An analysis of atomic manipulation, intermolecular resolution and the artefacts

of dynamic force microscopy



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Abstract

In this thesis we go through a journey of atomic manipulation of Pb dimers on Si(100), then we examine the limitations of AFM in intermolecular resolution and we take a closer look at a very promising technique named simultaneous STM/AFM which opens new horizons in the field but is part of an ongoing debate as it is still under development.

NC-AFM imaging of adsorbed Pb dimers on Si(100) provided detailed information of the Pb configuration, which agrees with previous STM studies. The lateral force required to move a Pb dimer is related to the adsorption of the dimer on the surface, the associated potential energy land scape and in some cases the interaction of the Pb dimer with its neighbouring dimers.

In the next part of this thesis we examine the adsorption of a small organic molecule (NTCDI) on Si(111)- (7×7) and we report two energetically preferable geometries among others.

In the last part of this thesis, we present an analysis of the crosstalk effect using an Omicron commercial qPlus sensor and a home built sensor with two system configurations and we compare them with a Createc commercial system. The results show that in order to avoid crosstalk the range of the STM operational pre-amplifier and the optimal electronics wiring play a major role.

List of publications

Sweetman A M, Jarvis S P, Sang H, <u>Lekkas I</u>, Rahe P, Wang Y, Wang J, Champness N R, Kantorovich L, and Moriarty P. Mapping the force field of a hydrogen-bonded assembly. Nature communications 5, 3931 (2014).

Jarvis S P, Sweetman A M, <u>Lekkas I</u>, Champness N R, Kantorovich L, and Moriarty P. Simulated structure and imaging of NTCDI on Si (1 1 1)-7 7: a combined STM, NC-AFM and DFT study. Journal of Physics: Condensed Matter, 27(5), 054004. (2014).

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Stirling J, <u>Lekkas I</u>, Sweetman I, Djuranovic P, Guo Q, Pauw B, Granwehr J, Lvy R, Moriarty P. Critical assessment of the evidence for striped nanoparticles PloS one 9.11 (2014): e108482

Sweetman A, <u>Lekkas I</u> and Moriarty P. Mechano-chemical manipulation of Sn chains on Si (100) by NC-AFM Journal of Physics: Condensed Matter 29.7 (2016): 074003.

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Chapter 1

Introduction

The first topographic image of a flat surface with atomic resolution was achieved in 1983 with the invention of the scanning tunnelling microscope (STM) [1]. The STM uses the quantum mechanical tunnelling current flowing between the tip and the sample as the imaging signal, and is therefore limited to study conductive surfaces. The invention of the STM introduced the family of scanning probe microscopy (SPM) techniques which has been widely used for imaging and manipulation of molecules, atoms and structures up to the scale of micrometers.

In SPM a probe raster scans a sample surface recording the interactions occuring in the tip-sample conjuction. The nature of the tipsample interaction can be used to map specific properties of the recorded surface into the form of an image. The first artificial atomic assembly came a few years later, in 1990 from Eigler and Schweizer, manipulating Xe atoms on Ni(110) surface spelling the IBM logo. (see Fig. 1.1(a) and (b) [2]).



Figure 1.1: The initial and the final STM topographic images for (a,
b) The construction of Xe atoms on a Ni(110) surface assembly and
spelling the IBM logo [2]; (c, d) Building a Au₂₀ chain on NiAl(110) [3].

This thesis covers the manipulation of metal dimers on a silicon surface, molecular adsorption, the intermolecular imaging and takes a closer look at simultaneous STM and AFM technique more specifically.

Molecular and atomic manipulation are commonly performed using STM. Some example where STM applies are on artificial nanostructures such as the formation of atomic wire [3], studying the properties of single-molecule devices [4–6], computation with individual molecules and doping of single molecules [7]. In addition, examining devices with interesting quantum mechanical properties [8–10], pick up of CO molecules [11], and manipulation of water clusters and lateral manipulation of atoms [12].

The atomic force microscope (AFM) was introduced shortly following the invention of the STM in 1986 [13]. AFM is another probe based microscope but uses the forces acting between the probe and the sample as the imaging signal (AFM will be described in particular detail in Chapter 2). Atomic resolution with AFM was claimed to be achieved on a Si(111) surface, but in those results the AFM image was appearing different than the STM image. The image acquired by AFM was lacking of defects and cornerholes on the surface which made it less accurate than the STM image [1]. The difficulty of achieving an atomically sharp tip from the regular contact between the tip and the sample made true atomic resolution impossible. Nine years later, Giessibl et al. [14] introduced a new tip-sensor (qPlus) for the AFM where in principle the tip would not come in contact with the surface and the so-called true atomic resolution was revealed in 1995 with the qPlus sensor (Fig. 1.2). This new-found atomic resolution capability paved the way for a rapid increase in the capabilities of NC-AFM.

Since then, a remarkable number of studies have been conducted on the manipulation of atoms and molecules not only on conducting surfaces but also on semiconducting and insulating surfaces. The advantage of the AFM is that it is not limited to conductive surfaces. Moreover AFM enables mechano-chemical force in the absence of bias voltage to be explored and exploited at the atomic level.

1.1 Atomic manipulation

From the invention of the AFM [13] to the first true atomic resolution [14] image ten years later, it took another decade for atomic manipulation to be achieved [15] with the AFM. This force in the absence



Figure 1.2: The first AFM image with 'true' atomic resolution. The three regions of image quality, are marked with dashed lines, starting from the marking of the lower quality regions of the image, until a few scan lines were achieved with high quality atomically resolved resolution. Adapted from [14]

of current flow between the tip-sample junction. This 'delay' is based on the different operational principles of these two systems (ie. STM and AFM), and hence on the instrumental complexity (Chapter 2).

In the AFM the tip-sample interatomic forces are responsible for the contrast and additional long range interactions. The long range forces equate to the van der Waals force, the electrostatic force and the magnetic-dipole interaction (if present) [16, 17].

The first atomic manipulation using chemical force alone was reported by Dujardin *et al.* in 1998 on Ge(111)-c(2 × 8)) using an STM tip without a current flow between the tip-sample junction. However, the changes in the tip-sample interaction during the manipulation could not be recorded [18]. In 2003 vertical manipulation was achieved by using a nanoindentation method on Si(111)-(7 \times 7) reconstruction [19]. After obtaining an image with atomic resolution, the AFM tip was placed on the selected adatom. A nanoidentation was performed with an open feedback loop while measuring the oscillation amplitude and the frequency shift channel. The process was stopped when a 'jump' was observed on the frequency shift channel and a new image was obtained with the same parameters (feedback loop on) with the previous image. Oyabu *et al.* reported that the adatoms were removed from the surface. In Fig. 1.3 the manipulation of the adatoms next to a cornerhole and central adatom are shown. This is the first example of vertical AFM manipulation where the interaction of the tip-sample system during the manipulation was recorded [19].

A few years later, the same group reported lateral manipulation of an adsorbate coming from the tip apex. The adsorbate was manipulated along the atomic rows of the Ge(111)-c(2 × 8) surface (Fig. 1.4) using the raster scan movement of the tip [20]. In the same experiment manipulation of Sn on the Ge(111)-(2 × 8) surface was reported. The manipulation was based on the influence of the presence of the tip on the local surface potential. Therefore the atoms could overcome the 1 eV energy barrier of the surface at low temperatures.

The first artificial atom assembly constructed using AFM came from Sugimoto *et al.* [21] who manipulated Sn atoms on the Ge(111)-c(2 × 8),



Figure 1.3: Sequence of topographic NC-AFM images showing two mechanical single atom vertical manipulation processes performed successively over the selected atomic positions of the Si(111)- (7×7) surface marked with a circle in (a) and (b), respectively. Vacancies created at the selected atomic positions (c). Adopted from [19].



Figure 1.4: Sequence of consecutive topographic NC-AFM images showing the lateral manipulation of an adsorbate deposited on top of a Ge(111)- $c(2 \times 8)$ surface. This adsorbate is manipulated by changing the slow scan direction (indicated by the arrows in each image), and by switching the tipsurface attractive interaction force from a value that induces the movement of the adsorbate (red arrows) to a value that does not (blue arrows) [20].

spelling out the Sn symbol at room temperature. After imaging the surface at tip-surface interaction forces that do not activate the interchange between Sn and Ge adatoms (Fig. 1.5(a)), the scan size was reduced and the tip fast-scan direction was aligned with the line connecting the centres of the adatoms selected for manipulation. The surface was imaged until the line connecting the centres of the adatoms was reached, and the slow scan was stopped at this position. Successive topographic scans over this line during which the tip-surface distance was gradually reduced led to adatom interchange. This process is monitored by a swap in the height signals associated with each adatom type (Fig. 1.5(b)). The surface area was imaged again without perturbing the adatoms (Fig. 1.5(c)). The Sn atoms were strongly bonded on the Si(111) surface. This protocol has been successfully performed on a variety of surfaces such as Sn on Si(111), In on Si(111) and on Sb substitutional atoms at the Si(111)-(7 × 7) surface [20].

When in close proximity to the surface, the tip changes the surface local potential, lowering the energy barriers for in-plane interchange diffusion below the point where the hopping rate is activated at room temperature and by the directionality of the movement of the tip, a potential path opens that allows the atom to move in a controlled manner. Also on the study of the lateral manipulation of the adatoms on Si(111)-(7 \times 7) was shown that the tip induces structural relaxations that weaken the adatom surface bonds and plays a major role on the local reduction of the natural diffusion barriers to adjacent adsorption positions, from 0.8 eV to 0.3 eV. When the tip is in close proximity with the surface in the above mentioned system, can cause vertical interchange between Sn



Figure 1.5: Sequence of topographic images illustrating the method for the controlled lateral manipulation of substitutional Sn adatoms in the Ge(111)-c(28) surface. (a) Imaging the surface and allying the tip in the direction as indicated by blue arrow, (b) The surface was imaged until the line connecting the centres of the adatoms (grey arrow) then the tip movement was continued by reducing the tip-surface distance, and (c) the final result of the manipulation process. Adopted from [21].



Figure 1.6: Sequence of NC-AFM topographic images describing the complex atomic patterning by vertical manipulation at room temperature [22].

atoms from the surface with Si atoms from the tip [22]. Fig. 1.6 shows the sequence of the images of the vertical interchange. The result is the silicon chemical symbol spelled with Si atoms on Sn layer.

A rather different type of atomic manipulation has been performed in our group by Sweetman *et al.* for the Si(100)-(4 \times 2) reconstruction. In this reconstruction the surface forms dimers with one atom sitting up and the other lower in the surface, a description of the surface and its properties is given in Chapter 3. The tip was positioned over the lower atom of the Si dimer and then it was approached closer to the sample until a tip-sample interaction due to the dimer flip was observed. The flip event is based on the covalent interaction between the tip and the sample [23]. In Fig. 1.7, step by step flipping of surface dimers is shown.

Terms and co-workers accurately determined the threshold forces for the manipulation of a single atom on a metal surface [24]. The vertical and the lateral forces were measured during the manipulation of a Co atom on a Pt(111) and a Cu(111) surface. The result was compared with



Figure 1.7: Sequence of stick and ball and NC-AFM topographic images showing the before and after manipulation of atoms from dimer fliping. Adopted from [23].

the manipulation of a CO molecule on a Cu(111) surface. The method that was used for the CO molecule is similar to that of Sugimoto and coworkers [21], as it was described above, but at cryogenic temperatures. The force required to move a Co atom on the Cu(111) surface was almost found to be an order of magnitude lower than the manipulation on Pt(111). The surface structure and the adsorption site of the Co atom are equivalent on both surfaces. In addition, in order to characterise the adsorption stability of the atom on the different surface they combined three-dimensional maps of the tip-sample interaction force for both cases and they calculated the tip-adatom interaction [24].

1.2 Molecular and sub-molecular imaging

Bartels *et al.* [25] introduced a robust method for functionalising the tip of the STM with a molecule. By appling a voltage pulse a CO molecule would be transfered from the surface to the tip and vice versa. Similarly in AFM, tip functionalisation was also investigated especially after the invention of the qPlus sensor, resulting in molecular and submolecular resolution. A variety of functionalised tips were investigated in order to achieve higher resolution, especially on organic molecules. The AFM tip was functionalized by picking up individual atoms or molecules, with vertical manipulation using the technique described by Bartels *et al.* The highest resolution was reported in 2009 with a CO- terminated tip (Fig. 1.8 (a)) and revealed the chemical achitecture of a pentacene molecule (Fig. 1.8 (b)) [26,27].



Figure 1.8: (a) Model of a CO-functionalised tip above a pentacene melecule [28]; (b) constant height AFM of pentacene molecule with CO-functionalised tip. Adopted from [26].

Sub-molecular imaging is now a common practice despite the fact that the CO tip functionalization has a 30% yield [26]. The architecture of molecules and especially asphaltines which posed a challenge for structural analysis have been reported [29]. Thermally induced cyclization cascades of enediynes have been studied with a CO tip and the structure of the reaction products were revealed. Fig. 1.9 shows the reactant and the products of the reaction. The sample was heated at 90°, resulting in three products and imaged with AFM [30].

Riss *et al.* reported a cyclic reaction of a polymer and the different bond length and contrast between the atoms along the molecule was illustrated [31]. Due to the feature contrast reported with this technique there has been exceptional interest in determing submolecular structure for C_{60} and the variation of the carbon-carbon bonds is also shown in C_{60} and polycyclic aromatic hydrocarbons [32].



Figure 1.9: Constant height AFM images (a)-(d). (a): The Reactant; (b)-(d): The products of the reaction; (e)-(h) The schematics of the molecules in (a)-(d) respectively [30].

In addition to CO- terminated tips, Cl- and O- terminated tips have been used to reveal submolecular resolution [33]. There are also cases where the tip was spontaneously functionalized via interaction with a surface-adsorbed molecule and the intramolecular resolution was resolved on Si(111) (7×7) of an NTCDI molecule [34]. The experimental results were compared with DFT calculations and show no significant difference between the hypothesis of having a NTCDI molecule attached on the tip and the oxygen pointing down with a CO-terminated tip.

The inter and intramolecular contrast has been reported with scanning tunnelling hydrogen microscopy (STHM). In this technique H_2 gas was released in the chamber. Eventually a H_2 molecule was trapped in the tip-sample conjunction by the Pauli repulsion and the mapping of the surface in conducted through the movement of the trapped H_2 in the tip-sample conjunction [35]. Fig. 1.10 shows stick and ball model and STHM images of the molecules.

Naturally the next step, now that sharp intra-molecular contrast has been established and the variation of the intra-molecular bonds have been reported, is to expand the study towards inter-molecular resolution. Self-assembly of molecules and supramolecular assembly play a key role in 21^{st} century chemistry and surface science due to the property of the molecules to be directed through non-covalent interactions, such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals or electrostatic forces. The first claim of the visualization of a hydrogen bond came from Zhang *et al.*, studing 8-hq molecular assemblies on a Cu(111) surface using AFM [36](Fig. 1.11). The authors claim that the contrast becomes visible due to short range Pauli repulsion. This claim of visualizing intermolecular bonds triggered intense debate



Figure 1.10: (a-d) Herringbone phase of PTCDA molecules on Au(111). (a) Structure model, molecular orientation and structure in analogy to bulk β -PTCDA. The molecular quadrupole moment and the unit cell are indicated. (b) Conventional STM image in constant height mode. (c) STHM image. (d) Superposition of the image from (c) with the structure of the herringbone phase in (a). White lines mark possible hydrogen bonds. [35].



Figure 1.11: AFM measurements of 8-hq assembled clusters on Cu(111). (A and B) Constant-height frequency shift images of typical moleculeassembled clusters and their corresponding structure models (C and D) [36].

about the capabilities and artefacts associated with AFM.

In 2014 Hapala *et al.* [37] introduced a model and analysis which took into account the flexibility of the tip apex, inspired by Pavlicek who showed high-resolution images of 'bonds' for DBTH molecules in areas where chemical bonds were absent [38]. In addition, the flexibility of the tip and the backround forces during imaging were taken into acount for correcting the length of the submolecular features [39,40] and the reactivity of the tip-molecule conjuction [41,42]. Haemaelaeinen *et al.* [43] studied a four bis(para-pyridyl)acetylene (BPPA) molecules form a tetramer stabilized by hydrogen bonds. This results in two nitrogen atoms from neighboring molecules being forced close together, without chemical or hydrogen bonds being formed between them, and with experimental results and calculations showing that a bond-like feature can



Figure 1.12: (top row) Experimental constant-height AFM images with a CO tip taken at different heights on top of the tetramer junction showing the appearance of both $C - H \dots N$ and N - N intermolecular contrast at close tip-sample distances. (bottom row) Simulated constant-height AFM images with a flexible CO tip at the given heights showing the appearance of the same intermolecular contrast. Adapted from [43].

be recorded in the absence of a chemical bond (Fig. 1.12).

Our group conducted a study on C_{60} self assemblies with a C_{60} terminated tip and the results show an inter-molecular contrast where hydrogen or halogen bonds are entirely absent [44]. Fig. 1.13 shows inter-molecular contrast captured in H₂O @ C_{60} and C_{60} assemblies. The DFT calculations show that this contrast is coming from the "swing" of the C_{60} molecule sitting at the apex of the tip.

In 2016 van der Lit *et al.* [45] imaged bis-(para-bezoicacid) acetylene (BPBA) molecules which contained polarized groups. The tips used in that experiment were either CO- (negatively charged) or Xe- (possitively charged) terminated. The images of the molecular "bonds" appear to differ due to the nature and the acting electrostatic forces of the tip [45]. Submolecular resolution was achieved due to the small size of the oxy-



Figure 1.13: Constant height AFM images (a): A six-layer film of H_2O @ C_{60} , (b): C_{60} molecules revealing connecting features between nearest neighbour molecules, (c) Line profile measurement along the white line shown in (a), and (d) Schematic of the C_{60} packing arrangement and locations of apparent intermolecular features. Adapted from [44].

gen atom sticking down, the chemical inertness of the CO molecule and at small tip heights which bring the O- atom and molecule within the Pauli repulsion, i.e. the increase in the kinetic energy of electrons due to the overlap of electron clouds of the tip and molecule and by taking into account the van der Waals (vdW) interactions. They showed that CO and Xe terminated tips provide different submolecular contrast. The submolecular contrast was, thus, driven by a combination of the attractive van der Waals forces, the repulsive Pauli interaction, and the electrostatic interaction that can be either attractive or repulsive.

1.3 Simultaneous force and current measurements

The simultaneous AFM/STM measurements are exceptionally important in modern nanoscience, since the technique can provide much more information than the AFM or STM alone. That was particularly important since measurements with the precision power of even a single electron charge were a milestone in the exploration of nanostructures [46]. In another case, the AFM/STM technique helped shedding light on the relationship between the strength of a chemical bond and the charge transport through that particular bond [47]; it was shown that in the cases of covalent or metallic bonds the attractive short range force reaches its maximum, the tunnelling barrier collapses and the current saturates at a value of one conductance quantum approximately. In addition, the formation of the covalent bond induces accumulation of electron density inside the tunnelling gap [48]. This information was useful in deciphering the tip-sample interaction in the SPM field itself where a tip is used to acquire images of atoms and molecules deposited on a surface, as well as in the atomic manipulation techniques: For example, in the case of tip-sample interactions with a weaker character than the covalent bonds (e.g. interaction between CO-functionalized tip and molecules deposited on a surface), weak electrostatic and Van der Waal interactions take place between the tip and the sample instead of covalent or metallic bonds. In this case the tunneling barrier does not collapse and the tunneling regime is preserved even when a mechanical contact between the tip and the sample is occurring, even though it is possible to observe current-on-distance phenomena for distances in which the Pauli force starts to dominate over the attractive bonding force [49].

Moreover, Weymouth et al used STM/AFM measurements to describe a phenomenon where the surface area beneath the tip can become charged on a local scale, generating a repulsive force between the sample and the tip and affecting the image contrast in AFM imaging. This effect affects directly the electrostatic attraction between the tip and the sample, as the electrostatic force is voltage dependent and is called phantom force [50].

In the next chapter, I cover the basic principles of the SPM with a particular introduction to basic STM and AFM principles of operation and explaining the theory behind the experimental techniques. All of the protocols of the methods used and sample preparations are shown in chapter 2 and chapter 3 respectively.

Chapter 4 discusses the imaging of a submonolayer coverage of Pb on Si(100) and its characteristics using NC-AFM. Additionally, in that chapter, I show a lateral manipulation process of a Pb dimer along the silicon rows of a Si(100) surface (more details about the surface characteristics can be found in chapter 3) and the force needed to break a Pb chain structure and move the dimer. Also I examine the transfer function and the excitation channel in order to make sure how reliably the force values are measured.

