Characterization of Epitaxial Graphene Grown on Silicon Carbide

Karaktärisering av epitaxiellt grafen växt på kiselkarbid

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Abstract

In this thesis work several manufacturing methods for graphene is discussed followed by an in-depth study of graphene grown by a high temperature sublimation method (sublimation of silicon carbide). The graphene surfaces studied have been grown by Graphensic AB, both graphene grown on the Si-face and the C-face of the silicon carbide were studied. Six graphene samples grown 4H-SiC substrates were examined for homogeneity and surface morphology as well as some surface roughness parameters using Atomic Force Microscopy (AFM). The graphene was studied to get a better understanding of the surfaces and the growth mechanisms to improve manufacturing parameters while also being informative for graphene sample customers. An additional graphene sample grown on 6H-SiC epitaxial layer was also studied to get a better understanding of the sublimation mechanism. If graphene could be manufactured in a cheap repeatable way the applications are endless and a new era of technology could emerge much like the silicon era that began several decades ago. In this thesis work the results are presented as topography images as well as tables and histograms in the results section. The growth on the Si-face is found to be well ordered when compared to the C-face which shows signs of a largely complex growth. The graphene on the Si-face lies on top of silicon carbide steps like a carpet with a buffer layer interface against the silicon carbide. On the C-face this buffer layer is not present but the graphene is deformed by buckling which is suspected to originate from differences in thermal properties between the graphene and the C-face. The influence of AFM settings for characterization of graphene while using intermittent mode have been evaluated and recommendations are given. Finally a method for evaluating the homogeneity of the graphene film is proposed but is in need of further verification.
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Chapter 1

Introduction

Today we live in the age of silicon nanotechnology, the base for the modern computerization is the silicon based transistor. The size of these transistors has been dropping considerably over the years, following Moore’s law that predicts that the number of transistors incorporated into a chip will double approximately every 24 months while their size should decrease by 30%. To be able to keep this development going is quite a feat by the scientists and engineers involved. We have now reached a state where the technology is so strong and cheap that people in the industrial world carries a smartphone in their pocket more powerful than the home computers were only years before. What makes this developing rate possible is the huge amount of money involved in the computer market (billions) which enables continuous research into making the silicon transistors smaller and more efficient. To date the smallest transistor made by Intel uses 22 nm technology (developed in 2011) [1], down from 32 nm in 2009 which is approximately as predicted by Moore figure 1.1.

However, the physical limit for how small the silicon transistors can be made industrially, while still functioning, is closing up (estimated stand still at 2026 [2]) and the industry is now on the hunt for a new wonder material. Graphene including epitaxial graphene grown by thermal decomposition of silicon carbide is an attractive enabling technology for integration of graphene into microelectronics. Graphene has superior electrical, thermal and mechanical properties when compared to silicon and it has been shown that it can be used in nanoelectron-
ics. Graphene transistors have been built with operating frequencies above a stunning 427 GHz [3]. However, large scale production of high quality graphene is still a challenge and progress in this field requires more understanding of the graphene growth mechanisms and the surfaces.

In this study graphene grown by the high temperature method (sublimation, see 2.2.4) on silicon carbide have been studied using AFM and optical microscopy, figure 1.2. All of the studied samples were manufactured and supplied by Graphensic AB and the research team behind the company. The samples were studied for morphology and homogeneity as well as surface roughness. This data can be used for understanding and optimizing the growth process while also being informative for customers of graphene samples. Since this study was performed with almost only AFM there have been no real way to determine the thickness of the graphene layers on the surfaces, only internal differences of surface steps could be measured. A method is proposed in this thesis where comparing the step heights on the surface of the samples to known values for graphene and silicon carbide heights can reveal homogeneity information.

Figure 1.2: An AFM topography scan of graphene grown on the Si-face of 4H-SiC. The graphene lies like a carpet on the steps of the silicon carbide.
Chapter 2

Background

2.1 Silicon carbide

2.1.1 History

Silicon carbide (SiC) is a compound that consists of silicon and carbon, it was discovered in 1891 by the American inventor Edward G. Acheson in an attempt to create artificial diamonds [4]. Mass production in the form of a powder started as early as 1893 where the SiC was manufactured for its great abrasive properties. In the early years after the discovery of SiC it was mostly used for abrasive purposes such as brake pads for cars but in the early 1900’s the electronic properties were recognised and SiC was incorporated in radio devices. Today SiC is used in many applications, ranging from high performance brake discs and cutting discs to small and sturdy transistors. The production has been refined and it is now possible to manufacture large SiC crystals, figure 2.1.

![Figure 2.1: 4H-SiC crystal from the early research, 22 mm in height and a diameter of 38 mm [5].](image)

One of the more recent applications for SiC was discovered only a few years ago when scientists discovered that SiC was a great substrate for large scale production of epitaxial graphene [6].

2.1.2 Properties

In 1991 it was realised that SiC was not only a hard material that could be used as an abrasive but also that it had a wide bandgap and could be used as a semiconductor [7]. The SiC has the advantage that it can withstand high temperatures, radiation and power applications that other common semiconductors like silicon can not, this is due to the strong $sp^3$ bonds in SiC. The SiC also displays high thermal conductivity as well as a high electric-field breakdown strength [7]. Most of the properties does slightly vary depending on which polytype of SiC that is examined, something that now will be explained further.
Polytypes

Silicon carbide is a special material in the sense that it can exist in many crystallographic forms, these forms are called polytypes and can be achieved by stacking the material in different ways. In 2012 the number of observed SiC polytypes was more than 250 [8]. To understand these polytypes the first step is to look at the tetrahedron formed by the carbon and silicon. The carbon is placed in the center of the tetrahedron with silicon at the vertices, *figure 2.2*. The distance between the C-Si and Si-Si is 1.89 Å and 3.08 Å, also the height of the tetrahedron (spacing between the layers in SiC) is 2.51 Å [5].

![Tetrahedron of carbon and silicon](image)

*Figure 2.2: Tetrahedron of carbon and silicon [9].*

By stacking these tetrahedrons and the tetrahedrons spun around their axis 180° it is possible to form all of the SiC polytypes. To label the stacking atom layers (the base layers of the tetrahedrons) are labeled A,B and C where A is the first layer of Si atoms. The second layer is called B if it is oriented in the same way as the underlying layer but is shifted so that the vertices of the new tetrahedrons are positioned on the peak atoms of the underlying layer. If the second layer is spun 180° and placed on the peak atoms of the underlying layer it is called C. This can be imaged as seen in *figure 2.3*.

![Stacking of SiC](image)

*Figure 2.3: Stacking of SiC, figure adapted from [8] and [5].*

The polytypes have been labeled in many ways over the years but one of the more accepted ones is the Ramsdell notation, nX. Where n is the number of stacking sequences required to describe the unit cell and X describes the crystal symmetry, C for Cubic, H for Hexagonal or R for rhombohedral [5]. For example 2H-SiC means that there are 2 tetrahedrons and that
the crystal is Hexagonal. 3C-SiC means that there are three stacked tetrahedrons and that the crystal is Cubic. In table 2.1 the three most common polytypes and their properties are listed.

Table 2.1: Three common SiC polytypes and some of their properties [7]

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Stacking sequence</th>
<th>Lattice constant (Å)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C-SiC</td>
<td>ABC</td>
<td>4.36</td>
<td>2.3</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>ABAC</td>
<td>3.08</td>
<td>3.3</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>ACBABC</td>
<td>3.08</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Surface orientation

Silicon carbide wafers can be cut from boules like the one in figure 2.1. The SiC is commonly cut in a way that produces the surface orientations (0001) and (0001̅), called the Si-face and C-face. The surface orientation describes what plane in the unit cell of the SiC that is exposed at the surface. The SiC unit cell is well described by the Bravais-Miller index \((hkil)\) where the Miller indices \(h, k, i\) and \(l\) each denote a plane orthogonal to the reciprocal lattice vector [10], see figure 2.4 for the Hexagonal unit cell and the aforementioned planes.

Figure 2.4: At the top the crystal structure of 4H-SiC and 6H-SiC is shown, cut parallel to the 1120 plane. The black line indicates the stacking sequence. In the lower part of the image the hexagonal unit cell is displayed. The vectors \(a_1, a_2, a_3\) are of the same length and oriented 120 degrees apart on a plane, vector \(c\) describes the height of the unit cell. The vectors are used to calculate the Miller indices \((hkil)\). Also displayed is a top view of the unit cell with some planes highlighted and to the right is a indicator for the (0001) "Si-face" plane and the (0001̅) "C-face" plane. Adapted from [9].

2.1.3 Manufacturing methods

Silicon carbide has been around for a long time now and thus many different ways of manufacturing have been developed. When production first began in the late 1800’s it was a simple
process of heating silica sand and petroleum coke to around 2500°C in a furnace. This process was later called the Ancheson process and produces SiC crystals with a wide spread in polytypes and purity [7]. It is not very useful for semiconductors nowadays but excellent for producing an abrasive product. Since then the processes of improving the manufacturing has been in steady forward motion and today it is possible to create large SiC crystals with only a specific polytype and high purity. One of the more recent production methods is the modified Lely process which can shortly be described as SiC growth by using a starting seed on which the crystal grows with certain polytype [5]. The non seeded Lely process produces SiC of a quality good enough to be used as a semiconductor but it has problems with controlling the polytype of the SiC which is critical for some applications.

The modified Lely process

The modified Lely process (commonly called physical vapor transport) still uses the sublimation of a SiC source but with a few additions and changes. The SiC source can be in the form of pieces of SiC or a powder placed at the bottom of a quasi-closed graphite crucible. At the top of the crucible a "seed" is placed. The seed is basically a substrate for the crystal to grow on, the orientation and polytype of the seed greatly affects the grown crystal. For example if a 4H-SiC crystal is desired it has to be grown on a seed with a 4H polytype (in research the cubic side of a 6H polytype) [5]. The crucible is placed in a reaction chamber with low pressure of inert gas and is then heated to growth temperature (1800-2600°C). The temperature should be highest at the source and lowest at the seed to supply a driving force for the growth. The source starts to sublime at a certain temperature and the Si-C species are then transported in vapor form to the seed where the surface is growing, figure 2.5.

