Single molecule conductance

Willems, R.

DOI:
10.6100/IR637876

Published: 01/01/2008

Citation for published version (APA):
Single molecule conductance

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Eindhoven,
on gezag van de Rector Magnificus,
prof.dr.ir. C.J. van Duijn,
voor een commissie aangewezen
door het College voor Promoties
in het openbaar te verdedigen
op dinsdag 14 oktober 2008 om 16.00 uur

doors

Ron Willems

geboren te Eindhoven
Dit proefschrift is goedgekeurd door de promotor:

prof.dr.ir. R.A.J. Janssen

Copromotor:
dr.ir. C.F.J. Flipse
Contents

1 Introduction ................................................................. 1
   Bibliography ............................................................. 4

2 Modeling single molecule conductance ................................ 7
   2.1 The theoretical models ............................................. 7
      2.1.1 The Self Consisted Field model ............................. 8
      2.1.2 The Coulomb blockade model ............................... 16
   2.2 Results and discussion ............................................ 21
      2.2.1 Results and discussion for the Self Consisted Field method .................................................. 22
      2.2.2 Results for the Coulomb blockade model ............... 31
   2.3 Conclusions ......................................................... 39
   Bibliography ............................................................ 40

3 Gold nanoparticle manipulation by AFM ............................. 41
   3.1 Introduction ......................................................... 41
   3.2 The experimental techniques ...................................... 42
      3.2.1 Electron beam lithography ................................ 43
      3.2.2 Atomic forces ................................................ 44
      3.2.3 The atomic force microscope ............................... 46
      3.2.4 AFM particle manipulation ................................. 48
      3.2.5 Seeding solution ............................................. 48
      3.2.6 Microwave irradiation ..................................... 49
   3.3 The setup ............................................................. 51
   3.4 Results and discussion ............................................ 52
      3.4.1 Creation of the lithographic contacts ...................... 52
      3.4.2 Manipulation of CGNP by AFM ............................... 52
      3.4.3 Microwave irradiation ..................................... 56
   3.5 Conclusions ......................................................... 61
   Bibliography ............................................................ 61

4 Electromigration of lithographic contacts .......................... 67
   4.1 Introduction ......................................................... 67
   4.2 The measurement techniques ...................................... 69
      4.2.1 Bilayer resist lithography and shadow-evaporation ...... 69
      4.2.2 Electromigration ............................................. 70
CONTENTS

4.2.3 The Simmons model ........................................... 72
4.3 The experimental setup ........................................ 72
  4.3.1 Sample fabrication ...................................... 72
  4.3.2 Electromigration ......................................... 73
  4.3.3 OPV-5 .................................................. 73
4.4 Results and discussion ........................................ 74
  4.4.1 Lithographic structure fabrication ....................... 74
  4.4.2 Electromigration of the contacts ......................... 74
  4.4.3 (No) measurements on molecules ......................... 77
4.5 Conclusions .................................................... 80
Bibliography ....................................................... 80

5 Scanning probe nanolithography of OTS monolayers on silicon 85
  5.1 Introduction ................................................ 85
  5.2 The measurement techniques ................................ 86
    5.2.1 Friction force measurements ............................ 86
    5.2.2 Modulated friction force imaging ....................... 87
    5.2.3 Local probe oxidation .................................. 88
    5.2.4 Electrostatic force microscopy ........................ 89
  5.3 The setup .................................................... 89
    5.3.1 Monolayer preparation ................................ 89
    5.3.2 AFM techniques ....................................... 90
  5.4 Results and discussion ..................................... 90
    5.4.1 Oxidation: OTS modification and SiO\textsubscript{2} growth 90
    5.4.2 Height imaging: dependence on scan direction ........ 92
    5.4.3 Electrical force microscopy on oxidized OTS layers .... 95
    5.4.4 Parameter space of OTS modification and SiO\textsubscript{2} growth 99
  5.5 Conclusions ................................................ 101
Bibliography ....................................................... 103

6 Thiophenol on Ag(111), topography and IETS 107
  6.1 Introduction ................................................ 107
  6.2 Theoretical modeling of IETS spectra ....................... 109
    6.2.1 Elastic conductance .................................. 109
    6.2.2 The inelastic channel ................................ 110
    6.2.3 A localized representation ............................ 112
    6.2.4 The used geometry and computational details ........ 112
    6.2.5 Modeling assumptions ................................ 115
  6.3 The measurement techniques ................................ 116
    6.3.1 Scanning tunneling microscopy ......................... 116
    6.3.2 The DOS of the sample ................................ 118
    6.3.3 Inelastic electron tunneling spectroscopy ............. 119
  6.4 The setup .................................................... 119
    6.4.1 The STM .............................................. 119
    6.4.2 The tip ............................................ 121
    6.4.3 Sample preparation ................................... 121
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5 Results and discussion</td>
<td>121</td>
</tr>
<tr>
<td>6.5.1 Topography of clean Ag(111)</td>
<td>121</td>
</tr>
<tr>
<td>6.5.2 Topography of thiophenol on Ag(111)</td>
<td>122</td>
</tr>
<tr>
<td>6.5.3 IETS and STS of thiophenol on Ag(111)</td>
<td>126</td>
</tr>
<tr>
<td>6.5.4 Computational results and comparison with measurements</td>
<td>135</td>
</tr>
<tr>
<td>6.6 Conclusions</td>
<td>144</td>
</tr>
<tr>
<td>Bibliography</td>
<td>145</td>
</tr>
<tr>
<td>Summary</td>
<td>153</td>
</tr>
<tr>
<td>Samenvatting</td>
<td>157</td>
</tr>
<tr>
<td>Dankwoord</td>
<td>161</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>165</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

Single molecule electronics, or in other words molecular electronics, is the field in which the electronic properties of individual molecules are studied. In this thesis, several approaches are investigated to perform electrical measurements on individual molecules.

One of the driving forces behind the field of molecular electronics is the miniaturization of electronics. Ever since the invention of the transistor, i.e. the basic component from which computer chips are built, in 1947 by William Shockley, John Bardeen and Walter Brattain [1], electronic components have been reduced in size to reduce the power consumption of individual components and increase the number of elements per unit area to increase the calculation power of electronic devices. This trend is described by Moore’s law and it states that the number of transistors that can be inexpensively placed on an integrated circuit is increasing exponentially, i.e. doubling approximately every two years [2].

To facilitate this miniaturization of electronic components ever more complex technologies have to be developed and employed. At the present time it are lithographic techniques that are used to create integrated circuits. Simply put, optical lithography is like taking a photograph with an old-fashioned camera. Instead of exposing the film in the camera, a lithography machine exposes a coating on a substrate to light. This exposed coating can then be used to selectively process specific areas of the substrate and to fabricate a chip. To keep up with Moore’s law, lithographic techniques had to be improved as well. Up to now, this has not been a problem, but in the not so distant future, optical lithography will no longer suffice for the production of even smaller electrical components and other methods will have to be found to sate the unquenchable thirst for ever smaller electronics. One such way could be the use of individual molecules as electronic components.

Besides making electronic components even smaller than they already are today, there is another important reason why people pursue molecular electronics. As mater-

---

1 Perhaps it is more accurate to say that Shockley, Bardeen and Brattain made the first practical transistor, since Julius Edgar Lilienfeld already patented the field-effect transistor principle in 1925 [2].

2 Initially Moore calculated a doubling every year [3], but later he refined the period to be two years.
1. Introduction

As materials become smaller and smaller, the way electrons propagate through them becomes different as well. For example, macroscopically conduction is described by Ohm’s law. However, Ohm’s law basically is an assemble average of all conduction pathways in a material and as this material becomes smaller in size, the number of pathways in it is reduced. Beyond a critical size, the number of pathways becomes so small that fluctuations around the average become important, thereby resulting in different electronic behavior. One is then said to enter the field of mesoscopic conduction. Shrinking down the size of the material even further, i.e. to a level where only one (or a few) pathway(s) is (are) available, the conduction of this (these) individual pathway(s) has to be taken into account. This regime is described quantum mechanically and it is in this regime that the conduction experiments of chapter 6 are performed.

There is great potential in the field of molecular electronics, as is evidenced by the many different publications on the subject. Effects that are being studied include, the electronic conduction through individual molecules itself [4–8], the effect of temperature [9, 10] on the conduction, the effect of an externally applied electric field on the (change of the) morphology of individual molecules [11] and the resulting conduction (change) [12, 13], magnetic effects of individual molecules like Kondo behavior [14–18] and the influence of atomic/molecular vibrations (of both the molecule and the substrate) [19–28] on the conduction.

Not only the effects that have been studied vary greatly, but the way in which samples/systems are prepared and measured also differ substantially. For example, Kubatkin et al. [5, 29] used the evaporation of metals under different incident angles to (directly) create metal contacts with a separation of only a few nanometers on which molecules were placed by evaporation. While this method resulted in very good conductance spectra, the process of fabricating the contacts is difficult and has a low success rate. Similarly, junctions created by electromigration [6, 7, 14, 18], i.e. the breaking of a metal wire by applying a sufficiently high current to it, have low success rates as well, as will (also) be seen later in this thesis. To increase this success rate mechanical break junctions [4, 30, 31] can be used to accurately and repeatedly (tens of thousands of times) make contact to an individual molecule and measure its conduction properties. However, incorporating a gate in a mechanical break junction is problematic and since the orientation of the molecule between the contacts is not known, it is hard (if not impossible) to model the conductance on the atomic scale.

The primary tools, used for the work that led to this thesis, are scanning probe microscopes, namely atomic force microscopes and scanning tunneling microscopes [26, 28]. Both methods/machines allow materials to be visualized and even manipulated on the nanometer scale. Scanning probe methods use a probe, also called a tip, which basically is a very sharp needle, to scan across a substrate surface, hence the name, and use the interaction between tip and surface to create an image of the substrate. Where for the atomic force microscopy this interaction consists of the atomic forces between the atoms of the tip and the substrate, it are (tunneling) electrons that move from tip to substrate (or vice versa) that govern this interaction in scanning tunneling microscopy.

In science, experiments are often supported by model calculations. In chapter 2 two elementary transport models, namely a Self Consistent Field model and a Coulomb model, were used to investigate the principles of conductance behavior of
(a single energy level of) a single molecule between two metal contacts. A number of parameters of both models were varied to gain insight into the processes that take place in a nanometer sized contact. Among others, it was found, that for the Coulomb model, using coupling constants whose magnitudes have a ratio that is far from unity, resulted in a polarity dependent Coulomb blockade behavior: for one bias polarity Coulomb blockade occurred, while for the other polarity it did not.

In order to be able to measure the conductance properties of individual molecules, it is necessary to controllably connect one molecule to the macroscopic world. As will become clear in the rest of this thesis, it is far from trivial to do so. Two methods are used to make metallic contacts with a gap between the contacts of only a few nanometers: In chapter 3 it is attempted to make a large gap between two electrodes smaller by moving colloidal gold nanoparticles into the gap by pushing them with the tip of an atomic force microscope. In chapter 4 the reverse is tried: Instead of making a smaller gap, a gap is actually formed in a metallic wire by controllably applying a high enough current to the conductor. This process is called electromigration. It is found that, while pushing gold colloids into a chain configuration resulted in electrically conducting wires, the accuracy required to controllably reduce the size of the gap to 1 to 2 nm in this fashion is lacking. Similarly, migration can be used to repeatedly create gaps of the desired size, but in all of the performed conduction experiments the presence of molecules could not be detected. As a result, the results of the calculations of chapter 2 could not be related to actual experiments either.

Another way in which atomic force microscopy has been employed in this work, is the local probe oxidation of a self-assembled monolayers. With local probe oxidation, an electric current is passed through a conductive tip, by applying a bias between tip and substrate, to selectively modify the surface area. In this fashion a pattern is written on the substrate. Such patterns could, for example, be used to selectively coat parts of the substrate with metals [32] and in this fashion create nano-scale electronic contacts. Before this can be done effectively, however, it is necessary to control the oxidation process. As is shown in chapter 5 two processes can occur when a bias is applied, namely the modification of the methyl end-groups of the molecules that form the monolayer into carboxylic acid groups, which is desirable, and growth of silicon oxide underneath the monolayer, which is undesirable. It is found that, depending on the oxidation conditions, i.e. the applied bias and the duration over which it is applied, a distinction can be made between these two processes. It is also observed that, depending on the scan direction, the end-group modification can be observed as either an increase or a decrease of the height of the modified areas due to cross-coupling, i.e. mixing, of the simultaneously recorded height and friction signals.

To successfully measure the conduction properties of individual molecules, scanning tunneling microscopy was used in chapter 6 to measure the conductivity of thiophenol molecules absorbed on a silver(111) substrate. It was found that the molecules form ordered monolayers on the substrate with a $3\sqrt{3} \times 3$ unit cell. The performed conduction experiments revealed vibrational features that could be related to the presence of vibrational modes of the thiophenol molecule as well as to phonon modes of the silver substrate. By comparing these conduction experiments with computational

---

3As will be seen later, the models of chapter 2 do not incorporate atomic/molecular vibrations and as such they can not be used to explain the conduction measurements of chapter 6.
1. Introduction

Simulations, it was determined that, depending on the exact position of the tip above the molecule, electrons can take different pathways through the molecule and thereby excite different atomic/molecular vibrations. Additionally, it has been observed that the conductance spectrum is asymmetric around 0 Volts, which is attributed to a realignment of the molecule due to its dipole interaction with the applied electric field, and has a characteristic dip for voltages below 40 mV that is thought to be caused by the interplay between the silver phonon modes and the thiophenol molecules.

Bibliography


1.0 Bibliography


1. Introduction


Chapter 2

Modeling single molecule conductance

Modeling of nanometer-sized conduction channels has been performed, using two different models, namely a Self Consistent Field model (SCF) and a Coulomb model. Both models, which are extensively reviewed by Datta [1], are explained in this chapter. Subsequently, the parameters of these models are varied to study the effects of these variations on the conductance plots generated with these models. Especially, the effect of changing the ratio of the coupling-constants on the conductance is discussed.

As will be seen later, the conduction experiments, as reported in chapters 3 and 4, proved unfruitful in the sense that no conduction measurements could be performed on single molecules. This, together with the fact that the theory in this chapter can not be applied to the results of chapter 6, leads to a situation where this theory can not be directly compared with the experimental data described in this work. Nevertheless, the results of this chapter give an insightful view into the fundamental aspects of conductance at the single molecule level.

2.1 The theoretical models

The models used in this chapter to describe a channel with dimensions in the order of a few nanometers are the Self Consistent Field model and the Coulomb blockade model. While both models have been described by Datta [1], a full derivation of both models is given in this chapter to better explain how the (final) formulas, that have been used for the actual calculations, were obtained.

For both models, which will be derived in the following sections respectively, the starting situation is a conduction channel with nanoscale dimensions. The channel is connected to source and drain contacts and coupled to a gate electrode via a thin insulating layer. By applying a potential difference $V_{SD}$ across the source and the drain, their chemical potentials $\mu_S$ and $\mu_D$, will no longer be equal. If there now lies an energy level $\epsilon$ of the channel between $\mu_S$ and $\mu_D$, then electrons can flow from source to drain (or vice versa, depending on the sign of the bias) via the channel and...
2. Modeling single molecule conductance

A current $I$ is established. By applying a gate voltage $V_G$ to the channel, the energy levels in the channel can be shifted up or down, thereby enabling the level $\epsilon$ to be placed between the two chemical potentials. A schematic representation of such a device is given in figure 2.1.

![Figure 2.1: A schematic representation of a channel containing a nano-sized conductor, connected to source and drain contacts and coupled to a gate via a thin insulating layer.](image)

2.1.1 The Self Consisted Field model

The first step in understanding how a small electronic conductor works, is to draw an equilibrium energy diagram. Here equilibrium signifies that no voltage is yet applied over the device. By using metals for the source and drain contacts, the resulting energy diagrams for the leads become continuous bands that are filled up to their respective chemical potentials $\mu_S$ and $\mu_D$, as indicated by the Fermi function:

$$f_A = f_0(E - \mu_A) = \frac{1}{1 + \exp((E - \mu_A)/k_BT)},$$  \hspace{1cm} (2.1.1)

where $E$ is the energy, $k_B$ the Boltzmann constant, $T$ the temperature and $A$ a parameter that should be replaced with $S$ and $D$ for the source and drain respectively. It is assumed that source and drain are made of the same material and therefore have the same chemical potential when no source-drain bias $V_{SD}$ is applied.

The channel itself has discrete energy levels $\epsilon$ and can only be occupied by electrons with energies corresponding to these levels. Now it is possible to draw an energy level diagram of the whole system, i.e. contacts and channel together, where the energy levels of the channel are filled for energies below $\mu = \mu_S = \mu_D$ and empty for higher energies, figure 2.2.
2.1 The theoretical models

Figure 2.2: A sketch of an energy diagram at equilibrium for a channel containing discrete levels, connected to metallic contacts. The full circles represent filled levels in the channel, whereas the open circles represent empty levels.

At this point no current can flow through the device, since no electrons in the leads have high enough energies to occupy the empty levels of the channel and likewise no electrons from the filled energy levels in the channel can move to either contact, because at these energies the levels of the contact are already filled.

By applying a voltage $V_{SD}$ over the source and the drain, which is equal to $\mu_D - \mu_S = qV_{SD}$, their respective chemical potentials are no longer equal. If there now lies an energy level in the channel between $\mu_S$ and $\mu_D$, then both leads will seek to bring this level in equilibrium with itself. The lead with a chemical potential higher than the level of the channel will try to do so by filling the channel with electrons, whereas the other lead will try to do so by emptying the channel of its electrons. As a result, these two balancing acts cause the channel to be in a non-equilibrium state where electrons are continuously entering and exiting the channel causing a current to be established.

How can the current now be derived mathematically? Conceptually it is easiest to consider a single level $\epsilon$ of the channel to lie between the chemical potentials of the contacts. The current flowing across the source-channel junction $I_S$ then is the
2. Modeling single molecule conductance

difference between the influx and outflux through the junction and can be written as:

\[ I_S = (-q) \frac{\gamma_S}{\hbar} (f_S - N) \]  

(2.1.2)

With \((-q)\) the charge per electron, \(\frac{2}{\hbar}\) the rate constant with which an electron, placed initially at level \(\epsilon\), escapes into the source contact (and vice versa) and \(f_S - N\) is the difference between in- and out-flux across the junction respectively. Here \(N\) is the average number of electrons in the channel. Note that, since the rate constants have the dimension per second and that of Planck’s constant \(\hbar\) is energy times second, \(\gamma_S\) and \(\gamma_D\) have dimensions of energy. A similar formula can be written down for the current \(I_D\) flowing through the channel-drain junction:

\[ I_D = (-q) \frac{\gamma_D}{\hbar} (f_D - N) \]  

(2.1.3)

In figure 2.3 the flows into and out of the channel are shown schematically.

By assuming steady state conditions, i.e. that there is no net flux into (or out of) the device \((I_S + I_D = 0)\), the number of electrons in the channel can be written as the weighted average of what the source and drain contacts would like to see:

\[ N = \frac{\gamma_S f_S + \gamma_D f_D}{\gamma_S + \gamma_D} \]  

(2.1.4)

Filling in this formula into equation 2.1.2 leads to:

\[ I = I_S = -I_D = \frac{q}{\hbar} \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} [f_S(\epsilon) - f_D(\epsilon)] \]  

(2.1.5)

This formula for the current is not yet fully correct. This can be seen as follows; when it is assumed, for the moment, that \(\mu_S > \epsilon > \mu_D\) and the temperature is taken low enough so that \(f_S \equiv f_0(\epsilon - \mu_S) \approx 1\) and \(f_D \equiv f_0(\epsilon - \mu_D) \approx 0\), then formula 2.1.5 reduces to:

\[ I = \frac{q}{\hbar} \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} = \frac{q \gamma_S}{2 \hbar} \quad \text{if} \quad \gamma_D = \gamma_S \]  

(2.1.6)

In this formula, an infinitely strong coupling \(\gamma_S\) would lead to an infinite current and therefore to an infinite conductance \(G\), since \(G \equiv \frac{I}{V SD}\). However, one of the main

1 The influx into the channel should be \(f_S(1 - N)\) and the outflux should be \((1 - f_S)N\), thereby taking the Pauli exclusion principle into account, but subtracting these two terms amounts to the same formula as that given in equation 2.1.2.

2 Looking at figure 2.3 one might wonder why arrows are also drawn for electrons flowing away from (into) the channel if the level of the channel lies below (above) the chemical potential of the leads. In this figure the filling of the energy levels of the leads is depicted as being a step function in the energy. This would only be true in the hypothetical case of the temperature being absolutely zero. In reality the Fermi functions cause the energy levels of the leads to be partially filled (emptied) above (below) their respective chemical potentials. Therefore it is still possible for electrons to flow away from (to) the channel and into (out of) the lead if the energy level of the channel lies below (above) the corresponding chemical potential.
2.1 The theoretical models

Figure 2.3: A sketch of an energy diagram, after applying a voltage over the device. This voltage causes the chemical potentials to be no longer equal and it then becomes possible for electrons to flow into or out of the channel from either electrode, indicated by the purple arrows, resulting in a current.

The real definition of the quantum of conductance is \( G_0 \equiv \frac{2q^2}{h} \) \cite{2}. To correct for this effect, it has to be realized that an increased coupling of the channel to the leads also results in broadening of the level of the channel. If this broadened level lies only partly inside the region of energy between \( \mu_S \) and \( \mu_D \), see figure 2.3, then this level can only partly contribute to the current.

The fraction, with which the channel can contribute to the current, is equal to the ratio of the effective width of the level, which is given by \( C \gamma_S \) (\( C \) being a numerical
2. Modeling single molecule conductance

**Figure 2.4:** The energy diagram shows a broadened level $\epsilon$ in the channel, that only partly lies between $\mu_S$ and $\mu_D$. As a result, the level only partly contributes to the current.

constant), and the difference in energy between $\mu_S$ and $\mu_D$:

$$\frac{\mu_S - \mu_D}{C\gamma_S} = \frac{qV_{SD}}{C\gamma_S}$$  \hfill (2.1.7)

By multiplying this ratio with formula [2.1.6] the current becomes:

$$I = \frac{q\gamma_S}{2\hbar} \frac{qV_{SD}}{C\gamma_S} \quad \rightarrow \quad G = \frac{I}{V_{SD}} = \frac{q^2}{2C\hbar}$$  \hfill (2.1.8)

As can be seen, the conductance approaches a constant value, that indeed is independent of the strength of the coupling.
2.1 The theoretical models

Before turning to the correct mathematical description of the broadening of the energy level, it is good to first consider why the level gets broadened in the first place. Since the energy level is coupled to the leads, electrons can move onto and away from the electronic level. As a result the lifetime $\tau$ of an electron on the level is finite. Heisenberg’s uncertainty principle then states that the energy level of the channel is broadened. As a result the energy level no longer resembles a delta function around $E = \epsilon$, but becomes a Lorentzian function with a width $\gamma = \frac{\hbar}{\tau}$ around $E = \epsilon$.

Mathematically it is now possible to take this broadening of the level into account by multiplying the current with the above mentioned Lorentzian, called the broadened density of state $D_\epsilon(E)$:

$$D_\epsilon(E) = \frac{\gamma/2\pi}{(E - \epsilon)^2 + (\gamma/2)^2} \quad \text{with} \quad \gamma = \gamma_S + \gamma_D$$  \hspace{1cm} (2.1.9)

and integrate over the energy $E$. Equation 2.1.5 then transforms into:

$$I = \frac{q}{h} \int_{-\infty}^{\infty} dE \ D_\epsilon(E) \ \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} \ [f_S(E) - f_D(E)]$$ \hspace{1cm} (2.1.10)

Similarly, the number of electrons in the channel becomes:

$$N = \int_{-\infty}^{\infty} dE \ D_\epsilon(E) \ \frac{\gamma_S f_S(E) + \gamma_D f_D(E)}{\gamma_S + \gamma_D}$$ \hspace{1cm} (2.1.11)

The channel potential

Another factor, that can influence the shape of the current-voltage characteristic, is the potential $U$ of the channel itself, because this potential can shift the level of the channel in energy and therefore this effect will have to be taken into account. The potential can be split into two parts:

$$U = U_L + U_0 \Delta N$$ \hspace{1cm} (2.1.12)

where $U_L$ is the part of the potential energy of the channel due to the externally applied biases $V_{SD}$ and $V_G$ [3,4]:

$$U_L = \frac{C_G}{C_E} (-qV_G) + \frac{C_D}{C_E} (-qV_{SD}) \quad \text{with} \quad C_E = C_S + C_D + C_G \hspace{1cm} (2.1.13)$$

with $C_S$, $C_D$ and $C_G$ being the source, drain and gate capacitances respectively [7] and $U_0$ being the single electron charging energy, which gives the change in potential energy due to one extra electron in the channel:

4One important thing to note, is that this broadened level still is only a single level and therefore can, integrated over energy, hold only one electron (if one ignores spin for the moment).

5The complete formula should also include the term $\frac{C_S}{C_E}$ for the source contact, but by assuming that the potential of the source is kept at zero, this term can be ignored.
2. Modeling single molecule conductance

\[ U_0 \equiv \frac{q^2}{C_E} \] (2.1.14)

and lastly, \( \Delta N = N - N_0 \) represents the change in number of electrons on the channel, with \( N \) (\( N_0 \)) being the number of electrons in the channel with (without) the biases applied. Taking this potential \( U \) into account, causes \( D_\epsilon(E) \) to be replaced by \( D_\epsilon(E - U) \), resulting in the following formulas for the current \( I \) and number of electrons in the channel \( N \):

\[
I = \frac{q}{\hbar} \int_{-\infty}^{\infty} dE \, D_\epsilon(E - U) \, \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} \left[ f_S(E) - f_D(E) \right] (2.1.15)
\]

\[
N = \int_{-\infty}^{\infty} dE \, D_\epsilon(E - U) \, \frac{\gamma_S f_S(E) + \gamma_D f_D(E)}{\gamma_S + \gamma_D} (2.1.16)
\]

As can be seen from equation (2.1.16), \( N \) has become a function of \( U \), i.e. \( N = N(U) \), and in equation (2.1.12) \( U \) is already defined as a function of \( N; U = U(N) \). The solution to this problem is to simultaneously, or in other words “self-consistently”, solve these two equations. Hence, the name “Self Consistent Field” for this model. Practically, an iterative procedure is used, where first a value for \( U \) is chosen (usually \( U = 0 \)) with which \( N \) is calculated. Next, equation (2.1.12) is used to calculate a new \( U \). If this new \( U \) is sufficiently close to the old \( U \), then the new \( U \) is used in equation (2.1.15) to calculate the current. If this is not the case, then the new \( U \) is used to calculate a new \( N \) and subsequently an even newer \( U \) as follows: \( U_{\text{new}} = U_{\text{old}} + \alpha[U_{\text{calculated}} - U_{\text{old}}] \), with \( \alpha \) being a positive number between 0 and 1, that is chosen to be as large as possible without causing the solution to diverge. This entire process is repeated until the \( U \) from iterative step \( X + 1 \) is sufficiently close to that of step \( X \). Here “sufficiently close” means that the difference in \( U \)’s is within a fraction of \( k_B T \).

The SCF model as used for the calculations

Now the current will be written in the manner that has been used for the actual calculations. With \( \mu_S = \mu_D = 0 \) and \( \mu_D = \mu_0 - qV_{SD} = -qV_{SD} \), and filling in \( D_\epsilon(E - U) \), equation (2.1.15) becomes\(^6\)

\[
I = \frac{q}{\hbar} \int_{-\infty}^{\infty} dE \, T(E - \epsilon - U) \left[ f_0(E) - f_0(E + qV_{SD}) \right] (2.1.17)
\]

Where \( T(E) \) is called the “transmission function”:

\[
T(E) = \frac{\gamma_S \gamma_D}{(E)^2 + (\gamma/2)^2} (2.1.18)
\]

Note that at this point equation (2.1.17) has the form of the basic Landauer formula [5] that captures the idea that “conductance is transmission”.

\(^6\) Note that now Planck’s constant, \( \hbar \), is used and no longer \( \hbar \), since \( h = 2\pi\hbar \).
2.1 The theoretical models

Since \( U \) is a function of \( V_{SD} \), it would be desirable to place the effect of the potential of the channel in the Fermi function and not in the transmission function, in order to see what the overall effect of the source-drain voltage is on the current. Mathematically this can be done by replacing symbol \( E \) in equation 2.1.17 with symbol \( C \), where \( C \equiv E + \epsilon + U \):

\[
I = \frac{q}{h} \int_{-\infty}^{\infty} dE T(E) [f_0(E + \epsilon + U) - f_0(E + qV_{SD} + \epsilon + U)]
\]  
(2.1.19)

By now filling in \( U \), equations 2.1.12, 2.1.13 and 2.1.14, into this equation, one obtains the formula as used for the calculations:

\[
I(V_{SD},V_G) = \frac{q}{h} \int_{-\infty}^{\infty} dE T(E) \left[ f_0(E + U_S(V_{SD},V_G)) - f_0(E + U_D(V_{SD},V_G)) \right]
\]  
(2.1.20)

with

\[
U_S(V_{SD},V_G) = \epsilon + \frac{q^2}{C_E} (N - N_0) - \frac{C_G}{C_E} (qV_G) - \frac{C_D}{C_E} (qV_{SD})
\]  
(2.1.21)

and

\[
U_D(V_{SD},V_G) = \epsilon + \frac{q^2}{C_E} (N - N_0) - \frac{C_G}{C_E} (qV_G) + (1 - \frac{C_D}{C_E}) (qV_{SD})
\]  
(2.1.22)

In these equations the units of energy are still in Joules, but it is preferable to do the calculations with the energy in units of electron Volts. This can be achieved by dividing all terms related to an energy, namely \( E, \gamma S, \gamma D, U_S(V_{SD},V_G), U_D(V_{SD},V_G) \) and \( k_BT \), by \( q \). Equations 2.1.20 to 2.1.22 then become:

\[
I(V_{SD},V_G) = \frac{q^2}{h} \int_{-\infty}^{\infty} dE_{eV} T_{eV}(E_{eV})
\]

\[
\left[ f_{0,eV}(E_{eV} + U_{S,eV}(V_{SD},V_G)) - f_{0,eV}(E_{eV} + U_{D,eV}(V_{SD},V_G)) \right]
\]  
(2.1.23)

here

\[
T_{eV}(E_{eV}) = \frac{\gamma S,eV\gamma D,eV}{(E_{eV})^2 + (\gamma eV/2)^2},
\]  
(2.1.24)

with

\[
U_{S,eV}(V_{SD},V_G) = \epsilon_{eV} + \frac{q}{C_E} (N - N_0) - \frac{C_G}{C_E} (V_G) - \frac{C_D}{C_E} (V_{SD})
\]  
(2.1.25)

and

\[
U_{D,eV}(V_{SD},V_G) = \epsilon_{eV} + \frac{q}{C_E} (N - N_0) - \frac{C_G}{C_E} (V_G) + (1 - \frac{C_D}{C_E}) (V_{SD}),
\]  
(2.1.26)

where the subscript “\( eV \)” is used to denote that the units of these parameters are in electron Volts. These three equations, are the final formulas used for the current-voltage calculations performed with the SCF model.
2. Modeling single molecule conductance

Besides directly displaying current voltage plots, it often is advantageous to show differential conductance plots derived from the current-voltage calculations. The differential conductance \( G(V_{SD},V_G) \) is obtained by differentiating equation 2.1.23 with respect to the source drain voltage \( V_{SD} \):

\[
G(V_{SD},V_G) = \frac{\partial I(V_{SD},V_G)}{\partial V_{SD}} \tag{2.1.27}
\]

### 2.1.2 The Coulomb blockade model

The Self Consistent Field (SCF) model described in the previous subsection basically is a model for a single level in the channel, containing a single electron. However, each energy level can contain not one, but two electrons. The simplest way to introduce a second electron in the level would be to take equation 2.1.9 and multiply it by two, i.e.:

\[
D_x(E) = 2 \cdot \frac{\gamma/2\pi}{(E - \epsilon)^2 + (\gamma/2)^2} \quad \text{with} \quad \gamma = \gamma_S + \gamma_D \tag{2.1.28}
\]

If one now assumes that this level is half-filled for a channel to which no bias is applied, then the chemical potential will lie exactly in the middle of the broadened density of states (DOS), figure 2.5.A and only a small bias will have to be applied for a current to flow.

However, it is possible for the degenerate DOS to split up in a spin-up and a spin-down part, separated by the single-electron charging energy \( U_0 \), figure 2.5.B. When a bias is now applied to the device, then initially no current will start to flow since no part of the DOS lies between the two chemical potentials and the device is said to be in the “Coulomb blockade” regime.

How can one now understand why the DOS splits up? In the SCF model, both peaks would have the same energy, in other words be degenerate, and therefore stay degenerate as long as they feel the same self-consistent potential \( U \). The thing to understand is that no electron feels a potential due to itself \[1\]. Suppose that first the spin-down level gets filled, then the spin-up level will increase in energy with an amount equal to \( U_0 \). However, since the spin-down level feels no potential due to itself it remains at the same energy, resulting in the splitting of both levels as shown in figure 2.5.B.

Clearly, simply using the SCF model and multiplying by 2 cannot be used to describe the Coulomb blockade effect and another method, i.e. the Coulomb blockade (CB) model, will have to be used. But before describing the CB model, it is important to understand when this model can be used. Basically, this is the case when the splitting of the DOS is “visible”, in other words when the tops of the spin-up and spin-down level lie further apart than the widths of the individual peaks of the levels, \( U_0 > \gamma \[7\] \) and when this splitting of the DOS is bigger than the thermal broadening of the leads, \( U_0 > k_BT \). Only when both of these conditions are fulfilled will Coulomb

---

\[7\] In literature this condition is normally referred to as the “small coupling limit”. A condition that is in general not fulfilled for a thiolate molecule attached to a metal substrate. This results in another reason why this theory can not be used to explain the results of chapter 6.
2.1 The theoretical models

Figure 2.5: The broadened density of state (DOS) of a spin-degenerate energy level, filled with one electron. A) The spin-up and spin-down levels are not split up, as a result the chemical potentials still lie in the center of the DOS and a current flows even under the application of a small bias. B) Splitting of the spin-up and spin-down levels occurs, resulting in a low density of states between the chemical potentials. As a result no current starts to flow when only a small bias is applied and the device is said to be in the “Coulomb blockade” regime.

blockade be observable. Otherwise the results from the SFC model and the CB model will be very similar.

To correctly describe the conduction through a nanometer-sized channel, it is necessary to use a multi-electron picture. In such a picture each single-electron level can have only two states: empty (0), or filled (1). Consequently a system containing $N$ one-electron states contains $2^N$ states, which quickly diverges as $N$ increases, making a direct treatment impractical. However, here a system containing only two levels is considered\(^8\) and a multi-electron approach is still efficient. The two single-electron levels can have four states, namely 00, 10, 01 and 11, which stand for; both levels unfilled, only the spin-up level filled, only the spin-down level filled and both levels filled respectively. The energy of these states $E$ can be written as a function of the number of electrons $N$ in the channel:

$$E(N) = \epsilon N + \frac{U_0}{2} (N - N_0)^2$$ (2.1.29)

Where $\epsilon N$ is the energy level of the channel times the number of electrons in the

\(^8\)Which is a reasonable assumption, because, in practice, filled states far below the Fermi level and empty states far above the Fermi level do not contribute to the current; only a few orbitals near the Fermi level do.
2. Modeling single molecule conductance

channel and the second term is the energy stored in a capacitor formed by the channel and the leads 9.

