

# The search for graphene



The Kamerlingh Onnes Laboratory

Leiden Institute of Physics  
Leiden University



J.A.M. van Ostaay

Bachelor Project in Physics

# The search for graphene

**Author:** Johannes Antonius Maria van Ostaay

**Student number:** 0422509

**Supervisors:** Prof. Dr. J. Aarts  
Dr. F. Galli

**Research conducted at:** “Magnetic and Superconducting Materials”  
The Kamerlingh Onnes Laboratory  
Leiden Institute of Physics (LION)  
Niels Bohrweg 2  
2333 CA Leiden

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**The picture on the cover:** AFM-picture of a graphene flake; picture is 10  $\mu\text{m}$  x 10  $\mu\text{m}$ .  
**Picture taken from:** <http://onnes.ph.man.ac.uk/nano/Images.html>

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# Chapter 1

## Introduction

A recent hype in the world of condensed-matter physics is a substance called “graphene”. This graphene is a single layer of graphite. Graphene is thus a monolayer of carbon atoms in a two-dimensional honeycomb lattice. Until recently it was thought that this could not exist in free nature. Recent discoveries disproved this believe and also showed that this special monolayer has very special properties: tuneable band gap, high mobility, anomalous quantum Hall effect, being described by the Dirac equation etc. etc.

To be able to do any experiment at all with graphene it is necessary to have a fabrication process for the graphene. There are few known methods: micromechanical cleavage, chemical exfoliation, epitaxial growth etc. Although some experimental groups try to invent a new process (see for example reference 2), most groups still rely on the method of micromechanical cleavage, or as I’m going to nickname it: “cleave-and-run”.

The cleave-and-run technique to make graphene is actually a bit of a primitive technique. With this technique the graphene is made by repeated peeling of graphite with adhesive tape. Although this technique is quite successful, this technique does have a big disadvantage: with this technique not only graphene is made but also a large amount of thicker graphite flakes. The most time-consuming part is therefore the search for the graphene on the substrate. The success of this technique is due to the pleasant fact that graphene becomes visible on a SiO<sub>2</sub>-layer that is placed on top of a silicon wafer. The requirements for the thickness of this SiO<sub>2</sub>-layer are very strict though and the contrast of the graphene is very low. This can be seen in figure 1 where a photo of graphene on top of the SiO<sub>2</sub>-layer is shown. In the next chapter I will describe the graphene and this “cleave-and-run” technique in greater detail.

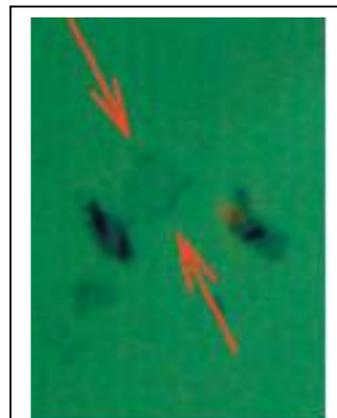
Although this technique works, the efficiency is very low. When the substrates are roughly 0.5 mm x 0.5 mm the average yield is 1-2 usable graphene flakes per ten substrates! This is very low yield, but the technique is able to (eventually) produce graphene and for most groups this is the most important aspect.

You might wonder what is made besides the graphene with the cleave-and-run technique. Off course that will be a lot of graphite flakes, but certain questions are sure to arise when one gives this subject more thought. Questions like: are the produced graphite flakes usually flat, do they vary a lot in height, what is the typical area of a graphite flake?

The answering of these questions is the motivation for the research I did: to investigate what are the properties of the produced graphite flakes when using the cleave-and-run technique. To this end substrates made with this certain technique have been scanned using an AFM.

In this report I will present the results that were obtained with my research and ultimately I will try to answer the question:

“What do you make with the cleave-and-run technique?”



*Figure 1:  
Photo of graphene  
made through a  
microscope. The  
graphene is indicated  
with the red arrows.  
Image taken from [4].*

### **Structure of this report**

The structure of this report will be the following.

In the next chapter, **chapter 2**, some theory concerning graphene will be presented and the cleave-and-run technique will be described in more detail. In **chapter 3** all the important machines and instruments I've used for my research will be explained. In **chapter 4** a brief description of my research will be given. The results will be given in **chapter 5**. In **chapter 6** the conclusions that could be drawn from the measurements will be summarized. After **chapter 6** the usual **acknowledgments** and **references** will follow. In the **appendices** some extra, technical information will be given: a list of interesting articles about graphene, the procedure I used to make my samples, the optimised AFM-parameters, some obtained pictures and the some qualifications of the AFM. At the end in the **acknowledgments** persons who were beneficial to my research will be thanked.

## Chapter 2

### Graphene

#### 2.1 A history of the wondrous graphene

Nowadays graphene is a hot topic in experimental and theoretical physics alike, but in earlier times things were a bit different.

Sixty years ago graphene was already a known topic in theoretical physics and was used for describing the properties of various carbon-based materials. The reason for this is the possibility to “make” all the graphitic materials from graphene: fullerenes or buckyballs are made by wrapping up the graphene, nanotubes by rolling it, graphite by stacking it etc.

Although it was researched in theoretical physics, the graphene was purely seen as a theoretical toy-model. The belief that graphene couldn't exist in the free state has its origin in the work of Landau and Peierls more than seventy years ago. They argued that strictly two-dimensional crystals were thermodynamically unstable. This argument was later extended by Mermin and experimental observations also seemed to support this. The discovery of graphene in 2004 by the group of A.K. Geim and K.S. Novoselov was therefore a big surprise. The existence of graphene seems to be in contradiction with the theory but in hindsight it is said that the produced two-dimensional graphene crystals are actually stuck in a metastable state, because they are extracted from a three-dimensional material, namely: graphite. The graphene can survive the thermal fluctuations thanks to its small size<sup>1</sup> and strong interatomic bonds. Another note about the stability of graphene: the graphite crystals have tendency of gently crumpling in the third dimension. This crumpling makes them intrinsically stable.

Since the experimental discovery of the graphene a lot of research has been on this material. It has been found that graphene has some very unique properties and these discoveries eventually made graphene a hot topic in condensed-matter physics.

#### 2.2 The special properties of graphene

Graphene is one of the strangest materials now known to men. I shall give a brief overview of some of the unique properties of graphene.

First of all, graphene has the unique property of being highly tuneable with respect to its charge carriers. Depending on the applied voltage  $V_g$  the charge carriers are either holes or electrons. The charge carriers are electrons for positive  $V_g$  and holes for negative  $V_g$ . The concentration  $n$  of electrons/holes is linear dependant on the voltage  $V_g$  and is given by equation [2.1]:

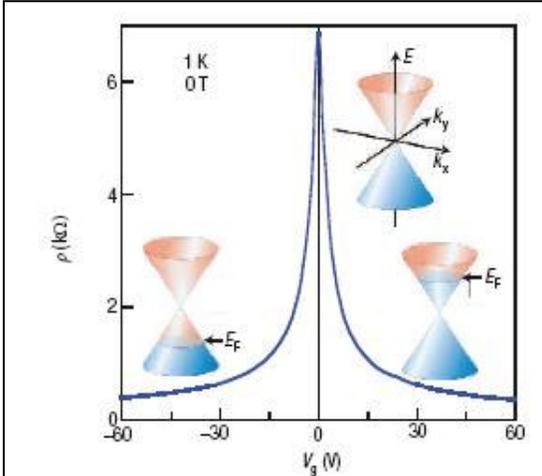
$$n = \alpha V_g \tag{2.1}$$

In equation [2.1] the coefficient  $\alpha$  is equal to:  $7.2 \cdot 10^{10} \text{ cm}^{-2}\text{V}^{-1}$ .

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<sup>1</sup> Graphene is typically smaller than  $10 \mu\text{m} \times 10 \mu\text{m}$ .

Another aspect of this ability to change the charge carriers is the dependence of the band gap between the valence and conductance band. For zero  $V_g$  the band gap is zero, but this band gap changes for finite  $V_g$ . For positive  $V_g$  there will be an overlap between both bands, for negative  $V_g$  the band gap will become positive.



*Figure 2:*  
*In this picture the resistivity  $\rho$  is plotted against the applied voltage  $V_g$ . In the inset the low-energy spectra are visible. In this case the mobility was equal to:  $\mu = 5,000 \text{ cm}^2/\text{Vs}$ . The properties described in the text are clearly visible. Image taken from [1].*

The second point of interest is the very high mobility of graphene. At ambient conditions this mobility  $\mu$  already exceeds  $15,000 \text{ cm}^2/\text{Vs}^2$  and this value is still limited by impurity scattering. It is said that the mobility of graphene might become as high as  $100,000 \text{ cm}^2/\text{Vs}$ . Unlike other materials this mobility  $\mu$  isn't influenced by the carrier concentration or doping. This high mobility results in an extreme electronic quality of the graphene.

The properties mentioned earlier can clearly be recognized in figure 2. In the insets of this picture the low-energy spectra for various values of  $V_g$  are shown. In these spectra the dependency of the band gap and the charge carriers on the applied voltage can clearly be seen. The graph of the resistivity  $\rho$  against  $V_g$  shows that the mobility  $\mu$  must be very high (in this case:  $\mu$  is  $5,000 \text{ cm}^2/\text{Vs}$ ). In the graph it can be seen that the point  $V_g = 0 \text{ V}$  is a special point: the resistivity is maximal,

the band gap is zero and the transition from electrons to holes as charge carriers occurs there. This special point therefore has gotten a name: the Dirac-point (this name will become clear later on).

The third special property of graphene is the observation of the quantum Hall effect (QHE) at room temperature. As the QHE is a quantum effect that one normally only sees at low temperature, this again indicates what a remarkable electronic quality graphene has. Furthermore the QHE seen in graphene isn't the normal QHE, but it is of a special kind: it is an anomalous QHE.

The normal QHE is the quantum-mechanical version of the Hall-effect and it means that the Hall conductance  $\sigma$  takes on quantised values as given in equation [2.2]:

$$\sigma = \nu \frac{e^2}{h} \quad [2.2]$$

In this equation  $e$  is the elementary charge and  $h$  is Planck's constant. In the "ordinary" QHE, the integer QHE,  $\nu$  takes on integer values. There is also another type of QHE where  $\nu$  can occur as a fraction. Normally the QHE is only observed in two-dimensional systems at low temperatures and in the presence of a strong magnetic field.

<sup>2</sup> For comparison: the mobility of sodium at ambient conditions is:  $\mu = 46 \text{ cm}^2/\text{Vs}$ .

For graphene the QHE is of the “ordinary” kind with the difference that there is a shift of  $\frac{1}{2}$  in the standard QHE sequence and that the conductance  $\sigma$  is four times as large, thus for graphene the conductance is given by equation [2.3]:

$$\sigma = \pm \frac{4(N + \frac{1}{2})e^2}{h} \quad [2.3]$$

The  $N$  in equation [2.3] can take on any positive integer value and zero.

In the next section this anomalous QHE will be explained.

The forth property that will be mentioned is the fact that single-, double- and few- (between 3 and 10) layer graphene<sup>3</sup> can easily be distinguished. When there are more than ten layers the two-dimensional character is lost and then the description as very thin graphite is better suited.

The last property that is worth to mention is the fact that graphene, unlike all the other substance in solid-state physics, needs to be described with the Dirac equation instead of the Schrödinger equation. The reason for this is the interaction of the electrons with the lattice of the graphene which gives rise to new quasiparticles. At low energies these quasiparticles can be accurately described by the (2+1)-dimensional Dirac equation with an effective speed of  $v_F = 10^6$  m/s. These massless quasiparticles have a charge of  $-e$  and are called massless Dirac fermions.

## 2.3 The mathematical graphene

As said before graphene needs to be described with the Dirac equation. For low energy  $E$  (low means here:  $|E| < 1$  eV) the quasiparticles within each energy valley can therefore formally be described with a Dirac-like Hamiltonian. This Hamiltonian is shown in equation [2.4]:

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \quad [2.4]$$

In this equation  $\hbar$  is the modified Planck’s constant,  $v_F$  is the speed of the quasiparticles and  $k_x$  and  $k_y$  are the components of the wavevector of the quasiparticles. With the two-dimensional Pauli matrix  $\sigma^4$  this equation can be written as:

$$\hat{H} = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{k} \quad [2.5]$$

In equation [2.5] one can see that the energy spectrum is linear. This was already visible in the insets of figure 2.

Although the linear spectrum is very essential for the understanding of graphene the fact that the honeycomb lattice of graphene is made up of two equivalent carbon sublattices  $A$  and  $B$  is even more important. These sublattices have been made visible in figure 3 on the next page. In figure 3 the lattice of graphene is shown including the unit-cell vectors and the two sublattices.

Due to the sublattices electronic states near zero  $E$  are compositions of the states belonging to the different sublattices. To account for the relative contributions of both

<sup>3</sup> The term graphene is not only used for the monolayer, but also for graphite that is less than eleven layers thick. From now on I will strictly use the word graphene to indicate the monolayer.

<sup>4</sup> My apologies for overuse of the letter sigma, but the use of the sigma for Pauli matrices and conductance is standard notation.

sublattices in the make-up of the electronic states of the quasiparticles two-component wavefunctions, spinors, need to be introduced. The index needed to indicate the sublattices is similar to the spin index and is called pseudospin. The  $\sigma$  in [2.5] also refers to this pseudospin in stead of the real spin of the electrons, whose effects are negligible for graphene.

Yet another new quantity is needed for the full understanding of graphene. This is the quantity “chirality”. This is the projection of  $\sigma$  on the direction of motion. In the form of an equation:

$$chirality = \frac{\boldsymbol{\sigma} \cdot \mathbf{k}}{\|\mathbf{k}\|} \quad [2.6]$$

For electrons this chirality is always positive and for holes this is always negative. Both pseudospin and chirality are conserved quantities. With the conservation of the quantities many electronic processes in graphene can be understood.