![Figure 2.5: The physical vapor transport process [5].](image)

The nucleation on the seed would be problematic if there were no defects present, the nucleation would have to start by making islands on the seed surface and it is not certain that a surface would start to form. Thankfully in reality there is no such thing as a "perfect"
crystal and dislocations are almost always present. At a dislocation there are positions that are favorable for the transported SiC to occupy, an example of such a nucleation at a screw dislocation is displayed in figure 2.6 a). The nucleation continues along the dislocations and steps are formed, for the screw dislocation the step growth will continue as a spiral around the origin of the screw dislocation. An example of a crystal grown by this "spiral growth" can be seen in figure 2.6 b). Naturally there are not just one dislocation on the seed but plenty, all of these can form step spirals that interact with each other, figure 2.6 c). The steps can either be of the SiC tetrahedron height for one step or any integer of that height for several steps that have bunched together, called step bunching [5].

Figure 2.6: a) Illustration of growth around a screw dislocation b) SiC bulk crystal grown by "spiral growth" c) Interaction between two growth spirals, image adapted from [5].

In order to grow large boules of SiC it has to be a relatively large distance between the source and seed (around 5 to 30 mm), this also increases the growth time as well as it causes more interaction between the vapor and the graphite crucible and this can cause problems. A troublesome defect that is commonly seen in films grown with this method are micropipes. Micropipes are holes that run all the way through the SiC films down to the seed or substrate and have a diameter of tens of micrometers or less [5]. It is not entirely determined how the micropipes are formed but a common idea is that they form around a dislocation in the seed like a circle because it is not energy efficient to form a crystal on the dislocation [11]. This leaves a "hole" in the first layer of the growing crystal and that is then continued throughout the rest of the layer leaving a crater all the way through, a micropipe. These micropipes can be very troublesome since in many applications it is desirable to have large areas that are free from defects and these pipes are big enough to cause problems. The number of micropipes have been considerably reduced over the years but some still remain.
2.2 Graphene

2.2.1 History

Graphene is the name of a two-dimensional monolayer of carbon atoms bound to each other with $sp^2$ bonds. The carbon is packed into a hexagonal honeycomb pattern and has several extraordinary properties. The discovery of graphene resulted in a Nobel prize which was awarded to Andre Geim and Konstantin Novoselov in 2010 for their research on single graphite layers in 2004. However, studies of graphene have been reported from the mid 1900’s [12] but back then it was mostly considered as dirt on other samples that were studied [13]. Graphene is the basic building block for many known forms of carbon such as fullerenes, carbon nanotubes and graphite, figure 2.7.

![Figure 2.7: A monolayer of graphene wrapped into buckyballs, folded into nanotubes and stacked into graphite [13].](image)

2.2.2 Properties

Graphene is a stable and strong material because of covalent carbon-carbon $sp^2$ bonds. The strong bonds give the graphene mechanical properties that far surpass other materials used in constructions today like steel and aluminium. The Young’s Modulus of graphene is 1 TPa [14], while steel and aluminium have values around 200 and 70 GPa [15]. The length of the carbon-carbon bond in the honeycomb lattice have been measured to be 1.42 Å [16] and the distance between graphene layers in graphite 3.54 Å. The mechanical strength of graphene was illustrated at the Nobel prize announcement by showing a cat lying on a 1x1m$^2$ graphene “hammock”. The cat could weigh up to four kilos and the monolayer graphene film would still hold it while weighing only a fraction of the cats whisker (0.77 mg). The graphene’s strength makes it ideal for implementation in applications such as foldable flat screens among others, figure 2.8.
Even though the mechanical properties of graphene look very promising the electric properties are even more interesting. Graphene is different compared to other materials in the sense that it has no band gap in the corners of the hexagonal Brillouin zone; the energy required for moving electrons from the valence band to the conduction band. This means that electrons can flow through graphene like in a free electron gas, with low electrical resistance. This gives amazing conduction and the mean free path of electrons in graphene have been measured to be in the micrometer region [18]. Recently there have been studies on graphene nanoribbons that have shown an electron mean free path of up to 58 µm [19]. The closed band gap can be illustrated in the energy-wave vector space (E-k space) correlation where a linear relation can be shown in the so called Dirac points. The name Dirac points comes from the fact that the electrons behave like massless particles in these points and are called Dirac fermions. The Dirac points in graphene lies at all the six corners in the graphene Brillouin zone, figure 2.9.

A interesting property of graphene is that a monolayer absorbs about 2.3% of white light making a monolayer clearly visible and opens up for some interesting applications [20]. These properties makes graphene a promising candidate for high power applications where the current carrying capabilities are higher than those achieved by silicon technology. Graphene can also be used for field emission transistors (FET’s) but here the closed band gap causes problems since it is not possible to turn the transistors off. There is, however, much research placed into inducing a small band gap into graphene and if successful the graphene FET’s would potentially be much faster than the silicon ones [3].

Graphene has the possibility to revolutionize our society but as with all new materials it is important to evaluate whether or not the material is safe for humans. There are reports of possible respiratory damage from inhaling small graphene flakes from Donaldson and associates [21]. This respiratory damage is however not something that is uniquely caused by inhaling graphene, many nanoparticles can cause damage when inhaled in large quantities. Another
recent study also showed that inhaling graphene flakes could cause inflammatory reactions in the lungs [22], graphene did however only cause inflammation at large quantities (carbon nanotubes caused the same inflammation at 20 times less concentration) and whether or not it was toxic could not be determined. Inhalation of large quantities of graphene flakes is unlikely in any of the possible graphene applications but it could be a danger in some manufacturing processes. Even though some graphene toxicity test have been carried out to some extent but research in the subject is needed.

2.2.3 Applications

The possible applications for graphene are staggering, a few of them are mentioned below.

Graphene Field Emission Display

A possible use for graphene is to build Field Emission Displays using erected graphene flakes on a substrate. The way a field emission display works is to apply a high electric field to a sharp object (the edge of graphene) causing it to emit electrons. These electrons then hit colored phosphore creating colored pixels. Graphene would work nicely in such a device with excellent electric properties as well as mechanical, this gives the option to mount the graphene on a flexible substrate and creating a flexible display [23].

Graphene Sensors

Graphene is a 2D film with great conductivity. If a molecule attaches itself to the graphene this will alter the conductivity of the graphene by a significant amount and it is large enough to detect. This opens up possibilities for using graphene as sensors able to detect small amounts of for example gas or other biological compounds. The sensitivity could be as high as picking up single atoms and the heat resistance of the graphene allows for a wide area of applications [23].

Batteries

Today the batteries made out of lithium ions and graphite anodes make up a large portion of what is used in our hand held devices and computers. There is always a demand for more power storage and battery lifetimes and graphene could be of use here. Using graphene as anodes instead of graphite could increase the capacity of the Lithium batteries since the graphene has superior conductivity, larger surface area and good chemical tolerance [23].

Transparent electrodes

Today’s flat screens, liquid crystal displays, touch screens, solar cell shielding (to name a few) all use transparent electrodes made by Indium Tin Oxide. Indium is scarce and the demand is ever increasing and prices rushing. Graphene could be an excellent replacement with great optical properties as well as the mechanical [23].

Transistors

As already discussed in the introduction graphene could come to replace silicon as the base material of choice for transistors. Graphene transistors can and have been constructed for some time, an example is the self aligned graphene transistor made by the University of California [3]. The transistors are manufactured according to figure 2.10 and the results from this scalable manufacturing method can be seen in figure 2.11.
Figure 2.10: Schematic of the self aligned graphene transistor A) A 50 nm gold film is deposited on a SiSiO$_2$ substrate followed by an atomic layer deposition (ALD) of a Al$_2$O$_3$ film B) Reactive ion etching process (RIE) is used to pattern the dielectric strips after a standard lithography process C) The gate sidewall spacer is formed by depositing a thin-layer Al$_2$O$_3$ film D) Unwanted Al$_2$O$_3$ film on the top surface of the gate metal and the substrate is etched away E) A layer of polymer with a glass transition temperature close to the thermal tape-releasing temperature is spin-cast before applying thermal releasing tape and peeling off the gate stacking F) The patterned top-gate stacks are peeled from the silicon wafer. After etching away the gold film the gate stacks can be transferred onto desired graphene substrate through a thermal releasing process G) The polymer is removed with acetone, leaving the gate stacks on top of graphene strips H) The source, drain, and top-gate electrodes are fabricated using electron-beam lithography, followed by deposition of 5-nm/10-nm Pd/Au metal film to form the self-aligned source and drain electrodes I) A cross-sectional view of the self-aligned device. Imported from [3].

Figure 2.11: A) Photo image of the self-aligned transistors on a glass substrate B) Optical image of self-aligned graphene transistors on 300-nm SiO$_2$Si substrate C) Scanning electron microscope image of a graphene transistor D) Cross-sectional transmission electron microscope image of the overall device layout. Adapted from [3].
When this process was done damage free the transistors exhibited a cut-off frequency of an astonishing 427 GHz which is an order of magnitude higher than transistors based on silicon.

2.2.4 Manufacturing methods

Since the interest for graphene skyrocketed only a few years ago methods for graphene production have been heavily researched. There are now hundreds of patents relating to graphene production [24], some of the more common processes are introduced below.

Mechanical removal of graphene flakes

When graphene was first recognised as an interesting material by Geim and Novoselov in 2004 they used mechanical exfoliation for producing the graphene [13]. The method had actually been around for many years in the form of simply rubbing graphite against a surface but Geim and Novoselov refined the method enough to get graphene flakes large enough to study. The method simply relies on exfoliation of graphite onto other substrates (can be done with a simple tape and lead pencil) in the hope to get nice graphene flakes. This is possible since graphite consists of hurdles of graphene sheets bond together by weak Van der Waals forces. A simple way of mechanical removal is to place a tape against a graphite crystal and then press it against a SiO wafer, leaving graphene on the wafer when the tape is removed, figure 2.12.

![Figure 2.12: Mechanical exfoliation of graphene using a tape [25].](image)

The refined method is to gently press a freshly cleaved graphite crystal onto a oxidized silicon wafer [26] instead of using a tape. This method has a chance to produce nice graphene but to get a flake with good enough quality can take days to several weeks if unlucky. This method does have some potential in the composite polymer, coatings, conductive ink, batteries industries to name a few [24]. Here the quality of the graphene is not the priority but rather the quantity. The mechanical exfoliation methods do have the potential to produce large amounts of graphene at low costs and are therefore viable in aforementioned applications.

Sonication

Another method for exfoliating graphene from graphite is sonication, described by Bunch and associates [27]. Flakes of graphite are placed in a dichlorobenzene solution and are sonicated
for approximately five minutes. Sonication means that sound waves are fed through the fluid with the graphite and that makes the graphite "shake". Since the bonds between the graphite layers are weak the layers of graphene that make up the graphite shakes off each other and floats away as graphene flakes, *figure 2.13.*

![Graphene flakes dispersed in liquid by sonication](image)

Figure 2.13: Graphene flakes dispersed in liquid by sonication [28].