In the multi-electron picture, the system has different possibilities \( P_\alpha \) of being in one of the \( 2^N \) states \( \alpha \), but all possibilities should still add up to one:

\[
\sum_\alpha P_\alpha = P_{00} + P_{10} + P_{01} + P_{11} = 1 \quad (2.1.30)
\]

In time, the system is continually shuffled between the states of the system and by assuming steady state conditions, there must be no net flow into or out of any state:

\[
\sum_\beta R(\alpha \rightarrow \beta)P_\alpha = \sum_\beta R(\beta \rightarrow \alpha)P_\beta \quad \text{with} \quad \alpha \neq \beta, \quad (2.1.31)
\]

where \( R(\alpha \rightarrow \beta) \) is the rate constant for going from state \( \alpha \) to state \( \beta \). Knowing these rate constants, allows for the calculation of the individual probabilities, which will be needed later, in order to calculate the current.

By assuming a specific model for the interaction of the channel with the surroundings, it becomes possible to calculate the rate constants. Here it is assumed that the interaction only involves the entry and exit of individual electrons from and to the source and drain contacts to the channel. The rate constants between states 00 and 10 (or 01) then become:

\[
R(00 \rightarrow 10) = R(00 \rightarrow 01) = \gamma_S \hbar f'_S + \gamma_D \hbar f'_D \quad \text{and} \quad (2.1.32)
\]

\[
R(10 \rightarrow 00) = R(01 \rightarrow 00) = \gamma_S \hbar (1 - f'_S) + \gamma_D \hbar (1 - f'_D) \quad (2.1.33)
\]

With the Fermi functions \( f'_S \equiv f_0(\epsilon_1 - \mu_S) \) and \( f'_D \equiv f_0(\epsilon_1 - \mu_D) \), which tell about the available electrons with energy \( \epsilon_1 = \epsilon - (U_0/2) \).

Similarly the rate constants between 10 (or 01) and 11 become:

\[
R(10 \rightarrow 11) = R(01 \rightarrow 11) = \gamma_S \hbar f''_S + \gamma_D \hbar f''_D \quad \text{and} \quad (2.1.34)
\]

\[
R(11 \rightarrow 10) = R(11 \rightarrow 01) = \gamma_S \hbar (1 - f''_S) + \gamma_D \hbar (1 - f''_D), \quad (2.1.35)
\]

where \( f''_S \equiv f_0(\epsilon_2 - \mu_S) \), \( f''_D \equiv f_0(\epsilon_2 - \mu_D) \) and the energy of the electrons is given by \( \epsilon_2 = \epsilon + (U_0/2) \).

9 The energy of the capacitor is given by \( Q^2/2C_E \), where \( Q \) is the net charge of the capacitor, \( Q = q(N - N_0) \). By now using equation 2.1.14, it is straightforward to derive formula 2.1.29.

10 Since the energies for states 10 and 01 are equal, so are their probabilities and consequently their rate constants.

11 It could be argued, that this multi-electron approach has been used in the SCF model as well, since applying this approach to a single electron level results in a formula that is equal to equation 2.1.15.

12 By taking \( N_0 = 1 \) in equation 2.1.29 and stating \( \epsilon_1 = E(1) - E(0) \), it follows immediately that \( \epsilon_1 = \epsilon - (U_0/2) \). Similarly, by stating that \( \epsilon_2 = E(2) - E(1) \), it follows that \( \epsilon_2 = \epsilon + (U_0/2) \).
2.1 The theoretical models

Because multiple electron entries (exits) have been excluded explicitly, transitions from states 00 to 11, and vice versa, are not allowed:

\[ R(00 \rightarrow 11) = R(11 \rightarrow 00) = 0 \] (2.1.36)

And because states 10 and 01 are indistinguishable, their rate constants are set to zero:

\[ R(10 \rightarrow 01) = R(01 \rightarrow 10) = 0 \] (2.1.37)

By filling in equations 2.1.32-2.1.37 in formula 2.1.31, it becomes possible to write the ratios for the probabilities as follows:

\[
\frac{P_{10}}{P_{00}} = \frac{P_{01}}{P_{00}} = \frac{\gamma_S f'_S + \gamma_D f'_D}{\gamma_S (1 - f'_S) + \gamma_D (1 - f'_D)} \equiv A \tag{2.1.38}
\]

\[
\frac{P_{11}}{P_{10}} = \frac{P_{10}}{P_{01}} = \frac{\gamma_S f''_S + \gamma_D f''_D}{\gamma_S (1 - f''_S) + \gamma_D (1 - f''_D)} \equiv B \tag{2.1.39}
\]

Where \( A \) and \( B \) are used as symbols to give shortened versions of equations 2.1.38 and 2.1.39.

Together with equation 2.1.30 and \( P_{10} = P_{01} \), equations 2.1.38 and 2.1.39 give the following expressions for the probabilities:

\[
P_{00} = \frac{1}{1 + 2A + AB} \tag{2.1.40}
\]

\[
P_{10} = P_{01} = \frac{A}{1 + 2A + AB} \tag{2.1.41}
\]

\[
P_{11} = \frac{AB}{1 + 2A + AB} \tag{2.1.42}
\]

Now that the rate constants \( R(\alpha \rightarrow \beta) \) and probabilities \( P_\alpha \) are explicitly known, it becomes possible to write down the formula for the current flowing from the source into the channel:

\[
I_S = -q \sum_{\alpha, \beta} (\pm) R_S(\alpha \rightarrow \beta) P_\alpha \quad \text{with} \quad \alpha \neq \beta \tag{2.1.43}
\]

Here “\( \pm \)” is + (−) if \( \beta \) has one more (less) electron than \( \alpha \) and \( R_S(\alpha \rightarrow \beta) \) represents the part of transition rate \( R(\alpha \rightarrow \beta) \) associated with the source contact.

Filling in the appropriate rate constants results in:

\[
I_S = \frac{q}{R} \left( 2\gamma_S f'_S P_{00} - \gamma_S (1 - f'_S)(P_{10} + P_{01}) + \gamma_S f''_S (P_{10} + P_{01}) - 2\gamma_S (1 - f''_S) P_{11} \right) \tag{2.1.44}
\]
2. Modeling single molecule conductance

Subsequently, filling in the probabilities into this equation gives the final formula for the current:

\[
I_S = 2\gamma_S \gamma_D \frac{q}{\hbar} \frac{\gamma_D f'_S (1 - f''_S) - f'_D (1 - f''_D)}{\gamma_S (f'_S + (1 - f''_S)) + \gamma_D (f'_D + (1 - f''_D))}
\]  

(2.1.45)

A similar formula can be set up for the current flowing from the drain into the channel:

\[
I_D = -q \sum_{\alpha, \beta} (\pm) R_D(\alpha \rightarrow \beta) \alpha \text{ with } \alpha \neq \beta
\]

(2.1.46)

With \(R_D(\alpha \rightarrow \beta)\) being the part of transition rate \(R(\alpha \rightarrow \beta)\) associated with the drain contact.

By again filling in the rate constants and probabilities it is easy to show that:

\[
I \equiv I_S = -I_D
\]

(2.1.47)

Re-writing the CB model to the form used in the calculations

Just as with the SCF model, it is advantageous to write the Coulomb blockade (CB) model in the form that has been used for the actual calculations.

The effect of the applied voltages on the energy level of the channel can easily be taken into account by adding the potential \(U\) of the channel to the energy levels \(\epsilon_1\) and \(\epsilon_2\) of the channel. Here \(U\) is:

\[
U = \frac{C_G}{C_E} (-qV_G) + \frac{C_D}{C_E} (-qV_{SD})
\]

(2.1.48)

This results in the Fermi functions to be written as follows:

\[
f'_S = f_0(\epsilon_1 + U - \mu_S)
\]

(2.1.49)

\[
f'_D = f_0(\epsilon_1 + U - \mu_D)
\]

(2.1.50)

\[
f''_S = f_0(\epsilon_2 + U - \mu_S)
\]

(2.1.51)

\[
f''_D = f_0(\epsilon_2 + U - \mu_D)
\]

(2.1.52)

By filling in equation 2.1.48, \(\mu_S = \mu_0 = 0, \mu_D = \mu_0 - qV_{SD} = -qV_{SD}, \epsilon_1 = \epsilon - U_0/2, \epsilon_2 = \epsilon + U_0/2\) and \(U_0 = q^2/C_E\), these equations become:

\[
f'_S(V_{SD}, V_G) = f_0(U'_S(V_{SD}, V_G))
\]

(2.1.53)

\[
f'_D(V_{SD}, V_G) = f_0(U'_D(V_{SD}, V_G))
\]

(2.1.54)

\[
f''_S(V_{SD}, V_G) = f_0(U''_S(V_{SD}, V_G))
\]

(2.1.55)

\[
f''_D(V_{SD}, V_G) = f_0(U''_D(V_{SD}, V_G))
\]

(2.1.56)

with

20
2.2 Results and discussion

\[
U'_S(V_{SD}, V_G) = \epsilon - \frac{q^2}{2C_E} - \frac{C_G}{C_E}(qV_G) - \frac{C_D}{C_E}(qV_{SD}) \tag{2.1.57}
\]

\[
U'_D(V_{SD}, V_G) = \epsilon - \frac{q^2}{2C_E} - \frac{C_G}{C_E}(qV_G) + (1 - \frac{C_D}{C_E})(qV_{SD}) \tag{2.1.58}
\]

\[
U''_S(V_{SD}, V_G) = \epsilon + \frac{q^2}{2C_E} - \frac{C_G}{C_E}(qV_G) - \frac{C_D}{C_E}(qV_{SD}) \tag{2.1.59}
\]

\[
U''_D(V_{SD}, V_G) = \epsilon + \frac{q^2}{2C_E} - \frac{C_G}{C_E}(qV_G) + (1 - \frac{C_D}{C_E})(qV_{SD}) \tag{2.1.60}
\]

Again, just as with the SCF model, the actual calculations have been performed with the units of energy in electron volts. Therefore, all energy related terms in equations 2.1.47 and 2.1.53 to 2.1.60, namely \( \gamma_S, \gamma_D, U'_S(V_{SD}, V_G), U'_D(V_{SD}, V_G), U''_S(V_{SD}, V_G), U''_D(V_{SD}, V_G) \), and \( k_B T \), need to be converted from units of Joules to units of electron volts, by dividing all these terms by \( q \). The formula for the current, as used for the calculations, then becomes:

\[
I = \frac{2q^2}{h} \frac{\gamma_{eV}}{\gamma_{eV}} \left[ f'_{s,eV}(1 - f''_{s,eV}) - f''_{s,eV}(1 - f''_{s,eV}) \right] \tag{2.1.61}
\]

where the subscript “eV” again denotes that the unit of the parameter is in electron volts. The Fermi functions become \( f'_{s,eV} = f_{0,eV}(U'_{s,eV}) \), \( f''_{s,eV} = f_{0,eV}(U''_{s,eV}) \), \( f'_{s,eV} = f_{0,eV}(U'_{s,eV}) \), and \( f''_{s,eV} = f_{0,eV}(U''_{s,eV}) \) respectively, with

\[
U'_{s,eV}(V_{SD}, V_G) = \epsilon_{eV} - \frac{q}{2C_E} - \frac{C_G}{C_E}(V_G) - \frac{C_D}{C_E}(V_{SD}) \tag{2.1.62}
\]

\[
U''_{s,eV}(V_{SD}, V_G) = \epsilon_{eV} - \frac{q}{2C_E} - \frac{C_G}{C_E}(V_G) + (1 - \frac{C_D}{C_E})(V_{SD}) \tag{2.1.63}
\]

\[
U''_{s,eV}(V_{SD}, V_G) = \epsilon_{eV} + \frac{q}{2C_E} - \frac{C_G}{C_E}(V_G) - \frac{C_D}{C_E}(V_{SD}) \tag{2.1.64}
\]

\[
U''_{s,eV}(V_{SD}, V_G) = \epsilon_{eV} + \frac{q}{2C_E} - \frac{C_G}{C_E}(V_G) + (1 - \frac{C_D}{C_E})(V_{SD}) \tag{2.1.65}
\]

Equation 2.1.61 is the final equation as used for the calculations. The differential conductance can simply be derived from equation 2.1.61 by taking its derivative to \( V_{SD} \):

\[
G(V_{SD}, V_G) = \frac{\partial I(V_{SD}, V_G)}{\partial V_{SD}} \tag{2.1.66}
\]

2.2 Results and discussion

The two models derived in the previous section are general in the sense that they can still be applied to any nanometer sized channel, connected to two leads and a gate,
2. Modeling single molecule conductance

regardless of dimensions and the materials used for those leads and gate. To be able to actually perform these calculations it will therefore be necessary to specify $U_0$, $C_G/C_E$ and $C_D/C_E$, or in other words specify the capacitances of the source, drain and gate. However, on these small scales it is not so easy to define these capacitances, since effects like self-capacitance and image charges have to be taken into account. But because the underlying physics of equations 2.1.23 and 2.1.61 is not altered by the choice of these parameters, it is possible to work with an estimate for the values of these parameters. Unless noted otherwise, the used estimates are $C_D/C_E = 0.49$ (from which $C_G/C_E$ can be derived) and $U_0 = q/C_E = 12$ meV. To give an indication about the correctness of the choice of the value for $C_D/C_E$, it is noted that from [4] a value of 0.42 can be derived for $C_D/C_E$.

Together with the other parameters used for the calculations, these estimates are listed in table 2.1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value (Unit)</th>
<th>Symbol</th>
<th>Value (Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q$</td>
<td>$1.602 \cdot 10^{-19}$ C</td>
<td>$\epsilon$</td>
<td>0.2 eV</td>
</tr>
<tr>
<td>$h$</td>
<td>$1.055 \cdot 10^{-34}$ Js</td>
<td>$\gamma_S$</td>
<td>$5.0 \cdot 10^{-3}$ A</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>$6.626 \cdot 10^{-34}$ Js</td>
<td>$\gamma_D$</td>
<td>$5.0 \cdot 10^{-3}$ A</td>
</tr>
<tr>
<td>$N_0$</td>
<td>1.0 -</td>
<td>$\mu_0$</td>
<td>0.0 eV</td>
</tr>
<tr>
<td>$T$</td>
<td>4.2 K</td>
<td>$k_B T$</td>
<td>$3.621 \cdot 10^{-4}$ eV</td>
</tr>
<tr>
<td>$C_D/C_E$</td>
<td>0.49 -</td>
<td>$U_0$</td>
<td>0.68 eV</td>
</tr>
<tr>
<td>$C_G/C_E$</td>
<td>0.02 -</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: The parameters used for the calculations. The parameters marked with A) are taken from [6].

2.2.1 Results and discussion for the Self Consisted Field method

For the SCF model, the effects of varying parameters, like the energy level of the channel and the temperature, on the current have been explored. These results will be shown in the following subsections, but before doing so, the concept of a “stability plot” is explained, in section 2.2.1.

The stability plot

By filling in the values as given in tabel 2.1 into equation 2.1.27, the differential conductance can be calculated and a $G(V_{SD}, V_G)$ plot, or in other words a “stability plot”, can be drawn, figure 2.6.A.

13Here it should be noted that the two models take two different things into account: The SCF model explicitly incorporates a broadening of the level in the calculation, which is not done for the CB model, while only the CB model actually incorporates the Coulomb blockade effect. As a result, it depends on the system under study which model is to be used.
2.2 Results and discussion

To explain what is happening in this figure it is advantageous to take a cross-section for one gate voltage, \( V_G = 5 \) V in this case, and compare the differential conductance \( G(V_{SD}) \), figure 2.6B, with the current \( I(V_{SD}) \), figure 2.6C. At zero source-drain bias both chemical potentials \( \mu_S \) and \( \mu_D \) are still equal and no current will flow. The differential conductance is zero as well. Increasing the voltage causes both chemical potentials to diverge, but as long as no part of the DOS of the energy level of the channel lies between the two potentials, the channel can not transport electrons and the current remains zero. Increasing the voltage even further causes part of the DOS the level of the channel to lie between the two potentials, resulting in an increasing current and hence the differential conductance increases as well. When the DOS lies completely between the two potentials, the current will have reached its maximum value and will remain constant upon further increasing the voltage. As a result the differential conductance will decrease to zero again, in effect \( G(V_{SD}) \) is a peak with its maximum at the same voltage as where the current has the steepest slope. By going to negative values of the voltage, the same behavior emerges, only with the polarity being reversed, the current for those voltages will be negative as well. The peak for the differential conductance will still be positive since both the voltage and the current are negative. By now changing the gate-voltage \( V_G \), the energy, at which the energy level \( \epsilon \) of the channel lies, changes as well. As a result, the source-drain voltage, where the differential conductance will be maximum, changes as well (for both positive and negative voltages).

Adding up various \( G(V_{SD}) \) traces, for a number of gate voltages, and plotting the intensity of the differential conductance with different colors, results in a stability plot such as shown in figure 2.6A, where the two crossing lines represent the maxima in the conductance. The gate-voltage, at which these two lines cross, is the point where the channel is said to be “in resonance” with the leads; even the smallest of source-drain voltages causes a current to flow. Also, the intensity of the differential conductance is maximum at this crossing point, since the current goes from its minimum to its maximum value here, without first reaching a plateau in the current at \( V_{SD} = 0 \) V and consequently the current has the steepest overall slope at this location.

The two lines in the stability plot themselves correspond to the two Fermi functions. This can be seen, by realizing that the positions of the lines change with voltage, both gate and source-drain voltage, and that only the two fermi functions contain terms with \( V_{SD} \) and \( V_G \) in it. By looking at equations 2.1.25 and 2.1.26 it becomes clear that the line with a negative slope, in \( (V_{SD}, V_G) \), corresponds to the source Fermi function. Since, in this case the factors before \( V_{SD} \) and \( V_G \) have the same sign, whereas for the drain Fermi function, these factors have opposite sign, resulting in a positive slope. To further demonstrate these points, the Fermi functions are plotted as function of source-drain and gate voltage, figure 2.7.

---

14 The peaks in figure 2.6B are not exactly equal in height. The same phenomenon is also observed in figure 2.13 and explained with equations 2.2.26 and 2.2.27.
15 Basically, one tries to keep the values of equations 2.1.26 and 2.1.27 constant while changing \( V_{SD} \) and \( V_G \). When the factors before \( V_{SD} \) and \( V_G \) have equal (opposite) sign, then the signs of the voltages need to be of opposite (equal) sign to keep \( U_{S,eV} (U_{D,eV}) \) constant. As a result, the slope of \( U_{S,eV} (U_{D,eV}) \) in \( [V_{SD},V_G] \) is negative (positive).
2. Modeling single molecule conductance

Figure 2.6: A) The stability plot of a nanometer sized channel containing a single electron energy level. The used parameters are given in table 2.1. At $V_G = 5V$ the vertical line shows where a cross-section of $G$ is taken. B) Shows this cross-section for $G(V_{SD})$ and C) for $I(V_{SD})$. 
2.2 Results and discussion

It can be seen, that the voltages, at which the Fermi functions change from 0 to 1, correspond to the voltages where the lines in the stability plot lie, proving that the lines in the stability plot really are due to the fermi functions. Not only that, but the change in the plot of the source Fermi function has a negative slope and that of the drain Fermi function has a positive slope.

Now that one can understands what a stability plot looks like, it becomes possible to look at what happens to such plots when the parameters of the calculation are varied. In the following subsections the effects of these changes will be discussed as well as how these changes in parameters relate to changes in a physical setup.

Changing the energy of the energy level

The first parameter to be varied is the energy level $\epsilon$ of the channel. This means, that the gate voltage at which the the level will be in resonance will change as well and this should result in the crossing point of the stability plot to shift to a different gate voltage. Experimentally, the variation of the energy level would be equivalent to the usage of a different molecule in between the leads.

Looking at figure 2.8 it can be observed that the shift of the crossing point along the gate voltage axis is the only change that occurs indeed. How can one understand this? In the previous subsection it has already been explained, that the lines in the stability plot are related to the positions where the Fermi functions change from 0 to 1. This will happen when the argument of the Fermi function becomes zero and
2. Modeling single molecule conductance

![Stability plots for different energy-levels of the channel. For A) $\epsilon = 0.2 \text{ eV}$ and for B) it is $0.1 \text{ eV}$. All other parameters are the same and given in Table 2.1.](image)

since only the energies around $E = 0$ will contribute to the current, this comes down to where equations 2.1.25 and 2.1.26 are zero. By now taking a lower energy level, namely $0.1 \text{ eV}$ instead of $0.2 \text{ eV}$, it can be seen that a lower gate voltage is required (for $V_{SD} = 0$) to make equations 2.1.25 and 2.1.26 equal to zero, consequently resulting in a shift of the crossing point to a lower gate voltage as well.

The effect of temperature

The next parameter to be varied within the SCF model is the temperature. The temperature effect is taken into account via the Fermi functions and it is well known that the bigger the temperature becomes, the more the step in the Fermi function, from 0 to 1, becomes smeared out in energy. This will result in the lines in the stability plot to become more smeared out, or in other words broader, as can be seen in figure 2.9.

From this figure it is clear that the lines in the stability plots become broader indeed as the temperature is increased. Another thing that can be observed is that the maximum differential current decreases from $30 \mu S$ to $5 \mu S$ as the temperature is raised from 4.2 $K$ to 293 $K$. By looking at figure 2.9D it can be seen, that changing the temperature only changes the voltage range over which the current goes from its minimum to its maximum value and not the minimum and maximum values themselves, which can be easily seen, since the density of states in the channel does not change. In other words, the slopes of the $I(V_{SD})$ lines decrease with increasing temperature. Since the differential conductance basically is this slope, its maximum value will decrease as well when the temperature goes up.

Varying the coupling constants: varying the absolute value

The last parameters to be varied for the SCF model are the rate constants $\gamma_S$ and $\gamma_D$. Since the molecule of each single-molecule-device will have a slightly different orientation with respect to the leads of similar devices, the coupling constants, or in other words $\gamma_S$ and $\gamma_D$, will vary as well from device to device. There are two ways
2.2 Results and discussion

**Figure 2.9:** Stability plots for different temperatures. For A) $T = 4.2 \, K$, for B) it is $77 \, K$ and for C) it is $293 \, K$. All other parameters are the same and given in table 2.1. D) shows the $I(V_{SD})$ traces at $V_G = 15 \, V$ for the three different temperatures in A) to C).

In which these $\gamma$’s can be varied: Firstly, by changing both $\gamma$’s in such a fashion that their ratio $M (M = \gamma_D/\gamma_S)$ remains constant. Secondly, by varying this ratio $M$.

First the magnitude of the $\gamma$’s was varied, with $M = 1$, and the results are displayed in figure 2.10.

What can be seen in the figure, is that for small values of $\gamma$, i.e. $\gamma_S = 0.005 \, eV$, the previously observed steps in the $I(V_{SD})$ plot are obtained as expected. But as $\gamma_S$ is increased to $5 \, eV$, the graph becomes a straight line with a slope equal to $\frac{q}{h}$, or in other words, the quantum of conductance.

That the conductance should approach the quantum of conductance has already been mentioned in section 2.1.1, but now a more formal derivation of this result is given. By taking equation 2.1.23 and using $\gamma_D = M \cdot \gamma_S$, with $M$ being a constant, one obtains:

\[
I(V_{SD}, V_G) = I_0 \int_{-\infty}^{\infty} dE \frac{M \gamma_S^2}{E^2 + \frac{\gamma_D^2}{\gamma_S^2} (1 + M)^2} \left[ f_0(E + U_S(V_{SD}, V_G)) - f_0(E + U_D(V_{SD}, V_G)) \right], \tag{2.2.1}
\]
2. Modeling single molecule conductance

Figure 2.10: $I(V_{SD})$ graphs for various coupling constants, with $\gamma_S = \gamma_D$ at $V_G = 15$ V. The numbers given on the lines of the graph are the corresponding values for $\gamma_S$ in eV. To more clearly show the $I(V_{SD})$ behavior for small $\gamma_S$, the inset shows the same data as the main graph, only for a narrower region of the current. All other parameters used for the calculations are given in table 2.1.

where $I_0 = \frac{q^2}{h}$ and all subscripts “eV” have been dropped. By now dividing both the enumerator and denominator by $\gamma^2_S$ and realizing that the differences of the two Fermi functions is 1 for $U_S > E > U_D$ and 0 for all other values of $E$ equation 2.2.1 becomes:

$$I(V_{SD}, V_G) = I_0 M \gamma_S \int_{U_S}^{U_D} d(E/\gamma_S) \frac{1}{(E/\gamma_S)^2 + (1 + M)^2},$$

which is a standard integral:

$$I(V_{SD}, V_G) = I_0 M \gamma_S \left[ \frac{2}{1 + M} \right] \left[ \arctan \left( \frac{U_D}{\gamma_S 1 + M} \right) - \arctan \left( \frac{U_S}{\gamma_S 1 + M} \right) \right]$$

16This can most easily be seen by looking at the limit of $T \to 0$. In that case, both Fermi functions become step-functions, with steps from 0 to 1, that are unequal only for $U_S > E > U_D$ and equal for all other values of $E$. 

28
2.2 Results and discussion

By now taking the Taylor expansion of the arc-tangent, the current can be written as:

\[ I(V_{SD}, V_G) = 2I_0 \gamma_S \left( \frac{M}{1 + M} \right) \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} \left( \frac{2}{(1 + M)\gamma_S} \right)^{2n+1} \left[ U_{D}^{2n+1} - U_{S}^{2n+1} \right] \]  \hspace{1cm} (2.2.4)

Writing out the first two terms gives:

\[ I(V_{SD}, V_G) = I_0 \cdot \left[ 4 \frac{M}{(1 + M)^2} (U_D - U_S) - \frac{16M}{3(1 + M)^4} \frac{1}{\gamma_S^2} (U_D^3 - U_S^3) + \cdots \right] \]  \hspace{1cm} (2.2.5)

Now it can easily be seen, that, in the limit of \( \gamma_S \to \infty \), all but the first term go to zero:

\[ I_{\gamma_S \to \infty}(V_{SD}, V_G) = I_0 \frac{4M}{(1 + M)^2} (U_D - U_S) \]  \hspace{1cm} (2.2.6)

Subtracting equations 2.1.25 and 2.1.26 from one another shows that \( U_D - U_S = V_{SD} \). Together with the fact, that \( \frac{4M}{(1 + M)^2} \) has its maximum value (of 1) for \( M = 1 \), this results in a maximum current \( I_{\text{max}} \) of:

\[ I_{\text{max}} = I_0 V_{SD}, \]  \hspace{1cm} (2.2.7)

which indeed increases linearly with applied source-drain voltage.

By dividing this current through the voltage, the maximum conductance \( G_{\text{max}} \) is obtained:

\[ G_{\text{max}} = \frac{I_{\text{max}}}{V_{SD}} = I_0 = \frac{q^2}{\hbar} \equiv G_0 \]  \hspace{1cm} (2.2.8)

Equation 2.2.8 shows that as \( \gamma_S \) goes to infinity, that the conductance reaches a maximum that indeed is equal to the quantum of conductance.

**Varying the coupling constants: varying ratio of the constants**

Secondly the ratio \( M \) of these coupling constants can be varied. Experimentally this corresponds to the situation when one of the ends of the molecule is more strongly bonded to one lead then the other end of the molecule is to its lead.

To see what can be expected, equation 2.2.4 is written slightly differently:

\[ I(V_{SD}, V_G) = 4I_0 \frac{M}{(1 + M)^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} \left( \frac{2}{(1 + M)\gamma_S} \right)^{2n} \left[ U_{D}^{2n+1} - U_{S}^{2n+1} \right] \]  \hspace{1cm} (2.2.9)

From this equation it can be seen, that if \( \gamma_D \) is a lot bigger or smaller than \( \gamma_S \), or in other words \( M \) approaches infinity or zero respectively, that the current will drop to zero. To verify this behavior, \( I(V_{SD}) \) is plotted for various values of \( M \), figure 2.11
2. Modeling single molecule conductance

Figure 2.11: Two $I(V_{SD})$ graphs for various ratios $M$ of the coupling constants, with $\gamma_S = 0.005 \text{ eV}$ and $\gamma_D = M \cdot \gamma_S$, at $V_G = 15 \text{ V}$. The numbers given on the lines of the graphs are the corresponding values for $M$. All other parameters used for the calculations are given in table 2.1.

As can be seen, the current indeed approaches zero when $M$ goes to zero or infinity. But how can one understand this result physically? To answer this question one only needs to look at the transmission function $T$, see equation 2.1.18, and realize that it is the product of the density of states $D$ and a term $Y$, which is a combination of $\gamma_S$ and $\gamma_D$ that signifies the overall rate with which electrons move from one electrode through the channel to the other electrode:

$$T(E) = \frac{\gamma_S \gamma_D}{(E)^2 + ((\gamma_S + \gamma_D)/2)^2} = \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} \frac{\gamma_S + \gamma_D}{E^2 + ((\gamma_S + \gamma_D)/2)^2} = Y \cdot D(E)$$

(2.2.10)

with

$$Y = 2\pi \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D}$$

and

$$D(E) = \frac{1}{2\pi} \frac{\gamma_S + \gamma_D}{E^2 + ((\gamma_S + \gamma_D)/2)^2}$$

(2.2.11)

When $\gamma_S \gg \gamma_D$, these equations become:

$$Y = 2\pi \gamma_D$$

and

$$D = \frac{4}{2\pi \gamma_S}$$

(2.2.12)

resulting in $T = 4\gamma_D$, which goes to zero because $\gamma_S \gg \gamma_D$. So, what physically happens when $\gamma_S \gg \gamma_D$, is that electrons can easily move from the source lead to the channel or vice versa, but not so easily from (to) the drain lead to (from) the channel, resulting in the overall rate $Y$ still to be limited by $\gamma_D$. On the other hand, the density of state goes to zero as $\gamma_S$ goes to infinity. As a result the transmission function, and therefore the current goes to zero. Similarly, the transmission function also goes to zero when $\gamma_D \gg \gamma_S$.

Another feature in figure 2.11 is that for small $M$ the shape of $I(V_{SD})$ becomes a staircase, whereas this shape becomes a straight line as $M$ becomes big. The reason
2.2 Results and discussion

for this is already given in the previous subsubsection; for small $\gamma$’s the shape of the current-voltage characteristic is a staircase and for big $\gamma$’s it is a straight line.

2.2.2 Results for the Coulomb blockade model

In section 2.2.1 the effects of changing the parameters of the model on the current-voltage characteristic and on the stability plot have been discussed for the Self Consistent Field model. In this subsection, the same will be done for the Coulomb blockade model. However, since both models are similar, changing some of the parameters, like the position of the energy level $\epsilon$ and the temperature $T$, will have the same effect as in the SCF model and it would be pointless to redo these calculations. Therefore, only the effect of varying the relevant parameters on the conduction, namely the single electron charging energy $U_0$ and the ratio $M$ between $\gamma_D$ and $\gamma_S$, will be discussed.

But before doing so, the stability plot for the Coulomb blockade model itself will be given.

The Stability Plot of the Coulomb blockade model

In subsection 2.2.1 it was shown, that the stability plot for a SCF model consists of two lines of maximum differential conductance, that correspond to the $[V_{SD}, V_G]$ combinations for which the arguments of the Fermi functions, i.e. $U_S(V_{SD}, V_G)$ and $U_D(V_{SD}, V_G)$, are zero.

Since there are 4 different Fermi functions in the Coulomb blockade (CB) model, it can be expected that there will be 4 lines of maximum differential conductance in the stability plot of the CB model and that each of these lines will correspond to a set of $[V_{SD}, V_G]$ combinations for which one of the arguments of the fermi functions ($U'_S(V_{SD}, V_G), U'_D(V_{SD}, V_G), U''_S(V_{SD}, V_G)$ or $U''_D(V_{SD}, V_G)$) will be zero. From figures 2.12 and 2.13 it can be seen that the above made assumptions are correct.

From figure 2.12.C it can be seen what happens to the current in the channel as the source-drain voltage is varied. Just as with the SCF model, at $V_{SD} = 0$ $V$ the chemical potentials of source and drain are equal and no current can flow. Similarly, increasing the voltage does not result immediately in a current since no energy level lies between the source and drain potential. When the voltage is increased to such an extent, that one spin-degenerate energy level lies between both potentials, two things happen. Firstly, one of the degenerate energy levels will start to transport electrons and a current is established. In figure 2.12.C this can be seen as the first step in the current. Secondly, since one of the two degenerate levels is now filled, the empty level experiences a potential due to the electron in the filled channel and as a result the empty channel is shifted up in energy. By increasing the voltage even further, this "up-shifted" energy level will come to lie between the source and drain potential as well, thereby also contributing to the current. This can be observed as the second step in the current. By going from zero to negative voltages, the same behavior can be observed, only with the polarity reversed.

One thing that can be seen in 2.12.C is that the first step in the current is twice as high as the second step. Physically, this can be seen as follows. At the first step, both levels are still degenerate and both spin-up and spin-down electrons can fill the
2. Modeling single molecule conductance

Figure 2.12: Several stability plots for the Coulomb blockade model. A) Shows a stability plot containing four lines of maximum differential conductance. B) A zoom in of plot A) that more clearly shows, that there are not two, but four lines of maximum conductance. C) shows an \( I(V_{SD}) \) plot and D) a \( G(V_{SD}) \) plot, both for \( V_G = 11.2V \), indicated by the white line in B). To show, that the lines of maximum differential conductance correspond to the \([V_{SD},V_G]\) combinations for which one of the arguments of the fermi functions will be zero, the four Fermi functions are plotted as functions of \( V_{SD} \) and \( V_G \); \( f'_S \) in A), \( f'_D \) in B), \( f''_S \) in C) and \( f''_D \) in D) in figure 2.13 respectively. The parameters used for the calculations are \( \gamma_S = \gamma_D = 50\mu eV \), with the rest of the parameters listed in tabel 2.1.

energy level and contribute to the current. At the second step, one level is already filled with an electron that has a spin and the only electrons that can contribute to the current due to the second level, are electrons with opposite spin, resulting in the step to be only half as high as the first.

Mathematically, this can best be seen by taking the following steps. For one gate voltage, the current reaches 5 different values of constant current as the source-drain voltage is varied. By calculating the current for each of these regions, it becomes possible to calculate the difference in current between these regions, or in other words the desired current steps can be obtained. Figure 2.14.A shows the same data as figure 2.12.C, only with the graph divided into five regions (A to E) of constant current.

In the limit of \( T = 0 K \), the Fermi functions reduce to step functions and the
2.2 Results and discussion

Figure 2.13: The Fermi functions corresponding to the stability plot of figure 2.12.B. The four Fermi functions are plotted as functions of $V_{SD}$ and $V_G$; $f'_S$ in A), $f'_D$ in B), $f''_S$ in C) and $f''_D$ in D) respectively. The parameters used for the calculations are $\gamma_S = \gamma_D = 50 \mu eV$, with the rest of the parameters listed in table 2.1.