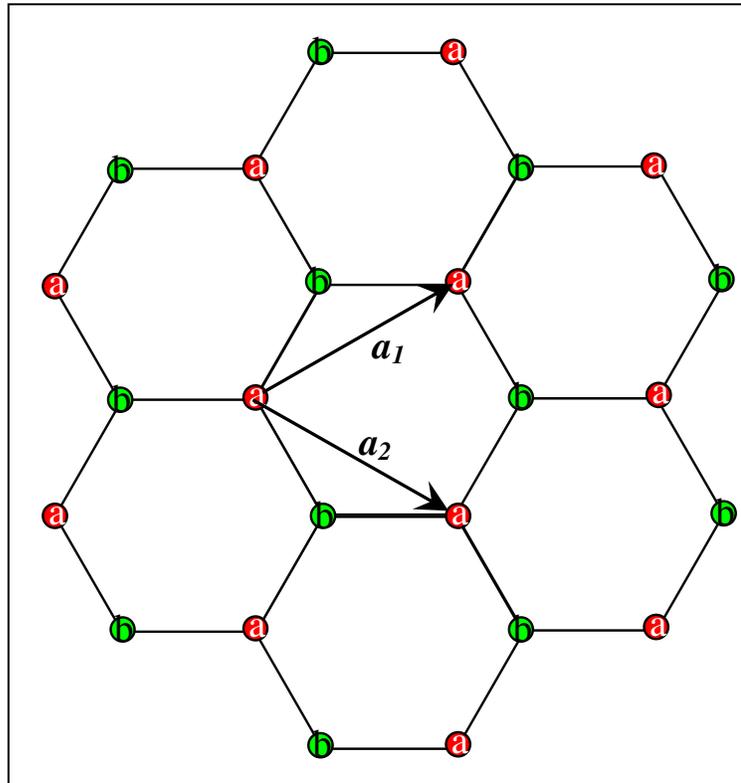
As an example the introduced concepts will now be used to explain the anomalous QHE that graphene exhibits. In equation [2.3] it was stated that the Hall conductance  $\sigma$  of graphene was given by:

$$\sigma = \pm \frac{4(N + \frac{1}{2})e^2}{h} \quad [2.7]$$

This differed from the normal Hall conductance as given in equation [2.2] by a factor 4 and a shift of  $\frac{1}{2}$ . The factor can be seen as a consequence of the double pseudospin and energy valley degeneracy. A

particle can namely be in one of the two sublattices and this particle can either be an electron or a hole. The shift of  $\frac{1}{2}$  is a result of the coupling between pseudospin and orbital motion. This coupling is clearly visible in the Hamiltonian in equation [2.5] and it gives rise to geometrical phase of  $\pi$  along cyclotron trajectories.

In this part I have given information about some of the most important and interesting properties of graphene, but graphene has much more interesting properties. For the interested reader I've included a selected list of articles in appendix A.



*Figure 3: The hexagonal lattice of graphene. The vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the unit-cell vectors of graphene with a lattice constant of  $a = 2.461$ . In this figure the two different sublattices have been marked. The red carbon atoms belong to sublattice A and the green one belong to sublattice B.*

## 2.4 The cleave-and-run technique

Now that some inside has been given in the wondrous world of graphene the time has come to explain one of the most important ways of fabricating graphene. I will describe the technique as most people would use it. In my case the last part, searching for the graphene with the microscope, was omitted, because I only needed to have the sample to do AFM on.

First of all you need to take some graphite (as pure as possible) and put that on adhesive tape. I will call this tape, tape A. I used a few sheets of HOPG, highly ordered pyrolytic graphite, that were obtained by peeling them of a block of HOPG. Then this adhesive tape A needs to be folded several times. The more times you fold, the better it is. After this another piece of adhesive tape is taken, called B, and the two pieces of tape must be pressed against each with the adhesive sides directing towards each other. Then tape B needs to be folded several times.

Then it will be time for some microscope work. Tape B needs to be looked at under an ordinary microscope to search for an area where there are large, flat graphite flakes.

When such an area has been found a clean substrate has to be pressed on the adhesive tape B at that specific area. Then the substrate will have to be cautiously removed. The substrate consists of a silicon-wafer with on top of that a layer of 290 nm  $\text{SiO}_2$ . The substrate needs to be pressed with  $\text{SiO}_2$ -layer down on the adhesive tape B.

This process causes some graphite flakes and graphene to get stuck to the substrate due to cleavage of graphite flakes and the Van der Waals forces. To remove all the glue that also found its way to the substrate the substrate needs to be cleaned by dipping and stirring it in the acetone. To prevent the loss of too much graphene flakes the use of an ultrasonic bath needs to be omitted.

With this process a sample will be made which contains a lot of glue and graphite flakes and might contain graphene flakes. To find out whether there is graphene or not the substrate needs to be scanned under the microscope with a large magnification. Due to the composition of the substrate it is possible to see the graphene as a very faint shadow on the substrate. An example of this was shown in figure 1. The differences between graphene and a few layers of graphene are subtle and to distinguish graphene from a few layer of graphene a lot of experience is required. The glue will appear as blue on the substrate and the graphite flakes can be anything from grey to green to yellow (for increasing thickness). It becomes easier to find the graphene when a computer is used to adjust the colour balance. In this colour balance the green light needs to be enhanced and the blue and red light needs to be slightly suppressed.

The reason that graphene is visible at all even though it is only one atomic layer is linked to a strong amplitude modulation. A  $\text{SiO}_2$ -layer on top of a silicon wafer has a distinct colour that depends on the thickness of the layer. For example: in the case of a layer of 290 nm thick the colour is purple. This apparent colour is the result of the interference between the two interfaces air to  $\text{SiO}_2$  and  $\text{SiO}_2$  to silicon. The reason that graphene is visible on this combination of  $\text{SiO}_2$  on silicon is due to a modulation of the relative amplitude of the interfering paths as a consequence of thickness dependent transparency. This relative amplitude modulation can then be made strongly visible with the correct chose of the thickness of  $\text{SiO}_2$ , which is 290 nm.

## Chapter 3

### Instruments and Machines

#### 3.1 Overview

For my research several machines and instruments were used. Some of those were very simple such as microscopes and spin coaters. Other machines and instruments weren't as simple to use or to understand. Therefore this chapter is dedicated to explain three machines/instruments that were of great use to my research and that could use some explanation.

I will explain the atomic force microscope, AFM, the e-beam process with the scanning electron microscope, SEM, and the e-gun evaporator.

When explaining these three apparatuses I will restrict myself to only explain the relevant parts/modes of these apparatuses. This means for example that I will not explain the SEM in great detail as being a wonderful microscope and a great machine to do e-beam lithography with, but just as the great machine to do e-beam lithography with.

Although this might be unnecessary to say, but I want to stress that the used parameters for the machines/instruments are given in the next chapter.

#### 3.2 The AFM

##### 3.2.1 The overview of the AFM

In this section the principle of the atomic force microscope, or AFM, will be explained. The AFM is able to measure atomic forces at the surface of a substance with the use of a cantilever with a microscale tip at the end.

The rough principle of the AFM is the following: the cantilever is held near (or very near) the surface of the substance one wants to measure and due to the forces that are present the cantilever will be deformed. This deformation is measurable as a laser shines on the cantilever. The deformation will therefore be visible through the deflection of the light that comes from the laser. This deflection is measured with the help of a photodiode, which converts the incoming light to a current. To prevent the tip from crashing in the surface a feedback mechanism is present that uses the converted current to determine in which way the cantilever should move. The movement of the cantilever is regulated by piezoelectric elements. In figure 4 on the next page an overview image of the AFM is being shown.

A note about the usefulness of the AFM: although the AFM indeed is able to measure the atomic forces that are present in the surface and in that way is able to indirectly see very small structures, the AFM isn't suited to look at atoms. The AFM is suited thought to see unit cell steps or atomic steps in the height (it is possible to recognize a flake as being of graphene which has a thickness of 0.4 nm by looking at the height of the flake). The reason that the AFM can't be used to see atoms has more to do with the size of the

cantilever tip than with the vertical resolution. For seeing atoms a STM<sup>5</sup> is needed. A great advantage of the AFM though is that an AFM is quite stable and that making pictures with an AFM is lot less difficult than with the more known STM.

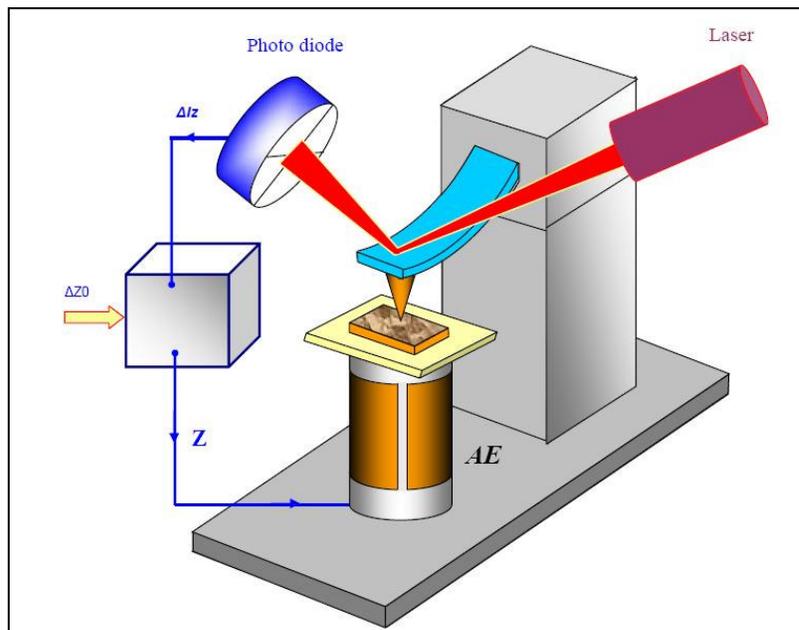


Figure 4: An overview image of the AFM. In this picture the main components of the AFM are being shown: the cantilever, the laser and photo diode, the feedback system (the grey box) and the piezoelectric element (the element called AE). Image taken from [8].

### 3.2.2 The AFM in detail: the feedback mechanism and the modes

In the last section a rough explanation was given of the principle of the AFM. There are two important subjects that deserve more attention. Those subjects will be explained in greater detail in this section. These are: the feedback mechanism and the operational modes of the AFM. As said before the AFM has a feedback mechanism that uses the converted current of the photodiode to determine the movement of the cantilever. To this end the photodiode is divided in four regions. This division is shown in figure 5.

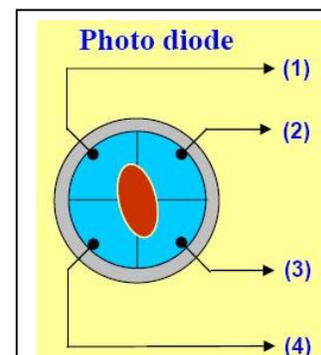


Figure 5: The division of the photodiode. Image taken from [8]

<sup>5</sup> In case you don't what that is: see reference [8].

For each region the differential current needs to be determined for the feedback mechanism. The differential current in region  $i$   $\Delta I_i$  is equal to the value of the photocurrent when the laser has been deflected due to the atomic forces  $I_i$  minus the reference value of the photocurrent when there isn't any deflection  $I_{0i}$ , thus:  $\Delta I_i = I_i - I_{0i}$ . The feedback mechanism then uses two differences of differential currents  $\Delta I_Z$  and  $\Delta I_L$ .  $\Delta I_Z$  is equal to:

$$\Delta I_Z = (\Delta I_1 + \Delta I_2) - (\Delta I_3 + \Delta I_4) \quad [3.1]$$

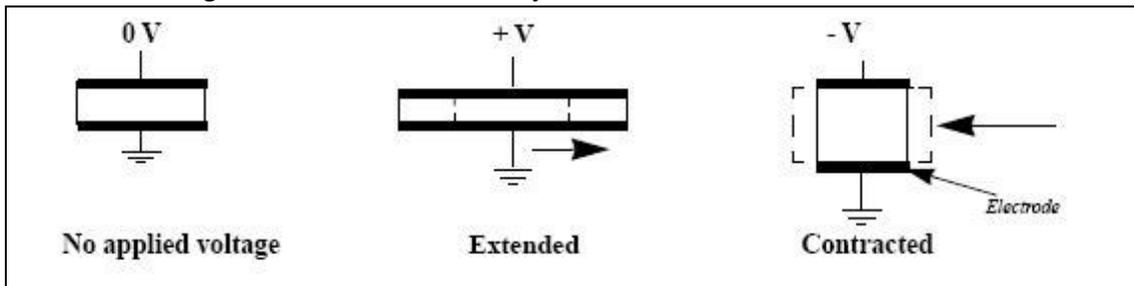
$\Delta I_L$  is equal to:

$$\Delta I_L = (\Delta I_1 + \Delta I_4) - (\Delta I_2 + \Delta I_3) \quad [3.2]$$

$\Delta I_Z$  is thus a measure for the influence of the forces in the vertical direction (perpendicular to the surface) and  $\Delta I_L$  is a measure for the influence of the forces in the lateral (horizontal) direction.

The feedback mechanism tries to keep  $\Delta I_Z$  at the value of zero by moving the cantilever up and down (depending on the value of  $\Delta I_Z$ ) with the help of piezoelectric elements. Usually the feedback mechanism doesn't use  $\Delta I_L$  as most forces (such as the Vander Waals forces) work in the vertical direction.

Piezoelectric materials have the unique property that their length changes when a voltage is applied to them. Their length increases for positive voltage and decreases for negative voltage in direction perpendicular to the direction of the voltage. This principle is shown in figure 6. The reason that piezoelectric elements are being used is that the change in their length is very small and can be accurately controlled (a typical value of the change in length is 400 nm for an applied voltage of 1000 V!). This is very important for the AFM as the height differences can be very small.



*Figure 6: The piezoelectric material.*

*From left to right: no applied voltage, a positive applied voltage and a negative applied voltage. Image taken from [10]*

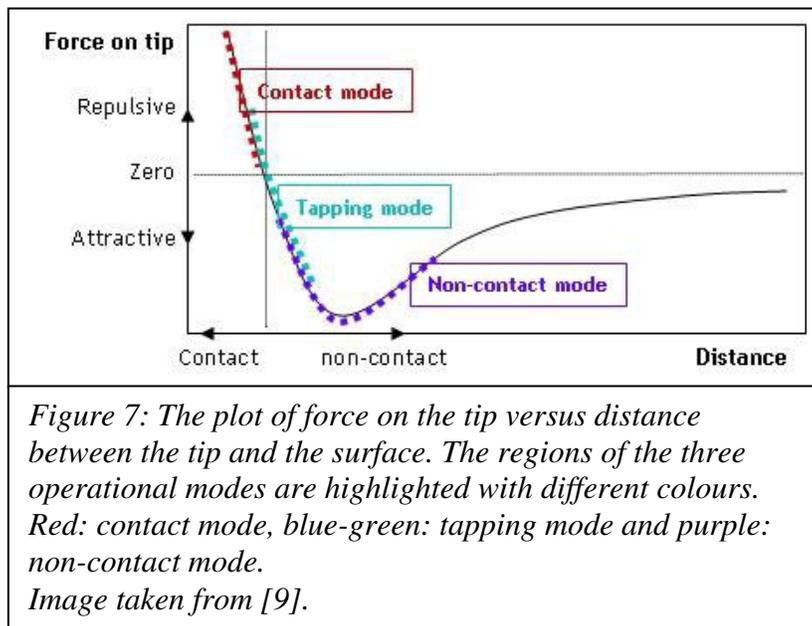
To regulate the feedback mechanism normally two parameters are being controlled: the integral gain, abbreviated as I gain, and the proportional gain, abbreviated as P gain. The I gain determines how fast the feedback mechanism responds; a high I gain means that the feedback is quick. The I gain shouldn't be too large as the feedback mechanism then starts to oscillate which severely decreases the quality of the image and also not too small as the feedback will then be too slow which causes deformations in the obtained picture.