In Chapter 5, I discuss the adsorption of NTCDI molecule on Si(111) and a NTCDI molecular assembly network on Ag passivated Si(111) where contrast is shown at the positions where hydrogen bonds are expected to be. Additional work has been conducted in order to understand the origin of the intermolecular contrast. The nature, size and flexibility of the tip has been a topic of a great interest since the revelation of the intermolecular resolution [37, 39–43, 51].

In the final results chapter 6, I discuss the so called crosstalk, effect as it was reported by Majzik *et al.* [52] and the crosstalk occurring in two commercial systems.

1.4 Summary

Overall the SPM is a powerful tool, able to support a vast range of experimental techniques including imaging and manipulation of atoms, characterisation of organic molecules and promising in the understanding of the electronic properties of surfaces. In this thesis we focus on two SPM techniques: the STM technique, which is useful for conducting and semiconducting surfaces and the AFM technique which also covers insulating surfaces. In particular, the AFM can be used as a manipulation tool to extract the mechanochemical force down to the single bond limit, as will be described in this thesis. A combination of the STM and AFM techniques, usually referred to as simultaneous STM/AFM, appears to be very promising, as it provides more information than STM or AFM alone, but its limitations have been under an ongoing debate.

Chapter 2

Theory of Scanning Probe Microscopy

The family of scanning probe microscopes (SPM) represent a large range of instruments that are used for the study of surfaces of a variety of materials in the range of a few micrometers down to the scale of Å. The core elements of any probe microscopy are the probe itself and the piezoelectric actuators used to position and move it across the surface.

The general operating method of an SPM can be described in six steps. Initially, the piezoelectric approaches the tip closer to the sample surface vertically, until the distance between tip-sample is ~ 1 nm (Fig. 2.1). There are several interaction mechanisms between the tip and the sample, such as tunnelling current or force, which would affect the tip approach. The scanner moves the tip parallel to the surface. To acquire an image the probe is scanned back and forth across the surface. Ideally the probe is moved a long distance linearly in one direction and the probe returned to the start position. Then the probe is moved a short distance perpendicular to the initial movement and the long linear motion is performed again. By repeating the long and short movements it is possible to build up a complete image. This process is known as raster scanning. By measuring the probe-surface interaction as a function of the position a map of the interaction is produced. Operating the microscope in this way is known as constant height mode. This mode requires that the z-position of the probe is kept constant.

In cases where the sample surface has large features or the x-y dimensions of the surface are tilted there is the risk of the apex of the probe contacting the surface. This may lead to probe wear and/or the destruction of the sample surface. To avoid these unwanted effects, a feedback loop is established such that a constant value of the probesample interaction is maintained. This is known as the topographic mode and the produced images are maps of constant interaction.

In the following section the basic principles of the two widly used SPM techniques are explained. The first SPM technique which was developed was the scanning tunnelling microscope (STM) by Binning, Rohrer, Gerber and Weibel [1].

2.1 Scanning Tunnelling Microscopy

When a voltage is applied to two metals separated by a thin insulating barrier, a tunnelling current can be measured between the electrodes. This quantum mechanical phenomenon was first reported by Giaever [53] in the context of applying a potential difference between two superconductors separated by an oxide layer (insulating film) and recording a current flow versus the applied bias voltage. Binnig *et al.* [1] subsequently extended this type of tunnelling experiment into a device that can scan and map conductive or semi-conductive surfaces with a probe by using the tunnelling current as the main and controlled interaction between the tip and the sample.

Fig. 2.1 shows the basic set-up of an STM. A sharp metal tip is positioned at a distance of less than a nanometre above the surface of a conducting sample and a voltage in the range of a few volts is applied between the tip and the sample. When the tip and the sample are brought in close proximity a small tunnel current can flow between them. This current is a strong function of the probe-sample separation and thus can be used to infer the topography of the sample. The direction of the tunnel current depends on the polarity of the bias. At negative bias, electrons tunnel out of the sample and the images show the sample states of the surface. While at positive bias, there is flow in the opposite direction and images show the empty states of the surface.

2.1.1 Tunnelling

Classically, when the potential barrier is greater than the energy of the electrons no current can flow between the tip and the sample. However, in quantum mechanics according to the Schrödinger equation a particle has a probability to pass to a region with larger potential than the potential of the particle. This region is called potential barrier. On the other hand, if the width of the potential barrier is finite and on the other



Figure 2.1: The principals of scanning tunnelling microscopy. When a potential difference is applied between the tip and the sample, and the tip is in close distance with the sample surface tunnelling current is established. A feedback mechanism reads the set-point of the current and regulates the tip-sample distance to keep the interaction constant. The piezocrystal is also responsible for the raster scan motion of the tip, contributing in the construction of an STM image.

side of the potential there is a region which demands lower energy than the energy of the particle, then there is a probability for the particle to be in the potential barrier and in the region beyond the barrier. This effect is known as quantum tunnelling. The current in STM is usually in the range of pA to nA. For reasons discussed below, the tunnel current has an exponential dependence on the tip-sample distance. When the current between the tip and sample increases by an order of magnitude the tip-sample distance decreases by approximately 1Å.

In Fig. 2.2 an energy diagram of an 1-D model of tip-vacuum-sample system is shown. The probability decays exponentially within the potential barrier. If a large number of particles are found in a region then only a small percentage will be able to penetrate the barrier.

In the case of a rectangular potential barrier of V_o with a width L in one dimension, the solution of the corresponding time independent Schrödinger equation is given by:

$$\Psi(z) = \begin{cases} Ae^{ikz} + Be^{-ikz} & z < 0\\ Ce^{-\kappa z} + De^{\kappa z} & 0 < z < L\\ Fe^{ikz} & z < L \end{cases}$$
(2.1)

For a particle to travel from left to right with $E < V_o$ the wave numbers are given by:

$$k = \sqrt{\frac{2mE}{h^2}} \tag{2.2}$$

and



Figure 2.2: Schematic showing an electron wave function incident on a 1D barrier. Initially the electron is travelling in the tip material, then the exponential decay of the wave function is shown in the vacuum area and finally the electron's wave function with a diminished amplitude is shown in the sample.

$$\kappa = \sqrt{\frac{2m(V_o - E)}{h^2}} \tag{2.3}$$

where *m* the mass of the particle, *E* is the kinetic energy of the particle and *h* is the Planck constant. These functions (Eq.2.1) and the derivatives must be continuous and continuously differentiable. So they must be equal at x = 0 and x = L. This gives four equations for the five coefficients A to F. The transmission coefficient is $T = |F|^2/|A|^2$, therefore is given by:

$$T = \frac{1}{1 + \frac{V_o^2 sinh^2(\kappa L))}{4E(V_o - E)}}$$
(2.4)

When the rectangular potential is high and has large width $\kappa L >>$ 1, the T becomes:
$$T \approx \frac{16E(V_o - E)}{V_o^2} e^{-2\kappa L}$$
(2.5)

The transmission probability and thus current have an exponential dependence. This dependence applies to the tunnelling current therefore for Eq.2.5 one order of magnitude increase is approximately 1Å, of z displacement closer to the surface.

The above one dimensional case can explain the current-distance dependence of the tunnelling current. The three dimensional description is moderately complicated and it has been shown by Bardeen [54] for quantitative description.

The transition probability between the tip and the sample can be demonstrated by applying first-order time dependent perturbation theory as:

$$T = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} [f(E_{\mu})[1 - f(E_{\nu} + eV)] - f(E_{\nu} + eV)][1 - f(E_{\mu})] \times |M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\nu})$$
(2.6)

where f(E) is the Fermi function and expresses the occupation of the states. E_{μ} is the energy of the electron states of the tip and E_{ν} is the energy of the electron states of the sample. V is the bias voltage applied to the sample and $M_{\mu\nu}$ is the transaction on tunnelling matrix element which takes into account the wave form overlap of the tunnelling electrons between tip (X_{μ}) and sample (Ψ_{ν}) . The Dirac function ensures that the tunnelling is elastic. The Eq. 2.6 in case of low temperatures and small bias can be written as:

$$T = \frac{2\pi e^2 V}{\hbar} \sum_{\mu,\nu} |M_{\mu\nu}|^2 \delta(E_{\mu} - E_F) \delta(E_{\nu} - E_F)$$
(2.7)

In this case, only electrons at the Fermi level E_F contribute to the tunnelling current. When using Eq. 2.7 to calculate the tunnelling current between the tip and the sample, the essential difficulty is the calculation of the matrix element $M_{\mu\nu}$.

Tersoff and Hamann developed a theory that enabled the interpretation of STM images [55]. They assumed the tip to be locally spherical and used s-like wave functions for the tip states. The following result for the tunnelling current between the tip and the sample was obtained:

$$T = \frac{32\pi^3 e^2 V(\Phi^s)^2 D_{tip}(E_F) R^2}{\hbar \kappa^4} e^{2kR} \sum_{\nu} |\psi_{\nu}(r_o)|^2 \delta(E_{\nu} - E_F), \quad (2.8)$$

where $\kappa = \sqrt{\frac{2m\Phi^s}{\hbar^2}}$ with the work function Φ^s of the sample surface. $D_{tip}(E_F)$ denotes the tip density of states at the Fermi level, and r_o and R are the center and the radius of the tip curvature, respectively. The important conclusion from the last equation is that the tunnelling current is proportional to the sample local density of states (LDOS) $\rho(r_o, E_F)$ at the Fermi level at the position of the tip. The LDOS at position r is in general defined as:

$$\rho(r, E) = \sum_{\nu} |\psi_{\nu}(r)|^2 \delta(E_{\nu} - E)$$
(2.9)

Therefore, if the assumption of s-wave tip states is justified, constantcurrent STM images show topographic maps of constant sample density of states.

2.2 Atomic Force Microscopy

Despite the STM's strengths it has one clear weakness. A current cannot travel through non-conducting materials. In order to address this issue atomic force microscopy was developed by Binnig in 1986 [13]. AFM utilises the motion of a cantilever to derive the forces acting on a probe attached at the end of the cantilever. The motion of the cantilever is detected from a frequency detection scheme with a laser beam reflected from the back of the cantilever, or using a qPlus sensor which was used in our case, Fig. 2.3. There are two commonly used types of imaging technique used in AFM, the contact mode and the non-contact mode.

2.2.1 Contact mode AFM

In contact mode, the force F acting on the probe translates into a static deflection of the cantilever:

$$F = -k\Delta x \tag{2.10}$$

where F the force of the cantilever, k the spring constant and Δx is the deflection of the cantilever. The more the cantilever deforms, the interaction force is stronger. This equation can only be used when the deformation of the cantilever is significantly larger than the deformations of the tip and the sample.

The first atomic resolution was obtained in contact mode AFM. It turned out, that the contrast mechanism was not the imaging with a single atom at the end of the tip, but rather scanning with a tip that



Figure 2.3: Schematic diagram showing the basic principle of an AFM. Incident laser is reflected onto a photo-diode split into four quadrants. As the cantilever is deflected due to interatomic forces the displacement can be traced with the movement of the laser and a height image can be mapped in 3D.

had a large contact area with the sample surface and periodicity similar to that of the surface. The lack of defects on the measured image led to the conclusion that atomic resolution in contact mode AFM is difficult to be achieved. On the other hand, interpretation of the data is uncomplicated and easy to do. A feedback control is used to keep the cantilever deflection constant during the scan and a topography image of constant force is recorded.

2.2.2 Non-contact mode AFM

In non-contact AFM, the cantilever is excited by a mechanical actuator to oscillate at its resonance frequency f_o . This enables a stable operation of the tip at small tip-sample distances without making contact with the sample surface. The NC-AFM technique operates in the attractive region of the Lennard-Jones potential. It is also an advantage that lowfrequency and periodic noise can be filtered out using a bandpass filter centred around f_o . The true atomic resolution, as it was called, was seen with non-contact AFM and it was called true due to the observation of the surface defects [14, 56]. There are two basic methods operating the NC-AFM: amplitude modulation (AM) and frequency modulation (FM).

Amplitude modulation

In AM-AFM, the actuator operates at fixed frequency with fixed amplitude. When the tip is close to the surface, the tip-sample interaction will shift the resonance either closer to the driving frequency or further



Figure 2.4: Response of a free cantilever (Blue) and a cantilever experiencing an attractive potential (Red) to being externally driven. By exciting a cantilever just off resonance any frequency shift will result in a change n the amplitude with different sign for positive and negative frequency shifts.

from the driving frequency. This will cause the amplitude to rise or fall respectively (Fig. 2.4). In this case the oscillation amplitude can be used as a feedback mechanism to adjust the tip-sample separation and keep the amplitude constant. To resolve atomic corrugations, a high Q factor, in the range of ~10⁴-10⁵, is desirable especially in ultra high vacuum conditions. The high Q factor increases the integration time that is required for the change in amplitude to decay ($\tau \sim \frac{2Q}{f_o}$). With high Q values the response time is long making the AM mode very slow. In this thesis the AM-AFM wasn't used so the technique is not described any further.

Frequency modulation

In frequency modulated AFM (FM-AFM) the cantilever always needs to be excited on resonance, even as the resonance changes due to the tip-sample interactions. The Q decays on a time scale of $\tau \sim \frac{1}{f_o}$, that resolves the time consuming process of the AM mode. In this case the deflection signal is a shift in the resonance frequency (Fig. 2.4). The signal is directed through a bandpass filter, phase shifted or locked and fed back to the system. A phase-locked-loop (PLL) determines the oscillation frequency, and the frequency shift is used as the imaging signal. In this report, only FM-AFM technique was used and therefore the AM-AFM will be omitted. This technique was used for this thesis and the feedback mechanism is described in subsection 2.2.8.

2.2.3 Theory of atomic force microscopy

There are two broad types of derived forces: a) the long range forces deriving from interactions between the probe and the sample structure, including van der Waals, electrostatic forces, magnetic forces and contact potential forces; b) The short range forces consist of the interaction force between the probe and the surface at the atomic scale (Fig. 2.5). Both types of forces are interesting in order to gain atomic resolution.

The movement of the cantilever can be described as a damped simple harmonic oscillator. This can be described by Hooke's Law:

$$F(z) = -kz \tag{2.11}$$



Figure 2.5: Force-Distance curves of van der Waals, electrostatic and short-range forces.

When the tip is close to the surface The interaction force is the sum of:

$$F_{sum} = F_{spring} + F_{damp} + F_{driv} = -kz \tag{2.12}$$

where $F_{damp} = -b\frac{dz}{dt}$ the damping force, $F_{driv} = A_o \cos(\omega t)$ the driving force, with max amplitude A_o and frequency ω , and the spring force is given by Hooke's Law.

In AFM a cantilever is characterised by its spring constant k, fundamental eigenfrequency f_o and quality factor Q. The quality factor is used to describe the width of the resonance peak of the cantilever and is given by:

$$Q = \frac{\omega_o}{2\beta} \tag{2.13}$$

where $\omega_o = \frac{\sqrt{\omega_o^2 - 2b^2}}{2\beta}$ is the resonance frequency and $\beta = \frac{b}{2m}$. For Q > 1, through substitution and rearrangement the effective constant b can be written as:

$$b = \frac{m\omega_o}{Q} \tag{2.14}$$

which lead to a full expression for the motion of the cantilever by:

$$m\frac{d^2z}{dt^2} = -kz - \frac{m\omega_o}{Q}\frac{dz}{dt} + A_o\cos(\omega t)$$
(2.15)

2.2.4 Interaction forces

The total interaction force between the probe and the sample can be expressed as:

$$F_{tot} = F_{vdW} + F_{el} + F_{chem} \tag{2.16}$$

 F_{vdW} represents the van der Waals interaction forces, F_{el} the electrostatic forces and F_{chem} the short-range chemical force.

van der Waals forces

Van der Waals interactions are caused by fluctuations of electron densities of the atoms leading to a dipole like interaction between atoms. As a result these forces are always attractive. For two atoms separated by r the van der Waals force goes as r^{-6} . On the macroscopic scale the van der Waals interactions can be calculated using the Hamaker approach which involves integrating over their respective volumes [57]. Using this approach a spherical tip of radius r and a distance z from the sample surface we get the following expression:

$$F_{vdW} = \frac{HR}{6z^2} \tag{2.17}$$

where H is the Hamaker constant which is strongly dependent on both tip and sample material.

Electrostatic forces

Long range electrostatic force occur when there is a potential difference between a tip and a sample. The tip-sample conjunction can be regarded as a parallel plate capacitor leading to a force interaction of:

$$F_{capacitance} = \frac{1}{2} \frac{dC}{dz} U^2 \tag{2.18}$$

where $\frac{dC}{dz}$ is the time and distant dependence capacitance of the conjunction. As there is a potential difference the electric field induces charge in the junction leading to a capacitive build up. The force form

the charge given by:

$$F_{charge} = -(q_s + CV)E_z \tag{2.19}$$

where q_s is the induced charge of the tip, E_z is the electric field, C is the capacitance and V the bias voltage applied. Finally the total electrostatic force is given by:

$$F_{el} = -(q_s + CV)E_z + \frac{1}{2}\frac{dC}{dz}V^2$$
(2.20)

Therefore the resulting force will always be attractive.

Chemical forces

The short-range chemical forces occur when the overlap between the electron wavefunctions of the tip and the sample, becomes significant. Depending on distance the chemical forces appear either attractive or repulsive. The most common model used to describe the potential interaction of the chemical force is the Lennard-Jones potential [58].

$$V_{LJ} = E_b \left[\left(\frac{z_o}{z}\right)^{12} - 2\left(\frac{z_o}{z}\right)^6 \right]$$
(2.21)

where E_b is the binding energy and z_o is equilibrium distance. The corresponding force derived from the Lennard-Jones potential is given by:

$$F = -\frac{dV}{dz} \tag{2.22}$$

2.2.5 Detecting atomic corrugation

We now derive the relation between the force interaction between the probe and the sample and the recorded oscillation frequency of the cantilever which is used as the imaging signal. For the harmonic oscillator model we can describe the unperturbed motion $(F_{drive} = A_o \cos(2\pi f_o t))$ where f_o is the resonance frequency). The resonance frequency $f_o = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}$ where m^* the effective mass of the cantilever and k is the spring constant. The force between between tip and sample will cause a change in k. Assuming small cantilever amplitudes and tip-sample distances then $k' = k - (\frac{\partial F}{\partial z})$ [59]. If the force gradient is small in comparison to k and constant in the z direction, then the frequency shift can be approximated to:

$$\frac{\Delta\omega}{\omega_o} = \frac{\Delta f}{f} = \frac{k_{ts}}{2k} = \frac{1}{2k} \frac{\partial F}{\partial z}$$
(2.23)

where $k_{ts} = \left(\frac{\partial F}{\partial z}\right)$. From the above expression we see that for small amplitudes Δf is directly proportional to the force gradient. However for large amplitudes which are commonly used in AFM, this simple relation breaks down. Dürig [60, 61] and Livshits [62] derived the following expression:

$$\Delta f = -\frac{f_o}{\pi k A_o} \int_{-1}^{1} F_{ts} [d_o + A_o(1+u)] \frac{u}{\sqrt{1-u^2}} du \qquad (2.24)$$

where $u = \cos(2\pi f_o t)$.

2.2.6 Force deconvolution

Sader and Jarvis derived an equation for obtaining the force from the frequency $shift^1$ in eq.2.24 [63].

$$F(z) = 2k \int_{z}^{\infty} \left(1 + \frac{a^{\frac{1}{2}}}{8\sqrt{\pi(t-z)}} \right) \Omega(t) - \frac{a^{\frac{3}{2}}}{\sqrt{2(t-z)}} \frac{d\Omega(t)}{dt} dt \quad (2.25)$$

This equation is used in this report in a MATLAB script for the deconvolution of the Δf spectra obtained during AFM measurements.

Another method was introduced by Giessibl to obtain the force from the frequency shift using an inverse matrix method [64]:

$$F_{ts,j} = \sum_{i=1}^{N} M_{ji} \Delta f_i \tag{2.26}$$

Welker [64] used a statistical model to describe the deconvolution quality as a function of the oscillation amplitude. He finds that both approaches fit reliably to the statical models for amplitudes of 300 pm but the Sader-Jarvis method has a lower coefficient of determination for an amplitude of 137 pm.

¹Also Saber and Jarvis introduce the on-off spectroscopy

2.2.7 Grid spectroscopy

In grid spectroscopy, multiple force spectra² are taken above a grid of positions on the x-y imaging plane [65]. Multiple measurements in z are taken for each force spectrum, the final data represents a three dimensional array of spatially separated Δf measurements. The interaction potential can be extracted from each spectrum resulting in the potential landscape in three dimensions.

