Confinement of charge carriers in bilayer graphene
Confinement of charge carriers in bilayer graphene

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.C.A.M Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op 17 mei 2013 om 12:30 uur

door

Augustinus Marius GOOSSENS

Master of Science in de natuurkunde
geboren te Lichtenvoorde
Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. ir. L.M.K. Vandersypen

Samenstelling van de promotiecommissie:

Rector Magnificus 
Prof. dr. ir. L.M.K. Vandersypen
Prof. dr. ir. L.P. Kouwenhoven
Prof. dr. P. Kim
Prof. dr. J.W.M. Frenken
Jun.-prof. dr. C. Stampfer
Prof. dr. Y.V. Nazarov

Voorzitter
Technische Universiteit Delft
Technische Universiteit Delft
Columbia University New York
Universiteit Leiden
RWTH Aachen
Technische Universiteit Delft, reservelid

Published by: A.M. Goossens
Printed by: Ipskamp Drukkers BV, Enschede
ISBN: 978-94-6191-728-7
Casimir PhD Series, Delft-Leiden 2013-15
Copyright © 2013 by A.M. Goossens
Electronic version available at http://www.library.tudelft.nl/dissertations
Contents

1 Introduction

2 Theoretical background of bilayer graphene confinement devices.
   2.1 Introduction
   2.2 Electronic band structure bilayer graphene
   2.3 Tunable band gap in double gated device
      2.3.1 Device working principle
      2.3.2 Background charges
   2.4 Quantized conductance
   2.5 Quantum Hall effect in bilayer graphene
   2.6 Quantum dots
      2.6.1 The constant interaction model of a single quantum dot
      2.6.2 Low bias regime
      2.6.3 High bias regime and excited states
   2.7 Hexagonal Boron Nitride

3 Device fabrication and measurement setup
   3.1 Introduction
   3.2 Electrostatic confinement in bilayer graphene: devices and electronic quality
      3.2.1 Quantum point contact
      3.2.2 Quantum dots
      3.2.3 Electronic quality
   3.3 Make and identify flakes
      3.3.1 Bilayer graphene
      3.3.2 Hexagonal boron nitride
   3.4 Raman spectroscopy
   3.5 Dry transfer method
   3.6 Cleaning graphene
   3.7 Lithography
   3.8 Measurement setups
## Contents

4 Double gated bilayer graphene devices with SiO$_x$ dielectrics
   4.1 Introduction ........................................ 36
   4.2 Fabrication ........................................ 36
   4.3 Band gap opening ................................... 36
   4.4 Split gate channel pinch-off ....................... 39
   4.5 Conclusion .......................................... 40

5 Mechanical cleaning of graphene
   5.1 Introduction ........................................ 42
   5.2 Heat cleaning ineffective ............................ 42
   5.3 Mechanical cleaning with contact mode AFM ....... 43
      5.3.1 Double gated device ........................... 45
      5.3.2 Discussions .................................... 45
   5.4 Conclusions ......................................... 48

6 Bubbles and wrinkles in graphene on hBN
   6.1 Introduction ........................................ 50
   6.2 Larger flat areas and larger bubbles .............. 50
   6.3 Bubble strain and substance ........................ 52
   6.4 Manipulating bubbles: substance .................... 53
   6.5 Dynamics of graphene on hBN ....................... 56
   6.6 Conclusion .......................................... 58

7 Gate defined confinement in bilayer graphene - hexagonal boron nitride hybrid devices
   7.1 Confinement in graphene ............................. 62
   7.2 Device fabrication .................................. 63
   7.3 One barrier: quantized conductance ................ 64
   7.4 Two barriers: Coulomb blockade .................... 67
   7.5 Conclusion .......................................... 69

8 Anomalous insulating state in bilayer graphene sandwiched in hBN
   8.1 Introduction ........................................ 72
   8.2 Fabrication ........................................ 72
   8.3 Anomalous insulating state ......................... 73
   8.4 Bias spectroscopy and magnetic field dependence .. 76
   8.5 Discussion and outlook ............................. 77

9 Reflection and Outlook
   9.1 Device platform ..................................... 81
   9.2 Confinement of bilayer graphene quasiparticles .... 84
   9.3 Bilayer graphene research .......................... 85

Bibliography .............................................. 89
## Contents

A  **Guide for fabricating double gated hBN/bilayer graphene/hBN**  
A.1 Substrate preparation and obtaining graphene and hBN flakes  
A.2 Dry transfer of graphene on top of hBN  
A.3 Annealing at $400^\circ{\text{C}}$  
A.4 Pattern contacts with EBL  
A.5 Etch graphene into channel  
A.6 Mechanical cleaning of graphene  
A.7 Dry transfer of top gate hBN flake on graphene  
A.8 Annealing at $250^\circ{\text{C}}$  
A.9 Pattern top gates with EBL  
A.10 Package and bond the device  

B  **Background resistance subtraction and alternatives for qpc conductance data**  

Acknowledgements  
Summary  
Samenvatting  
Curriculum Vitae
CHAPTER 1

Introduction

Imagine that your high school mathematics teacher has asked you in geometry class to provide him with a two-dimensional object. You are an eager student so you want to come back with the thinnest sheet possible. You sneak into the school kitchen and try to find some plastic wrap. Unfortunately the last piece has just been used and the supplier arrives only the day after tomorrow. Desperately you grab a piece of A4 paper from the copier and head back to the class room. The question rises if you did well. Is this A4 paper less two-dimensional than the plastic wrap because it is thicker? The mathematics teacher would say that both are two dimensional in the limit of thickness $d \to 0$. The number of dimensions of a system reflects the number of coordinates needed to describe the position of an object in that system. For example, an electron in a copper wire can move in all directions and three coordinates are needed to describe its position: it lives in a three-dimensional space. An electron bound to the nucleus of an atom cannot move in any direction, no coordinates are needed to describe its position: it lives in a zero-dimensional space. In 2004 A. Geim and K. Novoselov isolated graphene for the first time, a discovery for which they were awarded the Nobel prize.\cite{1, 2} Graphene is an atomically thin layer of carbon atoms ordered in a hexagonal lattice. Because it is only one atom thick there are two coordinates necessary to describe any position on the graphene flake. Hence graphene is an intrinsic two-dimensional material. Graphene can be isolated by peeling graphite (the material in the core of a pencil) with the help of scotch tape. This approach is more fancily called mechanical exfoliation. The next time somebody asks you to provide him with a two-dimensional object you know what to do: take a pencil and peel it with scotch tape until it becomes atomically thin.

Graphene has many amazing properties. Here I will list a few of them. Graphene is a gapless semiconductor where no backscattering is allowed. Carrier mobilities up to $1 \cdot 10^6 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ have been measured in suspended graphene.\cite{3, 4} That is almost three orders of magnitude larger than in silicon. Although graphene is conductive it absorbs only 2% of the light because it is only 0.34 nm thin.\cite{5} The in-plane covalent C-C bonding is very robust so the graphene membrane is very strong.\cite{6} Graphene has a theoretical Young’s modulus of 1 TPa which is 10 times larger than steel. The bending stiffness of the membrane is negligible which makes the material very flexible.\cite{7} Finally
Chapter 1. Introduction

Graphene is an impermeable atomic membrane: even helium atoms can not penetrate the thin sheet. These fantastic properties of graphene have triggered a huge interest in the material. Not only academia is obsessed with the ultra-thin material. Large companies as Samsung and Nokia are intensively researching graphene. In less than a decade graphene has developed from a Lunar park for fundamental physicists to a potential disruptive technology. Exemplary for this development is the appointment of graphene as a European Union Future Emerging Technology Flagship worth one billion euro in research grants over the next ten years.

The properties mentioned in the previous paragraph are all intrinsic properties of graphene. In reality graphene hardly ever occurs in its fully intrinsic form. The membrane is so thin that it will be affected by the nature of its surroundings. For example, when graphene is exfoliated on a rough substrate such as silicon oxide ($\text{SiO}_x$) it partially conforms to this roughness. A second example of the influence of a substrate on graphene concerns the electronic properties. Charged impurities in the $\text{SiO}_x$ substrate severely limit graphene’s mobility. Up to date suspended graphene is the most intrinsic form of graphene that has been obtained (see Fig. 1.1). Apart from having detrimental effects a substrate can also add functionality to graphene. The discovery of hexagonal boron nitride (hBN) as a suitable substrate has made huge impact on graphene research by enabling fabrication of graphene devices on a substrate with high electronic quality. More importantly, this discovery opened an entirely new field of two-dimensional layered heterostructures. hBN is a layered material like graphene, the sheets have a hexagonal crystal symmetry, but now the carbon atoms are replaced by boron and nitrogen atoms. Stacking graphene and hBN in the right order using the optimal thicknesses resulted in a field effect tunneling transistor with a room temperature current modulation a factor 10 better than in planar graphene field effect transistors. Further development of the transistor also involved using a layer of even another atomically thin layered material, tungsten disulfide (WS$_2$), to achieve an impressive current modulation up to a factor $10^6$ at room temperature.

The insulator WS$_2$ is a member of the family of two-dimensional transitional metal dichalcogenides (TMDCs) such as the semiconductor MoS$_2$, metal TaS$_2$ and superconductor NbSe$_2$. The possibilities of new devices are virtually limitless now we have mastered the control over two-dimensional layered structures.

In this thesis we use a Bernal stacked structure of two layers of graphene: bilayer graphene (BLG). Bilayer graphene is a two dimensional material that inherits many of the special properties of graphene. The electronic structure of bilayer graphene has many charming properties. First of all the quasiparticles are chiral and secondly they are four-fold degenerate. As bilayer graphene does not possess a band gap, conduction can be switched from electron to hole conduction. All these special electronic properties wonderfully come together in a demonstration of the quantum Hall effect in bilayer graphene measured by Novoselov et al. In this thesis we aim to further investigate the fundamental properties of quasiparticles in bilayer graphene. We do this by confining them to one-dimensional and zero-dimensional structures: quantum point contacts and quantum dots. A first feature to study is the four-fold degeneracy of the quasiparticles. Can we measure quantized conductance with steps of $4e^2/h$? Even more exciting would be to see four-fold shell filling in a quantum dot. Another question is if bipolar conduction still takes place in these low-dimensional structures. Can we empty...
Figure 1.1: Scanning electron microscope image of a suspended bilayer graphene device with a suspended gate. I developed this device in the group of Prof. dr. P. Kim at Columbia University in New York. As the top gate was connected to the graphene this device did not generate useful data.

a quantum dot from electrons and tune it into to a hole dot? In other words, can we observe the electron-hole crossover in bilayer graphene? It is also very interesting to investigate how the low-dimensionality makes the behavior of carriers different from higher dimensions. The electron-phonon coupling in graphene could be the ultimate limiter of mobility in suspended graphene. Low dimensionality will probably reduce the electron-phonon interaction. A field under intense research interest is graphene spintronics. Carbon has a low spin-orbit coupling due to the low atomic weight of the nucleus. Also the hyperfine interaction in graphene is weak because of the spinless nature of the abundant $^{12}C$ isotope in graphene. Consequently spins are predicted to live long in graphene. In practice the spin-lifetimes in graphene spin valves are unexpectedly short (up to 2.3 ns). Confining the carriers to zero dimensions might enhance these spin lifetimes and will give much insight in the physical mechanism behind spin decay.