After the sonication the solution is dripped onto a oxidized silicon wafer and dried off, leaving graphene flakes on the oxidized silicon. Again, now it is necessary to use for example an AFM to study the sample and look for suitable flakes of graphene and this can take a very long time.

**Unzipping of carbon nanotubes**

Nano-ribbons of graphene can be made from unzipping carbon nanotubes along their length. The nanotubes are "unzipped" by a chemical process that involves sulfuric acid and Potassium permanganate [29]. The acid breaks the carbon-carbon bonds of the nanotubes and they unfold into ribbons of graphene, *figure 2.14.* Many different sizes of ribbons can be made depending on the size of the nanotubes and the number of walls in the tubes.

!["Unzipping" of carbon nanotubes](image)

Figure 2.14: "Unzipping" of carbon nanotubes [28].

The method shows promise in making ribbons for nano-electric applications, however, there are problems with the process where the ribbons can (and usually do) get damaged by the acidic environment and gentler ways of opening them are needed [29].
Chemical Vapor Deposition

Synthesis of graphene using Chemical Vapor Deposition (CVD) was first reported in 2006 by Somani and associates [30] where they grew graphene on Ni-foils. Since then numerous CVD methods to synthesise graphene have been developed. The idea with CVD is to grow a substance on a substrate by exposing the substrate to a gas that contains the desired material as seen in figure 2.15 where hydrocarbon reacts with a copper substrate. The substrate reacts with the gas and the new surface is deposited. Somanis group used camphor and argon gas as a carrier at a temperature of about 800 °C which produced few layered graphene with folds. This is a common defect when growing graphene with CVD. The fold form because of the mismatch between the lattice of the graphene and the substrate. It is therefore important to choose a suitable substrate and the options with compatible lattices are limited.

![Chemical Vapor Deposition](image)

Figure 2.15: Chemical Vapor Deposition on a metal substrate, producing graphene [28].

Researchers at IBM grows graphene on Copper films using CVD [31]. A polymer, polymethyl-methacrylate (PMMA), is then added on top of the graphene through spin coating to add support before further processing. The graphene covered Copper films are then subjected to a corrosive acid and the Copper film corrodes away, figure 2.16. What is left is a monolayer of graphene attached to a polymer that can be placed on a substrate of the customers choosing. After placement on the new substrate the polymer can be dissolved leaving only one layer of graphene [31].

![Treatment of graphene grown on Cu](image)

Figure 2.16: Treatment of graphene grown on Cu, IBM [31].

Another interesting method developed at IBM is the Roll-Based production of graphene for use in electronics. The graphene is grown on a Copper stripe using CVD, a polymer is then added on the graphene and the stripe is thereafter rolled through an etching solution removing the Copper before being placed on the desired target, figure 2.17.
The quality of the graphene synthesised by CVD varies between methods and in some cases it is good enough to be used in nanoelectronics. However, the quality is still a problem for CVD since it is hard to control the growth and defects can easily form. There is also a considerable risk for defects when moving the graphene from the original growth substrate to the target. The method is expensive enough for this to be unacceptable since nanoelectronics are sensitive to defects and more research is needed to perfect the production [24].

**Epitaxial graphene growth on SiC**

Epitaxial graphene can be grown from a SiC substrate by sublimation under the right condition. The sublimation takes place since the silicon has a higher vapor pressure than carbon and therefore it evaporates from the SiC surface when heated to at least 1150°C. This is leaving the carbon on the substrate [32], *figure 2.18*. The temperature is increased to about 1400°C and graphene starts to form on the surface. A graphene layer has 38 carbon atoms/nm² and to produce that with sublimation at least 3 unit cells of SiC are needed yielding 36.5 carbon atoms/nm². The height of 3 SiC unit cells is 0.75 nm and a graphene layer spacing is 0.35 nm, thus the surface should withdraw with about 0.4 nm for every graphene layer grown [33].

![Figure 2.18: The Si-species leaving the substrate in the sublimation process of SiC](image)

These are the basics but then there are many different ways to perform the silicon sublimation and they greatly affect the quality of the graphene. At Graphensic AB the SiC is sublimed by placing a SiC wafer in a graphite crucible (the following description is from Graphensic’s patent [32]). The crucible is placed in a reaction chamber where the temperature and pressure can be controlled. The wafer is heated to 1400°C in two heating steps and with an inert gas pressure between 600-1100 bar. There are then additional heating steps up to about 1900°C. This produces a high quality graphene. The parameters of the production process can be manipulated to achieve monolayer graphene as well as few layered graphene if that is desired.
The epitaxial graphene grown by sublimation has the potential to replace silicon in high performance electronics because of its high quality [24]. That the epitaxial graphene is grown directly on the semiconductor SiC is also beneficial since there is no need to transfer the graphene for electronic applications (unlike the CVD on metal). The SiC substrate have steps in it that the graphene forms over like a carpet, figure 2.19. This phenomenon have been studied for the last few years but more research is needed to understand the mechanisms behind the graphene steps that forms when grown on SiC.

Figure 2.19: Graphene growth on a 4H-SiC surface with steps [28].

The understanding of the graphene formation on the Si-face is fairly well developed. The surface reconstructs into an interface layer between the graphene and SiC ($6\sqrt{3} \times 6\sqrt{3}R30^\circ$) where a "buffer" layer of carbon is formed, figure 2.20 (does not act like graphene because 30% of the carbon atoms have covalent bonds with the silicon at the surface) [35]. The growth process on the C-face is not yet fully understood but it is known that there is no interfacial layer.

Figure 2.20: The buffer layer on the (0001) side of SiC. Silicon atoms in orange and carbon in blue [36].
Chapter 3

Experimental

3.1 Characterization methods

3.1.1 Atomic Force Microscopy

The AFM was invented in 1986 by G. Binnig and C. F. Quate [37] based upon similar principles as the Scanning Tunneling Microscope (STM). The concept is to sweep a small tip over the surface to be studied in a raster motion. The tip is attached to a cantilever and when the tip moves because of interaction with the surface the cantilever deflects. The deflection is then recorded by a detector that registers how a laser beam is reflected on the cantilever. From this data an image of the surface can be produced, showing the topography of the surface as well as additional images depending on the mode of the AFM. The basic setup of an AFM is displayed in figure 3.1. The resolution of the AFM depends on the measurement mode but can be as high as 1 Å in the lateral direction and 0.1 Å in the vertical [38]. The AFM can be used to image samples that are not conductive, unlike the STM, which made the invention especially important for biochemists. There are two types of forces acting between the tip and sample, attractive and repulsive. The attractive forces act on a much longer range than the repulsive ones and consist mainly of polarization interaction (Van der Waals forces) between the atoms on the tip and the surface. There are, however, plenty of other attractive forces like capillary (if the AFM is operated in air), electrostatic forces, chemical bonding and magnetic forces to name a few. The repulsive force act on an atomic scale (Å) and their origin is the exchange interaction due to overlap of electron orbitals. When the repulsive is dominant the tip is said to be in contact with the surface.
The AFM can be operated in several different modes, intermittent, contact and non contact are the most common. In contact mode the tip is pressed against the surface of the sample and then dragged along the surface as the scans commence. This mode is best suited for stable surfaces since there is a risk that the tip will mechanically damage a soft surface [40].

In non-contact mode the tip oscillates over the sample without touching it during the sweeps. When the oscillating tip passes over the surface it is affected by forces acting from the surface. These forces affect the frequency and phase of the oscillations and can be measured to characterize the surface [40]. This mode is useful for imaging surfaces that are sensitive or highly reactive, for example liquids.

In intermittent contact mode (or tapping mode\textsuperscript{TM}) the tip is tapping against the sample surface at a high frequency during the scans. This reduces the risk of mechanically dragging particles around on the surface like in contact mode, however, there is a great risk to pick up particles with the tip or damaging it. In intermittent mode the images produced are not only topographic but can also show material properties due to the tip-sample interaction. Intermittent mode is suitable for most sample characterizations. The cantilevers used for intermittent mode are all constructed with a certain resonance frequency in mind. At this frequency the cantilever will have the largest amplitude. To tune the amplitude the user can choose at which frequency the cantilever should be oscillated as well as choosing the drive amplitude which is the voltage that drives the oscillations. This is done by plotting the amplitude of the cantilever versus the frequency, in such a plot it is also useful to include the phase of the cantilever figure 3.2.
When choosing the frequency it is important to pick one that is slightly to the left of the amplitude peak, this is to ensure that the amplitude does not pass the amplitude peak as the amplitude is increased by attractive forces when approaching the sample. The phase should also be set to zero at the chosen frequency if the user wishes to have useful phase imaging. To get information about the tip/sample interaction it is useful to do a spectroscopy, an amplitude/phase spectroscopy for example is done by moving the oscillating cantilever a set distance down towards the sample and plot the resulting amplitude/phase versus the distance. By looking at figure 3.2 it can be excepted that the phase would first slack behind as the amplitude is increased while approaching the sample to then get ahead as the cantilever is pressed against the sample and the amplitude decrease. Such spectroscopies can be useful to determine a good intermittent amplitude for imaging, as is shown later in the thesis work.

Artifacts

When running the AFM there are a few common artifacts that the user should be aware of to minimize the risk of mistaking them for real features of the surface. The condition of the tip is crucial to imaging and if the tip is damaged it will not give useful information and have to be replaced. For example the tip can pick up contaminants or debris from the sample and become ”dull”, only imaging the picked up contaminants instead of the surface. This can be recognized if the user is on the lookout for excessive repeated features on the sample that seem illogical and do not appear at the same places during repetend scans of the same surface. The contaminants on the tip can also create several new tips that all are engaged at the same time, producing overlapping images. It is usually hard to clean a tip and therefor they are more commonly thrown away and replaced when these artifacts occur. When changing tip because of contaminants it is also a good idea to clean the sample to prevent further loss of tips.

A possible artifact when using contact mode on highly reflective surfaces is the formation of a sinusoidal pattern on the sample with a period of about 1.5-2 \( \mu \text{m} \) [41]. This artifact is caused by interference between the reflected laser from the cantilever and reflections from the sample. This artifact gives a weak signal but if the samples are highly planar it will become easily distinguishable. Sometimes this artifact can be reduced by aligning the laser better however if the reflective area on the cantilever is small compared to the laser spot size this artifact will be hard to remove. One way to improve the image in the latter case is to switch cantilever to one with a more reflective coating if possible. If the feedback parameters are not correctly tuned it is possible to get trails on the images. These trails are the result of the tip hitting a particle or step on the surface and then not having time to adjust itself before the sweep is continued. This artifact can be removed by lowering the scan speed and/or increasing the feedback speed.