Currents for the different regions, as indicated in figure 2.14.A, can be written as follows:

\[
\begin{align*}
I_A &= -2I_0 \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D} \\
I_B &= -2I_0 \frac{\gamma_S \gamma_D}{\gamma_S + 2\gamma_D} \\
I_C &= 0 \\
I_D &= 2I_0 \frac{\gamma_S \gamma_D}{2\gamma_S + \gamma_D} \\
I_E &= 2I_0 \frac{\gamma_S \gamma_D}{\gamma_S + \gamma_D}
\end{align*}
\]

where $I_0 = q^2/h$. By subtracting these voltages from one another, the current steps are found:

\[\text{These formulas are derived for } V_G = 11.2 \text{ V. For other, i.e. higher, gate voltages the various Fermi functions will start to cross one another, see figure 2.12.B. However, this will result in similar formula's for the current in the different source-drain voltage regions and they will not be given separately.}\]
2. Modeling single molecule conductance

Figure 2.14: The current-voltage, A), and differential conductance-voltage, B), graphs for the Coulomb blockade model for $V_G = 11.2$ V, $\gamma_S = \gamma_D = 50\mu eV$ and the rest of the parameters given in tabel 2.1. The current-voltage plot is divided into five regions (A to E) of constant current. B) Shows the corresponding differential conductance plots for the transitions between these regions of constant current.

\[
\begin{align*}
\Delta I_{B\rightarrow A} &= I_B - I_A = 2I_0 \frac{\gamma_S^2 \gamma_D^2}{\gamma_S^2 + 3\gamma_S \gamma_D + 2\gamma_D^2} \\
\Delta I_{C\rightarrow B} &= I_C - I_B = 2I_0 \frac{\gamma_S \gamma_D}{\gamma_S + 2\gamma_D} \\
\Delta I_{D\rightarrow C} &= I_D - I_C = 2I_0 \frac{\gamma_S \gamma_D}{2\gamma_S + \gamma_D} \\
\Delta I_{E\rightarrow D} &= I_E - I_D = 2I_0 \frac{\gamma_S \gamma_D}{2\gamma_S^2 + 3\gamma_S \gamma_D + \gamma_D^2}
\end{align*}
\]

For this particular calculation $\gamma_S = \gamma_D$, which reduces equations (2.2.18) to (2.2.21) to:

\[
\begin{align*}
\Delta I_{B\rightarrow A} &= \frac{1}{3} I_0 \gamma_S \quad (2.2.22) \\
\Delta I_{C\rightarrow B} &= \frac{2}{3} I_0 \gamma_S \quad (2.2.23) \\
\Delta I_{D\rightarrow C} &= \frac{2}{3} I_0 \gamma_S \quad (2.2.24) \\
\Delta I_{E\rightarrow D} &= \frac{1}{3} I_0 \gamma_S \quad (2.2.25)
\end{align*}
\]

And indeed, the current steps closest to $V_{SD} = 0$, $\Delta I_{C\rightarrow B}$ and $\Delta I_{D\rightarrow C}$, are twice as big as the two steps furthest away from $V_{SD} = 0$, $\Delta I_{B\rightarrow A}$ and $\Delta I_{E\rightarrow D}$.
2.2 Results and discussion

The differential conductance should be proportional to these current steps and in general this is the case; in figure 2.14.B the peaks in the differential conductance corresponding to $\Delta I_{C \rightarrow B}$ and $\Delta I_{D \rightarrow C}$ are approximately twice the height of the peaks corresponding to $\Delta I_{B \rightarrow A}$ and $\Delta I_{E \rightarrow D}$. However, peaks $\Delta I_{C \rightarrow B}$ and $\Delta I_{D \rightarrow C}$ are not equal, which contradicts the results found in equations 2.2.23 and 2.2.24. To understand this, one has to look at how the Fermi functions change from 0 to 1 as the source-drain voltage is varied\(^\text{18}\). The terms responsible for these changes of the Fermi functions are:

\[
\frac{C_D}{2C_D + C_G}(qV_{SD})/k_BT \quad \text{for } f_S' \text{ and } f_S'' \quad \text{(2.2.26)}
\]

and

\[
\frac{C_D + C_G}{2C_D + C_G}(qV_{SD})/k_BT \quad \text{for } f_D' \text{ and } f_D'' \quad \text{(2.2.27)}
\]

For $T = 0$ K, used in equations 2.2.23 and 2.2.24, expressions 2.2.26 and 2.2.27 are equal (albeit infinity). Resulting in the transitions of all Fermi functions to be equal as well. Consequently, the steps in the current are also equal. For $T > 0$ K, used in figure 2.14.B, equations 2.2.26 and 2.2.27 are no longer equal. This results in different transitions for Fermi functions $f_S'$ and $f_S''$, compared to $f_D'$ and $f_D''$. Hence, the heights of the differential conductance peaks $\Delta I_{C \rightarrow B}$ and $\Delta I_{D \rightarrow C}$ in figure 2.14.B are also different.

Varying the charging energy $U_0$

The difference between Fermi functions $f_S'$ and $f_S''$ (and between $f_D'$ and $f_D''$ as well) is the charging energy $U_0 eV = q/C_E$, see equations 2.1.62 to 2.1.65. Therefore, by varying $U_0$, the difference between $f_S'$ and $f_S''$ (or $f_D'$ and $f_D''$) can varied as well.

Figure 2.15 shows several stability plots for various values of the charging energy $U_0$ of the channel.

As can be seen from the figure, the smaller the charging energy $U_0$ becomes, the closer together the lines of maximum differential conductance lie, or in other words, the lines where $f_S'$ and $f_S''$ (and $f_D'$ and $f_D''$ as well) are zero.

Varying the ratio between the coupling constants

The last parameter to be varied for the Coulomb blockade model is the ratio $M$ between the coupling constants $\gamma_S$ and $\gamma_D$. Just as with the Self Consistent Field model, unequal coupling constants can arise experimentally when one end of the molecule binds more strongly to the lead then the other end of the molecule does.

In figure 2.16 the stability plots for the three characteristic regimes of $M$, namely $M < 1$, $M = 1$ and $M > 1$, are shown, together with the corresponding current-voltage traces for $V_G = 11.2$ V.

For values of $M$ far away from unity it can be seen that parts of several of the lines of maximum differential conductance are missing, whereas they are not for $M = 1$.

\(^{18}\)Since all current steps are taken at one gate voltage, $V_G$ can here be assumed to be constant.
2. Modeling single molecule conductance

To understand this behavior one only has to realize that intensity of these lines is proportional to magnitude of the steps in the current, as show in the beginning of this subsection. By now filling in $\gamma_D = M \cdot \gamma_S$ into equations 2.2.18 to 2.2.21, the formulas for these current steps become:

\[
\begin{align*}
\Delta I_{B\rightarrow A} &= I_B - I_A = 2I_0\gamma_S \frac{M^2}{1 + 3M + 2M^2} \\
\Delta I_{C\rightarrow B} &= I_C - I_B = 2I_0\gamma_S \frac{M}{1 + 2M} \\
\Delta I_{D\rightarrow C} &= I_D - I_C = 2I_0\gamma_S \frac{M}{2 + M} \\
\Delta I_{E\rightarrow D} &= I_E - I_D = 2I_0\gamma_S \frac{M}{2 + 3M + M^2}
\end{align*}
\]

For $M = 1$ this gives the same result as for equations 2.2.22 to 2.2.25. However for ratios far from unity, $M \ll 1$ or $M \gg 1$, these equations become quite different. In the case of $M$ being far smaller than 1 the changes in current are given by

\[
\begin{align*}
\Delta I_{B\rightarrow A} &= 2I_0\gamma_S M^2 \\
\Delta I_{C\rightarrow B} &= 2I_0\gamma_S M \\
\Delta I_{D\rightarrow C} &= I_0\gamma_S M \\
\Delta I_{E\rightarrow D} &= I_0\gamma_S M
\end{align*}
\]

Not only do these formula’s give the correct ratios between the different differential conductance peaks, but they also explain why the absolute value of all four peaks goes down as $M$ is decreased.

Similarly, when $M \gg 1$, the following equations give the change in current:

\[
\begin{align*}
\Delta I_{B\rightarrow A} &= I_0\gamma_S \\
\Delta I_{C\rightarrow B} &= I_0\gamma_S \\
\Delta I_{D\rightarrow C} &= 2I_0\gamma_S \\
\Delta I_{E\rightarrow D} &= 2I_0\gamma_S / M \approx 0
\end{align*}
\]

Again, these formulas concur with the current-steps reported in figure 2.16 F. Basically, what happens here, is that, depending on the polarity of the applied voltage, the Coulomb blockade is lifted or not.

To understand what physically happens in these cases, it is necessary to look again at how $\gamma_S$ and $\gamma_D$ are defined. In equation 2.1.2 (2.1.3), \( \frac{\tau}{\hbar} = \frac{\gamma}{\eta} \) is defined as the inverse time it takes an electron to move to/from the energy level $\epsilon$ in the channel from/to the source (drain) contact. So, when $M$ is far from unity, it means that electrons can move easily through one of the lead/channel interfaces but not through the other. Therefore the interface with the lowest coupling constant acts as the mayor barrier for electron flow and electrons “pie-up” against this barrier. Depending on the polarity of the voltage, this pile-up will take place in the lead or in the channel.
2.2 Results and discussion

Figure 2.15: Stability plots for various charging energies of the channel; $U_0$ is 59, 24, 12, 2, 1 and 0.1 meV for A), B), C), D), E) and F) respectively. The coupling constants $\gamma_S$ and $\gamma_D$ are 50 $\mu$eV and all other parameters used for the calculations are listed in tabel 2.1.
2. Modeling single molecule conductance

Figure 2.16: Stability plots for the three characteristic regimes of $M$ together with the corresponding current-voltage traces for $V_G = 11.2$ V; $M \ll 1$, namely $M = 1/100$, for A) and B). For C) and D) $M = 1$. And for E) and F) $M \gg 1$, namely $M = 100$. The coupling constants are as follows; $\gamma_S = 50 \mu$eV and $\gamma_D = M \cdot \gamma_S$. All other parameters used for the calculations are given in table 2.1.
2.3 Conclusions

Only when the pile-up takes place in the channel will there be any Coulomb blockade, hence the polarity dependent Blockade phenomenon.

For example, if one looks again at $M \ll 1$, figure 2.16.B, then $\gamma_D \ll \gamma_S$ and $\gamma_D$ is the major barrier. By now taking a positive source-drain voltage, the electrons will flow from the source to the drain via the channel. Since the big barrier is the drain-channel interface, electrons pile up in the channel and long before the first electron exits the channel via the drain, a second electron enters the channel via the source. Since there are two electrons simultaneously on the channel, the Coulomb blockade effect has to be taken into account. When the bias is reversed however, electrons flow from drain to source, immediately encountering the big drain-channel barrier. When an electron does cross the barrier, it will exit the channel via the source contact, long before another electron enters the channel via the drain and no Coulomb blockade occurs. Looking at figure 2.16.B confirms that the Coulomb blockade effect does indeed occur for positive voltages, but not for negative values of the voltage.

2.3 Conclusions

In this chapter, the results of two models (as described by Datta [1]), describing the conductance of electrons through channels with dimensions in the order of nanometers, have been presented, namely the Self Consistent Field model and the Coulomb blockade model. For both models, the general outcome is a stability plot; i.e. a plot of the differential conductance as function of both source-drain and gate voltage. Various modeling parameters have been varied to see how the (differential) conductance of the channel changed because of these variations as well as the physical meaning behind these changes.

A change in the energy of the energy level of the channel is reflected in the shift of the crossing point of the lines of maximum differential conductance along the gate-voltage-axis.

Increasing the temperature, causes the width of the lines of maximum differential conductance in the stability plots to be increased. This results from the broadening of the step in the Fermi function with increased temperature, as is well known from literature [7].

For the Self Consistent Field model, increasing the coupling strengths of the channel to source and drain equally, results in the differential conductance to reach a maximum, namely the quantum of conductance. Setting the ratio between the source-coupling and the drain-coupling far from unity results in the current going to zero; the overall transfer-rate is still dominated by the smallest of the two coupling constants, while the density of states becomes broadened and therefore effectively goes to zero if either of the coupling-constants is increased.

Lastly, for the Coulomb blockade model, it is shown that Coulomb blockade only occurs for sufficiently large charging energies; if the charging energy is too low, then the splitting between the two levels is too small to be resolved. Finally, when the ratio between the coupling constants is far from unity, the Coulomb blockade becomes dependent on the polarity of the source-drain bias; in one direction the Coulomb blockade is lifted, in the other it is not.
2. Modeling single molecule conductance

Bibliography


Chapter 3

Gold nanoparticle manipulation by AFM

In this chapter an atomic force microscope (AFM) has been used to push colloidal gold nanoparticles (CGNP) between lithographically defined contacts. With this method it was attempted to create two conducting contacts with a spacing of 1 to 2 nm between them, that could subsequently be used to connect a single molecule to the macroscopic world and measure its conduction properties. Before making two contacts with a small gap in between them, fully connected wires were created in this fashion. For such wires no conduction could be measured as application of a voltage to the wire resulted in its destruction. To bypass the electrically insulating citrate shells that cover the CGNP and make the wire more conductive, the wires were coated with a thin layer of silver by applying an “enhancement” solution. While the silver indeed enhanced the conduction, it was determined that almost all of the current flowed through the silver and not through the gold colloids. Therefore it was attempted to remove the citrate shells of the CGNP by applying microwave radiation to the sample. Not only did microwave irradiation remove the citrate shell, but it also caused the colloids to melt and resulted in the coalescence of those colloids that touched one another.

3.1 Introduction

In order to measure the conductance of individual molecules, it is necessary to connect them to contacts in such a way that allows for electrical currents to be applied to such molecules. In this chapter a method for creating such wires is investigated.

A great variety of methods has been used to create ever smaller and smaller metallic wires and contacts that can be used for connecting various nano scale objects, like individual molecules [1, 2], colloidal particles [3–5] and carbon nanotubes [6, 7] to the macroscopic world. The use of mechanical break junction (MBJ) techniques [8–10] to create chains of gold atoms and measure their conductance has attracted a lot of attention over the last decade. Likewise, scanning probe microscopes (SPM), scanning tunneling microscopes (STM) [11, 12] and similar devices [13] have been used for
3. Gold nanoparticle manipulation by AFM

comparable experiments where a wire is created directly between the tip (of the SPM) and a substrate by first placing the tip in contact with the substrate and subsequently slowly pulling the tip away. Also, STMs and atomic force microscopes (AFM) have been used as probes that can be connected directly to nanoscopic objects like metallic wires [14] and thin films [15]. Alternatively small metallic wires can be created by placing a droplet of an aqueous solution, containing colloidal gold nanoparticles, between two metallic contacts and apply an alternating electric field. The alternating field causes the particles to align into a wire and to fuse into one another [16–18].

The various methods have advantages and disadvantages. For example, while the gap between two leads can be controlled accurately with STM, this method lacks the ability to add a gate electrode to the setup that is necessary to address electronic states of the molecule over an energy range of several volts without destroying the molecule under study. In the case of wires created from colloidal gold nanoparticles in an alternating electrical field a gate would be possible, but how the wire will be exactly formed on the nanometer level can not be controlled.

Therefore, the method chosen in this chapter for creating nanometer-sized contact wires is one where not only a gate can be used, but where the geometry of the leads can be controlled with nanometer precision. The method of choice consists of using an AFM to push CGNP across a substrate and align them into a wire configuration between two lithographically defined contacts (see [19,20] and references therein).

A major concern for the conduction properties of chains of colloidal particles is the shell of organic molecules around each of these particles. This shell is needed to prevent the CGNP from clustering [21] in the solution in which they are fabricated, but these molecules, citrate to be precise, are insulating and might result in non-conducting leads.

To gain insight into the effect of the shell, it is desirable to perform conduction experiments on chains of CGNP both with and without such a shell.

To remove the shell of the gold colloids, the CGNP are treated with microwave radiation. Besides the everyday use of cooking food with microwave radiation, microwaves have been used to create various kinds of metal colloids [22–25], as well as for (re)aligning the magnetic moments of nanoparticles [26, 27] and for controlling the packing order of colloidal particles on a substrate [28]. On the macroscopic scale microwaves are used to fabricate metal components by sintering of metal powders into the desired shape [29]. Recently Perelaer et al. used a combination of ink-jet printing and microwave sintering to create conducting lines of silver with widths of 100 to 200 µm [30].

3.2 The experimental techniques

Several experimental techniques have been used to create lines of colloids between two macroscopic leads. The used techniques are (electron-beam) lithography, AFM particle manipulation, the use of seeding solutions and microwave irradiation. A short description of each will be given in this section.

1Attempts are underway to incorporate a gate electrode into a MBJ configuration though.
3.2 The experimental techniques

3.2.1 Electron beam lithography

The word “lithography” comes from the Greek words lithos and graphein and literally it means writing in stone [31]. Not stone, but its modern counterpart, namely silicon, is used as a basis for writing the desired pattern on. The silicon is covered with a thin film of a radiation-sensitive material, poly(methylmethacrylate) (PMMA) in this case, figure 3.1.A. Exposing this film to an electron beam will cause the local dissociation of the molecules constituting the thin film and a hole will be burnt into it, figure 3.1.B. By controlling which parts of the film are exposed to the radiation and which parts are not, a predetermined pattern can be written into the film. This turns the thin film into a mask, on which metals can be evaporated to form the actual lithographic structures, figure 3.1.C. The metal evaporated onto the substrate is gold because gold does not readily react to the air and oxygen that are present at ambient conditions. However, gold does not adhere well to silicon oxide and in order to create metallic structures that are stable and robust, a thin layer of titanium is first evaporated unto the substrate to anchor the gold in place. In the last step, known as “lift-off”, the PMMA is removed, leaving behind the finished lithographic structure.

![Figure 3.1: Schematic representation of the lithography process used for creating nano-scale metallic contacts. A) A silicon substrate with a silicon oxide layer is covered with a PMMA film and gold is evaporated on top of it to prevent charging during exposure. B) Holes have been burnt into the PMMA layer with the E-beam. C) The complete surface (and in particular the holes) is partially filled up with evaporated Ti and Au. D) The PMMA layer is removed, leaving only the lithographic structures behind.](image)

Using electrons has several advantages. First, the De Broglie-wavelength of electrons is very small, i.e. 8.45 picometer for electrons with an energy of 20 keV. Thus writing with electrons gives, at least in theory, a resolution high enough for making structures with dimensions in the order of nanometers. Second, since electrons are charged particles, it is easy to focus them into a tight beam with magnetic lenses.
3. Gold nanoparticle manipulation by AFM

This gives the accuracy necessary to deposit the electrons on the desired location with nanometer precision.

However, there are other processes at work that reduce the resolution of E-beam lithography. First the beam coming out of the electron-beam lithography machine is already broader than the theoretical limit of 8.45 picometer due to modification of the beam as it is collimated. Second, when the beam hits the resist on the sample forward scattering occurs; its electrons undergo small angle scattering events and the beam-width will increase according to the empirical formula

\[ d_f = 0.9 \left( \frac{R_t}{V_b} \right)^{1.5} \]

where \( d_f \) is the broadening of the beam due to forward scattering in nanometers, \( R_t \) the thickness of the resist (also in nanometers) and \( V_b \) the beam voltage in kilovolts.

As electrons penetrate the sample’s substrate, then many of them will experience large angle scattering events, causing electrons to return through the resist a significant distance away from the point of entry, leading to additional broadening of the exposed area. This effect is called backscattering.

Finally there are the secondary electrons. As the primary electrons slow down, much of their energy is dissipated in the form of secondary electrons. They are responsible for the bulk of the actual resist exposure process. Since their range in resist is only a few nanometers, they contribute little to the broadening of the exposed area.

These broadening effects all have to be added to the beam width to get the total effective resolution of the beam. These broadening effects together are called the “proximity effect”.

3.2.2 Atomic forces

Before explaining how an AFM can be used to move particles across a substrate, it is necessary to explain how an AFM itself works. With atomic force microscopy, the forces between atoms are being probed and used to image a substrate’s surface. Many different interactions can play a role, like covalent bonds, Coulomb forces, ionic forces, dipole interactions, van der Waals forces, etc. The main forces involved in interatomic interactions are the attractive van der Waals forces and the repulsive interatomic force, which are due to the Pauli exclusion principle, and lead to the phenomenological Lennard-Jones potential \( w \) \([33, 34]\). Depending on the distance \( r \) between the two atoms the interaction/potential \( w \) can be positive (repulsive) or negative (attractive) and has the following form:

\[ w(r) = 4w_0 \left[ -\left( \frac{\sigma}{r} \right)^6 + \left( \frac{\sigma}{r} \right)^{12} \right], \]

where \( \sigma \) is the distance between the two atoms for which this potential is zero and \( w_0 \) is the minimum energy of the potential. This equation can be rewritten as:

\[ w(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^6 - 2 \left( \frac{\sigma}{r} \right)^{12} \right] \]

From [32], it is known that for a 20 keV potential difference, the beam hitting the substrate is 2 nm broad.
3.2 The experimental techniques

\[ w(r) = -\frac{C_6}{r^6} + \frac{C_{12}}{r^{12}}, \]  
\[ (3.2.3) \]

with \( C_6 = 4w_0\sigma^6 \) and \( C_{12} = 4w_0\sigma^{12} \).

It should be noted that equation 3.2.2 is only valid for the interaction between individual atoms. To obtain the macroscopic interactions between objects, equation 3.2.2 has to be integrated over the macroscopic bodies in question. Here the macroscopic objects to integrate over are a sphere of radius \( R \), separated from a flat surface by a distance \( r_3 \).

From literature \[34\] it is known, that integration of an interaction between two molecules of the form \( w(r) = -\frac{C}{r^n} \), results in an interaction \( W \) of the form:

\[ W(r) = -\frac{4\pi^2\rho_{sp}\rho_{su}CR}{(n-2)(n-3)(n-4)(n-5)} \frac{1}{r^{n-1}}, \]  
\[ (3.2.4) \]

if the geometric configuration to be integrated over is one of a sphere, with radius \( R \), above a flat surface and where \( \rho_{sp} \) and \( \rho_{su} \) are the number density of molecules, i.e the number of molecules per cubic meter, in the sphere and the surface respectively.

Using this transformation on both terms of equation 3.2.3 results in the following interaction potential \( W \) between a sphere of radius \( R \), separated from a flat surface by a distance \( r \):

\[ W(r) = A\sigma R \left[ \frac{1}{210} \left( \frac{\sigma}{r} \right)^7 - \left( \frac{\sigma}{r} \right)^2 \right], \]  
\[ (3.2.5) \]

with \( A = \frac{2}{3}\pi^2 w_0\rho_{sp}\rho_{su}\sigma^4 \).

The force \( F \) between sphere and surface can now be simply found by taking the negative of the gradient of the potential:

\[ F(r) = -\nabla W(r) = AR \left[ \frac{1}{30} \left( \frac{\sigma}{r} \right)^8 - \left( \frac{\sigma}{r} \right)^2 \right], \]  
\[ (3.2.6) \]

Figure 3.2 shows the graphical representation of equation 3.2.6, i.e the so-called force-distance curve, for typical \[35\] AFM parameters. For small distances the total force is positive (repulsive) and the tip is said to be in contact with the surface. \[4\]

Trapped electronic charges on tip and or substrate can lead to additional electrostatic forces. Their strength depends on Coulomb’s law and scales with \( 1/r^2 \). In addition, for operation of an AFM under ambient conditions, the formation of a water meniscus \[36,37\] between tip and substrate presents a major interaction that can change the amplitude of the van der Waals forces be several orders of magnitude. While such changes result in different values for \( w_0 \) and \( \sigma \), this does not change the general shape (and therefore the behavior) of the force-distance curve. \[3\]

\[3\]In first approximation, an AFM tip above a substrate can be modeled by a sphere above a flat surface.

\[4\]Note that a total of zero force does not mean that the atoms experience no forces, only that the total resulting force is zero.
3. Gold nanoparticle manipulation by AFM

Figure 3.2: A) A schematic representation of a tip with radius \( R \) separated from a flat surface by a distance \( r \). B) The force-distance curve of the model in A). The used parameters are \( w_0 = 3.79 \cdot 10^{-22} \) J, \( \rho_{sp} = \rho_{su} = 6.4 \cdot 10^{28} \) m\(^{-3} \) and \( \sigma = 0.34 \) nm and are taken from [35], \( R = 10 \) nm.

3.2.3 The atomic force microscope

From the previous section it is clear that atomic forces are present, but how can they actually be measured? In other words, how does an atomic force microscope (AFM) operate? Figure 3.3 shows the basic operation of an AFM.

Figure 3.3: A) Schematic image of an AFM setup. B) Detail image of the four-quadrant detector
3.2 The experimental techniques

The part of the AFM that interacts with the surface is the tip. Tips are thin needles made of Si or Si₃N₄ with a length of several tens of micrometers, a full tip cone angle of 30 degrees or less and a radius of curvature of 10 nm or below. The tip is attached to a cantilever that acts as a spring, that, depending on the forces acting on the tip, bends to a certain degree. The spring-constants for such cantilevers lie between 0.01 and 100 N/m. By virtue of Hooke’s law, the amount of deflection of the cantilever is a measure of the forces acting on the tip. AFM probes are commercially available in various dimensions, with many different spring-constants, radii of curvature, (metal) coatings on the probe, etc., leading to many different applications.

To read out this deflection, a laser is reflected of the back-side of the cantilever and falls onto a four-quadrant photo detector, see figure 3.3.B. By measuring the difference in intensity between the signals $S$ coming from the top and bottom quadrants of the detector, i.e. $([S_A + S_B] - [S_C + S_D])$, the deflection of the cantilever can be measured and it is used to measure the height (change) of the substrate. Similarly, the torsion of the cantilever can be determined from the difference between the intensity of the signals coming from the left- and righthand quadrants of the detector: $([S_A + S_C] - [S_B + S_D])$ and this signal is used to measure the friction force a tip experiences as it is scanned over the surface of the substrate. These signals are then fed into a computer for storage.

To actually make an image of a substrate, the AFM probe is moved parallel to the surface, by the movement of the piezo tube to which it is attached. This is done line by line: the AFM moves the tip in one direction, the fast-scan direction, and back again to scan a single line. Then the tube moves a small distance in the perpendicular direction, the slow-scan direction, and another line is recorded. To make certain that during scanning the AFM accurately follows the contours of the substrate, there is a feedback loop from the computer to the piezo tube to control the height of the probe. Depending on the operation mode of the AFM, contact mode or tapping mode, the feedback-loop operates differently.

For small distances, the force between tip and surface are positive, figure 3.2, and the AFM is said to operate in contact mode. As the tip is scanned across the surface, the corrugation of the surface causes the cantilever to bend. As a result the laser spot on the photo-detector moves up and down as well. The feedback-loop tries to keep the laser spot in the center of the detector, by moving the probe up and down in the vertical direction.

When the tip and surface are separated by a larger distance, the forces become negative and the tip is operated in either non-contact mode or in tapping mode. For both modes the tip is oscillated with a certain amplitude by a piezo-electronic resonator at the resonance frequency of the AFM probe. But where the tip still comes in contact with the substrate in tapping mode, it does not do so in non-contact mode. With tapping mode, the amplitude of the oscillation is set to a predetermined value. Depending of the distance between surface and tip, this amplitude is increased or decreased. The feedback-loop tries to keep this amplitude at its setpoint value by approaching or retracting the tip to or from the surface.

Though not used in this work, for non-contact mode the feedback-loop tries to keep the resonance frequency of the tip constant.
3. Gold nanoparticle manipulation by AFM

3.2.4 AFM particle manipulation

Besides imaging of the substrate, AFM can be used to manipulate the substrate. In this particular case CGNP are moved across the surface by pushing them with an AFM tip. Figure 3.4 gives a qualitative picture of what happens during an attempt to move a particle. The free oscillation amplitude $A_{\text{free}}$ is set to a specific (but for this discussion arbitrary) value. If the feedback loop is on, then by setting the (oscillation) amplitude-setpoint $A_{\text{set}}$ to a value lower than $A_{\text{free}}$, the tip will move closer to the surface, causing the surface forces acting on the tip to decrease the oscillation amplitude until $A_{\text{set}}$ is reached. The (zero-amplitude) tip-sample separation at which this happens is called $S_0$. The exact value of $S_0$ is not known, but is dependent on $A_{\text{free}}$ and $A_{\text{set}}$. By turning the feedback loop off, $S_0$ becomes a fixed distance. If the tip is now scanned over the surface, then as long as the (zero-amplitude) tip-sample separation remains constant (and equal to $S_0$), the oscillation amplitude will remain the same as well. However, as the tip approaches a particle, the tip-sample separation becomes smaller, causing the oscillation amplitude to decrease. When this oscillation dies out (the tip hits the particle), the cantilever starts to deflect. Deflection of the cantilever indicates that the tip applies a force to the particle, and the bigger the deflection, the larger the applied force will be. If this force becomes big enough, i.e, bigger than the forces holding the particle to the surface, then the particle will be moved [19, 20, 38].

3.2.5 Seeding solution

A seeding solution, also called an enhancement solution, is used to add extra metal to a metallic surface. For example, in literature, colloidal gold nanoparticles are used as probes to measure the presence of antibodies in biological tissue, but since such colloids are too small to be observed with light microscopes, they are made bigger by applying an enhancement solution containing silver ions to them [39, 40]. Similarly, scanning electron microscope (SEM) studies of organic tissue treated with gold colloids benefit from such enhancement as well [41].

The basic process that makes silver enhancement possible is the reduction of silver ions ($Ag^+$) to atomic silver ($Ag$), figure 3.5A. To provide these ions, a silver salt, either silver nitrate ($AgNO_3$) or silver lactate ($AgCH_3CH(OH)COO$), is dissolved in a citrate buffer solution.

To reduce the silver ions to silver a reductant is needed. The material of choice is hydroquinone ($C_6H_4(OH)_2$). Hydroquinone has an acid-base-equilibrium, figure 3.5B, and it is the di-anion that is formed by de-protonation of two $H^+$ ions that is the actual reducing agent. Upon reduction of the silver, the di-anion is oxidized to quinone ($C_6H_4O_2$), figure 3.5. In order for di-anion to remain available during the enhancement reaction, a buffer-solution is added to the hydroquinone di-anion mixture that keeps the pH of the solution constant.

By mixing the solution containing the silver ions with the solution containing the di-anions a redox reaction is started, figure 3.5 that results in the formation of atomic

\footnote{How $A_{\text{free}}$ is modified into $A_{\text{set}}$ not only depends on $S_0$, but also on the shapes and materials from which tip and sample are made. But since these two factors will not change significantly during the experiment they can be considered constant and will be left out of the rest of the discussion.}
3.2 The experimental techniques

Figure 3.4: The principle of moving a particle with tapping-mode AFM. As the tip approaches the particle the oscillation amplitude decreases and eventually the cantilever starts to deflect. The deflection indicates that force is being applied to the particle. If the deflection is large enough, the applied forces will be greater than the forces with which the particle clings the surface and the particle will be displaced. In this image $A_{\text{set}}$ is the amplitude-setpoint, $S_0$ the (zero-amplitude) tip-substrate separation, $R_p$ the radius of the particle and $D_{\text{max}}$ the maximum deflection the cantilever can experience in this situation.

silver [42]. This silver precipitates on the metal surface present, i.e. the gold colloids, causing the particles to grow and interconnect with one another.

3.2.6 Microwave irradiation

Microwave radiation is electromagnetic radiation with wavelengths between 1 mm and 1 m. The corresponding frequencies are 300 GHz and 300 MHz respectively. For heat to be generated in a material, microwaves need to enter the material and transfer their energy to it. This energy transfer takes place at the atomic and molecular level and the dielectric properties of the material ultimately determine the effect of the electromagnetic field on the material, the so-called dielectric response. There are many properties that contribute to the dielectric response. Among them are, electronic polarization, atomic polarization, ionic conduction, dipole polarization and Maxwell-Wagner polarization mechanisms. For microwave frequencies, dipole polarization is considered to be the most important mechanism for energy transfer [43,44].

Within materials there exists bound charge and free charge and the motion of the bound charge (due to the applied electromagnetic field) results in polarization. Polarization of electric charge where either the translational and rotational motion of the material is restricted results in a lag between the electromagnetic field and the polarization. This time lag, known as the relaxation time, is due to the dissipation of energy as heat within the material. Microwave heating is the result of this dielectric
3. Gold nanoparticle manipulation by AFM

Figure 3.5: Schematic representation of the chemical reactions that take place during the silver enhancement procedure [42]. A) Reduction of silver ions (Ag⁺) to atomic silver (Ag). B) The acid-base-equilibrium between hydroquinone (C₆H₄(OH)₂) and the di-anion. C) Oxidation of the di-anion to quinone (C₆H₄O₂). D) The total reaction.

Using the Poynting Vector Theorem [45], the power absorbed per unit volume $P$ can be written as [46]:

$$ P = 2\pi f \epsilon_0 \epsilon'' E^2, \quad (3.2.7) $$

where $f$ is the frequency of the applied microwave radiation, $\epsilon_0$ the electrical permittivity of vacuum, $\epsilon''$ the dimensionless dielectric loss factor and $E$ the root-mean-square amplitude of the internal electric field.

As energy is absorbed within the material, the electric field decreases as a function of the distance from the surface of the material. Therefore equation [3.2.7] is only valid for very thin materials. The penetration depth $d$ is defined as the distance from the sample surface where the absorbed power is only a factor $1/e$ of the power absorbed at the surface. The penetration depth is given by [46]:

$$ d = \frac{c}{2\pi f \epsilon''}, \quad (3.2.8) $$

with $c$ being the speed of light.

Only when the dimensions of the irradiated material are of the order of the penetration depth or smaller, is heating with microwave radiation effective. For gold the
3.3 The setup

The penetration depth of microwave radiation of 2.45 GHz ranges from 1.3 to 1.6 µm [30]. Since the used gold colloids are 10 or 15 nm in diameter, microwave heating is feasible.

3.3 The setup

The substrate, on which these devices are build, is always the same; Si with a 1 µm thick thermally grown SiO$_2$ layer, cleaned by emersion in several solutions, i.e. H$_2$SO$_4$, demineralized water, acetone and methanol respectively. The cleaning is performed in an ultrasonic bath and afterwards the sample is dried with N$_2$ gas.

To create the lithographic structures, a 80 nm thick layer of PMMA, 950 PMMA A2 from Microchem, U.S.A., is spin-coated from an anisole solution onto the substrate at 2500 rpm for 30 seconds. The substrate is baked at 175 °C for 1 h, and then a 12.5 nm gold layer is thermally evaporated onto the substrate to prevent charging. Next, the sample is placed in an electron beam (E-beam) lithography machine, a Raith150 with a LEO 1520 SEM with a Gemini column and a heated field emission source from Raith, Germany, and the structures are written with a 20 keV beam. After exposure, the thin gold layer is removed by placing the sample in a solution of KI$_2$H$_2$O = 4:1:40 (mass-ratios) for 6 seconds and subsequently placing it in a stopper and developer solutions, a 1:3 mixture of methyl isobutyl keton (MIBK) and isopropanol (IPA) and pure IPA respectively, for 30 seconds each. Then electron beam evaporation is used to deposit 7.5 nm of titanium on the substrate, followed by 15 nm of gold. Finally, placing the sample in acetone and using ultrasonic cleaning for 45 to 60 seconds is used perform lift-off of the PMMA.

For gold colloids to adhere to the substrate, a monolayer of [3-(2-aminoethylamino)-propyl]trimethoxysilane, or AEAPTS for short (Z-6020 from Dow Corning, U.S.A.), is applied to the surface, by placing the samples in a 100 times diluted aqueous solution of AEAPTS, followed by baking of the substrate at 110°C for 30 to 60 minutes. Unconjugated colloidal gold nanoparticles, 10 and 15 nm in diameter, were obtained from Ted Pella Inc, U.S.A. and administered to the sample by placing it in the pure CGNP solution for 1 minute and rinsing with demineralized water afterwards.