Nanopatterning graphene in nanoribbons and small islands has been a successful strategy for one-dimensional and zero-dimensional confinement. Unfortunately, as a result of the etching process that is used for nanopatterning, the edges of the devices are very rough. This edge disorder, aggravated by substrate-induced disorder, leads to rather irregular device behaviour. The ideal device would confine charge carriers in the bulk, far from (disordered) edges, have well controlled tunnel barriers, and enjoy all the design freedom offered by lithography. This can be achieved by confining the carriers in graphene electrostatically. Electrostatic confinement requires a band gap. In bilayer graphene, a band gap can be opened by applying a perpendicular electric field.

In the last alinea of the introduction I would like to outline this thesis in the light of the previous. In chapter I describe the theoretical background of the bilayer graphene electrostatic confinement devices. The following chapter is devoted to the methods used to fabricate and measure our devices. In this chapter I elaborate on the transfer method used to fabricate layered two-dimensional heterostructures. In
chapter 4 I describe measurements on double gated bilayer graphene devices with SiO$_x$ dielectrics. This chapter describes results that are influenced for a large part by the surroundings of the bilayer graphene. I devoted Chapter 5 to a description of the many interesting (but often unwanted) effects like bubbles that occur after transferring a graphene sheet onto another substrate, in this case hBN. Chapter 6 describes a newly invented cleaning technique: mechanical cleaning. I sweep a contact mode atomic force microscope tip over the surface and thereby remove residues from the graphene to enhance its electronic quality. These clean graphene sheets are used in electrostatic confinement devices made of hBN/BLG/hBN layered heterostructures in chapter 7. Confinement of charge carriers to one dimension shows quantized conductance in steps of $2e^2/h$ and confinement to zero dimensions shows Coulomb blockade. In the last chapter I report preliminary results on an anomalous insulating state observed in clean hBN/BLG/hBN layered heterostructures.
CHAPTER 2

Theoretical background of bilayer graphene confinement devices.

2.1 Introduction

The goal of this thesis is to study confined quasiparticles in bilayer graphene. In the introduction I explained briefly that I want to implement electrostatic confinement to study confined quasiparticles. Electrostatic confinement requires a band gap. Section explains how a band gap can be induced in bilayer graphene. As is described in section 2.3 this band gap can be used to induce an insulating state. Structuring the top gates of a double gated device in the lateral dimension allows to create insulating regions while leaving other regions conductive. The gate structures described in section 3.2 in the next chapter induce a small conductive channel or island.

To provide a theoretical background for the measurements presented in chapter 7 this chapter theoretically describes quantized conductance, the quantum Hall effect in bilayer graphene and the constant interaction model for quantum dots. We close the chapter with section 2.7 about the insulating layered material hexagonal boron nitride that we will use to encapsulate our bilayer graphene devices.

2.2 Electronic band structure bilayer graphene

P.R. Wallace worked out the electronic band structure of graphene in 1947 motivated by understanding the properties of graphite. Most probably he did not anticipate the impact of his work. With the discovery of carbon nanotubes and later graphene his calculations were of great relevance to many scientists. In this chapter we explain the band structure of bilayer graphene. Again for a large part based on the results that P.R. Wallace presented more than 60 years ago.

Bilayer graphene is a layered structure that consists of two coupled graphene monolayers. To understand the physics of bilayer graphene it is instructive to first look at the monolayer graphene case. Monolayer graphene is a carbon allotrope with its atoms ordered in a two dimensional, hexagonal structure. Each carbon atom has four valence
electrons and three of these are used for the formation of $sp^2$ hybridized orbitals that form three $\sigma$ bonds with the neighbouring atoms. The fourth electron occupies a $2p_z$ orbital which is perpendicular to the graphene plane. It overlaps with neighbouring $2p_z$ orbitals to form $\pi$ bonds. The $2p_z$ electrons are delocalized over the entire lattice and make graphene conductive.

Monolayer graphene has a unit cell in the form of a parallelogram with equal sides that contains two carbon atoms, the A and B atom. The collection of all the A atoms in the lattice is called the A sublattice and likewise there is a B sublattice. These sublattices are inequivalent because they cannot be connected by primitive lattice vectors. The sublattice degree of freedom is often referred to as the ‘pseudospin’.

Stacking two monolayers in the Bernal order (A-B) gives the bilayer graphene crystal structure. The A sublattice in the top layer is exactly on top of the B sublattice in the bottom layer. The B sublattice in the top layer is in the middle of the hexagon of the bottom layer. The same holds for the A sublattice in the bottom layer. Fig. 2.1b and b show the lattice structure of bilayer graphene. In panel a we show the unit cell (shaded in grey) spanned by the primitive lattice vectors $\vec{a}_1$ and $\vec{a}_2$. The unit cell contains four carbon atoms: A1/B1 in the bottom and A2/B2 in the top layer.

The reciprocal lattice of bilayer graphene is a hexagonal Bravais lattice. The first Brillouin zone is a hexagon. The corners of the hexagon are subdivided in two sets of triangular symmetry (just like the sublattices in real space). These subsets are inequivalent as they can not be connected by primitive reciprocal lattice vectors. This degree of freedom is called the valley degree of freedom. The two inequivalent valleys are labeled K and K’. These valleys are of particular importance as the valence and conduction band touch at these points as we will explain in the following paragraphs. For neutral bilayer graphene the Fermi level is located at the K-points.

To calculate the band structure in the tight binding description one needs to take into account the $2p_z$ orbitals on the four atomic sites in the unit cell. Hence the tight-binding Hamiltonian operates in the space of wave functions $\Psi = (\psi_{A1}, \psi_{B2}, \psi_{A2}, \psi_{B1})$ for the K-valley and $\Psi' = (\psi_{B2}, \psi_{A1}, \psi_{B1}, \psi_{A2})$ for the K’-valley [34]:

$$H = \pm \begin{pmatrix}
-\frac{1}{2}V & 0 & 0 & v\pi^\dagger \\
0 & \frac{1}{2}V & v\pi & 0 \\
0 & v\pi^\dagger & \frac{1}{2}V & \pm \gamma_1 \\
v\pi & 0 & \pm \gamma_1 & -\frac{1}{2}V \\
\end{pmatrix},$$  \hspace{1cm} (2.1)

where $\pi = p_x + ip_y$, $\gamma_1$ the overlap integral for A1 and B2, the plus (minus)-sign labels valley K (K’). The Hamiltonian takes into account the asymmetry $V = \epsilon_2 - \epsilon_1$ between on-site energies in the two layers. Within each plane nearest neighbour coupling $\gamma_0 = 3.16$ eV leads to in-plane velocity $v = \sqrt{3}/2a\gamma_0/\hbar \approx 1 \cdot 10^6$ m/s where $a$ is the graphene lattice constant. Note that this in-plane velocity is different from the Fermi velocity in bilayer graphene. The in-plane velocity is the Fermi velocity in monolayer graphene.

This Hamiltonian describes the dispersion relation $\pm E^2_\alpha(p)$ ($\alpha = 1, 2$) for the four
2.2. Electronic band structure bilayer graphene

Figure 2.1: a) Top view of the lattice structure of bilayer graphene. The top layer is black and the bottom layer is grey. The filled circles form the A sublattices and the open circles the B sublattices. b) Side view of the lattice structure of bilayer graphene. With the voltage source we indicate an applied potential difference between the layers of magnitude \( V \). c) The dispersion relation of bilayer graphene calculated for different interlayer potential differences. The dotted line is for \( V = 0 \), the dashed line is for \( V = 0.1\gamma_1 \) and the solid line for \( V = \gamma_1 \). The dispersion relation for monolayer graphene is plotted in light grey for comparison.

Valley degenerate bands \[34\] with:

\[
E_\alpha^2(p) = \frac{\gamma_1^2}{2} + \frac{V^2}{4} + v^2p^2 \pm \sqrt{\frac{\gamma_1^4}{4} + v^2p^2(\gamma_1^2 + V^2)},
\]  

(2.2)

where \( p \) is the magnitude of the momentum near the K-point.

The four bands are plotted in Fig. 2.1: for different values of \( V \). When the on-site energy difference \( V = 0 \) the bands are parabolic and the low energy conduction and valence bands touch at the K-points. When \( V \neq 0 \) a bandgap opens:

\[
E_g = \sqrt{\frac{V^2\gamma_1^2}{(V^2 + \gamma_1^2)}}.
\]  

(2.3)

In this paragraph we discuss the tight binding calculation for bilayer graphene in a more qualitative manner. The A1 and B2 atoms are directly below or on top of another atom. We refer to them as ‘dimer’, because the electronic orbitals are coupled by the interlayer coupling (\( \gamma_1 \)). The atomic orbitals on the dimer sites repel each
Chapter 2. Theoretical background of bilayer graphene confinement devices.

Figure 2.2: a) Side view of the lattice structure of bilayer graphene. We indicated in red and green the B1 and A2 sublattices that form the lower lying energy bands. b) On the left a cut through the low energy band structure of bilayer graphene at \(k_y = 0\). On the right a cut through the valence and conduction band. We indicated the pseudospin texture for \(\vec{k}\) in one of the valleys. In the other valley the texture is opposite. Note that the pseudospin texture is also opposite for electrons and holes. Unlike monolayer graphene where the negative \(k_x\) hole branch and positive \(k_x\) electron branch have the same pseudospin. c) The pseudospin texture for monolayer graphene.

other and form higher lying energy bands. These bands are \(\sim 0.4\) eV (\(\sim \gamma_1 \approx 0.38\) eV [35]) away from 0 energy and can be safely neglected for low energy transport properties. The lower lying energy bands touch at the K-points and are formed by the atomic orbitals on the B1 and A2 sites. Electrons hop from site B1 to A2 via the A1-B2 dimer. Direct tunneling from A2 to B1 is neglected here as the overlap integral \(\gamma_{A2-B1} \equiv \gamma_3\) is very small. [36]

From this point we focus on the low energy electronic band structure in the vicinity of the K and K’ points. In a first approximation the effective Hamiltonian for these bands becomes in the K, K’ valleys [37]:

\[
H_K = \left( \begin{array}{cc}
\frac{1}{2}V & -\frac{\hbar^2}{2m^*}(k_x - ik_y)^2 \\
-\frac{\hbar^2}{2m^*}(k_x + ik_y)^2 & -\frac{1}{2}V
\end{array} \right),
\]

\[
H_{K'} = \left( \begin{array}{cc}
\frac{1}{2}V & -\frac{\hbar^2}{2m^*}(k_x + ik_y)^2 \\
-\frac{\hbar^2}{2m^*}(k_x - ik_y)^2 & -\frac{1}{2}V
\end{array} \right).
\]

This Hamiltonian acts on the spinor \((\psi_{B1}, \psi_{A2})\). The Hamiltonian resembles the Hamiltonian for single layer graphene, but with a quadratic term on the off-diagonal elements. The term \(\frac{\hbar^2}{2m^*}(k_x + ik_y)^2\) describes an effective hopping from B1 to A2 sites. First a hop from B1 to A1 and then a transition via the dimer sites A1-B2 that generates an effective mass \(\sim \gamma_1\), followed by a hop from B2 to A2. The solutions of this Hamiltonian are massive chiral electrons with a parabolic dispersion relation \(E = \pm \hbar^2 k^2/2m^*, m^* = \gamma_1/2v^2\). The density of states is \(m^*/(2\pi\hbar^2)\) per valley and per spin, and the Fermi velocity is \(v_F = \hbar k_F/m^*\). Note that \(v_F\) is dependent on momentum unlike the Fermi velocity \(v\) in monolayer graphene.