Gird spectroscopy measurements take considerable time. The spacing in z should be much smaller than the amplitude of oscillation to have accuracy of the force deconvolution, and the z range needs to extend far enough where no chemical interaction is detected. Usually the z range is selected at least 1 nm above the sample surface and 1000 points are chosen to be collected during the spectra. The number of pixels or spectra position in x-y plane to obtain a grid spectra, are usually in the range of 30×30 . Assuming that the interaction time in each point is 10 ms, to complete the grid at least 5 hours are required. In our case the grids were obtained at 5 K and took up to 22 hours. In such long experiments, it is important to introduce a method to compensate for drift of the sample relative to the tip, for this we use atom tracking [66] which will be explained in the next chapter.

2.2.8 Feedback mechanism in FM-AFM

Fig. 2.6 shows the diagram of the frequency modulation AFM feedback loop. There are two options to either, obtain a topography image from

²Although the term force-distance spectra is technically incorrect, it is widespread in the NC-AFM literature.

the surface by keeping the z feedback loop closed (constant frequency shift mode) or when open the z feedback and obtain a frequency shift map of the surface (constant height mode).



Figure 2.6: Schematic diagram of the frequency modulation AFM feedback loop. The physical observables are listed in the box to the right. The z feedback loop can be open resulting in constant-height mode, or closed switching in constant-frequency shift mode.

In the phase locked loop, as shown in Fig. 2.7, a phase detector compares two input signals and produces an error signal which is proportional to their phase difference. The error signal is then low-pass filtered and used to drive a voltage-controlled oscillator (VCO) which creates an output phase. The output is fed through an optional divider back to the input of the system, producing a negative feedback loop. If the output phase drifts, the error signal will increase, driving the VCO phase in the opposite direction so as to reduce the error. Thus the output phase is locked to the phase at the other input. This input is called



Figure 2.7: Schematic diagram of the phase locked loop.

the reference.

2.2.9 Dissipation signal and transfer function

As was described before, the centre of the FM-AFM instrument is the cantilever oscilating at its natural frequency driven by the piezo, which shifts upon interaction with a sample. The oscillation amplitude of the cantilever is kept constant by an automatic-gain-controller (AGC Fig.2.8), which adjusts the amplitude of the drive signal used to actuate the cantilever by piezoacoustic excitation. The dissipation signal refers to any change in the drive amplitude which is either related to the tip-sample dissipative forces (real dissipation) or it is assumed to be caused by non ideal behaviour of the instrument (apparent dissipation). The electronic structure effects theory [67, 68] supports that friction can be observed not only when two objects slide past each other in contact but also when two surfaces keep a small finite distance of a few nm while sliding. This phenomenon can induce phononic and electronic excitations called phononic and electronic friction which results in a change of resonance frequency and dissipation [67, 68]. Also atomic instabili-



Figure 2.8: The transfer functions consists of the self-excitation loop (gray boxes). The evolution of the self-excitation signal is described within the loop. The cantilever tip interacts with the sample; the bias voltage between the two is adjustable. The AGC maintains a constant cantilever amplitude by modulating the drive amplitude; this is valid if the amplitude responce of the detection system is flat. Adopted from [70]

ties are likely to occur when two solid surfaces move to each other in close proximity leading to temperature dependent atomic scale topography and dissipation images, this theory is called adhesion hysteresis and predicts that dissipation occurs through reversible jumps of surface atoms when a tip is close to the surface resulting in dissipating energies [69].

The cantilever transfer function during the experiment (Fig.2.8) experiences disturbance due to tip-sample conservative interactions, resulting the self-excited oscillation frequency to change. Additionally, the perturbed cantilever damping increases with the additional damping related to the tip-sample dissipative interactions. Therefore the phase of the cantilever varies to compensate for changes in the excitation system phase response. In addition, Labuda *et al.* [70] attributes several dissipation signals to the frequency response of the piezoacoustic cantilever excitation system which can lead to a large apparent dissipation by the coupling of the frequency shift to the drive-amplitude signal. Finally Weymouth *et al.* [50] demonstrated that there is a strong impact of the tunnelling current on the measured force on samples with limited conductivity, producing a lowering of the effective gap voltage through sample resistance which in turn lowers the electrostatic attraction resulting in a repulsive force (phantom force) affecting the probe measurements.

In ref [52] after obtaining the transfer function, a long-range dissipation signal was measured to be correlated with the frequency shift. This apparent dissipation was corrected by using a linear dependence of the apparent dissipation signal on Δf and the apparent dissipation was subtracted. The short-range dissipation signal appears flat at large distances, and when in close proximity on the sample surface a minor increase of the dissipation signal appears due to the adhesion hysteresis [69].

Chapter 3

Experimental details

3.1 Silicon

Silicon belongs to group XIV of the periodic table, capable of sp^3 -hybridisation resulting in the formation of a tetrahedrally-bonded covalent crystal with a face-centred-cubic (FCC) crystal with a basis of two atoms (Fig. 3.1). The lattice constant of the Si crystal is 5.43 Å, and its valence-conduction indirect band gap is 1.12 eV. The electronic structure of silicon can be controllably changed using dopants. Boron dopants result in p-type materials, while nitrogen, phosphorous and arsenic lead to n-type materials [71].

3.1.1 Silicon(100) surface

Silicon (100) represents the exposure of the bulk crystal along the (100) plane. The bulk-terminated surface comprises a periodic square array of silicon atoms separated by a surface lattice constant of 3.84 Å. Each atom on the surface has two unsatisfied dangling bonds creating a high



Figure 3.1: The crystal structure of diamond, silicon and germanium, consists of a two atom basis arranged around a face centred cubic lattice [72].

surface free energy. Tromp *et al.* [73] imaged first the surface confirming a structural model derived from LEED experiments. The dimers on the surface can be either symmetric or buckled leading to a (2×1) reconstruction and a $p(2\times2)$ or $c(4\times2)$ reconstruction respectively (Fig. 3.2). The ground state of the surface was shown using low temperature AFM [74,75] confirming theoretical calculations [76,77] that the $c(4\times2)$ is the ground state. The two unsatisfied bonds of the symmetric dimer lead to degenerate electronic states at the Fermi level making the buckled state preferable. The upper atom of the buckled dimer gains charge from the lower atom, due to redistribution of charge, resulting in two types of silicon atoms at the surface [77–79].

STM images of the surface, obtained at higher temperatures show symmetric dimer chains which can be explained by rapid thermal flipflop of the buckled dimers. The flip-flop motion of the dimer takes place on a shorter time scale than the acquisition of each pixel in a STM image, thereby recording the average position of each dimer that



Figure 3.2: Different reconstructions of the silicon (100) surface. Adopted from [80].

is showing a symmetric state [73]. Also using low temperature STM, the (2×1) reconstruction has been reported [81,82] but in this case the flipflop motion is activated by tunnelling electrons. Low temperature AFM images also show the (2×1) structure [74,83] at high setpoints where the probe apex comes very close to the surface. In this regime the attractive forces between the tip and down atom of the buckled dimer can pull the atom into the up position forcing the dimer to flip. During the raster scan of the tip all of the down atoms will be pulled up, therefore the image will show only up atoms suggesting that all dimers appear unbuckled and symmetric. On the contrary, at low setpoints the tip sample interaction is weaker and the flipping dimers are rarely shown. Finally, Sweetman *et al.* provided information on the dimer flipping mechanism by extracting the forces that need to be applied in order to flip a dimer [23,75].

3.1.2 Silicon(111) surface

Silicon (111) represents the grown or cleaved silicon crystal in such a direction exposing the (111) plane. When the surface is exposed a large number of unsatisfied dangling bonds are created, resulting in a high surface free energy. The free energy of the surface can be reduced by the reconstruction of the surface, which is a rearrangement of the surface atoms. In the case of Si(111) surface when the silicon crystal is cleaved a reconstruction (2×1) is formed spontaneously. With an energy input such as anneal cycle, a (7×7) reconstruction is produced. Initially the surface is heated up to 1000°C. At this temperature the silicon dioxide is removed from the surface and the carbon contamination of surface



Figure 3.3: (a) An STM image of Si(100). Parameters $V_{bias} = -2$ V, $I_t = 20 \ pA$, $A_o = 90 \ pm$, at 77 K.

is diffused in the bulk, dropping the temperature rapidly to 900°C. At 900°C the surface is cooled down slowly and the surface atoms have enough energy to diffuse to their ground state. The (7×7) unit cell has only 19 dangling bonds as compared to the 49 of the unreconstructed surface in the same area. The Si(111)- (7×7) surface must be prepared in vacuum conditions due to the high reactivity of the silicon forming oxides in air. In ultra high vacuum conditions, 10^{-11} mbar range, the sample has a lifetime of approximately a month.

The (7×7) reconstruction is the most stable structure of the silicon (111) plane and is easy to fabricate with high quality. Takayanagi [85] used data from transmission electron diffraction experiments and to determine the dimer-adatom stacking fault (DAS) model. The (7×7) unit cell is spilt into two triangular halves each with 6 adatoms. These sit above the rest atoms, dimers surround and bisect the unit cell, and cornerholes are found at the vertices of the unit cell. The spacing of the adatoms is large compared to the atoms on most surfaces and the deep corner holes lead to a high corrugation. This, coupled with the ease of preparation, makes the (7×7) surface very useful for the testing and calibration of new scanning probe instruments.

The first atomic resolution AFM image of the Si(111)-(7×7) was produced by Giessibl [14]. Giessibl used the (7×7) surface to demonstrate the ability of the qPlus sensor [59] and to produce subatomic features [86]. The subatomic features were recorded as two crescents for each of the 12 adatoms and were separated by 2.2 Å. The interpretation of these images is that the tip has picked up a cluster of silicon and





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the point down atom is sp^3 hybridised with two dangling bonds, each of them acting as a 'subatomic' tip forming chemical bonds with the dangling bonds of the surface.

3.1.3 Silver-terminated silicon (111) surface

Silver atoms can be used to satisfy the dangling bonds of the Si(111) surface and reduce the surface energy. Depositing silver onto a Si(111)(7×7) structure annealed at ~ 480°C results in a $(\sqrt{3} \times \sqrt{3})$ R30° reconstruction. This reconstruction at room temperature appears to have a thermally averaged HCP (hexagonal close-packed), in the HCP configuration the Ag adatoms bond to each other forming Ag trimers the bonding is of covalent nature (Fig. 3.5). This results in a chained honeycomb arrangement of Ag trimers. At lower temperatures the inequivalent (IET) in size Ag trimers result from a 6° rotation between the Ag-Si bonds. Since the rotation can occur in two directions two asymmetric ground states can accrue which are chirmorphically symmetric and are usually reffered to as IETa and IETb [87].

3.2 Instrumentation

The Omicron system was used for obtaining serults in all of the result chapters in this thesis. Results from the Createc system were obtained by Dr. Samuel Jarvis and are included in chapter 5.



Figure 3.5: (Colour on-line) Top-down views of the (a) HCT, (b) IETa, and (c) IETb models of the Ag:Si(111) surface. Key: large (small) circles, Ag (Si) atoms; ellipses, Ag-Si bonds; light (dark) triangles, small (large) Ag trimers. Adopted from [87].

3.2.1 Omicron LT

Omicron GmbH supplied the second low temperature vacuum STM-AFM instrument (Fig. 3.6). The system has two main chambers; one is used for sample preparation and storage, and a second houses the scan head. Both chambers are pumped continuously with ion pumps and titanium sublimation pumps (TSPs) giving a base pressure of ${\sim}10^{-10}$ mbar in the preparation chamber and 10^{-11} mbar in the scan head chamber. The manipulator arm is cooled during long sample preparation to avoid out-gassing (and to prevent the silicon diode used to measure its temperature from being damaged). The probe/sample storage is located in the scan head chamber preventing the degradation of the samples whilst others are prepared. The system also has two bath cryostats for cooling the scan head down to either 77 K with LN_2 which can last up to 7 days or to 5 K with LHe which can last for 36 hours. The instrument can be used to perform conventional STM with etched tungsten probes or AFM using qPlus sensors supplied by Omicron. Coarse motion is provided by slip-stick motors. The system uses Matrix control electronics and software supplied with the instrument by Omicron. The system contains a load lock for sample exchange. This can be pumped by a turbo pump and open to the preparation chamber. Through the manipulator arm sample/sensors can be transferred to the scan head for use or storage.

3.2.2 Createc LT

The Createc low temperature STM/AFM, is a commercially available, from Fischer & Co GmbH, which is an ultra high vacuum (UHV) instru-



Figure 3.6: Omicron LT STM-AFM.

ment based on an instrument designed by Gehard Meyer ((Fig. 3.7)). It has a similar two chamber design as the Omicron system. The base pressure for the preparation chamber is typically in the low 10^{-10} mbar range whist the scan head pressure sits in the low 10^{-11} mbar range. The system has two main chambers; one is used for sample preparation and storage, and a second houses the scan head. Both chambers are pumped continuously with ion pumps and titanium sublimation pumps (TSPs) giving a base pressure of $\sim 10^{-10}$ mbar. The scan head is cooled by a bath cryostat that can be filled with either nitrogen or helium to cool the head to 77 K or 5 K, respectively. A second cryostat surrounds the first to prolong the lifetime of the liquid in the first.

Typically the helium lasts ~ 72 hrs and the nitrogen lasts over one week. When filled, the cryostat reduces the pressure in the scan head down into the 10^{-11} mbar range. The system contains a fast entry load



Figure 3.7: Createc LT STM-AFM.

lock for sample exchange and can be pumped by a turbo pump. A transfer arm allows movement of samples and probes/sensors into the preparation chamber. Transport between the preparation chamber and the scan head is achieved using the manipulator arm (which is also used to heat and cool the samples during preparation). The system is capable of conventional STM using etched tungsten wire probes or qPlus AFM with sensors supplied by Createc. The system uses electronics and software from the Nanonis SPM control system available from SPECS Zurich GmbH.

3.2.3 The sensors

In this report qPlus sensors [88] were used in both systems. In the Omicron system a qPlus commercial sensor and a home-built sensor were used to obtain results. The commercial qPlus sensor has a tuning fork with one prong firmly attached, in the other 'free' prong a tip is attached on the STM electrode of the tuning fork and the deflection signal is measured through the other electrode. The home-build sensor was part of the crosstalk project and it is explained in chapter 6.

The Createc sensor has a different design also using a tuning fork but the STM signal is collected by an external wire attached to the tip. Also the tip is attached at the end of the 'free' prong. More details about the sensors are given in Chapter 6.

3.3 Sample preparation

All of the samples and the sensors were introduced to the system through the load lock, as described in the following sections. Then, they were placed on the manipulation arm, in the preparation chamber and guided in the LT chamber. In the LT chamber, the samples were placed from the arm in the scan head by using a wobble stick. Most of the samples were prepared in the preparation chamber, only the Pb:Si(100) was prepared in the LT chamber. Full description of the preparation parameters for each sample is following.

3.3.1 Preparation of Pb:Si(100)

Boron doped Si(100) wafers $(2 \times 10^{19} \text{ dopants per cm}^2 \text{ and conductivity} 1 \text{ m}\Omega\text{cm})$ were introduced to the UHV system and placed on the ma-

nipulation arm. The sample was degassed by being heated at ~600°C for three and six hours. The manipulation arm holding the wafer was cooled at ~69 K with LN₂ flowing through the cryostat of the arm. The sample was then flashed to ~1200°C to remove the oxide layer from the surface, rapidly cooled to ~900°C and then slowly cooled down to the arm temperature (~20 minutes). The chamber pressure during the flashing part of the preparation was kept below 5×10^{-10} mbar. The low coverage of Pb was achieved by exposing the cold silicon wafer to the a molybdenum crucible containing high purity Pb (Goodfellow Cambridge Ltd.) heated by electron bombardment. The sample was kept cool to control the diffusion of the landing Pb atoms on the sample and prevent them from forming large structures.

3.3.2 Preparation of NTCDI on Si(111)

Clean boron doped Si(111)-(7×7) wafers $(2\times10^{19} \text{ dopants per cm}^2 \text{ and}$ conductivity 1 m Ω cm) were introduced to the UHV system. The surface was prepared by flash annealing the silicon wafers to 1200°C, rapid cooling to 900°C, and then slow cooling to room temperature. A low coverage of NTCDI was prepared by depositing the molecules from a standard Knudsen cell (heated to approximately 230°C) onto the room temperature substrate.

3.3.3 Preparation of NTCDI on Ag:Si(111)

The Ag- $\sqrt{3}$ surface was generated by exposing a Si(111)-(7×7) sample, held at a temperature of 550°C, to a flux of Ag from a Knudsen cell. NTCDI molecules were also deposited from a Knudsen cell at temperature 230°C, onto the Ag- $\sqrt{3}$ surface, which was at room temperature.

3.3.4 Preparation of $C_{60}/Ag(111)$

In the Omicron system, a Ag(111) on Mica surface was prepared by spattering a sample with Ar at 500 eV with gas pressure $\sim 1.6 \times 10^{-8}$ mbar and by annealing at $\sim 500^{\circ}$ C at a pressure of $\leq 1.6 \times 10^{-8}$ mbar. The C₆₀ molecules where deposited, while the sample was held at ~ 100 K, with a simple home-made evaporator incorporating a direct current heated Ta envelope with a small hole in one end with diameter of ~ 1 mm.

3.3.5 Preparation of $C_{60}/Cu(111)$

In the Createc system Cu(111) surface was prepared by spattering a sample with Ne at 600 eV with gas pressure 5×10^{-6} mbar and by annealing at ~650°C at a pressure of $\leq 5 \times 10^{-10}$ mbar. The C₆₀ molecules where placed in a home-made crucible resistively heated to ~350 ± 50°C with the sample held at ~70 K and deposited with thermal evaporation by exposing, the clean Cu(111) surface, to the C₆₀ flux.

3.4 Experimental methods

Measurements were performed at low temperature either at 77 K (LN_2) or 5 K (LHe). The tips were prepared by standard STM methods such as voltage pulses and controlled contact with the sample surface.

Atom tracking

The atom tracking device and software was provided from Philipp Rahe. In this method, the tip was positioned over a local maximum or minimum on the surface. Assuming that the maximum is radially symmetric, if the tip motion is set to circle the maxima in x and y, with z feedback off, the frequency shift should remain constant for NC-AFM mode. If the sample drifts relative to the tip in the x-y plane the frequency shift will no longer remain constant. The direction of tip movement to compensate for this drift can be calculated very simply by considering that to apply the circular motion sinusoidal signals are applied in x and y with a phase difference of 90°. The magnitude of the variation in Δf which is in-phase with the x component corresponds to the drift in x. Similarly the Δf variation 90° out of phase with x corresponds to drift in y. Thus, the drift in the x-y plane can be compensated with two feedback loops acting on the in-phase and quadrature outputs of a twophase lock-in amplifier, with Δf as the input and the x dither signal as the reference input. To combine drift compensation with other measurements the drift is measured above a stable point of interest for a set time. The drift in z is also calculated by setting low gain to the z feedback rather than switching it off. The z feedback should be too slow to react to the changes in Δf induced by the tip dither (these being corrected by the x and y loops), instead correcting for tip sample drift in z. By applying linear fits to the motion in x, y, and z the drift rate can be calculated, and compensated for during the measurement. For grid spectroscopy measurements presented in this thesis atom tracking was performed to update the drift rate between each spectra using specialised instrumentation designed by Rahe *et al.* [66].

Chapter 4

Characterisation and lateral manipulation of Pb atoms and dimers

4.1 Sub-monolayer coverages of Pb on Si(100)

As discussed in Chapter 3, in group IV of the periodic table the elements above Pb, (i.e. Sn, Ge, Si and C) have a stable or metastable allotrope in which they crystallize in the diamond cubic structure, involving covalent bonds. In the diamond structure, each atom is tetrahedrally coordinated, indicating that all four bonds are equivalent, having each attained the lowest possible energy. To explain this, in spite of the fact that two of the electrons are in s-orbitals and the other two in higher-energy p-orbitals, orbital hybridization is invoked, in which one of the electrons is "promoted" from an s-orbital to a p-orbital, and then all form four intermediate hybrid orbitals in a process called sp³ hybridization. The inert pair effect, which suggests that the s electrons are more tightly bound to the nucleus and therefore more difficult to ionize, affects the crystal structure of lead, because the promotion energy of a 6s-electron becomes larger than the amount of energy that would be released from the additional bonds formed [89]. Thus, rather than having the diamond-cubic covalent structure, lead forms metallic bonds, in which only the p-electrons are delocalized and shared between the Pb²⁺ ions, resulting in a face-centered cubic structure like those of the similarly-sized divalent calcium and strontium [90].