The P gain determines the amount of the error  $\Delta I_z$  is being used in the feedback mechanism. The higher this value is, the more sensitive the feedback becomes, but making the P gain too high can cause instability.

Now the feedback mechanism has been explained the basic overview for operations with the AFM will be given. First the sample needs to be mounted in the AFM and the laser needs to be aligned in such a way that it shines on the end of the cantilever. After that the reflected laser beam is directed to the photodiode (in my situation this was done with the help of a mirror which isn't shown in figure 4).

Then the cantilever is brought as close to the sample as possible without crashing the tip off course. (I also moved the cantilever in the horizontal direction) For this work normal screws are used, because the maximum range of a piezoelectric element is typically a lot less than 0.5mm. After this the tip is brought closer to the sample with the help of a stepper motor. Then the measuring starts and the cantilever scans over the area that one wants. The feedback mechanism tries to keep  $\Delta I_z$  as close to zero as possible during the scanning to prevent the crashing of the tip. For these things piezoelectric elements are being used. Although I said that the cantilever scans the area, the piezoelectric elements for the movements in the horizontal direction are usually beneath the sample itself. The AFM can be used in three different modes depending on the distance between the sample and the tip. These modes are from small distance to longer distance: contact mode (cm-AFM), tapping mode (tm-AFM) and non-contact mode.

In figure 7 a plot is shown of the force working on the tip as function of the distance between the tip and the surface. In this plot it is assumed that the interaction is purely Vander Waals, which is in most cases correct (and also in my case). In the plot the regions are shown of the three operational modes.



I will only discuss the contact and tapping mode in the next section as these modes are the most common.

### 3.2.3 Contact Mode AFM

When the AFM operates in contact mode, the distance between the tip and the surface is very small, hence the name contact mode. The force that works on the tip is then purely repulsive.

The big advantages of this mode are the high scan speed and the fact that with this mode the smallest structures are visible. In theory one could obtain “atomic” resolution. The big problem of course with contact mode is that due to short distance the tip and the sample could start to wear during the scanning. Therefore only hard materials (such as metals) can be scanned with contact mode and the cantilever needs to be quite flexible (also to increase the resolution). Typically the force constant of the cantilevers used for this mode varies from 0.01 N/m to 1.0 N/m.

### 3.2.4 Tapping Mode AFM

When an AFM operates in tapping mode, the distance between the tip and the surface will be larger than in tapping mode. The most important feature though is the oscillation of the cantilever that is present in this mode.

The cantilever will be oscillated near its resonance frequency and the amplitude of this oscillation will typically range from 20 nm to 100 nm. As the cantilever oscillates a bit above the surface, the tip will lightly “tap” the surface at given times. This explains the name tapping mode.

Although this mode is slower than contact mode, this mode causes a lot less wear of the tip and the lateral forces are completely absent in this mode. This means that this mode can be used to image soft materials (such as organic tissue or graphene) and that the lateral resolution will be higher than in the case of contact mode.

The cantilevers used for this mode needs to be harder than the ones for contact mode. A typical force constant for cantilevers is around 3.0 N/m.

## 3.3 The SEM and lift-off procedure

### 3.3.1 The SEM

The scanning electron microscope (SEM) is as the name implies a microscope that uses an electron beam to view a sample. In figure 8 a picture of a SEM is shown

A SEM can be used to view a sample with the help of an electron beam, but the SEM is also used to perform “electron beam lithography”.

The most important element of the SEM is a filament that when the SEM is operational is heated by a current that runs through it. Due to the heating the filament will start to emit electrons and these are used to look at the sample to structure the sample.



*Figure 8:  
A picture of a SEM. The SEM itself is on the left and the monitor on the right. Image taken from [12].*

When the SEM works as a microscope, the image of the sample is being made with the help of the reflected electrons that come from the sample. When the SEM is being used to structure the sample, the electron beam is only directed at the specific areas where one wants to modify the sample. Care is taken to avoid exposure of the rest of the sample. A few important parameters for the SEM are: the working distance, also called the WD, the beam current and the area dose.

As I used the SEM solely to perform electron-beam lithography these parameters will be explained in that context.

The WD is the distance between the sample and the point from where the electrons come from. The smaller the WD the smaller the write field of the SEM, but the more accurately the structure are being written.

The beam current which isn't the same as the current that heats the filament and causes for the emission, determines the beam spot and the write speed. These two quantities increase with the beam spot.

The area dose is the total amount of charge that is deposited per unit area when the electron beam exposes the surface. This area dose mustn't be too small or else the sample will underexposed and the lithography will fail, but also not too large as this will give rise to distortions, such as squares that become circles.

### **3.3.2 The lift-off procedure**

Electron beam lithography is a technique that uses an electron beam to write structures in the sample. There are several ways to perform the electron beam lithography. The one used in my research was the lift-off procedure.

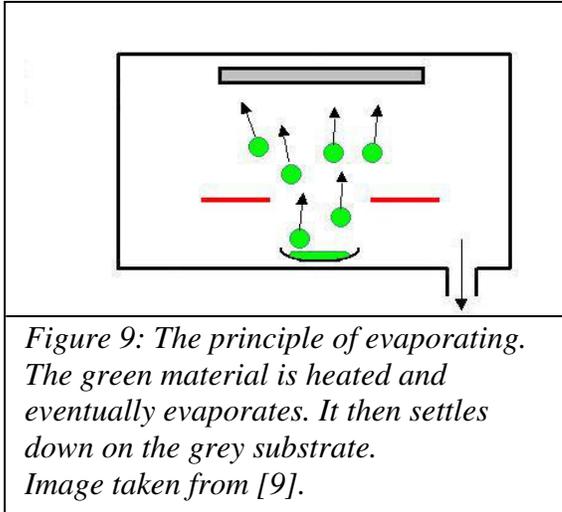
The lift-off procedure is for example used to make tiny structures.

The lift-off procedure consists of the following steps:

1. On the sample a substance called a resist is applied. To make this layer of resist homogenous a spin-coater is used which spins the sample with the resists at high speed.
2. The SEM is used to write structures in the layer of resist.
3. The resist is developed with a certain chemical and all the parts of resist that were exposed will be removed.
4. With the help of a special machine, called the evaporator (see next section) layer(s) of the desired material(s) of a certain thickness are laid on the sample.
5. A solvent is used to remove the rest of the resist. The desired structures of the evaporated material(s) on top of the sample are now finished.

### 3.4 The evaporator

The evaporator is a machine that is able to make very thin layers of metal on a substrate with the technique of evaporating. Thin layers means layers with a thickness between 1 en 50 nm. When evaporating is used to deposit a thin layer the following is done. The material that is going to be deposited is inside in bowl or hangs as a wire. Then the material is heated until it melts and starts to evaporate. Eventually the evaporated atoms will then settle down on the substrate which hangs upside at a certain distance from the bowl/wire. This principle of evaporating is shown in figure 9.



To successfully evaporate homogeneous thin layers on a substrate it is very important that the space in which the evaporating takes place is at ultra high vacuum (UHV). This UHV-condition means that the pressure before the evaporation can be started should be lower than 1.0 nbar (this is  $1.0 \cdot 10^{-4}$  Pa).

The evaporator that was used in my research used an electric current to heat the material. The bowls in which the material resided were in my case shaped like boats.

To reach the UHV-condition this evaporator was inside a cylinder which was being pumped by two turbo pump and one vacuum pump. One of these turbo pumps constantly pumped the cylinder and the other one was for the load lock. This load lock needed to be opened each time when a new substrate had to be brought in. This meant that the load lock each had to be pumped down again to UHV with the vacuum pump and the turbo pump.

## Chapter 4

### Description of the Research

#### 4.1 The goal of the research

As I already told in the introduction, the main goal of my research was to give a more quantitative answer to the question: “What do you make with the cleave-and-run technique?” It is clear that you make graphene and graphite flakes with this technique, but a priori it isn't clear what kind of graphene and graphite flakes are being made. As this technique doesn't provide you with a lot of graphene (as said in the introduction: 1-2 usable graphene flakes per ten substrates), the focus was on the graphite flakes. With my research I tried to find the properties of the produced graphite flakes.

My research consisted of the following steps:

Some clean substrates were taken and with the cleave-and-run technique these substrates were covered with glue, graphite flakes and maybe some graphene flakes. The substrates were 1 cm x 1 cm and consisted of a piece of silicon with a layer of 290 nm silicon dioxide ( $\text{SiO}_2$ ) on top.

Tapping mode AFM was done on these substrates to measure the dimensions of the produced graphite flakes. On the substrates the scanning with the AFM was done on a few locations per substrate to prevent the research of becoming too time-consuming. With time-consuming I really mean time-consuming: my substrates are 1 cm x 1 cm, the maximal scan range of the AFM is  $150\ \mu\text{m} \times 150\ \mu\text{m}$  and to scan such an area at least 77 minutes are needed (this will be explained later in chapter 5). This comes down to a minimal total scan time of about 5703 hours or 238 days for one whole substrate!

In the lines above a rough overview of my research was given. The rest of this chapter will be devoted to a more detailed description of my research. In the next section more will be told about the way to make the samples and in the last section the measuring with the AFM will be described in greater detail.

In this chapter I shall give most of the parameters that were used when operating the machines and instruments. These parameters can also be found in appendices B and C together with a few parameters that are either too technical or not relevant for the story.

## 4.2 Making the samples

In detail the fabrication of my samples will now be described. All the relevant parameters will be mentioned and can also be found in appendix B.

I will start to describe how the substrates were made. The substrates were made from a silicon wafer with a layer of 290 nm SiO<sub>2</sub> on top of it. This wafer was polished at the side of the SiO<sub>2</sub> and unpolished at the other side. With the help of a diamond cutter and a ruler squares of 1 cm by 1 cm were cut out of this wafer. As this cutting created a lot of dust the substrates were cleaned afterward by putting them for 2.5 minutes in the following solvents (in this order): acetone, isopropanol and distilled water. While the substrate was in this solvent ultrasound was present to get rid of all kind of particles that had got stuck on the substrate. After the cleaning in each solvent the substrate was dried by blowing nitrogen gas on it. This process was done for one substrate at a time and about six substrates were cleaned in this way.

After the substrates were made they were provided with markers. These markers consisted of a thin layer of chromium with a thicker layer of gold on top. The chromium was just as a sort of glue to keep the gold attached to the substrate. These markers were useful for the AFM-work as they made it easier to see whether the AFM-picture was distorted or not. They were used as reference structures to navigate easier through the substrate. As these markers were helpful, but not critically important for my research I will describe their fabrication in a few lines. The details and process parameter can be found in appendix B.

The production of the markers consisted of the following steps:

1. Spin coat PMMA on the substrate and bake this on a hot plate.
2. Use the SEM to do write the markers in the resist.
3. Develop the resist with the developer MIBK.
4. Evaporate a thin (around 3 nm) layer of chromium and a thicker (around 25 nm) layer of gold on the substrate with the evaporator.
5. Remove the rest of the resist with acetone.

I performed my measurements in total on three substrates. The design of the markers for the first substrate was a bit different from their design for the last two substrates.

In figure 10 the design of the markers for the first substrate is shown; in figure 11 on the next page this is shown for the other two substrates.

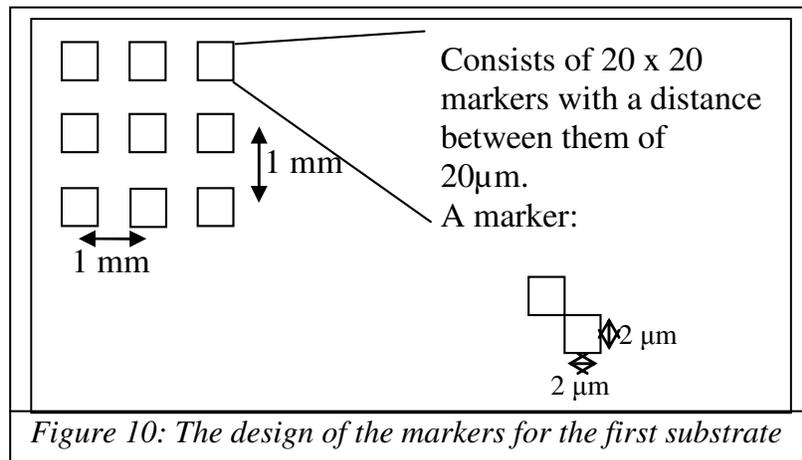


Figure 10: The design of the markers for the first substrate

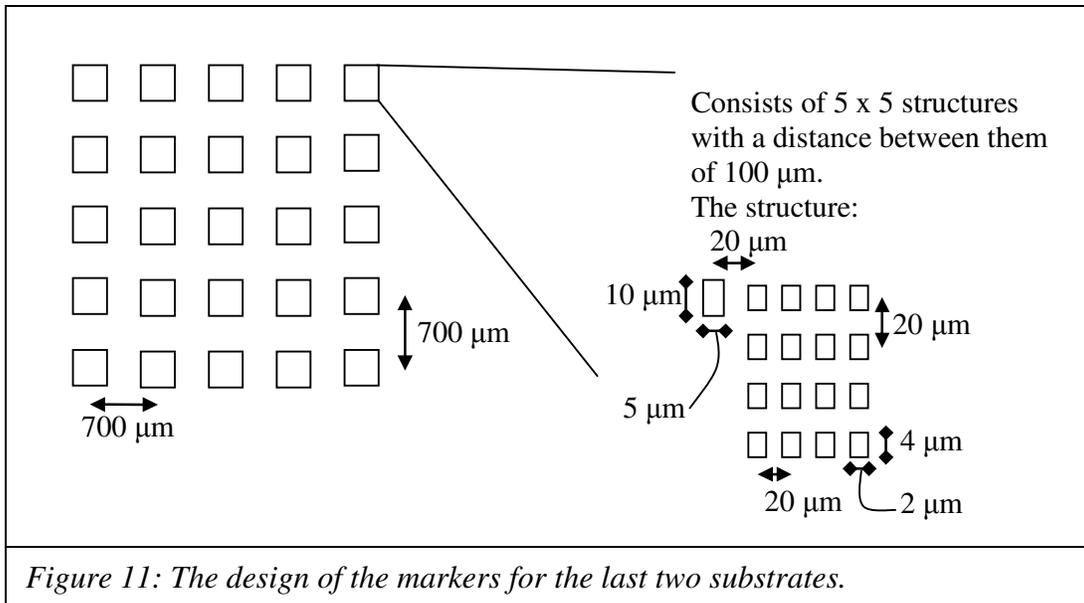


Figure 11: The design of the markers for the last two substrates.

