, paved the way for the development of a new, dynamic mode of operation. In this mode, the cantilever is constantly oscillated by a shaker piezo near its resonance frequency. The interaction between the tip and the sample can be measured by keeping the oscillation frequency constant and measuring the change in amplitude - the amplitude modulation mode (AM-mode). The other possibility is keeping the amplitude at a constant level and measuring the frequency shift, the frequency modulation mode (FM-mode). Although both modes are suitable for atomic resolution, the AM-mode is seldom applied. The reason lies in the measurement time under Ultra High Vacuum (UHV) conditions. The time response of the cantilever is $\tau = 2Q/\omega_0$ with Q as the Quality factor of the oscillation and ω_0 as the resonance frequency (Albrecht et al. [1991]). This leads to extremely high measurement times and thus limits the application of the AM-mode under UHV conditions.

To describe the motion of the cantilever quantitatively, the model of a damped driven harmonic oscillator in 1D can be applied:

$$m^* \ddot{z}(t) = -\alpha \dot{z} - kz(t) - kz_d(t)$$
 (2.10)

with the driving amplitude of

$$z_d = A_d \cdot \cos(2\pi f_d t) \tag{2.11}$$

The interaction between the cantilever and the sample surface can be described by an adapted spring constant $k' = k + k_{ts} = k - \frac{dF_{ts}}{dz}$ with k as the cantilever spring constant and F_{ts} as the surface sample force (Giessibl [1997]). With this adapted spring constant, the resonance frequency of the system is slightly shifted by Δf from f_0 . If the amplitude of the cantilever is small compared to the surface-sample distance, the frequency shift is roughly proportional to the force gradient:

$$\frac{\Delta f}{f_0} \approx -\frac{1}{2k} \frac{dF}{dz} \tag{2.12}$$

For larger amplitudes, the following expression was derived (Giessibl [1997]):

$$\Delta f \approx \frac{f_0^2}{A k} \int_{0}^{1/f_0} F_{ts}[z(t), \dot{z}(t)] \cos(2\pi f_0 t) dt \qquad (2.13)$$

This requires the excitation to be constant and the tip-sample forces to be much smaller than the Ak. Finally, this can be derived to:

$$\frac{\Delta f}{f_0} = -\frac{1}{\pi Ak} \int_{-1}^{1} F_{ts} \left(D + A(1+u) \frac{u}{\sqrt{1-u^2}} \right) du$$
(2.14)

This equation is often applied in AFM measurements that want to explore the interacting force between the tip and the sample. To achieve this Eq. 2.14 needs to be inverted. Sader and Jarvis [2004] developed an approximative approach which has proven to be highly accurate and is therefore applied in most cases. By applying Laplace transformation and modified Bessel function, the force can be calculated with:

$$F(z) = \frac{2k}{f_0} \int_{z}^{\infty} \left(\left[1 + \frac{\sqrt{A}}{8\sqrt{\pi(t-z)}} \right] \Delta f(t) - \frac{A^{3/2}}{\sqrt{2(t-z)}} \frac{\partial [\Delta f(t)]}{\partial t} \right) dt$$
(2.15)

with k as the spring constant and f_0 as the resonance frequency. In chapter 3, the spring constant which is required for calculating the absolute force in this formula, is analysed for the qPlus sensor type.

2.4 Submolecular Resolution With AFM

In the last years the resolution achievable with Atomic Force Microscopy and Scanning Tunnelling Microscopy has made a large leap. The history of STM and AFM has some significant milestones concerning the resolution. Since some of them were already mentioned in chapter 2.2.1, the most important steps are listed here in short:

- invention of the STM in 1982 (Binnig et al. [1982]; Binnig and Rohrer [1982])
- atomic resolution with an STM in 1983 (Binnig et al. [1983])
- invention of the AFM in 1986 (Binnig et al. [1986])
- first atomic structure with an AFM in 1990 (Meyer and Amer [1990])

- first real atomic resolution with AFM in 1995 (Giessibl [1995]; Kitamura and Iwatsuki [1995])
- first submolecular resolution with STM in 2008 (Temirov et al. [2008])
- first submolecular resolution with AFM in 2009 (Gross et al. [2009])

In subsequent chapters, we focus on the submolecular resolution with the AFM.



Fig. 2.3: First submolecular AFM images published by Gross et al. [2009]. A shows a model of a pentacene molecule, B is a constant current STM scan of the same molecule. Images C and D show submolecular resolution on pentacene molecules.

The beginning of submolecular resolution can be marked in 2009 (Gross et al. [2009]) with the submolecular resolution of a pentacene molecule shown in Fig. 2.3. High resolution was made possible by the functionalisation of the tungsten tip from a qPlus sensor. As elaborated in chapter 2.2.1 the highest resolution can only be achieved if the Pauli repulsion becomes the dominant force in the tip-sample interaction. Tungsten tips do not allow the resolution for the imaging of submolecular features as a large number of tip atoms contributes to the overall resolution. The sum of all atoms causes the van-der-Waals interaction to remain the dominant force until the tip jumps into contact with the surface.

To reach a higher resolution, the share of the van-der-Waals force needs to be kept to a minimum. This was achieved in the work by Gross et al. (2009). By applying a mixture of high currents and voltages as described in Bartels et al. [1997], they were able to pick up a CO molecule and perform AFM scans subsequently. The CO molecule turns during the adsorption to the tip, resulting in the oxygen atom to be the closest atom to the sample. After the pick up they deactivated the feedback loop and scanned in close proximity to the

sample. With this set-up the managed to resolve the hexagonal structure of the pentacene molecule (Gross et al. [2009]). This method has since been applied in various publications affirming the possibilities of this tool.

The contrast mechanism with the CO tip has mainly been assigned to the Pauli repulsion of the CO's oxygen electron orbital and the orbitals of the scanned sample (Gross et al. [2009]; Moll et al. [2010]). It has been explained by the increasing Pauli interaction caused by the dangling bond of the unsaturated oxygen atom targeted towards the sample overlapping with the orbitals of the sample's atoms. This thin extension of the tungsten tip allows to reduce the number of atoms which contribute to the van-Waals-interaction and thus increase the share of the short range forces in the overall interaction. In addition, Ellner et al. [2016] showed that beside the Pauli repulsion the contrast can also be attributed to short ranging electrostatic interactions. They observed a vacancy on a NaCI lattice which appeared as a protrusion if the tip-sample distance was larger than 500 pm. The vacancy was only correctly imaged as a depression for smaller tip-sample distances. The explanation for this effect is the negative charge distribution at the front of the CO tip. It is caused by the strong electronegativity of the oxygen atom at the tip apex. Thus, when approaching the Cl vacancy position a repulsive force is measured before the Pauli repulsion takes over and dominates the contrast mechanism.

Other results showed, that the images with this outstanding resolution of the functionalised tip cannot always be interpreted in a straightforward manner, even if the electrostatic interaction is taken into consideration. Some publications have shown that a CO tip sometimes displays bond-like features at locations at which a bond can be excluded with certainty (Pavliček et al. [2013]). In this publication they observed a bond-like feature on dibenzo[a,h]thianthrene (DBTH) molecules. These molecules are non planar and exist in two different configurations which resemble a V in one configuration and an upside down V in the other configuration. CO functionalised tips measure a ridge between the two uppermost atoms, which in this case are sulfur. This ridge, although imaged, does not exist but is an artefact caused by the high electron density between these two sulfur atoms. One other peculiar feature is the ridges of bonds that are sharper imaged than DFT calculations predict. These bond like features and the unexpectedly sharp bond ridges could be explained with a mobile CO molecule at the tip.

The CO molecule is not rigidly attached to the tungsten tip but has the ability to tilt in every direction (Hapala et al. [2014]). The CO molecule was simulated by a movable sphere attached to the tip apex. The overall force was calculated by a composition of three forces. This simulation allowed an explanation of the most important features observed in submolecular AFM publications and furthermore allowed to generate images with high accordance to the experimentally observed images. The simulations showed that the Pauli repulsion is the cause for the moveable sphere to be bent horizontally if the sample is approached too closely. This lateral relaxation results in a frequency shift which gives a similar appearance to that of a real existing bond. It also causes the ridge of a bond to appear much sharper defined than the electron orbitals actually are. With this model, the submolecular images created with a functionalised tip could be reproduced by Hapala et al. not only for CO tips but also for Xe tips.

In the publication by Guo et al. [2015] the high contrast in subTmolecular AFM measurements was compared with ab initio calculations for different samples. Their calculations support the assumption, that the sharp ridges and bond like features measured are partially caused by a tilting CO molecule. They also argue that the short range electrostatic interaction is not only dominating the contrast mechanism for large tip sample distances as shown by Ellner et al. [2016], but is also the dominating interaction in the imaging process during submolecular measurements.

Two other notable effects were observed by Gross et al. [2012]. First they were able to identify the bond order between two carbon atoms within polycyclic hydrocarbons and C60 fullerenes. By studying the contrast in the frequency shift image, they could observe, that a higher bond order results in a larger frequency shift. This was explained by a higher electron density within these bonds. The other important effect was that a higher electron density caused the CO molecule at the tip apex to tilt resulting in a deviation between the measured bond length and the actual length. This is of significant interest if the AFM is applied to determine the bond length in newly discovered compounds.

In conclusion, it can be stated that the submolecular measurements are suitable for determining both: bond lengths and the particular structure of a molecule. In the observation of bonds between single atoms or molecules one has to be cautions when interpreting the results, as the contrast caused by tilt or electrostatic interaction can lead to misguiding interpretations. To reduce the probability of these errors it is necessary to perform some scans at different heights above the sample. The achieved height overview allows to differentiate real bonds, which always appear as lines, from bond like features, which only appear as lines if approached very closely and also excludes an inverted contrast by short range electrostatic interactions.

2.5 The Experimental Set-Up

The experimental set-up applied in this thesis is explained briefly in the following.

The UHV (Ultra High Vacuum) LT (Low Temperature)-STM/AFM is a commercially available system purchased from ScientaOmicron (Taunusstein, Germany). All components for preparing and analysing the samples are under a UHV atmosphere. UHV, which is defined by a base pressure starting from 10^{-9} mbar down to 10^{-12} mbar. A pressure of the lower 10^{-11} mbar regime was achieved during the measurements in this work. The creation of such high vacuum conditions can only be achieved with an elaborated vessel and a system of pumps.



Fig. 2.4: Experimental set-up with the load lock.

Five different pumps are installed in this system.

• The rotary pump is used to pump the chamber from atmospheric pressure down to 10^{-3} mbar. This pump type is the only one installed in our set-up that is able to pump down from atmospheric pressure.

• The turbomolecular pump can be operated from 10^{-2} mbar down to 10^{-10} mbar. It consists of a fast rotating paddle wheel that gives every molecule an impulse out of the chamber. The rotary pump and the turbomolecular pump are used to create the first rough vacuum, since they are able to remove gas molecules out of the chamber.