When doing large scans an arcshaped-bow can be seen on the images. This is caused by
the piezo that moves the sample and the artifact can be removed by performing a second order planefit to the image.

### 3.1.2 Optical microscopy

A common method used for studying samples is the light optic microscope. Light is focused on a sample and the reflected or transmitted light can then be focused to produce an image, a simple schematic of the Reflective and Transmission light microscope is displayed in *figure 3.3*.

![Schematic of Reflective and Transmission light microscope](image)

**Figure 3.3**: A schematic of the Reflective (left) and Transmission (right) light microscope. The mirror is dichroic and transmits light as well as reflect it.

It is possible to see single layers of graphene on a wide variety of substrates depending on the relation between the reflective indexes of the materials. An example of the contrasts of graphene on a few substrates is displayed in *figure 3.4*. 

![Contrasts of graphene on substrates](image)
As can be seen from the diagrams the contrast for $\text{Al}_2\text{O}_3$ and silicon is negative, meaning that the graphene will appear as brighter than the substrate. The positive contrast for the Gold surface means that the graphene will appear as darker than the substrate. The contrast is rather low on all of the substrates for single layers of graphene but with computer enhancement of the contrast they are clearly visible. It has also been shown that graphene on SiC can clearly be seen with optical methods [43].
3.2 Samples

The examined samples during this study where both SiC substrates and graphene grown on SiC substrates by the aforementioned sublimation method, they are all listed in table 3.1.

Table 3.1: Sample names and specifications

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Specifications</th>
<th>Size</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC</td>
<td>7x7 Si-face 6H-SiC</td>
<td>7x7 mm</td>
<td>12 µm, epilayer</td>
</tr>
<tr>
<td>4H-SiC</td>
<td>7x7 Si-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Specifications</th>
<th>Size</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>6HG</td>
<td>7x7 Si-face 6H-SiC</td>
<td>7x7 mm</td>
<td>12 µm, epilayer</td>
</tr>
<tr>
<td>G465</td>
<td>7x7 Si-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
<tr>
<td>G503</td>
<td>7x7 Si-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
<tr>
<td>G506</td>
<td>7x7 Si-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
<tr>
<td>G507</td>
<td>7x7 C-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
<tr>
<td>G508</td>
<td>7x7 C-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
<tr>
<td>G509</td>
<td>7x7 C-face 4H-SiC</td>
<td>7x7 mm</td>
<td>350-370 µm</td>
</tr>
</tbody>
</table>

All of the graphene 4H-SiC substrates were cut with one side parallel to a (10\overline{1}0) plane with the flat parallel to the \(<11\overline{2}0>\) direction within ±5°, the surface orientation is on axis (0001) within ±0.25°. The 4H-SiC substrates are cut from wafers that in turn are cut from boules made by the modified Lely process. The substrates have been polished using Chemical Mechanical Planarization (or Polishing, also called CMP). In the CMP process the substrates are polished using an abrasive and corrosive chemical slurry while being held by a rotating pad that forces the substrate against a rotating flat board [44]. This causes the substrates to be polished in a non concentric way and tends to even out the topography of the substrates, making them planar. The 6H-SiC sample is a thin film epilayer grown on a 6H-SiC substrate at a temperature of 1800°C for 60 minutes.

The 4H-SiC Si-face samples have been sublimed at 2000°C for 10-15 minutes at a pressure of 850 mbar argon, this "recipe" have been developed over a few years and is believed to produce the "best" graphene. The 4H-SiC C-face has a slightly different "recipe" to achieve monolayer conditions, the reason for this is that the surface free energy of the C-face is less than two and a half (1700 erg/cm² for the Si-face and 750 erg/cm² for the C-face [45]) of the Si-face and thus the C-face starts to sublime at lower temperatures. For this study the C-face samples were grown at the slightly lower temperature of 1900°C with the rest of the parameters set to the same as for the Si-face. The 6H-SiC epilayer was sublimed using the same parameters as for the 4H-SiC Si-face.

The samples are transported and stored in cylindrical plastic containers, they are forced against a curved surface by a plastic spring securing the samples while making sure that the surface of the sample does not get damaged, figure 3.5.
3.3 Sample treatment

The 4H-SiC sample was exposed to the ambient for three weeks during the study and picked up contaminations from the atmosphere that made studies difficult. The sample was therefore cleaned using an ozone treatment where the sample is placed in a metallic chamber with a ultra violet light source. When the light source is engaged the photons interact with the ambient air inside the chamber and this is creating ozone. This ozone is highly reactive and reacts with the contaminants on the surface of the sample. These new molecules will now be less inclined to stay on surface and rather just flow up into the chamber. The 4H-SiC sample was exposed to 15 minutes of UV light and then left to react with the ozone for another 15 minutes. This treatment was not effective and is perhaps more suitable for other samples. Instead to clean the SiC or graphene surfaces one should consider using a low pressure furnace, heating the sample to around 700°C and continuously pumping out the released particles. The sample should then be left to cool in the furnace before being exposed to the ambient atmosphere again.

3.4 Experimental setup

The samples were studied with the Innova AFM. For contact mode the probe MSCT-MT-BF from Veeco (now Bruker) was used and for intermittent mode the NCS18/AIBS probe, figure 3.6.

![AFM tips](image)

Figure 3.6: The AFM tips used during the study. a) the intermittent probe NCS18/AIBS b) the contact probe MSCT-MF-BF with all five tips present c) the contact probe with only the two stiffest cantilevers remaining. [46][47]

The contact probe has 5 tips mounted on it so that the user has several choices for stiffness and frequencies. For this study the stiffest of the tips were chosen since the samples that were
studied were hard. Data for this tip can be seen in table 3.3. To be able to use this tip the other tips was mechanically removed since they would otherwise press hard against the sample and cause noise and damage during scans. This is a tricky procedure when done by hand and therefore it was decided to leave an additional tip intact to minimize risk of damaging the actual tip to be used. The intermittent mode tip data is found in table 3.2.

Table 3.2: NSC18/AIBS Tip data [47].

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>Tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>n-type silicon</td>
</tr>
<tr>
<td>Thickness</td>
<td>3 µm</td>
</tr>
<tr>
<td>Length</td>
<td>230 µm</td>
</tr>
<tr>
<td>Width</td>
<td>40 µm</td>
</tr>
<tr>
<td>Resonant frequency</td>
<td>75 kHz</td>
</tr>
<tr>
<td>Force constant</td>
<td>3.5 N/m</td>
</tr>
<tr>
<td>Radius</td>
<td>10 nm</td>
</tr>
<tr>
<td>Height</td>
<td>22.5 µm</td>
</tr>
</tbody>
</table>

Table 3.3: MSCT-MT-BF Tip data [46].

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>Tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.6 µm</td>
</tr>
<tr>
<td>Top layer coating</td>
<td>45 nm Ti/Au</td>
</tr>
<tr>
<td>Shape</td>
<td>Triangular</td>
</tr>
<tr>
<td>Resonant frequency</td>
<td>120 kHz</td>
</tr>
<tr>
<td>Spring constant</td>
<td>0.5 N/m</td>
</tr>
<tr>
<td>Length</td>
<td>85 µm</td>
</tr>
<tr>
<td>Width</td>
<td>18 µm</td>
</tr>
</tbody>
</table>

Only the G465 sample was studied with contact mode since it was too contaminated for intermittent mode. To achieve topography scans of G465 the same surfaces was scanned about four times in contact mode, sweeping away loose contaminations. This is a time consuming and dangerous task since it can damage the graphene, cleaning the surfaces by heating is highly recommended instead. All of the other samples were characterized using intermittent mode with settings described later in experimental section.

### 3.4.1 Innova Scanner

The Innova AFM controls the movements of the sample using a piezo tube scanner (INSC-090). The tube scanner is constructed as seen in figure 3.7 a). The scanner moves when a bias is placed over the contacts on the tube, causing the piezo material to contract or expand. This kind of scanner was initially developed for the Scanning Tunneling Microscopes (STM) because they were easier to manufacture and and control than scanners that used one piezo element for each direction which was the standard at the time. The tube scanner works great when scanning small areas (up to about 10 × 10 µm) but when the areas becomes larger the bow of the piezo becomes an issue. The bow comes from the way the piezo moves, figure 3.7 b), a bowing movement. This movement causes the actual surface topography to be placed on a plane that looks like a segment of a sphere with the radius of the piezoscanner height. This bow can be adjusted by applying a two dimensional planefit to the surface but distorting the data in this way is not without complications.
Figure 3.7: A schematic of the piezo tube and its movements, the blue color represents the piezo material and the yellow represents contacts a) The piezo tube scanner, the sample holder is placed on top of the piezo and the movements can be controlled by applying a voltage over the contacts. V1 controls the height while V2 through V5 controls the x-y movements b) A display of how the piezo needs to move to scan a quadratic scan area, highly exaggerated c) The plane on which the piezo moves the sample d) The resulted plane on which the surface is represented in an AFM scan, inverted from c) since the tip is held in contact with the sample.

The Innova microscope also has some difficulties with the measuring large scans. When the scan sizes increase to about 15 µm and beyond the height profiles measured from left to right and right to left starts to exhibit a bow characteristic in different directions. The reason for this is unknown but it is suspected that the software has some sort of built in “correction” for the data. Because of the fact that the left-right scan profile bow could not be explained (it should bow in the same way as the right-left scan) it was decided to only use the right-left scan during the study. A left-right, right-left height profile for a 20 × 20 µm scan displaying the problem can be seen in figure 3.8.
Figure 3.8: A height profile from a 20 × 20 µm scan. The light blue is the left-right scan and the dark blue is the right-left scan direction. The reason that the scans do not connect at the starting/ending points is that a 15% overscan is applied to eliminate defects from engaging and disengaging the sample.

3.4.2 Innova height sensor

As a way to get around the bowing issues the Innova microscope has an integrated optical height sensor. This sensor measures topography data by measuring how the piezo has actually moved the sample rather than measuring the voltage applied to the piezo. The resolution of such measurements should be too low for being useful when looking at atomic planes (the wavelength of the light used is likely much larger than the distances being measured) but by using some clever diffraction mechanics the manufacturer claims that the resolution is usable. A test of this sensor revealed that the sensor measures height in "steps" of about 4 Å which is not good enough for characterizing atomic planes. An example of the height sensor data from an atomically flat sample (4H-SiC substrate) reveals these steps, figure 3.9.
Thus the height sensor was not used during this study but could perhaps be useful when looking at more rough surfaces where the accuracy is acceptable.