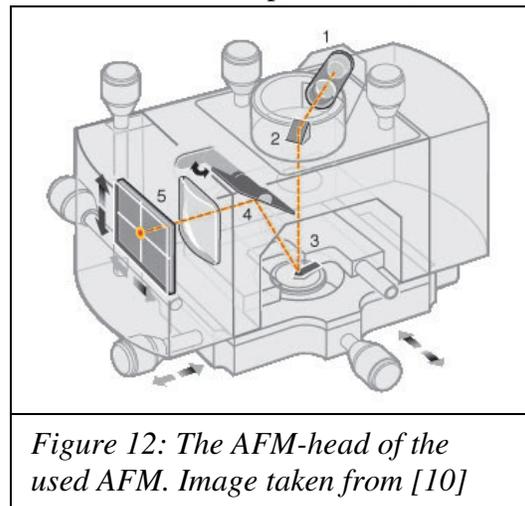
After the substrates were provided with markers they were again cleaned by putting those 2.5 minutes with ultrasound in: acetone, isopropanol and distilled water. As before the substrates were dried with nitrogen-gas after each solvent.

Then the cleave-and-run technique, as it was explained in section 2.4, was used and the samples were finished. They were called graphene/graphite-samples. The cleaning in the acetone that was also mentioned in section 2.4 lasted one minute and I again want to stress that no ultrasound was used this time. Otherwise this would remove almost all the flakes. After this cleaning the samples were dried with nitrogen-gas.

### 4.3 Measuring the samples

For measuring the samples the AFM was used in tapping mode. The AFM that I used, consisted of two main parts: the scanner and the AFM-head. With the scanner all the movements were regulated and the AFM-head contained the AFM-tip, the laser, the photodiode etc. A schematic image of this AFM-head is shown in figure 12.

The scanner was a so called J-scanner with a maximal scan area of 150  $\mu\text{m}$  x 150  $\mu\text{m}$ . For the scanning tapping mode AFM- cantilevers (which are also sloppy called AFM-tips) of the company Olympus were used. Their item number was AC240 TS.



The measuring was done in steps. First the AFM-tip was moved to a certain area of the sample and this area was scanned with the maximal scan range of  $150\ \mu\text{m} \times 150\ \mu\text{m}$ . Then this scanned picture was searched by eye for graphite flakes and as much graphite flakes as possibly could be identified, were scanned with a much smaller scan range. When the scanning of a certain area was finished, the AFM-tip was moved to a new area (moved at least over a distance of  $400\ \mu\text{m}$ ) and the whole process was repeated. In total 24 areas have been completely measured with this process. Of these areas 16 were on sample 1, 7 were on sample 2 and 1 were on sample 3. This unbalanced spread of the areas in the samples is due to logistic reasons. I did make sure that the areas that I measured on a sample were a bit spread over the sample in stead of being too much clustered. The one area on sample three was taken in the middle of the sample. When doing the scanning, there were some troubles/problems which had to be taken care of. Each problem will now be discussed and the used solution to counter it will be given. First there were some troubles with the drift, although there wasn't any glue used to stick the sample to a metal disk as the sample could be laid on the sample holder without any problem. The greatest problem was that the whole image could be shifted after a scan has been made. This shift varied a bit, but it sometimes was in the order of  $10\ \mu\text{m}$ ! The drift during the scanning was quite small and mostly in the vertical (z) direction. To make the drift as small as possible the sample was mounted in the AFM at the end of the afternoon of the day before I was going to perform measurements on it (if that was possible). This decreases the shift in the picture after each scan and the frequency with which these shifts occurred. Secondly the glue was quite a nuisance. If the drive amplitude wasn't high enough the glue caused real troubles, because the AFM-tip then got stuck in the glue or picked up some glue and the result was that the picture became very streaky. To make this problem as small as possible a relatively high drive amplitude was chosen. To reduce the glue problems it also helped to let the sample dry for a few days after it was produced before the measurements were started. Thirdly there was a bow-like deformation present for the largest scan area. This has nothing to do with drift and it wasn't possible to get rid of this deformation during the scanning. Although it could be removed when the pictures were enhanced with the software, it wasn't helpful as I needed to increase the Z limit<sup>6</sup> due to this deformation to keep my picture in the vertical range of the AFM. This at the other hand made the AFM less sensitive to changes in the height. The last point is about the detection of the graphite flakes. As I told before, first an overview picture was made and then I searched by eye for graphite flakes before zooming in. The big problems were that I had to use a picture that wasn't enhanced by software yet to search for those flakes, a lot of glue was present, the graphite flakes were sometimes very difficult to find due to their small size. The problem with the glue was that the glue spots tended cluster and these clusters sometimes looked like graphite flakes. There were a number of criteria that were used to determine whether something was a graphite flake or not.

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<sup>6</sup> The Z limit is the range in vertical direction of the AFM. This determines the vertical resolution as the smallest step size is equal to this Z limit divided by  $2^{16}$  steps (a 16-bits AD-converter was used).

In the end those criteria were the following:

- The form of a certain structure. Glue pulled harder at the tip than the graphite. Therefore the glue drops looked more like spikes and the graphite flakes were quite flat in comparison. Furthermore the glue didn't have any height structure at all while the graphite flakes had steps and other deviations in height.
- The shape. The glue drops were quite circular and the graphite flakes could have a lot of different shapes while a circular shape was quite rare.
- The streaks. Even with a high drive amplitude some glue still caused some streaks and other nasty effects that graphite can not cause. Thus if I saw a structure that caused a lot of streaks I knew for sure that that could not be a graphite flake.

This will now end the story about the measurement problems. In the next chapter a section will be devoted to the further and more quantitative description of the problems such as drift.

After the measurements had been made, the token pictures were enhanced with software. This removed the effects of the (slight) drift and the bow-like deformation. On these enhanced pictures it became easier to find the graphite flakes and quite some graphite flakes also have been found in this way. The problem with these graphite flakes was that there wasn't an accurate zoomed-in picture of them and this meant that I had to exclude the tiniest graphite flakes I found in this way as for those flakes the horizontal dimensions couldn't be measured accurately enough (or at all).

For each of the measurable flakes the following three values were measured: the effective width, length and thickness. In most cases these effective values were (rough) averages, but sometimes another value has been taken instead of the average. For example: if a flake has a height profile which is mostly 40 nm with one peak of 60 nm at the edge, then the effective height would be 40 nm and not 42.3 nm (which would be the average). The effective values are the values that would describe the flake the best.

These measured values were used to determine the area  $A$ , the quotient  $Q$  and the effective height  $h$ . The area  $A$  and the quotient  $Q$  were determined from the effective length  $l$  and width  $b$  in the following way:

$$\begin{aligned} A &= lb \\ Q &\equiv b/l \end{aligned} \tag{4.1}$$

One could also say that  $l$  and  $b$  could be seen as the effective length and width in such a way that they give the correct area (which is indeed what I tried to do).

The area  $A$  and the effective height  $h$  are understandable to use as quantity of interest, while the quotient  $Q$  probably needs some clarification.

The quotient  $Q$  ranges from 0 to 1 (as  $b \leq l$ ) and is an indication of the "squareness" (or "circularity", but graphite flakes usually aren't circular) of the flake. The higher  $Q$  is, the more the flake starts to look like a square (or in the case of a triangle: a triangle with a length that is two times its base due to my use of effective values) and the lower  $Q$  is, the more the flake starts to look like a needle.

These three quantities were used to see whether there was any correlation between shape ( $Q$ ), size ( $A$ ) and height ( $h$ ) of the graphite flakes and which shape, size and height was the most common. This was done by making histograms and determining important statistical parameters of  $Q$ ,  $A$  and  $h$  and making plots of  $Q$  and  $A$ ,  $Q$  and  $h$  and  $A$  and  $h$ . These diagrams can be found in the next chapter.

## Chapter 5

### Results

#### 5.1 Overview of the results

To summarise the last part of the last chapter:

With the AFM graphite flakes were measured as accurately as possible. Then with the taken pictures three important parameters were determined: effective length  $h$ , effective width  $b$  and the effective height  $h$ . From these the area  $A$  and the quotient  $Q$  were determined with equation [4.1]. Then histograms were made of  $Q$ ,  $h$  and  $A$ , statistical properties of these quantities were determined and various plots with these three quantities were made.

In the next section those diagrams will be presented, together with a few pictures that were made with the AFM. These diagrams will be interpreted and some observations about the form of the graphite flakes will be made.

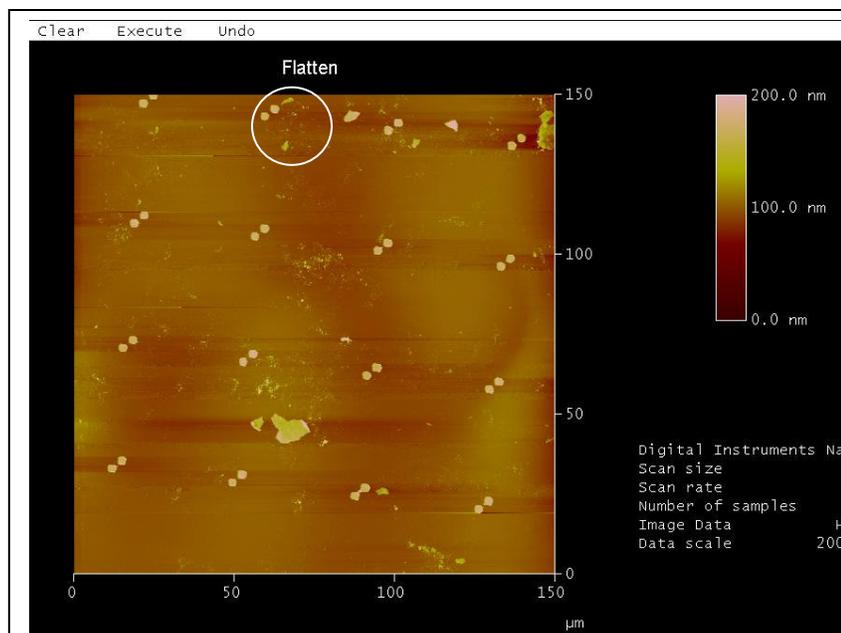
In the section after that some remarks will be made about doing AFM in order to say more about graphite flakes and how well the AFM is suited as a tool in the search for graphene.

After that it will be time to draw some final conclusion in the next chapter.

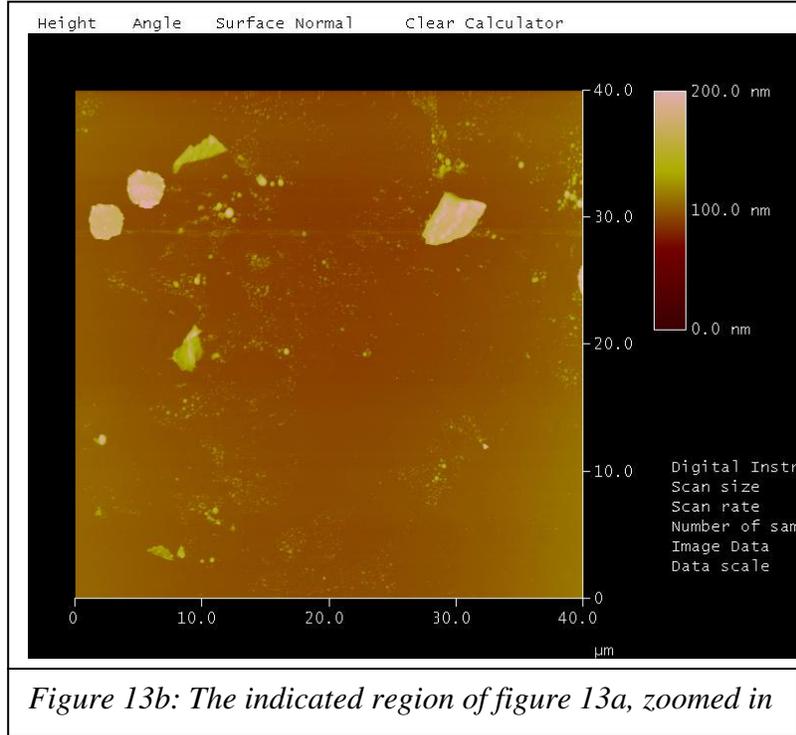
#### 5.2 Results concerning the graphite flakes

In this section the diagrams will be given which tell something about the properties of the graphite flakes that are made with the cleave-and-run method. Before this a few AFM-pictures will be shown to get an impression of the kind of pictures that are obtained when doing AFM on the graphene/graphite-samples.

In figures 13a and 13b the process of the measurements is shown. In figure 13a an overview picture is shown and in figure 13b on a part of this picture has been zoomed in. Both pictures have been enhanced with the software.

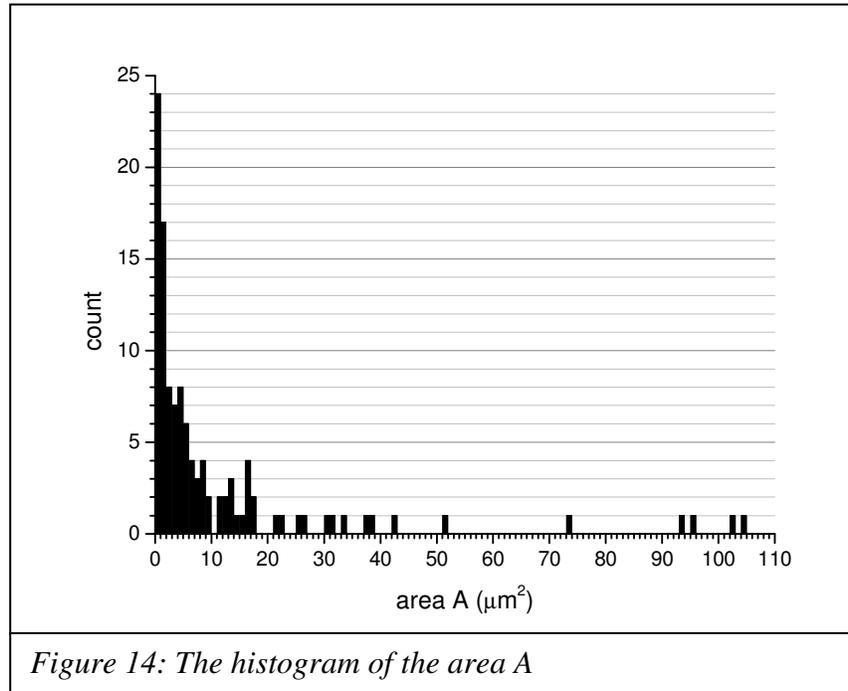


*Figure 13a: An overview picture made with the AFM  
On the region indicated with the circle has been zoomed in.*



Now the histograms of the area  $A$ , the quotient  $Q$  and the effective height  $h$  (from now I will start to call this just the height  $h$ ) will be given together with some conclusion that can be drawn when looking at these histograms. For these histograms the following step sizes were used: for  $A$  a step size  $\Delta A$  of  $1 \mu\text{m}^2$ , for  $Q$  a step size  $\Delta Q$  of 0.01 and for  $h$  a step size  $\Delta h$  of 1 nm.