To image the substrate a Dimension 3100, Veeco Instruments Inc., U.S.A., Scanning Probe Microscope, with a NanoScope IIIa controller, is used together with NSC35 AFM cantilevers (with resonance frequencies between 240 and 405 kHz and force constants between 6.5 and 27.5 N/m) and Hi'RES DP18 cantilevers (resonance frequencies between 60 and 90 kHz and a force constant of 2.0 to 5.5 N/m), both from MikroMasch, Estonia. Moving the gold particles across the substrate was done with the abovementioned AFM, NSC35 cantilevers and a home-build script for the Nanoscope control software.

After placing the colloids in the desired configuration, a silver seeding solution ("Silver Enhancing Kit" from British Biocell Inc., United Kingdom) is used to grow and connect the individual CGNP in the case where their shells are not to be removed. This is done by placing a droplet of enhancement solution on the sample for 1 minute and rinsing with demineralized water afterwards.

Microwave treatment was performed on a Emrys Liberator single mode microwave from Biotage, Sweden, by applying 2.45 GHz radiation to the sample with intensities
3. Gold nanoparticle manipulation by AFM

between 150 and 300 W.

XPS analysis of the sample is done on a small spot ESCA XPS machine of Vacuum
Generators, United Kingdom.

To measure the conductance of the samples, either a source measure unit, a Keithley 2400
from Keithley, U.S.A. or a HP 6625A System DC power supply from Hewlett Packard, U.S.A. was used.

3.4 Results and discussion

3.4.1 Creation of the lithographic contacts

The first step in placing colloids between lithographic contacts is the creation of these
contacts. Using the method described in section 3.3, lithographic structures were
successfully fabricated, as can be seen from figure 3.6.

3.4.2 Manipulation of CGNP by AFM

Having successfully created the contacts, the next step in creating a metallic wire,
build up out of CGNP, is applying these colloids to the substrate, as is explained in
section 3.3. Figure 3.7 shows a lithographic contact with colloids added to it.

The subsequent step consists of aligning these particles between two lithographic
contacts. To move a particle, first an AFM image is made in tapping mode to select
a particle. Then the tip is placed behind the particle, and subsequently the feedback
loop controlling the height of the AFM is turned off, the particle is moved in the
desired direction and finally the feedback loop is turned on again. Figure 3.8 shows
several steps of the successful alignment process of 4 CGNP between two lithographic
contacts.

After alignment of the particles into a wire, a voltage is applied to this wire and the
resulting current is measured. However, as the bias was increased on the wire shown
in figure 3.9A, the level of the current did not rise above $10^{-11}$ A, the threshold level
of the used Keithley 2400 source measure unit, and as a result the actual current
could not be detected. After the conduction measurements on such colloids, AFM
was used to observe what had happened to the CGNPs between the contacts. All
the gold colloids were completely removed from the gap, resulting in the destruction
of the contact 3.9B. A possible reason why the particles were removed is that the
application of the bias caused the particles to charge and repel one another.

To prevent the destruction of wires made up out of colloids during application
of the bias voltage, the whole substrate is treated with a silver seeding solution, to
grow and connect the individual particles to form a fully connected contact, after
alignment of the particles with the AFM. With the seeding solution applied, wires
were bonded to the sample and a voltage ramp was applied to the contact in figure 3.8
to measure its electrical conductivity. By ramping the voltage to 1 Volt, a current was
measured, as is shown in figure 3.10A. The figure shows several individual I-V traces,
corresponding to several separate voltage ramps. As can be seen, the current drops
slightly for subsequent voltage ramps. This is indicative for (the onset of) electron
migration. That is, when metal atoms are displaced either by electron wind diffusion
3.4 Results and discussion

Figure 3.6: A SEM image showing a typical example of lithographically defined contact electrodes. The black areas correspond to the SiO$_2$ background, while the grey areas are the 22.5 nm high metallic contacts. The gap between the two electrodes is 50 nm.

or electron scattering at impurity sites in the nanowire [47, 48]. For a more detailed description of electron migration the reader is referred to section 4.2.2. By ramping the bias to higher voltages, the effect of electron migration increases as well and eventually it will result in the destruction of the wire, as can be seen figure 3.10.B.

There are two ways in which electrons can now flow through the wire. Either there is conduction from contact to contact through the silver enhancement and/or the electrons tunnel from gold core to gold core. To determine whether or not the latter is true, the Simmons model [49] was used. With the Simmons model the
3. Gold nanoparticle manipulation by AFM

Figure 3.7: An AFM image showing a typical example of a lithographic contact with colloids added to it. The dark grey areas correspond to the SiO$_2$ background, while the light grey areas are the metallic contacts. The (almost) white objects on top of the contacts, indicated by the black arrows, are CGNP. There are also CGNP present between the contacts, as indicated by the white arrows.

Tunneling current flowing through a potential barrier of height $\varphi$ and width $L$ can be determined as function of the voltage. (See section 4.2.3 for details on the Simmons model.) Using AFM it was confirmed that the CGNP were touching one another. In that case, the distance between two gold cores is equal to twice the thickness of the citrate shell around these cores. The minimum shell thickness is estimated to be 0.3 nm$^7$, giving a total gap of 0.6 nm. Since there are 4 CGNP in the wire, there are

$^7$To obtain this minimum thickness it is assumed that a citrate molecule lies flat on a gold core.
3.4 Results and discussion

Figure 3.8: Six AFM images showing several steps in the alignment of 4 CGNP between two lithographic structures. The white arrows indicate which CGNP has been moved. Note that image A is the same image as the one shown in figure 3.7. Also note that images A to E were recorded with NSC35 cantilevers (with a radius of curvature of 10 nm), whereas image F was made with the much sharper Hi’RES DP 18 cantilever (with a radius of curvature of 1 nm).

3 barriers of 0.6 nm thick that will dominate the resistance of the wire. As a result, the effective bias that is applied over a single barrier is only 1/3 of the total applied bias. In a vacuum one would expect the height of the barrier to be equal to the work function of the gold, i.e. 5.4 eV [50], however, the presence of organic molecules (the citrate) on the gold will result in a lowering of the work function of the gold by about 1.6 eV [51] to 3.8 eV. Filling in these parameters and assuming that the CGNP have a circular contact area with a radius of 5 nm, which is used to estimate the cross section of the wire, the current can be plotted as a function of voltage, as has been done in figure 3.10 A.

Clearly, the curve calculated with the Simmons model displays a current that is far lower than the experimentally determined currents and the Simmons model cannot be used to explain these results. Therefore it is concluded that (the majority of) the current flows through the silver applied by the enhancement step.

There will also be two barriers of 0.3 nm thick, but since the tunneling current depends exponentially on the distance of the gap, the resistances of these barriers will be 2 to 3 orders of magnitude smaller than those of the 0.6 nm thick barriers.
3. Gold nanoparticle manipulation by AFM

![Figure 3.9: Two AFM images of a lithographically defined contacts (the white areas), where 6 CGNP have been pushed into a wire configuration (the grey line) between the contacts with an AFM tip. A) and B) show the contact before and after applying a voltage (of up to 1 V) to the wire respectively. After application of the bias the colloids have been removed and the wire is destroyed.](image)

While the silver enhancement is effective in creating a conducting wire, it would be desirable if one could omit both the silver enhancement and the citrate shells around the CGNPs. In this way the electrons would only be able to flow through the gold itself, and provided that the formed channel is wide enough, the conduction behavior should be Ohmic with a resistance in the order of a hundred Ohms [52, 53] and not 1 MΩ as was measured for this wire.

3.4.3 Microwave irradiation

Another sample, containing only CGNP, was placed in a microwave to see if electromagnetic radiation could be used to remove the organic shell of these CGNP. By irradiating the sample, it was heated up to an average temperature of 200 °C for 10 minutes and then rapidly cooled down to room temperature by cooling with pressurized nitrogen gas. To confirm the removal of the citrate shell, XPS measurements were performed on this sample after the microwave treatment. A reference sample that was not irradiated was probed by XPS as well (figure 3.11).

From the XPS data it can be seen that the majority of carbon has been removed from the sample after irradiation, a good indication that the citrate shell around the gold cores, consisting mostly of carbon, has been removed. Further evidence for this statement is the shift of the 4f gold peaks (inset figure 3.11.A) from 84.5 to 84.0 eV and from 88.2 to 87.8 eV, respectively, after the microwave treatment, since this is a shift towards their respective values for pure gold, namely 84.0 and 87.7 eV [54].

Besides a decrease in the carbon peak, the disappearance of the nitrogen peak at
3.4 Results and discussion

![Figure 3.10: I(V) characteristics of the contact shown in figure 3.8. Three individual voltage ramps to 1 V are displayed in A). The numbers 1, 2 and 3 on the graphs indicate the 1st, 2nd and 3rd times that a voltage is applied to the wire. Each graph shows non-linear conduction behaviour, but with a slightly lower conduction G for each subsequent voltage ramp. This is indicative for electron migration and eventually results in destruction of the wire, as is shown by the two consecutive voltage ramps to 5 V, indicated by the numbers 4 and 5 respectively, in B). The dashed line in A) corresponds to the Simmons model with the following parameters: \( \varphi = 3.8 \) eV, \( L = 0.6 \) nm and a circular cross section with a radius of 5 nm.](image)

401 eV can be observed after microwave irradiation, indicating the breakdown of the AEAPTS layer. This was confirmed by AFM analysis of the sample after microwave treatment, which shows gaps in the AEAPTS, figures 3.11.C. Furthermore, from this image it is clear the gold cores of the CGNP have survived the treatment intact.

To test whether or not CGNP, aligned in a chain/wire configuration, do not move across the substrate under the influence of the microwave treatment and thereby destroy this wire, a line of CGNP was created on another sample. This sample contained lithographic marker structures, for finding the line of CGNP back after microwave irradiation, but was otherwise identical to the previous samples; i.e. Si, with a SiO\(_2\) top layer, an AEAPTS monolayer and CGNP. Figure 3.12 shows the line lying next to a marker before and after the microwave treatment.

By comparing figures 3.12.A and B, it can be seen that, as long as individual CGNP are not physically touching, they remain on the same spot despite of the applied microwave radiation. A more striking feature is what happens when CGNP are touching; in this case they still do not move across the substrate but they do coalesce into larger particles. This indicates, that the local temperature at the CGNP rises above the melting point of gold\(^9\) and that the CGNP appear to form well-(inter)connected metallic wires.

\(^9\)The melting temperature of bulk gold is 1064.18 °C [50], but when the dimensions of the gold are reduced to a few nanometers, the melting temperature can become as low as 120 °C [55].
3. Gold nanoparticle manipulation by AFM

**Figure 3.11:** A) XPS data of two samples covered with CGNP one after microwave treatment and one without irradiation, with in the inset a zoom in on the gold peaks around 85 eV. The letters in the graph indicate the elements that are detected and the symbols between brackets indicate the specific atomic orbital of the element that is observed. B) and C) AFM phase images of the same samples as in A), without and with microwave treatment respectively.
3.4 Results and discussion

**Figure 3.12:** Four AFM height images of a line of CGNP connected to a lithographic marker. A) The line before microwave irradiation. C) A zoom in of A). B) After microwave irradiation. D) A zoom in of B). The black horizontal lines in A) and B) show where height profiles of the lithographic structure are taken. E) and F) show the respective height profiles of A) and B), or in other words, they show the (peak to peak) surface roughness of the lithographic structure before and after the microwave treatment.
3. Gold nanoparticle manipulation by AFM

Not only the CGNP are influenced by the microwave radiation, but the lithographic contacts as well; the (peak to peak) surface roughness of the structure has increased from 1-2 nm to 6-10 nm after irradiation, as can be seen in the line-traces of the AFM images, figure 3.12.E and F.

In order to perform conduction measurements on a microwave treated wire, another such wire was created between two lithographic contacts and microwave radiation was applied to it. After this treatment, a wire was created that stretched from contact to contact, figure 3.13.

![Figure 3.13: A) CGNP moved between two lithographic contacts with an AFM tip, before microwave treatment. B) Same as A), but after microwave radiation.](image)

Subsequently, the resistance of this wire was determined. Voltages up to 100 mV were applied and for this bias range the current did not rise above the detection threshold of 10 µA of the current meter, indicating that the resistance of the wire is 10 kΩ or higher. Since 18 CGNP of 10 nm in diameter were placed in the gap and the gap has a length of 60 nm, it can be ruled out that not enough particles have been placed in the gap to fully connect the two lithographic structures. Figure 3.13.B shows an image where a wire of gold particles seems to fully bridge the gap between the two contacts, but due to the convolution effect [56] in the imaging, caused by the non-zero dimensions of the (apex of the) AFM tip, gaps of a few nanometers in the wire can be easily masked. The convolution effect also prevents the determination of the exact shape of the colloid aggregates after microwave irradiation. In other words, how colloids will coalesce during the microwave treatment can not be accurately determined or controlled. Therefore, the method of melting and coalescing colloids by microwave radiation cannot be used to reliably create metal wires with nanometer accuracy.

10By using the Simmons model [49], see section 4.2.3 for more details on this model, it can be calculated that the gap between two gold electrodes, which has a resistance of 10 kΩ or more, has a length of at least 0.6 nm. This is a distance that can easily be masked by the convolution effect the AFM tip has on the imaging of the substrate.
3.5 Conclusions

In this chapter, the results of the AFM manipulation of CGNP with an AFM tip, as well as the effect of microwave irradiation on such colloids have been reported.

By using an AFM, colloids could be pushed into a wire configuration between two lithographically defined contacts. Applying a voltage to this wire resulted in the destruction of the wire without a successful measurement of the resulting current, indicating that the organic shell of citrate around the particles is insulating. By applying a silver seeding solution on a second chain of CGNP, a current could be measured. By modeling this current with the Simmons model, it was determined that the current flowed through the silver and that tunneling through the gold colloids alone is insufficient to explain the observed results.

To remove the insulating shell and thereby create metallic, well-conducting wires, the gold colloids were irradiated with microwave radiation. Not only did the microwave radiation remove the citrate, but it also caused the CGNP to melt and, provided that two or more colloids touched one another, to coalesce. However, coalescence of particles could not be controlled on the nanometer scale and, as a result, microwave irradiation could not be used to reliably and accurately create metallic wires with nanometer precision.

To be able to measure the conductance of individual molecules, a more accurate and reliable way of creating contacts with nanometer-sized gaps is needed. In the next chapter one such way, namely electromigration of thin metallic wires, is explored.

Bibliography


3. Gold nanoparticle manipulation by AFM


3.5 Bibliography


3. Gold nanoparticle manipulation by AFM


[34] D. Sarid, Scanning force microscopy with applications to electric, magnetic and atomic forces, Oxford University Press (1994).


3.5 Bibliography


Chapter 4

Electromigration of lithographic contacts

In this chapter, gaps, of a few nanometers in width, are created in lithographically defined metallic wires by applying a high enough voltage to these wires to reach current densities for which electromigration can take place. Subsequently these gaps are used to try to determine the conductance properties of individual molecules. It is found that the total resistance of the wire before electromigration is crucial for the formation of suited gaps: If, on one hand, the resistance is too small, the size-distribution of the produced gaps is too big for the gaps to be of use. On the other hand, if the resistance is too high, the formed gaps are too big to determine any tunneling current at all. Migration took place at a critical current density, irrespective of the total resistance of the circuit, and the voltage at which migration occurred increased linearly with the resistance of the wire. After migration and application of the molecules no conductance features could be observed that indicated the presence of a molecule in the gap.

4.1 Introduction

To connect individual molecules to macroscopic contacts, conductors are needed that have a separation distance of the order of the molecules to be probed, i.e. 1 to 2 nm. As can be seen in the previous chapter, it is difficult to create such gaps by first creating a structure that has a bigger gap, say 50 nm wide, and then subsequently reducing the size of this gap by placing gold colloids in it. In this chapter the reverse is attempted. Here a fully connected (and conducting) wire of nanometer-sized dimensions is created lithographically and by applying a high enough current(density) to it, a gap of a few nanometers is controllably created in the wire. This process, where passing a high enough current through a metal wire causes it to brake, is called electromigration [1] and it is the main failure mechanisms in microelectronic circuitry [2]. As will become clear in this chapter, by controlling the voltage at which migration occurs, this destructive effect can be used beneficially.
4. Electromigration of lithographic contacts

Durkan et al. systematically studied the failure of thin gold wires by electromigration [3–5]. They looked at how electron migration depends on the length and width of the wire as well on the oxide thickness of the silicon oxide underneath the wire. They found that the shorter the wire and the thinner the oxide, the higher the current density can be before migration starts to occur.

While Durkan et al. performed their research to be able to minimize electron migration in electronic contacts, at the same time others tried to use this mechanism to actually create gaps in small metallic wires. McEuen et al. were the first to use electromigration to controllably fabricate gaps with dimensions of approximately one nanometer in gold wires and to use such wires to measure the conductance of nanometer sized objects, i.e. colloidal cadmium selenide nanocrystals in their case [6].

Since McEuen et al. published their work, many others have used this technique to measure the conductance properties of both colloidal nanoparticles [7, 8] and individual molecules [9–22]. Interpretation of such electromigrated contacts has to be performed carefully. Not only can electromigrated junctions have resistances that can vary 6 to 8 orders of magnitude from device to device [6,23], but “clean” contacts, i.e. contacts to which no molecules have been added, can display various kinds of conductance behavior [24]. By adding a series resistor to the circuit [24,25] and/or using a feedback loop to control the migration process [26–28], structures can be created that have a narrower distribution of resistance values. Even with these precautions, the chance of creating a gap that is suited for the performance of conduction experiments on single molecules is far from 100% [24]. Van der Zant et al. show that, as a byproduct of the electromigration process, small metal islands can be formed in the gap created by electromigration and that these islands can give rise to Coulomb blockade phenomena just as easily as single molecules can [15,20,21]. Therefore, the presence of Coulomb blockade effects in conduction experiments performed on such electromigrated wires is not enough to determine whether or not a (single) molecule is present in the gap and other features, like molecular vibrations [19,22], will have to be present in the conductance spectra to prove that it are the conduction properties of a molecule that are being probed.

In this work nanometer sized gaps are also created by electromigrating lithographically defined metal wires. To keep the complexity of the fabrication process to a minimum, heavily doped silicon has been used in this work to act as a gate electrode, rather than a metal electrode [21,22], which would require an additional lithography step. Similarly, no active feedback was used during migration, only a series resistor was used to control the migration process.

After migration, molecules are applied to the wire to determine their electrical conduction properties. The used molecule, i.e. OPV-5 (see figure 4.1), is an oligophenylenevinylene derivative in which five benzene rings are connected through four double bonds. OPV-5 is chosen because the molecule has a fully conjugated carbon backbone, has a total length of 3.2 nm, which makes it suited for bridging a gap with a width of 2 nm and is thiol-terminated on both sides to allow chemical bonding to the gold contacts.

1 In other words, these junctions can have gap sizes that vary several nanometers from device to device.
2 An oxide of several tens of nanometers thick is used to prevent short circuits between the contacts.
4.2 The measurement techniques

4.2.1 Bilayer resist lithography and shadow-evaporation

In section 3.2.1 (electron beam) lithography in general is explained and the reader is referred to this section for a more detailed description of lithography itself. In this section the two additional steps are described that are required to fabricate the wires that will be used for electromigration, namely shadow-evaporation and the use of bilayer resists.

The atoms of the metal in the region of the wire that is to be migrated, need to be able to move across the surface of the substrate and therefore the bonding of these atoms to the substrate must be relatively weak. On the other hand, the rest of the wire needs to be robust and stable, thereby favoring a good adhesion of the metals to the substrate in these areas. To be able to fulfill both requirements, a method is needed that allows for selective evaporation of metals on the surface. The combination of bilayer resists and shadow-evaporation provides the required selectivity.

With bilayer resists two layers of resist are spincoated on a substrate, figure 4.2 A. Since the penetration depth of electrons in the resist that comprises the bottom layer is larger than the penetration dept of electrons in the resist that comprises the top layer, the area that is exposed is larger in the bottom layer compared to that of the top layer. As a result, (after exposure) a “bridge” of the top-layer resist is suspended over the substrate without any of the bottom-layer resist being present, figure 4.2 B. By evaporating the metals under different angles onto the substrate, this bridge creates a shadow on the substrate that allows for location-selective evaporation of the metals, figure 4.2 C. In the last step lift-off is applied and only the finished wire remains, figure 4.2 D. At this point, the description of bilayer resist lithography and shadow-evaporation is still general and the reader is referred to section 4.3.1 for the exact experimental details.
4. Electromigration of lithographic contacts

4.2.2 Electromigration

Electromigration is described as a mass flux under the influence of a high current density. Basically, there are two effects that contribute to electromigration, namely the “electron wind force” and the “direct force”. With the electron wind force being the momentum transfer to the moving atom due to its collision with the charge carriers and the direct force is taken to be the force exerted by the electric field on a (charged) impurity in the metal [2].

However, a full description of the electromigration effect is far from trivial. In order to include all fluxes and forces involved, one needs to look at the thermodynamics of irreversible processes [29]. In this particular case, three different fluxes $J$ are relevant: the electron particle flux $J_e$, the flux of metal atoms $J_m$ and the energy flux $J_u$. These fluxes are induced by forces (or potential gradients) $X_j$. The forces for the particles can be written as $X_j = -\nabla \mu_{ec}$. Here $\mu_{ec} = \mu + Z e \varphi$, with $\mu$, $Z$ and $\varphi$ being the chemical potential, the particle charge (-1 for electrons) and the electrostatic potential respectively. The other force is due to the temperature gradient; $X_u = \nabla (1/T)$, where $T$ denotes the temperature. Using the thermodynamics of irreversible processes [29], the following set of equations can be written down for the fluxes $J$:

Figure 4.2: A schematic representation of the formation of wires for electromigration experiments, by combination of shadow evaporation and the use of bilayer resists. A) A side view of two layers of electron sensitive resist that are spincoated on the substrate. B) After exposure a “bridge” of top-layer resist is suspended over the substrate. C) Evaporation of the metals under different angles. D) The resulting wire after lift-off. The numbers on the layers indicate the order in which the metals are evaporated onto the substrate. Note that the dimensions are not drawn to scale.
4.2 The measurement techniques

\[ J_m = -L_{m,m} \nabla \left( \frac{\mu_{mc}}{T} \right) - L_{m,e} \nabla \left( \frac{\mu_{ec}}{T} \right) - L_{m,u} \left( \frac{\nabla T}{T^2} \right), \quad (4.2.1) \]

\[ J_e = -L_{e,m} \nabla \left( \frac{\mu_{mc}}{T} \right) - L_{e,e} \nabla \left( \frac{\mu_{ec}}{T} \right) - L_{e,u} \left( \frac{\nabla T}{T^2} \right), \quad (4.2.2) \]

\[ J_u = -L_{u,m} \nabla \left( \frac{\mu_{mc}}{T} \right) - L_{u,e} \nabla \left( \frac{\mu_{ec}}{T} \right) - L_{u,u} \left( \frac{\nabla T}{T^2} \right), \quad (4.2.3) \]

where the phenomenological constants \( L_{i,j} \) relate all fluxes to all the forces, while obeying the Onsager relations \( L_{i,j} = L_{j,i} \). Equations 4.2.1 to 4.2.3 provide a general description of the system and include electromigration as well as thermoelectric effects and thermodiffusion.

Solving this set of equations is far from trivial and a number of assumptions are made to derive a simplified relation for the mass flux. First, for materials with a high conductivity, the \( \nabla \mu^e \) term can be ignored. Second, from Trouwborst et al. [25] it is known that the (local) temperature at which electromigration starts is independent of the temperature of the environment. This temperature independence indicates, that gap formation is due to a electromigration (at a critical temperature) and not to thermodiffusion via a temperature gradient. As a result thermodiffusion, i.e. the \( \nabla T \) term, can be ignored. Finally, it is noted that in practice all charge current is due to electron flux, resulting in \(-\nabla \phi = \rho j\), where \( \rho \) is the resistivity and \( j \) the current density. Using these assumptions, equation 4.2.1 transforms into:

\[ J_m = -L_{m,m}^* (\nabla \mu^m - Z^* e \rho j), \quad (4.2.4) \]

where \( L_{m,m}^* \) is defined as \( L_{m,m} / T \). An effective charge \( Z^* \) is introduced with \( Z^* = Z - L_{m,e}^* / L_{m,m}^* \). In other words, the atoms behave as if they have an effective charge \( Z^* \) and this effective charge is due to the momentum transfer from the electrons to the atoms. In general \( L_{m,e}^* / L_{m,m}^* \gg Z \), resulting in a net force acting on the gold atoms, that is in the same direction as the electron flow.

By noting that \( \nabla \mu^m = \Omega \partial \sigma / \partial x \) is the driving force due to stress \( \sigma \) [30], with \( \Omega \) being the atomic volume, equation 4.2.4 can be written as:

\[ J_m = -L_{m,m}^* (\Omega \Delta \sigma / L - Z^* e \rho j), \quad (4.2.5) \]

where \( \Delta \sigma \) is the stress build up over length \( L \). As long as \( \Delta \sigma < \Delta \sigma_{max} \) the electromigration force is balanced by the stress gradient and the atom flux is zero [30]. This defines a critical current density \( j_{min} \) below which migration takes place; \( j_{min} = \Omega \Delta \sigma_{max} / Z^* e \rho L \). From [31] an expression can be derived for the phenomenological constant \( L_{m,m}^* \):

\[ L_{m,m}^* = \frac{cD}{k_b T}, \quad (4.2.6) \]

where \( c, D \) and \( T \) are the concentration, diffusion constant and temperature of the material respectively and \( k_b \) is the Boltzmann constant.

\[^3\text{Thermodiffusion refers to the mass flux due to temperature gradients (which, in turn, can be due to Joule heating).}\]
4. Electromigration of lithographic contacts

By filling in this expression for \( L_{\text{m},m}^* \) into equation 4.2.5, the mass flux can be written as:

\[
J_m = A(j - j_{\text{min}}),
\]

(4.2.7)

where \( A \equiv cD^*e\rho/kT \). As shown above, a minimum current density is required for electromigration to occur. Trouwborst et al. show that the minimum current density needed to migrate a thin gold wire is \( 1 \cdot 10^{12} \text{ A/m}^2 \) [25]. As will be seen later, such values are easily reached experimentally.

4.2.3 The Simmons model

Once a gap has been formed in the metallic wire by electromigration, a bias can be applied over the migrated contacts to measure the tunnel current. Using the Simmons model [32, 33], this tunneling current can be used to estimate the distance \( L \) between the two contacts.

For small biases, the tunnel current \( I \) between two similar electrodes, separated by a thin insulating film, with a rectangular potential barrier of height \( \varphi \), is given by [32]:

\[
I = \frac{e^2AV_{sd}\sqrt{2m\varphi}}{4\pi^2\hbar^2L} \exp(-2L\sqrt{2m\varphi}/\hbar),
\]

(4.2.8)

where \( e, A, V_{sd} \) and \( m \) are the electron charge, the wire cross-section, the applied source-drain bias and the electron mass respectively.

4.3 The experimental setup

4.3.1 Sample fabrication

The silicon wafers are purchased from Silicon Quest International, Inc., U.S.A., are boron doped (p-doped), have a resistivity of 0.001 to 0.003 \( \Omega \cdot \text{cm} \) and are covered with a 30 nm layer of thermally grown \( \text{SiO}_2 \). The top- and bottom-resist layers are 950k \( \text{PMMA} \) A4 and \( \text{P(MMA-MAA)} \) EL9 respectively, where \( \text{PMMA} \) stands for poly(methylmethacrylate) and \( \text{P(MMA-MAA)} \) for poly(methylmethacrylate-methacrylic acid). Both resists are purchased from MicroChem Corp., U.S.A.

First the silicon wafer is cleaned by placing it in an oxygen plasma of 300 W, for 10 minutes. Next, \( \text{P(MMA-MAA)} \) is spincoated on top of the silicon substrate at 4000 rpm for 45 seconds from an ethyl lactate solution, resulting in a 300 nm thick layer. Then the sample is baked on a hotplate at 150 °C for 75 seconds. Subsequently the PMMA is spin coated on top of the \( \text{P(MMA-MAA)} \) at 4000 rpm for 45 seconds from an anisole solution, resulting in a 200 nm thick layer. Next, baking on a hotplate is performed at 180 °C for 75 seconds. The sample is exposed on a \( \text{VB6-HR} \) e-beam...
4.3 The experimental setup

lithography machine from Vistec Semiconductor Systems GmbH, Germany, using a 50 kV beam. These exposures were performed at IMEC in Leuven, Belgium. After exposure the samples are developed in a 1:3 mixture of methyl isobutyl ketone and isopropanol for 45 seconds. Immediately afterwards, a stopper solution, i.e pure isopropanol, is applied to the sample for 45 seconds to prevent further exposure of the resist layers. After drying the sample with nitrogen gas, metals are evaporated onto it. First, a 3 nm layer of titanium is evaporated under an angle of 0 degrees with the surface normal. Next, 10.5 nm of gold is evaporated under an angle of +17 degrees with the surface normal, resulting in a 10 nm thick layer. Subsequently another 10.5 nm of gold is evaporated, but now under an angle of -17 degrees with the surface normal. Finally 150 nm of gold is evaporated under an angle of 0 degrees with the surface normal. (Figure 4.2.D gives a graphical representation of how these metals are evaporated: The numbers in this figure represent the order in which the metals are evaporated onto the substrate.) Prior to lift-off, the sample is placed in an atmosphere that is saturated with acetone vapor. The vapor causes the resist layers to swell, resulting in the mechanical disconnection of the metals on top of the resist layers from the metals in the gaps in the resist layers. This rupture of the metal facilitates the lift-off that is performed subsequently by rinsing the sample with acetone. Lastly, the sample is rinsed with isopropanol and dried with nitrogen gas.

Scanning electron microscopy (SEM) was used to check that the structures were formed correctly after lift-off. The SEM that was used is a XL 30 ESEM-FEG from Koninklijke Philips Electronics N.V., the Netherlands.

4.3.2 Electromigration

The sample is placed in a flow cryostat, a OptistatCF-V from Oxford Instruments plc, United Kingdom. and is connected to a semiconductor characterization system, a Keithley 4200 from Keithley, U.S.A. for the electromigration and subsequent electrical analysis. Migration experiments were either carried out at room temperature (and atmospheric pressure) or at 4.2 K. For the low temperature measurements the cryostat is evacuated to a pressure of approximately $10^{-5}$ mBar, the sample is cooled down to 4.2 K. In either case, a voltage is ramped up from zero to a pre-determined value to perform the electromigration. Subsequently, the migrated wire is studied by applying both source-drain ($V_{SD}$) and gate voltages ($V_{G}$) and measuring the source-drain current ($I_{SD} = I$).

4.3.3 OPV-5

The OPV-5 molecules were obtained from Dr. Nicolai Stuhr-Hansen (University of Copenhagen). The molecules were used as received. To apply the molecules to the wires they were dissolved in ethanol at a concentration of 1 mM. A droplet of this solution was placed on top of the substrate carrying the lithographic wires for 12 to 18 hours. To prevent evaporation of the droplet during these hours, the application was performed in an environment that was saturated with ethanol vapor. After application of the molecules the sample was carefully rinsed with pure ethanol and left to dry.
4. Electromigration of lithographic contacts

4.4 Results and discussion

4.4.1 Lithographic structure fabrication

Lithographic structures were created, as described in sections 4.2.1 and 4.3.1. Figure 4.3 shows four SEM images of examples of successfully fabricated structures. In each of the SEM images the black background area is the SiO$_2$ substrate. The dark gray areas correspond to the thin (10 nm) gold layers that were evaporated under an angle of + or -17 degrees with respect to the surface normal. The light gray areas are the thick (150 nm) gold layers that were evaporated straight down. The created wires have a width of approximately 150 nm at the narrowest point and their total length, including the macroscopic contact pads (not shown), is 400 µm.

4.4.2 Electromigration of the contacts

With the successful creation of the lithographic structures it becomes possible to perform the electron migration experiments. Initially, no series resistor was used and the bias was applied over the lithographic structure alone. Figure 4.4 shows a typical migration experiment under these conditions.

At zero Volt, when the bias is increased, the current starts to rise initially. In this regime no migration takes place. In a typical experiment the slope of the $I(V)$ curve starts to becomes smaller at 230 ± 20 mV, indicating the onset of migration. When the voltage is increased only slightly further the current reaches a maximum ($22 ± 5$ mA at 240 ± 20 mV) and immediately afterwards (at 260 ± 25 mV) drops sharply. The latter indicates the major electromigration event. However, as can be seen from figure 4.4, the wire is not migrated completely, i.e. no complete gap is created in the wire, since the current does not drop to zero, but to a value of about 3.5 mA. Only when the voltage is raised to 600 mV does the current drop further and even then it does not drop all the way to zero.

The inset of figure 4.4 shows an electrical measurement of a wire after migration, the grey line, together with a fit from the Simmons model, the black line. The parameters used for the Simmons model are $L = 1.1$ nm, a cross section of $1020 \text{ nm}^2$ and $\varphi = 1.1 \text{ eV}$.

Wires migrated in this fashion, i.e. without a series resistor added, resulted in gaps that had tunnel currents ranging from $10^{-5}$ to $10^{-8}$ A and the overall success rate of creating gaps with dimensions of 1 to 2 nm was less than 35%.

To improve these statistics, a series resistor of 100 Ω was added to the setup. Figure 4.5.A shows a migration experiment with a 100 Ω resistor added in series. The maximum current (of 19.8 mA) is comparable to that of figure 4.4, but the voltage at which migration occurs is a lot higher, i.e. 2.2 V, compared to that of the migration experiment without a series resistor. That a higher voltage is needed to start migration is not surprising; From section 4.2.2 it is clear that the current needs to cross a critical current (density) before migration starts. Placing a resistor in series with the wire results in a larger overall resistance and a higher voltage will be needed

\[ \text{Since the wire in the inset of figure 4.4 was migrated at atmospheric pressure, the barrier height of the resulting tunneling gap is not equal to the work function of gold, i.e. 5.4 eV, but has a far lower value [34–36].} \]
4.4 Results and discussion

Figure 4.3: Four SEM images, showing lithographic structures created with bi-layer resist and shadow mask techniques. The four (almost) identical structures indicate that the production process consistently yields suitable structures.

to reach the same current level. As a consequence, a higher voltage will need to be applied to reach the current at which migration occurs as well.

As the voltage is increased and migration starts to occur, the resistance of the wire increases as well because the cross-section of the wire decreases during migration. Without any series resistor attached, this does not really matter because the voltage drop over the wire will still be equal to the applied bias, which is increased linearly with time. When a series resistor is added however, initially the majority of the applied bias is dissipated over the series resistor. When the bias is increased and migration starts to occur, the resistance of the wire increases, causing more of the applied bias to
4. Electromigration of lithographic contacts

![Graph of I(V) relationship](image)

**Figure 4.4:** A typical migration experiment without a series resistor added. The inset shows an I(V) graph (grey line) of a device after migration. The black line in the inset corresponds to the Simmons model, with the following parameters: $\phi = 1.1$ eV, $L = 1.1$ nm and a cross section of 1020 nm$^2$.

be dissipated over the wire as well. As a result, the bias that is effectively applied over the wire increases faster than when no series resistor is used. This faster migration results in a more powerful breaking process [24], as is evidenced by the fact that after the major drop in current, i.e. the major migration event, no current was measured for wires with a series resistor added to the wire (figure 4.5), while there still was a detectable current for wires without any series resistor (figure 4.4).