Sub-monolayer coverages of elements from group IV of the periodic table such as Ge [91,92] and Sn [93,94] on the Si(100) surface (Fig. 4.1a) form one dimensional structures perpendicular to the Si(100) dimer rows (Fig. 4.1b). Similar behaviour is reported for Pb. The Pb/Si(100) system is of great interest for the construction of atomic structures atom by atom. The literature has reported experimentally the position and stability of the Pb dimers and dimer chains on the Si(100) with STM studies [95–100]. Additionally theoretical models have been developed to describe the position of the Pb dimers and dimer chains predicting their mobility and structure on silicon (100) [101–103]. Before discussing our experiments regarding Pb on Si(100) surface, I will briefly review the reported topography and behaviour of sub-monolayer Pb on Si(100) surface, obtained by STM.

In 1994 deposition of Pb on Si(100)-(2×1) was studied with STM [73]. The Pb formed (2×2), $c(4\times8)$, (2×1) and $c(4\times4)$ reconstructions for 0.5 ML to 1.5 ML coverages at room temperature. STM images of Pb sub-monolayers on Si(100) showed long quasi-1D structures. The pe-


Figure 4.1: a) Ball and stick model of the Si(100) surface showing the $p(2 \times 2)$ and $c(4 \times 2)$ reconstructions. b) Ball and stick model of the orientation of the Pb chain growth on the Si(100) surface. Image adapted from [94].

riodicity along the Pb chain (Fig. 4.2) is equal to the distance between the Si dimer rows, which is $2\alpha_o$ or 0.77 nm [73]. The structural model in Fig. 4.3 shows the side view of the atomic structure of the Si(100)surface covered with a sub-monolayer of Pb. Moreover, the asymmetric positions of the Pb atoms placed with an upper and lower atom within the dimer is illustrated. These lines consist of asymmetric Pb dimers that grow in parallel and in the trenches between the underlying Si dimers [96]. The length of the bonds formed by the Pb atoms is ~ 3.13 Å, which is smaller than the bulk Pb nearest-neighbour distance of 3.5 Å(Fig. 4.3). In addition, the asymmetric structure of the Pb dimers is related to their electronic configuration. Each Pb atom has four valence electrons. When Pb is adsorbed onto the Si(100) surface, according to the parallel ad-dimer model, two electrons are used in the saturation of Si dangling bonds and another is used in the formation of a σ -type Pb-Pb bond. There is a remaining electron in each Pb atom of the dimer that is located in the *p*-type orbital perpendicular to the surface and it is thus possible to form a π bond. The formation of a double bond between two Pb atoms in a dimer is, however, not energetically favourable on the Si(100) surface. In order to achieve an energetically stable state between the Pb atoms, the Pb dimers are buckled by an angle of \sim 12.45°. The bond lengths of the Pb-Si are ~ 2.80 Å, and ~ 2.73 Å, for the upper and lower Pb atoms respectively [101]. Tunnelling spectra for the isolated Pb dimer chains exhibit a surface-state band gap of ~ 1.2 eV and are thus not metallic due to the local covalent chemical bonding, dimerization and buckling [97].

Sub-monolayer coverages of Pb dimers on the Si(100) surface have



Figure 4.2: a) Empty (taken at +1.2V) and b) occupied (taken at -1.2V) state images of the same area at 0.1ML of Pb/Si(100) The same D and S structures are indicated in (a) and (b); c) Termination of the chains that appear as bright (BT) and normal (NT) in empty states images [98].



Figure 4.3: Side view of the atomic structure of the Si(100) surface covered with 0.25 coverage of a monolayer of Pb. The plane is perpendicular to the surface and it passes through the Pb dimers [101].



Figure 4.4: :Large scale STM image overview image showing a low coverage of the Pb short chains on Si(100) surface. A bright termination (BT) [98] is shown. $V_{gap} = -2V$, $I_t = 20pA$, $A_o = 70pm$.

high mobility at room temperature [96]. Jure *et al.* studied the terminations of the Pb chains and suggested that there are two kinds of chain terminations and that the mobility is connected to the contrast shown in STM images [98] (Fig. 4.4). A single atom structure (denoted from now on with the letter S) is strongly bias dependent and appears bright in positive biases while in negative is hard to detect. The Pb dimer seems to exchange bright contrast between the upper and lower atom of the dimer according to the bias applied (Fig. 4.2(a) & (b)).

The normal termination (denoted with NT) features appear more or less as normal chain dimers whereas the bright termination (BT) maxima are brighter than normal chain dimers. The bright termination is claimed to be a single atom rather a dimer [98]. Defects on the substrate trap migrating atoms, creating a single structure which can capture other atoms and transform to a double structure. This seeds a nucleation process and longer chains can subsequently be build. The reverse process has also been observed. At room temperature, both buckled and flat Pb dimers can coexist. The same dimer appeared as bright termination and as normal termination in a sequencial image (Fig. 4.2) [99,100].

Theoretical studies also support the high mobility of Pb adatoms and ad-dimers on Si(100). Pb adatoms are found to diffuse on top of the Si(100) dimer row with an energy barrier of 0.31 eV. On the other hand, Pb dimers are energetically more stable but when oriented parallel to Si(100) dimer row they can diffuse along the row with an associated energy barrier of 0.32 eV [103].

4.2 Topography of the low coverage Pb/Si(100) surface

This section will provide information from a constant height NC-AFM overview of the a Si(100) surface after the deposition of low Pb coverage. In Fig. 4.5(a) the silicon surface can be observed as a white background while the silicon dimer rows are also faintly visible. The Pb atoms can be observed as attractive (dark blobs) and less attractive (bright blobs). It is important to note that the sample was kept at low temperature (the manipulation arm was cooled down with LN_2) during the deposition in order to restrict the natural mobility of the Pb atoms.



Figure 4.5: (a) Constant height overview image NC-AFM, the dashed lines on the upper right corner indicate the direction of the Si dimer rows; (b)-(e) illustrates Off-line zoom-in images of Pb dimer structures found in the overview image.(b) two dimers are located next to each other and both atoms of each dimer appears attractive; (c) a dimer Pb chain with an uncommon termination on the lower left corner; (d) illustrates the interaction of the less attractive adatom of Pb dimer with the scanning tip; (e) shows a Pb atom or dimer moving on the surface as result of the interaction with the scanning tip; (f) and (g) ball-and-stick models of the various Pb dimer structures (dark balls) and the silicon dimer surface (white balls). More information in the text. Parameters: $A_o = 70$ pm, $\Delta z = 0$ nm, $V_{gap} = 0$ V.

Under these conditions the Pb atoms tend to form dimers and dimer chains and Pb also clusters on the surface in two different ways which are the energetically more stable structures possible [98]; the first and less common structure appearing in Fig. 4.5(b) and the second and more common, chain structure appearing in Fig. 4.5(c). In the first case, the Pb dimers interact with the silicon surface in a way that both Pb atoms of the dimer are at an almost equal height from the dimers of the silicon surface and grow in parallel direction to the silicon dimer rows. They appear as two dark blobs in the constant height image (Fig. 4.5(b)). The ball-and-stick model of this structure is depicted in Fig. 4.5(f). For the more common structure of Fig. 4.5(c) the Pb dimers interact with the surface in such a way that one atom of the dimer locates clearly higher than the other. In that case the higher Pb atom appears as a bright blob while the other that sits lower appears as a dark blob in the constant height image (Fig. 4.5(c)). The ball-and-stick model for this structure appears at Fig. 4.5(g). Note that the structure at the lower left corner of the Fig. 4.5(c) is very rare and we can speculate that it resembles a combination of the two aforementioned structures; the majority of the imaged chains didn't have it.

In Fig. 4.5(d), a tip-induced modification of the Pb structure can be seen. In another case (Fig. 4.5(e)) a Pb atom or dimer (it cannot be clarified with certainty) interacts with the scanning tip and leaves a trace along the scan lines as the scanning progresses (Fig. 4.5(e) black arrows show the direction of the trace). Note that the structure shown in Fig. 4.5(e) in the dashed square looks similar to the aforementioned structure shown at the lower left corner of Fig. 4.5(c).

4.3 Lateral manipulation of the Pb dimers

Fig. 4.6(a) shows an STM image of an individual Pb dimer and a Pb chain. The atom-manipulation software from the Omicron system was used. The system allows the user to draw a path on the surface during the imaging process and to control the parameters such as gain, V_{gap} , Δf , ΔZ etc. which dictate the behaviour of the tip while following the path. In our case the tip was in constant height mode while moving along the manipulation path.

The paths of the tip are indicated with the black arrows in Fig. 4.6(b)-(d). The Pb dimer was firstly manipulated perpendicularly (Fig. 4.6(b) & (c)) and consequently in parallel (Fig. 4.6(d)) to the silicon dimer rows. The outcome of the manipulation was that the dimer disappears and the chain appears to be elongated (Figs. 4.6(e) & (f)). As the reader may assume, the goal of this experiment was to manipulate a Pb dimer in a way that would move it towards the Pb dimer chain. The nature of this method allows a series of simple and quick manipulations but the lack of a $\Delta f(x, z)$ map, which is explained later, restricts the calculation of the forces needed for the manipulation in order to be accurate.



Figure 4.6: Images (a) to (f) show a Pb dimer and a Pb chain on Si(100). In each case the black arrow indicates the manipulation path of the tip; a) STM image of Pb dimer and Pb chain; b) constant Δf NC-AFM image of the Pb chain prior to manipulation; c) constant Δf AFM image of the same region after the manipulation perpendicular to the Si(100) rows; d) constant Δf AFM image manipulation of the Pb dimer in parallel to the Si(100) rows; e) constant Δf AFM image of the expanded chain; Parameters: STM image: gain= 5.0%, I-setpoint: 10 pA, V_{gap} = -1.5 V, for the AFM images: gain= 5.0%, Δf -setpoint= -5.91 Hz; constant height AFM ΔZ = 0 nm, A_o = 90 pm, at 77 K; f) constant height AFM image of the dimer chain.

4.4 Collection of the short range Δf map

The sample was cooled down to 5K to achieve better control and accuracy for the manipulation of the Pb dimers. The first step in this method was to detect the area of manipulation and then pause the tip and reposition the scan in a way that the first scan line would meet the centre of the dimer selected for manipulation in a fashion that the trace direction of the tip would point towards the desired direction (Fig. 4.7(a)). Secondly, the long scan axis was disabled and the tip was retracted 1 nm away from the surface. During every trace line the tip was deepened by 5 pm and was set to scan along the trace once. When the tip reached the end of the trace line it was retracted by 200 pm of the relevant position and was set to move along the retrace to the beginning of the scan line. Consequently, the tip was deepened again by further 5 pm than the previous relative position and a new scan along the trace line was performed, followed by a new retrace with the tip pulled back by 200 pm from its relative position. This procedure was repeated several times as shown in Fig. 4.7(a) each time with the tip positioned closer to the surface by 5 pm.

During one of these transits of the tip along the trace line, the tip interacted with the Pb dimer which resulted in the movement of the Pb dimer towards the Pb dimer chain as shown in Figs. 4.7(b-before manipulation) and (c-after manipulation). Constant height scan was performed after each manipulation attempt in order to make the results visible.

The trace image when plotted in in-plane fashion presents a $\Delta f(x,z)$

map of the manipulation. From this map the first and the last 3 pixels from each side on the lines were removed to help address the effects of any drift/creep for the movement of the tip. The next 10 pixels in both ends from each scan line were averaged and used as an Off spectra for the calculations of the forces. For the calculations of the forces we used the Sader-Jarvis algorithm [63].

Fig. 4.7(b) is the image before and Fig. 4.7(c) is the image after the manipulation attempt. The red arrow indicated the path of the tip. The short range Δf is shown in Fig. 4.7(d), while the calculated energy, the lateral (F_x) and the vertical force (F_z) are shown in Fig. 4.7(d), (f), and (g) respectively. The maximum F_x is on the spot of the sawtooth shape of the short range Δf rather than the spot of the Δf drop.

The short range Δ f(x,z) map of the manipulation is shown in Fig. 4.7(d). From that the potential energy, the vertical and the lateral forces were calculated (Fig. 4.7(e)-(g)). Fig. 4.7(d) and (f) are presented in a way to show how the manipulation point was selected. The dashed line is placed on the observed 'jump' of the short-range Δ f traces and highlights the spot of the manipulation event.

The lateral force required to move the dimer is related to its adsorption on the surface, the associated potential energy landscape and in some cases with its interaction with neighbouring dimers as being part of a chain. The following method for acquiring the forces for each manipulation was similar to the one reported by [24,44]. All forces presented here should slightly underestimate the true tip-sample interac-



Figure 4.7: (a) Schematic of the tip path during the manipulation; (b)&(c) Constant height NC-AFM images also presented in Fig. 4.8(d)&(e) respectively;(d) In plane plot of the short range $\Delta f(x,z)$ recorded during the manipulation; (e) The calculated potential energy of the tip-sample interaction; (f) Calculated short range lateral force(F_x); (g)Calculated short range vertical force(F_z). The red coloured lines show the last line of the manipulation, the energy and the forces in (d), (e) and (f) $\mathfrak{G}(g)$ respectively.

tion, but we believe this systematic underestimation to be preferable to the greater uncertainties that would be introduced by attempting a longrange fit of the van de Waals and electrostatic background [104, 105].

4.5 Pb dimer manipulation

Fig. 4.8 shows consequent constant height NC-AFM images taken during the manipulation procedure presenting a complete manipulation of a Pb dimer. Between each pair of images shown, one manipulation attempt has been performed. In Fig. 4.8(a) two Pb dimer chains are shown, on the left a short Pb chain and on the right a longer chain. Each manipulation performed moved the top Pb dimer of the short chain towards to long chain which is used as a point of reference. After the first manipulation was performed, the top dimer of the top chain broke and a small Pb structure remained at the lower end of the short chain (Fig. 4.8(b)). The short chain broke as a result of tip interaction with the Pb dimer during the manipulation.

Fig. 4.9 illustrates the short-range Δf trace before the manipulation event (black line) plotted with the manipulation trace (red line). Fig. 4.9(a) illustrates the manipulation of the Pb dimer from the position shown in Fig. 4.8(a) to the position shown in Fig. 4.8(b), where the dimer breaks off from the chain. In this manipulation attempt the dimer performs multiple steps which are presented in the Δf trace as multiple 'hops' and the manipulation along the Si row is not one clear step but rather a combination of multiple steps. The manipulation from the



Figure 4.8: A to G: constant height NC-AFM successive images showing the surface topography before and after each manipulation. $V_{gap} = 0 V$, $A_o = 70 pm$, $f_o = 24349 Hz$ at 5 K.

position of the Pb dimer shown in Fig. 4.8(b) to the position shown in Fig. 4.8 (c) is depicted in the graph as a two step event. It is not clear why the manipulation shown in Fig. 4.9(b) occurred in two steps but it is possible that it is caused by the Pb dimer sitting in a metastable condition as a result of the first manipulation. Thus its interaction with the tip appears to be complicated. We can speculate that the dimer might not sit on the surface with an upper and lower atom, but in a different way which limits the dimer relaxation. Another explanation is baced on the attraction of the dimer by the tip, that might cause a 'pull' of the dimer towards the tip. Finally, in Fig. 4.9(c) a single step manipulation is shown. This manipulation pattern (single step) was recorded during all the manipulations performed from Fig. 4.8(d)to (g). The shape of the manipulation Δf traces indicate a 'sawtooth' pattern observed in AFM [44] and STM [11] experiments of adsorbate manipulations. During the manipulation the frequency shift decreases in magnitude indicating a 'pull' manipulation.

The distance measured for each step is ~0.8 nm which is approximately twice the surface lattice constant of the Si(100) surface 0.768 nm. The potential energy at the manipulation point for the extracted dimer was calculated between -0.3 eV to -0.5 eV. For the rest of the manipulation events the energy was in the range of -0.19 eV to -0.27 eV which is close to the calculated diffusion energy barrier of the Pb dimer on Si(100) at 0.32 eV [102, 103].

The lateral force F_x measured for breaking the short chain has been calculated ~-0.1 nN and the vertical force $F_z \sim -0.5$ nN. The F_x required



Figure 4.9: The traces of the first three manipulation events from Fig. 4.8(A)-(D); A)the trace before (black line) and during (red line) the manipulation event between the positions shown in Figs. 4.8(A) and (B); B)the trace before and during the manipulation event between the positions shown in Fig. 4.8(B) and (C); C) the trace before and during the manipulation event between the positions shown in Fig. 4.8(C) and (D); The traces of the rest of the manipulation events are omitted because they resemble the manipulation shown in (C).

to manipulate the Pb dimer by 0.8 nm was within a range of -0.035 \pm 0.01 nN while the F_z was -0.19 \pm 0.05 nN.

4.6 Additional interactions

The manipulation events shown in Fig. 4.10(a) & (b) are both acquired with the same tip (indicated from now on as tip-I) while the manipulation events shown in Fig. 4.10(c) and (d) are acquired with two different tips (indicated from now on as tip-II and tip-III respectively). For all tips a peak is observed at the initial stage when the tip approaches the atom (black arrow). This interaction indicates a pulling mechanism which has been observed with a variety of tip states. In Fig. 4.10(c)(taken with tip-II) shows cases where the tip pulls the Pb towards it and the Pb stays in the new position. In Fig. 4.10(d) the tip also pulled the Pb while approaching but in this case the Pb dimer has been pulled also towards the end of the manipulation line. Tip-II and tip-III show a manipulation distance around 0.4 nm which is very close to the surface lattice constant of Si(100). On the other hand, the distance of manipulation with tip-I is around 0.8 nm showing a bigger jump during the manipulation, which is in good agreement with diffusion theorerical studies [103].

We can speculate that the manipulation with the tip-II and tip-III might lead to a single atom manipulation. In both cases the lateral forces were calculated to be within the same range and the vertical forces seem dominant in all of them. The dominant vertical force sug-



Figure 4.10: Short range Δf with two different tips; A) The Pb dimer is pulled back from the tip; B) The Pb dimers was pulled back and then forward; C) The Pb dimer is pulled back from the tip and stays in the new position and D) the Pb dimer is pulled back and the forwards long the trace of the tip. $A_o = 70 \text{ pm}, f_o = 22,846 \text{ Hz}$ at 5 K.

gest a possible interaction on the surface potential lowering the energy barrier [106]. We didn't observe any change on the energy needed to move a Pb dimer. The energy barrier we measured (\sim -0.27 eV) is comparable to that predicted in the theoritical study of the diffusion barrier of Chan *et al.* (\sim 0.3 eV) [102, 103].

4.7 Transfer function and phase error

The transfer function was recorded right after the manipulation measurements taken with tip-II. Fig. 4.11 shows an in situ measurement, it is clear that a large in dissipation is recorded between -50 Hz to -33 Hz, this frequency range is away from any measured value during imaging or manipulation. On the transfer function we observe similar behaviour around the same frequency range. The manipulations took place at \sim -25 Hz where there is some disruption at the transfer function, smaller curves are reported also on the excitation signal.

In Fig. 4.12 the raw Δf with all the recorded channels during a typical manipulation are shown. The phase correction was calculated by comparing every pixel of the phase channel with the frequency from an in situ frequency sweep. The excitation peaks at the manipulation point are shown in the excitation and the amplitude channel. The phase error was of 0.5 Hz which is insignificant. On the other hand, due to the peak observed in the excitation channel around the manipulation Δf the results might be affected by the transfer function. In all of the data sets and with all the tips the force values were calculated within the same



Figure 4.11: Transfer function analysis. Left: Plot of the tuning fork excitation VS frequency shift during (Right) $\Delta f(V)$ measurement taken at imaging position of the tip ($\Delta Z = 0$ nm). The red dashed line indicates the large jump in the dissipation and the black dashed line indicates the dissipation at the frequency shift value where the manipulation attempts were performed.

range, therefore we can speculate that the results are reasonable. Also the large vertical force might be due to the atom building a bond with the tip.



Figure 4.12: Analysis of the role of phase error in manipulation measurements; a) the raw Δf map during a manipulation; b) the Phase recorded; c) the frequency error due to phase; d) the excitation during the manipulation and e) The amplitude during the manipulation. The excitation at the manipulation frequency follows similar behaviour with the one shown in Fig. 4.11 left. The phase shows a negligible error of ~0.5 Hz.

4.8 Future perspectives: Other types of manipulation

Fig. 4.13 shows two different types of manipulation. The before and after constant height AFM images of tip-III from a lateral manipulation are shown in Fig. 4.13(a)&(b) and the before and after image of a vertical manipulation are shown in Fig. 4.13(c)&(d). The manipulated atom appears to be mobile when interacting with the tip while scanning therefore the blurry contrast. Jure *et al.* [98] reported two types of Pb dimer chain terminations. It would be very interesting to conduct a further study on the characterisation and if necessary a re-definition of the Pb chain termination using NC-AFM.



Figure 4.13: Constant height AFM images (a) and (b) are the 'before' and 'after' image of a lateral manipulation with tip-III; (c) and (d) before and after image of a most likely vertical manipulation with tip-IV. $A_o =$ 70 pm, $f_o = 22,846$ Hz at 5 K.