The components of the spinor \((\psi_{B1}, \psi_{A2})\) are located on different layers in the bilayer system (see Fig. 2.2a). Hence the pseudospin degree of freedom in bilayer graphene is often referred to as the which-layer degree of freedom. The pseudospin
2.3. Tunable band gap in double gated device

2.3.1 Device working principle

In the previous section we showed that a band gap in bilayer graphene opens when sublattices B1 and A2 are at different potentials. The magnitude of the gap is roughly proportional to the magnitude of the potential difference (equation 2.3). The fact that the B1 and A2 sublattices are in different layers can be exploited to control the potentials by an external electric field perpendicular to the bilayer graphene plane. One way to induce this electric field is to use a gate below the graphene and a gate on top of the graphene: the so-called double gated device geometry. This geometry is illustrated in Fig. 2.3. Note that the gate electrodes can be also replaced by a layer of ionic dopants like potassium ions. In the remaining of this section we will explain
Chapter 2. Theoretical background of bilayer graphene confinement devices.

The physical background of the device concept and discuss from the viewpoint of an experimentalist the deviations from the simple models.

The gates with dielectrics induce displacement fields. For calculating the displacement fields we assume infinite parallel plate capacitors. This assumption is valid under the condition that $d_{BG}, d_{TG} \ll W, L$ where $d_{BG}, d_{TG}$ are the thicknesses of the bottom and top gate dielectric respectively and $W, L$ are the width and length of the capacitor respectively. The displacement field that the backgate induces is $D_{BG}/\epsilon_0 = \epsilon_{r,BG} V_{BG}/d_{BG}$. The displacement field that the top gate induces is $D_{TG}/\epsilon_0 = \epsilon_{r,TG} V_{TG}/d_{TG}$, here we divided out $\epsilon_0$ so that the $D/\epsilon_0$ has units $[V/nm]$.

In Fig. 2.3 we show the definition of the sign of the displacement fields. The difference of the two leads to a net carrier doping of the graphene

$$\sigma_{GR} = -en_{GR} = D_{BG} - D_{TG}, \quad (2.6)$$

where the number density $n_{GR}$ is positive for electrons and negative for holes.

The average of the two displacement fields creates a potential difference between the two sublattices.

$$D_{gates} = (D_{BG} + D_{TG})/2. \quad (2.7)$$

Now we continue to calculate the magnitude of the potential difference as induced by the gates. Here we treat the bilayer system as two parallel plates (perfect conductors) with a dielectric in between with $\epsilon_r = \epsilon_{GR}$. The back gate induces a charge density of $\sigma_1 = -\epsilon_0 D_{BG}$ on the bottom layer and the top gate induces a charge density of $\sigma_2 = \epsilon_0 D_{TG}$ on the top layer (see Fig. 2.3b). Since the magnitude of an electric field above an infinite plane with uniform charge density $\sigma$ is $\sigma/(2\epsilon_0 \epsilon_r)$, the electric field through the bilayer is $E_{GR} = (\sigma_2 - \sigma_1)/(2\epsilon_0 \epsilon_{GR})$, where $\epsilon_{GR}$ is the relative dielectric constant of bilayer graphene. The potential difference between the two layers is $V = E_{GR} c_0$, where $c_0 = 3.35$ Å is the interlayer distance. For low energies ($E \ll \gamma_1$) the magnitude of the gap is:

$$E_g = eV = e c_0 D_{TG} + D_{BG}/2\epsilon_{GR}. \quad (2.8)$$

In reality bilayer graphene is not a perfect conductor so it does not perfectly screen the electric fields of the gates. Hence the real induced gap is smaller. In refs. this effect is calculated self consistently or with density functional theory. In ref. the results of the calculations are checked with optical absorption measurements of the band gap and found to be accurate.

2.3.2 Background charges

In this subsection we elaborate on the influence of background charges on the displacement field applied to the bilayer graphene. We model the background charges as a uniform layer of dopants. In reality these dopants are randomly distributed and hence they also induce potential fluctuations that are better known as electron-hole
2.3. Tunable band gap in double gated device

![Diagram of a double gated bilayer graphene device](image)

**Figure 2.4:** a) Schematic representation of a double gated bilayer graphene device. For simplicity the bottom- and topgate dielectrics with relative dielectric constant $\varepsilon_r$ both have thickness $d$, so that the relative coupling is equal. The displacements fields of the backgate, topgate and graphene are respectively $D_{BG}, D_{TG}$ and $D_{GR}$. The top gate and back gate metals are indicated by the bold lines. $V_{BG}$ is the voltage on the back gate and $V_{TG}$ is the voltage on the top gate. There is a layer of dopants in the dielectric that has a charge per surface area of $\sigma_d$. b-f Schematic depiction of the behaviour of the device in panel a in different doping scenarios. The horizontal axis is the voltage on the topgate, the vertical axis is the voltage on the backgate. The diagonal solid line is drawn where $\sigma_{GR} = 0$, the diagonal dashed line is drawn where $D_{GR} = 0$.

This is a quite detailed discourse as it is of importance for the interpretation of the data in chapters 4 and 8.

Fig. 2.4a shows a schematic representation of a double gated bilayer graphene device. In this case positively charged dopants are present in the topgate dielectric. These positively charged dopants induce a negative charge in the graphene. This charge can be cancelled by a positive charge induced by applying a proportional negative voltage on either of the gates. The charged dopants generate an additional displacement field. The magnitude of the displacement field due to the dopant layer ($D_d$) can be calculated as follows. The dopant layer has positive charge density $\sigma_d$, this induces a charge $-\sigma_d/2$ on the graphene and $-\sigma_d/2$ on one of the gates. The displacement field that the layer induces is $D_d/\varepsilon_0 = \sigma_d/(2\varepsilon_0)$. The equation for the magnitude of the gap now also depends on the amount of dopants in the dielectric:

$$E_g = eV = e\varepsilon_0 \frac{D_{TG} + D_{d,TG} + D_{BG} + D_{d,BG}}{2\varepsilon_{GR}}.$$  \hspace{1cm} (2.9)

Now we define $D_{GR} = D_{TG} + D_{d,TG} + D_{BG} + D_{d,BG}$, where $D_{d,BG}$ and $D_{d,TG}$ are...
the displacement fields due to the dopants in the back gate and top gate respectively. In panel b-f of Fig. 2.4 we show how different arrangements of the dopant layer affect the position of the $\sigma_{GR}=0$ diagonal.

In Fig. 2.4, the situation is displayed for the trivial case of no dopants. The black diagonal line is where $\sigma_{GR} = 0$: $V_{TG} = \alpha V_{BG}$, where $\alpha = C_{BG}/C_{TG}$, where $C_{BG}, C_{TG}$ are the capacitances of the back gate and top gate respectively. At $V_{TG} = V_{BG} = 0$ the displacement field is 0. Along the diagonal $D_{GR}$ increases for $\sigma_{GR} = 0$. A band gap opens and the resistance of the bilayer graphene sheet will increase. Perpendicular to the diagonal, the field stays constant and $\sigma_{GR}$ increases, so the resistance decreases.

In Fig. 2.4c a layer of dopants is present in the dielectric of the back gate. When both top gate and back gate are grounded the graphene is doped with a charge carrier density of $-\sigma_d/2$ and $D_{GR} = \sigma_d/4$. By applying a voltage $-\Delta V_{BG} = \sigma_d/(2C_{BG})$ to the back gate and keeping $V_{TG}$ to 0, the charge carrier density goes to zero and the field induced by the dopants is cancelled so that $D_{GR} = 0$. With voltage $V_{TG} = -\Delta V_{TG} = \sigma_d/(2C_{TG})$ and $V_{BG} = 0$ the displacement field is $D_{GR} = \sigma_d/2$. In Fig. 2.4d the layer of dopants is in the dielectric of the top gate. The situation is now inverted: for $V_{TG} = -\Delta V_{TG}, V_{BG} = 0$ the graphene is charge neutral and no displacement field is present. For $V_{BG} = -\Delta V_{BG}, V_{TG} = 0$ the graphene is neutral, but a displacement field is present. Based on this observation one can tell from the minimum in resistance along the charge neutral diagonal where the excess charged impurities are located in the device. In Fig. 2.4e there are positively charged dopants present above and below the graphene. This shifts the diagonal with a voltage $-\Delta V_{TG}$ to the left and with a voltage $-\Delta V_{BG}$ right, because we need twice the voltage on the gates to make the graphene charge neutral again. Fig. 2.4f is a peculiar case. Here we have exactly the opposite amount of charge in the bottom and top gate dielectric. With no voltage on the gates, the graphene is neutral, but an electric field is present. Only applying a voltage $\Delta V_{BG}$ to the bottom gate and $\Delta V_{TG}$ to the top gate cancels the displacement field.

When the top gate metal is narrow and thus not coupling to the entire graphene flake, a horizontal band of large resistance occurs in a 2D-plot due to the areas of graphene that are not covered by the top gate. The position of this band in $V_{BG}$ is dependent on the amount and position of dopants. In Fig. 2.4e this band will occur at $V_{BG} = (D_{d,BG} + D_{d,TG})/C_{BG}$. If the graphene flake is only covered with top gate dielectric underneath the top gate metal such as our devices in chapter 4 $D_{d,TG}$ is obviously zero in that region.

In chapters 4, 7 and 8 we make use of the device structure described in this section. In those chapters we also elaborate on the insulating state the gap induces and how this insulating state was used to confine charge carriers in quantum point contacts and dots. In the section 3.2 we explain the theoretical background of the use of the band gap for electrostatic confinement in bilayer graphene. Moreover we elaborate on our considerations about constructing the devices.

### 2.4 Quantized conductance

In 1988 Van Wees et al. and Wharam et al. reported the first measurements of conductance through a quantum point contact.\cite{VanWees1988,Wharam1988} Surprisingly, they discovered
2.4. Quantized conductance

this conductance was quantized in steps of $\frac{2e^2}{h}$. The origin of quantized conductance is that transport is limited to a narrow 1D constriction with a width comparable to the Fermi wavelength ($\lambda_F$). In this constriction the charge carriers are confined in the lateral direction leading to a set of discrete wave vectors.

We explain quantized conductance in terms of an ideal quasi-one-dimensional conductor (see Fig. 2.5a). This quasi-one-dimensional conductor behaves as an electron waveguide of width $W$ that connects two reservoirs at potential $E_F$ and $E_F + \delta \mu$ (see Fig. 2.5). The net current is injected in a small energy window $\delta \mu$ above $E_F$ into $N$ one-dimensional subbands that can propagate at these energies. For such a one-dimensional conductor it is thought that all inelastic scattering takes place in the reservoirs following Landauer’s principle that conductance is transmission. The dispersion relation of the one-dimensional subbands is:

$$E_n(k_x, k_y, n) = E_n(k_y, n) + \frac{\hbar^2 k_x^2}{2m^*},$$

where $E_n(k_x, k_y, n)$ is the energy of the $n^{th}$ subband.