After migration it was attempted to determine the tunneling current of these wires, but in all cases where a 100 $\Omega$ series resistor was used, the current was too low to be detected, indicating that the formed gaps have widths of 2.2 nm and above. While a distance of 2.2 nm would be suitable for the molecules of interest, there is no guarantee that the distance between the two contacts is not far larger. As a result these contacts could not be used for measurements on single molecules.

To overcome this difficulty, a resistor with a variable resistance was placed in series with the wire and the total combined resistance of wire and resistor was set to 30 $\Omega$. Figure 4.5B shows a migration experiment where the total resistance was set to 30 $\Omega$. For this resistance, the migration takes place all at once as well, as indicated by the
4.4 Results and discussion

Figure 4.5: Two migration experiments with a resistor placed in series with the wire. In A) the resistance of the series resistor is 100 Ω and in B) the total resistance series resistor and wire is 30 Ω.

current dropping completely to zero, and after migration 88% of the structures have resistances that, by using the Simmons model of section 4.2.3, can be related to gaps that have widths between 1 and 2 nm.

Plotting both the maximum current density that runs through a wire and the voltage at which migration takes place as function of the total resistance before migration results in the graphs of figure 4.6A and B respectively. From these graphs two things are clear. First, the current density at which migration occurs, i.e. at $7.6 \cdot 10^{12} \text{ A/m}^2$, is independent of the initial resistance of the wire. As demonstrated by equation 4.2.7, this is because migration occurs above a minimum current density. Not only that, but this value is comparable to values found in literature for the current density at which migration occurs [3, 6, 24, 25]. Second, when the total resistance of the wire is increased, the voltage at which the wire is migrated increases linearly with it. As mentioned before and as dictated by Ohm’s law, this is because the higher the total resistance of the wire is, the higher the total voltage has to be to reach the same current (density).

4.4.3 (No) measurements on molecules

With the migration of the wires under control, the next step was the application of molecules to such migrated contacts and the determination of the conduction properties of the molecule.

Two different ways of performing these measurements were attempted. The first method consists of first migrating the wire and then applying the OPV-5 molecules. In the second method, the molecules are applied before migration. It has been argued, that applying the molecules before migration will lead to their destruction because of the high temperatures that are reached during migration. Trouwborst et al. [25] show

\[ \text{The samples have cross sections of 3000 nm}^2. \text{ With this value, the current density could be calculated from the measured currents} \]
4. Electromigration of lithographic contacts

Figure 4.6: The maximum current density, A), and voltage at which migration occurs, B), as function of the total resistance of both the wire and the series resistor. From left to right the points in both graphs are the averages for “no series resistor”, “a total resistance of 30 Ω” and “a 100 Ω series resistor” respectively and the error bars are the spreads in the corresponding averages.

that, provided that a suitable series resistor is incorporated into the electrical circuit during migration, temperatures do not rise above 460 K and that most molecules used in molecular electronics do not get damaged at these temperatures. Also, Osorio et al. [22] claim that they do not see a difference in device performance for both methods.
4.4 Results and discussion

Therefore it is believed, that both methods should work just as well.

However, for both methods, none of the total 76 conduction experiments that were performed on wires treated with molecules, resulted in a $I(V)$ measurement that showed either a Coulomb blockade effect and/or vibrational features. For example, figure 4.7 shows two $I(V)$ curves of a wire that was electromigrated. While one of the graphs was recorded before applying the molecules and the other after applying them, there is no significant difference between the two measurements. Both measurements show a linear tunneling current in the (sub)pico Ampere range, from which a gap size of approximately 2.1 nm could be determined. Both the migration and conduction experiments were performed in vacuum, indicating that the obtained results are not caused by outside contaminants. If molecules were present during the conduction experiments, one would expect a sudden increase in the current at several tens of millivolts, to values as large as 1 nA and above, see for example figure 1.C from Pasupathy et al. [10] or figure 2.A from Park et al. [9]. Such increases in current are clearly not observed in the measurements shown in figure 4.7. Combined with the fact, that the application of molecules to the contact did not result in any additional features in the current, it is concluded that no molecules were probed in these measurements and that, unfortunately, nothing further can be said about the conduction properties of these molecules.

![Figure 4.7](image_url)

**Figure 4.7:** Two current-voltage curves of an electromigrated wire, one graph was measured before and the other after applying OPV-5 molecules.
4. Electromigration of lithographic contacts

That not all such conduction experiments of single molecules on migrated wires are successful is known from literature as well. For example, only 8 out of 415 samples (1.9%) measured by Osorio et al. [22] resulted in data from which the presence of a molecule could be determined along with the nature of its conduction properties. Similarly, Yu et al. [20] performed measurements of $C_{60}$ molecules and only 5 out of 475 samples (1.1%) showed features, namely molecular vibrations of the $C_{60}$, that could be related to the presence of molecules in the electromigrated gap. For trimetal molecules containing either three copper or nickel atoms, Chae et al. [19] show that only 4 out of 160 (2.5%) and 7 out of 160 (4.4%) of their respective copper and nickel devices show vibrational features that reveal the presence of molecules.

Therefore, it is not surprising that the obtained yield is low. However, the expenditure of effort is considered to be disproportionately large compared to the obtained results and therefore it was decided to look for other ways to measure the conductance properties of individual molecules.

4.5 Conclusions

In this chapter the results on the electromigration of thin metallic wires has been reported.

After successful creation of the lithographic structures, by combination of shadow evaporation and a bilayer resist technique, these structures were migrated by applying a voltage over them. Without an additional series resistor, migration resulted in poorly defined structures were obtained and a low percentage of structures had suitable gap sizes. Adding a series resistor with a too high resistance to the circuit, resulted in gaps that were so large that no tunneling current could be determined after migration. By setting the total resistance of wire and series resistor to 30 Ω, gaps could be created that had widths between 1 and 2 nm with more than 85% efficiency.

As expected from literature, migration took place at a critical current density, namely at $7.6 \cdot 10^{12}$ A/m², irrespective of the total resistance of the circuit and as a result, the voltage at which migration occurred increased linearly with the resistance.

No conductance features could be observed in migrated wires treated with molecules that indicated the presence of a molecule in the gap.

Bibliography


4.5 Bibliography


4. Electromigration of lithographic contacts


4.5 Bibliography


Chapter 5

Scanning probe nanolithography of OTS monolayers on silicon

In this chapter, the effects of locally applying a bias on self assembled monolayers of octadecyl trichlorosilane (OTS) on silicon with an atomic force microscope tip are reported. It is found that two processes can occur, depending on the applied bias and the duration for which it is applied. The first process that can occur is the modification of the methyl end groups of the OTS to carboxylic acid groups. The second process is the growth of silicon oxide underneath the OTS-SAM. For the first process, a change in height was observed for the oxidized areas. This change in height was not only unexpected, but turned out to be scan direction dependent as well; scanning the AFM tip from left to right resulted in observing the modified surface areas as hills, whereas for the opposite scan direction, from right to left, these areas were observed as valleys. By using modulated friction measurement, i.e. applying an oscillatory movement parallel the scan direction of the tip, it was determined that this scan direction effect is caused by the cross-coupling of the height and friction force signals of the AFM. By using electrostatic force microscopy (EFM) it was determined that charges are present after oxidation. These charges, however, are not the cause of the surface-reactivity, because the charges disappear in time, while the reactivity does not.

Note that part of the work reported in this chapter has already been published in literature [1].

5.1 Introduction

Scanning probe nanolithography, or in other words local probe oxidation, is a technique where the tip of a scanning probe microscope (SPM), either a scanning tunneling microscope (STM) or, as is the case in this chapter, an atomic force microscope (AFM), is used to modify the surface of a substrate by applying a bias between
5. Scanning probe nanolithography of OTS monolayers on silicon

substrate and tip. This technique is a convenient and versatile route towards the preparation of nanostructures [2–6]. Firstly because this technique is relatively easy to employ without the need for expensive instrumentation, i.e. focused ion/electron beam, and secondly because the methods can be performed in a parallel fashion utilizing a multiple tip approach and therefore covering large substrates [7–10].

Using local probe oxidation on conducting and semi-conducting substrates, several groups have demonstrated sub 20 nm patterning of surfaces, as well as the application of these patterns in, both positive and negative etching procedures of, for example, silicon substrates [11–15]. Self assembled monolayers (SAMs) of simple molecules have been employed as resist layers, thereby improving the resolution of the obtained patterns [13] and have even been claimed to increase the oxidation speed of the underlying SiO$_x$/Si compared to the oxidation speed of the bare substrates [16, 17]. The oxidative scanning probe lithography of organic self-assembled monolayers, e.g. octadecyl trichlorosilane on silicon, has recently gained a lot of interest because it offers a very versatile platform for the build-up of complex systems [18–23], that in the future might be used to fabricate nano-scale (electronic) devices. Although the important conditions for the local probe oxidation of silicon to silicon dioxide, namely humidity, bias voltage and pulse duration, have been studied extensively [14, 24–26], the role of the SAM remains under-researched [27].

In this chapter the influence of the applied bias voltage and the pulse duration on the local oxidation of OTS monolayers on SiO$_x$/Si is discussed. This is done in terms of the formation of carboxylic acid end groups and/or the oxidation of the underlying silicon as observed by lateral force microscopy. This information is correlated to observed line heights obtained by contact-mode imaging in different directions as well as electrostatic force imaging.

5.2 The measurement techniques

For an explanation of the basic operation principle of the AFM the reader is referred to chapter 3.

5.2.1 Friction force measurements

Besides measuring the topography, an AFM can also be used to measure the friction force the tip generates as it is moved across the substrate. Since the tip has to be in continuous contact with the surface to perform friction measurements, only contact mode can be used for these experiments.

With height measurements the fast-scan direction is usually chosen to be parallel with the long-axis of the cantilever of the AFM probe, see figure 5.1, to facilitate the bending of the cantilever. For friction force measurements, the fast-scan direction is chosen perpendicular to the long-axis of the cantilever, figure 5.1, because in this configuration the friction force between tip and substrate cause the tip to stick as it is dragged across to the surface. As a result the cantilever gets tordated and the friction signal can be measured (separately from the height signal).
5.2 The measurement techniques

5.2.2 Modulated friction force imaging

Normally when performing friction force measurements, the tip is scanned from left to right (or vice versa) in one continuous motion in the fast-scan direction, see figure 5.2A. With modulated friction force microscopy (MFFM) [28–31], a sinusoidal oscillation is added to the motion in the fast-scan direction, figure 5.2B, at the resonance frequency of the cantilever. During imaging the z-defection and the magnitude of the lateral resonance (MAG) are measured. The magnitude of the lateral resonance is a measure for the friction the tip experiences in the lateral direction and can therefore be compared to, for example, the friction signal in friction force microscopy (FFM).

Figure 5.1: A) The fast scan direction parallel to the long-axis. B) The fast scan direction perpendicular to the long-axis.

Figure 5.2: The effect of modulated friction on the motion in the fast scan direction. A) No modulated friction: a continuous motion in the fast scan direction. B) With modulated friction the tip is oscillated back and forth in the fast scan direction in addition to the overall scanning motion.
5. Scanning probe nanolithography of OTS monolayers on silicon

5.2.3 Local probe oxidation

With local probe oxidation, the AFM is used in contact mode. When the tip is in contact with the surface a bias is applied to it (the substrate is grounded) and a chemical reaction takes place that modifies the surface. Since a bias is applied, the tip needs to be conductive. By using metal-coated tips, this is taken care off.

![Figure 5.3: A schematic representation of scanning probe nanolithography; A conducting tip is placed in contact with a substrate, where here the substrate consists of a silicon wafer (with an approximately 1 to 2 nm thick layer of native oxide) with an octadecyl trichlorosilane monolayer on top of it. When a bias voltage is applied to the tip (the substrate is grounded), the surface underneath the tip is locally oxidized. If the tip is simultaneously moved across the surface, modified areas can be selectively created. These areas can later be used as templates in subsequent reaction steps.](image)

The presence of water and the formation of a stable water meniscus between tip and substrate is a crucial requirement in the local probe oxidation of, for example, metallic or semi-conducting substrates [32]. Water present in the meniscus is decomposed by the electrical current and its decomposition products cause the substrate to become (further) oxidized, irrespective of whether a layer of native oxide is present [27, 35, 36] or not [32]. However, if the process of oxidative probe lithography is applied to a self assembled monolayer of OTS on a silicon support, figure 5.3, the role of water becomes more complex, as the result of the oxidation will be a competition between a number of processes that may occur at different time scales depending on the applied bias voltage. Moreover, the hydrophobic surface properties make the meniscus formation more difficult. The first reaction that can take place

---

1Unless special care is taken to passivate a silicon surface, the presence of water in the atmosphere causes the growth of a “native” layer of silicon oxide on the substrate. This oxide is 1 to 2 nm thick [33, 34] and is required to chemically bond the OTS molecules to the surface.
5.3 The setup

is the conventional oxidation of silicon under the OTS monolayer [27]. While this process requires the diffusion of charged species through both the highly hydrophobic OTS monolayer and the native oxide, it occurs nevertheless 2. Competing with this reaction is the (partial) oxidation of the methyl end groups (-CH$_3$) of OTS, effectively converting them to carboxylic acid end groups (-COOH) [20].

It should be noted that it takes two separate experiments to measure the patterns created by local probe oxidation. In the first experiment the actual pattern is created using local probe oxidation and in the second experiment one or more of the above-mentioned methods are used to determine the structure that has been produced in the previous experiment.

5.2.4 Electrostatic force microscopy

To measure the charges induced into the substrate by local probe oxidation, EFM is used. EFM is a so-called two-pass technique [37, 38]: In the first pass the topography of a single scan line is determined, using tapping mode in this particular case, and in the second pass the tip is lifted and kept at a fixed height above the substrate. During this second pass a DC voltage $V_{DC}$ is applied between substrate and tip. Applying this bias results in a shift $\Delta f$ in the resonance frequency of the tip [37]:

$$\Delta f \propto \frac{\partial^2 C}{\partial r^2} (V_{DC} - V_{substrate})^2,$$  \hspace{1cm} (5.2.1)

where $C$ is the capacitance between tip and sample, $r$ the height of the tip above the substrate and $V_{substrate}$ the potential, or in other words the charge, of the substrate.

During the second pass, the feedback-loop tries to reduce the frequency shift to zero by applying a DC voltage $V_{DC}$ to the tip that cancels out the potential of the substrate. Hereby $V_{DC}(x,y)$ is a direct measure of the local distribution of charges on the substrate.

5.3 The setup

5.3.1 Monolayer preparation

Unless stated otherwise, all materials were used without further purification. Toluene and octadecyl trichlorosilane were obtained from Aldrich, U.S.A. Bis-cyclohexane (BCH) was obtained from Fluka, U.S.A and was distilled over sodium before use. Silicon wafers, p-doped, with a resistivity of 7-21 $\Omega$cm and a native oxide layer, were obtained from Infineon, Germany.

Monolayers of OTS on Si/SiO$_x$ were prepared by dipping the substrate in a 2 mM solution of OTS in BCH for 30 seconds followed by sonication in toluene. This process was repeated, if necessary, until the wafers emerge dry from the solution and the water

---

2Xie et al. [27] show, that while the presence of OTS reduces the amount of oxide that is formed, it does not stop this formation completely.

3By using Fourier transformed infrared measurements, Maoz et al. confirmed that the (electrical) oxidation of an OTS layer results in the formation of carboxylic acid end groups [20].
5. Scanning probe nanolithography of OTS monolayers on silicon

contact angle was 118° (as determined with a DSA10 contact angle measurement device made by Kruss, Germany).

5.3.2 AFM techniques

Oxidative scanning probe nanolithography was performed on a Solver P47H atomic force microscope (made by NT-MDT, Russia) that was placed in a home-built chamber with controllable humidity. Oxidation experiments were carried out at room temperature at 55-58% relative humidity using titanium nitride-coated tips, model NSG01, from NT-MDT, Russia. Oxidation patterns were made in “vector mode” at 2 µm/s and parameters as pulse height $V$ (-5 V < $V$ < -10 V) and pulse duration $t$ (0.01 ms < $t$ < 1000 ms) were systematically varied, while contact force, temperature and humidity were kept constant. Oxidized patterns were imaged afterwards in contact mode (using the same tip) and in tapping mode, using DP18 tips from Mikromasch, Estonia. The modulated friction force experiments have been performed on a Probe NanoLaboratory (PNL) Ntegra AFM from NT-MDT, Russia. It should be noted that for all three of these AFMs from NT-MDT the propagation direction of the laser light of the AFM is perpendicular to the long-axis of the cantilever. As will be seen in section 5.4.2 this will have an effect on the measured height signal.

5.4 Results and discussion

5.4.1 Oxidation: OTS modification and SiO$_2$ growth

Figure 5.4 shows an example of two oxidation experiments performed with different oxidation conditions. For both cases the relative humidity was set to 55-58%. The left column, figure 5.4.A and B, shows the height and friction images of four oxidation experiments for which the bias voltage and the pulse duration were set to -7 V and 10 ms respectively. In the right column, a set of height and friction images is displayed that were obtained after oxidation at a bias of -7.5 V with a pulse duration of 50 ms.

In both cases the change in the friction signal between the OTS background and the oxidized lines indicates a change in interaction between surface and tip, due to the modified surface area. However, when comparing the height images one can observe that the line oxidized at -7.0 V displays an apparent decrease in height of about 0.3 nm, whereas the lines oxidized at -7.5 V show an increase in height of, in this case, about the same magnitude. The areas with a decrease in height are thought to result from local oxidation of the OTS monolayer, namely by the formation of carboxylic acid end groups (−COOH) on the OTS molecules [19]. The conditions, at which an increase in height is observed, are ascribed to the degradation of the OTS monolayer, accompanied by the growth of the underlying silicon dioxide layer. The growth of the underlying silicon oxide has been shown before to cause an increase in height [35,36], whereas the “observed” decreases in heights are caused by a cross-coupling effect.

The scale bar for figure 5.4B and D is in units of Amperes and not in Newtons as one would expect. The reason for this is, that what is initially detected with the AFM is the current signal coming from the four-quadrant photodetector. From this current signal the friction force signal can be derived.
5.4 Results and discussion

Figure 5.4: A typical example of height, A) and C) and friction images, B) and D), of the local probe oxidation of an OTS monolayer performed for two different sets of conditions; For A) and B) -7.0 V and 10 ms. For C) and D) -7.5 V and 50 ms). Local oxidation of the top methyl groups of OTS to carboxylic acid end groups can be followed by a negative height contrast, as shown in A). Degradation of the OTS monolayer and the oxidation and growth of the underlying silicon/silicon-dioxide causes an increase in height, see C).

between the height and lateral deflection signals of the laser detector\textsuperscript{5}. Because the negative height contrast has been observed on three independent AFMs and with numerous cantilevers, it is concluded that a rotated positioning of the photodetector array [39] is not the cause of this cross-coupling.

\textsuperscript{5}Here “observed” is placed between brackets because both the methyl and carboxylic acid end-groups have almost exactly the same height and no height contrast should be observed.
5. Scanning probe nanolithography of OTS monolayers on silicon

5.4.2 Height imaging: dependence on scan direction

In the previous section it is shown that there is a cross-coupling between the height and the lateral deflection signals. In this section a possible explanation for this cross-coupling is given: the torsion of the cantilever gives rise to a height deviation, see figure 5.5.

Here it is important to note that, for the AFMs that were used for these experiments, the propagation direction of the laser light of the AFM is perpendicular to the long-axis of the cantilever.

On areas with high friction, but without corrugation, the friction will cause torsion in the cantilever. Depending on the scan direction, this torsion will be clock-wise or counter-clockwise. When imaging is performed from left to right, figure 5.5.B, the torsion is clockwise. As a result the incidence angle of the laser with the surface normal becomes larger and the angle of reflection becomes larger as well. Therefore the position at which the laser hits the photodiode becomes lower, resulting in an artificial negative height contrast, or in other words in an artificial depression or valley. When the imaging direction is reversed, i.e. from right to left, the torsion will be counter-clockwise, figure 5.5.C. Now the angle of incidence of the laser with the surface normal of the cantilever decreases, resulting in a smaller reflection angle. The laser hits the photodetector at a higher position and it thereby gives rise to an artificial positive height contrast, i.e. hills.

These cross-talk effects on the observed height will also be superimposed on any existing “real” corrugation. In case of conversion of the top methyl groups of an OTS monolayer to carboxylic acid end groups, no “real” change in height is to be expected, as indicated by the contrast inversion. Nevertheless a superposition of these cross-talk effects with height effects that are much smaller than the topography effect cannot be excluded.

Figure 5.6 displays a typical example of a set of oxidation features created at different bias voltages but with a constant pulse duration of 10 ms, imaged in two different scan directions. One can clearly observe that for structures created at mild conditions, i.e. at -6.5 and -7 V, the observed negative height is reversed and appears to be positive when the structures are imaged in the opposite scan direction. As will be shown in figure 5.7, for biases of –9 V there also is a difference in the observed height for the two different scan directions, but since both heights will be positive, the contrast is not so striking as for the two lower biases.

The graph in Figure 5.7 shows the observed height with respect to the background for a set of oxidized lines formed at bias voltages between -6.5 and -9 V, when imaged at opposite scan directions. The observed difference in height between both imaging directions is, 0.6±0.2 nm. The observed height and friction contrast furthermore change with applied load (data not shown), indicating a correlation between the friction and the height image. The origin of the negative height contrast is contributed to the creation of large local differences in friction due to the different surface properties between the unchanged OTS and the oxidized lines. The oxidation does not only induce charges in the surface, as will be discussed later, but it also locally changes
5.4 Results and discussion

Figure 5.5: A schematic drawing of how torsion of the cantilever can cause cross-talk between the height ($\Delta Z$) and friction/lateral force (LFM) signals. The top row of images shows the torsion of the cantilever during scanning and the bottom row shows the effect of this torsion on the deflection of the laser on the photo-diode. Note that the propagation direction of the laser light is perpendicular to the long-axis of the cantilever. A) The tip is scanned over part of the OTS surface with low friction, i.e. no oxidation, and as a result the laser spot stays in the center of the photo-diode. B) If the tip passes from left to right over parts of the OTS surface with high friction, i.e. after oxidation, torsion in the cantilever causes the laser deflection to shift laterally (LFM) and a bit in the vertical direction ($\Delta Z$) as well. If the scan direction is reversed C), the laser LFM and height signal $\Delta Z$ will have inverse sign. In the drawing the position of the laser diode has been fixed with respect to the piezo. The torsion on the cantilever and the vertical deflection have been exaggerated for clarity.

The contact angle of a droplet of water on (the methyl ($-\text{CH}_3$) end-groups of) OTS is 105-108 $^\circ$ [13], indicating a very hydrophobic surface. After oxidation, the end-groups are transformed into carboxylic acid ($-\text{COOH}$). These end-groups form hydrogen bonds with the water molecules that are present [40]. Therefore the oxidized substrate is highly hydrophilic.

the surface from hydrophobic to hydrophilic leading to differences in the amount
5. Scanning probe nanolithography of OTS monolayers on silicon

![Figure 5.6: Contact mode height images of three sets of three squares oxidized with pulses of 10 ms at -9.0, -6.5 and -7.0 V. Image A) shows the result after oxidation when the fast imaging direction is set from left to right (arrow). Image B) shows the same area as in A), but measured with the reversed fast scan direction.](image)

of adsorbed water.

In order to measure the real height, and not the height related to the above mentioned cross-coupling effect, modulated friction force microscopy [28-31] has been used to visualize oxidation patterns on OTS. Figure 5.8A displays a square area of oxidized OTS. This square has been made by raster imaging of a $2.5 \times 2.5 \mu m^2$ area with an electrically biased tip ($-8$ V). The formed -COOH end groups on the surface were imaged with an apparent height because the image was recorded with the fast scan direction from right to left. The bright dot in the center of the square is silicon dioxide, generated during the approach cycle of the tip. When the same area is imaged (again from right to left) using the modulated friction force imaging mode, the apparent height of the areas consisting of -COOH end groups decreases to zero. In this method the tip is laterally excited while remaining in contact with the surface. The resulting rapid backward/forward motion in the fast scan direction causes the apparent height, that is assigned to cross-coupling, for both directions to average out, resulting in a zero net height. This is in good agreement with the near zero height change that one would expect upon conversion of the methyl end-groups of the OTS monolayer to carboxylic acid groups. Therefore, modulated friction force imaging proves that the observed height changes are caused by the cross-coupling of the height and lateral force signals. The dot in the center of the square, which consists of silicon dioxide, is caused by a real topographic change, since silicon dioxide takes up more volume than silicon, and therefore the height of this dot is not affected by this measurement technique. Additionally, the magnitude of the lateral excitation is recorded. The interaction between tip and surface is different for oxidized OTS
5.4 Results and discussion

Figure 5.7: The observed height in contact mode images. In the graph the observed height for oxidized lines is plotted against the applied bias voltage at which they were written for the two scan directions.

and unaffected OTS. Therefore the magnitude of lateral excitation can be used as a measure of friction, see figure 5.8.C.

5.4.3 Electrical force microscopy on oxidized OTS layers

Besides the conversion of methyl end groups into carboxyl groups, local probe oxidation results in the formation of residual charges onto the surface. This is demonstrated by EFM. In this two-pass scanning method the tip is resonating at a small amplitude above the surface with typically a small bias applied to the tip.

In figure 5.10.A and B the height and friction images of a set of oxidations are displayed respectively. The oxidations were performed according to the scheme in figure 5.9, i.e. a total of twelve sets of three identical squares were written at six different bias voltages and with two different pulse durations for each voltage. The oxidation biases and pulse durations were selected to obtain oxidation of the OTS monolayer as well as oxidation of the silicon substrate. From the friction image, figure 5.10.B, it can already be observed, that for two of these settings (-5.7 V for
5. Scanning probe nanolithography of OTS monolayers on silicon

10 ms and -6.2 V for 10 ms) there is hardly any detectable increase in the friction contrast. For these settings, no change in the height could be observed on the OTS monolayer either. At the same time, squares oxidized at higher bias voltages (-8.5 V for 1 and 10 ms and -8 V for 10 ms) caused the degradation of the OTS layer to be accompanied by growth of silicon oxide, as evidenced by the increase in height of
5.4 Results and discussion

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Oxidation Conditions</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8.5 V</td>
<td></td>
<td>1 ms</td>
</tr>
<tr>
<td>-8.0 V</td>
<td></td>
<td>10 ms</td>
</tr>
<tr>
<td>-7.5 V</td>
<td></td>
<td>10 ms</td>
</tr>
<tr>
<td>-6.7 V</td>
<td></td>
<td>10 ms</td>
</tr>
<tr>
<td>-6.2 V</td>
<td></td>
<td>50 ms</td>
</tr>
<tr>
<td>-5.7 V</td>
<td></td>
<td>10 ms</td>
</tr>
</tbody>
</table>

Figure 5.9: A schematic representation of 12 sets of 3 squares, each with their corresponding oxidation conditions, i.e. the applied bias and pulse duration. The squares in the scheme represent with which conditions the squares in figures 5.10 and 5.11 have been written.

Figure 5.10: For different bias voltages and pulse-durations, sets of three squares have been oxidized. See figure 5.9 for which set of parameters corresponds to which set of three squares. The resulting height- and friction images are shown in A) and B) respectively. See figure 5.11 for the corresponding EFM measurements these structures compared to the no-oxidized areas of the substrate.

The presence of residual charge was demonstrated by EFM-imaging (figure 5.11).
5. Scanning probe nanolithography of OTS monolayers on silicon

Figure 5.11: For different bias voltages and pulse-durations, sets of three squares have been oxidized. EFM was used to identity the presence of residual charges on the surface. Images were recorded in a two-pass mode technique with the lift height set to 19.9 nm in A) and B) and to 50 nm in C) and D). Applying a positive bias (+1 V) leads to a negative phase shift, see A) and C), while applying a negative bias (-1 V) leads to a positive phase contrast, see B) and D), indicating the presence of negative surface charges. See figure 5.10 for the corresponding height- and friction images.

to D) [41,42]. The oxidized squares are exactly the same squares as in figure 5.10 and the oxidations were performed according to the scheme in figure 5.9. Negative surface charges were present in all structures except for those where no friction contrast could be observed. The observed contrast is inverted upon changing tip bias and it decreases with increasing lift-height. The intensity of the signal showed little correlation with the height of the applied bias voltage. However, the duration of the applied pulse does show correlation with the EFM-signal intensity: the longer pulses show stronger contrast, as, for example, is shown for the structures marked with ◆ and ■ (−6.7 V: 10 and 50 ms respectively) and also for the squares marked with ▶ and ◆ (−7.5 V: 1 and 10 ms). During oxidation, charges may be induced at the surface in the form of
5.4 Results and discussion

carboxylic acid anions, by incomplete formation of the silicon dioxide or by trapped charged species in the silicon dioxide layer as reported for the anodization of Si [27]. It is unlikely that the observed charges are positioned at the acid group (i.e. the air interface) because oxidation and imaging are all done at ambient conditions and about 60 minutes have passed between oxidation and EFM-imaging, leaving ample time for charge recombination. It should be noted, however, that in another example (data not show), in which the EFM imaging was performed two days after oxidation, no signal could be observed. Nevertheless, this lack of charge does not influence the reactivity with respect to subsequently performed surface modification techniques, such as e.g. the site-selective binding of nanoparticles. The fact, that the pulse duration seems to be a factor in increasing the total charge at the surface, indicates that diffusion processes of reactive species through the hydrophobic OTS monolayer acts as a rate limiting step [41,42]. If oxidation of the OTS to form surface carboxylic acid groups is desired, oxidations should be performed at small time-scales.

5.4.4 Parameter space of OTS modification and SiO₂ growth

The onsets of oxidation, i.e. the start of formation of carboxylic acid groups as well as the start of silicon dioxide growth, have been evaluated in terms of the height of applied bias and the pulse duration. Scanning was performed from left to right, therefore an increase in height of the oxidized areas compared to the un-oxidized regions could be related to the growth of silicon oxide, while a decrease in height could be related to the formation of carboxylic acid groups. Figure 5.12 shows the results of a series of experiments in which a number of lines was oxidized where the applied bias voltage was varied between –5.5 and –9 V, but the pulse duration was kept constant at 10 ms. The oxidation experiments were performed using TiN-coated tips at room temperature and at 54% relative humidity. The different symbols in the graph represent different oxidation experiments. The oxidized lines were analyzed in terms of the apparent height of the respective lines after oxidation as compared to the unchanged flat OTS background. To ensure that a good comparison can be made between individual images, all imaging has been performed using the same tip and using the same deflection set point. In the plot three distinct regimes can be discerned; one part where zero height change is observed (the regime marked “A”), one part with only negative heights (the regime marked “B”, between -7.5 and -6 V) and a part in which both a negative height and a positive height are observed at the same time (regime marked “C”). The AFM images, figures 5.12 A to C, above the graph show a typical example for each of the regimes.

In regime “A” (bias voltages above -6 V) no change in height and no friction contrast were observed. Therefore we can conclude that for a TiN-coated tip, the applied bias for a 10 ms pulse should be below -6 V to induce any change in the monolayer. At biases between a -6.5 and -7.5 V a clear friction contrast has been observed that is accompanied by an apparent decrease in height of about 0.25 nm. Lines written at these biases and displaying this kind of height and friction contrast behavior, can be ascribed to the local formation of carboxylic acid end group functionality [3,19–23].

At more negative bias voltages, two effects can be observed simultaneously; when looking at the oxidized lines created at bias voltages below -7.5 V, the center part
5. Scanning probe nanolithography of OTS monolayers on silicon

Figure 5.12: The observed height plotted for different voltages. D) The observed height for oxidized lines is plotted as a function of the applied bias. The pulse length is 10 ms for all voltages. Typical contact mode AFM height images are displayed for each of the observed regimes. In regime A) no change in height is observed, in B) a negative height is found and in C) the central part of the oxidized lines have a positive height surrounded by areas with negative height contrast. The z-scale is 1.0 nm for all images.
negative height contrast remains nearly constant. The increasing height contrast at the center of the lines is ascribed to the local degradation of the OTS monolayer and the simultaneous formation of silicon oxide in the substrate, whereas at the edges the end groups of the OTS monolayer are converted into -COOH groups. The increasing line height with decreasing bias voltage is consistent with the work on the local anodic oxidation of silicon substrates [24, 25].

These experiments have been repeated for different pulse durations and from the obtained results the parameter space in which the local oxidation of OTS is initiated, as well as the conditions at which silicon dioxide is formed, could be determined. In Figure 5.13, the window for OTS oxidation, as observed for a TiN-coated tip, is displayed. At conditions in the white region of the graph, i.e. highly negative bias and long pulses, the OTS monolayer is degraded and the growth of silicon dioxide dominates. At conditions in the grey area of the graph, no oxidation effects were observed. In the black area of the graph, only carboxylic acid groups are formed. Note that to the bottom of the graph, i.e. short pulses, one is limited by the AFM: the shortest pulses that can be generated are 0.01 ms. To the top of the graph, the total oxidation time needed for oxidations increases exponentially, and increasing experimental noise, induced by drift and creep effects, is observed in that case.

It should also be noted that for other TiN tips, small variations are possible, but in that case the onsets of both OTS and Si oxidation generally do not shift more then 0.5 V. For tips with different conductive coatings (Pt, Au, W$_2$C) the onsets may lie at different positions altogether, making oxidation of OTS feasible at bias voltages as high as -4.0 V [43].

5.5 Conclusions

When performing local probe oxidation experiments on OTS monolayers, there are in principle two reactions that can take place: firstly, the conversion of the top methyl groups of the OTS molecules in the monolayer into carboxylic acid end groups, and secondly, the local probe oxidation of the silicon substrate, resulting in the local growth of silicon dioxide.

The formation of silicon dioxide leads to an actual increase in height, whereas the formation of acid groups leads to a change in height that depends on the scanning direction of the AFM tip and is a result of cross-talk between the friction and the height signals. This cross-talk effect was confirmed by using modulated friction force imaging.

The fact that the observed height changes sign when the scan direction is reversed, has been used as an indication for the formation of carboxylic acid end groups. These observations were used to determine the parameter space in which either reaction takes place. It was found that, for a fixed bias voltage, the formation of silicon dioxide takes longer than the conversion of OTS to carboxylic acid end groups. In general, the oxidation of OTS takes one to two orders of magnitude less time than the growth of silicon oxide. For different TiN-coated tips these onsets may shift up to 0.5 V but the trends are the same.