The other pumps in the system are not suited for this purpose as they belong to the group of entrapment pumps. These pumps do not remove the remaining gas out of the chamber but trap the molecules inside of it. The way the entrapment is done differs for each pump type. As long as the pump is able to trap more molecules than it releases, the result is sinking pressure.

- The ion-getter pump is applied if the pressure drops below 10⁻⁴ mbar and it operates down to 10⁻¹² mbar. It works by ionizing the remaining molecules and accelerating them with an electric field onto a target. In our case, this target is a titanium block. Titanium combines the advantage of being very reactive and binding molecules with a high melting point and a low outgasing rate.
- The titanium sublimation pump works down to pressures of 10^{-12} mbar. It is basically constructed of a titanium rod, which can be resistively heated. The temperature reached by the rod leads to the sublimation of titanium gas. This gaseous titanium instantaneously condensates on the cold chamber walls. Similar to the ion-getter pump, the condensated titanium absorbs gas molecules in the chamber. Depending on the remaining pressure, the time between two sublimation cycles has to be adjusted, because the titanium will be saturated at some point.
- The last pump utilized in our system made it possible to reach pressures of about 10^{-12} mbar. The cryo-pump is not a pump, which has been installed to create a better vacuum, but is a side effect of working at liquid helium temperatures. As a large part of the chamber is cooled down with liquid helium and liquid nitrogen for the measurements, the temperature in this part is extremely low. Liquid helium temperature is sufficiently low to trap nearly all remaining gas molecules. When a molecule hits the cooled areas, it condensates on the wall and can be kept there as long as the temperature is kept low.

The pumps alone do not have the capability of reaching the vacuum within a reasonable amount of time, as a large amount of molecules is adsorbed on the chamber walls and they only desorb very slowly into the chamber. To accelerate this process, a system bakeout is required. For this procedure the chamber is heated up to 120° C and kept there for at least two days. The high temperature increases the gas pressure of the adsorbed molecules which then can be removed by the pumps once they reach the gas phase. The other important result of the bake-out process is the removal of the entrapped molecules in the ion-getter pump's titanium blocks. After two days the system pressure decreases to the lower 10^{-8} mbar range. During cool-down all filaments in the chamber are manually degassed. In the end, the ion-getter pumps are turned on to reach the desired pressure.



Fig. 2.5: The experimental set-up seen from the side. The manipulator on the right is used to transfer the sample from the preparation chamber to the analysis chamber or for molecule evaporations.

The UHV system consists of two major chambers connected by a plate valve shown in Fig. 2.4 and Fig. 2.5. The preparation chamber has a load lock connected to it for inserting all samples and probes into the vacuum vessel. This chamber is named preparation chamber as it has several devices for preparing the sample eg. cleaning, coating etc. The valve between the two chambers prevents a contamination of the second chamber. This is necessary because the preparation chamber is often exposed to higher gas pressures for sputtering or to molecule beams during evaporation. The second chamber is the analysis chamber, which houses the microscope itself (cf. Fig. 2.6). This chamber is designed to keep a sample temperature of 5 K for at least two days and to minimize all vibrations that would disturb the measurement. The cooling of the sample is achieved by a two stage cryostat. The outer containment is filled with liquid nitrogen, the inner with liquid helium. Liquid nitrogen has a much higher thermal capacity than liquid helium, and is therefore well suited to

block the heat flow from the outside to the inner crysotat to which the microscope is connected. To reach the desired temperature of 5 K, it is necessary to additionally block the infra-red radiation from the chamber and the windows. Therefore the AFM is surrounded by a shielding. The outer shield is connected to the liquid nitrogen cryostat and absorbs most heat radiation from the outside. The inner shield is connected to the liquid helium cryostat and blocks the remaining radiation. For mounting a sample or a probe into the chamber, the shielding can be turned open and closed again for the measurement. When the shielding is closed, the movement of the probe can be visually controlled by a camera that observes the AFM from the outside through a set of infra-red blocking windows. The samples and probes are moved with an OMNIAX (VacGen, Taunusstein) manipulator. This manipulator has a heating filament which allows the sample to be heated up to 1400° C, and with the help of a liquid flow cryostat the sample can be cooled down to 25 K.

For the detection of atomic or submolecular structures it is necessary to be able to move with subatomic precision. This is achieved via the use of piezo electric drives connected to high precision voltage controls. By applying a voltage to a piezo electric material the crystal cage structure can be deformed highly controllable, which allows move-



Fig. 2.6: View into the analysis chamber. In the background the AFM itself with the golden tripod and the qPlus sensor can be seen.

ments of the probe in the pm range. For this purpose a special tailored piezo tube for the fine movement. For the coarse approach of the AFM is mounted onto a walker which can travel with a few milimeters per second. The coarse motion of the piezo tube is controlled with a piezo actuator which allows travel range of roughly $1 cm^2$. This is the area which can be used later for the measurement.

For the measurement of small forces (pN) and currents (pA) and (nA), the complete electronic setup must match the requirements. The electronics used for this purpose are high precision amplifiers with a high signal to noise ratio. For the reduction of vibrational noise disturbing the measurement, the system has two damping stages. To reduce noise from the building, the whole system is decoupled with the High Performance Laminar Flow Isolator S-2000 (Irvine, California). The microscope itself is decoupled from the chamber by being held with springs. To reduce the movement of the free microscope, it is slowed down with an eddy current damping.

3 The qPlus Sensor: Performance and Calibration

3.1 Introduction

This chapter is based on the publication of Falter and Stiefermann (Falter et al. [2014]) published in Beilstein Journal of Nanotechnology under public license. The article has been slightly adapted and shortened.

Atomic force microscopy (AFM) allows the imaging of surfaces with true atomic resolution and resolving the intra-molecular structure of molecules (Gross et al. [2009]). Furthermore, the non-contact AFM technique has the capability of quantifying the interaction forces acting between the probing tip and the sample site with atomic precision. Recent achievements of this force spectroscopy method manifest in the identification of the chemical identity of single atoms in an alloy (Sugimoto et al. [2007]) or the measurement of the force applied during the controlled manipulation of molecules or atoms over a surface (Ternes et al. [2008]; Langewisch et al. [2013]). Nc-AFM experiments at the atomic scale usually demand well defined environments, such as ultrahigh vacuum (UHV) and low temperatures (LT). For these conditions, force sensors based on quartz tuning forks in the qPlus-design (Giessibl [2000]) have been proven to routinely provide stable operation and sufficient sensitivity to achieve highest resolution in non-contact-AFM experiments. The AFM we applied in this work as well as many commercially available AFM are using this sensor type.

Common AFM sensors are micro-fabricated from silicon or silicon nitride with an already integrated tip. Their spread in geometric parameters is within a low range and the characterization of their geometric parameters has been presented extensively by theory and experiments (Senden and Ducker [1994]; Sader et al. [1995, 1999]). Quartz tuning fork force sensors in contrast are usually hand-made and, even though they are commercially available, they are far from mass production and therefore exhibit a large spread of geometric parameters. The precise knowledge of the sensor stiffness k_{qPlus} is crucial for quantitative interpretation of force spectroscopy measurements. Early spectroscopy experiments compared relative forces with high accuracy for which the stiffness of the sensor was not needed. Latest measurements of the absolute interaction force impress by their force resolution but suffer from the large error and spread in the determination of the geometric factors of the qPlus sensors. The stiffness of the force sensor is necessary for the transformation from the experimental frequency shift data $\Delta \omega$ to forces. Therefore, a force measurement can only be as precise as the determination of all factors in the force transformation formula Eq.(Giessibl [1997]).

$$\frac{\Delta\omega}{\omega_{res}} = -\frac{1}{\pi a k_{qPlus}} \int_{-1}^{1} F(z+a(1+u)) \frac{u}{\sqrt{1-u^2}} du$$
(3.1)

Inversion of this formula is necessary to calculate force vs. distance curves from the measured frequency shift versus distance data and can be solved by several approaches (Giessibl [1997]; Dürig [1999]; Hölscher et al. [1999]; Sader and Jarvis [2004]) with high accuracy. All of these formulas contain the stiffness of the sensor k_{qPlus} as prefactor and therefore directly suffer from an inaccurate determination of the spring constant.

In this chapter we present a fork sensor in the qPlus design with standard lab equipment. Our results reveal that a large spread of stiffness exists even in a series of commercially sold sensors. This finding underpins the urge of the individual characterization of each sensor. The standard equation to calculate the stiffness from the geometric dimensions is the beam formula. Comparison of our experimental results with the formula show large discrepancies up to a factor 5. In the next step, we used extensive Finite Element Method (FEM) modelling of the precise tuning fork sensor geometry to understand these deviations. The simulations show quantitative agreement with the beam formula if the beam origin is shifted to the position of zero stress onset inside the tuning fork base and if torsional effects are included as well. Comparison with experimental spring constant data still show that the spring constant is overestimated by FEM and beam formula. This effect is attributed to a small but non-negligible angle between the tip wire axis and the surface normal of the tuning fork prong.

3.2 Experiment

The quartz tuning fork, originally used in common wrist watches as frequency normal constitutes the centerpiece of a force sensor in the qPlus design. Fig. 3.1 shows micro-

graphs from Scanning Electron Microscopy (SEM) of a bare tuning fork (typeDS26, Micro Crystal AG, Switzerland). These tuning forks are micro fabricated from piezoelectric quartz which is electrically contacted by gold electrodes placed onto the quartz substrate. The dimensions of the tuning fork can be easily measured by SEM images as labeled in Fig. 3.1a) and b). The tuning fork has an overall length of $l_{TF} = 3548 \ \mu m$ and a width of $w_{TF} = 651.4 \ \mu m$ at the widest point while the substrate has a thickness of $t_{TF} = 120.8 \ \mu m$. Fig. 3.1c) was taken from a derivative of the same type of tuning fork which differs only by some additional grooves at the basis compared to the tuning fork of images a) and b). At this point it should be noted that all experiments and simulations presented in this chapter were carried out for both types (with and without grooves). However, no differences were found in the stiffness of the sensors of the two types, and therefore only one set (without grooves) is presented here. In the qPlus design of ncAFM force sensors, one prong, and the end of the basis is fixed onto a carrier (usually from marcor) with epoxy glue. This type of fixation breaks the original quadrupole design, where both prongs are oscillating around a forceless point that is found within the quartz body between the prongs. A very sharp tip etched from metal wire is attached to the end of the free prong, again with epoxy glue.