The total number of occupied subbands is $N$ such that $E_N < E_F$. The current per unit energy interval injected into one subband is the product of group velocity $v_n = \frac{1}{\hbar} dE_n(k)/dk$ and one-dimensional density of states $\rho_n = g(\frac{2}{\pi} dE_n(k)/dk)^{-1}$, where $g$ is the degeneracy of the system:

$$I_n = \int_{E_F}^{E_F + \delta \mu} e v_n \rho_n dE = \frac{ge}{\hbar} \delta \mu.$$  

(2.11)

The current is thus independent of energy and subband number. It follows that the current is equally distributed over all subbands. This is the basis of conductance.
Chapter 2. Theoretical background of bilayer graphene confinement devices.

quantization. The total current is now

\[ I = \sum_{n=1}^{N} I_n = N \frac{2e}{h} \delta \mu = N \frac{ge^2}{h} V_{bias}. \] (2.12)

It follows that the conductance of the quasi-one-dimensional channel is

\[ G = \frac{I}{V_{bias}} = N \frac{ge^2}{h}. \] (2.13)

In Fig. 2.5b we visualize quantized conductance in k-space. The allowed wave vectors in the Fermi disc are indicated by the horizontal lines. The circle indicates the position of \( k_F \). The current is carried by the states in the grey shell. We took a square well lateral confining potential in this illustration. The one-dimensional subbands correspond to pairs of lines with \( k_{y,n} = \pm n\pi/W \) where \( n \in \{1, 2, 3, 4, \ldots\} \). The square well is a simple approximation of the lateral confinement potential. In reality it is better described by a harmonic potential. In this thesis we still use the square well description as it simplifies calculations and provides reasonable accuracy.

### 2.5 Quantum Hall effect in bilayer graphene

The motion of an electron in a large magnetic field becomes circular due to the Lorentz force acting on the particle. The radius of the orbit is the cyclotron radius \( r_c = \frac{\hbar k_F}{eB} \). When the sample size is larger than the cyclotron motion \( (W > r_c) \), electrons can traverse full circles in the sample. In this regime the coupling of the magnetic field to the electrons yields interesting quantum effects. In this section we will study the effect of the magnetic field. Especially how the quantization of the areal size of the electron orbits leads to the formation of so-called Landau-levels and the quantum Hall effect.

A magnetic field modifies the canonical momentum \( \vec{p} \) via the vector potential \( \vec{A} \) defining the magnetic field as \( \vec{B} = \nabla \times \vec{A} \):

\[ \vec{p} = m \vec{v}. \] (2.14)

We can write for the Hamiltonian in a two-dimensional system:

\[ H = \frac{(\hat{P} + e\vec{A})^2}{2m} + e\vec{A} + U(x, y), \] (2.15)

where \( \hat{P} \) is the momentum operator and \( U(x, y) \) is the potential in which the electrons move.

First we assume an infinite, unbounded two-dimensional system so that \( U(x, y) = 0 \). The Schrödinger equation gives the following eigenvalues for the energy of the electrons:

\[ E_n = (n + \frac{1}{2})\hbar \omega_c, \] (2.16)
2.5. Quantum Hall effect in bilayer graphene

where \( n \in \{0, 1, 2, 3, 4, \ldots \} \) and \( \omega_c \) is the cyclotron frequency due to the classical Lorentz force acting on the electrons, \( \omega_c = eB/m^* \).

\( n \) labels the different levels of the system. These levels are called Landau-levels. Put in words, the result of a perpendicular magnetic field is that the uniform density of states transforms into a discrete density of states. These discrete states, the Landau-levels, are consequently highly degenerate.

Now we impose boundaries to the system: \( U(x, y) \) has a finite value throughout the system and is not constant at the edges. For the energy of an individual state we can write:

\[
E_n = (n + \frac{1}{2})\hbar\omega_c + U(y) + \frac{\hbar^2k_x^2}{2m^*}.
\] (2.17)

This equation is illustrated in Fig. 2.6a. The fat line is the potential energy \( U(y) \). The thin lines are the equally spaced Landau-levels. At the edges their energies bend upwards. The electrochemical potential of the system lies in between the 1\textsuperscript{st} and 2\textsuperscript{nd} Landau-level. The two Landau-levels that are below \( \mu \) in the bulk cross \( \mu \) at the edges of the samples. Only at this spatial position free states are available: edge channels form. These edge channels have the same one-dimensional nature as the channels in a QPC. Consequently the two-terminal conductance of the system is also described by equation 2.13. Now \( N \) is given by \( n \) of the highest occupied Landau level. In a Hall-bar geometry these edge channels lead to an exactly quantized Hall conductance \( (G = Ng^2/2e^2 \), where \( g \) is the degeneracy factor) that was first observed in 1980 by K. von Klitzing et al. \cite{47}. This effect is known as the integer quantum Hall effect (IQHE).

The Landau levels in bilayer graphene are different than in a conventional two-dimensional electron system (2DES). The electrons in bilayer graphene are chiral. In section 2.2 and Fig. 2.2 we explain how this chirality gives a Berry’s phase of \( 2\pi \). This changes equation 2.16 into the following expression for the energy of the quasiparticles.

Figure 2.6: a) Electron states in a two-dimensional electron system (2DES) channel subjected to a perpendicular magnetic field. b) Schematic drawing of a top view of the 2DES channel in real space. There are 2 Landau levels below the electrochemical potential and hence two modes are available for transport. Panel a is the energy representation along the dashed line.
in bilayer graphene \[36]\: 

\[ E_n = \pm \hbar \omega_c \sqrt{n(n-1)}. \] (2.18)

The consequence is that for \( n = 0,1 \) states with \( E_n = 0 \) occur.\[16\] Moreover the degeneracy of this zero energy Landau-level is twice as high as the other levels. When a perpendicular electric field is applied to the system, a band gap opens and the zero energy Landau-level splits in two. Here we would like to note that energy of the Landau levels in bilayer graphene depends linearly on magnetic field, just as in conventional 2DEGs. This is in contrast to monolayer graphene where the energy has a square root dependence on magnetic field.\[33\]

### 2.6 Quantum dots

#### 2.6.1 The constant interaction model of a single quantum dot

In figure Fig. 2.7 a quantum dot is schematically depicted. The disc shaped island in the middle represents the quantum dot. It is connected via tunnel barriers to the source and drain electrodes. The source and drain are reservoirs and are filled up to the electrochemical potentials \( \mu_s \) and \( \mu_d \). The dot is capacitively coupled to a plunger gate (PG) and a backgate (BG). By varying \( V_{PG} \) or \( V_{BG} \) the number of electrons in the dot can be changed. Adding one electron to the dot costs energy, the electrochemical potential:

\[ \mu(N) = U(N) - U(N - 1), \] (2.19)

where \( U(N) \) is the total energy of the dot with \( N \) electrons in the ground state. \( U(N) \) can be calculated using the constant interaction model which is based on two assumptions.\[48\] First, the Coulomb interactions among electrons in the dot and
between electrons in the dot and the environment are described by a constant capacitance, \( C_\Sigma \), independent of the number of electrons in the dot. The capacitance, \( C_\Sigma \), is the sum of all the capacitances:

\[
C_\Sigma = C_S + C_D + C_{BG} + C_{TG} + C_{PG} + C_{SC},
\]

(2.20)

where \( C_S \) and \( C_D \) are respectively the capacitances of the source and drain electrode to the island. \( C_{BG}, C_{TG} \) and \( C_{PG} \) are respectively the capacitances of the back gate, top gate and plunger gate to the island and \( C_{SC} \) is the self capacitance of a circular disk:

\[
C_{SC} = 4 \epsilon_r \epsilon_0 D,
\]

(2.21)

where \( \epsilon_0 = 8.854 \cdot 10^{-12} \text{ F/m} \), \( \epsilon_r \) the dielectric constant and \( D \) the diameter of the dot.

The second assumption is that the single-particle energy level spacing is independent of the number of particles in the dot.

With these two assumptions the equation for \( U(N) \) is given by:

\[
U(N) = \left( -e(N - N_0) + C_S V_S + C_D V_D + C_{BG} V_{BG} + C_{TG} V_{TG} + C_{PG} V_{PG} \right)^2 + \frac{N}{2 C_\Sigma} \sum_{n=1}^{N} E_n,
\]

(2.22)

where \( e \) is the electron charge, \( eN_0 \) is the charge in the dot at zero gate voltage and \( E_n \) is the energy of the single particle levels. The electrochemical potential of the dot now becomes:

\[
\mu(N) = U(N) - U(N - 1)
\]

(2.23)

\[
= 2E_C(N - N_0 - \frac{1}{2}) - \frac{2E_C}{e} (C_S V_S + C_D V_D + C_{BG} V_{BG} + C_{TG} V_{TG} + C_{PG} V_{PG}) + E_N,
\]

where \( E_C = \frac{e^2}{2C_\Sigma} \) is the charging energy of the dot. The electrochemical potentials for different \( N \) form a ladder as shown in the schematics in figure 2.8. The absolute position in energy depends linearly on the gate voltages. This dependence is the same for different \( N \), thus by varying the gate voltages the whole ladder of electrochemical potentials can move up or down while the distance between the levels remains constant. The spacing between successive electrochemical potentials is the addition energy, the energy needed to add one electron to the dot:

\[
E_{add} = \mu(N + 1) - \mu(N) = 2E_C + \Delta E.
\]

(2.24)

The addition energy consist of two contributions. First the charging energy \( (E_C) \) which is purely electrostatic and second the energy spacing between two quantum levels \( \Delta E \) due to confinement.

From here we will discuss electronic transport through the dot. This is a useful tool to map out different properties of the dot such as the different capacitances and the single particle energy level spacing.
Chapter 2. Theoretical background of bilayer graphene confinement devices.

Figure 2.8: Schematic diagrams (horizontal axis is the position x and vertical axis is the energy) of the electrochemical potentials of the quantum dot for different gate voltages and bias voltages. 

a) $\mu_s \leq \mu(N) \leq \mu_d$, so the number of electrons fluctuates between $N$ and $N-1$.

b) No allowed electrochemical potential is inside the bias window, so the system is in Coulomb blockade, transport is blocked.

c) The bias window is opened so far that electrons can be transported via two electrochemical potentials. The number of electrons fluctuates between $N-1$ and $N+1$.

d) In the previous panels we neglected excited states. In this diagram we show the energy of the first excited state depicted by the grey line. Transport can now take place via two channels. The number of electrons on the dot still fluctuates between $N$ and $N-1$ because of Coulomb blockade.

2.6.2 Low bias regime

Electron transport through the dot is only possible when an electrochemical potential in the dot is within the bias window: $\mu_s \leq \mu(N) \leq \mu_d$ (Fig. 2.8a). The bias window is opened by creating an imbalance between source and drain with a bias voltage: $V_{bias} = \mu_s - \mu_d$. When there is no electrochemical potential of the dot inside the bias window the number of carriers is fixed and no current flows through the dot (Fig. 2.8b). This regime is called Coulomb blockade. Bringing the dot consecutively in and out of the Coulomb blockade regime with the gate, will give a data set like Fig. 2.9b. When the level spacing $\Delta E$ is small in comparison to $E_C \Delta V_{gate} = e/C_{gate}$, the peak spacing $\Delta V_{gate} = E_{add}/\alpha$ where $\alpha = C_{gate}/C_{\Sigma}$.