The presence of negative charges on the surface after oxidation was confirmed
5. Scanning probe nanolithography of OTS monolayers on silicon

Figure 5.13: Graph showing how the oxidation of an OTS monolayer on silicon, in contact with a TiN-coated tip, depends on the applied bias voltage and pulse duration. The silicon oxide growth (white area) and OTS oxidation (black area) have been determined from the appearance of a negative or positive height contrast. All images, used to determine these onsets, were recorded from left to right, therefore formation of -COOH end groups and growth of silicon dioxide could be related to a negative and a positive height contrast respectively. For low voltages and pulse durations (grey area) no changes in the OTS monolayer are induced.

with electrostatic force microscopy. These charges, however, are not influencing the mechanism of reactivity of subsequent surface functionalization steps, as these charges disappear in time whereas the surface-reactivity does not.
5.5 Bibliography

Bibliography


5. Scanning probe nanolithography of OTS monolayers on silicon


5.5 Bibliography


5. Scanning probe nanolithography of OTS monolayers on silicon


Chapter 6

Thiophenol on Ag(111),
topography and IETS

Three scanning tunneling microscopy (STM) techniques have been used to study a self-assembled monolayer (SAM) of thiophenol (TP) molecules on a Ag(111) substrate, namely scanning tunneling microscopy, scanning tunneling spectroscopy (STS) and inelastic electron tunneling spectroscopy (IETS). From the topography imaging it follows, that the SAM consists of domains that each have a periodic structure with a $3 \times 3\sqrt{3}$ unit cell. The IETS measurements show vibrational contributions of both the thiophenol molecules and the silver substrate. By comparing the measurements with the calculations, it was observed, that depending on the exact position of the tip on a thiophenol molecule, electrons can take different pathways through the molecule and thereby excite different molecular vibrations. Besides the position of the tip, its composition also plays an important role in the generation of the IET spectrum, as is evidenced by the differences in the calculated spectra of the gold and tungsten tips. The STS measurements reveal a non-symmetric $\frac{dI}{dV}$ curve around 0 Volt and the origin of this asymmetry is attributed to the spatial reorientation the molecule undergoes due to the applied electric field. For voltages up to 40 mV a dip is observed in the $\frac{dI}{dV}$ spectra and it is attributed to the silver phonon modes; it is thought that the bonding of the thiophenol molecules to the substrate pronounces the presence of the phonon modes in the $\frac{dI}{dV}$ signal.

6.1 Introduction

In the late fifties the first tunneling experiments were performed on silicon and germanium $p-n$-junctions. [1, 2] About a decade later it was found that for low bias voltages ($< 1$ V) the tunneling spectra obtained on thin oxide tunnel junctions, contained features that correspond to the molecular vibrations of the material in the tunneling barrier [3, 4] and thus the field of IETS was born. Since then, many different metals-oxide-metal systems, often with small molecules evaporated on the oxide, have been studied using IETS, see for example [5] and references therein.
6. Thiophenol on Ag(111), topography and IETS

The major advantage of IETS, compared to other techniques that enable molecular vibrations to be measured, like Electron Energy Loss Spectroscopy (EELS) and infrared spectroscopy, is its sensitivity: IETS is about 10 times as sensitive as other techniques [6]. However, one of the drawbacks of IETS performed on such semiconductor-junctions, is, that the molecules, that are being probed, are buried in a complex environment that is difficult to characterize. Quickly after the invention of the STM in 1981 by Binnig and Rohrer [7,8], it was realized, that this technique could also be employed to probe vibrational excitations [9,10], thus removing the need to encase the molecules under study in another material. It was not until 1998 however, that Ho and coworkers managed to perform the first IETS experiments with an STM [11] (STM-IETS). In the decade that has followed, many different systems have been studied using STM-IETS, though most of them consisted of a a single small molecule on a metal surface [6,12–17]. The majority of these studies resulted in IET spectra where the observed features were attributed to both (solely) molecular vibrations and vibrations that arise due to the interaction between molecule and substrate.

When a (conjugated) molecules lies flat on a metal substrate, it has a strong interaction with this substrate and its electrical and vibrational properties are strongly influenced by the metal [18]. To reduce the influence of the substrate as much as possible, it is attempted to position the molecule as perpendicular as possible on the metal surface. This is done by applying the thiophenol to the substrate in such quantities that there are no molecules present individually, but that they form a SAM.

It could be argued that by using a SAM, instead of individual molecules, it becomes uncertain whether on measures the conduction properties of a single molecule or not. However, as the tunneling current is exponentially dependent on the distance between the tip and the molecule\(^1\), it is unlikely that tip also probes the neighboring molecule, especially if the corresponding topography image resolves the individual molecules\(^2\).

IETS measurements have been performed on SAMs [19–23], but only once in a STM configuration [24]\(^3\). In these non-STM experiments, hundreds if not thousands of molecules still contribute to the current and the IET spectra obtained from such measurements are ensemble averages and give no information on the contributions of the individual molecules themselves. Therefore the results of this chapter deal with IETS measurements done in a STM configuration on a SAM of thiophenol molecules on Ag(111).

The molecule of choice is thiophenol, also called benzenethiol or phenylmercaptan. The thiol-group binds strongly to a metal substrate, thereby reducing the chance of this molecule being picked up by the tip of the STM during an experiment. Another reason for choosing thiophenol is that it is a conjugated molecule and conjugated molecules allow current to be passed through them. Thiolates have already been extensively studied with STM [25–33] and though it is well established, that they form self assembled monolayers (SAM) on metal substrates, no STM-IETS has yet

---

\(^1\) Each additional Ångström of separation results in a tunneling current that is approximately one order of magnitude smaller.

\(^2\) Because in order to resolve the individual molecules, the tunneling electrons have to pass through a single molecule.

\(^3\) Okabayashi et al. have performed STM-IETS on a monolayer, but that was for a non-conjugated molecule and the tip actually touched the molecules during the measurement [24].
been performed on these systems.

For the substrate, Ag(111) is chosen, because both the orientation [34, 35], the STS spectrum [36, 37] as well as the phonon modes [38–40] of silver are well known. Similarly, for thiophenol applied to a silver substrate, both the orientation [32, 41] and the molecular vibrations [42] of the thiophenol are known as well.

Scientific experiments form the basis on which theories and mathematical models are build to describe and explain the obtained results. The reverse is also true: experimental data are compared with models to verify whether or not the experimental data can be trusted to be correct and to gain a better insight in the processes that are physically taking place as well.

Here, a combination of computational methods have been used to perform calculations on a cluster of noble metal atoms, on which a single thiophenol molecule has been placed, to gain insight in how the exact position of the STM tip above the molecule influences the IETS spectrum. The method used has been derived by Troisi et al. [43–45] and builds on the Landauer-Imry approach [46,47] for tunneling transport.

6.2 Theoretical modeling of IETS spectra

In this section the general formalism for the perturbative simulation of IET spectra will be given. As already mentioned, this theory has been developed by Troisi et al. and the reader is referred to the literature for a more detailed discussion on this formalism [43–45].

6.2.1 Elastic conductance

Just as in chapter 2, the starting point is the Landauer formula [48]:

\[
I = \frac{g_c}{e} \int_{-\infty}^{+\infty} dE \, T(E) \left[ f_L(E) - f_R(E) \right],
\]

(6.2.1)

where \( g_c \) is the quantum of conductance, \( T(E) \) the transmission function and \( f_L(E) \) and \( f_R(E) \) are the Fermi distribution functions of the left and right contacts respectively. Note that \( g_c \) times \( T(E) \) basically is the (energy dependent) conductance of the device.

However, where the models of chapter 2 are derived for a single (spin degenerate) energy level and do not take molecular vibrations into account, the model given in this section will be used to model a device that has not a single level but a complete density of states and since the aim of this model is to generate a simulated IET spectrum, it is essential that molecular vibrations are included.

As a result, a different expression for the transmission function will have to be found. The elastic component of the conduction \( g^e(E) \) through a channel with multiple energy levels is given by [48,49]:

\[
g^e(E) = g_c \, \text{Tr}[\Gamma^L(E) G(E) \Gamma^R G(E)\dagger],
\]

(6.2.2)

with \( \text{Tr} \) indicating the trace taken over the matrix \( (\Gamma^L(E) G(E) \Gamma^R G(E)\dagger) \). Here \( \Gamma^L \) and \( \Gamma^R \) are twice the imaginary part of the of the self energy matrices \( \Sigma^L \) and \( \Sigma^R \).
6. Thiophenol on Ag(111), topography and IETS

associated with the interaction of the molecular subsystem with the left and right electrodes, or in other words \( \Gamma^L = i(\sum^L - \sum L, \uparrow) \). \( G \) is the matrix representation of the retarded Green function operator and it is related to the molecular Hamiltonian \( H \) by:

\[
G(E) = (E - H + i\epsilon)^{-1}.
\]  

The Hamiltonian depends on the nuclear coordinates \( \{Q_\alpha\} \) of the molecule and consists of several parts:

\[
H(Q_\alpha) = H_L + H_R + H_M(Q_\alpha) + V, \tag{6.2.4}
\]

where \( L, R \) and \( M \) stand for the left and right electrode and the molecule respectively and \( V \) is the interaction between the subsystems. The molecule considered here is an “extended molecule”: the subsystem of the molecule is chosen large enough to make certain that the properties of the remaining electrodes can be considered to be close to those of pure metals. In this context it means that subsystem \( M \) extends until all the vibrational modes relevant to IETS are localized within it and that \( V \) does not depend on \( Q_\alpha \). In section 6.2.4 a brief description will be given on how all the parameters of the Hamiltonian are calculated.

### 6.2.2 The inelastic channel

To derive an expression for the inelastic part of the current, the interaction of the tunneling electron with the vibrational level of the molecule is treated perturbatively, allowing exchange of a single vibrational quantum per tunneling electron and assuming that the molecule is in its ground vibrational state \( ^4 \) For a discussion on these assumptions, the reader is referred to [44], where a detailed derivation of the following equation is given. Since the Green’s function matrix elements are parametrically dependent on nuclear coordinates \( \{Q_\alpha\} \ tag{\text{2.6}} \) the Green’s function can be expanded around the equilibrium position \( \{Q_\alpha\} = 0 \) using a Taylor series:

\[
G_{i,j}(E, \{Q\}) \simeq G_{i,j}(E, 0) + \sum \alpha \left( \frac{\partial G_{i,j}(E, \{Q_\alpha\})}{\partial Q_\alpha} \right)_{Q_\alpha = 0} Q_\alpha. \tag{6.2.5}
\]

Basically, the first order correction to the Green’s function, and thus to the current, comes from the motion of the atoms of the molecule around their respective equilibrium positions, or in other words from the molecular vibrations \( \alpha \).

By using the following definition:

\[
G_{i,j}^\alpha = \frac{1}{\sqrt{2}} \left( \frac{\partial G_{i,j}(E, \{Q_\alpha\})}{\partial Q_\alpha} \right)_{Q_\alpha = 0}, \tag{6.2.6}
\]

the inelastic contributions to the conductance due to mode \( \alpha \), separated in left to right \( (L \rightarrow R) \) and right to left \( (R \rightarrow L) \) parts, can be written as:

\( ^4 \) Or in other words, the system is in the low temperature limit, i.e. \( k_B T \ll \hbar \omega_\alpha \)

\( ^5 \) Note that the used coordinates are dimensionless.
6.2 Theoretical modeling of IETS spectra

\[ g^\text{inel}_{\alpha}^{(L\to R)}(E) = g_c \text{Tr}[\Gamma^L(E) G^\alpha(E) \Gamma^R(E - \hbar \omega_{\alpha}) G^\alpha(E)^\dagger] \] \hspace{1cm} (6.2.7)

\[ g^\text{inel}_{\alpha}^{(R\to L)}(E) = g_c \text{Tr}[\Gamma^R(E - \hbar \omega_{\alpha}) G^\alpha(E) \Gamma^L(E) G^\alpha(E)^\dagger] \] \hspace{1cm} (6.2.8)

respectively, where \( G^\alpha \) is the matrix representation of equation 6.2.6 and \( \hbar \omega_{\alpha} \) is the energy of vibrational mode \( \alpha \).

The inelastic contribution to the current from mode \( \alpha \) is

\[ I^\text{inel}_\alpha = I^\text{inel}_{\alpha}^{(L\to R)} - I^\text{inel}_{\alpha}^{(R\to L)}, \] \hspace{1cm} (6.2.9)

\[ I^\text{inel}_{\alpha}^{(L\to R)} = \frac{1}{e} \int_{-\infty}^{+\infty} dE \ g^\text{inel}_{\alpha}^{(L\to R)}(E) f_L(E)[1 - f_R(E - \hbar \omega_{\alpha})] \] \hspace{1cm} (6.2.10)

\[ I^\text{inel}_{\alpha}^{(R\to L)} = \frac{1}{e} \int_{-\infty}^{+\infty} dE \ g^\text{inel}_{\alpha}^{(R\to L)}(E) f_R(E)[1 - f_L(E - \hbar \omega_{\alpha})]. \] \hspace{1cm} (6.2.11)

In this model the elastic and inelastic components are additive and therefore:

\[ I = I^\text{el} + \sum_\alpha I^\text{inel}_\alpha. \] \hspace{1cm} (6.2.12)

Equations (6.2.10) and (6.2.11) imply that when a bias \( V \) equal to \( \hbar \omega_{\alpha} \) is applied, that an inelastic channel \( \alpha \) opens up and remains open for larger bias. A plot of \( d^2I/dV^2 \) versus \( V \) therefore shows a peak for \( V = \hbar \omega_{\alpha} \) (or \( -\hbar \omega_{\alpha} \)), as is explained in detail in section 6.3.3 and the integral below the peak \( W_\alpha \) is \( g^\text{inel}_{\alpha}^{(L\to R)} \) (or \( -g^\text{inel}_{\alpha}^{(R\to L)} \)).

At low bias, the energy dependence in equations and can be neglected and \( E \) can be set to the Fermi energy \( E_F \). The integrated intensity \( W_\alpha \) of the peak due to mode \( \alpha \) in the IET spectrum is given by:

\[ W_\alpha = g_c \text{Tr}[\Gamma^L(E_F) G^\alpha(E_F) \Gamma^R(E_F) G^\alpha(E_F)^\dagger] \] \hspace{1cm} (6.2.13)

To show that equation (6.2.13) is correct one only has to consider that the integral below one peak of the IET spectrum occurring at \( V = \hbar \omega_{\alpha} \) is simply the difference between the conductance measured for energies above and below the peak. Mathematically this comes down to:

\[ W_\alpha \equiv \int_{\hbar \omega_{\alpha}/e - \Delta V}^{\hbar \omega_{\alpha}/e + \Delta V} dV \frac{d^2I}{dV^2} \] \hspace{1cm} (6.2.14)

\[ = \left( \frac{dI}{dV} \right)_{V = \hbar \omega_{\alpha}/e + \Delta V} - \left( \frac{dI}{dV} \right)_{V = \hbar \omega_{\alpha}/e - \Delta V} \] \hspace{1cm} (6.2.15)

\[ = \left( \frac{dI^\text{inel}}{dV} \right)_{V = \hbar \omega_{\alpha}/e + \Delta V} - \left( \frac{dI^\text{inel}}{dV} \right)_{V = \hbar \omega_{\alpha}/e - \Delta V} \] \hspace{1cm} (6.2.16)
where $\Delta V$ is an arbitrarily small voltage interval and the last equality derives from the fact that only the inelastic conductance, due to mode $\alpha$, changes around $V = \hbar \omega_{\alpha}$ (provided that no other vibrational modes are active in the interval $[\hbar \omega_{\alpha}/e - \Delta V \cdots \hbar \omega_{\alpha}/e - \Delta V]$).

### 6.2.3 A localized representation

Now that the equations describing the system are defined in the previous section, it becomes possible to choose a basis set with which the actual calculations will be performed. Any basis set that is appropriate for the one-electron wave function can be used to build the matrices in equations 6.2.2 and 6.2.13. It is convenient to use localized atomic orbitals. Because the overall system is described by a linear combination of atomic orbitals and molecular orbitals, the choice of the basis can still describe delocalization within the molecule.

Mathematically, $\Gamma_L$ can be defined as [43,44] (with a similar formula for $\Gamma_R$):

$$\Gamma_{ij}^L = 2\pi \sum_{\lambda} V_{\lambda i} V_{\lambda j}^* \delta(E_{\lambda} - E), \quad (6.2.17)$$

where $\lambda$ is an index running over the left electrode states and $V_{\lambda i}$ and $V_{\lambda j}$ are the molecular or atom/electrode couplings.

### 6.2.4 The used geometry and computational details

Calculation have been performed for two kinds of tip, namely a tip consisting of a gold dimer and a tip consisting of 10 tungsten atoms. Both calculations follow the same procedure and only for the gold tip is the full procedure explained. For the tungsten tip, only the points at which the calculation deviates from that of the gold tip are the differences mentioned.

#### The gold tip

The geometry used for the calculations with the gold tip is illustrated in figure 6.1. A single thiophenol molecule is bonded to a cluster of gold atoms on a $fcc$ absorption site of the gold and makes an angle of 40 degrees with the surface normal. The spheres above the molecule indicate the different positions of the tip that have been used for the calculations. Each sphere actually represents the atom of the tip that is closest to the molecule.

The tip consists of a dimer of gold atoms and is placed 0.43 nm above the molecule. In order to make certain that the tip does not have discrete electronic levels, like those of an individual atom, the effect of broadening is included in the self-energy terms $\Sigma$ (and thus in $\Gamma$, since $\Gamma = i[\Sigma - \Sigma^\dagger]$).

Since the entire geometry is a composite system, several different kinds of computations have to be performed in order to calculate a single IET spectrum, namely

---

6A number of assumptions have been made in order to be able to perform the calculations. Some of these assumptions differ from the actual experiment. These assumptions and the effect they will have on the calculation will be discussed in section 6.2.5.
6.2 Theoretical modeling of IETS spectra

Figure 6.1: A schematic top view, A), and side view, B), representation of the system used in the calculations: A single (dark grey) thiopenol molecule is placed upon a cluster of (light grey) gold atoms. The calculation has been performed several times, with the STM tip on different positions above the molecule. The (almost black) spheres (with the numbers) above the molecule indicate these different positions at which the STM tip was placed for the separate calculations. The Greek letters $\alpha$ and $\beta$ are labels for the top two (almost white) hydrogen atoms.

(A) the isolated molecule properties, (B) the molecule-electrode interaction and (C) the electrode local density of states.

(A) The vibrational frequencies of the isolated molecule and the matrix elements $G_{nm}(E)$ and $\partial G_{nm}(E)/\partial Q_\alpha$ are derived from density functional theory (DFT) calculations at the 6-31G$^*$/B3LYP level. By now using this calculation level, the effect of
6. Thiophenol on Ag(111), topography and IETS

the metal substrate on the on the molecular vibrations is not included. Similarly, the phonon modes of the metals are not included in the IET spectrum either. The calculations have been performed on the thiophenol molecule, so on a molecule containing an $S-H$ termination instead of a $S-Au$ end group. To eliminate the vibrational modes coming from the $S-H$ group, the mass of the $H$ atom of the $S-H$ group was artificially set to infinity.

(B) The electrode-molecule interaction is computed by performing a cluster calculation (also on the B3LYP level) on a model system consisting of nine gold atoms and a benzene thiolate. It is assumed that the $S$ atom is on a fcc-like absorption site and that the $S-C$ bond has a length of 0.285 nm. A 6-31G* basis set has been used for the organic part and a “Lanl2mb” basis set [50, 51] and pseudopotential for the gold atoms. This cluster has been used to compute the Hamiltonian matrix elements between the $S$ and Au atomic orbitals.

(C) The local density of states (LDOS) at the Fermi energy on the gold surface is calculated by using a tight binding model for metallic gold and a very large cluster of atoms to simulate the LDOS of the Au(111) gold surface. The tight binding parameters were obtained from first principle (B3LYP) using small cluster calculations with the same pseudopotential and basis set used for the calculation of the molecule-metal interaction [52].

Using the LDOS of the gold surface at the Fermi energy, together with the matrix elements computed in (B), the matrix elements of $\Gamma^L_\alpha$ and $\Gamma^R_\alpha$ can be calculated as follows:

$$\Gamma^L_\alpha = 2\pi \sum_k V_{ki} V_{kj}^* LDOS(E_F)_k,$$

where $k$ is an index running on the molecular orbitals on the left electrode, $i$ and $j$ correspond to the orbitals on the molecule and $V_{ki}$ (and $V_{kj}$) are the couplings between these two groups of orbitals, as calculated in step (B).

The Tungsten tip

For the calculation with the tungsten tip, the actual geometry of the tip is shown in figure 6.2.A. The tip consists of 10 W atoms and the geometry is extracted from a body centered cubic (BCC) structure, since that is the crystal structure that tungsten has. Figures 6.2.B and C give a top and a side view respectively of the different positions where the tip has been placed for the calculations. The spheres indicate the positions of the lowest atom of the tip for the different calculations. The calculations were performed at heights of 0.36 and 0.46 nm above the height of the highest hydrogen atom.

The tip configuration of figure 6.2.A has been used to compute the local density of states of the tungsten tip and only the lower 5 atoms of the tip are assumed to be coupled to the molecule. For the rest, the calculations are the same as those for the gold tip.
6.2 Theoretical modeling of IETS spectra

Figure 6.2: The geometry used for the tungsten tip. The specific shape of the tip is shown in A). A schematic top view, B), and side view, C), representation of the system used in the calculations. The calculation has been performed several times, with the STM tip on different positions above the molecule. The spheres (with the labels) above the molecule indicate these different positions at which the (bottom atom of the) STM tip was placed for the separate calculations. Note that images A), B) and C) are not drawn to scale.

6.2.5 Modeling assumptions

The model described in the previous sections to simulate an IET spectrum differs in two (major) ways from the experiments, as reported in section 6.5.3. In the experiments the tip is made of tungsten and the substrate is silver, but in the model both the tip and the substrate are made of gold.\footnote{Initially, only the calculations with the gold tip were performed. At a later stage, the calculations with the tungsten tip were performed as well.} The reason for this is that the model has previously been used to model an IET spectrum of two gold wires in a cross-wire
6. Thiophenol on Ag(111), topography and IETS

geometry with molecules in between the wires [23]. One can then wonder how these difference might affect the computation.

Regarding the substrate, not much of a difference is expected when the gold is replaced by silver, since for both metals, the valence electrons are in a s orbital and the inter atomic distances in the (111) crystallographic direction are 0.288 and 0.289 nm for gold and silver respectively [53].

Two discrepancies can be expected for the (gold) tip. Namely the position of the Fermi levels of the metals will be different and the specific orbitals of tip and molecule that couple together will vary as well. In the model used for these calculations the Fermi energy ($E_F$) is a parameter that has to be entered into the code manually and from previous work it is known that the exact value of $E_F$ does not alter the structure of the computed spectra, provided that the change in value is not too big [44]. The IET spectra are essentially independent of the choice of the Fermi energy when the energy differences between $E_F$ and both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are larger than 0.4 eV [43], which they are in this case. As a result, the difference in Fermi levels for the different metals is considered to be irrelevant for the calculation.

For the overlap of the different orbitals it is not so easy to determine if there will be a difference in the calculations for the different metals. From Hagelaar [54], however, it is known that if different orbitals contribute to the current, that different vibrations can be excited. Therefore it is possible that the calculations will differ from the measurements.

Clearly, for the tungsten tip these latter two discrepancies are not expected to occur. As a matter of fact, by comparing the results of the calculations for the different tips with one another, it becomes possible to get an estimate on the effect the shape and composition of the tip will have on the calculations.

6.3 The measurement techniques

The STM is the first machine that enabled people to image individual atoms in real space and it operates on the quantum mechanical tunneling principle. As will be explained in this section, STM can be used to measure both the topography, the density of states (DOS) and the IET spectrum.

6.3.1 Scanning tunneling microscopy

As its name says, a STM operates on the tunneling principle, but what is meant by that? Tunneling is a quantumechnical phenomenon where a particle, e.g. an electron, can be transmitted through, rather than over, a potential energy barrier, e.g. a vacuum gap between two metallic conductors, provided that the distance over which the tunneling occurs is small, i.e. in the order of a few nanometers. This is something that would not be possible with classical Newtonian physics, where a particle can never have a potential energy greater than its total energy. Though this tunneling is possible in the quantum world, the wave function $\psi$ of the electron drops exponentially inside the barrier as:
6.3 The measurement techniques

\[ \psi \propto e^{-z \sqrt{2m(U_0 - E)/\hbar^2}} \]  \hspace{1cm} (6.3.1)

where \( z \) is the width of the barrier and \( U_0 \) its height, \( E \) the energy of the electron and \( m \) its mass and \( \hbar = h/2\pi \) the reduced Planck’s constant, see figure 6.3.A.

![Diagram showing the tunneling principle and Fermi energies](image)

**Figure 6.3:** A) Schematic picture showing the tunneling principle: An electron with an energy lower than that of the barrier, i.e. \( U_0 \), tunnels into the barrier, thereby lowering its wave function amplitude from \( \psi_{in} \) to \( \psi_{out} \). B) Schematic representation of how a tunneling current is established in a STM experiment; The densities of state of tip and sample, \( \rho_t \) and \( \rho_s \), are filled up to their respective Fermi energies and together with the overlap of the wave functions, \( \psi_{t,i} \) and \( \psi_{s,j} \), of tip and substrate, they determine the tunneling current.

As a bias is applied to the STM-setup, electrons will start to tunnel through the gap and a current starts to flow, figure 6.3.B. By, for the moment, considering only elastic currents at absolutely zero temperature, the current \( I \), that flows between a metallic tip and a sample, as function of the applied bias \( V \), can be described by the well-know Bardeen formula [55]:

\[ I(V) = \frac{4\pi e}{h} \int_0^{eV} \rho_s(E_{F,s} - eV + E)\rho_t(E_{F,t} + E)|M(E_{F,s} + E)|^2 dE \]  \hspace{1cm} (6.3.2)

Here \( \rho_t(E) \) and \( \rho_s(E) \) represent the amount of energy levels available at energy \( E \), the so-called Density Of States (DOS), for the tip and substrate respectively and \( |M(E)|^2 \) stands for the tunneling probability. The energies up to which DOS of the tip and substrate are filled when no bias is applied are given by their respective Fermi energies \( E_{F,t} \) and \( E_{F,s} \). The height of the barrier \( U_0 \) is approximated by \((\phi_t + \phi_s - eV)/2\), where \( \phi \) is the work function of the material, or in other words, the minimum energy needed to remove an electron from the material to the vacuum.
6. Thiophenol on Ag(111), topography and IETS

Alternatively, the current can be written in another way, that gives a clearer insight into the tunnel probability $|M(E)|^2$:

$$I(V) = \frac{2\pi e}{h} \int_{0}^{eV} \sum_{i,j} |M_{ij}(E_{F,s} + E)|^2 dE$$  (6.3.3)

Now $M_{ij}(E)$ is a tunneling matrix element and contains information about the shape of the tip and sample wave functions ($\psi_{t,i}$ and $\psi_{s,j}$) and their overlap at energy $E$. The Bardeen expression for $M$ is a first order approximation and is written as:

$$M_{ij}(E) = -\frac{\hbar^2}{2m} \int \int d\vec{S} (\psi_{t,i}^* \nabla \psi_{s,j} - \psi_{s,j} \nabla \psi_{t,i}^*) \delta(E - E_i) \delta(E - E_j) dS$$  (6.3.4)

where the surface integral is taken over any arbitrary surface $\vec{S}$ that lies entirely within the vacuum barrier region that separates tip and sample. By modeling the tip wave functions $\psi_{t,i}$ as a single s-orbital, as was done for the first time by Tersoff and Hamann [56], the tunneling probability becomes: $M_{ij} = M_j \propto \psi_{s,j}$. Since $|M_j|^2 = |\psi_{s,j}|^2 \equiv \rho_s$, equation 6.3.3 simplifies, for small voltages, to:

$$I(V) \propto eV \rho_s(E_{F,s})$$  (6.3.5)

It should be noted, that equation 6.3.5 does not hold, when any other atomic orbital is used to model the apex of the tip.

From equations 6.3.1 and 6.3.5 it can be seen that the tunneling current depends exponentially on the tunneling distance $z$. It is this strong distance dependence that is used in STM. To measure the topography of a substrate, the STM is used in constant current mode, that is, the current $I$ is set to a certain setpoint value (typically between 1 pA and 10 nA). As the tip of the STM is scanned over the substrate (in the $x$ and $y$ directions), a feedback loop continuously maintains the current at its setpoint value, by moving the tip away from or towards the substrate in the $z$ direction. The actual movement of the tip, in both $x$, $y$ and $z$ directions, is performed by piezo-electric actuators that are of such quality, that accurate displacements of less than 10 pm are possible.

By scanning the tip over the substrate and recording the change in tip-height $\Delta z$ at each $(x,y)$ position, a topographic image of the surface is created.

6.3.2 The DOS of the sample

The first derivative of the current $\frac{dI}{dV}$ gives information about the charge density distribution of the sample. This can most easily be seen in the Tersoff-Hamann approximation, as by taking the first derivative of equation 6.3.3 one gets:

$$\frac{dI}{dV}(V) \propto \rho_s(x, y, E_{F,s} + eV)$$  (6.3.6)

Note that the tunneling current not only depends on the tip-sample distance $z$, but laterally it also depends on the DOS of the sample at that position (i.e. the local-DOS or LDOS $\rho_s(x, y)$), as can be seen in equation 6.3.2. As a result, the image obtained with an STM is not 100% topographic.
6.4 The setup

It should be noted, that in determining the DOS from \( \frac{dI}{dV} \), the information comes from the elastic tunneling current. That means, that the electrons have the same energy before and after tunneling. When electrons lose energy during tunneling, this gives rise to inelastic processes and these are described below.

6.3.3 Inelastic electron tunneling spectroscopy

With IETS, as an electron tunnels, it can scatter off the molecule and thereby lose an energy \( \hbar \omega \) equal to the vibrational energy quantum of the molecule, see figure 6.4.A. This process is only possible if there is an empty state available, which is the case for \( eV \geq \hbar \omega \). For energies below \( \hbar \omega \) the electron can tunnel only elastically, but at this energy an extra inelastic tunneling path opens. This gives rise to a kink in \( I \) at \( \hbar \omega \).

As can be seen in figure 6.4.B, a kink in \( I \) gives rise to a step in \( \frac{dI}{dV} \) and peak in \( \frac{d^2I}{dV^2} \) and it is the latter quantity that is measured in IETS.

When an inelastic channel is opened at \( eV = \hbar \omega \), this does not automatically lead to an increase in the conductance. If the level is close to resonance (\( E_m < \Delta \), where \( E_m \) is the position of the electronic state with respect to the Fermi energy of the leads and \( \Delta \) is the width of this state), elastic tunneling through virtual emission and reabsorption of a vibrational quantum starts to become important [57]. This two-phonon process is depicted in figure 6.4.E. For both direct and two-phonon tunneling the initial and final states are the same. Since IETS processes are coherent processes, electrons taking different paths can interfere and depending on the exact position of \( E_m \) with respect to \( E_F \) this interference can be destructive or constructive. As a result, the total current is a combination of an always positive inelastic part and a interfered elastic signal and the IETS feature can be a peak, a dip or even a derivative-like shape [16, 57, 58]. The important issue to note here is that the spectrum should be anti-symmetric, that is, that when a peak (dip) appears at \( eV = +\hbar \omega \) a dip (peak) will appear at \( eV = -\hbar \omega \). In general the magnitude of the peak and the dip are not the same. This is due to the asymmetric bias dependence of the lead-molecule coupling factors [59].

6.4 The setup

6.4.1 The STM

To perform the experiments, an ultra high vacuum (UHV), low temperature, STM has been used, namely a LT STM, made by Omicron Nanotechnology GmbH, Germany. In the setup that is used the tip is grounded and the bias is applied to the sample plate. The piezo controllers and STM software are a SPM 100 and XPM Pro, version 1.2.2.0, respectively and are made by RHK Technology, Inc., USA. The STM is already equipped with vibrational dampening systems, but to further reduce mechanical vibrations, the entire setup is placed on an active dampening system, model AVI 400S by Stable Table Ltd., Switzerland, and the island on which the STM setup stands is mechanically decoupled from the rest of the building. The main chamber of the STM setup has a base pressure of \( 10^{-11} \) mBar and below and is cooled down to 4-5 K to get rid of thermal noise in the current signal.
6. Thiophenol on Ag(111), topography and IETS

Figure 6.4: A) A diagram illustrating the mechanism of IETS. When the energy difference between tip and sample is large enough \( (eV \geq \hbar \omega) \), electrons can excite a vibrational quantum \( \hbar \omega \) of the adsorbate and still tunnel into the empty states of the sample. B) In \( I(V) \) curves, inelastic processes emerge as kinks at the vibrational threshold value \( \hbar \omega \). These kinks in \( I(V) \) show up as steps in the first derivative and peaks in \( d^2I/dV^2 \), that is being measured in practice. C) and D) represent energy the diagrams for direct (elastic) and inelastic tunneling respectively. E) If the molecular electronic level is close to resonance \( (E_m < \Delta) \), a third tunneling process becomes important, in which an electron emits and reabsorbs a vibrational quantum while tunneling. In this two-phonon process, the initial and final state of the electron have the same energy and hence, this process is elastic.

For performing the STS and IETS measurements, two additional lock-in amplifiers, model SR830 DSP from Stanford Research Instruments, Inc., USA., were connected to the STM, to measure the first and second derivative of the tunneling current. The AC voltage, \( V_{AC} \), that has to be superimposed upon the DC voltage, \( V_{DC} \), for the lock-in amplifiers to work, is supplied by a frequency generator that is incorporated in these lock-ins.
6.5 Results and discussion

6.4.2 The tip

In order to be able to image with the STM, tips were made from tungsten wire, by etching the wire in a NaOH solution (8.5 gr NaOH per 50 mL H2O) while applying a 3.3 V, DC bias over the wire. The resistance of the wire in etching solution is determined to be 263 Ω, resulting in an etching current of 12.6 mA. Scanning Electron Microscopy (SEM) was used to verify that the etched tips have a radius of curvature equal to 50 nm or smaller. Next the tip is placed in the preparation chamber of the STM, which has a base pressure in the order of 10⁻⁹ to 10⁻¹⁰ mBar, to remove any oxide on it. This is done by annealing the tip to the point where it starts to glow by bombarding it with electrons, i.e. e-beam heating. (To prevent deformation of the tip, the glow-time is kept to a few seconds.)

6.4.3 Sample preparation

The silver sample is a single crystal with a surface orientation in the (111) direction, purchased from Surface Preparation Laboratory, the Netherlands. To clean it, it is placed in the preparation chamber of the STM. There the sample is first annealed at 500°C for 45 minutes to remove physisorbed contaminants on the surface, followed by an argon sputtering treatment (at 1500 V, 1.8 µA and an argon pressure of 10⁻⁶ mBar) for 15 minutes to remove any contaminants not removed by annealing. The last step in the cleaning process is another annealing step at 500°C for 15 minutes to obtain atomically flat silver terraces.

Thiophenol was purchased from Sigma Aldrich, with a purity greater than 99.5%, and used as received. Thiophenol molecules were adsorbed onto the silver surface from the gas-phase at room-temperature. The sample was placed in the fast-entry chamber of the STM, which has a base pressure of 10⁻⁷ mBar. There the nozzle of a needle-valve was placed a few centimeters away from the Ag substrate. Since thiophenol is a liquid at room temperature and its vapor pressure is 2 mBar [60], opening this needle valve caused some of the thiophenol to vaporize and enter the fast entry chamber in the gas-phase. There the thiophenol was applied to the substrate at a pressure of 2·10⁻⁶ mBar for 20 minutes.