Commonly, spring constants between $k_{qPlus} = 1800 \ N/m$ and 2000 N/m are used for the force transformation. These values are estimated from the geometric dimensions of the free prong of the tuning fork and the Young modulus of quartz using the beam formula according to Eq. 3.2.

$$k_{beam} = E_{\text{Quartz}} \frac{w}{4} \left(\frac{t}{\Delta L}\right)^3 \tag{3.2}$$

In this equation, w and t are the width and thickness of the free prong, respectively, and E_{Quartz} is the Young modulus of quartz. Since the tip wire is not necessarily placed at the very end of the prong $\Delta L = L - L_0$ denotes the effective lentgh of the free beam, i.e. the wire position L along the prong with respect to the beam origin L_0 . Comparison with Fig. 3.1 a) shows that a certain ambiguity exists in the position of this beam origin L_0 . At the beam base, the cross-section of the prong broadens before ending in the rigid basis. We here chose the point before the broadening as the zero point L_0 as commonly done in the nc-AFM literature. Inserting our measured values of $\Delta L = 2139 \ \mu m$, $w = 207.3 \ \mu m$ and $t = 120.8 \ \mu m$ into Eq. 3.2 together with the Young modulus of quartz of $E_{\text{Quartz}} = 78.7 \ GPa$ results in a stiffness of the free prong of $k_{qPlus} = 1898.88 \ N/m$. This is within the range of reported spring constant values $k_{qPlus} = 1800 \ N/m$ (Giessibl [2000]) and $k_{qPlus} = 2000 \ N/m$ (Albers et al. [2008]), while the latter was calculated with a different



Fig. 3.1: Determination of the geometric dimensions of a quartz tuning fork (Micro Crystal, type DS26 used for qPlus-force sensors. (a) Sideview of tuning fork made from quartz (b) Topview of tuning fork for measurement of the wafer thickness (c) Sideview of alternative geometric layout of DS26-type tuning fork with groves at the basis (cf. arrows). Images made by Jens Falter.

Young modulus of $E_{\text{Quartz}} = 79.1 \ GPa$ to correct for the non-orthogonal crystallographic cut through the substrate of the tuning forks.

However, all these calculations are barely in agreement with the actual qPlus sensor. The force is applied through a metal wire glued onto the free prong. Therefore, the force application point is defined by the position of the glue point. Since these sensors are handmade it is obvious that this length cannot be regarded as constant for all sensors. The broadening of the beam towards the basis and the unknown Young modulus of the material limit the usage of the beam formula for the description of the tuning fork stiffness. Even influences and therefore spread in the individual stiffness of these sensors have recently been reported (van Vörden et al. [2012]). Possible methods are the determination of the stiffness by adding some mass to the prong and analyzing the change of the dynamic oscillation (Cleveland et al. [1993]) or static deflection (van Vörden et al. [2012]) of the cantilever. Alternatively, the stiffness can be estimated from thermal excitation (Berger et al. [2013]). Here we employed a very simple and easy to implement method to measure the stiffness of the tuning fork sensors only using a micrometer screw and a scale. The setup for such a measurement is shown by the photograph in Fig. 3.2.



Fig. 3.2: Photograph of the experimental setup. Not shown in the picture is the micrometer caliper 1, which pushed or pulled the whole setup towards or from the scale. The Macor body 3, carrying the tuning fork sensor 4 is fixed to the holder 2. The Inlet shows the enlarged aperture of the tuning fork. The tuning fork is glued to a glass substrate, which transferred the force to the scale and delivered the mass needed for the pulling experiments. The setup for this experiment was designed by Jens Falter.

To validate this measurement method we assembled a test sensor similar to the qPlussensor setup. A quartz tuning fork was glued on the identical scheme as in a qPlus sensor onto a Macor body as well as a tungsten wire with a diameter of $d_{W-wire} = 50 \ \mu m$ was glued onto the free prong. This sensor is mounted onto a traverse which can be lowered by a micrometer screw (Mitutoyo, type 110-164) with an accuracy of $\Delta z = 5 \ \mu m$. Below the traverse, a scale is located (KERN & Sohn GmbH, type: KB 120-3) with a mass resolution of $\Delta m = 1$ mg. The stiffness of the sensor can be measured by pushing the sensor onto the scale with the micrometer screw while simultaneously measuring the weight increase on the scale. By lowering the end of the wire into a fresh droplet of Torr Seal epoxy glue, it can be mechanically fixed onto a glass substrate resting on the scale (cf. Fig. 3.2). After the glue is cured out at room temperature, the stiffness can be measured in both directions, pushing (increasing mass on scale) or pulling (decreasing mass on scale). A reference experiment was performed with a bare Marcor carrier (without tuning fork) to measure the stiffness of the experimental setup k_{scale} (mainly the scale compliance), which was $k_{setup} = 5952 N/m$ in our case. The stiffness of the tuning fork can then be evaluated by Eq. 3.3 representing a series of both stiffnesses.

$$k_{tuningfork} = \left(\frac{1}{k_{measurement}} - \frac{1}{k_{setup}}\right)^{-1}$$
(3.3)

With this setup, the stiffness of the bare tuning fork was measured as a function of the position of the force application point, i.e. the tip wire. The diagram in Fig. 3.3 shows linear slopes recorded by pushing along different positions of the tuning fork prong. The position was determined from photographs taken through a stereo microscope during the experiment. The result of the position dependence is then compared with the values predicted by the beam formula (Eq. 3.2) using the effective beam length $\Delta L = L - L_0$ with respect to the force application point L. Table 3.1 lists the measured stiffnesses as well as the values calculated from the beam formula. While for long prongs (large ΔL values), the measurement seems to be roughly within the range of the calculation, for shorter prongs (small ΔL) a drastic discrepancy between the measured stiffness and the calculated value is found (up to a factor 5 of larger, cf. last column).

In fact, a deviation between the experimental tuning fork stiffness and the beam formula is not unexpected. Previous simulations suggest that the zero point has to be chosen differently as commonly done using the beam formula (Simon et al. [2007]). These findings motivated our detailed analysis of the mechanical tuning fork properties by the Finite Element Method (FEM) using the software Comsol Multiphysics (V.41a).



Fig. 3.3: Diagram of a "push" experiment to measure the stiffness of the free prong of a qPlus sensor by the slope of the fit to the data points with an error of approx. 1%. The deflection of the prong starts at position 20μ of the micrometer screw. The spring constant had been calculated in the range of increasing forces. The effective stiffness increases for decreasing effective prong length, i.e., for tip positions located further to the beginning of the prong. The stiffness was calculated from the slope.

Position in μm	Measurement (push exp.) spring const. in N/m	Calculation (beam formula) spring const. in N/m	Measurement Calculation
408	65427	357386	5.46
604	33784	120717	3.53
1085	6315	20576.3	3.25
1630	3088	4986.39	1.61
1653	4135	4719.32	1.93
1994	2000	2690.12	1.80

Table 3.1: Comparison of the measurement of the stiffness with the calculation using the beam formula for the identical position at the prong.

3.3 FEM Simulations

Special care was taken to make the geomtetric model of the qPlus sensor in the FEM software as realistic as possible, including glueing points as well as a metal tip. Also, three samples made from "Torr Seal" in a sample geometry accordant to DIN EN ISO 527 were tested in a tensile test to obtain a realistic value of the Young modulus of the glue for the FEM simulations. Two of the Torr Seal samples were cured at a temperature of $100^{\circ}C$ resulting in $E_{\text{TorrSeal}} = 6500 \ GPa$ and $6000 \ GPa$ respectively. The third sample was cured at room temperature (RT) resulting in a Young modulus for $E_{\text{TorrSeal},RT} = 4000 \ GPa$. As our home build qPlus sensors are cured out in an oven, the value of $E_{\text{TorrSeal}} = 6000 \ GPa$ was used in our FEM simulations for the epoxy glue. The geometry of the simulated model is depicted in Fig. 3.4 in more detail. The sophisticated geometry of different sub-geometries is meshed by tetrahedral elements, which allow a very fine mesh at the boundary lines as well as the boundary areas between the sub-geometries (in particular at the force application point from the wire through the glueing droplet into the free prong).

In the next step, a force was applied through the vertical axis of the wire and the displacement of the free prong was analyzed. Interestingly, a closer look at the stress distribution reveals that the stress is reaching several hundred microns into the basis of the tuning fork. Fig. 3.5 shows the stress contribution within the tuning fork caused by a loading force of $F_{load} = 1 - 100 \ mN$ and resulting in a displacement of the very end of the free prong of $x_{end} = 50 \ \mu m$. Since the tip was attached to the side of the tuning fork as it is also the case in commercial qPlus sensors, the different stress contributions of torsion and normal stress are color coded as the comparative Van Mises stress (VMS). The color code represents stress values from minimal stress of $\sigma_{VMSmin} = 0 \ N/m^2$ (red) to maximum values of $\sigma_{VMSmax} = 2.5 \cdot 10^8 \ N/m^2$ (violet). The stress minimum in the basis is marked by the dashed circle.

This finding suggests that the zero point L_0 , as origin for the length of the cantilever, has to be adjusted when calculating the stiffness with the beam formula. To demonstrate this effect we first plot the stiffness in a diagram using the zero point at the end of the narrow beam, i.e. $L_0 = 0$ as a reference curve. The logarithmic plot shows that the spring constant versus beam length curve (gray curves) does not follow a certain power law, e.g. ΔL^{-3} as expected from Eq. 3.2. For direct comparison we also plotted the results from the beam formula of Eq. 3.2 as a red solid line, thus depicted as a straight line in the logarithmic plot.



Fig. 3.4: Image of the geometric model reflecting the geometry of an actual qPlus sensor. The model includes a tip attached to the free prong with a droplet of epoxy glue. The sophisticated geometry is meshed with tetrahedral elements to better account for the transition between the individual geometry elements. The material properties were taken from literature, as for the Young modulus of the epoxy glue, tensile experiments were carried out to determine a realistic value for the crucial connection of the force application point between the metal tip and the prong.



Fig. 3.5: Van Mises Stress. Analysis of the stress caused by the bending of the free prong. In contrast to the model for the beam formula, where a cantilever is infinitely fixed on one end, the stress in the quartz tuning fork reaches beyond the end of the prong far into the basis of the tuning fork. The origin of the minimal Van Mises stress is indicated by arrows pointing into the dashed circle (see inset).

Motivated by the non negligible stress reaching into the tuning fork basis, the results from the FEM simulation are plotted for different beam origins L_0 reaching into the tuning fork base. The resulting set of curves is plotted in the diagram of Fig. 3.6, where the new effective origin L_0 was adjusted in a range from $-1200 \,\mu m$ to $200 \,\mu m$. Here, in the transition regime between the two extreme L_0 positions, a linear behavior can be identified at an effective origin of $L_0 = 700 \,\mu m$, which is located "inside" the tuning fork's basis with respect to the conventional origin at $L_0 = 0$. For the new origin $L_0 = 700 \,\mu m$ we find quantitative agreement between simulations and beam formula for larger tip wire positions $\Delta L > 1500 \,\mu m$, which is usually the case. Only if the tip wire is closer to the basis, some deviations occur where the beam formula is systematically overestimating the stiffness. Therefore, we conclude that the beam formula can still be used to estimate the tuning fork prong spring constant, if the beam origin is set to the new effective position $L_0 = 700 \,\mu m$ (for the here used tuning forks) and if the tip wire position is more than 1500 μm away from the origin.