3.5 Surface roughness

When characterizing surfaces one aspect of interest is its roughness, the meaning of roughness in this context is measurement of how much the surface height differ from the mean height of the surface. There are several ways to measure this roughness and here some ways are listed.

**Roughness average** \((R_a)\)

This is an arithmetical mean deviation method which consists of summing up the absolute value of all the height differences of the sample and divide them by the number of measurement points; resulting in a value that describes the average deviation of all points from the median line. This value is calculated with the formula:

\[
R_a = \frac{1}{N} \sum_{i=1}^{N} |z_i - z^m|
\]

Where \(N\) is the number of measurement points, \(z\) is the actual height and \(z^m\) is the mean height value.
Root Mean Square ($R_q$)

The Root Mean Square (RMS) method calculates the square of all the height deviations from the median height on the surface, divides by the number of measurement points and finally takes the square root of the result. This measurement is slightly more sensitive to large changes in the height deviation than the $R_a$ measurement and is often chosen for statistical purposes. The RMS value is calculated with the following formula:

$$R_q = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_i - z_{i}^m)^2}$$

Maximum height profile ($R_t$)

This value describes the greatest distance between the largest peak and the lowest valley on the sample. This value is not good for statistics because it effectively only measures the difference between two points on a sample but for some requirements it can be useful. The value is calculated from:

$$R_t = | \min_{1 \leq i \leq N} (z_i - z_{i}^m) | + | \max_{1 \leq i \leq N} (z_i - z_{i}^m) |$$

Leveling

All these surface roughness measurements are more or less flawed since they depend greatly on factors like the scan size examined or the overall curvature of the sample. A leveling is needed to find the mean height of a surface. The leveling is done mainly to correct two things, the tilt of the sample from the mounting in the AFM and the bow movement from the piezo. Further leveling can be done if the surface is curved but the main interest lies in the topography that follow the curve. These leveling operations can be done in several ways and this affects the roughness measurements. An example of the leveling steps for a $60 \times 60$ $\mu$m scan window of sample G465 is displayed in figure 3.10.

Figure 3.10: a) the raw topography data of sample G465, a $60 \times 60$ $\mu$m scan b) the height profile drawn in a) (black) and a first order polynomial fitted to the height profile (red)
Not much can be seen in the data from figure 3.10 since the sample is tilted, which can be seen in the profile on the right that corresponds to the line drawn on the topography data. The black line is the actual topography data and the red line is a 1D polynomial fit to that data. To remove the effect of the tilt the data needs to be fitted to the red line, a so called leveling to a first order polynomial, figure 3.11.

Figure 3.11: a) topography data, leveled with a first order polynomial b) the height profile drawn in a) (black) and a second order polynomial fitted to the height profile (red)

The topography data have been leveled with a first order polynomial to account for the tilt of the sample. This data still does not seem to represent the surface well, it displays the artifact discussed in 3.4.1. In the profile on the right the black line is the topography data adjusted by a first order polynomial and the red line is a second order polynomial fitted to the data. This seems to be a good adjustment for the scanner artifact and the data leveled with a second order polynomial is displayed in figure 3.12.

Figure 3.12: a) the final topography after adjusting for both tilt and scanner bow is displayed b) the height profile drawn in a)

On the profile on the right in figure 3.12 a noticeable curvature is still present on the sample. This curvature could be a part of the surface but the curvature is similar on several scans and could therefore be yet another Innova artifact with an unknown origin. It should be noted that this is a simplification of process, the leveling is done in both x and y direction and takes
into account all profiles in the data. From the leveled data it is finally possible to determine the mean height of the surface topography. The mean height is simply a 0D polynomial fit (a straight line) to the topography data. Looking at the profile from figure 3.12 and applying the mean line brings a new problem, figure 3.13.

Figure 3.13: The profile from figure 3.12 in black and the mean line in red.

If a roughness calculation like RMS would be applied to a surface with the profile as in figure 3.13 then the value would almost exclusively represent the curvature of the surface and not the actual topography. This can be dealt with in quite a few ways, for example fitting the data once again to in this case a 3D polynomial or take a smaller scan size to collect the surface statistics. If another polynomial fit is applied there becomes a problem with the credibility of the statistics, if it is allowed to modify the actual surface then it can be sculpted further to fit the users needs (like a low RMS value). To select a smaller scan size, in this case at least below $20 \times 20 \, \mu m$, runs the risk of not representing the entire surface in a good way while eliminating most of the curvature of the sample. The scan size greatly affects the roughness values and when presenting such data it is important to also include the scan size in the result. An example of this effect can be seen in figure 3.14 where the RMS for G465 has been calculated for different scan sizes but on the same general area.

Figure 3.14: RMS value versus scan size comparison for sample G465.

It is clear that the two largest scan sizes pick up a good amount of the curvature while the
RMS stabilize at the $20 \times 20 \, \mu m$ scan size. The same trend can be seen on other samples as well (see appendix A) and therefore the $20 \times 20 \, \mu m$ scan size is chosen for the RMS measurements.

### 3.6 Calibration

The Innova calibration was checked for lateral and vertical accuracy with three calibration samples, *table 3.4, figure 3.15*. As seen in *table 3.4* the AFM was found to be highly accurate and no additional calibration was needed.

Table 3.4: Measurements of calibration samples.

<table>
<thead>
<tr>
<th>Calibration Sample</th>
<th>Designed step height</th>
<th>Designed Pitch</th>
<th>Measured step height</th>
<th>Measured pitch</th>
<th>Difference in step height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample from Digital Instruments</td>
<td>200 nm</td>
<td>2 $\mu m$</td>
<td>200 nm</td>
<td>2 $\mu m$</td>
<td>0%</td>
</tr>
<tr>
<td>Digital Instruments, P/N 498-000-026 3D reference</td>
<td>200 nm</td>
<td>10 $\mu m$</td>
<td>206 nm</td>
<td>10 $\mu m$</td>
<td>3%</td>
</tr>
<tr>
<td>NT-MDT, T163b Si Calibration sample STEPP</td>
<td>0,314 nm</td>
<td>N/A</td>
<td>0,316 nm</td>
<td>N/A</td>
<td>1%</td>
</tr>
</tbody>
</table>
Figure 3.15: Calibration samples and height profiles a) The 200 nm step height sample from Digital Instruments b) The 3D reference sample from Digital Instruments also with step heights of 200 nm c) The STEPP calibration sample with steps of 0.314 nm.
Chapter 4

Results and Discussion

4.1 Intermittent mode configurations

Most of the step heights were measured using the AFM intermittent mode. When using this mode special care should be taken to use proper settings. There is a discussion in [48] where graphene layers on silicon oxide are measured with different amplitudes of the cantilever producing anomalies in the nm regime for the height of the layers. Such large anomalies can not be accepted when measuring heights in the Å regime as is done in this study and therefore this behaviour of the intermittent mode was investigated. The first test was run on a graphene layer grown on the Si-face of the SiC. Three steps were measured with different set-point amplitudes resulting in figure 4.1. The measurements were taken in both scanning directions.

![Figure 4.1: To the left is the topography scan of 3 steps on sample G506 with the profile for step measurements marked. On the right is the profile of the steps.](image)

The steps were measured with a set-point amplitude ranging from 102.3 nm to 62 nm in steps of 3.1 nm and are presented in figure 4.2. The free amplitude was 105.4 nm.
As can be seen from figure 4.2 the step heights are consistent up until an amplitude of about 88 nm. This can to a large degree be explained by the attractive forces between the tip and the sample. When the tip closes in on the sample surface it is attracted by forces and they can vary over the sample. The magnitude of the forces can depend on contaminations, different compositions and steps that are giving rise to more contact area. It is also important to push hard enough as well to get through any possible layers of moist that can be present on the sample since it is examined in air. These effects can be seen in the phase of the cantilever oscillations when the tip is attracted by the sample. The amplitude is increased and the phase is lagging behind. At some distance the cantilever will be close enough to the sample to mostly experience repulsive forces from hitting the surface and at this point the phase should be back to its original state. A spectroscopy measurement of the amplitude and phase can thus reveal which amplitudes that are appropriate when running the intermittent mode on the sample, figure 4.3.
The spectroscopy suggests that the set-point amplitude in this case should be lower than 93 nm to be in the repulsive region. This result corresponds well with the step measurement result from earlier where the step height became consistent just slightly below that value. The same type of experiment was performed on a single graphene step on the C-face, sample G508, for consistency, figure 4.4.

The free amplitude of the cantilever was 106.2 nm and the graphene step was measured with amplitudes ranging from 103 nm to 62.5 nm in steps of 3.1 nm, figure 4.5.
Figure 4.5: The step height measured versus the amplitude of the cantilever, for both scan directions.

Just like in the previous test the step height becomes notably more stable at an amplitude of about 88 nm. An amplitude/phase spectroscopy measurement is made again to confirm previous results, figure 4.6.

Figure 4.6: Amplitude/phase spectroscopy measurement taken on sample G508, to the left the original spectroscopy and on the right the appropriate amplitudes for measuring are marked.

From the spectroscopy measurement the predicted set-point amplitude threshold for stable results is around 96 nm, again a reasonable match with the step height measurement. The conclusion can be drawn that one should take care to have the repulsive side of the tip-sample interaction dominating. These tests show that this region seems to be consistently at around 80% and lower of the free amplitude, one should however always make an amplitude/phase spectroscopy measurement first to confirm this to be on the safe side since the measurements in the attractive region are not consistent.
4.2 Silicon carbide

Before studying the grown graphene the SiC substrates were first examined with the purpose to get a better understanding of the surfaces. The first sample to be studied was the thin 6H-SiC film followed by the 4H-SiC substrate.

4.2.1 6H-SiC

The 6H-SiC sample displays a very well ordered surface with even steps propagating in the same direction, possibly a great substrate for graphene growth. In figure 4.7 two topography scans are displayed as well as a histogram over the step heights.