6.5 Results and discussion

6.5.1 Topography of clean Ag(111)

Before actually applying thiophenol to the clean Ag(111) substrate, its topography was measured to verify that the cleaning procedure had been performed correctly. As is shown in figure 6.5.A, flat terraces have indeed been formed. From the histogram in figure 6.5.B it is clear that the steps between the terraces are 0.24 nm high, which is in excellent agreement with the height of a mono-atomic step of silver in the (111) direction. In other words, the steps are mono-atomic. As a result, it can be concluded

9The silver-silver interatomic distance is 0.289 nm [53] and Ag has a Face Centered Cubic (FCC) unit cell. From its geometry it then immediately follows, that to find the step height in the (111) direction, the interatomic distance has to be multiplied by a geometric factor of \( \sqrt{6}/3 \), which indeed results in a step height of 0.24 nm.
that the cleaning procedure was correctly performed.

6. Thiophenol on Ag(111), topography and IETS

Zooming in, on one of these terraces, resulted in the observance of individual dots on the (111) surface in a hexagonal pattern, as can be seen in figure 6.6. The average distance between the tops of these dots is $0.30 \pm 0.02$ nm, which is in perfect agreement with the interatomic silver-silver distance as measured before with both STM [34] and atomic force microscopy (AFM) [35]. Therefore it can be concluded that figure 6.6 displays an atomically resolved Ag(111) surface.

6.5.2 Topography of thiophenol on Ag(111)

Having verified, that the surface is suitably prepared, thiophenol molecules are applied to it from the gas-phase and the topography of these molecules on the silver substrate is studied with STM. So far, thiol-containing molecules have mostly been applied from a solution to the substrate [27–32]. In this work however, the molecules are applied from the gas phase, to reduce contaminants on the surface as much as possible.

The resulting topography, as shown in figure 6.7, is a self assembled monolayer of thiophenol molecules on silver(111). Figure 6.7A shows that the molecules form domains on the substrate, which have typical sizes between 10 and 20 nm. From figure 6.7B it is clear that each of these domains is build up of periodically repeating units.
6.5 Results and discussion

Figure 6.6: A STM topography image of a atomically resolved Ag(111) surface. The obtained interatomic distance is $0.30 \pm 0.02$ nm. The image was recorded at a bias of -400 mV and a tunneling current of 0.2 nA.

Figure 6.7: STM topography images of thiophenol applied to an Ag(111) surface. A) Domains ranging in size from 10 to 20 nm can be observed. B) Each of these domains contains a periodic structure. Both images were recorded at a bias of -400 mV and a tunneling current of 0.2 nA.

Zooming in on one of these domains, allows for this periodic structure to be determined. This is shown in figure 6.8 where two different kinds of unit cells are superimposed upon the topography data. The sizes of the vectors of the smaller of the two unit cells, figure 6.8C, are $\Gamma_1 = \Gamma_2 = 0.53 \pm 0.04$ nm, resulting in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice.
6. Thiophenol on Ag(111), topography and IETS

The sizes of the vectors of the larger unit cell, figure 6.8D, yield $\Delta_1 = 0.82\pm0.02$ nm and $\Delta_2 = 1.67\pm0.06$ nm, and therefore this periodic structure has a unit cell of $(3 \times 3\sqrt{3})$.

In order to understand these two kinds of unit cells it is necessary to understand what is exactly being observed with the STM. Therefore it is necessary to know the exact orientation of the thiophenol molecules on the substrate. From literature it is known that the thiol-end-group binds to the silver [62] (and references therein) and that the angle $\theta$ the molecule makes with the surface normal lies between 24 and 37 degrees [32,41]. From reference [32] it is also known that the azimuthal angle $\xi$ is zero degrees, or in other words, the plane of the phenyl ring of the molecule is perpendicular with the surface of the substrate. This orientation is shown in figure 6.9 and from it is clear, that the highest part of the molecule, the part that is supposedly imaged by the STM, consists of the molecule’s top two hydrogen atoms [11]. Consequently, distances $B_1$ and $B_2$ in figure 6.8B correspond to the length and the height difference between the top two hydrogen atoms of a thiophenol molecule respectively and these distances can be used to calculate the angle $\theta$ the molecule makes with the surface normal. From $B_1 = 265$ pm and $B_2 = 90$ pm it follows that $\theta = 32$ degrees, which is in excellent agreement with the abovementioned literature. From this it can be concluded that it are indeed the hydrogen atoms of the thiophenol that are imaged. Therefore, at least a part of, the current flows through these hydrogen atoms. As will be seen in the next section, this is important for determining the correct assignment of some of the IETS features to the molecular vibrations.

Now it is clear what is observed with the STM, the two periodicities can be explained. For the smaller periodicity, i.e. the $(\sqrt{3} \times \sqrt{3})R30$ unit cell, each point of the cell corresponds to a single thiophenol molecule. However, the molecules still have one orientational degree of freedom, namely the rotation angle $\varphi$ around the surface normal. Under the influence of van der Waals forces, the molecules orientate themselves on the substrate with different angles $\varphi$, resulting in the larger $(3 \times 3\sqrt{3})$ unit cell.

It is not always possible to resolve the internal structure of the thiophenol molecules. As is shown in figure 6.10, the resolution can be limited to observing the individual molecules or even only resolving the $(3 \times 3\sqrt{3})$ unit cell.

---

10 Here Wood’s notation [61], i.e. $(\sqrt{3} \times \sqrt{3})R30$, has been used for the expression of the unit cell. The thiophenol unit cell is build up out of vectors that have sizes that are $\sqrt{3}$ times bigger than the vectors that span the unit cell of the silver substrate. The orientation or the thiophenol unit cell vectors is rotated by 30 degrees compared to those of the silver substrate, hence the “$R30$” suffix.

11 As will be shown later, the resolution of the STM images is not always good enough to resolve the individual hydrogen atoms. As a result, one can sometimes only observe the individual molecules or even only the larger larger periodic structure.

12 It can be easily seen that the points of the $(3 \times 3\sqrt{3})$ periodicity all correspond to points on the $(\sqrt{3} \times \sqrt{3})R30$ periodicity.
6.5 Results and discussion

Figure 6.8: STM images of individually resolved thiophenol molecules on the Ag(111) substrate. A) The topography of the substrate. The white diagonal line shows where the height profile of B) has been taken. B1 and B2 indicate the length and height difference between the two points marked in B) respectively and their values are as follows: B1 = 265 pm and B2 = 90 pm. C) and D) show the same data as in A), but this time with two different periodic structures, including their respective unit cells, superimposed on top of it. The sizes of the unit cell vectors are as follows: for C) $\Gamma_1 = \Gamma_2 = 0.53 \pm 0.04$ nm, and for D) $\Delta_1 = 0.82 \pm 0.02$ nm and $\Delta_2 = 1.67 \pm 0.06$ nm. The image was recorded at a bias of -400 mV and a tunneling current of 0.2 nA.
6. Thiophenol on Ag(111), topography and IETS

6.5.3 IETS and STS of thiophenol on Ag(111)

Inelastic electron tunneling spectroscopy (IETS) and scanning tunneling spectroscopy (STS) have been performed on these SAMs of thiophenol on silver(111). Figure 6.11 shows such measurements. The $I(V)$ spectrum, figure 6.11.A, displays the tunneling current and the oscillations on the graph are caused by the applied modulation signal $V_{AC}$.

Figure 6.11.C shows the second derivative of the current, or in other words the

![Diagram of a thiophenol molecule on Ag(111)](image_url)

**Figure 6.9:** A schematic representation of the orientation of a thiophenol molecule on the silver(111) substrate. The angle with the surface normal, the azimuthal angle and the angle around the surface normal are represented by $\theta$, $\xi$ and $\varphi$ respectively.
6.5 Results and discussion

IET spectrum, and several peaks and dips can be observed. The anti-symmetric peak (dip) at 96 ± 7 (−92 ± 8) mV is attributed to the \( CH \) out-of-plane bending mode \( (\gamma CH) \) \[42\]. The peak at positive voltage shows a much higher intensity than the dip at negative voltage; their intensities are 2.0 and -0.9 nA/V\(^2\) respectively. As is explained in section 6.3.3, this could be due to the asymmetry in the tunnel contact. Another anti-symmetric peak (dip) is visible at 19 ± 3 (−16 ± 4) mV. For these energies no vibrations have been observed for thiophenol on silver \[42\] and the observed IETS features can not be assigned to a molecular vibration of the thiophenol. Besides molecular vibrations, the IET spectra can also include contributions from the tip and sample electrodes themselves \[63\]. For silver, surface phonons have an energy of 20 meV \[38–40\], indicating that the observed IETS features can be ascribed to this silver phonon mode \[14\]. Although this interesting feature can be found in almost all IETS experiments, it is never explicitly mentioned, except for \[64\] and \[54\]. In fact,

As can be seen more clearly in figure 6.16 there is a small shoulder at 111 mV, that could be related to another \( CH \) out-of-plane vibration. However due to the broadening of the spectrum it is very hard to see this feature clearly and care should be taken in interpreting it.

Another surface phonon mode has been measured for silver(111) \[38,39\], but since this mode occurs at 10 meV it cannot be used to explain the features in the IET spectrum.
6. Thiophenol on Ag(111), topography and IETS

the work of Taylor [63] is the only systematic study of the phonon contributions from the electrode to the IETS signal. Lastly there is the feature at 52 ± 4 (−54 ± 4) mV. According to the theory of Galperin et al. [57] this feature could be a molecular vibration that, for positive bias, shows up as a dip instead of a peak. This would then be caused by a two-phonon process whereby an electron emits and re-absorbs a vibrational quantum, see section 6.3.3. For such two-phonon process to occur, the vibrational level needs to be close to resonance, i.e. close to the Fermi level of the system. However, this would imply that the vibration found at +20 mV, which lies even closer to the Fermi level, would also have to appear as a dip, since it would also be close to resonance. Clearly this is not the case; the feature at +20 mV is a peak. Also, in literature dips have been found in experimental STM-IET spectra [16] for positive voltages, but in that case all features at positive bias were dips and not a mix of dips and peaks. Therefore it is unlikely that the feature at 52 mV is a molecular vibration and it is considered to be an artifact, i.e. it is thought to be the minimum between the other two peaks.

The first derivative $\frac{dI}{dV}$, as shown in figure 6.11B, corresponds, in first order, to the density of state (DOS) of the system. The data indicate, that, even for low voltages, the DOS does not go to zero, despite the fact that thiophenol itself has a bandgap of several eV; the HOMO and the lowest LUMO for thiophenol bonded to silver lie at -1.09 and 2.55 eV respectively [65]. Hybridization of the $sp$-electrons of the silver with $\sigma$ and $\pi$ electrons of the thiophenol molecule, results in the broadening of the HOMO and LUMO levels and the formation of states near the Fermi-level, the so-called metal induced gap states (MIGS) [65–69].

In figure 6.11B it can be seen that the $\frac{dI}{dV}$ signal is non-symmetric around 0 V, a result that differs from the density of state calculation performed for thiophenol on Ag(111) by Heimel et al. [65]: for voltages up to ±400 mV Heimel et al. find a density of states that is symmetric around zero Volt. In the same paper [65] Heimel et al. show that a dipole is present in the thiophenol-silver system and that it is comprised of two parts, namely the intrinsic dipole of the molecule and the interfacial dipole that is the result of the bond formation between the docking group of the molecule and the metal surface. By applying a bias over tip and substrate, this dipole will try to align itself along the field lines between tip and substrate. From literature it is known that alignment of the dipole of the molecule with the applied field can lead not only to conformational changes of the molecule [70] and to changes in the current [71], but can even result in an non-symmetric $\frac{dI}{dV}$ spectrum [72]. In this particular case, the alignment of the dipole with the field causes the angle the molecule makes with the surface normal to be varied. Depending on the sign of the electric field, the angle the molecule makes with the normal of the surface will be increased or decreased. Since the molecule will change its orientation, the overlap of the wave functions of tip and molecule will vary as well. The derivative $\frac{d}{dV}$ of equation 6.3.2 is proportional to the overlap of the wave functions between substrate and tip, i.e. $\frac{d}{dV}(V) \propto |M(E_{F,s} + eV)|^2$. Since this overlap will be non-symmetric in voltage, due to the reorientation of the molecule under the influence of the electric field, the first derivative of the current will be asymmetric as well. As a result, the first derivative of the current can no longer be considered to solely represent the DOS of the substrate. This fact explains the difference between the results in figure 6.11B.
6.5 Results and discussion

Figure 6.11: dI/dV and IET spectra. The $I(V)$, $dI(V)/dV$ and $d^2I(V)/dV^2$ spectra are shown in A), B) and C) respectively. Figure D) shows $dI/dV$, where the measured graph is a zoom-in of the data in figure B) and the calculated graph is the numerically integrated $d^2I/dV^2$ signal of figure C). The spectra are taken from $-400$ mV to $+400$ mV with $4$ mV steps and are the average of $20$ individual scans. The parameters for the AC voltage are $V_{AC} = 20$ mV, $1060$ Hz. The STM tip was placed above the substrate at a bias of $-400$ mV and a tunneling current of $0.2$ nA. $T = 4.8$ K

and the results of Heimel et al. [65]: Heimel et al. show a spectrum that represents the pure DOS of the substrate and they do not incorporate the effect of an externally applied electric field in their results.

One way to prove that the asymmetry in the first derivative spectrum is caused by a change in the overlap of the wave functions of the tip and the substrate, is to measure $dI/dV$ for different tip-substrate separations. The further away the tip is from the substrate, the smaller the electric field will be (for the same applied bias). Therefore the dipole will be affected less by this field and the change in the orientation of the molecule will be less as well. As a result the $dI/dV$ spectrum is expected to be more symmetric.

From 0 to 40 mV there is a strong decrease in the $dI/dV$ signal, the so-called zero bias feature (ZBF). In literature this ZBF is observed on several occasions [22, 23, 73].
but its physical origin is not fully understood. Nevertheless, some comments can be made about it. Since the ZBF has been observed for different molecular species, namely for thiolate-molecules with a backbone that is either conjugated (this work), non-conjugated [22], or partially conjugated [23] and for carbon monoxide [73] as well, it is unlikely that it is specifically the thiophenol molecule that is the cause of this feature. Not only did Kushmerick et al., Troisi et al. and Gregory et al. [22,23,73] use different molecules in their experiments, but they used a different metal as well, i.e. gold instead of silver. Similarly, for nitric oxide (NO) on Rh(111) Hagelaar [74] also observed a strong increase in his $\frac{dI}{dV}$ signal for voltages up to 50 mV. Therefore, this effect is substrate independent as well. From the discussion above it is already known that the second derivative spectrum, $\frac{d^2I}{dV^2}$, has a contribution at 20 mV that has been associated with the phonon modes of the silver substrate. Numerically integrating the second derivative gives a curve that, for small voltages, is comparable to the measured first derivative (figure 6.11.D), leading to the interpretation that the increase in the $\frac{dI}{dV}$ signal for 0 to 40 mV is also caused by these phonon modes. However, for pure silver(111) the $\frac{dI}{dV}$ signal does not show an increase in the signal around 0 V, but is completely flat and featureless [36,37].

A possible explanation is that the silver surface phonons at 20 meV [38,39] couple to the molecule and form a Kondo like feature in the first derivative and a Fano-like shape in the second derivative, which is more pronounced than the phonon mode would be by itself. To be able to speak about a Kondo effect, a small system, for example a magnetic impurity atom, has to be coupled to a continuum of free electrons, namely the free electrons of the substrate. Since the silver-sulphur bond between the molecule and the substrate is strong [62], this results in strongly bound electrons (localized in energy) that act as scatterers for mobile electrons and this bond can be considered to be an impurity. For coupling of this impurity to the substrate to occur, it is needed that the impurity is close to the electrode, which it certainly is in the case of the AgS bond. While the feature in $dI/dV$ occurs at 0 V, as it should be in the case of a Kondo effect, it is a dip and not a peak, as is usually the case for Kondo behavior. Twenty years ago, Baratoff and Persson not only predicted the presence of a Kondo like feature for STM-IETS measurements on molecules chemisorbed on a metal surface, but they also predicted that the $dI/dV$ signal should show a “fingerprintlike decrease”, as is the case in the measurement shown in figure 6.11.B (as well as in figure 6.12.B) [76,77]. Baratoff and Persson relate this phenomenon to “elastic contributions, involving virtual phonon emission and reabsorption, which vary rapidly near the inelastic threshold”, a process that is similar to the mechanism proposed by Galperin et al [57] to describe the appearance of dips in the IET spectrum for positive voltages. What is thought to give rise to the Kondo like dip in $dI/dV$ in this work, is the interference that occurs between, on one hand, the tunneling channel in which electrons tunnel directly from the tip to the (continuum) states of the substrate and, on the other hand, the tunneling channel through the orbital of

---

15 These spectra from literature do show a step-like feature at -67 mV that is due to the onset of the Shockley surface-state band [75], but since the entire substrate is covered by thiophenol molecules in this work, this surface effect is not present and cannot be used to explain the observed ZBF.

16 For a brief explanation of the mechanism of virtual phonon emission and reabsorption the reader is referred to section 6.3.3.
the (localized) \( AgS \) bond. Both channels can interfere because both of them involve elastic tunneling. For direct tunneling this is self-evident, since there is no interaction of the electron with the molecule that allows for the loss of vibrational energy. For tunneling through the \( AgS \) bond it is believed that there is virtual phonon emission and absorption of the silver surface phonons at 20 meV that leads to elastic tunneling as well.

Experimentally, such a fingerprint like decrease has been observed in scanning tunneling spectroscopy studies of single-atom magnetic impurities on noble metal surfaces, where the decrease in \( dI/dV \) was attributed to be a Kondo effect where interference between the various tunneling pathways resulted in a dip, rather than a peak, as well. \[78–80\]. The Kondo effect is usually regarded as a spin-related phenomenon, namely the coherent exchange of the spin between a localized state (impurity) and a Fermi sea of delocalized electrons. Lately however, it is shown that the role of the spin could be replaced by other degrees of freedom, \[81–83\] and it is therefore possible that thiophenol, a non magnetic molecule, can give rise to a Kondo like effect when it is attached to a silver surface.

By looking ahead and comparing figures 6.11.C, 6.12.C and 6.13.A with one another it can be observed that the peaks around 20 meV have both different intensities (heights) and widths. More specifically, the higher the peak, the broader it becomes as well. From literature it is known that the widths (FWHM) of IETS peaks do not depend on their heights \[84\], while the height and width of a peak are related in the case of a Fano resonance \[85\]: the stronger the coupling of the impurity with the phonon mode, the higher and broader the Fano peak will become. Not only do these facts give further credence to the notion that the feature observed at 20 mV in the IET spectra is indeed a Fano resonance, the different heights and widths of these peaks also explain why no \( CH \) vibration can be observed in figure 6.12.C. As the Fano resonance becomes very high and broad, it masks the presence of any phonon modes beneath it, including the \( CH \) out of plane vibration at 90 meV in the case of figure 6.12.C.

Another example of an IET spectrum recorded on thiophenol on Ag(111) is shown in figure 6.12, together with the accompanying \( dI/dV \) graph. The white dot in the topography image of figure 6.12.A shows where the spectra were recorded. Just as with figure 6.11, the \( dI/dV \) signal is found to be non-symmetric and the graph also displays a strong increase of the signal for 0 to 40 mV. For a detailed description of these features, the reader is referred to the discussion above about the \( dI/dV \) spectrum of figure 6.11.

The second derivative shows a number of features; at \( 22 \pm 4 \) (-23±4) mV there is a peak (dip) in the spectrum and it is ascribed to the above mentioned Kondo effect, where the phonon modes of the silver substrate [38–40] couple to the molecule. Compared to the results of figure 6.11, the phonon modes in this experiment have a far larger intensity. As already mentioned above, it is reasoned that this (Fano) peak is larger in intensity because of a stronger coupling of the molecule to the substrate.

At around 160 (-160) mV there is another feature, but it is very small, indicating a weak electron phonon coupling. This feature is ascribed to the \( CC \) stretch mode \( (\nu_{CC}) \) at 164 mV [42]. However, the noise present at this feature makes a clear assignment to a molecular vibration difficult and care must be taken with the
Figure 6.12: Graphs of an IETS experiment. The topography is shown in A), where the white dot indicates the position where the $dI(V)/dV$ and $d^2I(V)/dV^2$ spectra, shown in B) and C) respectively, were recorded. Figure D) shows $dI(V)/dV$, where the measured graph is a zoom-in of the data in figure B) and the calculated graph is the integrated $d^2I(V)/dV^2$ signal from figure C). The spectra are taken from −400 mV to +400 mV with 4 mV steps and are the average of 29 individual scans. The parameters for the AC voltage are $V_{AC} = 20$ mV, 1060 Hz. Imaging was performed at a bias of −400 mV and a tunneling current of 0.2 nA. $T = 4.8$ K

interpretation of this peak (dip). At 104 ± 4 (−99 ± 5) mV there is third feature. For positive voltage this feature is a dip, whereas the other two features are peaks. Similar to the reasoning applied to the dip found at +52 mV in figure 6.11 C, this feature is not considered to be a molecular vibration; the feature at +22 mV is a peak and the two phonon-processes that can occur near resonance and lead to dips in the second derivative of the current for positive bias [57] do not play a role. Therefore the feature is thought to be the minimum (maximum) between the two other peaks (dips)

Clearly, a different molecular vibration is observed in figure 6.12 compared to that of figure 6.11. While the increased intensity and width of the peak at 22 mV might explain the disappearance, i.e. masking, of the peak at 90 mV, it can not explain why
6.5 Results and discussion

there now is a peak visible at 160 mV. A possible reason for this is, that electrons can take different tunneling paths through the molecule and thereby excite different vibrations; In the work by Troisi et al. [23], it is shown that there are multiple ways for an electron to tunnel from the tip to the molecule (or vice versa). The first route is by tunneling to the \( \sigma \)-orbital of the hydrogen atom of the molecule and then moving to the \( \pi \)-orbital of the conjugated part of the molecule by the out of plane \( CH \) vibration. With the second route, the electron tunnels directly from the tip into the \( \pi \)-orbital of the carbon backbone and excites a vibration over there. The first route is evidenced in figure 6.11 whereas the second route is observed in figure 6.12.

It should be noted, that in the work of Troisi and his colleagues [23], both vibrations are measured simultaneously, while in this work they are measured in separate experiments. This can be explained by the different kind of setups that have been used; Troisi et al. worked with a cross-wire geometry that involves multiple (hundreds if not thousands of) molecules in parallel, thereby enabling different pathways to be taken simultaneously. In this work, a STM configuration is used that, due to the exponential decay of the tunneling current, measures the current (and its derivatives) on a single molecule. Depending on the exact position of the tip on the substrate, either one of the possibilities pathways is followed and one of the vibrations is observed. Since the exact position of the tip on the substrate could not be determined for the experiment in figure 6.11 due to poor topography imaging, it is impossible to verify that the tip was placed on a different position of the sample compared to that of figure 6.12.

![Figure 6.13](image.png)

**Figure 6.13:** An IET spectrum, A), with its corresponding topography image in B). The white dot in B) represent the location on which the IET spectrum in A) was recorded. The spectrum is taken from –400 mV to +400 mV with 4 mV steps and is the average of 10 scans. The parameters for the AC voltage are \( V_{AC} = 20 \) mV, 1060 Hz. The topography image was made at a bias of –400 mV and a tunneling current of 0.2 nA. \( T = 4.8 \) K.

To verify that, depending on the position of the tip on the substrate, different vibrations can be observed, another IETS experiment has been performed, see figure 6.13. In this experiment the tip was placed exactly above one of the thiophenol
molecules, whereas for figure 6.12 A this was not the case. The IET spectrum of figure 6.13 shows a peak (dip) at 22 ± 4 (−23 ± 4) mV, which is attributed to the Kondo effect where the molecule is coupled to the phonon modes of the silver substrate [38–40]. At 91 ± 3 mV a small peak is observed that is assigned to the γCH vibration at 92 mV [42]. At negative bias, no dip is observed around −92 mV, but the combination of the noise present at this voltage and the presence of the feature at −69 ± 5 mV, which has a width of 56 mV at its base, can mask the presence of this vibration. Especially since the amplitude of the vibration observed for positive bias is small, it can be expected that the feature at negative bias is small as well. A dip (peak) is observed at 64 ± 4 (−69 ± 5) mV. Similar to the previous two IETS experiments, this feature is not ascribed to a molecular vibration; Since the feature at +22 mV is a peak, not a dip, it indicates that two-phonon processes [57] do not occur in this experiment and that for positive bias all observed molecular vibrations should appear as peaks in the IET spectrum, which is not the case for the dip at 64 mV.

By comparing the IETS results of figure 6.12 with those of figure 6.13 it can be seen, that performing IET spectroscopy on various positions on the surface, results in the excitation of different molecular vibrations. As discussed above, this is thought to be related to the position of the tip on the substrate; different positions on the substrate allow for different tunneling paths to be taken through the molecule, which results in the excitation of different molecular vibrations [23]. In the next section, this point is addressed in further detail.

By comparing the IET spectra of figures 6.11 and 6.13 it can be seen, that the peaks of both the phonon modes at 20 mV and the γCH vibrations at 92 mV have different intensities for both experiments. Just as with the comparison between the intensities of the peaks at 20 mV of figures 6.11 and 6.12, these differences are ascribed to a different coupling of the molecule to the substrate.

For the latter these differences in intensity are thought to be the result of different orbitals of the tip contributing to the current [54]. From the work of Hagelaar [54] it is known that changes in the intensity of the IETS signal can be related to a difference in the imaging of the surface by the STM tip. Hagelaar shows that when different orbitals of the tip contribute to the tunneling current that this not only results in a different topography, but in the observation of IETS features with different intensities as well. Though the relation between the tip orbitals contributing to the tunneling current and the resulting STM image is not explicitly known in this work, it is clear that the obtained imaging is not always the same (see figure 6.10) and the imaging was certainly different for these two IETS experiments 17. Therefore, these differences in the intensity of the IETS peaks at 20 mV is ascribed to the variation of the orbitals of the tip that contribute to the tunneling current.

For electrons to pass from tip through the molecule to the silver substrate, or vice versa, they will have to move through the CS and AgS bonds as well, but no IETS features are observed in the spectra that correspond to molecular vibrations of these bonds. A possible reason for not observing these vibrations in the IET spectra is, that

17The quality of the imaging, that accompanies the data of figure 6.11 was so poor, that no topographic features could be discerned and as such it is not taken up in this work. Nevertheless, from this fact it can still be concluded, that there is a clear difference between the imaging of both experiments, since figure 6.13 A does show a topography with discernable features.
6.5 Results and discussion

the energies at which these vibrations occur lie close to the energies of the vibrations that are observed. For example, the AgS stretch mode ($\nu_{AgS}$) lies at 30 meV [42], which is close to the phono mode of the silver at 20 meV. Since the full width at half maximum (FWHM) of the peak at 20 mV is on average 30 meV, it is possible that the silver phonons mask the presence of the $\nu_{AgS}$ vibration.

6.5.4 Computational results and comparison with measurements

The results for both the gold and the tungsten tip are presented in this section.

Results for the gold tip

Using the model described in section 6.2 IET spectra were calculated for the six different positions shown in figure 6.1. The results are shown in figures 6.14 and 6.15.

The output of a single calculation consists of the vibrational energies, together with the respective intensities of these vibrations, of the 33 vibrational modes of the thiophenol molecule $^{18}$, as indicated by the vertical bars in figure 6.14.A to F. To create an actual IET spectrum out of these bars, each of the 33 intensities is multiplied by a Gaussian with a width $W$ $^{19}$ equal to:

$$W = \sqrt{(W_I)^2 + (1.7V_{AC})^2 + (5.4k_BT/e)^2},$$

where $W_I$ is the intrinsic line width broadening (which is set to 4 mV [84]), $V_{AC}$ is the modulation signal, $k_B$ is the Boltzmann constant, $T$ the absolute temperature and $e$ the elementary charge. Using the same values as for the experimentally determined IET spectra, namely $V_{AC} = 20$ mV and $T = 4.8$ K, results in a total width $W$ of 34 mV. Adding all the broadened vibrational peaks together, results in the IET spectra of figure 6.14.

As can be seen from figure 6.14 the results of the calculations differ for the different STM positions above the thiophenol molecule. The calculated intensities of each of the 33 vibrational modes are different for the three separate positions, resulting not only in spectra with different magnitudes, but with different shapes as well. For position 1, figure 6.14.A, the major contribution is from mode 15, while for position 3, figure 6.14.C, the main mode is number 8. In between positions 1 and 3, i.e. at position 2, the major contribution to the spectrum lies more or less halfway between those of positions 1 and 3 (albeit at a much lower overall intensity), as can be seen from figure 6.14.B, since both mode 8 and 15 contribute with (almost) equal intensity. The results for positions 4 and 5 are very similar to those of figure 3, only is there an intensity difference between them. For position 6 it is mode 19 that gives the largest inelastic contribution.

$^{18}$The number of internal (molecular) vibrations that a non-linear molecule has is equal to $3N - 6$, where $N$ is the number of atoms out of which the molecule is build up. In the case of thiophenol $N = 13$.

$^{19}$This width $W$ is the full width at half maximum (FWHM) and not the standard deviation $\sigma$ of the Gaussian. The relation between $W$ and $\sigma$ is as follows: $W = 2\sqrt{2}\ln(2)\sigma$. 

135
6. Thiophenol on Ag(111), topography and IETS

Figure 6.14: Several graphs showing the calculated IET spectra for different tip positions above the molecule. Graphs A, B, C, D, E, and F correspond to the IET spectra calculated with the STM tip placed at positions 1, 2, 3, 4, 5, and 6 of figure 6.1, respectively (as is also indicated by the encircled numbers in the figures). The positions of the bars in each of these graphs show the vibrational energy and their heights show the intensity of all calculated molecular vibration modes. The numbers on some of the bars are labels that specify the specific vibration mode. Applying a FWHM broadening of 34 meV to each of these bars, resulted in the full IET spectra shown in A) to F).
6.5 Results and discussion

To more clearly show the difference between the separate positions, all spectra of figure 6.14 are plotted in one graph in figure 6.15 (for both positive and negative bias). From figure 6.15 it is clear, that there are large intensity differences between the different positions. Not only that, but the intensities of the graphs taken on positions next to the molecule (positions 4 to 6) can actually be higher than those taken at positions above the molecule (positions 1 to 3). For example the spectra calculated for position 5 has the highest overall intensity. However, one should take into account that these IETS spectra are normalized, i.e. \( \frac{d^2I}{dV^2}/(dI/dV) \) is plotted instead of \( d^2I/dV^2 \). As a result, the plotted intensity is a measure for the ratio between inelastic and elastic tunneling that takes place (at that energy) and not an absolute measure for the (inelastic) tunneling current.

![Graph showing the same IETS data as in figure 6.14 but now all spectra are plotted in one single figure (to better show the variation of the IETS signal as function of the tip position) and both positive and negative biases are depicted.](image)

Figure 6.15: A graph showing the same IETS data as in figure 6.14 but now all spectra are plotted in one single figure (to better show the variation of the IETS signal as function of the tip position) and both positive and negative biases are depicted.

To get further insight into what happens at the different tip positions, the energies and intensities of the major modes contributing to the IET spectra at these positions are given in table 6.1 together with the corresponding schematic representations of

\[ \text{The higher the normalized intensity, the larger the percentage of inelastic tunneling is.} \]
6. Thiophenol on Ag(111), topography and IETS

The movement of the atoms of the molecules for the different vibrational modes. The plus (+) and minus (-) signs indicate the (simultaneous) out-of-plane and into-plane movement respectively. The Greek letters $\alpha$ and $\beta$ indicate the top two hydrogen atoms and correspond to the $\alpha$ and $\beta$ of figure 6.1.

<table>
<thead>
<tr>
<th>Peak Nr</th>
<th>Voltage (mV)</th>
<th>Intensity (1/V) @ position</th>
<th>Normal mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22</td>
<td>0.68</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.32</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>84</td>
<td>0.91</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.68</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>89</td>
<td>0.87</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>107</td>
<td>1.63</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.15</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>118</td>
<td>2.79</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.76</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>134</td>
<td>1.19</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>159</td>
<td>1.34</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: The vibrational energies and intensities of the most important vibrational mode of thiophenol, together with a schematic representation of the motion of the atoms of the molecule for each mode. The plus (+) and minus (-) signs indicate out-of-plane and into-plane movement respectively. The Greek letters $\alpha$ and $\beta$ indicate the top two hydrogen atoms.
6.5 Results and discussion

By combining the results of figures 6.1 and 6.14 and table 6.1 it can be seen that for position 3, the tip is above hydrogen atom $\beta$ and that the major contribution comes from mode 8, which has a large (out-of-plane) movement amplitude of hydrogen atom $\beta$ but no movement of hydrogen atom $\alpha$. However, when one goes to position 1 (above hydrogen $\alpha$), the major contribution comes from mode 15, which has a large (out-of-plane) movement amplitude of hydrogen atom $\alpha$ and a not so large amplitude for hydrogen atom $\beta$. From these results it can be concluded that, depending upon the exact position of the STM tip above the thiophenol molecule, the electrons can indeed take a different path through the molecule and thereby excite different molecular vibrations, as was proposed in the previous section.

For the spectrum calculated at position 4 the ratio between the intensities of the individual (normalized) vibrational modes is almost the same as those of the spectrum calculated at position 3, as can be seen by comparing figures 6.14.C and D. In other words, the shapes of both spectra are similar. Their overall intensities, however, are not, as can most easily be seen from figure 6.15. That the shapes of both spectra are similar can be seen as follows: since position 4 lies closest to position 3 and tunneling drops exponentially with distance it is therefore to be expected that the spectra of these positions have a similar character. The spectrum at position 5 is also similar in shape to that of the spectrum at position 3. Since position 5 lies (almost) as close to position 1 as it lies to position 3, one might expect a spectrum that has a character that is a combination of the characters of both positions 1 and 3, but apparently the character of position 3 dominates. Why this is so is not 100% clear.

At position 6, it is mode 19 that dominates, but why this is the case is not clear. However, since the overall (normalized) intensity of the IET spectrum at position 6 is far lower than the intensity of all other spectra, which indicates that only a small part of the tunneling occurs inelastically, it means that a small increase in the occurrence of a specific molecular vibration has a relatively large influence on the spectrum.

To see how representative the model is, its results are compared to an actual IETS measurement. Figure 6.16 shows both the calculated data of figure 6.14.C (position 3) and the IETS signal of figure 6.11.C, where for the latter the $d^2I/dV^2$ signal has been normalized by dividing it by the (simultaneously recorded) $dI/dV$ signal.

From figure 6.16 it can be seen that there is a good match between the experiment and the calculation; both methods give peaks at around 20±3 and 90±5 mV and even the intensities are within a factor 5±2 of one another. From the fact, that the overall intensity of the calculation is higher than the intensity for the measurement, it can be concluded that the model slightly overestimates the (relative) inelastic contribution compared to the elastic one.

What can also be seen, is that the exact positions of the maxima of the peaks around 20 and 90 mV occur are slightly different for the calculation and the measurement. For the peak around 90 mV this is not so surprising, since there are many vibrational modes that contribute to the IETS signal in that energy range (as can be seen in figure 6.14) and changing the position of the tip above the substrate can easily shift the energy where the maximum of the calculated spectrum occurs to a value above that of the position of the measured maximum. For example, at position 1 of the calculation, figure 6.14.A, the maximum of the spectrum occurs at 117 mV, which is an energy well above that found for the measured spectrum.
6. Thiophenol on Ag(111), topography and IETS

Figure 6.16: The measured and calculated IET spectra of figures 6.11.C and 6.14.C (position 3) respectively.