Fig. 3.6: Diagram showing the result of the FEM simulation shifted by the origin. While for too large or too small chosen positions of the origin, the curves show a non linear behavior, the ΔL^3 behavior can be identified in the transition/middle for a new origin position of approx. $L_0 = 700 \ \mu m$.

In the next step, we want to investigate the influence of torsional motion of the tuning fork prong, which may also play an important role. While the beam formula only considers normal forces applied orthogonal to the prongs axis, in the qPlus sensor configuration, the wire-tip is attached at the side causing in addition to the bending of the prong also a torque around the beams axis. To evaluate the influence of the torsion, the simulation was repeated with the tip positioned in the center of the prong (indeed some experimentalists attach the wire-tip on the face side of the free prong to avoid torsion during the AFMexperiments). In our FEM simulations the position was chosen such that tip is on top of the prong (TOT), allowing us to vary the position of the force application point, for direct comparison to the results from the so far discussed tip on side (TOS) configuration.



Fig. 3.7: Comparison between tip on side (TOS) and tip on top (TOT) configurations as possible origin of the deviation between FEM simulation and experiment. The deviation was found to be larger than the contribution of torsion in the TOS configuration.

Fig. 3.7 shows the result of the FEM simulation in the two configurations, TOS (blue) and TOT (green). While for large positions, the deviation between the two configurations is negligible, in the regime of small position values, a deviation can be noticed. The contribution caused by the torsion can be calculated analytically by the following relation:

$$\Phi_t = \frac{TL}{GI_T} \tag{3.4}$$

The influence of torsion can be calculated with equation 3.4, in which Φ_t is the angle of twist in radians, L the length at which the force is applied, G the shear momentum,
and I_T the second momentum of area of the prong. To calculate the exact influence of the torsion the overall spring constant, the tuning fork has to be seen as a system of two springs connected in series. The red curve in the diagram shows the result from the simulated TOS-configuration where the effect of the torsion is corrected for with the above equation. The torsion corrected curve coincides well with the curve simulated for the TOS configuration of the qPlus sensor.

These results also demonstrate that torsion has a negligible influence at the end of the prong, as the torsion spring constant is decreasing linearly whereas the deflection spring constant decreases with ΔL^{-3} . Only if the tip is mounted closer to the origin of the tuning fork body, the torsion has an increasing influence on the overall spring constant. This influence results in a smaller increase of the global spring constant as the torsion spring constant is not increasing as fast as the deflection spring constant. This effect is obvious in the area of smaller ΔL -values, in which the TOS curve shows a recognizably lower spring constant, than the TOT-curve.



Fig. 3.8: FEM simulation result displaying the influence of a tilted tungsten wire on the resulting spring constant versus a non tilted wire. It is obvious, that a strongly tilted tip causes an increasing influence of torsion. Thus during the assembly one should also focus on the angle between tuning fork and wire, trying to keep it as small as possible.

Before we proceed by finally comparing the FEM and modified beam formula results with the experimental spring constants, we consider one further important issue related to the hand-made qPlus sensor fabrication. Since the wire is glued on the prong very often a small tilt of the wire's long axis with respect to the prong surface normal can not be excluded. Unfortunately, the torsion caused by the non central fixation of the tungsten wire increases, when the wire is not perfectly mounted to the tuning fork. Therefore we conducted further FEM simulations considering a possible wire axis tilt, with the results shown in Figure 3.8. This figure demonstrates clearly that even a small misalignment of the wire-axis can lead to large deviations of the effective spring constant, in particular for wire fixation points close to the tuning fork base.



Fig. 3.9: Comparison of the Experiment (including tilt of the qPlus sensor towards the force application axis) with FEM simulations and calculation using the beam formula with the new origin $L_0 = -700 \,\mu m$ for both. The non tilted experiment still shows a deviation from the simulations and calculations respectively. This is possibly caused by some tilt of the sensor towards the force application axis where small angles cannot be completely avoided in the experimental procedure.

As the final step, Figure 3.9 now displays the comparison between the experimental results (black square markers), the FEM simulations including a small 5° tilt (green triangles), and the modified beam formula (red line). First we note that the experimental spring constant results show a considerable spread, where almost identical tip positions may still exhibit differences of a factor of three in the most extreme cases, while differences of 50% are typically found. This spread in the individual spring constants is most likely due to tip

axis misalignments during the qPlus fabrication. In fact, the spread in spring constants agrees with the range of misalignment angles considered in Figure 3.8.

Despite this scatter in the individual data we find overall that there is a decent agreement between the measured spring constant values and the FEM results with a 5° tilt included, which is a realistic average value for careful manual tip fixation procedures. Furterhmore, we can now directly compare how well the origin shifted beam formula agrees with FEM data and experimental values. Again, in the regime of large ΔL values ($\Delta L > 1500$) the agreement between experiment and simulations/beam formula is acceptable, if the shifted origin method is applied. Please note that the scatter between the individual experimental data points is larger than the difference between beam formula and FEM data with 5° tilt angle.

From this section we conclude that using the conventional beam formula for calculation of the spring constants of tuning forks results in a dramatic overestimation of the beam compliance. However, the origin shifted beam formula can be used to estimate the qPlus spring constant for $\Delta L > 1500$. Still in this case a typical error of 50% remains, which is mainly due to angular misalignment effects during the tip wire fixation to the free prong. For more precise spring constant determination, as required for quantitative force spectroscopy experiments, individual calibration of the used tuning fork sensors is mandatory.

3.4 Summary And Conclusion

In this chapter a simple method of measuring the spring constant of tuning fork sensors using a micrometer screw and a scale was presented. The experimental results are compared to the beam formula and FEM-simulations revealing the limits of the commonly used models for the determination of qPlus sensor stiffness. The combination of finite element method simulation with experimental measurements allowed a comprehensive understanding of the spring constant behavior alongside the whole length of the prong. This knowledge finally opens the opportunity of adapting the beam formula by shifting the origin of the beam formula and thus making it a reliable tool for the k determination in the area around the last millimeter of the prong.

Since the beam formula is calibrated in the present study, it can be used for the determination of spring constants of qPlus sensors by measuring the effective length between the force application point at the glueing droplet attaching the wire to the prong and the shifted coordinate for the zero point of $\Delta x_0 = -700 \ \mu m$ into the basis. This length can either be measured from SEM images of tuning fork sensors or even simpler by microscopic photography. Whenever a more precise value of the spring constant is needed, the presented method to measure the stiffness directly can be applied to the sensor after the AFM spectroscopy experiment to provide a precise value for the further analysis of the forces.

4 Diamondoids on surfaces

This chapter gives a short introduction to diamondoids and their scientific applications. Diamondoids are the smallest diamond-like molecules which consist out of fully sp^3 hybridized carbons.

For most polycyclic hydrocarbons, the adapted von Baeyer IUPAC (Hellwich [2002]) nomenclature is used which, however, proves to be cumbersome in many cases. The naming of diamondoid molecules can be approached differently. As all polymantanes consist of an aggregation of adamantane, a nomenclature that made use of these very regularstructured molecules was developed. The nomenclature of Balaban and Schleyer [1978] is a simplified, yet precise method of describing all diamondoids. By having four possible directions that a cage can be attached to the next one, a molecule can be named by a list of numbers between 1 and 4 indicating the direction of the next cage. By writing one number in brackets, a cage that is a junction with two attached cages can be marked recognizable. In Fig. 4.1 the naming of a pentamantane molecule is exemplified.

Fig. 4.2 shows an overview of some of the existing diamondoids. Adamantane is the smallest diamondoid existent with only one isomer, similar to the two larger diamondoids diamantane and triamantane. From tetramantane upwards, which already has three isomers and one pair of enantiomers, several possibilities exist of how the cages can be attached.

The history of diamondoids starts in the year 1932 when Czech scientists S. Landa, V. Machacek and M. Mzourek discovered the first diamondoid, adamantane, as an ingredient of crude oil (Landa and Machacek [1933]). By distillation they were able to isolate adamantane and could study some of its properties like the melting and boiling point. As the dissolved amount of adamantane in oil is very small, early attempts were made to synthesize it. The first successful synthesis was finally achieved in 1941 by Vladimir Prelog (Prelog and Seiwerth [1941a, b]), the first diamantane synthesis followed in 1965 (Cupas et al. [1965]; Courtney et al. [1972]). However, the method applied to assemble carbon cages to diamondoids was not able to create higher diamondoids (Osawa et al.



Fig. 4.1: Stick model of [1213]pentamantane. The numbers start with the direction of the adjacent carbon cage in relation to the first cage, so four numbers are sufficient to describe a diamondoid with five carbon cages.

[1980]). In 2010 a different method was presented wich allowed the synthesis of higher diamondoids. The highest diamondiod that could be created this way was pentamantane (Dahl et al. [2010]). The relatively low yield in the synthesis of higher diamondoids is still an issue that has to be overcome, as for now the amount is not high enough for commercial applications. Until today higher diamondoids up to undecamantane that consists of eleven carbon cages, could be extracted out of petroleum sources with a different technique (Dahl et al. [2003]). Since the percentage of polymantanes in petroleum is rather low, a commercial extraction is also very unlikely.

Graphene is manifold object to research but with no large-scale commercial application yet. Diamondoids, in contrast, already have some applications. Adamantane derivatives are applied as a pharmaceutical against Parkinson's disease, HIV, diabetes, and Hepatitis (Wanka et al. [2013]). Due to their unavailability in larger amounts, higher diamondoids are not part of a commercial product yet. Research has already shown that higher diamondoids can be applied in several areas beside the pharmaceutical applications e.g. as polymer additives (Archibald et al. [1991]; Malik et al. [1991]; Zheng et al. [2000]), monochromatic electron emitters (Roth et al. [2010]; Narasimha et al. [2016]), or even molecular machines (Karlen et al. [2005]; Chu et al. [2013]).



Fig. 4.2: Different diamondoids starting with the smallest, Adamantane, going up to Heptamantane (Molecular data obtained from School of Chemistry, University of Bristol [2017])

Diamondoids appear to have a broad variety of possible applications and therefore are an interesting sample system for research. Some STM scans (and no AFM scans) of diamondoids have been made already. However, the knowledge about the self-assembly or rotational structure of diamondoids is only rudimentary up to now. The structure of self-assembled monolayers grown with evaporated diamonds are of large interest as the separation of diamondoids, especially isomers, is rather complex and a new more efficient method would open a window to various applications.

4.1 [121] Tetramantane - Self-Assembly Process

In the following chapter, the results of our research on the self-assembled monolayers of [121]tetramantane are presented. After a short introduction to previous research results, our observations during the analysis of [121]tetramantane with STM and AFM scans are shown. Our aim was a comprehensive examination of the self-assembled structure of [121]tetramantane on a suitable substrate. Hence, the key corner stones for this project are:

the determination of the mode of growth, the reconstruction geometry, and the rotation of the molecules themselves. The results constitute the basis for any further required steps toward the application of [121]tetramantane.