![Figure 4.7: Topography scan of 6H-SiC from AFM a) 15 × 15 µm scan, the 6H-SiC surface displays steps that are 200 to 500 nanometers in width and with lengths of several hundred micrometers b) 5 × 5 µm scan of the same surface c) Histogram over the step heights from both the scans with a binary of 0.25 nm.](image)

One interesting thing to note here is that all of the step heights on the sample become even integers when divided by the unit cell height of SiC (0.25 nm). This is not surprising but will prove useful later on in the study (in the graphene section of the results). Even though the surface is well ordered there are some defects, for example micropipes. To find such a defect the film was first examined in a transmission light microscope where features such as micropipes can be found by changing the focal plane from the backside of the transparent sample to the top side. If the feature examined follows the focal plane all the way through the sample it is possible that it is a micropipe. One such defect was found and is displayed in figure 4.8 where the defect was first found with a transmission optical microscope and then imaged with an AFM, shown as a 3D image in figure 4.9 to get a better sense of the scale.
Figure 4.8: a) Optical transmission image of the 6H-surface, the focal plane is roughly on the backside of the sample and the assumed micropipe is marked with a red circle, when moving the focal plane upwards towards the surface of the sample the defect stayed with the focal plane b) A transmission image of the surface for reference, taken at the edge of the 6H-SiC sample.
It should be noted that the images are not taken on the same spot on the 6H-SiC sample. In the figure 4.8 b) it is possible to see the actual steps of the surface as white lines in some places.

Figure 4.9: A possible micropipe on the 6H-SiC surface. The micropipe has a diameter of 8 µm and is assumed to go all the way through the 6H-SiC film to the substrate. The scan size for the AFM 3D image is 15 × 15 µm and the height scale goes from -2.4 µm to 0.5 µm.

The height scale of the topography scan again shows that it is probably a micropipe since the AFM tip is roughly 3 µm long and it fell all the way down and could not reach the bottom of the feature. It can also be seen that even though the surface suffers such a seemingly large defect it realigns fast and in about 15 steps from the defect the steps have straighten out again.

4.2.2 4H-SiC

The main substrate for all the graphene samples studied were 4H-SiC. The 7 × 7 mm substrates are cut from a wafer as described in 3.2. The substrates are marked with an ”x” on the backside to make it clear which side that is the Si-face and C-face, figure 4.10.
Since the substrates have been polished they are highly planar and do not display much topography other than some fine polishing scratches, figure 4.11. The step structure that was seen on the 6H-SiC is hidden beneath the amorphous top layer from the polishing but is again revealed when the graphene is grown since the amorphous layer is sublimed. A schematic of a profile cut in the polished surface is displayed in figure 4.12.

The highly planar surface of the SiC is a crucial parameter in the graphene growth since graphene starts to form where it is easiest to do so. Defects on the surface are therefore prone to generate multiple graphene layers more than on other places on the sample causing a disruption in the homogeneity of the graphene. The increase of quality of the graphene grown on SiC can be linked to the increased quality of the SiC growth and preparation.
4.3 Graphene

4.3.1 6H-SiC graphene

The 6HG sample is not regularly produced by Graphensic as the high steps on the substrate causes a rather irregular growth. This sample is therefore not included in the surface roughness measurements among other things later on. It is, however, a good example of how the sublimation of the SiC steps behave, in figure 4.13 two scans of 6HG is displayed.

![Figure 4.13: a) a 15 × 15 µm topography scan of 6HG b) a 5 × 5 µm topography scan of 6HG](image)

The sublimation has caused the straight and well ordered steps seen in figure 4.7 to become more ”curved” and in the 5 × 5 µm scan the sublimation process at the edges of the steps is clearly visible. The sublimation starts where it is ”easiest” to do so, which is at dislocations or step edges. When the original substrate steps consists of such a large amount of SiC unit cell layers as in this case the steps sublime into several small steps at the step edges. An example of this is displayed figure 4.14 where a scan over the steps edges is shown as well as a schematic over the sublimation process.
Figure 4.14: a) a $2 \times 2 \, \mu m$ topography scan of 6HG, clearly displaying the sublimation steps at the step edges b) a schematic of the sublimation at the steps, the orange lines are SiC and the black are graphene layers.

The schematic of the sublimation is in the ideal case and in reality there is a possibility that the sublimation chooses other ways.
4.3.2 Surface roughness parameters

To calculate the roughness parameters for the 4H-SiC graphene samples three $20 \times 20$ $\mu$m scans were taken on different places on each sample. The individual scans were taken at least 400 $\mu$m apart from each other in an attempt to see weather there were large differences in the statistics depending on the area studied. Three roughness parameters were calculated for each scan and sample, the result are displayed in table 4.1. In figure 4.15 there is a sample of the topographies used for the roughness calculations, only one scan for each sample is displayed and the rest can be found in the appendix, part B.

Table 4.1: Surface roughness measurements for the graphene samples, all values are in nm. Discussion follows in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS Scan 1</th>
<th>RMS Scan 2</th>
<th>RMS Scan 3</th>
<th>$R_a$ Scan 1</th>
<th>$R_a$ Scan 2</th>
<th>$R_a$ Scan 3</th>
<th>$R_t$ Scan 1</th>
<th>$R_t$ Scan 2</th>
<th>$R_t$ Scan 3</th>
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<tbody>
<tr>
<td>G465</td>
<td>0.62</td>
<td>1.99</td>
<td>2.46</td>
<td>0.49</td>
<td>0.77</td>
<td>0.76</td>
<td>5.34</td>
<td>70.1</td>
<td>82.1</td>
</tr>
<tr>
<td>G503</td>
<td>1.27</td>
<td>0.98</td>
<td>1.21</td>
<td>1.01</td>
<td>0.70</td>
<td>0.85</td>
<td>11.5</td>
<td>29.9</td>
<td>31.0</td>
</tr>
<tr>
<td>G506</td>
<td>0.61</td>
<td>0.94</td>
<td>0.93</td>
<td>0.50</td>
<td>0.76</td>
<td>0.74</td>
<td>4.36</td>
<td>7.35</td>
<td>11.6</td>
</tr>
<tr>
<td>G507</td>
<td>1.82</td>
<td>1.41</td>
<td>1.82</td>
<td>1.37</td>
<td>1.05</td>
<td>1.28</td>
<td>33.2</td>
<td>31.4</td>
<td>35.8</td>
</tr>
<tr>
<td>G508</td>
<td>1.53</td>
<td>1.48</td>
<td>1.41</td>
<td>1.11</td>
<td>1.00</td>
<td>1.07</td>
<td>34.5</td>
<td>96.3</td>
<td>39.8</td>
</tr>
<tr>
<td>G509</td>
<td>1.05</td>
<td>1.03</td>
<td>1.05</td>
<td>0.80</td>
<td>0.81</td>
<td>0.81</td>
<td>23.8</td>
<td>29.9</td>
<td>23.9</td>
</tr>
</tbody>
</table>
Figure 4.15: A sample of the scans used for the surface roughness calculations. The topography images are all $20 \times 20 \, \mu \text{m}$ and the samples are a) G465 b) G503 c) G506 d) G507 e) G508 f) G509.

As can be seen in table 4.1 G465 is standing out as producing rather inconsistent statistics. The reason for this is that the sample picked up a considerable amount of contaminants between the first scan and the second two (the last scans were taken about 2 months after the first one). This is also clearly evident in the $R_t$ values that are very high because of the large contaminants. The statistics for this sample should therefore not be considered in too much detail. Later it will be discussed how the contaminated scans can be treated to solve the contamination problem.
The $R_t$ values are generally only useful to see if there are any large contaminations on the sample. If the $R_t$ value is high and differ to a high degree between the scans then the sample probably has large contaminations and if the $R_t$ value is low then the surface is likely flat and clean. For the RMS values it can be seen that they differ significantly for the Si-face samples, 23% for G503 and 35% for G506. This difference between the scans comes mainly from the curvature of the surface (which could be an artifact), while the steps on the surface are mostly the same in height and number. To get better coherence in the statistics one could consider doing smaller scans. For the C-face the statistics are more coherent with a 22% difference for G507, 8% for G508 and a very low 2% for G509. Still weather or not these statistics are useful to describe the surface is questionable.

When left in their containers the graphene samples picks up contaminants, the larger of those contaminantins are round with a typical diameter of 500 nm and a height of 40 nm. This should not be a problem for the usefulness of the graphene but for roughness calculations it is detrimental. To get rid of the contaminations the samples should be heated to around 700°C while pumping out the contaminations. During this study this was, however, not possible and thus other methods where implemented to solve the problem. On sample G465 the contaminations were removed by solving the Laplace equation with the borders around the contamination as a source to generate new data. This is of course manipulation of the raw data and should not be considered as acceptable for generating statistics. Nevertheless this method was implemented just to see what results it would give. The results are displayed in table 4.2 and in figure 4.16 the topography scan before and after the corrections is displayed.

Table 4.2: Surface roughness parameters for G465 where scan 2 and 3 have been corrected for the large contaminations, all values are in nm.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>RMS Scan 1</th>
<th>RMS Scan 2</th>
<th>RMS Scan 3</th>
<th>$R_a$ Scan 1</th>
<th>$R_a$ Scan 2</th>
<th>$R_a$ Scan 3</th>
<th>$R_t$ Scan 1</th>
<th>$R_t$ Scan 2</th>
<th>$R_t$ Scan 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>G465</td>
<td>0.62</td>
<td>0.93</td>
<td>0.797</td>
<td>0.49</td>
<td>0.70</td>
<td>0.64</td>
<td>5.34</td>
<td>13.6</td>
<td>9.73</td>
</tr>
</tbody>
</table>

Figure 4.16: a) A scan of G465 with large contaminations b) The contaminations have been removed by solving the Laplace equation in a small area around the contaminations to calculate the new data.

As can clearly be seen a lot can be done with image software to manipulate the data, the RMS values now differ by 32% (as opposed to the earlier 75%) which is more in line with the values of the other Si-face samples.
4.3.3 4H-SiC graphene on the Si-face

The graphene grown on the Si-face shows a well ordered growth with distinct steps that can be followed over long distances. An example of this can be seen in figure 4.17 where the steps can be followed for the entire scan of 60 × 60 µm.