4.9 Conclusions

Using the NC-AFM technique it was possible to acquire an image of Pb atoms and dimers on a semiconducting surface as well as manipulate a Pb dimer using mechanochemical force. We measured the lateral force required for the manipulation event, within a range of -0.035 ± 0.01 nN, and determined that the lateral force required to move a Pb dimer is related to the adsorption of the dimer on the surface, or the position of each atom of the dimer 'sitting' on the surface, the associated potential energy land scape and in some cases the interaction of the Pb dimer with its neighbouring dimers.

Chapter 5

Adsorption and origins of inter-molecular contrast of NTCDI molecule

In this chapter we investigate the adsorption of naphthalenetetracarboxylic diimide (NTCDI, Fig. 5.1) on Si(111)-(7 \times 7) and on silverterminated silicon (Ag:Si(111)), using a variety of methods such as STM and NC-AFM supported by DFT calculations. The experiments were carried out for two main reasons: Firstly, in order to determine the complete molecular adsorption geometry of the NTCDI molecule and to reveal its chemisorption interaction and to provide more information of NTCDI molecular adsorption on metallic and semiconducting surfaces, since an apparent lack of relevant information on the subject was observed in the literature. Secondly, given the particular importance of hydrogen bonding in a bewildering array of scientific fields such as biology, chemistry and material's science, DFM was used to provide inter and intra molecular resolution of the NTCDI molecular assembly



Figure 5.1: Ball-and-stick structure of NTCDI molecule.

on a semiconducting surface (Ag:Si(111)), with a spontaneously functionalised tip and DFT calculations to investigate the origins of the aforementioned resolution.

5.1 Topography of NTCDI on Si(111) with STM/AFM

The structure of a NTCDI molecule is shown in the ball-and-stick model in Fig. 5.1. The back-bone of the molecule consists of fourteen carbon atoms terminated with an imide group on each end. From a previous study of the PTCDA on Si(111)-(7×7) system¹ by Nicoara *et al.* [107], the C=O units are expected to have a covalent interaction with the surface adatoms.

Fig. 5.2 shows STM images of a sub-monolayer coverage of NTCDI

¹The PTCDA molecular structure is also a planar molecule structure like that of NTCDI, but PTCDA molecule is larger with more aromatic rings, therefore a similar behaviour is expected.

on the Si(111)- (7×7) surface. The overview image in Fig. 5.2(a) shows the appearance of surface after the deposition of a low coverage of NTCDI. The defect density of the surface seems to be high due to a number of native adatoms defects, potentially caused by CO and/or water contamination during the deposition, but also there is an increase of bright features corresponding to adsorbed NTCDI molecules. In particular, we observe several bright (dashed circles) and dark (dotted ellipses) features each with a characteristic size, appearance and location on the Si(111)- (7×7) unit cell. The high-resolution STM images in Figs. 5.2(b) and (c) show the characteristic bright and dark features with more detail of the lobe-like structure. The bright features shown in Fig. 5.2(b), when imaged with positive bias, appear as a number of five parallel stripes aligned perpendicular to the direction "cutting" each half of the 7×7 unit cell. The dark features towards the bottom right of the molecule correspond to surface adatom vacancies. The darker features with less detailed contrast in STM images, shown in Fig. 5.2(c), can easily be mistaken for clusters of adatom vacancies. The reason why we can conclude that the observed features in Fig. 5.2(b) and (d) correspond to actual NTCDI molecules is the fact that a primary identifying characteristic of the cluster features are consistent in size and alignment with the Si(111)- (7×7) unit cell. This characteristic is its consistent location of the molecule above the silicon dimers which divide each half of the unit cell, similar to the location of the bright feature shown in Fig.5.2(b) which is a typical high resolution image of an adsorbed NTCDI molecule. Fig. 5.2(d) and (e) show less commonly observed features. In particular, Fig. 5.2(d) shows an example of an almost structureless bright feature which will be explained later on. A

slightly more distinctive but also more rare structure is shown in Fig. 5.2(e) which is similar to the observations of PTCDA adsorption within a corner hole of the Si(111)-(7×7) surface.

Fig. 5.3 shows STM and NC-AFM images of a number of adsorbed NTCDI molecules appearing as a mixture of brighter and darker features similar to those seen in Fig. 5.2(b) and (c). The STM and NC-AFM images shown in Figs. 5.3 (a) and (b), respectively, were acquired immediately after one another over the same region of the surface. A minor change of the tip during the transition to NC-AFM was observed but the STM contrast was not significantly changed. By overlaying the adatom structure on the NC-AFM image we can identify that the features in Fig. 5.3(a) correspond to planar adsorbed NTCDI molecules located above the connecting dimers between the two halves of the 7×7 unit cell.

Additional NC-AFM images, confirming the adsorption locations of the NTCDI molecules, are shown in Fig. 5.4 (a) and (b), resolving intramolecular structure and the adatom arrangement of the surface. Note that the alignment of the NTCDI molecule with the underlying adatoms in Fig. 5.4 (a) can more clearly be observed in Fig. 5.5 (c), which was taken at a larger tip-sample separation over the same molecule, with the same tip.



Figure 5.2: a)STM image of the Si(111)-(7×7) surface following deposition of a low coverage of NTCDI. b)Typical high-resolution image of an adsorbed NTCDI molecule appearing as a bright feature relative to the surrounding silicon adatoms, highlighted with dashed circles in (a). c)Adsorbed NTCDI in another configuration, appearing as a dark feature similar to a large vacancy defect, highlighted with dashed ovals in (a). Less commonly observed features are shown in (d) and (e) potentially corresponding to alternative adsorption sites of NTCDI. In (b)-(e) the 7×7 unit cell is indicated by a black dashed line. Parameters: (a)+1.5 V/70 pA, scan size = 20 nm × 2 0nm, T = 77 K,(b) and (c) +1.5 V/70 pA, T = 77 K, (e)+2 V/1.25 nA, T = 5K.



Figure 5.3: High-resolution a) STM and b) constant height NC-AFM images showing a number of adsorbed NTCDI molecules. The overlaid structure of the silicon surface and the surface unit cell (black dashed lines) shows that the dark and bright features observed in STM correspond to two planar adsorption geometries perpendicular to one another with respect to the 7 × 7 unit cell. Parameters: a) +1.5 V/40 pA, b) $\alpha_o = 280pm, T = 77K.$



c) and d) for Geometry 1 and 2, respectively. Alternative non-planar calculated structures are shown in e)-h) which we term Geometry 3-6, respectively. Parameters: $a)\alpha_o = 110pm$, scan size: 4.1nm × 4.1nm b) $\alpha_o = 110pm$, scan and 2, are shown in a) and b), respectively. The lowest energy DFT structures for each adsorption site are shown in Figure 5.4: High-resolution NC-AFM images of each of the two adsorption positions, which we term Geometry 1 sixe: $3.27nm \times 3.27nm, T = 5K$.



Figure 5.5: Distortion of adsorbed NTCDI molecule. a)Side views on ball-and-stick model of NTCDI in Geometry 1 shows curvature of the NTCDI molecule induced by surface adsorption. b) Calculated electron density difference plotted as plane cross-section intersecting the Si-O bond. Red represents density depletion and blue density excess over the range of $\pm 0.05e/\alpha_o$. c) NC-AFM image of the same molecule shown in Fig. 5.4 a, taken at an increased tip-sample distance of 50 pm. d) and e) show the calculated total electron density plotted at distance 1 Å, and 2 Å, above the molecular plane respectively. Parameters: $a)\alpha_o = 110pm$, scan size: 4.1 nm × 4.1 nm, T = 5 K.

5.2 Density functional theory simulations

All of the calculation included in this chapter were performed by Dr. Samuel Jarvis. Using DFT calculations of the combined NTCDI:Si(111)- (7×7) system, the adsorption mechanism and geometries adopted by NTCDI were studied thoroughly. The comparison of high-resolution images showed that there are two planar adsorption geometries, shown in Figs 5.4 (c) and (d), which match the observation as shown in Figs 5.4 (a) and (b) (Geometry 1 and 2) respectively. The NTCDI molecule is adsorbed via covalent bonds between the C=O and the underlying silicon adatoms. The small size of the NTCDI molecule allows the formation of four Si-O bonds near the centre of the unit cell in two perpendicular directions. This explains the two different appearances between the experimental STM results at the same surface site.

If fewer Si-O bonds are formed, then alternative adsorption sites can be produced; namely four unique geometries have been found as shown in Figs. 5.4 (e) to (h) (Geometries 3 to 6). The basic difference is that in the latter cases two covalent bonds are formed instead of four. In all those cases, however, the NTCDI molecule appears asymmetric, which indicates that it is strongly tilted towards the molecular plane [108]. This means that the NTCDI molecule is adsorbed on the surface at a region of the molecule which bends the molecule itself, thus, its projection as we see in the acquired NC-AFM images appears asymmetric. Another notable difference between Geometries 1, 2 and 3 - 6 is the strain-induced curvature of the NTCDI molecule caused by the molecule-surface distortions required to form the Si-O bonds. For example, in Fig. 5.5 (a), we can see that the distance between the central carbon and the peripheral nitrogen atoms is ~ 0.2 Å, and ~ 0.35 Å, for Geometry 1 and 2 respectively whereas in Geometries 3 - 6 the same distance varies between ~ 6.8 to ~ 7.8 Å, across the short and long axis of the Si(111)-(7×7) unit cell, respectively. This is because the Si-O bonds formed between the NTCDI and the surface atoms in Geometries 3 - 6 induce an electron density difference that increases the adsorption of NTCDI significantly. The separation of the oxygen atoms in NTCDI is 7.2 Å, across the short axis and 4.6 Å, across the long axis.

In Fig. 5.5 (c) experimental NC-AFM images, taken at large tipsample separation where tip-induced perturbations are reduced, we observe distortions in the NTCDI structure. Comparing the tip-sample distance in Fig. 5.4 (a) and Fig. 5.5 (c) the distance is 50pm larger for the latter. At close tip-sample distances (Fig. 5.4 (a)) the central aromatic rings of the molecule appear brighter than its periphery. In our simulations this feature can be reproduced by using total electron density (TED) as a first order approximation for the expected image. It can be generally considered that the TED is related to the force responsible for intra-molecular resolution. This has been confirmed in many simulations so that we can say that the TED can be used to predict the observed contrast [32]. On the other hand, there have been circumstances where the TED is unrelated to the observed contrast [37]. The effect seems to be noticeable at larger separation, shown in Figs 5.5 (d) and (e) where the tip-sample distance is 1 Å, and 2 Å, above the molecular plane respectively. Especially in Fig. 5.5 (e) the central two carbon rings appear to be more "dense" compared to the outer edges of the molecule.



Figure 5.6: Corner-hole adsorption of NTCDI. a)NC-AFM image of a NTCDI molecule adsorbed at the corner hole site of the Si(111)- (7×7) surface. Two calculated geometries for the corner hole position are shown in b) and c) termed Corner 1 and Corner 2. Scan parameters for the image shown in (a) are $\alpha_o = 280$ pm, scan size: 3.5 nm × 3.5 nm, T = 5 K.

Fig. 5.6 (a) shows a rare example of the NTCDI molecule adsorbed in the corner hole position where the Si(111)-(7 \times 7) adatoms appear as bright triangular features due to a repulsive tip-sample interaction [109]. There are two stable geometries which can in principle include a corner hole bonding position (Figs. 5.6 (b) and (c)), but in practice the geometry shown in Fig. 5.6 (b) is more consistent with the observations.

In Fig. 5.6 (a) the NTCDI molecule sits inside the corner hole where four Si-O bonds are formed while for the alternative geometry shown in Fig. 5.6 (c) the NTCDI molecule bonds with two surface adatoms which leads to the molecule being drawn to one site of the corner hole.

The corner-hole effect leads to a reduction of the adsorption height of the NTCDI molecule which is measured as the distance in Z between the undistorted surrounding Si adatoms and the highest point of the NTCDI molecule. Thus in Geometry 1 and 2 the maximum z distance is measured at 2.5 and 1.97 Å, respectively while in Fig. 5.6 (a) the same distance is measured at only 1.6 Å.

5.2.1 Stability of the NTCDI calculated geometries

Based on the calculated adsorption energies it can be deduced that Geometry 1 is the most stable structure followed by Geometry 2 which is higher in energy by more than 0.5eV (Table 5.7). The tendency of the NTCDI and Si(111)-(7×7) system to form these two geometries is due to the fact that the increased number of Si-O bonds between the adatoms of the surface stabilise the structure. The next more stable Geometries are 3 and 5 since they have only two Si-O bonds. Finally, even though Geometries 4 and 6 have also two Si-O bonds they are significantly less stable because they require the molecule to be deformed in order to bond with the surface (see Fig. 5.4).

In the cases where the NTCDI molecule is adsorbed in a corner hole, the geometries which should be the least stable according to the calculations appear to be more stable experimentally. This is most likely explained by the absence of van der Waals forces in our simulations, which, if included, would increase the adsorption energy to a much more stable value. To explain why we only observe the Corner 1 structure, we suggest that this might potentially be explained by a complex potential energy surface. Due to its relatively small adsorption height and the recessed nature of the molecule in the Corner 1 position, it is reasonable

Figure 5.7: table

Relative adsorption	energies for calculated geometries of NTCDI or	ļ
$Si(111)-7 \times 7.$	N refers to the total number or Si-O bonds.	

	N	Figure	$E_{\rm ads}$
Geometry 1	4	4(c)	-3.21
Geometry 2	4	4(d)	-2.67
Geometry 3	2	4(e)	-2.24
Geometry 5	2	4(g)	-2.22
Corner 2	2	6(c)	-1.79
Geometry 6	2	4(h)	-1.44
Geometry 4	2	4(f)	-0.80
Corner 1	4^{a}	6(<i>b</i>)	+0.14

^aBonding involves 2nd layer silicon rather than adatoms.

to expect that the energy barriers required to exit this configuration might be significant enough to effectively 'trap' the molecule in this unfavourable position. We note that observing molecular adsorption in the corner hole position was a particularly rare occurrence. Although possible, in principle, a full statistical experimental analysis of each geometry would require taking many images over large surface areas with minimal changes to the STM tip.

5.3 Simulated STM images

In order to examine the electronic structure we attempted to simulate STM images using the Tersoff-Hamann approximation, as a supplementary method to NC-AFM images. Geometries 1, 2, 3 and Corner 1 were chosen since they were the most energetically stable structures from an
energy point, and in addition Corner 1 was the most stable corner hole adsorption configuration.

Fig. 5.8 shows simulated STM images plotted as both images of constant height (bottom) and contours of constant current (top) using a sample bias of +1.5 V, chosen to match the majority of experimental observations. Considering first Geometry 1, shown in Fig. 5.8 (a), we note that the calculated image contains many of the qualitative features observed in the experimental data. In particular, in addition to reproducing the overall bright appearance of the molecule we observe a similar shape where the central part of the molecule appears much wider (topto-bottom in Fig. 5.8 (a)) than each of the imide terminations. Due to the absence of a finite tip radius in our calculations, the features contributing to this overall shape can be clearly observed, particularly in the constant height image which shows five lobes of similar brightness making up the central band, alongside two smaller, less intense, lobes which appear at each end. Interestingly, in contrast to a previous report on PTCDA [31] we find that the simulated STM at positive biases appears dominated by the HOMO and HOMO-1 orbitals, whereas images at negative biases (not shown) are dominated by the LUMO orbital, presumably due to shifts or splitting of the molecular orbitals caused from the bonding configuration of the molecule on the surface.

Moving onto the additional calculated geometries we instead find more limited agreement. For Geometry 2 in particular (Fig 5.8 (b)), which is observed as a dark feature in experiments (Fig. 5.2 (c)), we see a very similar appearance to the images calculated for Geometry 1, i.e. appearing brighter than the surrounding Si(111)- (7×7) adatoms. Similar features in the simulated STM are also observed for the Corner 1 geometry. Although in this case the molecule does appear with a reduced brightness, it is likely a consequence of the reduced moleculesurface separation and not due to significant changes to the electronic structure. Finally, for the metastable Geometry 3 we once again observe a bright appearance for the molecule, however, in this case the non-planar geometry significantly reduces the number of internal features visible in the images, similar to some of the defect-like features observed in experiment. We therefore tentatively suggest that Geometry 3 and potentially Geometries 4 6, might explain surface features such as that shown in Fig. 5.2 (d).

We therefore conclude that whilst the simulations show some similarities to the experimental images particularly Geometry 1 and 3 the simple Tersoff-Hamann approach is not sufficient to provide a complete model of the NTCDI:Si(111)- (7×7) system. Indeed, Nicoara *et al.* show [107], using an in-house Greens function code [110], that in order to provide better agreement with experiment more complete simulations are needed, requiring the inclusion of a model silicon tip cluster [111].

5.4 NTCDI assembly on Ag:Si(111)

After having examined the intramolecular contrast and the adsorption of the NTCDI molecule on the metallic Si(111)- (7×7) reconstruction our interest was focused on the NTCDI molecular assembly on a silver-



Figure 5.8: Simulated constant height current (top) and constant z (bottom) STM images for the a)Geometry 1, b)Geometry 2, c)Geometry 3 and d)Corner 1 calculated structures. All images are calculated using sample bis voltage +1.5 V. Scan sizes are 3.8 nm \times 3.8 nm and 1.6 nm \times 1.6 nm for the constant current and constant height images respectively.



Figure 5.9: a) Constant current feedback STM image of an NTCDI island. $V_{gap} = +2 \ V, I_t = 20 \ pA$, oscillation amplitude ($A_o = 0.275 \ nm$, b 0 Constant Δf feedback DFM, $\Delta f = -13 \ Hz$, $A_o = 0.275 \ nm$, c) Constant height DFM at $\Delta z = -0.1 \ nm$, $A_o = 0.275 \ nm$. Image size $7.2 \times 5.5 \ nm$. Data collected at 77 K.

terminated Si(111) surface. It is important to reiterate that this surface is covered with a monolayer of Ag and that it is semiconducting, rather than metallic, in order to gain a deeper understanding of the inter-molecular forces of the bonded NTCDI molecules on a non reactive surface. Fig. 5.9 depicts a NTCDI island on Ag:Si(111) imaged with three different methods. Fig. 5.9 (a) shows the initial STM image of the same NTCDI island, in Fig. 5.9 (b) we see the constant Δf image of the same island, and, finally, in Fig. 5.9 (c) the constant height DFM image of the island. The most noteworthy points of the DFM image are the well resolved intramolecular contrast and the clarity of the maximum contrast at the expected positions of the hydrogen bonds between the molecules. Similar results have been produced by Zhang *et al.* [36] in DFM images of 8-hydroxiquinoline on Cu(111) and by Kichin *et al.* with PTCDA on Au(111) with STHM [35].

Fig. 5.10 shows the evolution of contrast in the NTCDI assembly as

a function of tip-sample separation. In Fig. 5.10 (d) the contrast in the expected positions for hydrogen bonds appears to be particularly sharp.



Figure 5.10: (a)-(d) Constant height DFM images of an NTCDI island acquired with a different tip-sample separation in each case. Parameters: $A_o=275 \text{ pm}, T=77 \text{ K}, \text{ image size } 3.3 \times 3.3 \text{ nm}, a)\Delta z=-17 \text{ pm}, b)\Delta z=-67 \text{ pm}, c)\Delta z=-125 \text{ pm} \text{ and } d)\Delta z=-175 \text{ pm}, where \Delta z \text{ is relative to that}$ associated with the Δf setpoint used for atom tracking.

5.5 Mapping tip-sample forces

Atom tracking enabled 3-D force spectroscopy was used to quantify the forces and the energies involved in the observed intermolecular contrast. Fig. 5.11 shows the short-range force curves for a molecular assembly of NTCDI molecules taken at the centre of the carbon ring (red color), above an intermolecular region (blue color), in a void region between the molecules (purple color) and above a C-C bond (green color). It can be seen that the intermolecular and intramolecular contrast is sharp only when the tip-sample distance is small enough to record the force value after the turn-around of the force. It is generally accepted that this feature is not produced by hydrogen bonding interaction but its rather an artefact, as it was discussed in the Chapter 1. Another observation from Fig. 5.11 is that the force curves measured above the C-C bond in the NTCDI molecule have very subtle differences between them, especially at the centre of the carbon rings and at the edges of the molecule where the supposed hydrogen bonds are formed, due to the nature of the tip-sample system.