4.1.1 STM Analysis

4.1.1.1 Earlier Results

[121]tetramantane has been studied earlier by Wang et al. [2008]. In their study, they sublimed [121]tetramantane onto an Au(111) surface and studied the molecules at 5 K with an STM. They were able to show that [121]tetramantane assembles in large islands with a lattice constant of 11.4 Å x 8.3 Å. In the next step, they dragged out a single tetramantane molecule with an STM tip and scanned it with different voltages applied to the tip before moving the molecule again and repeating the scan. The results of these scans were then compared to DFT computations. With the knowledge of the molecules' orientation in the DFT scan, they identified three different orientations of tetramantane on the gold surface. In combination with scanning tunnelling spectroscopy, Wang et al. also resolved electronic and vibronic properties of the tetramantane molecules.



Fig. 4.3: Left: ball and stick model of [121]tetramantane. Right: wireframe model of [121]tetramantane with the directions of the adjacent carbon cages indicated by arrows, with a number for each direction written below.

The Au(111) reconstruction, also called herringbone reconstruction, that was used as a substrate in these measurements can have a striking influence in the self-assembly process

of other types of molecules as shown by Zint et al. [2016]. Beside the face centred cubic (fcc) domain, the Au(111) surface also appears to have a hexagonal closed packed domain (hcp) which has been shown to interact with molecules adsorbing on the surface. Therefore, we used copper as a substrate material. Copper has a face centred cubic (fcc) structure with a sixfold symmetry in the (111) direction. In addition, it does not show any irregular surface reconstruction that could interfere with the self-assembly process.

4.1.1.2 Submonolayer Coverage Preparation

[121]tetramantane consists of four carbon cages assembled as shown in Fig. 4.3. The sample applied in our studies was over 99% pure [121]tetramantane.



Fig. 4.4: STM image showing the rim of a tetramantane island.

The Cu(111) crystal was prepared by numerous sputter-annealing cycles. An atomic-clean surface was achieved by sputtering with Ar^+ ions, with energies ranging from 800 to 1500 eV, followed by annealing steps ranging from room temperature to 850 °C. The [121]tetramantane molecules were sublimated at 38 °C onto the precooled sample. The sublimation was done with a home built evaporator made of a stainless steel tube mounted onto a steel omicron sample plate. Prior to the experiment, the evaporator had

been outgased at temperatures of up to 900 °C. This procedure reduced the probability of contaminating our sample with components of the stainless steel tube during sublimation. To achieve stable controlled sublimation conditions, the heating stage of the manipulator (VACGEN, Great Britain) was only used as a position for the evaporator in thermally equilibrated conditions. The sample held by the mag-probe was kept at room temperature during the whole sublimation procedure. The time span between the beginning of the sublimation and the mounting of the sample was approximately 15 minutes.



Fig. 4.5: STM images of two different orientations of the 3×4 reconstruction on a [121]tetramantane island. a) and b) show the up and down scan of the same position. The vector length of the orientation is thus 7.68 ± 0.1 Å and 10.2 ± 0.1 Å. After one complete cycle, the scanning angle was turned about 90° to eliminate possible errors by the piezo, shown in images c) and d). This procedure allows a precise lattice constant determination.

4.1.1.3 Structural Analysis By STM

Similar to the observation by Wang et al., we observed that tetramantane, sublimed onto a Cu(111) surface at room temperature, assembles in large monolayer islands (cf. Fig. 4.4). Hence, the mode of growth, the first corner stone mentioned, can be identified as Frankvan-der-Merwe-growth, which is characterised by the flat growth of adsorbed monolayers. Due to the preferred interaction of the adsorbed molecule with the substrate, the complete substrate is covered with a monolayer before a second layer can be observed (Frank and van der Merwe [1949a, b, c]). The islands' sizes are only limited by the size of the copper terraces of the substrate. Several different samples were prepared, and the measurements were repeated in order to create a suitable island size and number. Fig. 4.4 shows a large island of tetramantane on the copper surface. The resolution in the STM is sufficient for identifying single molecules. However, the images showed no submolecular contrast which would allow the identification of a single molecule's orientation. Despite this limitation, the images are suitable to determine the other corner stones.

The reconstruction of tetramantane could be identified with the images in Fig. 4.5. They demonstrate that [121]tetramantane assembles in a single phase. All images depict the same area of the sample, whereas a) and c) show the up-scan, c) and d) the down-scan. Additionally, the scans on the right side are rotated by 90° . This helped exclude possible errors due to creep or drift effects altering the measurement of reconstruction vectors. A possible explanation for the disruption in the phase is the growth process during the island assembly. In the sublimation process, several different initial crystallisation nuclei form, which merge into large islands. These different initial islands are likely to be the cause for the 60 degree symmetry of the observed phase. With the lattice constant of copper(111)= 2.55 Å (Drexler et al. [1992]), a possible superstructure of [121]tetramantane is a 3×4 reconstruction on copper. The second step necessary for the superstructures's identification is the knowledge of the molecules' orientation with respect to the copper orientation. We were able to identify this orientation with a scan that had molecular resolution on the tetramantane islands and atomic resolution on the copper substrate in the same image (cf. Fig. 7.4). Knowing the underlying copper subtrate's orientation, we were able to link this single orientation to all scans of this measurement cycle. Image c) indicates that tetramantane only assembles in orientations according to the 60° symmetry of the copper substrate. The coloured rhomboid-shaped areas represent the directions of other islands observed in this cycle. All islands stuck to the 60° symmetry of copper. Hence, the superstructure can be distinctively identified as the assumed 3 x 4 reconstruction.

The images in Fig. 4.5, as well as five other images not shown here, reveal that the molecules organize very precisely in the 3×4 reconstruction. The theoretical values for the reconstruction vectors are 7.66 Å and 10.2 Å with a 60° angle in-between as shown in Fig. 4.7; the measured values are 7.68 ± 0.1 Å and 10.2 ± 0.1 Å with an angle of $60^{\circ} \pm 0.1^{\circ}$. The reason for this nearly perfect alignment can either be found in the molecule-substrate interaction, or be a result of the molecules' geometry.



Fig. 4.6: a) shows an STM image with molecular resolution on [121]tetramantane in combination with the atomic resolution of the Cu substrate. The directions of the domains are highlighted with the coloured rhomboids. b) shows an enlargement of the red rhomboid on copper. c) shows all rhomboids gathered from of all measured reconstructions within this cycle. All reconstructions align with the 60° symmetry of the underlying copper substrate.

Analogous to the work by Wang et al. mentioned earlier, lattice constants of 11.4 Å x 8.3 Å for [121]tetramantane on Au(111) were experimentally determined. These lattice constants are also close to the theoretical values of the 3 x 4 reconstruction on Au(111) with 11.53 Å x 8.68 Å. Both findings suggest that the substrate-molecule interaction could have a significant impact on the self-assembly structure of the tetramantane islands.

The bare STM images were suitable for the determination of the surface reconstruction but could not



Fig. 4.7: Animation of the 3x4 reconstruction on a Cu(111) surface. A possible position of the tetramantane molecule is shown.

be used directly to gain further knowledge about the rotation of the single molecules.

By taking the molecules' geometry into account, however it was possible to draw a second conclusion concerning the orientation on the substrate. The tetramantane molecules have a maximum length of 9.128 Å and a diameter of 6 Å. Assuming the molecules stood "upright" on the substrate as shown in Fig. 4.9, the gap between them would be more than one copper lattice constant and would allow the molecules to pack much closer than observed. Since this is not the case, this position does not appear likely.



Fig. 4.8: The geometrical calculation delivered these three orientations of [121]tetramantane as the most probable ones.

The next step for the orientation identification required the combination of the STM images with the results of a self-programmed routine. For this calculation, a tetramantane molecule and its three closest neighbours were simulated in a ball and stick model. The basic idea behind this was the reduction of possible molecule orientations fitting into the 3×4 reconstruction observed. The calculation started with a single molecule that was rotated around the x, y and z axes. After that, the observed 3×4 reconstruction was generated out of four molecules with the chosen rotation.



Fig. 4.9: Animation of the "upright" orientation of the [121]tetramantane molecule on the copper substrate. This orientation was excluded from the calculations.

definite answer.

To determine whether this orientation was favourable, the minimal distance between the closest atoms of the adjacent molecules was calculated. Solutions that contained an overlap of two molecules were rejected. The solutions were sorted by distance between molecules, the best solution containing the maximum distance. Finally, this calculation was done for every possible rotation, except those with the molecule standing "upright" (cf. Fig. 4.8). The routine made it possible to break the number for the molecules' orientation down to three major ones. This means that the three orientations can still be slightly changed in the tilt, but can be interpreted as representatives for a group which contains a number of solutions with very similar appearance. This was a rough approach and did not consider forces or the substrate and therefore did not allow to conclude which orientation was favoured. Thus, the results of this routine can only be interpreted as clues to the possible orientations and not as a

4.1.2 Submolecular Resolved AFM Analysis

In further research the exact orientation of [121]tetramantane could be distinctively identified with the help of submolecular AFM scans. Fig. 4.10 shows a tetramantane island with high resolution AFM. This island is not yet completely reconstructed in the earlier mentioned 3 x 4 structure. Besides, the clearly resolved molecules all appear to have the same height as well as the same side facing towards the tip. The only difference is the rotation on the plane. However, the side facing the tip can be assumed to be the same side as in the STM scans. By taking a look at a single molecule it is possible to identify five bright spots (highlighted by red circles) belonging to each molecule. They are the completing element required for the last corner stone, the precise rotation identification. The comparison of the bright spots with a model of the molecule demonstrates that only one rotation allows the existence of five single hydrogen atoms facing towards the tip as depicted in Fig. 4.11.



Fig. 4.10: AFM scan of a tetramantane island at a Δz of 140 pm. The red circles emphasize the five bright dots every molecule shows. Three dots are of similar brightness, the other two appear much darker. Scan done by Daniel Ebeling.

4.1.3 Summary

In addition to the submolecular analysis of flat molecules, the combination of STM and AFM proved to be a very powerful instrument in the structure determination of bulky self-assembled diamondoids. With the knowledge of the exact structure of the molecules at hand, the information gathered by scanning only one side is sufficient for a comprehensive analysis. With the help of the STM, the growth mechanism, the 3 x 4 reconstruction of [121]tetramantane on copper, as well as the alignment of the molecules according to the underlying copper structure were determined. The subsequent CO-functionalised AFM scans finally made it possible to identify the orientation of the [121]tetramantane molecules on the surface.