2.6.3 High bias regime and excited states

Coulomb blockade can not only be lifted by applying a gate voltage, but also by increasing the source drain bias. In Fig. 2.8 the bias is increased so that two electrochemical potentials are in the bias window. The $V_{bias}$ for which this situation occurs is exactly $E_{add}$ of the dot. When plotting the current versus $V_{bias}$ and the $V_{gate}$, the nonconducting areas form diamonds. These diamonds are called Coulomb diamonds and are shown in Fig. 2.9b. Many properties of the quantum dot can be extracted from the Coulomb diamonds. The height of the diamonds is the addition energy, $E_{add} = \frac{e^2}{C_{\Sigma}}$ (when $\Delta E = 0$). When $\Delta E > k_BT_e$ ($T_e$ is the temperature of the electrons in the dot) lines of enhanced current will appear parallel to the edges of the diamonds. This is transport through excited states (Fig. 2.8d). Also the ratio
between the sum capacitance and the gate capacitances can be calculated:

\[
\frac{C_{\Sigma}}{C_G} = \frac{1}{\alpha} = \frac{1}{\beta} + \frac{1}{\gamma},
\]

(2.25)

where \( \beta \) and \( \gamma \) are the slopes of the left respectively right side of the diamond. Moreover, from these slopes the source and drain capacitances can be calculated, once the gate capacitances are known. For the upper left edge of the diamond \( \mu(N) = \mu_s \) holds, which leads to the following expression for \( \beta \) and the drain capacitance:

\[
\beta = \frac{C_G}{(C_G + C_D)},
\]

\[
C_D = \frac{C_G}{\beta} - C_G.
\]

(2.26)

From the other slope, where \( \mu(N) = \mu_d = 0 \), the source capacitance can be calculated using:

\[
\gamma = \frac{C_G}{C_S},
\]

\[
C_S = \frac{C_G}{\gamma}.
\]

(2.27)

Summarizing this section, it costs electrostatic energy to add an extra electron to an isolated system. This leads to the observation of Coulomb blockade. When the system is small enough confinement will create discrete quantum levels. Bias and gate spectroscopy are very valuable tools to extract relevant parameters about the system.

### 2.7 Hexagonal Boron Nitride

hBN has a layered structure like graphite as is shown in Fig. 2.10. A monolayer hBN has a hexagonal lattice structure with a lattice mismatch relative to graphene.
Chapter 2. Theoretical background of bilayer graphene confinement devices.

Figure 2.10: a) Top view of the lattice structure of hBN. The lattice constant $a$ is indicated. b) Side view of the lattice structure of hBN. The interlayer spacing $c_0$ is indicated.

of only 1.7 %.[12] The carbon atoms in one sublattice are replaced by boron and in the other sublattice by nitrogen. The stacking order is not Bernal as in graphite but eclipsed: the boron atoms in one layer are on top of the nitrogen atoms in the other layer. The different on-site energies of the boron and nitrogen atoms puts the different sublattices at a different potential and a large band gap (5.97 eV) opens.[50] This large band gap makes hBN an excellent insulating layer so it is suitable as a gate dielectric. The relative dielectric constant of hBN is found to be $\epsilon_r = 3.0 - 3.9$ (see chapters 5 and 8).

The layered structure gives hBN an atomically flat surface. Any corrugation induced carrier density fluctuations will be absent. Most importantly due to the strong ionic in-plane bonding the hBN is relatively inert and free of surface charge traps and dangling bonds.[12] This is the main cause for the immensely improved electronic quality of graphene on hBN.

hBN can be obtained by mechanical exfoliation as we explain in chapter 3.[51] Note that by selecting flakes based on height measurements, the thickness of dielectrics can be tuned with a precision of 0.33 nm, the mono-atomic layer thickness of hBN. Efforts in growing large-area hBN crystals by chemical vapor deposition (CVD) are increasing.[52, 53] Recently groups reported on growing lateral graphene-hBN heterostructures.[54, 55]
CHAPTER 3

Device fabrication and measurement setup


3.1 Introduction

In the first section of this chapter we discuss the device design of bilayer graphene electrostatic confinement devices. In the other sections of this chapter we will review the techniques we used to fabricate double gated graphene devices. In the last paragraph we shortly describe the measurement setup we used. We structured the chapter around the dry transfer method that we adapted from ref. [12]. We used this method to fabricate double gated bilayer graphene devices with the graphene sandwiched in hexagonal boron nitride (hBN) to enhance the electronic quality. The general procedure for making a graphene on hBN device is as follows:

1. Make and identify bilayer graphene (BLG) and hBN flakes
2. Transfer the BLG on top of an hBN flake
3. Remove residues by annealing at at 400 °C
4. Pattern contacts with electron beam lithography (EBL) and etch BLG into a channel
5. Remove residues by thermal annealing and/or mechanical cleaning
6. Transfer top hBN flake
7. Pattern top gates with EBL

For a detailed step-by-step guide to make hBN/bilayer graphene sandwiches we refer to appendix A.
Chapter 3. Device fabrication and measurement setup

Figure 3.1: a) Top view of the design of a QPC top gate structure. The width is chosen to be 1 μm to avoid parallel conduction. \[ \text{b) Top view of the design of a QD top gate structure where } L \text{ is the diameter of the dot. The dot in the graphene will extend underneath the top gates (see chapter 4).} \text{c) Three dimensional depiction of the full double gated bilayer graphene QD device. In chapter 7, Fig. 7.1 we elaborate on the elements in this device image.}

3.2 Electrostatic confinement in bilayer graphene: devices and electronic quality

In this thesis we aim to confine charge carriers in graphene with electrostatics. In section 2.3 we describe the double gated bilayer graphene device we will use to implement electrostatic confinement. By patterning the top gates we tailor the insulating state to only exist in certain parts of the bilayer graphene. In Fig. 3.1 we show the top gate patterns for a quantum point contact (QPC) and quantum dot (QD).

3.2.1 Quantum point contact

First we consider the case of a quantum point contact as shown in Fig. 3.1a. With this QPC we intend to measure quantized conductance (see 2.4). In this device the top gate consists of two split gates. The regions in the bilayer graphene below the split gates can be depleted. Now a narrow conduction channel is formed that can host transverse standing waves of electrons or holes that form discrete modes. In Fig. 3.1 we show a schematic drawing of the device structure.

The first requirement for observing quantized conductance is that the Fermi wavelength ($\lambda_F$) should be in the order of the channel width. The Fermi wavelength for bilayer graphene is given by:

$$\lambda_F = \frac{2\pi}{\sqrt{\pi n}}. \hspace{1cm} (3.1)$$

For a typical carrier density of $10^{12}$ cm$^{-2}$, $\lambda_F \sim 35$ nm.

The second requirement for observing quantized conductance is that the mean free path ($\lambda_{mfp}$) of the charge carriers is larger than the length of the narrow channel. The mean free path is dependent on carrier density and mobility as follows, valid for
the regime $\lambda_{mfp}k_F \ll 1$

$$\lambda_{mfp} = \frac{\hbar\mu}{e}\sqrt{n},$$  \hspace{1cm} (3.2)

where $\mu$ is the drift mobility that relates the drift velocity of carriers to the electric field ($v_d = \mu E$). For a mobility of $10,000 \text{ cm}^2/\text{Vs}$ and a carrier density of $10^{12} \text{ cm}^{-2}$, $\lambda_{mfp} \sim 100 \text{ nm}$. Based on these numbers for $\lambda_{mfp}$ and $\lambda_F$ we chose in the device designs for a separation of $\sim 50 \text{ nm}$ between the gate’s apexes (see chapters 4 and 7).

### 3.2.2 Quantum dots

The second device design that we consider is a quantum dot as shown in Fig. 3.1b. The purpose of this device is to confine electrons/holes to a zero-dimensional state. In essence we create a small island in the bilayer graphene that is coupled to bilayer graphene reservoirs by two tunnel barriers. These tunnel barriers are formed at the apexes of TG1 with TG2 and TG3 (see Fig. 3.1b, essentially two split-gate geometries in series). To make sure that the channels below the split gates can be pinched off, we placed the apexes closer together than in the QPC design ($\sim 30 \text{ nm}$). With the gate labeled PG we intend to sweep the levels in the dot without changing the barriers too much.

To observe the quantum mechanically confined states in the dot we need to make the dot small enough so that the charging energy $E_C$ and the level spacing $\Delta E$ are larger than the thermal energy of the electrons: $E_C, \Delta E \gg k_b T_e$. $T_e$ is the temperature of the electrons. This temperature is measured to be not larger than 83 mK in chapter 7 which leads to a thermal energy of 7 $\mu$eV. The level spacing of a circular QD can be estimated by

$$\Delta E = \frac{\hbar^2\pi}{m^*L^2},$$  \hspace{1cm} (3.3)

where $L$ is the diameter of the dot.

A level spacing of 100 $\mu$eV ($\sim 10 \cdot k_b T_e$) corresponds to a dot diameter of approximately $\sim 200 \text{ nm}$. The level spacing is relatively large because of the low effective mass of carriers in bilayer graphene. When the charging energy also needs to be resolved, $C_{\Sigma}$ cannot be larger than $\sim 0.8 \text{ pF}$. In reality our dots are slightly larger than 200 nm (see chapter 7).

For a quantum dot device the requirement on the electronic quality is as follows: the carrier density should be approximately uniform over the quantum dot region. In other words the electron-hole (e-h) puddles should be minimized. The result of too much carrier density fluctuates is that the dot falls apart in multiple dots. The requirement on the charge density fluctuations is quantified by the charge density inhomogeneity $\Delta n_{\text{imp}}$ and the correlation length of these fluctuations.

### 3.2.3 Electronic quality

In the previous sections we discussed the requirements for electronic quality for QPC’s (long $\lambda_{mfp}$) and QD’s (low $\Delta n_{\text{imp}}$). The microscopic origin of $\Delta n_{\text{imp}}$ is mostly
charged impurities in the substrate.\textsuperscript{57, 58} Corrugations of the graphene due to for example substrate roughness do not have a direct influence on $\Delta n_{\text{imp}}$.\textsuperscript{57} The charged impurities not only introduce residual doping, but also act as long range scatterers. The dominant scattering mechanism in graphene is still debated, but charged impurity scattering is believed to be an important scattering mechanism.\textsuperscript{10} Thus reducing the amount of charged impurities around the graphene will bring us closer to meeting the electronic quality requirements of both the quantum dot and the quantum point contact.

For our SiO$_x$ samples the charge density inhomogeneity was in the order of $10^{12}$ cm$^{-2}$ (see chapter \textsuperscript{3}). In graphene on a SiO$_x$ substrate without a SiO$_x$ top gate dielectric these fluctuations can be reduced by an order of magnitude.\textsuperscript{59} For bilayer graphene the correlation length of electron hole puddles on SiO$_x$ is 10-20 nm.\textsuperscript{41, 60, 59} The typical mobility for topgated devices on SiO$_x$ is 2000 cm$^2$V$^{-1}$s$^{-1}$. This leads to a mean free path of $\sim$ 20 nm.