In Fig. 5.12 (c) the complete tip-NTCDI island - Ag- $\sqrt{3}$ system was simulated while the position of the simulated² tip at an initial height of 0.6 nm with respect to the molecular surface is marked with 'X' symbols. The tip-sample separation was then reduced in small steps of 0.1Å, towards the surface. The total energies were calculated to obtain the tip-sample force. Then we compared $\frac{\partial F}{\partial z}$ and the maximum attractive force with the forces we measured for the short-range curves. It was found that the best agreement out of all the tip apices we tested was the O-down orientation as presented in Fig. 5.12 (b) and particularly in the negative force gradient region as shown in Fig. 5.12 (a). There were also alternative tip structures, such as a H-terminated and an Agterminated silicon cluster, that we considered and had good agreement with the experimental force spectra acquired above the C-C and carbon ring positions. This suggests that all the tips would be capable of intramolecular resolution but not all of them are suitable for recording intermolecular contrast, since the intermolecular location was generally overestimated or failed to become sufficiently repulsive (Fig. 5.12 (d)-(f)).

²Simulations were carried out by Lev Kontorovich and co-workers.(Appendix A)



Figure 5.11: Quantifying the short-range forces responsible for the intermolecular contrast in an NTCDI assembly. Short-range curves for a NTCDI molecular assembly, which were acquired at the centre of a carbon ring, above C-C bond, above a hydrogen bond region, and in a void void region between the molecules are plotted in red, green, blue and purple, respectively. The curves were extracted from a spectroscopy grid acquired at 5 K. Slices through the spectroscopy grid acquired at the z values labelled as 1-6 on the force curves are shown as images 1-6 to the right. Note, in particular, the absence of intra- and intermolecular contrast in the region of the force curve where the force gradient is positive. Distinct intermolecular contrast appears only when the force gradient becomes negative, that is, when the repulsive component of the tip-sample interaction is sufficiently large to cause the force gradient to change sign. The oscillation amplitude here was 110 pm.



force curves overlaid in the negative force gradient region of the tip-molecule interaction. Inset: complete calculated F(z) curves, including the data for the bare surface position (that is, X in Fig. 3c) whose minimum lies at a much smaller tip-sample separation. (b) Ball-and-stick model of the full simulated system with an O-down oriented NTCD1 Calculated F(z) curves for alternative tip structures: H-down NTCDI, H-terminated and an Ag-terminated silicon tip~(side-on~view).~(c)~Top-down~schematic~of~the~simulated~NTCDI~island~with~spectral~sites~marked~as~crosses.~(df)Figure 5.12: Comparison of experimental and calculated tip-sample interactions. (a) Calculated (-) and measured (Δ) cluster, respectively.

5.5.1 TED versus density depletion

When a total electron density (TED) calculation was performed³ for the NTCDI island adsorbed on the Ag- $\sqrt{3}$ surface the results showed a poor agreement between the TED distribution and the constant height DFM images of intermolecular contrast, despite earlier works following a similar approach suggesting a good agreement [14]. Namely the TED distribution showed that the electronic density in the intramolecular region was over an order of magnitude smaller than that of the C-C bond regions, as shown in Fig. 5.13. In contrast, the DFM images as shown in Figs 5.10 and 5.11 do not show a striking difference in the sharpness of the contrast for intra- and inter-molecular resolution. We can deduce certain conclusions from the above.

To examine the role of tip-sample interactions in our system we calculated both the TED and the electron density difference (EDD), (where $EDD = TED_{system} - TED_{isolated-surf.}$), and also the isolated NTCDI tip at each step of the F(z) calculation. The two densities were summed together and subtracted from the TED of the full system. The remaining EDD describes the interaction caused by the tip. By comparing the magnitude of the TED and the EED it was found that the tip interaction in the C-C areas is only ~0.8% while 11% is affected in the intermolecular location.

Both the TED and EDD were plotted as x-y slices positioned at 50 pm above the NTCDI molecular plane in Fig. 5.14. This position was chosen to intersect the EDD in the region of highest density. To quantify

³The TED calculation were carried out by L. Kontorovich, H. Sang and S. Jarvis



Figure 5.13: Total electron density slices taken in x-y plane positioned 500 pm above the NTCDI molecular plane. a), Total electron density plotted to highlight the differences in charge in the H-bonding regions and carbon backbone. b), The same plot as (a) with the addition of a 3D isosurface plotted at 0.08 e/a_0^3 , the minimum at which we observe charge in the H-bonding regions (see legend on the right).

the effect of the molecular probe on the electronic density we calculated the TED and EDD with the O-down NTCDI tip at each tip-sample separation from the calculated F(z) curves. The same lateral positions as the force spectra in Fig. 5.12 were chosen to facilitate a comparison with our experimental data. Fig. 5.14 (a), (b) are the TED and EDD maps above a NTCDI C-C bond, and an intermolecular contrast, respectively, at a tip-sample separation corresponding to Position 1 in Fig. 5.11.

Summarising the above, it is shown that four major factors can contribute to the variation of the level of appearance of inter and intra molecular contrast in our experiments: the nature of the tip, the flexibility of the tip [112, 113] and the size of the tip are three factors which directly relate to the tip itself while the forth factor is the possible appearance of a displacement of the NTCDI molecule at the tip apex. All these factors can affect the inter and intra molecular contrast to a point where artefacts appear in the acquired NC-AFM images taken which could mislead us to conclude that hydrogen bonds are depicted on the images. In the recent literature, the origins of the inter and intra molecular contrast have been studied more thoroughly and more information has been provided. Namely, Moll et. al [51], using a CO- terminated tip on a pentacene molecule provided evidence that the Pauli repulsion is mainly responsible for the high resolution NC-AFM images while the van der Waals and electrostatic interactions only add a diffuse attractive background with no atomic contrast. Later, Hapala et al. [37] demonstrated a flexible tip model where the lateral and the vertical relaxations of the probe particle are closely coupled. In the area between the neighbouring potential "basins" the vertical position of the probe particle also



Figure 5.14: Relaxed and frozen electron densities. (a) Calculated TED (left) and EDD (right) plots for an O-down NTCDI tip at the C-C location of a networked NTCDI at a tip-sample separation of $z \pm 250$ pm; (b) Equivalent plot for the H-bond location. Note comparable intensity of EDD features in a and b. (Density scale represented in units of electrons per bohr³). EDD plotted at 50 pm above molecular plane. (c) Slice through the three-dimensional force field, also corresponding to z value +1. The green and blue lines indicate the positions of the line profiles for the C-C bond region, and hydrogen-bond region which are shown in (e); (d) Simulated image of hydrogen-bond region generated by fixing all atomic coordinates and the electron density of the tip and sample. This slice was taken from a simulated three-dimensional force field and was selected on the basis of a best match to the experimentally measured forces. The dotted lines through the C-C bond (green in (c)) and the intramolecular bond region (blue in (c)) regions represent the positions of the simulated line profiles shown in f. (e) Upper: experimentally measured force profile across an intramolecular C-C bond. Lower: experimental force profile for the hydrogen bond region. (f) Line profiles through the simulated three- dimensional force field, at the Hbond and C-C bond positions. Compare the experimental profiles in (e). Note that the small oscillation of the force observed for the simulated hydrogen-bond region arises from a numerical artefact owing to the finite self-consistent field (SCF) grid size used to calculate the density.

becomes very sensitive to the precise position of the tip, thus producing the sharp image features in the AFM images. Haemaelaeinen *et al.* [43] used the model introduced by Hapala *et al.* to demonstrate that intermolecular features may appear even in molecular assemblies known to devoid of intermolecular bonds naturally, thus supporting the idea that intermolecular features can appear as artefacts in NC-AFM. Also, the electrostatic forces and outer most electron distributions of the sample were demonstrated to play a role in the appearence of intermolecular constrast of organic molecules in NC-AFM [39, 42].

Regarding how the size of the tip affects intermolecular contrast, Jarvis *et al.* used a C_{60} molecular assembly imaged with a C_{60} terminated tip and showed that increasing the size of the tip produces the appearance of strong intermolecular contrast on the image even though it is naturally non-existent [44]. Finally in our work, we have provided information that in 'frozen' systems, where the tip relaxation is not taken in account for the calculations and only the electronic density of the un-relaxed system contributes to the tip-sample force, the force curves show similar overall trends to the fully relaxed system, which is in agreement with the finding described above and suggest that the intermolecular artefact in NC-AFM images is of multiple origins. In addition, an interesting point was discovered in our calculation, which is shown in Fig. 5.15, where a CO- terminated tip was also used in order to extract the intermolecular contrast forces. These forces were matching with the NTCDI termination having an O- pointing down. That revealed, that the imaged contrast was suspected to containing artefacts given that the force measured above the C-C covalently bonded area was close in value



Figure 5.15: Calculated F(z) for CO terminated tip overlaid with O:NTCDI. Oxygen-down NTCDI data is shown as dashed lines with CO data shown as solid lines.

to the force measured above the area of the supposed H-bonds, using DFT calculations.

5.6 Conclusions

In this chapter, we examined the adsorption of a small organic molecule (NTCDI) in Si(111)- (7×7) and we report that there are two energetically preferable adsorption geometries among others. In the second part of the chapter, we studied an NTCDI molecular assembly in Ag:Si(111)

with a particular interest in the intermolecular features recorded in between the NTCDI molecules of the molecular assembly. Resent studies have shown that the nature of these arise from several factors that need to be taken into consideration especially when recording a contrast on alleged hydrogen or halogen bonds. An interesting finding in our results is the similarity of the force measured on the C-C bond and the hydrogen bond.

Chapter 6

A closer look at simultaneous STM and AFM measurements with a qPlus sensor

With the introduction of the qPlus sensor [88] there has been an increasing interest in the simultaneous STM and AFM measurements with NC-AFM and specifically with a qPlus sensor. The possibility of measuring the interaction forces simultaneously with the flow of electrons between the tip and the sample opens a new horizon in the understanding of elemental processes of the electron transport on surfaces [50] and in clarifying the relationship between the short-range force and the tunnelling current in metal contacts [47]. In the case of qPlus sensors, due to their self sensing properties, the presence of the tunnelling current may introduce an undesired interference, or crosstalk, between the current and the deflection channel. Majzik *et al.* [52] studied the crosstalk and introduced a new qPlus sensor design which exploited the findings of their study to limit the crosstalk effect.

The crosstalk phenomenon

Crosstalk in electronics, is any phenomenon by which a signal transmitted on one circuit or channel of a transmission system creates an undesired effect in another circuit or channel. Crosstalk is usually caused by undesired capacitive, inductive, or conductive coupling from one circuit, part of a circuit, or channel, to another [114].

The crosstalk phenomenon, in the qPlus sensor configuration, as defined by Majzik *et al.* [52], occurs when an interference between the tunnel current and deflection channels leads to undesired modulation of the tuning fork motion or undesired electrical disturbance. The combination of an oscillating ground potential with the presence of a stray capacitance between the wires connecting the electrodes to the amplifiers may induce couplings between the channels. This, in turn, leads to artificial modulation of the detection channel.

Majzik *et al.* [52] has proposed that the crosstalk phenomenon is controlled by three major parameters: (i) the resonant frequency of the fork (f_o), (ii) the stray capacitance (C_c) between the wires connecting the electrodes to operational amplifiers, and (iii) the maximum amplitude of the modulation of the virtual ground potential, considering the signal is within the bandwidth of the STM operational amplifier (OPA). An Operational Amplifier is fundamentally a voltage amplifying device designed to be used with external feedback components such as resistors and capacitors between its output and input terminals. These feedback components determine the resulting function or 'operation' of the amplifier and by virtue of the different feedback configurations whether resistive, capacitive or both, the amplifier can perform a variety of different operations, giving rise to its name of 'operational amplifier'. An operational amplifier is basically a three-terminal device which consists of two high impedance inputs, one called the inverting input, marked with a negative or 'minus' sign, (-) and the other one called the noninverting Input, marked with a positive or 'plus' sign (+). The ideal OPA regulates the difference at the input terminals to zero and prevent any charge built up at the input. Any amplifier should ideally have a bandwidth suited to the range of frequencies it is intended to amplify, while too narrow a bandwidth will result in the loss of some signal frequencies, too wide a bandwidth will allow the introduction of unwanted signals and it will lower the signal resolution for small currents.

A current-to-voltage converter as shown in Fig. 6.1 converts the tunnelling current I_t to a voltage signal V_{out} . In order to achieve that the input current floats to the OPA at the virtual ground potential (V_g) . Following that, the current passes through a feedback resistor (R_f) connected in parallel between the V_{out} and V_g which induces a voltage drop equal to the value of $R_f \times I_t$. In parallel to the R_f a capacitor (C_f) is connected to the R_f and C_p represents the parasitic capacitance of the feedback resistor. The OPA ends up changing its output voltage because of the potential difference between the input terminals, compensating



Figure 6.1: Circuit diagram of a current to voltage converter where R_f is the feedback resistance with the parallel capacitance C_f ; C_i is the input capacitance, C_p is the parasitic capacitance and V_g is the virtual ground potential. OPA is denoted with blue colour. Adopted from [52].

the voltage drop and making sure the potential difference between the input terminals is zero. Because the inverting input is kept at the ground potential this terminal is denoted the virtual ground V_g . The slew rate is the maximum rate at which an amplifier can respond to an abrupt change of input level.

In FM-AFM mode when the tip is closer to the sample surface the resonant frequency changes by Δf because of the forces acting between the two [115] (see Chapter 2). It is also possible to observe a current flowing between the tip and the sample if they are conductive and differ-

ent bias is applied. The tunnel current (I_t) depends on the tip-surface distance (z) given by: $I_t = I_o e^{-2\kappa z}$ (Fig. 6.2(a), (b)), where I_o is the measured current when the displacement of the cantilever oscillation is zero and κ quantifies the decay of the wave in the tip-sample conjunction. In this case due to the oscillating cantilever from the AFM mode, the current signal is periodic. The frequency spectrum of the I_t shows higher harmonics of the modulation signal, Fig. 6.2(c). The I_t passes through a feedback resistor (R_f) . As z increases, the I_t drops causing a drop at the voltage between the input terminals. The operation amplifier (OPA) tries to compensate the voltage drop by changing its output voltage (V_{out}) to ensure zero potential difference between the terminals. The relationship between the V_{out} and I_t is $V_{out} = - R_f I_t$.

The tunnelling current, I_t , is converted to a voltage signal V_{out} with a current to voltage converter (IVC). The optimal function of the IVC occurs as long as the value of the virtual ground potential is kept constant. To achieve that V_{out} must vary in order to compensate. The slew rate of the OPA determines how fast V_{out} can counteract the voltage change, by producing the same voltage on the output but with opposite sign in order to keep the voltage difference between the input terminals at zero. $V_{out} = \frac{-R_f I_t}{1+2\pi f R_f C_p}$, where f is the frequency of the IVC response and C_p is the parasitic capacitance of the R_f in the IVC. If f is small the term $2\pi f R_f V_c$ tends to zero, therefore is negligible. But if f is $\geq \frac{1}{2\pi R_f C_p}$ then the value of C_p becomes the dominant term of the equation. Therefore for small frequencies C_p plays a minimal role in how V_{out} varies. On the contrary, for larger frequencies the value of C_p is constant, the fluctuation of



Figure 6.2: (a): The effect of z modulation on (b): the tunneling current, and (c): the frequency distribution FFT. Adopted from [52].

 V_{out} becomes smaller for higher frequencies. The combination of small differences between V_{out} and V_g at higher frequencies may pose a problem to the OPA to keep V_g constant with precision due to the finite response time of the amplifier.

As explained before, the OPA tries to keep the virtual ground constant as stable as possible, but Fig. 6.2 shows that I_t contains frequency components much higher than the resonant frequency of the tuning fork, stemming from the higher current flow when the tip comes closer to the surface during the oscillation cycle of the cantilever. This can lead to the OPA not being able to keep the virtual ground (V_g) constant due to speed limit of the amplifier. In order to determine the optimal slew rate of the OPA the following formula should be used [52]:

$$\frac{dV_{out}}{dt} = 2\pi f V_{out}^{peak} \cos(2\pi f t)$$

where V_{out}^{peak} is the output voltage at the peak of the amplitude signal, and at t =0, the maximum values are given by [52]:

$$(\frac{dV_{out}}{dt})_{max} = 2\pi f V_{out}^{peak}$$

Majzik *et al.* [52] tested the set-up shown in Fig. 6.3(a), with various stray capacitance values (C_s), resonant frequencies, and maximum amplitudes of the ground potential. The results show that the maximum current, can be estimated by the following formula [52].

$$I_{C_s}^{MAX} = C_s 2\pi f V_{out}^{peak}$$

 $I_{C_s}^{MAX}$ can also be called the degree of the crosstalk because as it can be seen from the above formula is only dependent on f and V_{out}^{peak} which together are responsible for the appearance of the crosstalk as described.

Fig. 6.3 B shows that large C_s values, especially exceeding 1 pF, can cause a significantly altered V_d output over time. As a consequence, crosstalk appears at high values of C_s . In addition, the current magnitude also depends on the frequency f_o . Therefore crosstalk can appear when the sensor is operated at higher frequencies, but for the purposes of our experiment the sensor were operated only at their resonance frequencies.

Finally, as the crosstalk depends on the speed of the amplifier response, the same analysis was carried out by Majzik *et al.* [52] with two different OPAs. The OPA with higher slew rate decrease the modulation of the virtual ground at higher C_s values. This implies that high slew rate OPAs can provide minimum crosstalk even in a circuit with a relatively high C_s value.

The crosstalk effect affects the deflection signal directly, as shown in the result section of this chapter. The dissipation signal refers to any change in the drive amplitude which is either related to the tip-sample dissipative forces (real dissipation) [67–69] or it is assumed to be caused by non-ideal behaviour of the instrument (apparent dissipation) and it is indirectly affected by the crosstalk effect as it is intrinsically derived from the response signal of the cantilever [70].



Figure 6.3: (a): The coupling between the deflection and the tunneling current channel is established by the stray capacitance C_s . To show the effect of the cross talk, signals shown in Fig.6.2 (b): The signal in the deflection channel is altered significantly at the output V_D for C_s values exceeding 1 pF. Adopted from [52].

6.0.1 The Systems

In this work two low temperature systems were used; a Scienta Omicron GmbH and a Createc low temperature STM/AFM, commercially available from Createc Fischer & Co GmbH (design based by Gerhard Meyer, Chapter 3). Fig. 6.4 illustrates a simplified schematic diagram of the Omicron electronic circuit, Matrix control electronics and software supplied with the instrument by Omicron, of the pre-amplifiers for the STM and the AFM signals. The Omicron system uses MATRIX electronics which contain a IVC H3 pre-amplifier with two internal feedback resistors at the first stage I/V-converter with bandwidths of 800 Hz at a maximum current of ± 3.3 nA and of 40 kHz at maximum current of ± 333 nA, respectively, for the detection of the STM signal. Our Createc system is using Nanonis Createc interface controller electronics and a simplified schematic diagram of the electronic circuit of the Createc system in shown in Fig. 6.5. The Nanonis electronics are equipped with a Femto DLPCA-200 pre-amplifier which provides seven bandwidth\range options starting from 7 kHz at maximum current of ± 100 nA up to 200 kHz at maximum current of $\pm 10\mu$ A.

6.0.2 The Sensors

Two types of sensors were used on the Omicron system: a commercial qPlus and a home-built (HB) qPlus sensor. On the commercial Omicron qPlus sensor a quartz tuning fork is glued on the ceramic substrate and the tip is glued on the side of the prong on top of the electrode that feeds the STM signal. The STM electrode which is in contact with the



Omicron LT SPM circuit using Omicron commercial qPlus sensor

Figure 6.4: Simplified schematic diagram of the electronics of the Omicron LT UHV system using an Omicron commercial qPlus sensor. TP1 - 4 represent the test points.



Createc LT SPM circuit using commercial qPlus sensor

Figure 6.5: Simplified schematic diagram of the relevant signal paths of the Createc LT system using a Createc commercial qPlus sensor.

tip is connected with the STM leg of the sensor with conductive epoxy. The other electrode of the tuning fork provides the AFM signal coming from the deflection of the prong (Fig. 6.6a). The design of the HB sensor is based on the design and methods of Majzik *et al.* [52] (Fig. 6.6b). The Createc system uses a sensor with a tuning fork and with a separate wire for the tunnelling current. One prong of the tuning fork is fixed on a ceramic substrate. The tip is attached on the end of the free prong with non-conductive epoxy and a Au wire connects the tip with the STM contact of the holder. In this system, the sensor collects two AFM signals which are fed to the system, where the final deflection is measured Fig. 6.6c.

6.0.3 Construction of the HB sensor

For the construction of the HB sensor, which was part of this thesis (Fig. 6.6b), a Au Omicron plate was used as the base of the sensor. On top, a Cu substrate was glued with non-conductive epoxy on the base and on the side of the AFM leg. On the Cu substrate a piezo crystal cantilever provided by Prof. Giessibl (sensor qPlus C in Ref. [116]) was glued with non-conductive epoxy. The STM electrode of the piezo crystal cantilever was grounded on the Cu substrate which was connected to the Au base with conductive epoxy. The AFM electrode of the cantilever was connected to the Au electrode of the sensor plate with a Au wire. A tungsten wire of 50 μ m diameter was used for tip and it was attached at the front of the prong with non-conducting epoxy. A Au wire connected the tip to the Cu rod. The Cu rod was connected with conductive epoxy on the STM leg of the sensor plate and on the Cu substrate with non-conductive epoxy (Fig. 6.6b).