4.1.4 Outlook

Our measurements on [121]tetramantane give the first comprehensive clues as to how these molecules assemble on a copper surface. For possible applications as electron emitters, the



Fig. 4.11: Scheme of [121]tetramantane molecule as it is found on the copper surface. The red coloured hydrogen atoms represent the five bright spots in the AFM scan. The green coloured hydrogen atoms belong to the binding end. For simplification, the lower half of the tetramantane is hidden in the right image and only the upper atoms facing towards the tip are depicted.

knowledge can be of significant influence on how the substrate or the molecules themselves have to be adapted to the desired state. The knowledge of the assembly on other surfaces and on copper under varying conditions is still not fully developed. Therefore, future research should focus on the determination of the behaviour on other substrates and different sublimation conditions. Furthermore, to facilitate the application as electron emitters the analysis of the self-assembly process of functionalised tetramantane is necessary.

4.2 [123]tetramantane - Chiral Molecules

The analysis of [121]tetramantane showed the high potential of the analysis of diamondoid molecules with STM and AFM combined. [123]tetramantane is an isomer of [121]tetramantane. The difference between them is the position of the last carbon cage. In contrast to [121]tetramantane, [123]tetramantane can be constructed in two different ways, which results in the existence of two chiral enantiomers of the same molecule. The sample in this study is a mixture consisting of racemate. The aim of our research was to find out if the two different molecule versions can be differentiated and also identified directly with the help of STM or AFM.

In earlier studies by Pechenezhskiy et al. [2013], [123]tetramantane has already been analysed with an STM, revealing that on Au(111) it assembles in islands in a hexagonal structure, with the vector length $|a| = |b| = 9.8 \pm 0.1$. They sublimated the same mixture of [123]tetramantane as used by us, onto the gold sample at a temperature ranging from 30° to 40°. They were not able to differentiate the two chiral versions with the STM. The STM image itself does not have the resolution that allows a differentiation of the two different versions. Analogous to chapter [121]tetramantane, the research on [123]tetramantane was done to clarify the characteristics of the self-assembled structures with an additional focus on the structural differences caused by the chirality.

4.2.1 Chirality

As the following chapter deals with the chirality of [123]tetramantane, a short introduction to chiral molecules is given here.

Chirality is a characteristic often occurring in nature. It means the object, after being mirrored, can not be transformed into the original state by rotation, independent from the axis at which this operation is done. An easier understanding can be achieved with the example of the human hand. If the right hand is mirrored, it becomes the left hand, and no rotation can transform a left into a right hand. This is the reason why this feature is called chirality, derived form the Greek word for hand. Other known examples are the snail shell or the corkscrew. Both exist in two different enantiomorphs.



Fig. 4.12: Wireframe model of [123]tetramantane. The number between the bullets names the direction of the next carbon cage attached for both isomers.

In chemistry, chirality is analogous to the biological-macroscopic world. Molecules can also exist in two different appearances. These molecules, in the abstract above called "variations", are called enantiomers in chemistry and will therefore be called this way in the following. [123]tetramantane can be constructed by attaching the carbon cages as shown in Fig. 4.12. Both are [123]tetramantane, but it is not possible to transform one enantiomer into the other by rotating it.

To distinguish the chiral molecules, the Cahn-Ingold-Prelog-Convention (Cahn et al. [1966]) is applied, which separates the molecules into "right handed" (R) and "left handed" (S). In our case, the notation "plus" (P) for "right handed" and "minus" (M) for "left

handed" is used. This notation was developed specifically for axial chiral molecules.

Although chirality seems to be only a small discrepancy, the effects it can have on chemical reactions range from none to severe. The Thalidomide affair is a commonly known case in which chirality had a detrimental effect. The medical agent of Contergan, thalidomide, is a chiral molecule. Its R-enantiomer had the desired effect against morning sickness of pregnant women, whereas the S-enantiomer caused deformities in newborns (Jacques et al. [2015], Eriksson et al. [2000]). This dramatic example shows the importance of a differentiation between chiral molecules and the need to test both enantiomers before an application as a pharmaceutical. The different impacts of two enantiomers can be understood by considering the reaction partners. In many cases, these partners are chiral as well and therefore exhibit favoured reaction paths with one of the two enantiomers. An example in which the effect of chirality can be experienced without any lab equipment is the molecule "Carvone". Both enantiomers have a strong, but completely different odour. One smells like spearmint the other like caraway seed (Russell and Hills [1971], Friedman and Miller [1971]). The explanation for the different odour is similar to that of the different effects of Contergan. The nasal receptors are chiral as well and thus recognize each enantiomer differently.

4.2.2 Structural Analysis By STM

4.2.2.1 Submonolayer Coverage Preparation

We started the measurement of [123]tetramantane again with STM scans. The sublimation was carried out similarly to the sublimation in chapter 4.1. A new gun was built and cleaned in an isopropanol bath with subsequent UHV-tempering to remove any possible contamination. The copper crystal was cleaned with several sputter-annealing cycles and subsequently exposed to the tetramantane gun. We carried out the first sublimation with the gun and the sample both at room temperature. The gun was positioned on the cooling station of the manipulator while the sample was held by the mag-probe. The sublimation time was 10 minutes. The transfer from the preparation chamber was also done at room temperature and took about 3 minutes.

4.2.2.2 Hexagonal Structure Resolved By STM



Fig. 4.13: Large STM scan of [123]tetramantane. The structure at hand does not show the well-ordered patterns of [121]tetramantane.

The first scan on [123]tetramantane carried out with 5 nA setpoint and -100 mV gap voltage(Fig. 4.13) showed that these molecules, similar to [121]tetramantane, also assemble according to Frank-vander-Merwe-growth in significant monolayer islands on the copper substrate. The [123]tetramantane islands seem to be less ordered and show no directly visible reconstruction. On the large scale, they seem to assemble in a hexagonal lattice which is not perfectly ordered. Fig. 4.14 depicts a zoom in on the island. It resolves the substructure of the tetramantane island. Most of the molecules appear to have the same side

facing towards the tip. But, if resolved higher, it can also be seen that the molecules do not arrange in a highly ordered pattern. This finding proves that, under the given circumstances, no separation of the tetramantane with different chiralities takes place. Instead the irregular structure is a strong indicator that the islands consist of both chiralities and therefore are not able to create a well-ordered structure. Additionally it can also be observed, that some molecules are facing the tip with a different side. These molecules seem to be blurred out or distorted.

Image 4.15 shows a Fourier filtered image of the tetramantane island seen in Fig.4.13. The Fourier filter allows clarify the reconstruction of the island by removing all features of the single molecules. The image shows slightly distorted hexagonal reconstruction. An explanation for this can be the mixture of the two different enantiomers within the island. Because of the slight difference between the enantiomers it is not possible for the molecules to arrange in a perfect pattern as observed in the scans of [121]tetramantane. The hexagonal structure formed by the molecules has a vector length of $a = b = 8.1 \pm 0.5 \, pm$ and an angle of $62^{\circ} \pm 1^{\circ}$ between both vectors. In the paper by Pechenezhskiy et al. [2013] the vector lengths on an Au(111) surface were determined to 9.8 pm for each direction. This is another evidence for the non-negligible interaction between the molecules and the substrate as mentioned earlier.



Fig. 4.14: Left: A zoom in on an STM image of a [123]tetramantane island shows that a well structured order is only visible in regard to the next neighbours (setpoint: 0.76 nA, gap voltage: -10 mV). Right: Further enlargement of structure. Most molecules have the same height, indicating that they are facing the tip with the same side. Some are distorted which could be caused by a different rotation and thus different height (setpoint: 3.25 nA, gap voltage: -30 mV).

4.2.3 Submolecular Resolution On [123]tetramantane By AFM

The STM images already recognized submolecular features. However, these images are insufficient to clearly identify the orientation of the molecule, and especially the exact enantiomer. To reliably distinguish the enantiomer, it is inevitable to clearly image its chiral end-group. As the submolecular resolution with an AFM already proved to be suitable for the identification of certain molecular features of the diamondoids, the same method was applied here.

The high resolution required for this purpose could be achieved with a functionalised tip. The potential of these tips has already been discussed in chapter 2.4. The major challenge with the CO tip was the imaging of the very bulky tetramantane molecules, which is a relatively new operating mode for these measurements (Moreno et al. [2015]; Pawlak et al. [2012]). Moreno et al. applied a combination of scans with and without feedback loop. In order to achieve submolecular contrast they scanned each line first with the feedback loop enabled and afterwards with a deactivated feedback loop again. During the second scan the tip approached to a distance at which submolecular features became visible. In order to avoid crashes the topographical information gathered for each point in the first scan was fed as an offset value to the tip in the second scan. With the tip "remembering" the topography of the sample during the high resolution images they could resolve the upper structure of a C60 molecule. Beside these few examples, most molecules that have



Fig. 4.15: Fourier filtered image of the [123]tetramantane island with a rhomboid indicating the reconstruction.

been resolved submolecularly with a functionalised tip were flat in comparison to the diamondoids (Gross [2011]). The bulky character of [123]tetramantane makes it difficult to image the whole structure - here, only the side showing upwards during the scans is resolved.

4.2.3.1 Single Molecule Coverage Preparation

For the imaging of the enantiomer's chiral end-group, the scan of [123]tetramantane located within an island is not very suitable. The best experimental conditions for this kind of measurement are isolated molecules. Surrounding molecules can lead to misinterpretations of the scan result, as the orbitals of two adjacent molecules can appear as a bond. This interference needs to be excluded to achieve valid results. In the previous measurement results it could be seen that the sublimation of [123]tetramantane on a sample at room temperature inevitably leads to the formation of islands. To avoid this formation, three different approaches were tested. The first approach was sublimating in the same set-up as before, but for a shorter time. We assumed that this approach would decrease the overall number of sublimated molecules on the sample and could therefore produce single molecules. It was carried out with the evaporator between 22° and 30° C onto a crystal at room temperature and took 2 minutes. The result was that less molecules could be observed. However, these molecules still assembled in islands with sizes over $100 nm^2$.

The second approach was to sublimate for one minute onto a cooled sample. The cooling stage of the manipulator was well-suited for this test. But because the evaporation gun had to be mounted in the manipulator, the sample could only be held with the magprobe which has no cooling possibility. Therefore a different set-up was tested. With the limited options given, we had one other possibility to cool the sample for the sublimation which is depicted in Fig. 4.16. The sample was mounted in the AFM until it reached 5 K. Afterwards, it was grabbed with the wobble stick and held over the evaporation gun for several seconds and then directly mounted back into the AFM (left image of Fig. 4.16). However, by grabbing the sample with the wobble stick, a thermal contact between the wobble stick at room temperature and the sample at 5 K was made. To avoid warming up the sample, the wobble stick was pre-cooled at the shielding of the AFM: first for 20 minutes at the outer liquid nitrogen shield and afterwards for 30 minutes at the inner liquid helium shield. With this procedure, the lowest sample temperature outside the AFM could be achieved, and it assured that the sample warmed up as little as possible during the sublimation. The scans showed that this method led to smaller islands compared to the first one, but still no single molecule could be observed. Pulling single molecules out of the islands proved to be challenging and often resulted in picking up the molecule.