Both $\lambda_{mfp}$ and $n_{\text{imp}}$ do not meet our requirements for graphene on SiO$_x$, so we need to find another device platform. Suspended graphene has a longer $\lambda_{mfp}$ and a lower $\Delta n_{\text{dis}}$.\textsuperscript{11} However, it is highly desirable to develop substrate supported devices. These devices allow for more design flexibility and easier integration. Hexagonal boron nitride (hBN) is the almost ideal substrate for QPC’s and QD’s in bilayer graphene (see section \textsuperscript{2.7}).\textsuperscript{12} The mobility of bilayer graphene on hBN is in the order of several tens thousands cm$^2$V$^{-1}$s$^{-1}$\textsuperscript{12} and the carrier density fluctuations of single layer graphene on hBN go down to $2.5 \cdot 10^{11}$ cm$^{-2}$\textsuperscript{61}. Entire encapsulation of the graphene in hBN is most desirable. This will protect the graphene from any detrimental environmental influences.

Summarizing, QPC’s and QD’s should have device dimensions as described in Fig. 3.1. The bilayer graphene needs to be encapsulated in hBN flakes to ensure large enough electronic quality. In the next section we start describing the fabrication of these devices by explaining mechanical exfoliation of bilayer graphene and hBN.

### 3.3 Make and identify flakes

#### 3.3.1 Bilayer graphene

For our devices we used mechanically exfoliated graphene. The source materials were natural graphite and KISH graphite. For most devices we used blue tape for mechanical exfoliation (NITTO DENKO SPV 224P). We start deposition by sticking a relatively large piece of graphite on the tape ($\sim$ 0.5 cm in diameter). Then we fold the tape and stick it together, followed by slowly tearing the tape apart. We repeat this stick-and-tear process on different areas of the tape and thereby we spread the graphite over its surface. We continue till the piece of tape is covered with graphite. Too many of these stick-and-tear steps results in small graphite pieces. This lowers the chance of creating large graphene flakes. Then we stick the tape to the target substrate, rub it with a light plastic object and tear the tape off the substrate. This will leave graphene and graphite crystals on the surface of the target substrate.

Graphene absorbs only 2 % of the light. The human eye could see graphene against a light background. Unfortunately the visibility is just at the limit of our
3.3. Make and identify flakes

![Diagram showing theoretical calculation of contrast values for different graphene layers.](image)

**Figure 3.2:** a) Theoretical calculation of the contrast values for green light ($\lambda = 550$ nm) for single layer graphene (blue), bilayer (green) and trilayer (black) as a function of the thickness of the PMMA layer. In the inset we show a schematic of the model we used for the calculation. The calculation was performed with the following parameters: $n_{Si} = 4.08 + 0.041i$, $d_{Si} = \infty$; $n_{AQS} = 1.58 + 1.83i$, measured with the ellipsometer, $d_{AQS} = 50$ nm; $n_{PMMA} = 1.59$; $n_{gr} = 2.7 + 1.4i$, $d_{gr} = n \cdot 0.34$ nm with $n$ the number of layers. b) Optical microscope image of a Si/Aquasave/PMMA substrate with graphene flakes at 5x magnification. The location of the graphene flakes is indicated with the box, the graphene flakes are not visible as they are too small. The yellow flakes are thicker graphite flakes. The green/yellow feature is a spincoating ‘comet’ caused by an impurity on the substrate. c) 50x magnification. Flake 1 (has also a small monolayer part) and 2 are bilayer graphene, the contrast is 9%. Flake 3 is monolayer graphene, the contrast is 5%. These contrasts are lower than in the theoretical calculation. The calculation assumed one wavelength, the RGB green channel value is an integration over many wavelengths.
capabilities. To render the graphene more visible, we use substrates covered with a thin film of a specific thickness. The optical path in a part that is not covered with graphene is different from the optical path in a part of the wafer that is covered with graphene. This results in a contrast that can be optimized by tuning the thickness of the substrate. For conventional graphene on SiO$_x$ devices we used purple colored 285 nm oxide wafers. The graphene flakes are visible as dark purple colored patches. The optical contrast of graphene $C$ now increases to about 5 %. We measure the contrast of a flake by taking an image with the microscope CCD-camera and loading the image in Adobe Photoshop. We read out the green channel value of the RGB-color space in the area with the flake ($I_{grn,flake}$) and in the area around the flake ($I_{grn,background}$). The contrast $C$ is then defined as:

$$C = \frac{I_{grn,background}}{I_{grn,flake}} - 1. \tag{3.4}$$

The graphene intended for transfers we deposit on a polymer stack of ±50 nm Aquasave (AQS) and ±390 nm polymethylmethacrylate (PMMA, 950k a6, Microchem Corporation) on top of a bare silicon wafer. The AQS layer is a sacrificial layer used to separate the PMMA from the Si substrate, it can be replaced with any water soluble polymer. By using a Fresnel solver we calculated which thickness of PMMA gives the optimal contrast (Fig. 3.2a). Then we tuned by trial and error the thickness of the PMMA to get the same purple color as the SiO$_x$. The contrast for graphene on these substrates is roughly the same as for graphene on the SiO$_x$ substrates. This approach can be used to engineer the thickness of any thin film dielectric substrate for maximizing the contrast of graphene.

On substrates with enhanced contrast it is easy to identify flakes that are only a few $\mu$m$^2$ large with an optical microscope. A student can learn to identify graphene flakes already after half an hour of practice. For our devices we need bilayer graphene. Bilayer graphene absorbs twice as much light as single layer graphene so it can be easily distinguished when a monolayer graphene flake is present next to the bilayer as reference. Often there is no reference in the microscope’s field-of-view and thus we make ourselves a reference system. We read out the contrast of each flake that looks like a mono- bi- or trilayer. For each substrate we plot this contrast in a histogram and we find three peaks with quite some spread for for mono- bi- and trilayer. As the number of flakes is usually below 20 and the contrast values have a large spread statistics is not very reliable. It is not possible to do statistics over multiple substrates as the contrast varies from substrate to substrate from 3-7 % for monolayer graphene, 8-14 % for bilayer and 13 to 22 % for trilayer. These variations are largest for the substrates with a polymer coating. Spincoating never gives large-area thickness uniformity. Moreover spincoating in different conditions yields different layer thicknesses. The settings of the microscope-camera, the intensity of the lamp and the magnification also play a role in the contrast value. It is important to control these parameters. After contrast-based identification of bilayer graphene flakes we always use Raman-spectroscopy as an independent method to distinguish bilayers from monolayers and trilayers (see section 3.4).

---

1 Aquasave is sulfonated polyaniline varnish, produced by Mitsubishi Rayon Co., Ltd.
3.3. Make and identify flakes

3.3.2 Hexagonal boron nitride

Hexagonal boron nitride (hBN) was obtained by mechanical exfoliation of small crystals made in the group of prof. K. Watanabe.\textsuperscript{[64]} We need the hBN flakes both below the bilayer graphene and on top. Hence we need to deposit crystals on SiO\textsubscript{x} coated substrates, but also on substrates with the polymer stack to facilitate transferring the flakes. hBN is a dielectric with a band gap of 5.8 eV\textsuperscript{[50]} so it does not absorb visible light. However, interference of different light paths in the stack leads to different colors for different hBN thicknesses. Few layer hBN is purple, just a bit darker than the substrate, around 10 nm the flakes turn dark blue, around 50 nm light blue and then around 70 nm yellow. This data is obtained by matching microscope images to atomic force microscope (AFM) height images.

There are two requirements for the thickness of the bottom hBN flakes. They should be $>\sim 10$ nm to smoothen out the roughness of the underlying SiO\textsubscript{x} and keep the graphene flake far away from charged impurities. They should be $<\sim 70$ nm to ensure the metal film for contact and gate leads can be continuous across the edge of the hBN flake and make proper electrical contact. For the top gate hBN flake the thickness is determined by the gate pattern. There should be a $\sim 1 : 1$ ratio between the smallest distance between two gates and the thickness of the hBN to ensure that the potential variations induced by the gate occur on a similar length scale as the lateral gate dimensions. In Fig. 3.3a we show an optical microscope image of a blue hBN flake with a thickness of 52 nm. The size of hBN flakes with a suitable thickness ranges from $10 \times 10 \mu$m\textsuperscript{2} to $50 \times 50 \mu$m\textsuperscript{2}.

After mechanical exfoliation hBN flakes are generally not clean. A typical surface is displayed in Fig. 3.3b and a zoom of that surface in Fig. 3.3c. The same observation is made in ref. \textsuperscript{[65]}. Annealing the hBN flakes at 500 °C in Ar:H\textsubscript{2} environment removes the residues, although some flakes remain contaminated. An image after annealing is...
shown in Fig. 3.3d. From experience we know that the flakes with uniform thickness and regular edges have cleaner and smoother surfaces (no folds or terraces). Ref. [65] claims that annealing at 500 °C in Ar:O$_2$ gas environment removes all organic contaminants and leaves the hBN flakes unaffected.

The origin of the residues is unclear. We think that they might be tape residues, but we cannot rule out that the hBN crystals are not as clean as we expected. Ref. [64] reports on carbon atom impurity levels of $10^{18}$ cm$^{-3}$ in the as-grown hBN crystals. That means for a typical flake of $10 \times 10 \mu$m$^2 \times 10$ nm ~ $10^{-6}$ impurity carbon atoms. If the impurities are all located at one surface we think this amount is substantial and detectable.

For PMMA substrates annealing at 500 °C is not an option. Another method to remove the residues is mechanical cleaning (see chapter 5). However, mechanical cleaning is time consuming for surfaces larger than 10 µm$^2$. These two reasons motivated us to adopt a new method to deposit the hBN flakes that reduces residues drastically. We do not use NITTO tape for exfoliation and replace it with two polydimethylsiloxane (PDMS) stamps. PDMS is a viscoelastic material. It behaves as a viscous substance when pressure is applied slowly. Thus PDMS conforms to any substrate irregularity (hBN flake) and sticks to that surface. When pressure is applied instantly PDMS behaves as an elastic solid. After we deposited the hBN flake we remove the stamp quickly from the surface. The top of the hBN crystal sticks well to the PDMS, the bottom sticks to the substrate and the crystal cleaves at a plane in between.

### 3.4 Raman spectroscopy

Raman spectroscopy is a very powerful tool to characterize graphene. [66, 67] Graphene has three characteristic peaks in its Raman spectrum: a D-peak ($\sim 1350$ cm$^{-1}$ at $\lambda = 514$ nm), G-peak ($\sim 1582$ cm$^{-1}$) and 2D-peak ($\sim 2700$ cm$^{-1}$). These peaks correspond to different vibrational modes of the graphene lattice. [66] From the position of the G-peak doping and strain levels in graphene sheets can be extracted. [68, 69] The presence of a D-peak reveals missing carbon atoms in the lattice: it gives information about lattice defects and edges. While fabricating devices we use Raman to distinguish bilayer from single layer and trilayer graphene.

The 2D-peak in bilayer graphene consists of four Lorentzians with different amplitude. This gives rise to a broad peak with a characteristic shoulder as can be seen in Fig. 3.4a. In monolayer graphene the 2D-peak is a narrow, single Lorentzian peak. In trilayer it is a broad peak (6 Lorentzians are needed to fit) without the characteristic shoulder.