Furthermore the important statistical properties of the three quantities of interest will be given in three tables.



In the histogram of the area A, as is shown in figure 14, it is clearly visible that the produced graphite flakes have a strong tendency to be of a small size. Almost all the produced graphite flakes are smaller than  $20 \mu\text{m}^2$  and the largest count is found for  $A \leq 1 \mu\text{m}^2$ . This can also be clearly seen in table 1 where some statistical data has been listed for the area A.

**Table 1: Statistical data for the area A**

Quantity	Value
Average	$11.5 \mu\text{m}^2$
Standard deviation	$20.5 \mu\text{m}^2$
Minimal value	$0.29 \mu\text{m}^2$
Maximal value	$104.86 \mu\text{m}^2$
25%-percentile <sup>7</sup>	$1.20 \mu\text{m}^2$
Median	$4.14 \mu\text{m}^2$
75%-percentile	$12.48 \mu\text{m}^2$

In this table this strong tendency for small areas is shown again: 75 per cent of all the flakes were smaller than  $12.48 \mu\text{m}^2$  and half of them are also smaller than  $4.14 \mu\text{m}^2$ . Another thing that can be observed from both the histogram and the table is that although there is a really strong tendency for small areas, some flakes with a much larger area are still found. These are really rare: only 6 flakes were seen with an area larger than  $50 \mu\text{m}^2$ , but they influence the average and the standard deviation so much that these do not represent the properties of the area very well, because they've become much too large. The histogram of the area A shows an exponential behaviour. I therefore tried to fit this exponential behaviour just to see how well this would describe the distribution of the area

<sup>7</sup> A x%-percentile is that value for which x % of the measurements is below that value. A 25%-percentile of  $1.20 \mu\text{m}^2$  in this case means that 25% of the samples have an area smaller than  $1.20 \mu\text{m}^2$

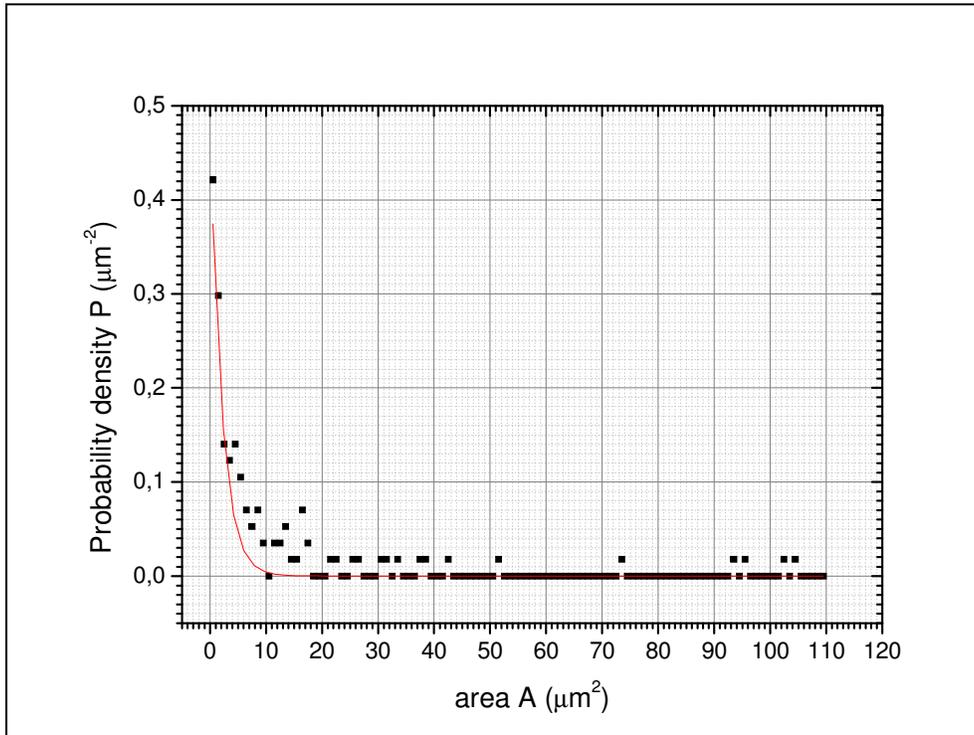
A. For this end I made of plot of the approximate probability density and this plot was fitted with the exponential distribution:

$$P(A) = Ce^{-AC} \quad [5.1]$$

In this equation [5.1]  $C$  is a constant which needs to be determined by the fit. This form of the distribution is needed to ensure the normalisation condition:

$$\int_0^{\infty} P(A)dA = 1 \quad [5.2]$$

The approximate probability density was determined by dividing the data set of the area in bins with a size of  $0.5 \mu\text{m}^2$  and by determining the frequency of the number of data points in each bin (this is just the way to make a histogram). The approximate probability density was then found by dividing those frequencies by 114(the total number of data points) and  $0.5 \mu\text{m}^2$  (the bin size). The result of this work is shown in figure 15.



*Figure 15: The probability density of the area A.  
The fit of this distribution is shown with red. The probability density is fitted with that of the exponential distribution:  $P(A) = Ce^{-AC}$ .  
The result of the fit is:  $C = 0.47 \pm 0.03 \mu\text{m}^{-2}$  and a  $R^2$  of 0.89281*

As can be seen in the diagram and at the value of  $R^2$ <sup>8</sup> the probability density can indeed be reasonable well be described with the exponential distribution with the constant  $C$  being equal to  $0.47 \mu\text{m}^{-2}$ .

<sup>8</sup>  $R^2$  is parameter that is used to fit graphs. The higher this number is, the better the fit is.  $R^2 = 1$  means a perfect fit.

In figure 16 below the histogram of the quotient  $Q$  is shown. As can be seen in this histogram the quotient  $Q$  has a large spread and no clear behaviour is visible. The largest peak is found at a quotient of 0.7 and most of the samples have a quotient the falls in the range from 0.4 to 1.0.

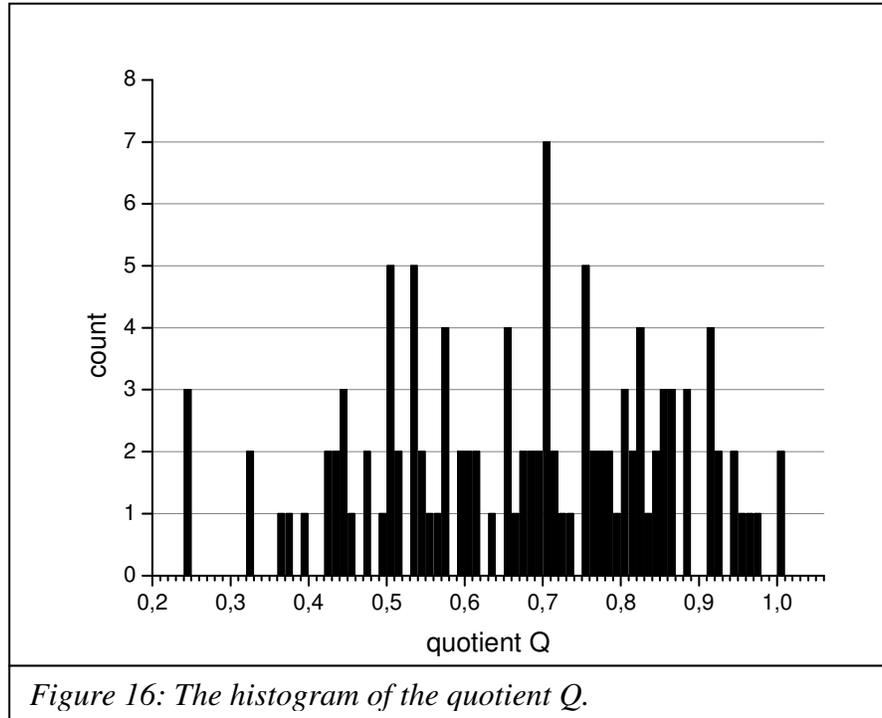


Figure 16: The histogram of the quotient  $Q$ .

In table 2 where some statistical data is shown for the quotient  $Q$  this same behaviour is seen again.

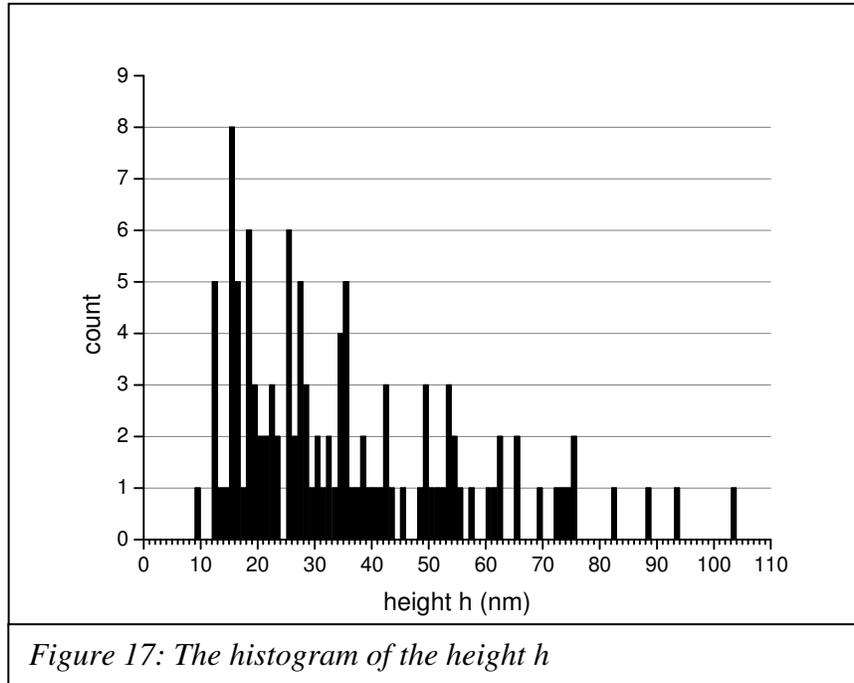
**Table 2: Statistical data for the quotient  $Q$**

Quantity	Value
Average	0.67
Standard deviation	0.18
Minimal value	0.24
Maximal value	1.00
25%-percentile	0.54
Median	0.70
75%-percentile	0.82

According to this table 75 per cent of the data has a  $Q$  that is greater than 0.54 and half of the samples has a  $Q$  between the 0.54 and the 0.82. From this fact it can be concluded that the produced graphite flakes tend to have a shape that is more square-like than needle-like. The data also seems to be quite symmetrical as the average value and the median are more or less the same.

The relatively large standard deviation indicates what already was seen in the histogram: there is quite some spread in the  $Q$  and the cluster around 0.7 is quite weak.

In figure 17 below the histogram of the height  $h$  is shown. In this histogram a strong tendency for the clustering around heights of 16 nm, 26 nm and 36 nm is visible. The clustering around 16 nm is by far the strongest and most of the samples have a height between 12 nm and 44 nm. Although there is some clustering present the height of the samples is still quite spread out and the peaks are weak. One remarkable feature is though that there are no flakes with a height smaller than 9 nm.



In table 3 some statistical data is shown for the height  $h$ .

**Table 3: Statistical data for the height  $h$**

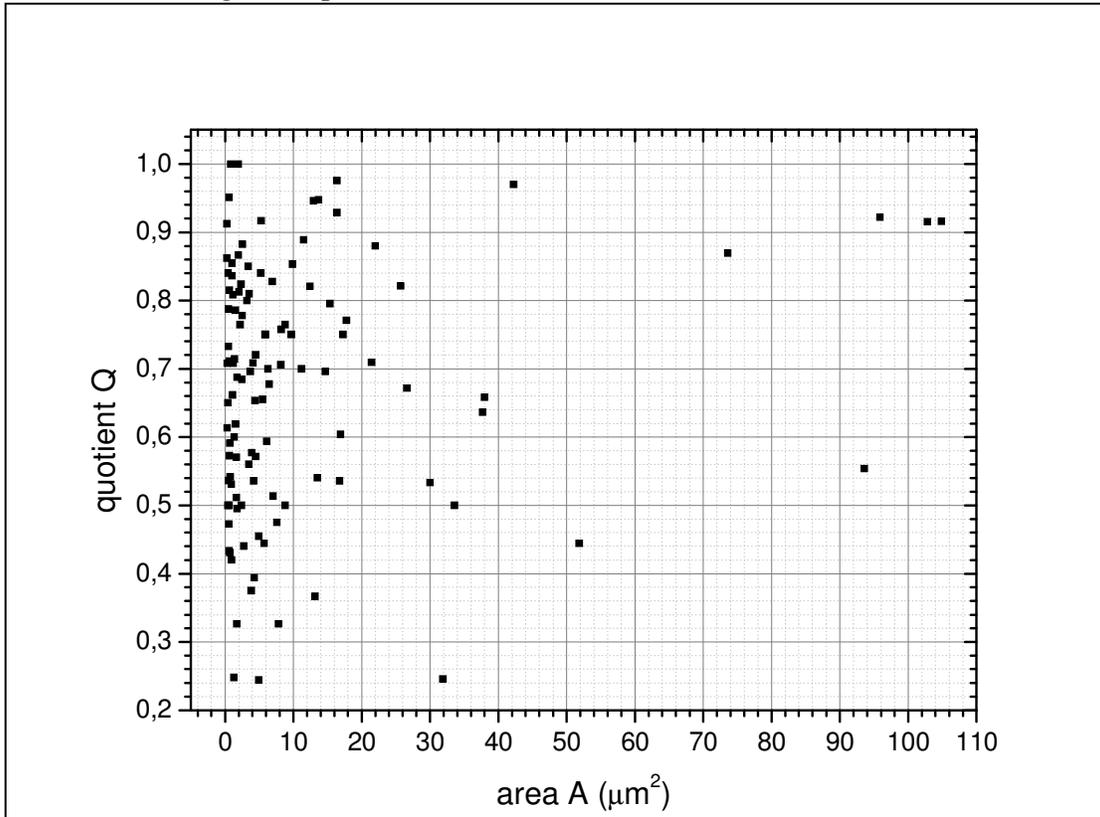
Quantity	Value
Average	35.5 nm
Standard deviation	20.1 nm
Minimal value	9.1 nm
Maximal value	103.3 nm
25%-percentile	19.4 nm
Median	29.7 nm
75%-percentile	49 nm

The value of the 25%-percentile and the 75%-percentile confirm my earlier statement that most of the samples have a height between 12 nm and 44 nm. The statistical data namely suggest that 75 per cent of the samples have a height between 9 nm and 49 nm.

The relatively large spread of the height  $h$  can be seen in the large standard deviation of 20.1 nm (this roughly half of the range in which 75 per cent of the samples are found). The average value is larger than one would expect by looking at the histogram, but this is due to the presence of a few samples with a much larger height than the rest.

After showing the histogram and statistical properties of the three quantities of interest the correlation between these quantities will be investigated by plotting them against each other. In these plots each data point represent a graphene flake.