As this approach showed that a reduced temperature does lead to a reduced island size, the final method was to sublimate directly onto the sample in the AFM as depicted in the right image of Fig. 4.16. This was the coldest possible arrangement with our set-up, as the sample was actively cooled during the procedure. During the sublimation, the sample temperature rose from 5 K to 13 K, which was caused by the infra-red radiation reaching the sample when the shielding was opened. For the sublimation, the gun was positioned directly in front of the passage to the AFM. To target the sample with the manipulator it was necessary to position the manipulator as high as possible to get a direct path to the sample. In addition to the higher z-position of the manipulator, the gun was tilted between 10° and 20° . This was the estimated angle the gun needed to have to target the sample. To make sure the sample was hit, the sublimation was started at 10° and slowly turned to 20° . After positioning the gun, the procedure was started by opening the cryo-shields and



Fig. 4.16: Left: Evaporation set-up for the cold sublimation. The sample is taken out of the AFM and held directly above the molecule gun for a short time. After that, it is remounted into the AFM to keep the sample temperature as low as possible. Right: The sample stays in the AFM and the molecule beam is directed onto the cold sample.

was stopped by closing the shields again after 10 minutes. Subsequently, the temperature dropped to 5 K within the first minute. For the CO molecule pick-up, the pressure of the preparation chamber was adjusted to $5 \cdot 10^{-8}$ mbar with the leak valve. Afterwards, the plate valve to the analysis chamber and the shielding of the AFM were opened. To stop the adsorption, the shielding and the valves were closed after 10 minutes.

4.2.3.2 Measurement Protocol For Submolecular AFM Scans

Measurements were started with an STM overview scan to identify the adsorbed CO molecules on the copper surface. After a CO had been observed, the STM tip was moved on top of the molecule for the pick-up procedure. One common method of picking up a CO molecule is the earlier mentioned Bartels method (Bartels et al. [1997]). We found that it was sufficient to apply single voltage pulses (without any further actions) to successfully pick up a CO molecule. The pulses used for a successful pick-up ranged from 3 V to 5 V, depending on the tip's sharpness. This proved to be the most important quality for a successful CO pick-up: the sharper the tip was the faster a CO molecule could be attached to it. Therefore, the frequency shift of the sensor during the STM scans was monitored. A shift smaller than 2 Hz at a set-point 20 pA and a gap voltage of 200 mV indicated that the tip was sufficiently sharp. If the frequency shift was larger, the tip was conditioned with spectroscopy curves up to several hundred nanometers into the substrate and voltage pulses up to 10 V. However, an attached CO did not automatically mean good resolution for the AFM scans. A subsequent STM scan clarified if the CO was attached correctly without any tilt or misplacement. When these images showed doubled or blurred-out fea-

tures a good resolution in the AFM was still possible, but unlikely.

The best location for the AFM measurements was on clean copper substrate near a single molecule. This location allowed the imaging of the molecule with no influence caused by neighbouring molecules. The other advantage of this position was of technical nature, as crashes during the scan could be avoided by a sample tilt calibration close to the area of interest ("detect plane" mode). The calibration was necessary since during the constant height AFM scans the feedback loop is deactivated. A tilted sample could therefore cause the tip to crash, as the tip wouldn't be retracted in case of a close approach. The farther this calibration was done from the location of the measurement, the more inaccurate it could be with respect to the scan area. This originates partially in the piezo's geometry and partially in the piezo creep. The piezo creep increases the further the piezo has to move between two positions. In addition to that, the piezo's tube geometry requires it to bend if moved within the possible scan area. This bend causes a higher z discrepancy between the left and right edge of a scan. The phenomena can be understood with the comparison to a thread pendulum. For small angles, the pendulum has only a small discrepancy in the height of the mass. If the angle increases, this deviation increases faster.

In addition, all the factors that had to be considered for a successful measurement with submolecular resolution, a precise measurement protocol had to be followed if a sufficient success rate was to be achieved. The protocol step short list is found in the Appendix.

Although the "detect plane" mode corrected any tilt, the tip crashed frequently. The cause for these crashes could be identified as the remaining piezo creep. Usually it can be reduced by only applying small voltages to the piezo. However, the voltages depend on the piezo's position and can therefore not be kept small all the time. To guarantee stable measurement conditions the piezo creep had to be suppressed, which was achieved by the implementation of a measurement routine for the MATRIX software. The concept for this procedure was to halt the scan after every scan line with the bias turned on and with the feedback loop subsequently enabled. This position was then used as the new reference position for the Δz value. Our procedure made sure that, even with a fast drifting sample, the entered Δz value was always kept constant. Furthermore, this routine allowed to start the AFM measurements directly after the CO pick-up and thus increased the overall time window for submolecular measurements. The remaining x/y-drift disappeared faster than the z piezo creep. It could be reduced significantly analogue to the z piezo creep by choosing a position for the scan with the x and y position of the piezo close to zero. In

this position, no or only a small voltage was applied to the scanner tube.

4.2.3.3 First Submolecular Resolved AFM Scan Of Chiral Molecules

The aim of a low molecule coverage was overachieved, which required fast STM scans over an area of $100 nm^2$ to find a single tetramantane molecule.



The first successful submolecular scan of a dimer of [123]tetra-

mantane molecules is shown in

Fig. 4.17: Dimer of [123]tetramantane.

Fig. 4.17. This scan was carried out with a qPlus sensor with the resonance frequency of 19303 Hz and a Q-factor of 24000. For the necessary resolution, the scan speed was limited to 16000 μs per data point. The excitation amplitude was 2.5 mV and 0.5 mV gap voltage to minimize the current between tip and sample.



Fig. 4.19: Three AFM scans on a [123]tetramantane molecule with different heights (STM image on the upper right). The lines between the hydrogen atoms (highlighted in green) do not depict actual bonds but are caused by the increasing Pauli repulsion. The closer the tip approaches the surface, the more artefacts can be seen.

[123]tetramantane molecules exhibit five bright spots, analogous to [121]tetramantane. Again these spots are five hydrogen atoms facing the tip. In contrast, the tilt observed here is different. It is not alongside the line of the three outer hydrogen, but 90° turned. For a better understanding, the tilt is visualized with fading arrows in Fig. 4.18. The question at hand was, whether this tilt is caused by a bond between the two molecules, or if it is caused by the chiral CH_2 -end group and therefore characteristic of [123]tetramantane on cop-



Fig. 4.18: Tilt of the two tetramantane indicated by the fading arrows.

per (depicted in Fig. 4.22). For clarification, the next measurement was done on a single molecule without other molecules interacting with it.

Fig. 4.19 shows a scan series of the same molecule at different heights. The five bright spots are clearly visible in all scans. The tilt observed earlier with the two molecules is visible again, which is a direct indicator that the tilt is not a result of the interaction between the molecules, but rather a characteristic of the molecule itself. The other important observation is that the closer the tip approaches the molecule, the more artefacts can be seen due to the increasing Pauli repulsion. The white lines between the hydrogen do not indicate a bond, instead, bond like features are caused by the same effect as already mentioned in chapter 4.1. The close proximity to the molecule tilts the CO and results in these features.

The tilt of the observed molecules could also be a result of the different orientation on the substrate. To exclude this possibility, the position of each observed molecule was compared to the underlying copper grid. In Fig. 4.21 all molecules scanned with the AFM in this measurement are represented with a red cross in a polar graph with their angles in respect to an arbitrary other molecule. The angles observed are all a multiples of 60° . In addition to that, one molecule has been accidentally rotated by the tip. The comparison of the images before the rotation and after shows, that it also has been rotated by a multiple of 60° . The graph and the rotation image show that the tetramantane molecule always adsorbs corresponding to the underlying copper grid, and therefore the different tilt directions observed can not be the result of a different adsorption but must be a property of the tetramantane itself.



Fig. 4.21: AFM image of a [123]tetramantane molecule before and after it was rotated by the AFM tip. The tip turned the molecule by a perfect multiple of 60°. This in combination with the image on the right side showing the angle of all single molecules measured with respect to an arbitrary one shows, that [123]tetramantane always aligns corresponding to the underlying copper substrate. Scan of the molecule done by Daniel Ebeling.



Fig. 4.20: AFM images of single [123] tetramantane molecules. The molecules are tilted into two different directions and can not be transformed into the other by rotation.

In Fig. 4.20 two single [123]tetramantane molecules are shown for comparison. Both molecules are mirrored images of each other. By taking a closer look at both images, it becomes visible that the tilt in each image is exactly opposite to that in the other image. This is the definition of a chiral molecule and an indicator, that two different chiralities of the [123]tetramantane exist. The other explanation is that [123]tetramantane is only adsorbed on another side and therefore faces the tip differently. With the images at hand, this problem can not be solved. To allow a clear explanation of this effect, a closer look at the exact molecule geometry is necessary. The distinctive identification of the molecule's chirality the difference between both enantiomers has to be understood. In the position observed with the five hydrogen atoms facing towards the tip, the hydrogen atoms, which allow for the enantiomer determination. can be found about 123 pm below the hydrogen atoms.



Fig. 4.22: The orientation of the molecule as observed in experiment with the hydrogen facing upwards (highlighted in green). In this orientation, the different enantiomers can be distinguished by the position of the hydrogen (highlighted in magenta). These hydrogen are located $123 \, pm$ below the green hydrogen.

Fig. 4.22 shows both enantiomers in the orientation found on the surface. For imaging the chiral end within a scan, it is necessary to move the tip roughly 120 pm closer to the surface. Fig. 4.19 shows that this is not possible in a constant height scan on top of the molecule. At this distance, the repulsive forces increase to a level at which the CO molecule at the tip is lost or the complete tetramantane molecule is picked up. This challenge was met with a dynamic approach: the combination of a constant height scan on top of the molecule and a variable height scan at the chiral end-group. The tip scanned the molecule beginning with the non-chiral end and slowly moving upwards to the chiral end-group located at the upper end of the molecule in this image. In this direction, it was possible to scan the whole molecule at a fixed height first and approach it further when the location of the possible end-group appeared. Therefore, the scan direction had to be rotated according to the upper two images in Fig. 4.23. The scan started at the bottom of the image and moved up row by row. After the row with the two hydrogen was passed, a protocol was manually activated. This let the tip approach the surface gradually until the tip was roughly 120 pm closer to the sample. To control if the two different molecule tilts correlate to the two enantiomers, both molecule types were scanned this way.

The result can be seen in the lower four images of Fig. 4.23. The approach showed the predicted result. The left and the right molecule are the two different enantiomers of [123]tetramantane. By comparison with the ball and stick model, the left molecule can be



Fig. 4.23: AFM scan of both observed tilts. After scanning the molecule for a first image, a second image was made in which the tip approached the surface roughly 120 pm after passing the last green highlighted hydrogen atoms. The scan shows, that the two molecules tilted in opposite directions indicate the two different enantiomers. This allows for a clear identification of the enantiomer just by checking the molecule's tilt. In the last image, the upper half with the chiral end of the tetramantane has been laid on top of the AFM scan illustrating the difference between both enantiomers.

identified as the M-enantiomer and the right as the P-Enantiomer.