![Figure 4.17: A large topography scan (60 × 60 µm) of sample G506 (Si-face).](image)

The steps are well ordered but a curvature of the entire sample is clearly visible at these large scan sizes (again, possibly an artifact). This curvature looks large but taking a look at the scale reveals that it the surface is actually quite flat, only a change in height of about 20 nm for distances of 30 µm. A closer look at the surface is displayed in figure 4.18 which is a 20 × 20 µm scan.
As mentioned earlier the steps are uniform and well ordered with a typical step width of 0.5 µm and length of at least 60 µm but likely much longer. To try and determine the step compositions a large number of steps (a total of 100) were measured for their height and the results can be seen in figure 4.19. The steps are measured by drawing a profile consisting of five adjacent line profiles along the steps.
As can be seen the steps height are varied on a large span from 0.4 to 2.7 nm but focused around 0.5 to 1.35 nm (73% of the total amount of steps). To try and determine the composition of the steps we can now guess the composition by stacking unit cells of SiC and layers of graphene until they agree with the height of the step (similar to what is done by Culbertson and associates in [49]). This method does not give any conclusive evidence at all concerning the actual composition but it gives us an idea whether the step affects the graphene layers or not. A MatLab script was created to calculate the possible step compositions. The script only considers steps that include a SiC step (step heights of 0.354 nm or integers of that height could of course still be single steps of graphene but they are unlikely since the dominating graphene growth formation comes from sublimation where the surface needs to reside to produce a graphene layer). The script varies a SiC step in terms of the SiC unit cell height (0.25 nm) from 1 to 10 unit cells (0.25 to 2.5 nm) and on each side of the steps graphene layers are stacked from 1 to 10 layers. Since it is assumed that graphene is grown over the entire surface the buffer layer is present everywhere and can therefore be neglected. This produces a “library” of 1000 possible step compositions including step heights from 0 to 5.65 nm. The reason that more possibilities are not included (like more graphene steps) is that the maximum step height measured during the step height measurements was never larger than 3.2 nm and according to the manufacturers earlier measurements of graphene layers they never reach more than 10 layers. For the G506 sample we examine the 4 top peak step heights with the script, 0.50 nm, 0.85 nm, 1.05 nm and 1.20 nm. The script prompts the user for a step height and searches its library for matching compositions, it then produces a visual result. The step heights need to be rounded off to the nearest half Å before they can be entered into the script, ie a 0.42 nm step should be entered as 0.40 nm and a 0.54 nm step as 0.55 nm. The first step to be evaluated is the 0.5 nm step, figure 4.20. It is unfortunately hard to read some of the results because of the format of a page, the interested reader is encouraged to run the script for him/her self to see the results better, see the appendix, part C for the code.
Figure 4.20: 20 matching step compositions for the 0.50 nm step height. The results are presented visually with the SiC unit cell steps in orange and graphene layers in black. GL stands for graphene layer.

The script reveals 20 matching compositions within the constraints described earlier. Even though there are 20 matches it is possible to say something about what is the most likely composition. Except for the compositions with a 2 SiC unit cell difference and an equal amount of graphene on both sides of the step (half of the matches) the graphene layer difference (5 graphene layers) in the other compositions make them unlikely since it would be very rare for the sample to sublime 15 SiC unit cells more at one side of just one step. It can thus be deduced that for the 0.50 nm step the most probable composition of the step is that the graphene layer remains constant. The second step up for evaluation is 0.85 nm, figure 4.21.

Figure 4.21: 19 matching step compositions for the 0.85 nm step height.

19 matching step compositions are found and again they reveal some information. There are no compositions that show an unchanged graphene layer, thus one can say with high certainty that the graphene layer is disrupted at these steps. Again the steps with large graphene layer differences are unlikely and we are left to consider a 2 SiC unit cell step with a graphene difference of one (9 matches). Next up is 1.05 nm, figure 4.22.
This step has only half the matches of the other steps with 10 matches. It can be seen that the step is likely composed of 7 SiC unit cells and a graphene layer difference of 2 as lowest. It should, however, be noted that this step is an integer of the graphene step height, thus it could also be a difference of 3 graphene layers on a flat of the SiC, this is unlikely though as mentioned before. Finally we evaluate the step with the most counts, 1.2 nm figure 4.23.

18 matches are found with quite different compositions. The most likely ones are the 2 SiC unit step with a graphene layer difference of two but the 9 SiC until cell composition is not entirely unlikely. The only certain thing is that the graphene layer is disrupted. A small example of what could be achieved with this method (should it be verified to give good results) is displayed with a $3 \times 3 \mu m$ topography scan of G506, figure 4.24.
In this small example it is found that there is at least a strip of graphene of about 1.5 $\mu$m that is continuous along the sample. If this method is found to be reasonable accurate then this could be done at much larger scale, the same 20 $\times$ 20 $\mu$m scans used for surface roughness would also give much information about the graphene homogeneity.

Two more Si-face grown graphene surfaces was studied, G465 and G503. G503 is similar to G506 with the same step widths and the same continuity, G465, however, displays a frequent defect in the steps, commonly in the form of a cut out half circle. These defects are about 0.5 $\mu$m in radii and with an average distance from each other of about 3 $\mu$m but sometimes as long as 10 $\mu$m. An example of the defects can be seen in figure 4.25 where a 30 $\times$ 30 $\mu$m scan is displayed and then a zoomed in picture of a defect.
Figure 4.25: a) a $30 \times 30 \, \mu\text{m}$ topography scan of sample G465 b) zoomed in topography of a step defect c) the two height profiles from b).

It is hard to say how these defects affect the graphene layer by only studying them with AFM. Other methods would perhaps reveal more. In the same way as before the step heights for G465 were measured, displayed in figure 4.26.
Again there is a wide spread in the step heights, from 0.25 to 2.65 nm. There is one distinct peak in the step height histogram at 1.2 nm, this step have already been evaluated in figure 4.23 and it was deduced that the graphene layer must have a difference of two at the steps. The three following highest peaks are at 0.65, 1.0 and 1.25 nm and those are now evaluated, 0.65 nm in figure 4.27.

Figure 4.27: 16 matching step compositions for the 0.65 nm step height.

For the 0.65 nm step there are 16 matches. From the results it is clear that the most probable composition is 4 SiC unit cells and a graphene layer difference of one layer. Now the
1.0 nm step is evaluated, *figure 4.28*.

![Figure 4.28: 15 matching step compositions for the 1.0 nm step height.](image)

There are 15 matches and the composition with the 4 SiC unit cell step and continuous graphene layer is the most likely, also making up 10 of the matches (63%). Finally the 1.25 nm step is evaluated, see *figure 4.29*.

![Figure 4.29: 15 matching step compositions for the 1.25 nm step height.](image)

15 matches are found for this step as well. The composition with the highest probability is the 5 SiC unit cell step with a continuous layer of graphene.

The G503 sample was studied in the same way with the results displayed in *figure 4.30*. 

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This sample comes in with the smallest range so far for the step heights ranging from 0.35 to 2.15 nm. The top peaks are 0.50, 0.85, 1.00, 1.20 and 1.25 nm, all of which have already been encountered and evaluated. The 0.50, 1.00 and 1.25 nm steps are believed to have a continuous layer of graphene while the 0.85 and 1.20 nm steps have a disrupted graphene layer.

4.3.4 4H-SiC graphene on the C-face

The growth on the C-face of SiC is clearly a complex one compared to the Si-face, let us start by looking at figure 4.31 which is a $20 \times 20 \mu m$ scan of sample G509.
The step propagation is from the top-right corner to the bottom-left corner. The steps are highly irregular and the terraces have a width that vary from 1 to 4 µm. The steps differ in height considerably, from 0.42 nm at the lowest steps to 4 nm at the highest. On the steps there are ridges in the graphene, these ridges have a typical height of 1.7 nm (20 ridges were measured with a span in height from 0.7 to 4 nm with 75% near 1.7 nm ±0.2 nm). The origin for these ridges is not clear but there are a few different lines of thought. One idea is that they appear when graphene grains that started growing close to each other on the steps meet. When the graphene grains grown over the steps they could curl up into nanotubes and when they meet another grain a ridge forms between them [50]. Another idea is that the ridges form by thermal induced buckling when the sample cools down after the sublimation [33]. The thermal contraction of the C-face SiC substrate compared to the graphene could be large enough to produce the stress during cooling. More study of the thermal properties would, however, be needed to confirm this. A closer look at the ridges on G508 indeed revel that their structure is advanced and hard to explain, figure 4.32.

Figure 4.31: Topography of sample G509 (C-face), discussion is found in the text.
The examined ridge is about 130 nm wide and it is very probable that more than a few graphene sheets have all curved up in a bow structure over the SiC surface. This is expected since the growth parameters were such that one should expect several graphene layers on this surface. The ridge has three peaks at 2.7, 4.8 and 6 nm which is a considerable rise. The profile should, however, not be interpreted as the actual profile of the ridge since the AFM only captures the height differences and the ridge probably has more to it than the AFM reveals. There is also a possibility of a ”double tip” artifact in the imaging where the tip have two tips, creating a ”shadow” and making the ridge seem larger than it is. The graphene grains resulting from this wrinkling have a size of at most about 3 × 3 μm² but are commonly even smaller. On the graphene grains it is also possible to find small steps of about 0.42 nm, this corresponds well to the height of a step where the graphene layer thickness changes as will be shown later in the thesis work.

Even though the steps are irregular at the edges they are continuous over large distances which can be seen in a larger scan such as figure 4.33.
Some steps can be followed at least 50 µm before they are fully covered by another step but there is no clear order in the structure, the step pattern looks somewhat like large disorder fish scales. Even though the individual steps are hard to follow they interchange with each other in the same propagation direction giving the surface at least some order.

Step height measurements are commenced on the C-face in the same way that was previously done on the Si-face, starting by measuring the step heights from G509, and the result is shown in figure 4.34.
Figure 4.34: Step heights of 100 steps measured from sample G509, source is figure 4.31 and appendix.

The step heights range from 0.25 to 3.25 nm with a fairly equal spread between the step up until about 2 nm. The four top peaks are at 0.25, 0.40, 0.45 and 1.35 nm, none of these step heights were peaking on the Si-face samples so they all need to be evaluated, starting with 0.25 nm, figure 4.35.

Figure 4.35: 20 matching step compositions for the 0.25 nm step height.

There are 20 matches, one composition with 1 SiC unit cell step and an equal layer of graphene and two others with a graphene difference of 5 layers. The most probable composition is then the 1 SiC unit cell step. The next step for evaluation is 0.40 nm, figure 4.36.
Figure 4.36: 19 matching step compositions for the 0.40 nm step height.

There are 19 matching compositions with the most likely one being a 3 SiC unit cell step with a constant graphene layer. It should also be mentioned that the same step height is measured for 1 additional layer graphene on graphene in [51] and [48] however the origin for that step height is not explained. The next step is 0.45 nm, figure 4.37.

Figure 4.37: 18 matching step compositions for the 0.45 nm step height.

18 matches are found and the composition that is most probable is the 1 SiC unit cell step with a two layer graphene difference. Finally the 1.35 nm step is evaluated, figure 4.38.
Figure 4.38: 13 matching step compositions for the 1.35 nm step height.

There are 13 matches and the most probable composition is the one with 4 SiC unit cell steps and a graphene layer difference of one layer. The other two C-face grown graphene samples studied (G507, G508) both displayed much the same characteristics as the G509 sample, a histogram over the step heights from G507 is shown in figure 4.39.

Figure 4.39: The step heights of 100 steps measured from sample G507 (see appendix B for source topography).