In figure 18  $A$  and  $Q$  are plotted, in figure 19  $A$  and  $h$  are plotted and finally in figure 20  $Q$  and  $h$  are plotted. Each of these plots will be supplied with the observations that can be made when looking at the plots.



*Figure 18: The plot of the area  $A$  and the quotient  $Q$*

In the figure above, figure 18, the area  $A$  and the quotient  $Q$  are plotted in the same diagram. As can be seen the figure doesn't show a very strong correlation between the two quantities. The only thing that can be really said without a reasonable doubt is that the spread in  $Q$  becomes smaller when  $A$  becomes larger. This can only be said beyond reasonable doubt for  $A \leq 18 \mu\text{m}^2$ . For small  $A$   $Q$  can vary from 0.24 to 1.0 and for larger  $A$  this range becomes very quickly smaller. Although this could also be due to the limited amount of graphene flakes that were measured.

It seems as if there isn't any correlation at all. Even if there is a correlation between  $A$  and  $Q$ , this correlation is very weak.

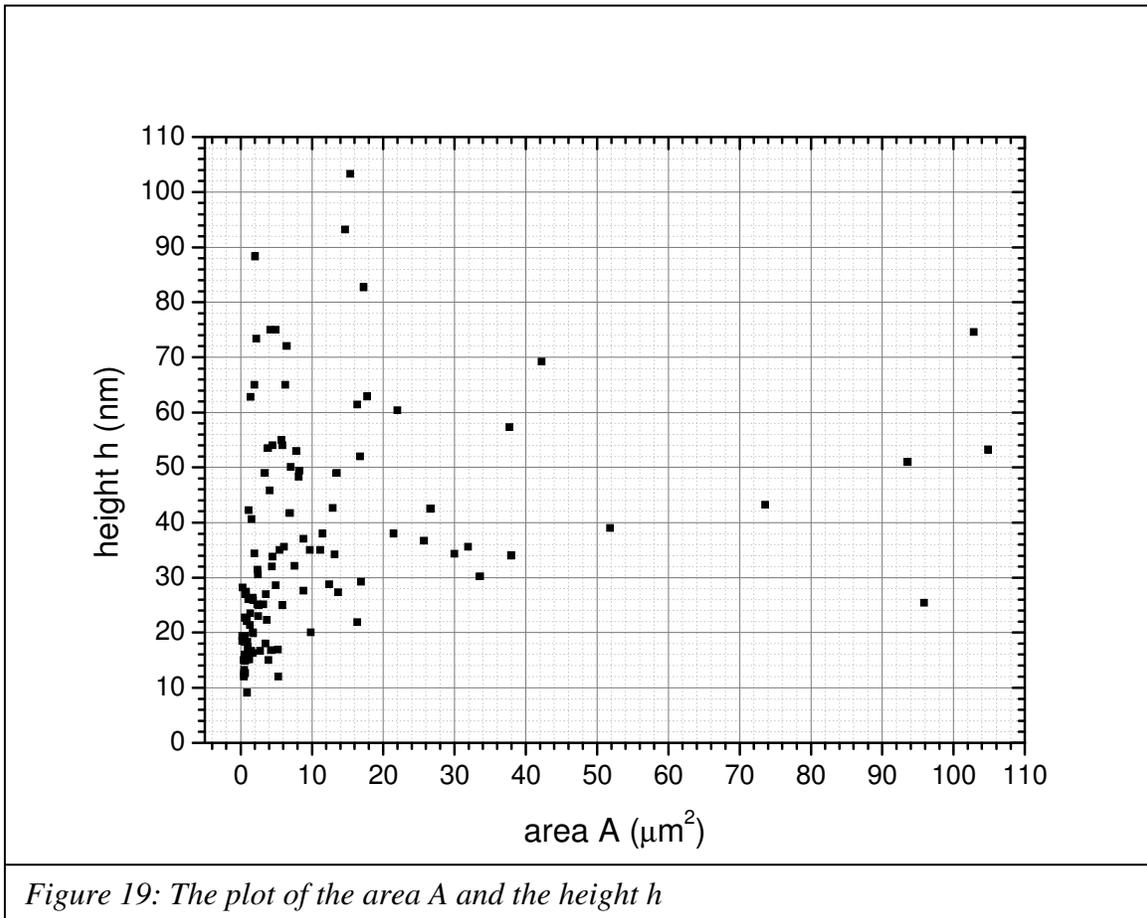


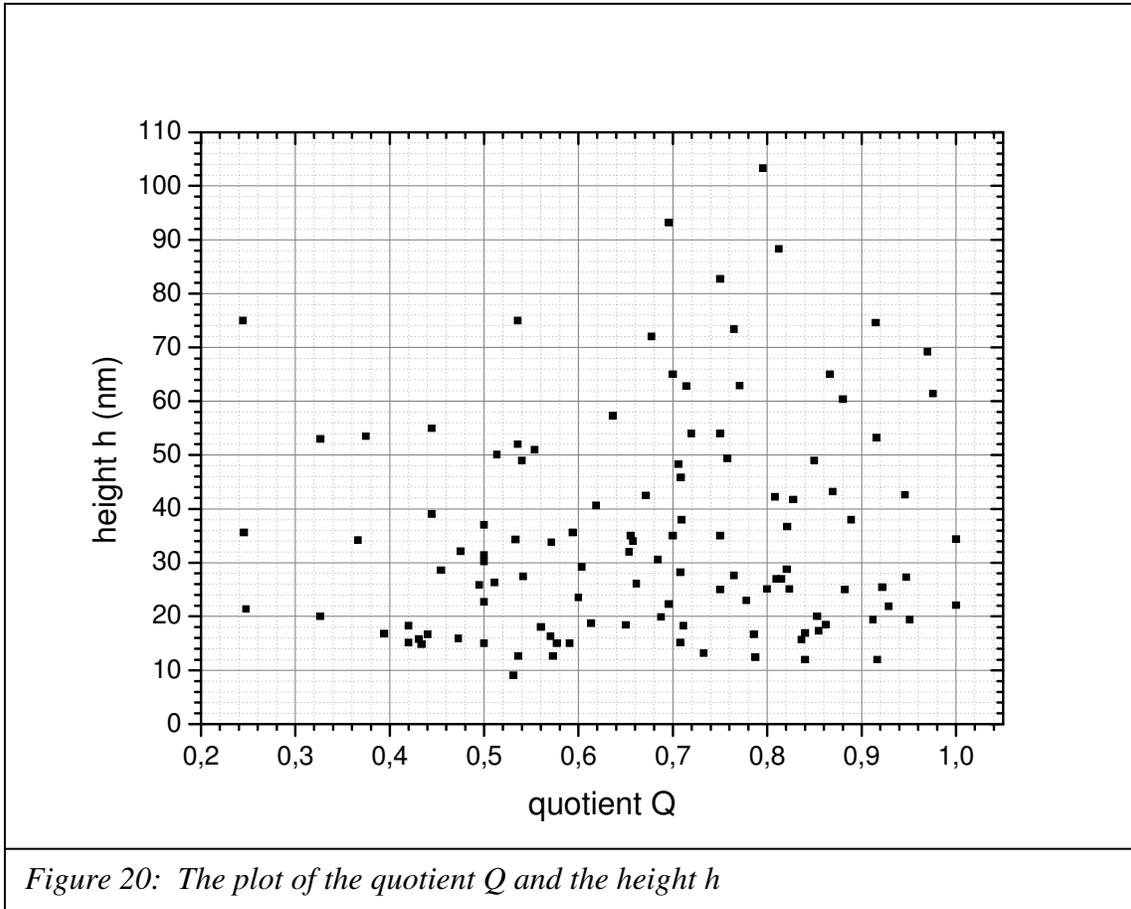
Figure 19: The plot of the area  $A$  and the height  $h$

In the figure above the area  $A$  and the height  $h$  are plotted in the same diagram. In the figure strong clustering can be seen around  $h = 16 \text{ nm}$  and  $A = 1 \mu\text{m}^2$ . Other striking features are:

- The lower limit of the height generally increases with the area.
- When the area is between  $2 \mu\text{m}^2$  and  $18 \mu\text{m}^2$ , the height varies a lot more than for an area of around  $1 \mu\text{m}^2$  or above  $20 \mu\text{m}^2$ .
- When the area is between  $2 \mu\text{m}^2$  and  $18 \mu\text{m}^2$ , the spread in the height increases (a bit) with the area in a periodic way.

It seems that the increase in the height goes hand in hand with the increase of the area and up until an area of  $18 \mu\text{m}^2$  I can say with certainty that the spread in the height increases a bit with the area in a periodic way. I can't say too much about the behaviour of the height for larger areas as there are only 16 data points with an area larger than  $18 \mu\text{m}^2$ .

It is certain that there is a correlation between the height and the area, but due to the very limited amount of data points for larger areas the dependency of the height and the area can only be clearly seen and described for area smaller than  $18 \mu\text{m}^2$ .



*Figure 20: The plot of the quotient  $Q$  and the height  $h$*

In figure 20 the quotient  $Q$  and the height  $h$  are plotted in the same diagram. If there is any correlation between the quotient and the height, then it must be extremely weak. When looking at figure 20 you'll probably get the impression that the data points seem to be better scattered more or less at random. Although there are indeed some clusters around  $h = 16$  nm and  $Q = 0.7$ , these clusters don't have anything to do with a correlation as these clusters can be explained from the height and quotient distributions alone.

This ends the results concerning the properties of the graphite flakes. In the next section some results will be given in the light of doing AFM on the graphene/graphite-samples and how well the AFM is suited to search for graphene.

### 5.3 Results concerning the AFM-work

This section will be devoted to the quantitative description of the quality of the AFM for the scanning of the graphene/graphite-samples. A shorter version of this section can be found in appendix which is a bit more technical.

First something will be said about the speed of the AFM. To make a scan of the image a total time of 512 seconds or 8.5 minutes is needed. Due to the glue, which even with the right precautions caused some problems, it was obligatory to first let the machine make one or two scans before a good overview picture could be made. After these scans the image has lost most of its streakiness and the image could be scanned properly. Therefore to make the overview picture already 17-25.5 minutes were needed.

Then came the part where I zoomed in on a certain area with the AFM. This zooming took about 10 minutes on average. The biggest reason for this relatively long time was a shift that sometimes occurred after a scan and which could be in the order of 10  $\mu\text{m}$ !

During this zooming in on an area the AFM scanned about four times as fast as normal and this saved a lot of time. After having zoomed in again 8.5 minutes were needed to scan and this gives a needed time of 18.5 minutes per zoomed-in area. On average about three zoomed-in (or attempts of zoomed-in) pictures are made per overview picture. An average time of 77 minutes is therefore needed to scan an area of 150  $\mu\text{m}$  x 150  $\mu\text{m}$ .

Earlier it was already calculated that you then need about 5703 hours to scan the whole substrate of 1 cm x 1 cm.

In this whole calculation it is assumed that nothing goes wrong and that the sample has had enough time to completely thermalise. Therefore in reality about 25 per cent extra time (on average) was needed and this makes point that I want to make even stronger: the AFM isn't fast enough to search for graphene; it just takes too much time!

The second point will be about the resolution of the AFM. In the vertical direction a height variation of about 0.09 nm was measurable in theory. For the zoomed in pictures this was even better. This resolution is quite good and in principal it should be possible to see very thin graphite flakes and even graphene (0.4 nm thick). In the pictures height steps of 3 nm and folds were clearly visible.

The horizontal resolution however also needs to be taken into account. For the large overview picture of 150  $\mu\text{m}$  x 150  $\mu\text{m}$  the area per pixel was 0.293  $\mu\text{m}$  x 0.293  $\mu\text{m}$ . A typical zoomed-in picture was about 25  $\mu\text{m}$  x 25  $\mu\text{m}$  and then this area per pixel was about 49 nm x 49 nm.

To see whether this resolution is good or bad, this needs to be compared with the typical dimensions of the graphite flakes. As could be seen in the last paragraph graphite flakes tend to be very small and one finds a lot of graphite flakes that have an area that is 1  $\mu\text{m}^2$  or even smaller. On the large overview picture this would be less than 25 pixels!

Therefore even if these small flakes can be seen on the overview picture, they contain too much bit noise to be properly measured. And it is very questionable if such a flake would be visible on a picture that is not enhanced due to effects that will be mentioned later; 25 pixels on 512<sup>2</sup> pixels is only 0.23 % of the total area! Only on a zoomed-in picture is it possible to see these small flakes clearly and in their full glory; they are then typically covered by 400 pixels. The moral of this: it is only possible to see all of the graphite flakes correctly when a relatively small scan area is used. This at the other hand increases the measure time by a considerable amount.

This same story also holds for graphene as a graphene flake typically has an area of around  $1 \mu\text{m}^2$ <sup>9</sup>.

The third point will be about the drift. There were actually two special kinds of drift apart from the normal drift that were teasing me during my research. Both of them will be mentioned and explained.

First you had the most annoying kind, namely the kind which shifted the image.

This shift was quite unpredictable in occurrence and size. This shift was triggered by two events: the scanning of an image had been finished and the cantilever was going to make a new image by moving in the reverse direction (as compared to the direction of the first image) and the moving of the cantilever when there was zoomed in. This shift could be quite large (up until  $15 \mu\text{m}$ !), but this shift was more annoying than harmful as it didn't influence the measurements.

Although this kind of drift occurred less often and became smaller when the sample had been in the AFM for quite a while (a whole night), this kind of drift could never be completely removed.

Second there was the bow-like deformation of a flat surface. Due to this the flat surface of my sample looked like it was curved. This was strongly size dependent. It was present on all of the overview pictures, but on most of the zoomed-in pictures this was very weak or absent. It did become less when the sample had been thermalised and it was typically smaller than  $3 \mu\text{m}$ .

Although the bow-like deformation could easily be removed with software enhancement of the picture, it did cause some problems. It forced me to increase the Z limit which decreases the resolution and it made it a lot harder to recognise the graphite flakes on the pictures that weren't software thus it became harder to find the graphite flakes during the scanning.

The fourth point will be about the glue and how well the AFM could handle it.

The glue that was present on the sample could really be a nuisance unless the measures that were described in section 4.3 were taken. These measures were to let the sample dry a few days before starting to do measurements on it and to use a high drive amplitude to prevent the AFM-tip from getting stuck in the glue. With these measures taken the AFM could handle the glue quite well. It was even possible to make nice pictures of the glue. One such picture is present in appendix C.

Even with all the precautions the glue could still incidentally cause streaks in the picture. When an overview picture was going to be made the AFM always needed to make a few test scans before the obtained image was stable enough. The reason for this phenomenon is that the sample then locally needs to be thermalised, but my impression during the measurements was that due to the glue the time before the sample was locally thermalised increased. My argument for this statement is that most of distortions that were present during this time were around the glue.