Figure 6.6: Photographs of the three types of sensors. (a):Omicron qPlus sensor; (b):Home built qPlus sensor; (c): Createc commercial qPlus sensor. Under each sensor, a schematic representation presents additional details.

The tip was shortened and sharpened after it was attached to the cantilever with the drop-off method [117]. The tip was submerged in a 2M NaOH solution with a ring shape electrode immersed in the solution, close to the surface, while the desired length of the tip was left above the solution surface. A voltage was applied and a current of 10 mA flowed between the anode, tip, and the cathode, electrode due to the potential difference. A drop in the current indicates that the tip has been etched, then the sensor was pulled back, and then rinsed initially with water to remove the remaining NaOH followed by isopropanol (IPA) for further cleaning. The sensor was then transferred to the microscope. The tip was treated with pulses and crashes on the sample surface until sub molecular resolution was achieved.

6.1 Crosstalk identification from imaging channels

In this section, a description of the imaging methods with constant height AFM with or without applied bias voltage (U_s) is provided using eight different configurations based on three different sensors (Omicron commercial, Omicron HB and Createc commercial sensor), followed by corsstalk identification from the imaging channels and a comparison of the results taken with each system configuration

6.1.1 Omicron LT

Commercial qPlus sensor

Submolecular resolution in constant height AFM at $0mV U_s$ of a C₆₀ island on Ag(111) was achieved. Ag(111) was chosen because is known to be able conduct high current flow due to its metallic nature and the C₆₀ molecules can facilitate the acquisition of high sub-molecular resolution images where any possible distortions would be clearly detectable [44]. For the tunnel current images, the contrast has been recorded in the range of pA. To characterize and identify any distortion on the channels in the presence of current, a gradual increase/decrease was applied in the U_s . In the case of the commercial qPlus sensor the voltage was changed from -19 mV to +19 mV in steps of +4 mV. Lower and higher U_s from the ones illustrated here were applied but the tip-sample system was unstable and the tip changes or crashes occurred. When U_s was applied, the contrast in the Δf , amplitude and excitation changed and it appeared to be similar to the contrast recorded on the current channel.



Figure 6.7: Constant height images of C_{60} islands on Ag(111) surface taken with a commercial qPlus sensor. I-L show the profile lines on each channel. The black profile line is from image A (+0.36 mV) and the blue is from image E (-19 mV). The data were acquired at $f_o = 23,756 \text{ Hz}$ and $A_o = 90 \text{ pm}$.

Fig. 6.7 shows images taken at 0.36 mV which for our system is the offset that measures 0 mV, and + 19 mV for each channel. Profile lines on top of the C_{60} islands in both cases (with and without U_s) are plotted to show the distortion of the signals. The distortion caused by the current is shown on the amplitude and the excitation channels. The subtracted images and the profile lines of A - D with E - H of Fig. 6.7 are shown in Fig. 6.8.

HB qPlus sensor

For a deeper understanding of our measurements a battery was connected at TP1 (Fig. 6.4) and bias was applied to the sample while the current channel was grounded, the U_s that was applied on the sample was measured externally with a multimeter.



Figure 6.8: Subtracted images A-D and profile lines E-H from Fig. 6.7.

In similar fashion, the HB sensor was tested. Starting by taking an image at 0V and increasing/decreasing the U_s gradually to $\pm 19mV$ with a step of $\pm 2mV$. The contrast between the frequency shift, the amplitude and the excitation was distorted in the presence of the current. The distortion of each channel is shown in Fig. 6.9 E-H. The profile lines show the difference between the absence and the presence of the current signal on each channel.

The subtracted images illustrate that the distortion in the Δf channel is smaller than the Omicron commercial sensor, while in the extracted images there is a clear difference in all of the channels between the absence and the presence of the current. The level of distortion in this case (Fig. 6.10) in the Δf , amplitude and excitation is in the range of 3Hz, -9pm and 0.24mV respectively. The profile lines show a clear difference, but resemble those of Fig. 6.7.



Figure 6.9: Constant height images of C_{60} islands on Ag(111) surface. The data were obtained with HB sensor. In image B the operational amplifier was in the range of 3.3nA therefore detailed features of the C_{60} molecules in low tunnel current were recorded. I-L show the profile lines on each channel. The black profile line is from image A (+0.36 mV) and the blue one is from image E (+19 mV). The data were acquired at $f_o = 22,756$ Hz and $A_o = 70$ pm.



Figure 6.10: Profile lines and subtracted images from Fig. 6.9.

Evaluating the noise level of the images

In order to quantify the level of crosstalk we have detected the minima and the maxima current values of each image. This means that the level of the background noise for an error estimation needs to be considered. A script was created where five points on the substrate and five in-between the molecules of the island were collected. From those points a circle with 5 pixel radii was drawn and the values within were averaged while the standard error of each was calculated. Fig. 6.11 shows the noise level on the substrate and within the C₆₀ island. The level of the noise appears negligible compared to the values recorded at minima and maxima current.

In order to examine if there is any electronic influence acquired from the STM pre-amplifiers (Fig. 6.4) and to get a deeper understanding of the effect taking place with both sensors, an external battery was introduced and U_s was applied to the sample in similar fashion as described above. The bias was gradually changed from 0mV to $\pm 8mV$ with a step of 4mV. The tunnel current electrode of the system was grounded, therefore the current couldn't be recorded. To ensure that the measurements were obtained in a similar regime as the illustrated data in Fig. 6.9, after obtaining an image at a specific U_s the tip was placed on top of the surface and the continuous signal of the Δf was recorded, then the tip was pulled back a few nm from the contact point. The tunnel current electrode was then grounded and the same U_s was applied to the sample from the battery. The applied bias was measured with a multimeter. The tip was then returned to the surface by measuring the Δf continuous signal. When the Δf reading was equivalent



Figure 6.11: Each plot shows the background noise of the relative channel on the bare Ag and in between the C_{60} molecules of the island. Taken with the Omicron commercial sensor.



Figure 6.12: Constant height images of C_{60} islands on Ag(111) surface. The images were obtained with the HB sensor. G-I show the profile lines on each channel. The black profile line is from image A (+0.36 mV) and the blue is from image E (+8 mV). The data were acquired at $f_o =$ 22,756 Hz and $A_o =$ 70 pm.

to the previous signal from the Matrix electronics, the tip was engaged and left for a few seconds in order to avoid creep in the z axis. Then the measurement was obtained at the same U_s as the previous one. In this way the measurements were taken in a sequential fashion and the results from both system configurations could be compared directly during the measurement. The amplitude and the excitation channels appeared distorted Fig. 6.12.

The subtracted images (Fig. 6.13) show the image contrast difference


Figure 6.13: Profile lines and subtracted images from Fig. 6.12

between 0V and $\pm 8mV$ U_s. The distortion was recorded and measured in this case where the current electrode of the system was grounded. The magnitude of the distortion in each channel is in the same order of magnitude with the operational amplifier. In all of the configurations of the Omicron LT system, in the presence of current, a distortion was recorded.

In the case of semiconductors, the effect of phantom force suggests that in the presence of current, the Δf channel measures a force which is independent of the directionality of the tunnelling current [50].

6.1.2 Quantification of the crosstalk effect from the images: Omicron LT

The aim of this study was to compare the commercial Omicron qPlus sensor with the HB Omicron sensor and with the Createc commercial qPlus sensor. The results for the Omicron system, with the commercial qPlus sensor, show that at even moderate currents, crosstalk and distortion were recorded in all of the channels. The distortion was recorded with the HB Omicron sensor in higher currents compared to the commercial qPlus. To analyse the results a script was developed which reads and stores the maximum and the minimum current values within each image, acquired at positive and negative U_s respectively. From the data shown in Figs. 6.7 and 6.9 the highest current values were collected from each image. Then the values at the same positions were collected from the frequency shift, amplitude and excitation channels and plotted against the current (Fig. 6.14). Images taken at $U_s = 0V$ were used in both, the negative and the positive case presenting a reference point for both. The tip state during imaging became unstable at the higher U_s that were used, in all of the cases for the Omicron system with both sensors and electronic configurations. During imaging, force spectra were acquired to measure the force. Negative spectra from the imaging position were performed starting at $U_s = 0$ mV.

A similar procedure was applied for the data shown in Fig. 6.9, and combined with the former data result in Fig. 6.14. For the data collected with attached battery due to the lack of the current channel the stored locations from the channels shown in Fig. 6.9 were used and the result is similar to Fig. 6.14 where the bottom row is plotted versus the applied U_s as a proxy for I_t . To rule out the phantom force effect [50], we used the image obtained at $U_s = -19$ mV. In this image the minimum current was located and a profile line along the fast scan axis crossing the point of the minimum current was drawn. The profile lines of the current and the Δf /amplitude/excitation channels were plotted. Fig. 6.15 show the profile lines taken at the minimum current, the peak of the current appears to be in the same location as the peak of the Δf , amplitude and excitation channels.

The Omicron commercial sensor operated with Matrix electronics shows that the distortion of the Δf signal is stronger when the current tends to negative values, the amplitude is suppressed while the excitation increases. In the positive part the distortion of the Δf seems smaller than the negative part, but the physical amplitude appears to increase while the excitation is tailing to zero volts (Fig. 6.14 top row).

The HB sensor operated with MATRIX electronics records large distortion on the Δf channel when the current is positive, while the physical amplitude decreases and the excitation increases. In negative currents the distortion of the Δf appears smaller than the positive regime, the amplitude is constant while the excitation is tailing to zero (6.14 bottom row). In Sec. 6.4 possible explanations for the difference of the behaviour between the two Omicron sensors is provided.



Figure 6.14: Comparison between frequency shift (left), amplitude (centre) and excitation channels (right) against the maximum current values. From the current channel of each case the highest current point was collected and compared with the respective point in the channels of frequency shift, amplitude and excitation. The points were collected from the data shown in Figs. 6.7 & 6.9. The top row shows the three graphs of the Omicron sensor and the bottom row the graphs of the home built sensor. The red and the blue lines represent the images taken in negative and positive bias respectively. The black line in the centre graphs illustrates the A_{vib} set point in each case.

6.1.3 Createc LT

In this system two different measurements took place using constant height AFM. Initially after achieving molecular resolution the current range was set to 10 μ A corresponding to a bandwidth of 200 kHz. The U_s was set to - 1.43 mV and at + 1.5 V. A shift in the Δf signal was



Figure 6.15: Profile lines of the Δf , amplitude and excitation at the maximum current value are plotted.

measured in the range of ≈ 2 Hz where the high U_s measurement is more negative than the low U_s, (Fig. 6.16 *I*) due to the large change in the electrostatic forces at the higher U_s. Other than the long range electrostatic regime and the difference in the current (Fig. 6.16 *J*) the amplitude and the excitation channels remain similar without significant changes (Fig. 6.16 K & L)

The current pre-amplifier gain was then switched to 100 nA. Fig.



Figure 6.16: Constant height images of C_{60} islands on Cu(111) surface A-H taken with the Createk system. The black profile line in the graphs in I to L represents the data obtained at $U_s = -1.43$ mV and the blue profile line the data taken at $U_s = +1.5$ V. Data were acquired at $f_o = 20,041$ Hz and $A_o = 300$ pm. Image acquired by Dr. Samuel Jarvis.



Figure 6.17: Constant height images of C_{60} islands on Cu(111) surface. The black profile line in the graphs in I to L represents the data obtained at $U_s =_1 .5$ V with current range 100 nA and the blue profile line the data taken at $U_s = +1.5$ V With current range 10 μ A. The data where acquired at $f_o = 20,041$ Hz and $A_o = 300$ pm. Image acquired by Dr. Samuel Jarvis.

6.17 demonstrates the difference in the two current ranges at the same U_s . The profile line of the low current range (Fig. 6.17 E - H) images show a large distortion in all of the channels. Due to the limitation of the pre-amplifier, the current saturates at lower values than before.

The results presented here, from the Createc system, show that there is no effect on the amplitude, the excitation and the frequency shift signals even at several hundred nA when the system and the signal paths are set up correctly. Most of the problems are due to the electronics and wiring of the Omicron system.

6.2 Quantification of the force spectra obtained with each system

The images acquired with AFM, as discussed above, showed a distortion in the presence of current. In order to have a more detailed view of the distortion as well as quantify it, site-specific on-off spectroscopy was used: to briefly explain the technique the "On" spectra was taken over a single C_{60} molecule, while the "Off" spectra were taken away from the molecules, over the Ag surface in order to subtract the long range force interactions from the total force spectra. This, in theory, should leave only the short range force interaction between the the tip and the molecule on the surface.

6.2.1 Omicron Commercial sensor

On-off spectroscopy was performed in all of the systems with various U_s , in order to have a closer look at the distortion caused with the increasing current. For the Omicron commercial sensor spectra were obtained within the range of $U_s = \pm 19$ mV. Fig. 6.18 shows the force curves obtained at -19 mV, 0 mV and + 19 mV in three different amplitude feedback values at 1%, 10% and 100%, in order to see the amplitude feedback dependence on the force curves. Due to the nature of the NC-AFM technique the amplitude need to be kept constant, by decreasing the amplitude feedback a larger distortion was expected due to the slow response of the feedback mechanism to keep the oscillation amplitude constant.

At amplitude feedback of 1 % when the I_t is positive, the physical amplitude initially increases (at 0.05 nm) and the excitation remains constant. At 0 nm distance the amplitude decreases while the excitation also decreases. For negative current values at amplitude feedback of 1 % the amplitude decreases while the excitation increases. The amplitude feedback response in close proximity of the tip-sample fails to keep the drive amplitude constant. For amplitude feedback of 10 % at positive I_t the amplitude increases and the excitation tails to zero. For negative I_t the amplitude decreases and the excitation increases. At feedback of 100 % for positive I_t , the amplitude increases while the excitation tails to zero, while at negative I_t the amplitude decreases by 40 pm. The excitation increases up to 10 V.

Since comparing the force spectra obtained at minimum and maximum bias voltages alone does not provide enough information for each amplitude feedback, all force spectra obtained at 0 mV from this data set were used to calculate the standard deviation (STD) of those measurements. The STD curve which was calculated this way (blue line) is plotted against the force curves obtained with various U_s , in order to see where the force curve deviates and to compare it with the current curve (green line).

In the case of the Omicron sensor with amplitude feedback of 1%, it can be seen that in both the positive and the negative bias voltage, the red curve coincides with the blue curve (Fig. 6.19). If the red curve de-



Force spctra obtained with Omicron commercial qPlus sensor

Figure 6.18: Force spectra on top of the C_{60} molecules obtained with different amplitude feedback using MATRIX electronics with the commercial Omicron sensor. The force, I_t , amplitude and excitation are shown.

viates from the blue curve that means that there is a significant change in the force which should be caused by the presence of the current. This doesn't appear to be the case. Namely, in the positive bias voltage cases,(Fig. 6.19 a-d) it can be seen that the current is exponential in all cases and doesn't appear to have any unexpected values with the only exception the case of +19 mV where the curve does not follow the blue curve, and also the slope of the current changes compared to the other cases (Fig. 6.19 e). This abrupt change in the current signifies that the tip is closer to the surface than the rest of the cases or in other words, that the distance between the tip and the surface decreased.

In the case of the negative bias voltage (Figs. 6.19 f-j) it can be observed that the current follows a similar exponential curve at -4mV, -8mV and -12mV (Figs. 6.19 f,g,h) while at -16 mV and -19mV the slew-rate of the current changes which is depicted at the slope of the curve (Figs. 6.19 i, j). Namely a sudden jump of the current is observed at around 3.2 nA while the jump in the case of -19 mV appears when the tip is farther from the surface compared to the -16 mV.

Comparing the behaviour of the force and current between the positive and the negative bias voltage, we can observe that the maximum current reaches a value of around +0.8 nA and -0.8 nA in the +4 mV and -4 mV cases respectively. In the +8 mV and -8 mV cases the current maximum values are around +1.5 nA and -1.5 nA respectively (Figs. 6.19 a, b, f, g). But in the rest of the cases (+/-12 mV, +/-16 mV and +/-19 mV) the maximum current is different between the positive and the negative bias voltages. In addition, the jump in the current appears at a larger distance between the tip and the surface at the negative bias voltage cases compared to the positive ones. In all cases the force (red line) appears to be unaffected by the changes in bias voltage and current.

In the case of the amplitude feedback of 10% and more specifically at positive bias, there can be seen little deviation between the red and the blue curves mainly in the +12 mV, +16 mV and +19 mV (red and blue curves denoting again the force curve obtained with applied U_s and the standard deviated curve of all the spectra obtained at zero voltage respectively). In all cases there appears to be a jump in the current which implies that the tip close proximity changes dramatically (Fig. 1 a-e in Appendix B). The current jump occurs at around 0.7 nA at +4mV and +8 mV and at around 2.2 nA, 3.5 nA and 4.8 nA at +12 mV, +16 mV and +19 mV respectively.

In the negative bias voltage cases the deviation between the red and the blue curves are more obvious, especially at the higher voltages. The current curve appears to jump at the same z where the deviation between the force curve and the zero voltage spectra curve occurs. This is strong evidence that the tip-sample proximity changed and the tip came very close to the surface abruptly due to amplitude's increase (Fig. 1 f-j in Appendix B).

The comparison between the positive and the negative bias voltage shows that the maximum values of the current are generally higher at negative bias voltage. This implies that the tip reaches closer to the surface with negative bias voltage applied. The greatest abnormali-



Omicron commercial sensor amplitude feedback 1%

Figure 6.19: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different U_s using MATRIX electronics with the commercial Omicron sensor with amplitude feedback of 1%. In the force window the blue curve is the standard deviation curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied U_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.

ties in the force curve and the current curve coincide, showing that the tip-sample distance in those case was changed due to the amplitude's increase.

In the case where the amplitude feedback is 100% the behaviour of the system resembles that of the amplitude at 10% but with sharper deviations (Fig. 2 in Appendix B). At the positive bias voltage the red/blue curve deviation is more obvious at the +12 mV onwards while again at negative bias voltage the effect is much more obvious. Again in +/-16 mV and +/-19 mV we can assume that the tip was disturbed.

As a first result judging from all the cases described above, it can be seen that increasing the amplitude feedback worsens the behaviour of the system with regards to the crosstalk effect; higher amplitude feedbacks increased the distortion of the signal and produced unwanted behaviour of the tip. Another conclusion can be seen that for different bias voltages the crosstalk kicks in at different current values. This makes it difficult to predict at which current value the crosstalk kicks in with accuracy. Ideally it would be helpful to see the appearance of the crosstalk after a certain bias voltage, always the same, even in different amplitude feedbacks, but this is not happening in our case. Finally, the current appears to affect the excitation and the amplitude channel besides the force as can be seen in Fig. 6.18.

6.2.2 Omicron HB sensor

For the HB sensor, spectra were obtained within the range of $U_s = \pm 50$ mV with MATRIX electronics, Fig. 6.20. The force curves (Fig. 6.20 left column) of the HB sensor at applied U_s appear to be affected by the change of the current. The amplitude and the excitation channels show similar behaviour to the one of the min/max depicted points in Fig. 6.14, bottom row. When the current is negative the amplitude remains constant while the excitation tails to zero. In positive currents the amplitude decreases while the excitation increases. The physical amplitude is within a similar range, around A_o , in both cases while the excitation on the home built sensor was measured an order of magnitude smaller that the commercial sensor.

Force curves of the HB sensor with the battery set-up (Fig. 6.20 right column) show that the force is affected by the presence of the current but the amplitude is stable compared to the Omicron commercial sensor and the HB sensor with MATRIX electronics system. The excitation in the presence of negative U_s decreases while in positive U_s increases, revealing a similar behaviour for both electronic configurations. The changes on each channel don't seem to be significant when compared with the other two configurations.

The blue line in Figs. 3 in Appendix B and 4 in Appendix B denotes the curves taken at 0 mV which is the standard deviation of the curve obtained by the MATRIX electronics and the external battery with the HB sensor. In principle in both configurations we expect to see an overlap in 0 volt curve, therefore in this case both of these curves were used



Figure 6.20: Force spectra on top of the C_{60} molecules obtained using MATRIX electronics (left) and with the external battery (right) with the HB sensor. The force, I_t , amplitude and excitation are shown.

in order to determine the range of the standard deviation of the 0 mV curves.