The substrate influences the intensities of the different Raman peaks. In Fig. 3.4b we show spectra of bilayer graphene on SiO$_x$ and hBN (same flake). The intensity of the G-peak ($I_G$) and 2D-peak ($I_{2D}$) is very different for the two substrates. In Fig. 3.4c we show a spectrum of a different bilayer graphene flake on hBN obtained with a larger laser power to prove that the graphene is still totally intact. The 2D-peak has a pronounced shoulder and there is no D-peak present.
3.5 Dry transfer method

The substrate has a huge impact on the electronic quality of graphene. Bilayer graphene on SiO$_x$ devices exhibit mobility of typically $\sim 2000$ cm$^2$V$^{-1}$s$^{-1}$ and sometimes has large residual doping. Removing the SiO$_x$ from underneath the graphene makes the graphene free standing and greatly increases its mobility after current annealing. For stability and fabrication flexibility it is preferable to make graphene devices on a substrate. hBN substrates are atomically flat and do not contain charged impurities. In ref. high mobility in graphene on hBN substrates is reported. A crucial breakthrough in this paper is the development of a special method to transfer the graphene from one substrate to an exact location on another substrate (in this case an hBN flake). In this method extreme care is taken to reduce water residues and is thus named ‘dry transfer method’. We adapted the dry transfer method in Delft to our needs.

The Delft dry transfer method consists mainly of four steps as illustrated in Fig. In step A we take the Si/AQS/PMMA chip with graphene (see subsection) and glue a Lexan frame with double sided tape on the chip. This frame serves as a support for the PMMA film and as a flotation device. Step B is to float the Lexan frame with attached substrate in DI water. The sacrificial AQS layer dissolves and the PMMA separates from the silicon chip which sinks to the bottom. The graphene is on top of the PMMA so it will never be in contact with water. In step C we take a glass slide with a hole that contains a conical metal piece and mount it to a micromanipulator that enables precise xyz-movement (Fig. The metal piece has a hole all the way through to make it possible to see the graphene and substrate with target hBN flakes (the PMMA film is transparent). By looking through the hole with the microscope we carefully align the graphene to the center of the hole and attach the Lexan frame to the glass slide. A side view of the attachment is drawn in step D. Here it is visible that the metal piece pushes out the PMMA and thereby flattens...
Chapter 3. Device fabrication and measurement setup

Figure 3.5: Illustrations of the steps of the dry transfer method. For explanation we refer to the text.

the film to enhance transfer yield. We put the substrate with target hBN flake on a custom made heater (Fig. 3.6) that we set to 105 °C to evaporate any humidity that is still on the hBN or graphene surfaces. Moreover the heat promotes adhesion between graphene & hBN and PMMA & SiOₓ (the glass transition temperature of PMMA is 105 °C). When the systems are in thermal equilibrium we carefully align the graphene and hBN on top of each other and bring them in contact. Just after contact we heat to 140 °C to promote adhesion and then we slowly cool down. When the temperature of the system is <60 °C (the flash point of acetone) we drop a few drops of acetone through the hole in the metal piece to dissolve the PMMA film on the substrate with the hBN/graphene stack.

We use this same Delft dry transfer method for transferring and aligning the top gate hBN flake.

3.6 Cleaning graphene

Cleaning graphene is crucial to obtain high electronic quality devices. We have different techniques at our disposal: chemical cleaning, thermal cleaning (annealing), current induced cleaning and mechanical cleaning. In the introduction of chapter 5 we elaborate on these different methods for cleaning graphene and in the rest of that chapter we extensively describe our newly developed mechanical cleaning method.

After the transfer of graphene on top of the hBN flake, we clean the stack in
3.7 Lithography

For fabricating contacts and gates on the devices we use standard lithography techniques. Patterns are defined with an electron beam pattern generator (EBPG) in a layer of PMMA. We evaporated metals with electron beam evaporation followed by acetone. As chemical cleaning with organic solvents always leaves some residues we anneal the samples as well. At this stage we heat the samples slowly to 400 °C in a tube oven (1” Lindberg Blue M) in forming gas environment and anneal them there for ~ 3 hours before slowly cooling down to room temperature. This treatment is very effective in removing polymer residues from the transfer. Annealing has also other effects on our samples. In chapter 6 we describe bubble formation and movement after annealing at these elevated temperatures. After lithography we also applied annealing to clean the samples, but then it was much less effective. Therefore we also use mechanical cleaning as described in chapter 5.

When using too high temperatures, annealing can induce chemical modification of the graphene. In Fig. 3.4b we show Raman spectra of the same flake that is partly on hBN and partly on SiO_x. The flake was annealed at 800 °C in an Ar:H_2 environment. The spectrum taken on SiO_x shows a broad D-peak, indicating defects in the graphene lattice. Surprisingly the D-peak feature is totally absent in the spectrum taken on hBN. So hBN not only improves the electronic quality of graphene, it also reduces the chemical reactivity of graphene. This effect was observed as well in ref. [70]. That paper concludes that the low residual doping of graphene on hBN leads to its reduced chemical reactivity. Contrary to the general belief, the substrate roughness induced sp^3 hybridization of graphene does not seem to play a large role in the reactivity of the graphene.
Chapter 3. Device fabrication and measurement setup

Figure 3.7: Picture of the sample holder in the dilution refrigerator. On the green PCB a socket is soldered that holds a 32-pin PLCC carrier that contains the sample. The PCB in the upper part of the picture contains the two stage cryogenic RC-filters. The cylinders in the lower part are the Cu-powder filters. Around the sample space we slide a cu-cylinder that acts as a Faraday cage. (Image courtesy of V.E. Calado)

lift-off. For the devices described in chapter 4 we evaporated a layer of SiO$_x$ in the same run as the metals for the top gates. For creating a Hall bar geometry in the graphene sheet we define a PMMA mask with the EBPG and etch away the graphene with an oxygen plasma in a reactive ion etcher. Extensive recipes for lithography can be found in appendix A.

3.8 Measurement setups

The electrical measurements were carried out in various setups. We used a probestation with and without vacuum chamber to quickly test the quality of the samples at room temperature. For most experiments described in this thesis we needed millikelvin temperatures. These temperatures were necessary for two reasons. First to create an insulating state with large enough resistances in bilayer graphene and second to be able to resolve the quantum mechanical phenomena we were hunting for. To reach mK temperatures we used a dilution refrigerator: Leiden Cryogenics MCK-50 with a base temperature of $\sim 20$ mK. The compact system allowed for quick sample turnover, a very useful feature when working with graphene samples.

The fridge was wired for low noise DC electrical measurements. In Fig. 3.7 we show the sample holder with Cu-powder and two stage RC-filters that filter respectively from 100 MHz to above 40 GHz and 10 kHz to 500 MHz. Moreover, at room temperature we installed $\pi$-filters that filter from 10 MHz to 10 GHz. The DC-resistance of each wire was 2.53 k$\Omega$ at low temperature. At $\sim 35$ mK we measured an electron temperature of $\sim 69$ mK (chapter 7).

For all our electrical measurements we have used battery powered, optically isolated
3.8. Measurement setups

measurement boxes to minimize interference and noise from the environment. These so-called IVVI racks are developed in-house by ing. R. Schouten. Their modular design allows for the optimal match of measurement setup to the measurement requirements.
CHAPTER 4

Double gated bilayer graphene devices with SiO$_x$ dielectrics

A.M. Goossens, X.L. Liu, L.M.K. Vandersypen

In this chapter we report on an insulating state created by opening a band gap in a double gated bilayer graphene device. The device has silicon oxide dielectrics. The maximum square resistance is $R_{\square} = 10$ M$\Omega$ at a displacement field of $D_{GR}/\epsilon_0 \sim 0.75$ V/nm at $T = 26$ mK. We pattern the top gate into a split gate geometry with which we can electrostatically induce a narrow conduction channel in the bilayer graphene. No signs of ballistic transport in the channel are observed. Nevertheless we can pinch off the channel to a resistance of $\sim 200$ k$\Omega$. 

35
Chapter 4. Double gated bilayer graphene devices with SiO$_x$ dielectrics

4.1 Introduction

Bilayer graphene consists of two graphene sheets overlaid in the Bernal stacking orientation. In monolayer graphene the unit cell has two basis atoms A and B. The ensembles of A and B atoms constitute the two sublattices. When these sublattices have a different potential a gap opens in monolayer graphene. In bilayer graphene the two sublattices that make up the lower lying energy bands are the ensembles of two atoms B1 and A2 in the different layers of the bilayer system. A transverse electric field puts the different layers and thus the B1 and A2 atoms at a different potential. This results in the opening of a band gap between the lowest lying energy bands. The magnitude of the band gap is proportional to the magnitude of the electric field. This unusual property of bilayer graphene has generated much interest in the search for an increased on/off ratio for graphene field effect transistors.

In this chapter we report on measurements with double gated bilayer graphene devices with SiO$_x$ gate dielectrics. We first reproduce the results in ref. [28] that prove an electrically insulating state can be created by applying a transverse electric field. We use this result to electrostatically induce a narrow conductance channel with a split gate device geometry. No signs of ballistic transport in the channel are observed. Nevertheless we can pinch off the channel to a resistance of $\sim 200$ kΩ.

4.2 Fabrication

First, we take a heavily doped silicon wafer with 285 nm thermally grown SiO$_x$. We clean the wafer with piranha (3:1 H$_2$SO$_4$:H$_2$O$_2$). Then we apply a monolayer of hexamethyldisilazane (HMDS) to make the surface hydrophobic and prevent water to be trapped in between the graphene and SiO$_x$. The next step is graphene deposition with the conventional mechanical exfoliation technique. Bilayer graphene flakes are distinguished by measuring optical contrast with the substrate. We make contacts to the flakes with standard electron beam lithography, electron beam deposition of 5/50 nm Ti/AuPd and lift-off. To remove processing residues we annealed the device at 350°C in N$_2$:H$_2$ atmosphere. We define the gates by electron beam lithography, electron beam evaporation of 20/5/50 nm of SiO$_2$/Cr/Au and lift-off. The sample has one gate that runs entirely over the graphene (strip gate) and two devices that are patterned to form a small channel (split gate). Each of the devices has their own set of contacts. Fig. 4.1a shows an optical image of the full sample. A scanning electron micrograph of a split gate device (Fig. 4.1b) reveals a narrow channel. The distance between the gates is designed to be only $\sim 20$ nm wide.

4.3 Band gap opening

To demonstrate the band gap opening that leads to an insulating state we use the strip gate device in the sample. We first need to open a gap before we can create depleted regions. The approach we take is as follows. We put a large voltage on the back gate to open a gap. This voltage also induces doping in the graphene (n$_{GR} \neq 0$).
4.3. Band gap opening

Figure 4.1: a) Scanning electron microscope (SEM) image of the sample with one strip gate device and two split gate devices. The graphene not covered with a gate is also not covered with SiO$_x$ dielectric. The strip gate has length $L = 1 \, \mu m$ and width $W = 1.7 \, \mu m$ b) SEM image of the middle device of the sample. The gates are 1 $\mu m$ wide and designed to be separated by 20 nm at the apex. The opening angle to the constriction is 60 degrees. c) Schematic side view (not in actual proportions) at the position of the blue dashed line in panel b.

We can use the strip gate to tune the Fermi level inside the gap by biasing the gate with a voltage of magnitude

$$V_{TG} = \frac{C_{BG}}{C_{TG}} V_{BG},$$

where $V_{TG}$ is the voltage on the strip gate, $C_{BG}$ the capacitance of the back gate, $C_{TG}$ the capacitance of the strip gate and $V_{BG}$ the voltage on the back gate.