The last point will be about the identification of the graphite flakes. For this purpose all of the aspects that were mentioned above played a roll: the resolution, the drift and the presence of the glue.

As the vertical resolution of the AFM was very good, the identification was only limited due to horizontal resolution. This was especially true for the overview picture. When

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<sup>9</sup> According to S. Russo and M. Cracuin

zooming in on the picture a lot of new, small graphite flakes were found and only on the zoomed-in pictures were graphite flakes accurate enough measurable.

With respect to identification of the graphite flakes the drift was very annoying. The shift after almost each scan made it harder to zoom in on the wanted area, but it at least didn't make it harder to identify a graphite flake. The bow-like deformation was actually much worse, as this deformed the image and could cause the picture to go (almost) out of the range of the AFM at the edges of the pictures. The graphite flakes that were at those edges could then only be seen after the picture had been enhanced with the software. The glue mostly caused a lot of confusion as the glue could resemble the graphite flakes quite well if the glue droplets were in a cluster. With the help of the criteria that were described in section 4.3 it was possible to distinguish the glue from the graphite flakes. The morale of this story is that the AFM is only partly suited to scan the graphite flakes and is very poorly suited to search for graphene

I will summarize the main arguments:

- Scanning a substrate with an AFM takes too much time. The AFM can scan large areas and the AFM can scan very precisely, but the AFM can only combine those two qualities when the scanning speed decreases drastically.
- It isn't very easy to identify the graphite flakes on the larger scale of the overview picture due to the presence of confusing glue droplets and the inability to use the enhanced pictures to zoom in. This last part isn't a fault of the AFM-technique, but more the fault of the software that used to control the AFM.
- Due to the bow-like deformation the range of the AFM needed to be quite large. Although this doesn't make the smallest step size in the height too large, this does make it harder to find relatively small changes in the height.

This ends this section about the quality of the AFM when scanning the graphene/graphite-samples. Now the conclusions will follow.

## Chapter 6

### Conclusion and recommendation

#### 6.1 Conclusions

The conclusions of this research can be separated in two different parts. A part about the properties of the graphite flakes that are produced when the cleave-and-run technique is used to make graphene and a part that discusses the effectiveness of the AFM as tool to investigate these properties.

About the properties of the produced graphite flakes as seen by the AFM the following conclusions can be drawn:

- The area of these flakes tends to be small: 75 per cent of the flakes are smaller than  $12.48 \mu\text{m}^2$  and 25 per cent of the flakes are smaller than  $1.20 \mu\text{m}^2$ . The spread in the area is not large, although some really large flakes (larger than  $50 \mu\text{m}^2$ ) can be found. The number of flakes falls off exponentially with increasing area.
- The quotient of the flakes can vary a bit, but is mostly between 0.5 and 0.9. A peak in the histogram is found at a quotient of 0.7 and the spread in the quotient is relatively symmetric around 0.7. These values of the quotient imply that the produced flakes tend to have a shape that is more likely to resemble a square than a needle.
- The height of the flakes varies less than the area, but more than the quotient of the flakes. The height is mostly between 9 nm and 49 nm and no flakes have been found that are thinner than 9 nm (roughly 23 layers of graphene). A few peaks can be found in the histogram: around 16 nm, 26 nm and 36 nm, but these peaks aren't very strong.
- There isn't a very strong correlation between the area and the shape of the flake. The only thing that can be said is that the spread in the quotient decreases for increasing area, but this can only be said beyond reasonable doubt for an area smaller than  $18 \mu\text{m}^2$  due to the limited amount of found flakes with an area larger than  $18 \mu\text{m}^2$ .
- The correlation between the area and the height of the flake is quite strong. In the plot of these two a strong cluster can be seen around a height of 16 nm and an area of  $1 \mu\text{m}^2$ . Furthermore the lower limit of the height seems to increase with the area and last but not least: the spread in the height seems to vary in a periodic way with the area. This last point can only be said to be true beyond reasonable doubt for an area smaller than  $18 \mu\text{m}^2$ .
- The correlation between the height and the shape of the flake is either very weak or absent.

One important note: all these conclusions about the graphite flakes are the conclusions about the flakes as seen with the AFM. It is very possible that the real properties of graphite flakes are a bit different than the ones that I've found with my research. I should

actually say that the properties that I've found are the properties of the graphite flakes that could be imaged correctly with the AFM using my measuring method. I'm afraid that due to my measuring method some of the smaller flakes have been missed which of course influences all of the statistics. At other hand: this method could effectively reduce the time needed to do all the measurements.

About the effectiveness of the AFM to investigate the properties of these flakes the following conclusions could be drawn:

- The AFM is very slow if one wants to precisely measure all the graphite flakes that can be found on a larger area (such as  $150\ \mu\text{m} \times 150\ \mu\text{m}$ ). This is correlated to the fact that the AFM needs to operate with a smaller scan area to be able to see all the flakes (accurately enough).
- The resolution (in all the directions) of the AFM is good enough to see all details of the graphite flakes as long as scan area isn't too large. Scan areas of about  $20\ \mu\text{m} \times 20\ \mu\text{m}$  or in that order are perfectly suited for observing these flakes. The quality of the imaged flakes was good enough to be able see small height steps, folds etc.
- Identification of the graphite flakes on the substrate is quite hard due to the presence of the glue on the samples which causes confusion, the inability of the software to let the user use software-enhanced picture to zoom in and the bow-like deformation which is strongly present on larger picture, but almost completely absent on the zoomed-in pictures. With some experience though this will become a lot less problematic. One big problem that remains is the relatively large Z limit that is required due to the bow-like deformation. This makes it very hard to identify very thin graphite flakes or graphene.
- The glue on the sample in the beginning proved to be a problem, but with a few measures this problem can be easily solved. These measures were: letting the sample thermalise, letting the glue dry, setting a high drive amplitude and making a few test scans before the real scan is made.

The main conclusion can be: the AFM is precise enough to image the graphite flakes very accurate and the glue doesn't prove to be a hurdle which can't be taken, but the AFM just isn't fast enough (at least: when it is in its mode where it is precise enough) to measure all the graphite flakes on a large area within a reasonable time.

## 6.2 Recommendations

Concerning the work I have done improvements can be made:

- In order to say more about the properties of the graphite flakes that are produced with the cleave-and-run technique the number of scanned graphite flakes needs to be increased. Now only 114 flakes have been scanned and although this is already enough to do some statistics on the data set, more accurate statements can be made when this number is drastically increased.
- To continue the last point: care must be taken to minimise the effects of the AFM on the measurements as with the technique that I used not all graphite flakes that could be found, have been taken into account.

- Another measuring technique needs to be found. Although the AFM is accurate enough, it isn't fast enough. It literally takes ages before enough graphite flakes (about thousands of flakes) have been scanned to make strong founded statistical statements. One suggestion is to use an optical microscope as the colour of the graphite flake on the sample depends on the thickness as can be read in reference [7]. With the help of the computer this could be made automatic and I'm sure of it that this is a lot faster than the AFM-technique. Scanning the sample with an optical microscope when searching for graphene normally takes about 2 hours; this is a lot less than the days that an AFM requires.

One final note about the title of my report: "The search for graphene". The search for graphene with the AFM has proved to be unsuccessful, but a lot has been learned about the graphite flakes that are also produced with the cleave-and-run technique. The search for graphene should be continued but definitely not with an AFM!

## References

### Material used per chapter

I will give a list of the material I used to write a certain chapter. The numbers in this list refer to the references stated in the list of references on the next page.

**Chapter 1 Introduction:** [1], [2], [3], [4]

**Chapter 2 Graphene:** [1], [2], [3], [5], [6], [7]; this chapter has been based on [1]

**Chapter 3 Instruments and Machines:** [8], [9], [10], [11], [12]

**Chapter 4 Description of the Research:** [10]

**Chapter 5 Results:** [3]

**Chapter 6 Conclusions and Recommendations:** [3], [7]

## List of references

- [1] The article:  
A.K. Geim and K.S. Novoselov  
*The rise of graphene*  
Nature Materials **6**, 183 (2007)
- [2] The supplement of the article:  
K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos,  
I.V. Grigorieva, A.A. Firsov  
*Electric Field Effect in Atomically Thin Carbon Films*  
Science **306**, 666 (2004)
- [3] Private communication with Saverio Russo and Monica Cracuin:  
Explanation of the cleave-and-run technique to make graphene as it is done at the  
university of Delft.
- [4] The supplement of the article:  
Jannik C. Meyer, A.K. Geim, M.I. Katsnelson, K.S. Novoselov, T.J. Booth and  
S.Roth  
*The structure of suspended graphene sheets*  
Nature **446**, 60 (2007)
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*Solid State Physics 2<sup>nd</sup> edition*  
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- [6] The website:  
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- [7] The article:  
S. Roddaro, P. Pingue, V. Piazza, V. Pellgrini and F. Beltram  
*Colors Of Graphite On Silicon Dioxide*
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V.L. Mironov, The Russian Academy of Sciences Institute of Physics of  
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[10] The book:

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[11] The website of the MSM Nano Lab of the University of Leiden

[12] The website:

[nano.mtu.edu/afm.htm](http://nano.mtu.edu/afm.htm)

# Appendix A

## List of interesting articles about graphene

In this appendix a list will be given of recommended, interesting articles about graphene. Each article will be supplied with a bit of extra information about the reason why I recommend this.

I will divide the articles in three sections: experimental articles, theoretical articles and fabrication article (there is only one).

### Experimental articles

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov  
*Electric Field Effect in Atomically Thin Carbon Films*  
Science **306**, 666 (2004)

This is the first experimental article about graphene. This is the article in which the first discovery is being described.

2. A.K. Geim and K.S. Novoselov  
*The rise of graphene*  
Nature Materials **6**, 183 (2007)

This is a well written article about graphene which gives an overview of some of the stunning properties of graphene. This article is quite easy to read.

3. Jannik C. Meyer, A.K. Geim, M.I. Katsnelson, K.S. Novoselov, T.J. Booth and S.Roth  
*The structure of suspended graphene sheets*  
Nature **446**, 60 (2007)

In this article the structure of suspended graphene sheets and the crumpling that it exhibits is discussed in detail. In the supplement a nice optical micrograph of graphene can be found!

4. K.S. Novoselov, E. McCann, S.V. Morozov, V.I. Fal'Ko, M.I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin and A.K. Geim  
*Unconventional quantum Hall effect and Berry's phase of  $2\pi$  in bilayer graphene*  
Nature Physics **Advance Online Publication**, (2006)

In this article the unconventional QHE that graphene exhibits, is being discussed in greater detail.

5. S. Roddaro, P. Pingue, V. Piazza, V. Pellgrini and F. Beltram  
*Colors Of Graphite on Silicon Dioxide*  
Can be found on the website of the MSM Nano Lab

This is the first article (that I found) that gave a satisfactory explanation for visibility of graphene on 290 nm SiO<sub>2</sub> on Si.

6. A.C. Ferrari, J.C. Meyer, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth and A.K. Geim  
*Raman Spectrum of Graphene and Graphene Layers*  
Phys. Rev. Letters **97**, 187401 (2006)

In this article another way of identifying graphene is mentioned, namely with the use of the Raman spectrum. The Raman spectrum seems to depend quite critically on the number of layers.

7. Hubert B. Heersche, Pablo Jarillo-Herrero, Jeroen B. Oostinga, Lieven M.K. Vandersypen and Alberto F. Morpurgo  
*Bipolar supercurrent in graphene*  
Nature **446**, 56 (2007)

In this article the research on the Josephson effect in mesoscopic junctions consisting of a graphene layer contacted by two closely spaced superconducting electrodes is being presented. In the article it is stated that at zero charge density a finite supercurrent can still flow through graphene.

8. Claire Berger, Zhimin Song, Xuebin Li, Xiaosong Wu, Nate Brown, Cécile Naud, Didier Mayou, Tianbo Li, Joanna Hass, Alexei N. Marchenkov, Edward H. Conrad, Philip N. First, Walt A. de Heer  
*Electronic Confinement and Coherence in Patterned Epitaxial Graphene*  
Science **312**, 1191 (2006)

This article describes research done on graphene that is epitaxial grown and has been patterned with nanolithography methods. The focus of this research was the electronic properties of the graphene. A lot can be found about the behaviour of graphene in the presence of a magnetic field.

9. P. Mallet, F. Varchon, C. Naud, L. Magaud, C. Berger and J.-Y. Veuille  
*Electron states of mono- and bilayer graphene on SiC probed by STM*  
arXiv: cond-mat/07024063v1 (2007)

This article tells about STM-work that has been done on graphene. Some nice STM-pictures of graphene are included.

## Theoretical articles

1. S.Reich, J.Maultzsch, C. Thomsen and P. Ordejón  
*Tight-binding description of graphene*  
Physical Review B **66**, 035412 (2002)

In this article a tight-binding description of graphene is given and it shown that this tight-binding description becomes a lot better when up to the third-nearest neighbors are being used.

2. M.A.H. Vozmediano, M.P. López-Sancho, T. Stauber and F. Guinea  
*Local defects and ferromagnetism in graphene layers*  
arXiv: cond-mat/0505557v1 (2005)

This tells about the effects of local defects on the electronic structure of graphene. One of these effects is the creation of ferromagnetic moments caused by electron-electron interactions.

3. Z.F. Wang, Huaixiu Zheng, Q.W. Shi, Jie Chen, Jinlong Yang and J.G.Hou  
*An insight into the electronic structure of graphene: from monolayer to multi-layer*  
arXiv:cond-mat/0703422v1 (2007)

An article about the band structure of one to four layers of graphene. Also the local density of states (LDOS) is being calculated for these four situations. One of the conclusions is that graphene and few-layer graphene can be identified by measuring the  $d^2I/dV^2$  in a STM.

4. V.P. Gusynin, S.G. Sharapov and J.P. Carbotte  
*Anomalous Absorption Line in the Magneto-Optical Response of Graphene*  
Physical Review Letters **98**, 157402 (2007)

This article tells a bit more about the absorption spectrum of graphene. This is critically depended on the Landau quantisation which also causes the anomalous QHE to arise in graphene. The complete theoretical calculation of the conductance of graphene can be found in the next article which is quite complicated.

5. V.P. Gusynin and S.G. Sharapov  
*Transport of Dirac quasiparticles in graphene: Hall and optical conductivities*  
Physical Review B **73**, 245411 (2006)

This is typically an article that you would only read if you had the desire to see a complete, complex calculation of a result that is given in an article. This article isn't recommended for readers that aren't too fond of theoretical calculations.

## **Fabrication article**

1. N. Staley, H. Wang, C. Puls, J. Forster, T.N. Jackson, K. McCarthy, B. Clouser and Y. Liu  
*Lithography-free fabrication of graphene devices*  
Applied Physics Letters **90**, 143518 (2007)

In this article a way to make structure out of graphene is described that doesn't rely on lithographic methods. A nice article for those readers that are more interesting in the fabrication of devices made of graphene.