In the two lowest images, the upper parts of the diamondoids are laid over the AFM scan to illustrate the chiral ends. The resulting image can be used to identify the enantiomer of the molecule by measuring the tilt direction. With this help, the identification of a large number of tetramantane molecules on the surface is possible. A submolecular AFM scan takes significantly longer than an STM scan. So, the logical next step in order to increase the efficiency of identifying enantiomers was to determine if the STM images of [123]tetramantane could also be used for identifying the enantiomers. For this aim, a series of AFM and STM images of the same molecule were compared in Fig. 4.24. To guarantee comparable conditions, the scanning parameters were the same in all images, with 0.2 V, 10 pA as well as constant current mode. The comparison between the M- and P-enantiomers shows that the round protrusions in the scans differ in the position in which they are found on [123]tetramantane. In the M-enantiomer it is located on the top/left position; in the P-enantiomers it is in the bottom/right position. In this case, the protrusion correlates with the highest hydrogen atoms. This is a clear indicator of the chirality, although it can not be seen as clearly as in the AFM. Evidently, it is not possible to convert the STM image of the M-enantiomer into the P-enantiomer and vice versa by rotation. In order to recognize this less visible feature for the enantiomer identification, a larger number of scans is necessary to obtain more data. This would help to clearly assign single features in the STM scans to the respective enantiomer. It could also be the case that, with a changed voltage or a different current, the features change and become more visible.



Fig. 4.24: Series of STM and AFM scans of both enantiomers. The STM images of the enantiomers differ slightly in their appearance. The only deviation in the images that can be observed is the round protrusion in the STM images. It can be found either on the right/bottom side, if dealing with P-enantiomers, or in the left/top side for M-enantiomers. Lower right scan done by Daniel Ebeling. In the previous paragraphs we were able to identify the single enantiomer by linking the tilt observed in the [123]tetramantane molecules to the chiral end-group. One possibility to check our findings was to compare the positioning of the enantiomers in dimers. If the identified enantiomers in the dimer fit according to the molecule model, this is further support verifying our variable height measurements. For this purpose, the number of molecules on the sample was increased by a new evaporation directly into the AFM. The scans depicted in Fig. 4.25 and Fig. 4.27 show the different dimers observed in these scans.



Fig. 4.25: Images a) and b) show an P-P dimer of [123]tetramantane and images c) and d) show an M-M dimer [123]tetramantane.

Fig. 4.25 contains both mono-enantiomeric dimers observed. Images a) and b) show the dimers as they were observed in the scan, images c) and d) are the corresponding inlays with a [123]tetramantane molecule. The enantiomers were identified only by comparing the tilt direction of the molecules in the scan. Our identification fits the models causing no overlap between the two enantiomers.

To verify this finding, the P-P dimer from Fig. 4.25 was taken and two M-enantiomers were laid over the scan in Fig. 4.26 image c) instead. The proximity between the two molecules leads to an overlap, making this attribution unlikely. This supports the enantiomer iden-



Fig. 4.26: a) is a [123]tetramantane dimer observed in the scan, b) shows an inlet of two P-enantiomers as identified by the tilt, c) shows an inlet of two M-enantiomers.

tification made in Fig. 4.25. Beside the mono-enantiomeric dimers, we also imaged mixed enantiomeric dimers throughout the scans. In Fig 4.27 these dimers are depicted.



Fig. 4.27: Three different mixed [123]tetramantane enantiomer dimers with their corresponding molecule model inlays beneath them.

For all three dimers, according to our identification, the corresponding enantiomers are laid over the scan in the images beneath. The identification does not lead to an overlap of two molecules. In Fig. 4.28 the enantiomer identification in image b) is tested by switching the enantiomers, which leads to an overlap in image c). This overlap is another conclusive evidence for our previous enantiomer identification based on the tilt observation.



Fig. 4.28: a) is a mixed enantiomeric [123]tetramantane dimer observed in the scan, b) shows the inlet of two enantiomers as identified by the tilt, c) shows an inlet of the opposite enantiomers.

4.2.4 Summary

The STM and AFM scans in this chapter gave new insights into the adsorption properties of [123]tetramantane. The STM scans could be used to identify the assembly structure of [123] tetramantane on a copper (111) surface. It could be seen that, under the tested circumstances, [123]tetramantane assembles in large monolayer islands. These islands did not have the pronounced reconstruction shown by earlier [121]tetramantane scans. The lack of a highly regular structure could be due to a different rotation of the molecule on the surface but is much more likely caused by the mixture of both enantiomers. This is supported by the fact that a different rotation would result in a different height. And, as already shown with [121]tetramantane, a well-ordered structure is energetically more feasible than an irregular one. As the molecules had enough time and energy to structure themselves before the STM scans were performed, it is more likely that this was not achieved due to the imperfectly matching enantiomers. It also was not possible to achieve a resolution with the STM that gave further information about the molecule orientation on the surface or the type of enantiomer scanned. Therefore, AFM scans with a functionalised tip were performed. These scans finally produced the desired information about the orientation and the enantiomer analysed.

This is the first time that an AFM was successfully used to image the chirality of two enantiomers. The AFM has the capability of not only observing the tilt or any other characteristic caused by the chirality, but also directly imaging the chiral group. This is a new and highly reliable method of differentiating enantiomers. Its potential lies in a very precise identification of other possible enantiomers. With the help of the scans we could link the observed tilt of the molecule directly to the specific enantiomer, and hereby open the door to a fast identification of large islands of [123]tetramantane. The observed dimers gave further proof to the chiral identification, and also showed that the observed tilt was not caused by the molecule-molecule interaction, but by the molecule-substrate interactions of the enantiomers. It also demonstrated, that the submolecularly resolved AFM images can be used to identify the orientation and enantiomer in groups of molecules.

4.2.5 Outlook

With the possibility of a fast identification of the racemate with the help of the AFM, further steps should be undertaken in the future. The potential to scan large islands and to identify enantiomers with the AFM is a powerful tool to investigate the self-assembly process of [123]tetramantane. In future research, the self-assembly process of [123]tetramantane on different substrates could be analysed by measuring a larger number of dimers to determine for example whether a enantiomer separation takes place with a different sample or preparation protocol. The AFM tip can also be used to manipulate single molecules. This feature, applied to separate the molecules, would open the door to manually created structures. As already shown in our analysis, there is a good chance that the STM scans could be sufficient for chirality identification. If this approach is further pursued, the scanning time could be decreased significantly. With enough information at hand, an automatic structure identification program could be written to support the manual analysis. With the scan speed in STM exceeding the scan speed of AFM by far, and in combination with an automatic structure identification, large islands could be characterised within seconds.

5 Conclusion And Outlook

In this work, we presented new data needed for the spring constant determination of qPlus sensors in AFM, which were applied afterwards with CO functionalized tips to gain new insights into the structure and orientation of self-assembled diamondoids.

In the first part of this work, we introduced a new method for the determination of the spring constant for qPlus-sensor type designs. In experiments and simulations we found the origin for the calculation of the spring constant to be located within the bulk glass body of the quartz tuning fork. With the correct origin for the beam formula it is now possible to accurately calibrate qPlus sensors, which in turn allows the measurement of absolute forces in the nanoscopic regime with a new level of precision. The deviation between the formerly used origin of the spring constant and the newly determined origin caused a minimum change of 60% rising up to over 500% in the effective spring constant. The new accurate origin is particularly interesting for the determination of absolute forces on the nanoscopic scale, especially of bottom-up approaches, since the strength of molecular bonds between single molecules can be determined without any approximation errors. It is one important step towards the analysis of two-dimensional molecular structures, which is indispensable for a successful implementation of self-assembled monolayers in future applications.

In the second part of this work, the structures of self-assembled diamondoid monolayers were comprehensively analysed with the application of STM and AFM. For the first time, diamondoids were sub-molecularly resolved with CO-functionalised AFM. The combination of both techniques allowed to determine distinctively the mode of growth, the identification of the adsorption structure, and the intra-molecular orientation. In addition, the chirality of small, bulky [123]Tetramantane molecules could be visualized for the first time, which could be the first element for a new method of molecular structure identification. With a combination of constant and variable height microscopy modes, we were able to show that the AFM is a suitable instrument for the identification of threedimensional enantiomers or other smaller three-dimensional molecules. In future research, this technique can also be adapted to the geometry of other molecules to identify the chirality. Furthermore, the combination of AFM and STM could allow a faster identification of a large number of molecules. This could be achieved by the distinct identification of molecules with sub-molecular AFM scans and a subsequent correlation of the AFM and STM images. If the existence or ratio of enantiomers in unknown samples have to be determined, this technique would allow a faster, more precise identification. A final step could be the development of automated techniques for enantiomer separation with the help of SPM techniques, for example by the application of different substrates or the induced growth of mono-enantiomeric islands through the selective manipulation with SPM.
Appendix

Check list for the successful application of the constant height scans for sub-molecular measurements.

- Retract the tip and adjust the AFM parameters: Find correct resonance frequency, adjust the amplitude to a small value that still is not over-damped, adjust phase, and turn on the PLL.
- Fast STM scan with CO-tip to find suitable area for AFM scan.
- Zoom in on area of interest.
- Start the "detect plane" feature of the MATRIX software to detect the tilt of the scan area. Important: When starting this feature, the outer rim of the scanning area should not have any protrusions or depressions. The tilt of the scanning area is averaged over the outer lines, and therefore these irregularities have a large effect on the overall tilt.
- Stop the STM scan.
- Enter a higher Δz value than the default STM scan setting (setpoint: 20 pA and gap voltage: 0.2 V) to avoid crashing the tip.
- Deactivate the feedback loop.
- Decrease the bias from 0.2 V to -0.005 mV.
- Start the AFM scan.
- Slowly approach the surface by manually decreasing the Δz value until the desired contrast appears.
- Start measurement again with a low speed of 0.16 seconds data acquisition time per data point and sufficiently high resolution (depending on scan size; e.g. 250 lines x 500 points for a 1.5 nm x 3 nm scan).



Fig. 5.1: Two photographs of the sublimation procedure directly outside of the AFM are shown. Left: Side view of sublimation procedure. The sample is held by the wobble stick and positioned directly over the evaporation gun, which is mounted in the manipulator. Right: Front view showing the open shielding and the wobble stick positioned over the manipulator.

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Declaration of Authorship

I declare that I have completed this dissertation single-handedly without the unauthorized help of a second party and only with the assistance acknowledged therein. I have appropriately acknowledged and cited all text passages that are derived verbatim from or are based on the content of published work of others, and all information relating to verbal communications. I consent to the use of an anti-plagiarism software to check my thesis. I have abided by the principles of good scientific conduct laid down in the charter of the Justus Liebig University Giessen "Satzung der Justus-Liebig-Universität Gießen zur Sicherung guter wissenschaftlicher Praxis" in carrying out the investigations described in the dissertation.

Cologne, November 26, 2017

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