The origin of the peak around 20 mV is more subtle to explain. For the measurements it was concluded that the observed peak corresponds to a Fano resonance that is due the coupling of the phonon modes at 20 mV [38–40] to the molecule, but the phonon modes of the metal contacts are not explicitly taken into account in the calculation, making a direct comparison between experiment and calculation difficult. For the calculation it is mode 2 at 22 mV that gives the major contribution to the IET spectrum in that energy range. It could be argued that binding of the thiophenol to the silver substrate and/or the interaction that one thiophenol molecule has with its neighbors in the SAM results in a shift of the IETS peak towards the measured value of 19 mV. However, since the calculation was performed on a single molecule and not on a SAM it is impossible to estimate the influence that neighboring thiophenol molecules have on one another. Nevertheless, it would be desirable to determine whether it is the phonon mode of the silver substrate, or the (shifted) C-S out of plane vibration of the thiophenol, or a combination of both, that gives rise to the peak found at around 20 mV. Two conceptually straightforward options

\[^{21}\text{This mode corresponds to the } \gamma_{\text{CS}} \text{ (C-S out of plane) vibration Joo et al. found in their Raman measurements at 23 mV [42] for pure thiophenol.}\]
6.5 Results and discussion

to determine which effect(s) contribute(s) to the peak at 20 mV would be to include the phonon modes of the contacts in the calculation and perform the calculation on an entire monolayer instead of a single molecule. However, practically it would be very difficult to implement these improvements in the model [43, 86]. To determine whether the silver phonon modes are present or not, an IETS measurement could be performed on pure Ag(111).

While the measured IET spectrum of figure 6.11C matches well with the calculations, this is not the case for the spectrum of figure 6.12. Figure 6.17 shows the measured spectrum of figures 6.12C together with the calculated spectrum of figure 6.14C (position 3). There still is a good match between measurement and experiment for the peak around 20 mV, but while the calculation predicts a major contribution of the \( CH \) out of plane vibrations (around 90 mV) \(^{22}\), no peak is visible in that energy range for the measured spectrum. Similarly, there is no good match of the measured spectrum with the spectra calculated for the other five locations.

![Figure 6.17: The measured and calculated IET spectra of figures 6.12C and 6.14C (position 3) respectively.](image)

\(^{22}\)Which were also observed experimentally [23, 42].
6. Thiophenol on Ag(111), topography and IETS

The measured and calculated spectra is not hard to explain, since the calculated spectra do not take the Kondo effect into account.

**Results for the tungsten tip**

Another set of IETS calculations has been performed with a tungsten tip (whose configuration and positioning is depicted in figure 6.2). The results are shown in figure 6.18.

![Image](image.png)

**Figure 6.18**: The IETS results obtained with the tungsten tip. In A) the effect of the height of the tip above the molecule on the IET spectrum is shown. B) shows how the IET spectra depend on the (lateral) position of the tip above the molecule. In C) and D) the identical locations for the gold and tungsten tips are compared: C) shows the results for position 1 of the gold tip, which corresponds to position A2 of the tungsten tip and D) shows the results for position 3 of the gold tip, which corresponds to position D2 of the tungsten tip. In D) the experimental results of figure 6.11 are depicted as well. The labels A1 to D2 refer to the positions of the tungsten tip above the substrate, as defined in figure 6.2. Similarly, the numbers 1 and 3 refer to the positions of the gold tip above the substrate, as defined in figure 6.1.

From figure 6.18 it is clear that (small) variations in the height of the tip above the molecule hardly influence the outcome of the (normalized) IET spectrum. For the
6.5 Results and discussion

other three lateral positions (data not shown) the effect of this height difference was very small as well. Provided that the height variation of the tip is not too large, this behavior is to be expected; a small variation in the height will not result in different overlap of the wave functions and, as a result, the IET spectrum is the same. If this height difference is large, it is quite possible that the overlap becomes different, resulting in a different IET spectrum. One way to establish when the height variation is big, would be to perform additional calculations at different heights of the tip above the molecule and see at what height the spectrum starts to change significantly.

Just as with the gold tip, the exact shape of the spectrum depends on the lateral position of the tip above the substrate (as can be seen from figure 6.18.B) and is indicative of different vibrations being excited at the various positions.

Since two positions of the tungsten tip correspond to those of the gold tip it is possible to perform direct comparisons between the tips and this has been done in figures 6.18.C and D. Figure 6.18.C shows the results for position 1 of the gold tip, which corresponds to position A2 of the tungsten tip and figure 6.18.D shows the results for position 3 of the gold tip, which corresponds to position D2 of the tungsten tip. For both positions it is clear that both the overall intensity, as well as the line shape, are not exactly the same for the gold and tungsten tips.

The overall intensity of the spectrum is approximately five times higher for the gold tip compared to the tungsten tip. This might at, first glance, seem to be a big difference, but the most important thing is that the overall intensity is “reasonably close”, i.e. within one order of magnitude, to the intensity of the measurements, which is for both tips. Also note, that even for the same tip, i.e. the gold tip in this case, the intensity can vary in magnitude by more than a factor of five as well.

For both tips, the CH out of plane vibrations contribute strongly to the IET spectra, but while these vibrations completely dominate the spectrum in case of the gold tip, it is the CS stretch vibration at 134 mV that has the largest contribution to the spectrum for the tungsten tip.

Figure 6.18.D also shows the experimentally obtained IET spectrum of figure 6.11.C. It can be seen that the shape of the spectrum of the gold tip more closely resembles the experimental data than that of the tungsten tip, while the overall intensity of the measurements lies closer to that of the tungsten tip.

From the comparison between the gold and the tungsten tips it is clear that the tip configuration has a considerable effect on the calculated spectra. Not only that, but, compared to the gold tip spectrum, the spectrum for the tungsten tip overestimates the CS stretch vibration. As a result, the gold tip spectrum more closely resembles (the shape of) the measured spectrum. These two observations indicate, that the role that the tip has on the spectra is significant and needs to be studied in further detail. The way to do so, would be to perform additional calculations with tips of the same material, preferably tungsten, but with different geometries and different amounts of atoms constituting the tip.
6. Thiophenol on Ag(111), topography and IETS

6.6 Conclusions

In this chapter, results on the topography, as well as the IETS, of thiophenol, deposited on silver(111), have been reported.

For the clean silver substrate, atomic resolution of the substrate has been achieved. The orientation of thiophenol molecules on the Ag(111) substrate was measured. The angle that the molecules make with the normal of the surface was determined to be 32 degrees. From this orientation it followed, that the top hydrogen atoms of the thiophenol molecules are measured by STM. This indicates that, at least part of, the current flows through these hydrogen atoms. The periodic structure that the thiophenol molecules form on the silver surface is determined to be a $(3 \times 3\sqrt{3})$ overlay structure.

The IET spectra showed vibrational modes of the thiophenol molecule. The vibrations that are found are the $\text{CH}$ out of plane vibration ($\gamma_{\text{CH}}$) at 92 mV and a vibration at 160 mV that is most likely related to the $\text{CC}$ stretching mode ($\nu_{\text{CC}}$) of the benzene ring at 164 mV.

Both molecular vibrations were not observed simultaneously in one and the same IETS experiment, but in separate ones. This might be due to the fact that the different spectra were recorded at different positions on the sample. Resulting in the electrons taking different pathways through the molecule and thereby exciting different molecular vibrations.

At 20 mV another vibrational mode is observed, irrespective of the molecular vibration that is observed simultaneously, and on the basis of the experimental data it is assigned to the phonon mode of the silver substrate.

No molecular vibrations have been observed for the AgS and CS bonds. The reason for this could be that the vibrations that have been observed mask the AgS and CS vibrations.

From experiment to experiment the intensity of the observed IETS peaks (and dips) varied. Since the observed topography varied from experiment to experiment as well, it is thought that these differences, in both topography and in IETS, correspond to different contributions of the orbitals of the tip to the tunneling current. However to really verify this statement, modeling is needed where the tip-orbitals contributing to the current are (simultaneously) related to both the topography and the IETS signal.

The scanning tunneling spectroscopy measurements resulted in non-symmetric $\frac{dI}{dV}(V)$ spectra. Since the molecule can also be considered to be a dipole that will align itself with the field lines between substrate and tip when a bias is applied, it can be argued that, depending on the polarity of the bias, the molecule will change its orientation with respect to the substrate by increasing or decreasing the angle it makes with the normal of the silver surface. This polarity dependent change in orientation of the molecule causes a change in the overlap between the wave functions of the molecule and those of the tip, resulting in a non-symmetric $\frac{dI}{dV}(V)$ spectrum.

A strong decrease of the $\frac{dI}{dV}(V)$ signal is observed for voltages up to 40 mV. By comparing the first derivative with the simultaneously recorded $\frac{d^2I}{dV^2}(V)$ signal, this increase is related to the presence of the phonon mode of the silver substrate. Since studies in literature of the $\frac{dI}{dV}(V)$ spectrum of pure Ag(111) do not show any features
6.6 Bibliography

around 0 V, it is concluded that interference between two elastic tunneling paths, namely direct tunneling into the continuum of the silver substrate and tunneling through the orbitals of the localized AgS bond via virtual phonon emission and reabsorption of silver surface phonons, gives rise to a Kondo-like effect. As a result of this Kondo-like effect, the presence of the silver phonon modes is more pronounced and therefore these modes are observable, as a dip, in the first derivative signal as well.

The IETS calculations show that the intensity and the shape of the IETS spectrum depends upon the exact position of the STM tip above the substrate and that this is caused by the electrons taking different pathways through the molecule and therefore excite different vibrations. For the gold tip, a comparison between the calculated and measured spectra revealed a good match in both positions (at least of the peaks at 20 and 90 mV) and intensities of the peaks. However, further study is needed to elucidate the exact nature of the peak at 20 mV.

The calculations also revealed that the obtained spectra depend on the shape and the material of the tip as well, as was evidenced by the different spectra that were obtained for the calculations with the gold and tungsten tips. The fact, that the calculations for the gold tip more closely resembled the (shape of the) measured spectrum than those of the tungsten tip, while the actual measurements were performed with a tungsten tip, indicates that the role of the tip on the spectra has to be studied in greater detail.

Generally, the IETS measurements contribute to the understanding of the conductance of single molecules and more specifically, to the molecular vibrations that are excited by the (trajectory of the) electron that passes through the molecule. Such knowledge is not only of fundamental interest, but may also contribute to applications in the area of organic electronics.

Bibliography


6. Thiophenol on Ag(111), topography and IETS


6.6 Bibliography


6. Thiophenol on Ag(111), topography and IETS


6.6 Bibliography


6. Thiophenol on Ag(111), topography and IETS


[74] Private communication with J. H. A. Hagelaar. The $dI/dV$ data of nitric oxide (NO) on Rh(111) was recorded simultaneously with the $d^2I/dV^2$ data of figure 5.2 from [54].


6.6 Bibliography


[86] Private communication with A. Troisi.
Summary

Single molecule conductance

This thesis represents an excursion into the world of molecular electronics, i.e. the field of research trying to use individual (organic) molecules as electronic components; in this work various experimental methods have been explored to connect individual molecules to metallic contacts and determine their electronic properties.

The drive for this research is twofold. On the one hand there is the rush towards ever smaller electronics. Using individual molecules in integrated circuits would further shrink the size of electronic components. On the other hand, different theories have to be used (and developed) to describe the conductance of electrons through matter as the dimensions of the material in question become smaller and smaller. This is because the (conduction) properties of a material change with changing size. In other words, research into the field of molecular electronics yields new fundamental insights into the interaction of electrons with matter at the nanoscale.

In this thesis two elementary models, namely a Self Consistent Field model and a Coulomb model, have been used to investigate the conduction properties of (a single energy level of) a single molecule between two metal contacts. Various parameters of these two models were systematically varied to see what their influence is on the conductance. In particular, the effect of the coupling (of the molecule to the metallic leads) on the conduction was studied carefully for both models. For the Self Consistent Field model it was shown, that, for symmetric coupling constants, the conductance reaches a maximum, namely the quantum of conductance, as the magnitude of the couplings becomes large. For highly non-symmetric coupling constants though the conductance drops to zero. In case of the Coulomb model it was observed that using coupling constants whose magnitudes have a ratio that is far from unity, resulted in a polarity dependent Coulomb blockade behavior: for one bias polarity Coulomb blockade occurred, while for the other polarity it did not.

These model calculations were performed to back up the two kinds experiments that were designed and performed to measure the electrical properties of a single molecule between two metallic contacts.

The first method consisted of pushing colloidal gold nanoparticles in between two lithographically defined metallic contacts (to reduce the size of the gap between these two electrodes to a few nanometers) with the tip of an atomic force microscopy (AFM) and subsequently apply molecules to the (in size reduced) gap. It was found
that a fully connecting chain of colloids, so without any molecules yet added to the device, did not conduct at all. The reason for the lack of conduction turned out to be the presence of an electrically insulating shell (of citrate molecules) around each colloid. Using microwave radiation, it was attempted to remove this shell. While microwave irradiation removed the shell and even caused individual colloids to melt and coalesce, the process could not be controlled to the extent that metallic contacts with a separation of 1 to 2 nm could reliably be produced.

In the second method the reverse was attempted: Instead of reducing the size of the gap, it was attempted to controllably create a gap of nanometer dimensions from a fully connected metallic structure, to which molecules could subsequently be applied. The process by which these gaps were created is called electromigration and basically consists of applying a high enough current(density) to a metallic wire to break it. It was found that to reliably create gaps with dimensions of 1 to 2 nm, it was necessary to add a series resistor to the system to obtain the correct overall resistance value. Too low a resistance value, i.e. no series resistor added, resulted in gaps that had size-distributions that were too large for the gaps to be of use. Too high a resistance value, namely too large a series resistor, resulted in gaps that were also useless, because for these gaps the exact gap size could not be determined, since the tunneling current flowing through these gap was too low to be determined. With the correct overall resistance, 30 Ω for these particular kind of structures, gaps with dimensions of a few nanometers could be reliably made more than 85% of the time. Placing an individual molecule in such a gap turned out to be more troublesome, as none of the 76 created structures resulted in a electrical measurement on a single molecule.

As an alternative to creating nanometer sized contacts, local probe oxidation has been performed on self-assembled monolayers (that consist of octadecyl trichlorosilane molecules on a silicon(oxide) substrate). With local probe oxidation, which is an AFM technique, an electric current is passed through a conductive tip (by applying a bias between tip and substrate), to selectively modify the surface area. In this fashion a pattern is written on the substrate as the tip is scanned across the surface. From literature it is known that such patterns could, for example, be used to selectively coat parts of the substrate with metals and in this fashion create nano-scale electronic contacts. Before this can be done effectively, however, it is necessary to control the oxidation process. Two processes can occur when a bias is applied, namely the modification of the methyl end-groups of the molecules that form the monolayer into carboxylic acid groups, which is desirable, and growth of silicon oxide underneath the monolayer, which is undesirable. It was found that, depending on the oxidation conditions, i.e. the applied bias and the duration over which it is applied, a distinction can be made between these two processes. It is also observed that, depending on the scan direction of the AFM, the end-group modification can be observed as either an increase or a decrease of the height of the modified areas due to cross-coupling, i.e. mixing, of the simultaneously recorded height and friction signals of the AFM.

To truly measure the conduction properties of individual molecules, scanning tunneling microscopy was used to measure the conductivity of thiophenol molecules absorbed on a silver(111) substrate. It was found that the molecules form ordered monolayers on the substrate with a $3\sqrt{3} \times 3$ unit cell. The performed conduction
experiments revealed vibrational features that could be related to the presence of vibrational modes of the thiophenol molecule as well as to phonon modes of the silver substrate. By comparing these conduction experiments with computational simulations, it was determined that, depending on the exact position of the tip above the molecule, electrons can take different pathways through the molecule and thereby excite different atomic/molecular vibrations. The calculations also showed that the composition of the tip has an important effect on the obtained IET spectrum as well. Additionally, it has been observed that the conductance spectrum is asymmetric around 0 Volts, which is attributed to a realignment of the molecule due to its dipole interaction with the applied electric field, and has a characteristic dip for voltages below 40 mV that is thought to be caused by the interplay between the silver phonon modes and the thiophenol molecules.
Samenvatting

Geleiding door individuele moleculen

Dit proefschrift beschrijft een excursie in de wereld van de moleculaire elektronica, oftewel het onderzoeksveld waar men probeert individuele (organische) moleculen als elektronische componenten te gebruiken. In dit proefschrift zijn verschillende experimentele methodes toegepast om individuele moleculen aan te sluiten op metalen contacten en de elektronische eigenschappen van deze moleculen te bepalen.

Er zijn twee belangrijke drijfveren voor dit onderzoek. Aan de ene kant is er het streven naar immer kleiner wordende elektronica. Door in geïntegreerde circuits gebruik te maken van individuele moleculen, kan de omvang van elektronische componenten sterk verkleind worden. Aan de andere kant moeten er nieuwe theorieën gebruikt (en ontwikkeld) worden om de geleiding van elektronen door materie te beschrijven als de grootte van het materiaal in kwestie afneemt. Dit komt doordat de (geleidings)eigenschappen van een materiaal veranderen als de grootte van het materiaal verandert. Met andere woorden, onderzoek op het gebied van moleculaire elektronica levert nieuwe fundamentele inzichten op over de interactie van elektronen met de materie op de nanometerschaal.

In deze thesis zijn twee elementaire modellen, namelijk een Self Consistent Field model en een Coulomb model, gebruikt om de geleidings eigenschappen van (enkel geleidingsniveau) van een individueel molecuul tussen twee metalen contacten te onderzoeken. Verschillende parameters van deze modellen zijn systematisch gevarieerd om het effect van deze variaties op de geleiding te bepalen. Vooral het effect van de koppeling (van het molecuul aan de metalen geleiders) op de geleiding is uitvoerig bestudeerd voor beide modellen. Voor het Self Consistent Field model is aangetoond dat, voor gelijke (ofwel symmetrische) koppelingsconstanten, de geleiding een maximum bereikt, namelijk het geleidingsquantum, als de waarde van deze koppelingsconstanten groot wordt. Voor ongelijke (niet-symmetrische) koppelingsconstanten valt de geleiding af naar nul als de constanten groot worden. In het geval van het Coulomb model blijkt dat voor (sterk) niet-symmetrische koppelingsconstanten het Coulomb blokkade effect afhangt van de polariteit van de aangebrachte spanning: Voor een polariteit treedt er wel Coulomb blokkade op, maar voor de andere polariteit niet.

Deze modelberekeningen zijn uitgevoerd om de metingen te ondersteunen van twee verschillende experimenten, experimenten die ontworpen en uitgevoerd zijn om
de elektrische eigenschappen van een enkel molecuul tussen twee metalen contacten te bestuderen.

De eerste methode bestaat uit het positioneren van colloïdale goud nanodeeltjes tussen twee lithografische contacten met behulp van de naald van een atomaire krachten microscoop (AKM) (om de grootte van dit gat te reduceren tot enkele nanometers) en het vervolgens moleculen aan te brengen in dit (verkleinde) gat. Het bleek dat een keten van volledig verbonden colloïdale deeltjes, dus nog zonder toevoeging van moleculen aan het sample, niet geleidt. De reden voor het gebrek aan geleiding is de isolerende schil van (citraat) moleculen die om elk colloïd heen zitten. Met behulp van microgolfstraling is getracht om deze schillen te verwijderen. Alhoewel bestraling met dergelijke straling deze schillen inderdaad weg haalt en zelfs de colloïden doet versmelten, kon dit proces niet dusdanig gecontroleerd worden dat er, met zekerheid en op betrouwbare wijze, metalen contacten gevormd worden met een onderlinge afstand van 1 à 2 nm.

Bij de tweede methode wordt het omgekeerde geprobeerd: In plaats van het kleiner maken van een gat, wordt er geprobeerd om, op gecontroleerde wijze, een gat met dimensies van enkele nanometers te maken in een volledig verbonden metalen draad. Het proces waarmee deze gaten gemaakt worden heet electromigratie en het komt er op neer dat er een voldoende grote stroom(dichtheid) door de draad geleid wordt om deze te breken. Het is gebleken dat, om gecontroleerd gaten van 1 a 2 nm in lengte te maken, het nodig is om een serieweerstand toe te voegen zodanig dat de totale weerstand van de draad de juiste waarde heeft. Als de totale weerstand te klein is (in dit geval was er geen serieweerstand toegevoegd), resulteerde dit in gaten met een afstandsbelijning die te groot is om betrouwbaar gebruik te kunnen maken van de contacten. Echter als de totale weerstand te groot is, in dit geval door een te grote serieweerstand te gebruiken, zijn de gevormde gaten ook onbruikbaar omdat de gemeten tunnelstroom te laag was om de gat grootte te bepalen. Met een correcte totaal weerstand, 30 Ω voor deze structuren, kon er in meer dan 85% van de gevallen betrouwbaar een gat gemaakt worden met afmetingen van enkele nanometers. Het plaatsen van een enkel molecuul in een dergelijk gat leverde meer problemen op, omdat niet één van de 76 gemaakte structuren resulteerde in een geleidingsmeting aan een enkel molecuul.

Als een alternatief voor het creëren van contacten met nanometer dimensies, is “local probe oxidatie” toegepast op zelf geassembleerde monolagen (die bestaan uit octadecyltrichlorosilaan moleculen op een silicium(oxide) substraat). Met “local probe oxidatie”, een AKM techniek, wordt er een stroom door een geleidende naald gestuurd (door het aanbrengen van een spanning tussen naald en substraat) om selectief het oppervlak van de monolaag te modificeren. Op deze wijze wordt er, door de naald over het oppervlak te bewegen, een patroon geschreven op het substraat. Uit de literatuur is bekend dat dergelijke patronen, bijvoorbeeld, gebruikt kunnen worden om selectief een deel van het substraat met metaal te bedekken en op deze wijze gebruikt kunnen worden om elektronische contacten te maken op nanoschaal. Voor dat dit echter effectief gedaan kan worden, moet het oxidatieproces onder controle gebracht worden. Er zijn namelijk twee processen die kunnen optreden; de modificatie van de methyleindgroepen van deze moleculen tot carboxylgroepen, wat gewenst is, en de groei van silicium oxide onder de monolaag, wat niet gewenst is. Uit het onderzoek
volgde dat, afhankelijk van de oxidatie condities, namelijk de aangebrachte spanning en de duur van het aanbrengen van deze spanning, onderscheid gemaakt kan worden tussen deze twee processen. Ook bleek dat, afhankelijk van de scanrichting van de AKM, de eindgroepmodificatie waargenomen kan worden als dan wel een toename, dan wel een afname van de hoogte van de gedomineerde gebieden, dit ten gevolge van kruiskoppeling, oftewel mixen, van de tegelijk opgenomen hoogte- en frictie-signalen van de AKM.

Om daadwerkelijk de geleidingseigenschappen van individuele moleculen te meten, is een scanning tunneling microscoop (STM) gebruikt om de geleiding van thiofenol moleculen, geabsorbeer op een zilver(111) substraat, te bepalen. Uit het onderzoek bleek dat de moleculen een geordende monolaag op het oppervlak vormen met een $3\sqrt{3} \times 3$ eenheidscel. De uitgevoerde experimenten lieten vibrationele aspecten zien die toegeschreven konden worden aan de aanwezigheid van vibrationele modes van zowel het thiofenol molecuul, als aan fonon modes van het zilversubstraat. Door deze experimenten te vergelijken met modelberekeningen, is bepaald dat, afhankelijk van de exacte positie van de STM-naald boven het molecuul, elektronen verschillende paden door het molecuul kunnen nemen en daardoor verschillende atomaire/moleculaire vibraties kunnen aanslaan. De berekeningen toonden ook aan dat de samenstelling van de tip ook een belangrijke invloed heeft op de waargenomen vibraties. Daarnaast bleek ook dat het geleidingsspectrum niet-symmetrisch is rond 0 Volt. Dit effect wordt toegeschreven aan de heroriëntatie van het molecuul door de interactie van het dipool van het molecuul met het aangebrachte elektrische veld. In het zelfde geleidingsspectrum is een typisch dal zichtbaar voor voltages lager dan 40 mV en het vermoeden bestaat dat dit dal veroorzaakt door de interactie van de zilfer fonon modes met de moleculen.
Dankwoord

Het werk dat nu voor je neus ligt is het resultaat van vijf jaar lang hard werken. In deze periode heb ik veel geleerd, zowel vakinhoudelijk als daarbuiten. Dit zou me nooit gelukt zijn zonder de hulp en steun van vele mensen en bij deze wil ik hen dan ook van harte bedanken.

Allereerst is er mijn copromotor en dagelijkse begeleider Kees Flipse. Ondanks het feit dat het, zeker in het begin, stroef liep tussen Kees en mezelf prijs ik me gelukkig om met Kees samengewerkt te hebben. Zijn bezieling en enthousiasme hebben me meermalen geholpen om net dat beetje extra te geven en ik ben er ook dankbaar voor dat ik van zijn gedegen en grondige theoretische kennis gebruik heb mogen maken. Wat ik echter het meest waarder aan Kees is dat hij me als persoon heel erg serieus heeft genomen, ook al zag ik dat in het begin niet.

Enthousiasme is belangrijk, maar de rode draad vasthouden en de voortgangen bewaken net zo. Gelukkig kon ik in dat opzicht altijd mijn promotor René Janssen rekenen. Naast de inhoudelijke beslommeringen heb ik René altdijd als een prettige persoon ervaren en ik zou hem hiervoor dan ook graag willen bedanken, alsmede voor de prettige tijd die ik heb mogen ervaren in zijn vakgroep M2N (Molecular Materials and Nanosystems). En René, nogmaals mijn excuses voor je bril.

Om te promoveren heb je, naast een promotor, een copromotor en een proefschrift, ook een promotiecommissie nodig. Ik zou dan ook (in willekeurige volgorde) Ulrich Schubert, Henk Swagten, Alessandro Troisi, Wim de Jonge, Paul Koenraad en Bert Koopmans willen bedanken voor de tijd en moeite die ze in mijn werk gestoken hebben.

De hoofdmoot van dit werk heb ik natuurlijk zelf gedaan, maar ik zou niet zover gekomen zijn zonder de samenwerking met anderen. Ik heb het geluk gehad om in de groep van Ulrich Schubert met Daan Wouters en Stephanie Höppener te mogen samenwerken. Naast de fraaie resultaten die we samen gehaald hebben, heb ik veel lol met beiden gehad. Hiervoor bedank ik hen dan ook graag van harte. Alhoewel er uiteindelijk niks van de inspanningen, die ik samen met Jeroen van Herrikhuysen geleverd heb, in dit proefschrift terecht zijn gekomen, ben ik Jeroen veel dank verschuldigd voor het werk dat hij gedaan heeft en voor onze prettige samenwerking. Daarnaast wil ik Alessandro Troisi bedanken voor zijn bijdragen aan mijn proefschrift. Zonder zijn vibratie-berekeningen aan thiophenol zou hoofdstuk 6 niet geworden zijn wat het nu is. Mijn dank hier voor.

Door samenwerking komt kennisoverdracht tot stand en van de bovenstaande mensen heb ik veel geleerd. Kennisoverdracht kan echter ook de andere kant op
gaan en ik ben dan ook blij dat ik in mijn samenwerking met een aantal studenten zelf ook de nodige kennis heb kunnen overdragen. Zo wil ik graag Filipe Rodrigues de Lima Pinheiro, Ondřej Vaculík en de studenten van het practicum bedanken voor de prettige samenwerking die ik met hen heb mogen meemaken.

Men zegt wel eens dat je tijdens je promotie één professor te vriend moet houden, namelijk je eigen promotor, en honderd technici. Oké, honderd zijn het er niet geweest, maar wel beduidend meer dan het aantal professoren, inderdaad die éne, dat me bijstand. Zonder de technische expertise van al deze mensen zou het me niet gelukt zijn om mijn experimenten te brengen tot waar ze nu gekomen zijn. Gerard Wijers zou ik graag willen bedanken voor de ondersteuning bij de STM (voor als het apparaat weer eens vast liep, al dan niet door mijn eigen toedoen) en alle kleine (en minder kleine) dingen die hij altijd in een mum van tijd voor me maakte de afgelopen jaren. Op elektronisch vlak kon ik altijd bij Wijnand Dijkstra en Rein Rumphorst aankloppen, iets wat ik dan ook veelvuldig gedaan heb. Niet alleen heb ik altijd met veel plezier met beide heren samengewerkt, maar vooral Rein zou ik graag ook bedanken voor de interessante en vaak verwarrende gesprekken waarmee hij de koffiekermer verrijkte.

Als je werk zich afspeelt in maar liefst vier verschillende vakgroepen, van ook nog eens vier verschillende faculteiten, dan is het niet verwonderlijk dat er ook technici van buiten je eigen vakgroep een bijdrage leveren aan je werk. Zo stonden Erik Jan Geluk en Barry Smalbrugge altijd voor me klaar in de cleanroom als ik weer wat nodig had, mijn dank hier voor. Met Peter Nouwens heb ik vele uren achter het bond-apparaat doorgebracht terwijl hij piep-kleine draadjes probeerde te bevestigen aan mijn samples. Het bonden was soms wel eens moeilijk, lees onmogelijk, en dan verbaasde het me elke keer weer hoeveel geduld Peter kon opbrengen en het toch nog één keertje opnieuw probeerde. Hier heb ik grote bewondering voor. Bij werktuigbouwkunde was het Marc van Maris die me, zowel vak-inhoudelijk als mentaal, ondersteunde en ik prijs me gelukkig met Marc samengewerkt te hebben. Behalve alle hulp die ik op het technische vlak van deze mensen heb mogen ontvangen, was het altijd gezellig om met hen tijdens de werkzaamheden over van alles en nog wat te kletsen.

Ondanks al deze ontvangen expertise ging er soms toch nog wel eens wat mis en dan is het prettig om te weten dat er mensen zijn die er voor zorgen dat fouten niet herhaald worden. Daarom zou ik Wim Verseijden graag willen bedanken voor de inzichten die hij me gegeven heeft om van het lab een veiligere omgeving te maken. Ook Jef Vekemans zijn hulp bij het neutraliseren van het “aroma” van thiophenol wordt door mij en de rest van de vakgroep erg op prijs gesteld. Ook het IMEC in Leuven, België, heeft Laurent Francis en Jos Moenens het mogelijk gemaakt dat ik de lithografische structuren had om mijn onderzoek te doen. Het was een hele toer om telkens mijn samples onbeschadigd van Eindhoven naar Leuven (en terug!) te krijgen, maar het eindresultaat mocht er wezen en daar ben ik Laurent en Jos dankbaar voor. Om (individuele) moleculen door te meten heb je nodig: inderdaad, moleculen en aangezien ik nog steeds niet weet wat de Suzuki koppeling en dergelijke inhouden, is het maar goed dat anderen zich over de synthese van de benodigde moleculen ontfermd hebben. Voor deze syntheses wil ik Nicolai Stuhr Hansen van de universiteit
van Kopenhagen, Denemarken, en Bert de Boer van de universiteit van Groningen
dan ook hartelijk bedanken.

Soms zitten dingen tegen en dan is het goed om bij mensen aan te kunnen kloppen
die verstand van je probleem hebben. Zo hebben Marius Trouwborst van de univer-
siteit van Groningen en Edgar Osorio van de universiteit van Delft zich meerdere
malen voor me ingezet als ik met de handen in het haar zat en dat waardeer ik zeer.
Vooral Marius wil ik graag bedanken omdat hij geheel belangeloos een keer helemaal
vanuit Groningen naar Eindhoven is gekomen om me op weg te helpen met mijn
experimenten.

In veel landen wordt een promotie gezien als een studie waar de student zelf voor
moet betalen. Hier in Nederland heb ik het geluk en voorrecht dat promoveren een
betaalde baan is. Ik zou dan ook graag de stichting voor Fundamenteel Onderzoek
der Materie (FOM) willen bedanken voor de financiële ondersteuning.

Een vakgroep is meer dan een verzameling wetenschappelijk experts. Na vijf jaar
met mensen te hebben samengewerkt kun je wel stellen dat ieder van hen toch op zijn
minst een goede bekende is geworden en een aantal van hen kan ik gelukkig tot mijn
vrienden rekenen. Ik wil al mijn (ex)collega’s dan ook, in willekeurige volgorde, be-
danken voor de leuke tijd die ik met ze gehad heb in de vakgroep en daarbuiten: Joris
Hagelaar, Erwin Rossen, Gheorghe Tănăsă, Jiří Červenka, Klára Maturová, Jean-
Michel Wulveryck, Juan Amir, Hans Gommans, Marco de Ridder, Frank Janssen,
Marc Ponjée, Martijn Kemerink, Marta Fonrodona Turon, Alexandre Nardes, Dimitri
Charrier, Yinxin Liang, Erik Roelung, Kevin van de Ruit, Simon Mathijsen, Rik van
Laarhoven, Cristina Popa, Paul Sieben, Jan Maarten Kramer, Gunnar Timmermans,
Friso Wittebrood, Nicolae (Nick) Podaru, Marzena Schoutese-Brzezinska, Arnoud
Denier van de Gon, Siebe van Mensfoort, Reinder Coehoorn, Marco Carvelli, Peter
Verhoeven, Lars Peters, Marije Haverhals, Stefan van Reenen, Thomas Lemmens, en
Wijnand Germs, allemaal van harte bedankt.

In de koffiekamer van onze vakgroep kom je niet alleen vakgroepgenoten tegen,
maar ook (ex)werknemers van het bij ons in het gebouw gevestigde Calipso B.V.
Ook zij hebben me altijd met veel lol en plezier bijgestaan met raad en daad en dat
waardeer ik zeer. Hidde Brongersma, Niels Kuijpers, Rik ter Veen, Erwin Timmer-
man, Theo Bijvoets en Arie Knoester dank jullie wel.

Als promovendus moet je zo nu en dan eens wat langer door werken en dan is
het goed dat er s’avonds de nodige morele ondersteuning is in de persoon van onze
portier Toon Wouters. Toon, bedankt voor alle kletspraatjes.

Het gros van mijn werk heeft zich afgespeeld op de universiteit, maar achter de
schermen hebben mijn ouders op het thuisfront ook zeker een belangrijke rol gespeeld.
Ze hebben me altijd voor 100% gesteund en me meermalen de nodige moed ingespro-
kend. Ik kan ze hiervoor niet genoeg bedanken. Ook Joost, mijn broer, wil ik graag
bedanken voor zijn steun en relativerende woorden. Naast steun was er ook de nodige
interesse in mij en mijn werk, niet alleen van mijn ouders, maar ook van mijn vrienden
en familie, ik ben ze hier dan ook erg dankbaar voor.

Tenslotte is er nog een iemand die ik graag in het bijzonder wil bedanken. Bregje
je bent mijn grote steun en toeverlaat. Dank je wel dat je er voor me bent.
Curriculum Vitae

Oktober 13, 1978  Born in Eindhoven, the Netherlands

1991 - 1997  Grammar school, Rythovius College, Eersel

1997 - 2003  M. Sc. in applied physics, Eindhoven university of technology, Eindhoven


Traineeship at departemento de Oceanografía Física, división de Oceanología, Centro de Investigación Científica y de Educación Superior de Ensenada (CICESE), Ensenada (Baja California), México. Subject: A laboratory study of eddy generation on a right-angled corner, supervised by dr. O. U. V. Fuentes and prof. dr. ir. G. J. F. van Heijst