Again a wide spread is seen in the step heights ranging from 0.25 to 3.1 nm, similarly to the previous C-face sample the steps are spread more or less evenly from 0.25 to about 2 nm. The four largest peaks are at 0.40, 0.45, 0.85 and 1.20 nm, all of these steps have been previously evaluated. The 0.40 nm step is believed to have a constant graphene layer while the 0.45, 0.85 and 1.2 nm steps have a disrupted graphene layer. The final sample to have its steps measured was G508 and the results are presented in figure 4.40.
The spread is again similar to the other C-face samples ranging from 0.25 to 3.2 nm with the main volume of heights from 0.25 to 2 nm. Three main peaks are found at 0.65, 0.90 and 1.00 nm. The 0.65 and 1.00 nm steps have already been evaluated and the 0.65 nm step was found to facilitate a one graphene layer difference while the 1.00 nm step has a continuous graphene layer. The evaluation for the 0.90 nm step is shown in figure 4.41.

Figure 4.40: The step heights of 100 steps measured from sample G508, see appendix for source topography.

16 matching compositions are found and the one that is most likely to be correct is the one with a 4 SiC unit cell step and a difference of one graphene layers. One striking feature of all the C-face sample studied was that they all showed a large amount of contaminations. The contaminations are always present at the edges of steps and on the ridges, it is reasonable to belike that this is because the graphene on the C-face consists of many layers and they have

Figure 4.41: 16 matching step compositions for the 0.90 nm step height.
many dangling bonds at the edges. These dangling bonds, combined with the lack of the buffer layer that exists on the Si-face causes contaminations to stick a lot easier to the C-face. The same reasoning goes for the ridges, when the graphene layers buckle up there is a chance that they create structures that leave dangling bonds.
Chapter 5

Conclusions

The first conclusion in this thesis is regarding the intermittent amplitude needed for step height measurements on graphene. It was concluded that set-point amplitude should be set to lower than 80% of the free amplitude should be used while also consulting the amplitude/phase spectroscopy for confirmation. As for the surface roughness parameters it was concluded that they were consistent for the C-face (and therefore useful) while picking up too much overall curvature on the Si-face to be useful. The RMS values for the C-face landed between 1.03 to 1.82 nm (different samples) with a highest difference for scan on the same surface of about 8% (one sample had a difference of 22% but it was caused by contaminations). For the Si-face the difference between the scans were much higher, 23% at best, while ranging in RMS from 0.61 to 1.27 nm. The leveling and scan areas were shown to be very important for the RMS values and after some testing the raw data from the Innova was leveled with a second degree polynomial and the scan size was set to 20 × 20 µm. From the study of the 6H-SiC epilayer it was concluded that the steps all were integers of the SiC unit cell height. The study of the 4H-SiC substrate reveled a highly flat surface with little remaining markings from polishing.

The graphene studies of the the Si-face displayed a highly well ordered graphene growth with distinct steps that had even edges and propagation. The step terrace width for all of the Si-face samples was found to be near 0.5 µm and had lengths of at least 60 µm but likely a lot more. The G465 sample stood out by having some defects on the edges of the steps and by being more contaminated than the other samples.

The C-face graphene growth showed a complex growth with ridges and uneven steps. The width of the ridges indicated that the graphene layer was composed of several graphene layers on all samples. The C-face graphene was also found to have plenty of contaminations.

A total of 653 steps were measured during this study, 100 for each graphene sample and 53 on 6H-SiC. The step heights for the C-face were found to have a larger range than the ones on the Si-face but no real pattern could be found concerning the step distribution.

Outlook

Continued work is needed in many areas concerning these surfaces. For the C-face the ridges need to be studied with other microscopic methods like scanning tunneling microscopy or transmission electron microscopy to find out more concerning their compositions and then perhaps shine some light on how they are formed and how to prevent it if at all possible. The contaminations on the C-face are also a problem that needs to be studied further, the exact elemental composition of the contaminations needs to be evaluated if any attempt to find their origin is to be made. An X-ray photoelectron spectroscopy study could be useful in this endeavour.
A new way to evaluate the step heights is proposed in this thesis where the step compositions is guessed using stacking of SiC unit cells and graphene layer heights. This method does however need confirmation by other evaluation methods for the step compositions (such as Low Energy Electron Microscopy, Raman and Kelvin probe measurements coupled with AFM). Should this method be confirmed to work to a high degree then it could be used coupled with the surface roughness parameters to give homogeneity data for graphene sample customers.
Bibliography


Appendix

part A.

Table 5.1: Measurements of RMS for sample G465

<table>
<thead>
<tr>
<th>Scan size (µm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.666</td>
</tr>
<tr>
<td>10x10</td>
<td>0.955</td>
</tr>
<tr>
<td>30x30</td>
<td>4.38</td>
</tr>
<tr>
<td>60x60</td>
<td>9.01</td>
</tr>
</tbody>
</table>

Table 5.2: Measurements of RMS for sample G509

<table>
<thead>
<tr>
<th>Scan size (µm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x2</td>
<td>0.859</td>
</tr>
<tr>
<td>10x10</td>
<td>1.04</td>
</tr>
<tr>
<td>30x30</td>
<td>4.21</td>
</tr>
<tr>
<td>60x60</td>
<td>9.01</td>
</tr>
</tbody>
</table>

part B.
Figure 5.1: Topography of sample G507 (C-face), used for step heights

Figure 5.2: Topography of sample G507 (C-face), used for step heights
Figure 5.3: Topography of sample G507 (C-face), used for step heights

Figure 5.4: Topography of sample G508 (C-face), used for step heights
Figure 5.5: Topography of sample G508 (C-face), used for step heights

Figure 5.6: Topography of sample G508 (C-face), used for step heights
Figure 5.7: Topography of sample G509 (C-face), used for step heights

Figure 5.8: Topography of sample G465 (Si-face), used for step heights
Figure 5.9: Topography of sample G465 (Si-face), used for step heights

Figure 5.10: Topography of sample G503 (Si-face), used for step heights
part C.

The MatLab code for the step height script:

```
%Step composition guesser for graphene on SiC
%The SiC step is from 1 to 9 SiC unit cells
%The Graphene layers range from 0 to 10 on both sides on the step
%The calculated library contains 1000 steps (many are the
%same step height but with different compositions)

%Clears the workspace and figures
clc
clear
clf
close all

%Step input
search = input('Please enter a stepheight (nm) to evaluate, rounded to the closest half integer (1.05 0.55 0.70 etc): ');

%Sends the user back if incorrect input is used
test = 0;
test = isa(search,'numeric');
if test == 0
    return
end
```
%Initial values
i = 0;
l = 0;
Final = zeros(10,10);

%Vector with lower graphene heights
LowerG = zeros(1,10);
while l < 10
    l = l + 1;
    LowerG(l) = 0.35*(l-1);
end
l = 0;

%Vector with SiC step heights
SiC = zeros(1,10);
while l < 10
    l = l + 1;
    SiC(l) = 0.25*l;
end
l = 0;

%Matrix with the left side SiC and graphene
UpperG = zeros(10,10);
while i < 10
    i = i + 1;
    u = 0;
    while u < 10
        u = u + 1;
        UpperG(i,u) = SiC(i) + 0.35*(u-1);
    end
i = 0;
end

%Calculation of step heights
Stepheights = zeros(10,10);
while l < 10
    l = l + 1;
    i = 0;
    while i < 10
        i = i + 1;
        u = 0;
        while u < 10
            u = u + 1;
            Stepheights(i,u) = abs(UpperG(i,u) - LowerG(l));
        end
    end
A = reshape(Stepheights,100,1);
k=0;
    while k < 100
        k=k+1;
        Final(1,k) = A(k);
    end
end

%Delete the "tail" of the numbers
H = (round(100*Final)/100);

%Find the desired step
[k,m] = ind2sub(size(H),find(ismember(H,search)));

%k row, m column
%For every 10 columns the upper graphene layer increases by 1
%The column 23 for example is 2 graphene 3 SiC unitcells on left side
%Row is the number of graphene on the lower side 1=0 layer 3=2 layers etc

%Printing out how many matches that were found
X = [num2str(length(k)), ' matching step compositions were found'];
disp(X)

%If there are no matches end the program
if length(k)<1
    return
end

%Initial values to handle exceptions
error = zeros(10,3);
n=0;
o=0;

%Handling exceptions, if a value is larger than 90 it needs to be handled separately
while o < length(k)
    o=o+1;
    if m(o)>89
        n=n+1;
        error(n,1) = 1;
        error(n,2) = m(o);
        error(n,3) = o;
        m(o) = 0;
    end
end

%Convert to string for separation
r = num2str(m+10);

%SiC unitcells
rr = str2num(r(:,1));
% Graphene layers, upper side
rr2 = str2num(r(:,2));

% If any values were larger than 90 they are treated here
v=0;
if error(1,1) == 1
    while v < n
        v=v+1;
        rr2(error(v,3))=error(v,2)-90;
        rr(error(v,3))=10;
    end
end

% And here
m=0;
while m < length(k)
    m=m+1;
    if rr2(m) == 0
        rr2(m) = 10;
        k(m) = k(m)+1;
    end
end

% Print out of the step compositions
o=0;
while o < length(k)
    o=o+1;
    p=k(o);
    X = ['Step composition:', num2str(rr2(o)), ' SiC unit cells,
        Graphene layers (upper/lower):', num2str(rr(o)),', ', num2str(p)];
    disp(X)
end

% Vectors for plotting
o=0;
x = [0 10];
x1 = [0 5];
x2 = [5 10];
y = [0 0];
SiCstep = [0.25 0.25];
Graphenelay = [0.35 0.35];

% Plotting
figure('Color',[1 1 1]);
set(gcf,'units','normalized','outerposition',[0 0 1 1])
while o < length(k)
    o=o+1;
    q=0;
    w=0;
end
d=0;
p=k(o);

X = [ num2str(rr2(o)), ', SiC, GL (upper/lower):',
     num2str(rr(o)), ', ', num2str(p) ];

subplot(ceil(sqrt(length(k))),ceil(sqrt(length(k))),o);
title(X)
hold on
axis([0 10 -0.5 10]);
axis off
b=plot(x,y);
set(b,'Color',[1 .4 0]);

while q < rr2(o)
    q=q+1;
    a=plot(x1,siCstep*q);
    set(a,'Color',[1 .4 0]);
end

while w < rr(o)
    w=w+1;
    plot(x1,rr2(o)*siCstep+Graphenelay*w,'k');
end

while d < k(o)
    d=d+1;
    plot(x2,Graphenelay*d,'k');
end