## Appendix B

### Fabrication of the samples

In this appendix the fabrication process of the samples will be given again in a very short way with all the parameters including the ones that weren't present in section 4.2.

#### Cutting the wafer

- Wafer: 290 nm SiO<sub>2</sub> on Si
- Substrate size: 1 cm by 1 cm
- Substrates cleaned: 2.5 minutes acetone, isopropanol and distilled water (with ultrasound).
- In between and at the end: dry with N<sub>2</sub>-gas.

#### Providing the substrates with markers: e-beam lithography

- Spincoat PMMA A4 4000 rpm:  
ramp1: 2s  
ramp2: 4s  
time: 50 s
- Bake 90 sec 180 °C on hot plate
- SEM, exposure parameters:  
I: 0.1 nA  
Area dose: 207.4 nAs/cm<sup>2</sup>  
WD: 8 mm  
Magnification: 100 times  
Write field: 800 μm x 800 μm
- Development:  
40 sec in MIBK: IPA 1:3 (stir gently)  
40 sec in IPA  
Dry with N<sub>2</sub>-gas
- Evaporating  
Substrate 1: first 5 nm Cr, then 30 nm Au  
Substrates 2 and 3: first 3 nm Cr, then 25 nm Au (gives markers that are smoother on the top)
- Evaporating; parameters:

Quantity	Recipe		Substrate 2		Substrate 3	
Initial pressure (in mbar)	< 1 · 10 <sup>-6</sup>		2.1 · 10 <sup>-7</sup>		1.1 · 10 <sup>-6</sup>	
	Cr	Au	Cr	Au	Cr	Au
Voltage U (in V)	1.5	2.5	4.6	2.2	1.83	2.24
Current I (in A)	3 x 25	3 x 60	3 x 28	3 x 55	3 x 24	3 x 52
Rate (in Å/s)	0.3	2.5	0.2	2.9	0.3	2.5
Thickness (in nm)	3	25	3	25	3.2	26.0

- Note: when evaporating sample 2 the Cr-wire was very thin and actually needed to be replaced. This explains the high voltage.

### **Providing the substrates with the flakes**

- Substrates cleaned: 2.5 minutes acetone, isopropanol and distilled water (with ultrasound).
- In between: dry with N<sub>2</sub>-gas.
- Apply the cleave-and-run technique as explained in section 2.4
- Clean 1 minute in acetone (stir, don't use ultrasound!) and dry with N<sub>2</sub>.

## Appendix C

### Details of doing AFM on the graphene/graphite-samples

In this appendix some extra information will be given concerning the AFM-work on the graphene/graphite-samples.

First of all I will give a list of the parameters that could (and were) adjusted including a short description. If these parameters have a unit, it will be given behind their name in brackets.

Second the optimised values of the parameters will be given. For parameters that still needed to be changed the range will be given in which these parameters were changed.

Third an AFM-picture of glue and an AFM-picture with a lot of small graphite flakes will be shown in order for the reader to clearly see the differences between glue and graphite flakes in the hope that the reader can form an image of the glue droplets that were present on the samples.

At the end the “raw” data will be given on which the graphs in section 5.2 were based. These “raw” data consists of the effective length, width and height of the graphene flakes and this data is ordered in a table.

#### List of AFM-parameters

- Lines/sample: this is the total number of lines in which the samples will be divided and the total number of bits in which one line will be divided. The total number of bits is the square of this value.
- Integral gain: abbreviated as I gain; already explained in section 3.2.2.
- Proportional gain: abbreviated as P gain; already explained in section 3.2.2.
- Drive amplitude (mV): the voltage of the signal that determines the amplitude with which the cantilever was forced to exert its oscillatory motion.
- Scan rate (Hz): the number of lines scanned per seconds.
- Drive frequency (kHz): the frequency with which the cantilever was driven.
- Scan size ( $\mu\text{m}$ ): the length of the side of the square that forms the scan area.
- Z limit: the range in vertical direction of the AFM. This determines the vertical resolution as the smallest step size is equal to this Z limit divided by  $2^{16}$  steps (16-bits AD-converter).

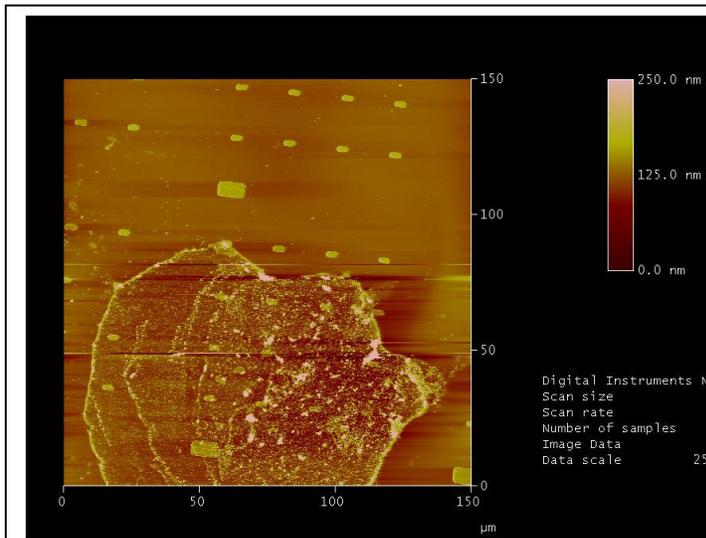
#### Values of the AFM-parameters

- Lines/sample: 512
- I gain: 0.8000 although sometimes 0.700 could be used and sometimes 0.900 needed to be used.
- P gain: 3.000
- Drive amplitude: 1000 mV, although for one area 1500 mV was needed
- Scan rate: 1.00 Hz

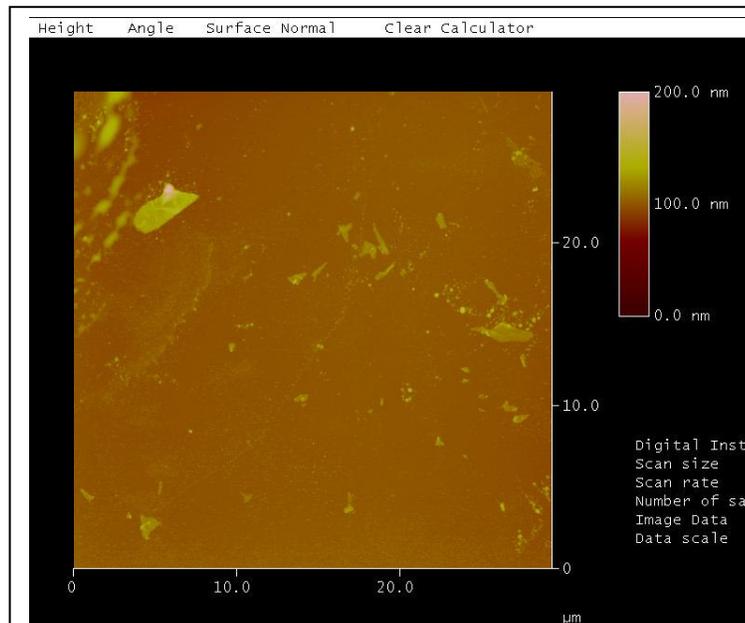
- Drive frequency: depended on the cantilever; the parameter varied from 76.0147 kHz to 79.4582 kHz
- Scan size: for the overview scans: 150  $\mu\text{m}$ ; for the zoomed-in scan varied from 16.4  $\mu\text{m}$  to 45.2  $\mu\text{m}$ . Typical for zoomed-in: 20-30  $\mu\text{m}$ .
- Z limit: for the overview scans: mostly 3.0  $\mu\text{m}$  (with a lot of drift: 6.0  $\mu\text{m}$ ); zoomed-in: 1.0  $\mu\text{m}$  (for the larger ones) or 500 nm (for the smaller ones).

## AFM-pictures of glue and graphite flakes

In figure A1 the picture with a lot of glue is shown. In figure A2 the zoomed-in picture with a lot of small graphite flakes is shown.



*Figure A1: The AFM-picture with a lot of glue.*



*Figure A2: The AFM-picture with a lot of small graphite flakes*

## The “raw” data

To save some space the table has been cut in three parts. The two first parts are shown on this page and the third part is shown on the next page.

In this table  $l$ ,  $b$  and  $h$  are the effective length, width and height respectively.

Number	$l$ ( $\mu\text{m}$ )	$b$ ( $\mu\text{m}$ )	$h$ (nm)
1	7.7	4.9	57.3
2	4.2	2.1	37
3	3.7	1.9	50.1
4	3.4	2.9	20
5	7.5	4	34.3
6	1.3	0.56	15.8
7	5	4.4	60.4
8	2.8	2.1	54
9	2.5	2.1	16.9
10	3.1	2.1	72
11	2.8	2.1	25
12	3.6	3.2	38
13	2	1.6	25.1
14	11.4	2.8	35.6
15	1.2	0.65	27.4
16	0.58	0.5	18.5
17	6	2.2	34.2
18	6.3	4.23	42.5
19	9.2	8	43.2
20	2.6	1.5	15
21	3.4	2.6	27.6
22	3.3	1.5	28.6
23	2.9	2.4	41.7
24	6.6	6.4	69.2
25	10.6	9.7	74.6
26	3.2	1.2	53.5
27	2.5	1.4	18
28	2.1	1.7	27
29	2.9	1.9	35
30	2	1.7	49
31	13	7.2	51
32	2.6	1.7	32
33	5.6	4.6	36.7
34	2.5	1.8	54
35	5.6	3	52
36	7.6	5	34
37	4	2.8	35
38	3.9	3.2	28.8

Number	$l$ ( $\mu\text{m}$ )	$b$ ( $\mu\text{m}$ )	$h$ (nm)
39	2.4	2.2	12
40	3.6	2.7	35
41	4.5	1.1	75
42	2.8	1.5	75
43	0.92	0.75	27
44	2.3	0.75	20
45	1.8	0.92	26.3
46	3.6	1.6	55
47	1.5	0.9	23.5
48	1.1	0.55	22.7
49	0.82	0.78	19.4
50	5.3	3.2	29.2
51	3.8	3.6	27.3
52	4.2	3.9	21.9
53	8.2	4.1	30.2
54	10.2	9.4	25.4
55	5.5	3.9	38
56	5	2.7	49
57	4.6	3.2	93.2
58	3.4	2.4	48.3
59	1.6	0.99	40.6
60	1.6	1.1	19.9
61	0.65	0.46	28.2
62	4.8	3.7	62.9
63	1.7	1.3	73.4
64	2.2	1.1	31.4
65	1.7	1.5	25
66	1.6	1.3	88.3
67	1.9	1.3	30.6
68	3.2	1.9	35.6
69	3.7	3.5	42.6
70	4.1	4	61.4
71	10.7	9.8	53.2
72	4.8	3.6	82.7
73	3	2.1	65
74	4.9	1.6	53
75	2.3	1.6	22.3
76	1.4	1	62.8

Number	$l$ ( $\mu\text{m}$ )	$b$ ( $\mu\text{m}$ )	$h$ (nm)
77	1.3	0.86	26.1
78	4.4	3.5	103.3
79	3.3	2.5	49.4
80	10.8	4.8	39
81	1.8	1.4	23
82	1.9	0.94	25.9
83	1.1	0.65	15
84	1.5	1.3	65
85	2.4	1.7	45.8
86	1.2	0.97	42.2
87	0.57	0.52	19.4
88	0.97	0.52	12.6
89	0.75	0.63	12
90	1.3	0.69	9.1
91	1.7	1.4	25.1
92	4	1.9	32.1
93	3.3	1.3	16.8
94	1.4	1.1	16.7
95	1.1	0.92	15.7
96	1.2	0.52	14.8
97	0.97	0.69	18.3
98	0.8	0.63	12.4
99	1.1	0.63	12.6
100	1.1	0.52	15.9
101	0.86	0.63	13.2
102	0.8	0.52	18.4
103	0.75	0.46	18.7
104	1.5	0.63	18.3
105	1.5	0.63	15.1
106	1.7	0.97	16.3
107	1.3	0.92	15.1
108	0.92	0.92	22.1
109	2.3	0.57	21.4
110	0.92	0.46	15
111	2.8	1.6	33.8
112	1.1	0.94	17.3
113	1.4	1.4	34.4
114	2.5	1.1	16.7

## Appendix D

### The effectiveness of the AFM when searching for graphene

In this appendix the effectiveness of the AFM to investigate the properties of the produced graphite flakes will be discussed, just like in section 5.3. In this appendix this discussion will be more in the style of a telegram, will focus more on the numerical aspect and some technical details that were omitted in section 5.3 will be given here.

#### The speed of the AFM

- Per scan: 512 seconds => 8.5 minutes
- One/two scans needed to stabilise the image
- Total average time/ overview picture: 21 minutes
- Zooming in on area: 10 minutes
- Zoomed-in area, total average scan time: 18.5 minutes
- On average: zoom in three times per overview picture: 3 x 18.5 minutes = 55.5 minutes
- Total average scan time( with correction): (21 + 55.5) x 125 % = 96 minutes

#### The resolution of the AFM

- Vertical resolution: depends inversely on the Z limit.

Picture	Z limit	Smallest step in the height
Overview	6 $\mu\text{m}$	0.092 nm
Overview	3 $\mu\text{m}$	0.046 nm
Zoomed-in	1 $\mu\text{m}$	0.015 nm
Zoomed-in	500 nm	7.7 pm

- Horizontal resolution: depends on the number of bits and the scan area
- Overview picture, area per pixel: 0.293  $\mu\text{m}$  x 0.293  $\mu\text{m}$
- Typical zoomed-in picture of 25  $\mu\text{m}$  x 25  $\mu\text{m}$ : 49 nm x 49 nm / pixel
- Flake of 1  $\mu\text{m}^2$  (occurs a lot): only 25 pixels on overview => bit noise!  
400 pixels on the zoomed-in => much more detail!

#### The drift of the AFM

The drift that caused shifts:

- Range from 1  $\mu\text{m}$  to 15  $\mu\text{m}$ . (estimated values)
- Occurrence: Practically always before thermalising, roughly half till three-quarters of the time after thermalising.

Bow-like deformation:

- Normally smaller than 3  $\mu\text{m}$ , but once a Z limit of 6  $\mu\text{m}$  was needed!
- Remedied with software-enhancement: auto plane fit of order 2 or 3; if this didn't worked: flatten, order 2 or 3.
- The order depended on the form: parabolic (2<sup>nd</sup> order) otherwise 3<sup>rd</sup> order

## **Glue and the AFM**

- Needed drive amplitude: 1000 mV, once 1500 mV was needed.
- Type of distortions around glue: long streaks that come from the glue, a periodic pattern appears in the surface (which isn't caused by wrong gains), image can start to go out of range at the beginning of the glue spot when the drive amplitude isn't high enough.

## **Identification of the graphite flakes**

This has been completely described in section 5.3. There is nothing that can be added anymore.

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