Regarding the Omicron home built sensor at the positive bias voltage the current curve reaches up to around 0.8 nA and the slope of the force curve (red) does not deviate from the blue curves between +1 mVand +14 mV of bias voltage (Fig. 3 a-g in Appendix B). At +14 mV and +20 mV though, the force curve starts deviating from the blue one while the maximum current rises to around 25 nA. The effect becomes much stronger at +50 mV (Fig. 3 h, i , j in Appendix B). A paradox in those measurements is that the maximum current fluctuates while the bias voltage increases; at +10 mV has a higher value than +12mV for example and while it reaches a maximum of 25 nA at +20 mVit becomes much lower (around 7 nA) at +30 mV. It is possible that the electrostatic force or another factor has affected the state of the tip which later flipped back to its original state giving those unexpected results in the process. If the tip had changed state permanently we would expect to get altered images when using the tip before and right after the measurements are taken which was not the case. It is important to note that the region of 50 nA was not even possible to be reached with the Omicron commercial sensor without any tip permanent changes.

At negative bias voltage there are no major deviations between the red and blue curves between -1 mV and -20 mV. On the other hand at -30mV the red curve begins to deviate clearly from the blue one (Fig. 4 in Appendix B). The current curve follows an irregular pattern of change, compared to the increase of bias voltage, similar to the positive bias voltages. Again we can speculate that the explanation for the measurements is what we described for the positive bias voltage case. Comparing those results with the respective positive bias voltage it can be seen that there is a higher deviation of the force for positive bias as well as more electrostatic force which affects the current curve more than that of the positive bias.

In cases where the current distortion is not affecting the measured force and no deviation is observed, a distortion can be observed in the amplitude and the excitation channels (Fig. 6.20). This indicates the existence of an additional effect that we believe represents a new kind of cross talk. These results are different than those of the Omicron commercial sensor.

In the HB sensor with the battery configuration (Fig. 5 in Appendix B), it can be observed that the force deviation (red line) from the zero volts curve (blue line), begins at very low bias voltage. Even at +1 mV it gives a small curve deviation which increases gradually onwards. The blue line that was used here is exactly the same as the one used in Figs. 3 and 4 in Appendix B. The negative bias voltage follow a similar pattern. These results have been obtained without measuring the current in order to avoid the current pre-amplifier distortion and the bias is applied by external battery. The amplitude in this configuration is steady in contrast with the amplitude in all the previous configurations where the amplitude follows the current fluctuations. The excitation on the other hand change in a similar fashion with the MATRIX electronics of the HB sensor but it is an order of magnitude smaller than that (Fig.

(6.20). The fact that the amplitude and excitation levels are much more stable in this configuration indicates that the current measurement (via the current pre-amplifier) by itself introduces a crosstalk effect to the system as described by Majzik *et al.* [52].

The Omicron sensor shows a strong dependence on the directionality of the current, particularly at negative current values where the Δf and the excitation appear to be affected. The opposite behaviour was recorded with the HB sensor, at positive currents the Δf and the excitation appear to be affected. We believe that due to the dependence on the directionality of the current there is no connection to the phantom force [50]. Additionally the phantom force as it's reported shows a few pm distance between the current and the Δf peak, in our case the maximum current and the maximum Δf values are overlapping Fig. 6.15.

6.2.3 Createc

On the Createc system a clear distortion was recorded at high I_t and at small range of the current pre-amplifier (at 100 nA). When the range of the pre-amplifier increases there is a clear trend indicating the recovery of the distortion in all of the channels as is shown in Fig. 6.17. For the Createc system $\Delta f(z)$ were obtained from 0 V up to + 1.5 V in the current pre-amplifier ranges such as 10 μ A, 1 μ A, 100 nA and 10 nA (Fig. 6.21). An interesting effect is the change of the force curve when the current changes Fig. 6.21 (left). When the range of the preamplifier is getting smaller the lowest point of the force is getting larger while the amplitude and the excitation channels do not show any distortion. On the spectra obtained in Fig. 6.21 right, at the pre-amplifier range of 10 μ A the force is getting stronger while the current increases. The amplitude and the excitation channels have similar behaviour as before. The change in the measured force for the Createc system shows that even when the range of the current pre-amplifier is large, the high current still has a direct influence on the force curve. These changes in force could be due to a real electrostatic or current based force. Since the forces are distorted quite consistently and the excitation channel remains unaffected we could conclude that this is not the cross-talk as described by Majzik *et al.* [52].

At the current pre-amplifier range of 100 nA the system appears to become saturated at lower values of nA. At +20 mV the noise at the force curve (red) is evident. In addition the deviation from the zero volts curve is also obvious. Higher bias voltage leads to higher deviations and from +200 mV onwards the force turnaround of the curve has changed and at +500 mV ceases to exist or cannot be measured. (Fig. 6 in Appendix B) A noteworthy remark is that the current slope remains unaffected and the amplitude and the excitation are not affected by the current changes too. This provides further support to the theory that the pre-amplifier of Omicron electronics introduces a crosstalk effect to the system. In other words, the Omicron system wiring is responsible for the introduction of at least one type of cross-talk to the system.

At the pre-amplifier range of 1 μ A, the current appears to behave irregularly from +50 mV onwards but the force does not deviate considerably. On the other hand the data have a lot of noise (Fig. 7in



156 6.2. Quantification of the force spectra obtained with each system

Figure 6.21: Force spectra on top of the C_{60} molecules obtained using Createc LT and Nanonis electronics. On the left the U_s was at +1.5 V and the gain was ranging; On the right the gain is stable at 10 μ A while the U_s varies.

Appendix B). Compared to the measurements of the 100 nA range, the force turnaround stops at higher volts (+1.5V). This is logical since the range of the pre-amplifier is increased and thus the current does not saturate as much. Overall it is clear that the create system can handle much higher current values than the Omicron commercial one.

In the Createc with Nanonis electronics configuration, the range is increased at 10 μ A, which means that the system is more resilient to high voltage and the current doesn't saturate as much. The red curve deviates considerably from the blue one at +1 V while the force turnaround disappears at +1.5 V. The bias voltage and the current increase linearly. (Fig. 8 in Appendix B). This could mean that the tip never changed configuration even temporarily or the behaviour is caused by an unknown cause. Looking at the force spectra at Fig. 8 in Appendix B shows that there are no changes in the excitation and amplitude which are almost constant in agreement with the theory that the pre-amplifier of Omicron electronics introduces a crosstalk effect to the system. On the other hand, determining the point where crosstalk kicks in for the Createc system is difficult because of the noise of the data. It is possible to filter the data in order to get a clearer image but lateral filtering of the force curve changes the position of the force and the position of z therefore such a filtering might give unreliable results for this cause.

6.3 Measuring electronic coupling in the Omicron electronics configuration

In the results acquired by the Omicron system we can clearly see how the system itself can introduce distortion. A 7265 Dual Phase DSP Lock-in Amplifier was attached in several test points (TPn Fig. 6.4) in the Omicron LT system in order to check for electric coupling within the system. Measurements took place with and without tip or sample. In the electronic configuration of the Omicron LT system U_s is applied on the sample and the current is detected from the sample while the STM electrode of the tip is grounded. Fig. 6.22a shows the behaviour of the force (F_N) by applying a dither on the sample through the current preamplifier (TP2). There is a coupling between the current pre-amplifier and the force which can be seen from the values of the solid black curve. A smaller coupling is shown in the case of the HB sensor when the sample is removed (red dashed line). In the rest of the cases, the curves seem to overlap with the no-tip and sample curve (blue dashed line). At the bottom row of Fig. 6.22b, F_N is measured with the dither applied directly on the sample. The highest coupling is measured from the Omicron commercial sensor, while the HB sensor curve has smaller difference with the no-tip and sample curve than the commercial sensor but it is not overlapping the solid blue curve Fig. 6.22c.

When a dither is applied at the TP2 and we obtain the signal from F_{n-out} , the Omicron commercial qPlus sensor with sample configuration lead to additional signal in F_N (Fig. 6.22a) at the same frequency but phase shifted, therefore it results in a different behaviour for positive

and negative current (Fig. 6.18). This also means that the signal could be different for a different sensor. When the amplitude feedback loop is increased the outcome becomes worse which might be caused from the sensor's excitation. In the absence of the sample the behaviour of the system is very different as virtually no capacitance is observed or measured. That suggests that the sample and the sensor works synergistically towards the appearance of a capacitance. When the HB sensor replaced the commercial sensor the additional signal in F_N , in the presence of the sample was much lower to the commercial sensor and similar to the no-tip configuration. This can be seen at the Fig. 6.22a where the solid red line overlaps with the solid blue one. This indicated that the additional coupling of the HB sensor is negligible for this configuration. A reason for that can be that the coupling is reduced by adding a separate Cu tip wire and isolating the tunnelling current path with respect to the AFM electrodes. An interesting finding is that in the absence of sample the HB sensor appears to have the highest coupling compared to the other two equivalent configurations. This might suggest an increased sensitivity of the HB sensor. The effect of the interaction between the HB sensor and the sample appears to be exactly the opposite than the interaction measured between the Omicron sensor and the sample; while, the Omicron commercial/sample configuration increases the additional F_N the HB/sample one mitigates the measured noise level.

Applying the dither directly on the sample (TP1), in Fig. 6.22b, and measuring the F_N produced an increased capacitance for both of the sensors in the presence of the sample. In the absence of the sample the capacitance was negligible. This configuration by passes the Omicron electronics and results in a system identical to the battery system shown in the results section. In the final graph the dither is applied directly on the tip (TP5) and the F_N of the Omicron commercial configuration shows the biggest capacitance. The HB configuration shows a lower capacitance than the no-tip/no-sample configuration. That can be explained also from the separate Cu wire collecting the tunnel current signal. An obvious abnormality in these measurements is the seemingly random spikes and negative spikes appearing in some of the curves. This might be due to the higher harmonics coming either from the operational amplifiers involved in each case or the tip, the fact that the spikes are consistent and appearing at specific frequencies makes it even more difficult to be addressed either as a physical phenomenon or an artefact, we mostly believe that is of an artefact nature.

6.4 Origins of the crosstalk effect in our findings

In this section we attempt to explain the origin of the crosstalk effect in the Omicron system. The first source of crosstalk can be the STM pre-amplifier. If the bandwidth of the pre-amplifier is too small a charge built-up occurs which leads to the appearance of an average potential of the additional electrostatic force across the tip-sample conjunction, which directly affect the measurement of the sensor. Another source of crosstalk could be the additional excitation of the cantilever by electrostatic forces appearing between the tip-sample conjunction and the



Figure 6.22: Frequency sweep of the sample Top: Dither Input from the STM pre-amplifier of the MATRIX electronics (TP2 6.4), Output measured from F_N (TP4 6.4); Bottom: Dither Input applied directly to the sample (TP1 6.4), Output measured from F_N

frequency resonator which again originates from the charge built-up on the quartz cantilever.

Additionally, in the Omicron commercial sensor, another possible source of crosstalk stems from the coupling capacitor due to the geometry of the STM and AFM electrodes on the tuning fork (Fig. 6.6A). The crosstalk coupling capacitor of this type of sensor would be zero with an ideal STM pre-amplifier, but will not be zero with an STM pre-amplifier not keeping the input at virtual ground. This then couples into the qPlus signal path and would lead to crosstalk via the amplitude feedback loop. It should be frequency stable with resonator frequency, but would disturb the amplitude feedback loop as it was shown in Fig 6.18. If there is a resistor instead of the STM pre-amplifier (or a slow STM preamp), we then have a voltage divider, and the additional electric potential on the tip is non-zero. In that case, the relative size of coupling capacitance and the capacitance of the tip-sample conjunction would then determine which component is the dominant.

The latter source of crosstalk can explain the different behaviour of the Omicron commercial sensor and HB sensor observed in Fig. 6.14; the internal wiring of the HB sensor appears to provide a better grounding for the sensor resulting in smaller coupling capacitance which in turn, leads to better behaviour of the sensor in higher currents than the Omicron Commercial sensor. On the other hand in the Createc system, where the STM pre-amplifier has larger bandwidth than the Omicron system and the internal wiring is not coupling according to our results, there is no evidence of crosstalk measured.

6.5 Conclusions

We compared an Omicron commercial qPlus sensor, a HB qPlus sensor with MATRIX electronics and external battery and a commercial Createc qPlus sensor. In the Omicron system with the commercial qPlus sensor, the increase of the current influences the Δf , the amplitude and the excitation channels. The HB sensor has a similar performance to the Omicron commercial qPlus sensor in our system regarding the crosstalk effect. In the case of the Createc system, when the range of the STM operational amplifier is large the imaging of the systems seems stable. By comparing the two systems and by testing the MATRIX electronics we report that when the range of the STM operational amplifier and the system wiring are optimal the crosstalk effect can be eliminated.

Chapter 7

Conclusions

Throughout this thesis the AFM was used as an atom manipulation device and for high resolution imaging, while another complicated technique was tested, called simultaneous STM and AFM.

Submonolayer coverage of Pb dimers and dimer chains on Si(100) was imaged with constant height NC-AFM. The recorded contrast, shows two different position of the dimer atoms. The Pb dimer sits in a buckled position with an upper and a lower atom. The top atom appeared to have smaller frequency shift than the bottom atom. In some cases both of the Pb atoms within a dimer appeared with high frequency shift contrast but we believe that the tip presence is responsible for interacting with the dimer while imaging it. Also, mobile Pb dimers on the surface were recorded interacting with the scanning tip leaving traces on the image.

Controlled manipulation of Pb dimers in parallel and perpendicular to the silicon dimer rows was recorded at 77 K, then the sample was cooled down to 5 K for highly controlled manipulations and to extract the force needed to move a Pb dimer along the silicon rows. We broke a Pb dimer from a Pb chain and it was manipulated laterally on the silicon dimer rows. The force for the breaking of the chain and for single step manipulation is reported. Two different types of manipulation distances were recorded at 0.5 nm and at 0.8 nm.

Molecular adsorption is reported, particularly for individual NTCDI molecules on Si(111). The NTCDI molecule was imaged to be adsorbed in four different geometries while two of them are more common than the others, as it was proved by the frequency of the geometries appearing in STM and constant height AFM images which was additionally supported with DFT calculations. The NTCDI molecule found in common geometries tilts the ends of the molecule towards the surface while its centre sits higher.

Intermolecular contrast and force spectra on the intermolecular positions were reported for the NTCDI molecular assembly on Ag:Si(111). The intermolecular contrast raised a big debate in the scientific community and drove a number of scientific groups to study this effect. A large amount of literature was written on the topic, which is discussed in the relevant chapter. Intermolecular contrast can be a result of multiple artefacts and false assumptions regarding the capabilities of the technique. The inter and intra molecular resolution is affected by the size of the tip, the nature of the tip, the tip-sample imaging distance and the bonding of the under-study system. All of these factors need to be taken into consideration when an inter-molecular contrast is resolved. In the final chapter of this work, we take a closer look to the simultaneous STM/AFM measurements. The so called corsstalk effect according to the literature was supposed to be suppressed by the new qPlus design introduced by Majzik *et al.*. Two commercial systems the Omicron and Createc were tested. For the purpose of conducting these experiments a home built qPlus sensor was devised based on Majzik *et al* and was compared with a commercial qPlus sensor and the Createc qPlus sensor. The results show that the crosstalk is not only caused by the geometry of the electrodes and the current pre-amplifier, but also from the wiring of the Omicron system. That conclusion is supported by the results obtained with the Createc system where the pre-amplifier can handle high tunnelling current flow and the electronics of the system is wired differently. Therefore, it can be concluded that results obtained from simultaneous STM/AFM should be used with caution.

Chapter 8

Future perspectives

While this thesis has demonstrated the potential of lateral manipulation of Pb dimer on Si(111) surface, inter-molecular resolution, and the spontaneous STM/AFM technique many opportunities for extending the scope of this thesis remain. This section presents some of these directions.

For the manipulation of Pb dimer on Si(111), two different distances of lateral manipulation were reported. As a future perspective, I suggest that DFT calculations will provide useful information for the interaction between the tip and the dimer during the manipulation, since in all of the cases the vertical force was dominant. Since a specific contrast of the manipulated dimer is recorded, a controlled vertical manipulation needs to be explored as well, in order to gain a better understanding of the interaction.

In this thesis, in chapter 5, the intermolecular contrast shows that in close proximity between the tip and the sample, we observe an artificial contrast. For future work, I recommend a comparison of the grid spectra of hydrogen bonded network with non-bonded networks which could provide information about the 'safe' distance between the tip and the sample in order to avoid intermolecular contrast that rises form artefacts.

In chapter 6 the simultaneous STM/AFM technique is discussed in greater detail, which is a very interesting and complex method. It is shown that in every system some crosstalk effect is present. In the Omicron system it is shown that the crosstalk is caused by the wiring configuration of the MATRIX electronics. I recommend for future work a wire re-arrangement of the system in a trial-and-error fashion until no form of crosstalk can be detected.

Appendix A

DFT calculations for the NTCDI island - Ag- $\sqrt{3}$ system simulation

DFT calculations were carried out using the CP2K code [118, 119]. The algorithm implemented in the code is based primarily on using Gaussian basis set for evaluating most terms in the Hamiltonian; however, an on-the-fly conversion is made to a plane wave basis set to calculate the electrostatic energy. Goedecker, Teter and Hutter pseudopotentials and the Perdew-Burke-Ernzerhof generalized gradient approximation method [120] were used. In all calculations the dispersion interaction was approximately taken into account using the DFT-D3 method as suggested by the study by Grimme *et al.* [121] Geometry relaxation in most calculations was run until the forces on atoms that were allowed to relax were no more than 0.01 eV/A. Electronic density plots were generated using the XCrySDen code [122].

Appendix B

Force spectra plotted with the current curve

The measured forces with the current are shown here. In the following images the force spectra analysis is shown and it is thoughrouly explained in Chapter 6.



Omicron commercial sensor amplitude feedback 10%

Figure 1: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different V_s using MATRIX electronics with the commercial Omicron sensor with amplitude feedback 10%. In the force window the blue curve is the curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.


Omicron commercial sensor amplitude feedback 100%

Figure 2: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different V_s using MATRIX electronics with the commercial Omicron sensor with amplitude feedback 100%. In the force window the blue curve is the curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.



Figure 3: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different positive V_s using MATRIX electronics with the HB sensor. In the force window the blue curve is the standard deviated curve of the spectra obtained at zero voltage while the red indicates the force curve obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.



Figure 4: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different negative V_s using MATRIX electronics with the HB sensor. In the force window the blue curve is the standard deviated curve of the spectra obtained at zero voltage while the red indicates the force curve obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.



Battery home built

Figure 5: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different negative V_s using the battery configuration with the HB sensor. In the force window the blue curve is the standard deviated curve of the spectra obtained at zero voltage while the red indicates the force curve obtained with applied V_s ; In this case the current was not measured due to the electronic configuration.



Figure 6: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different V_s using Createc system with Nanonis electronics. The current pre-amplifier range was of 100 nA. In the force window the blue curve is the curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.



Figure 7: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different V_s using Createc system with Nanonis electronics. The current pre-amplifier range was of 1 μ A. In the force window the blue curve is the curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.



Figure 8: The zoomed-in measured force spectra on top of the C_{60} molecules obtained at different V_s using Createc system with Nanonis electronics. The current pre-amplifier range was of 10,0 μ A. In the force window the blue curve is the curve of all the spectra obtained at zero voltage while the red indicates the force curved obtained with applied V_s ; The zoomed in I_t spectra with green line shows the behaviour of the current at each position of the tip.

Appendix C

Additional datasets

Additional datasets are included that show similar behaviour to the crosstalk effect. Figure 9 shows an example of a C_{60} island where the U_s vary in areas of the same image. In this case we cropped areas of the image from each U_s zone of the current channel and the Δf data collected with MATRIX electronics and the battery configurations respectively. The variation of the Δf and the amplitude channel seems negligible compared to the excitation channel where the changes in the case of the battery configuration are in the range of mV. Another example with similar behaviour is shown in Figure 10.

Figure 11 shows the plots from a Ag step edge. The correlation between the Δf and the excitation in the presence of the current follow similar a fashion with the results taken on the C_{60} islands. In the case of the MATRIX electronics configuration, when the current becomes more positive the excitation increases. In the battery configuration when the positive current increases the excitation decreases.



Figure 9: Area selection of another C_{60} island. Top row: The full current image; Bottom row: the cropped area. Top rows is maxima taken from the MATRIX electronics. Bottom row the results taken from the battery set up.



Figure 10: Area selection of another C_{60} island. Top row: The full current image; Bottom row: the cropped area. Top rows is maxima taken from the MATRIX electronics. Bottom row the results taken from the battery set up.



Figure 11: The data plotted represent The maxima on the Ag(111) step edge. Top rows is maxima taken from the MATRIX electronics. Bottom row the results taken from the battery set up.

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