Fig. 4.2 shows the resistance as a function of $V_{BG}$ and $V_{TG}$ at 26 mK. Along the large resistance diagonal $V_{BG}$ and $V_{TG}$ obey equation 4.1 and hence the carrier density in the graphene $n_{GR} = 0$. From the slope of the diagonal we extract the capacitance ratio between back gate and top gate $\frac{C_{TG}}{C_{BG}} = 32$. If we assume the dielectric constant of evaporated SiO$_x$ to be the same as thermally grown SiO$_x$ $\epsilon_{r, SiO_x} = 3.9$, the top gate dielectric is $285/32 = 9$ nm thick. This is much smaller than the thickness of 20 nm measured during evaporation. In the inset we plot the resistance $R_{MAX}$ along the $n_{GR} = 0$ diagonal. The resistance has a clear minimum at $V_{BG} = -3.4 \, V$ (and $V_{TG} = 1.1 \, V$). To both sides along the diagonal the resistance increases and thus a band gap is opened. $\frac{C_{TG}}{C_{BG}}$ is even more dramatically demonstrated in Fig. 4.2b, which shows a square resistance $R_{\square} = R_{MAX} \cdot W/L > 10 \, M\Omega$. There is not much increase in resistance on the negative displacement field side. We currently do not understand why the insulating behaviour is dependent on the sign of the applied electric field.

The displacement field induced by the gates $D_{gates} = (D_{TG} + D_{BG})/2$ at the minimum resistance point is not zero. As we showed in Fig. 2.4 $D_{gates}$ is not the only displacement field that acts on the graphene. Also charged impurities in the dielectric can impose a displacement field. Knowing the thicknesses of the dielectrics and their $\epsilon_r$ we calculate that the resistance minimum in Fig. 4.2b is at $D_{gates}/\epsilon_0 = 0.22$
Figure 4.2: a) Measurement of the resistance of the strip gate device as a function of $V_{BG}$ and $V_{TG}$ ($T = 26$ mK, $V_{bias} = 52 \mu$V). The data has been corrected for contact resistance by subtracting the resistance measured at $V_{TG} = -1.84$ V from each trace in back gate voltage. In the inset we show the resistance $R_{MAX}$ at $n_{GR} = 0$ (orange for panel a and blue for b). In panel b it was hard to extract this for $V_{BG} < -40$ V due to large fluctuations in the data. b) Same measurement as in panel a, but now for a different gate range. Also this data has been corrected for contact resistance by subtracting the resistance measured at $V_{TG} = 8$ V. ($T = 26$ mK, $V_{bias} = 52 \mu$V) In this measurement the position of the diagonal has changed due to a shift in doping levels. The coupling between back gate and top gate is still the same. The displacement is $+7.96$ V in back gate voltage. The offset in back gate is now $V_{BG} = +40.046$ V. The minimum in resistance along the diagonal is still at $V_{BG} = -3.4$, so the diagonal only shifted in top gate voltage. We can conclude that there are more dopants in the top gate dielectric. Now the minimum is at a displacement field induced by the gates of $D_{gates} = 0.35$ V/nm.

V/nm. The minimum is much more shifted in $V_{TG}$ than in $V_{BG}$. This means the majority of charged impurities resides in the top gate oxide. This is not surprising as the top gate oxide is an evaporated oxide and consequently of much lower quality than a thermal oxide. The 1.1 V shift in top gate voltage translates to a negatively charged impurity density of $n_{imp} = 2.7 \cdot 10^{12}$ cm$^{-2}$ in the top gate dielectric (Fig. 2.4). The -3.4 V shift in back gate voltage corresponds to a positively charged impurity density of $n_{imp} = -2.6 \cdot 10^{11}$ cm$^{-2}$ in the back gate oxide. This is more than an order of magnitude lower than for the top gate oxide.

Previous studies on double gated bilayer graphene devices reported that band transport was not the dominating transport mechanism in gapped bilayer graphene at low temperatures. Ref. [28] concludes a variable range hopping (VRH) mechanism for transport at temperatures of $\sim 50$ mK. Ref. [30] reports a more extended study of temperature dependence and concludes that for temperatures $< 80$ mK and $D < 2.5$ V/nm VRH should be the dominant transport mechanism. The same observation was made in ref. [74] for a device with Corbino geometry. Based on those references we can assume that we have VRH in our device considering our experimental parameters. For VRH in a two dimensional system, the resistance scales as $R = R_0 e^{(T_0/T)^{1/3}}$. When $R_0$ would be independent of $D_{GR}$, setting $T_0 = 0$ at $D_{GR} = 0$, we would be able to
4.4 Split gate channel pinch-off

We have shown that a band gap can be opened in graphene and that it can be used to induce insulating regions. Now we can pattern the top gates in order to confine the charge carriers in bilayer graphene to pre-defined one-dimensional or zero-dimensional regions: quantum point contacts or quantum dots. Here we realized a device with split gates separated by \( \sim 20 \text{ nm} \) at their apex (see Fig. 4.1b). In Fig. 4.3, we show that the device behaves qualitatively similar to the strip gate device in Fig. 4.2. The regions below the gates can be pinched off but the transport is dominated by the regions uncovered by the gates as the magnitude of the resistance is much lower than in Fig. 4.2a and b.

The electric field induced by the split gates naturally extends to the regions between them. The extent of the field is roughly proportional to the voltage on the split gates, so by increasing this voltage we can narrow and eventually pinch off the channel. In Fig. 4.3b we show a sweep of the split top gates at a back gate voltage of \(-80\text{ V}\). We observe depletion of the constriction. The maximum resistance of our splitgate device was almost 200 k\( \Omega \). This is much larger than the resistance quantum of \( \frac{1}{4e^2} = 6.47 \text{ k}\Omega \). On the flanks of the pinch-off curve we do not see any hints of quantized conductance. This is probably due to the short mean free path. The mobility of our device was \( \sim 1750 \text{ cm}^2/(\text{Vs}) \) (4-terminal measurement) which results in a mean free path of about 10 nm at a typical carrier density of \( 10^{12} \text{ cm}^{-2} \). We estimate the size of the constriction to be approximately 20 nm, so the electrons could

![Image](image_url)

**Figure 4.3:** Resistance as a function of \( V_{TG} \) and \( V_{BG} \) for the split gate device in Fig. 4.1b \((T = 26 \text{ mK}, V_{bias} = 100 \text{ } \mu\text{V})\). b) Linecut in conductance at \( V_{BG} = -80\text{ V} \). We did not correct for any background resistances in these plots.

eextract \( T_0 \) as a function of \( D_{GR} \). However, from the data in ref. [28] it is obvious that \( R_0 \) is dependent on \( D_{GR} \), so we could not extract \( T_0 \). We did not measure temperature dependence of transport.
not traverse the constriction ballistically, a requirement for formation of standing waves in the constriction and thus observation of quantized conductance.

4.5 Conclusion

Concluding, we reproduced the results in ref. [28] and measured a maximum square resistance of $R_\square = 10 \, \text{M}\Omega$ at a displacement field of $D_{GR}/\epsilon_0 \sim 0.75 \, \text{V/nm}$ at $T = 26 \, \text{mK}$. Furthermore we made a split gate device. The primary goal of the experiment was to see quantized conductance, but due to the low sample quality we could not observe plateaus in the pinch-off curves. An encouraging result is the fact that we could see depletion of the channel as the maximum conductance was much larger than the conductance quantum. We can conclude that the disorder dominated gapped state will not be limiting for low-dimensional quantum confinement devices. The results reported in this chapter pave the way to use the split gates in other devices, for example the tunable tunnel barrier in electrostatically defined quantum dots in bilayer graphene.

The success of electrostatic quantum confinement devices will depend on the electronic quality of the bilayer graphene. SiO$_x$ substrates limit the mobility severely so that mesoscopic effects such as quantized conductance will be obscured. Regular quantum dot behaviour will be hard to observe because of potential fluctuations. STM measurements that map the Dirac point (at $D_{GR}=0$) show a RMS disorder $\Delta E_{\text{dis}} = 19 \, \text{meV}$. From temperature dependent transport measurements a value of $\Delta E_{\text{dis}} = 21.5 \, \text{meV}$ is extracted. The disorder that causes these potential fluctuations also induces local electric fields complicating the situation even further. For future experiments the graphene flake needs to be suspended or supported by a high quality substrate like hexagonal boron nitride, realized in refs. [11] and [12] respectively. The technique developed in ref. [12] we use to create quantum confinement devices that show quantized conductance and coulomb blockade. These results we report in chapter 7 of this thesis.
CHAPTER 5

Mechanical cleaning of graphene

A.M. Goossens, V.E. Calado, A. Barreiro, K. Watanabe, T. Taniguchi, L.M.K. Vandersypen

Contamination of graphene due to residues from nanofabrication often introduces background doping and reduces electron mobility. For samples of high electronic quality, post-lithography cleaning treatments are therefore needed. We report that mechanical cleaning based on contact mode atomic force microscopy removes residues and significantly improves the electronic properties. A mechanically cleaned dual-gated bilayer graphene transistor with hexagonal boron nitride dielectrics exhibited a mobility of $\sim 36,000 \text{ cm}^2/\text{Vs}$ at low temperature.

\hspace{1cm}

5.1 Introduction

High electronic quality is demanded for many graphene experiments \[76, 10\], but is not easily realized. Graphene samples for electronic measurements are typically made with lithographic methods. Lithography makes a myriad of devices possible, but always leaves resist residues behind. Making contacts to graphene with shadow mask evaporation solves this contamination issue, but this method has many drawbacks concerning the flexibility of the fabrication process. Hence cleaning after lithography is a crucial step towards obtaining high electronic quality samples. There are different methods at hand: chemical cleaning \[77\], thermal cleaning (annealing in an oven) \[78, 79\] and current-induced cleaning \[80, 11\]. Each of these can be very useful but has its own limitations.

In this chapter we present an alternative cleaning method: mechanical cleaning. Scanning a contact mode atomic force microscope (CM AFM) tip over a graphene surface removes residues, removes doping and improves the electronic mobility without damaging the graphene.

5.2 Heat cleaning ineffective

We demonstrate the effectiveness of this method for 4 bilayer graphene on hexagonal boron nitride (hBN) samples. hBN flakes are deposited by mechanical exfoliation on silicon wafers coated with a silicon oxide (SiO$_2$) layer of thickness $t_{SiO_2} = 285$ nm. On top of the hBN we transfer a bilayer graphene flake using a dry transfer method following the protocol of \[12\] (at a temperature of 100 °C to remove any water absorbed on the surface of the graphene and hBN flakes). Samples are subsequently annealed in an oven at 400 °C (Ar 2400 sccm, H$_2$ 700 sccm) to remove residues induced by the transfer process. Cr/Au electrodes are fabricated using electron-beam lithography. We annealed the samples again (same flow rate as the first annealing step) to remove fabrication residues. Trying to clean the graphene, we performed multiple annealing steps at temperatures from 300 °C to a maximum of 440 °C.

After the final annealing step, the samples were often still contaminated. The tapping mode AFM (TM AFM) image of sample A (Fig. 5.1a) shows lots of deposited material outside the marked window. The roughness in this area is $\sim 1$ nm. Before lithography all samples were almost atomically flat with a roughness of at most 0.2 nm (limited by the resolution of the AFM).

We characterize the electronic quality of the samples via the residual doping and field effect mobility. Fig. 5.1b (lower trace) shows the conductivity of sample B as a function of the backgate voltage at room temperature (RT) in vacuum. From this and similar traces for the other devices, we extracted the charge neutrality point ($V_{np}$) and mobility ($\mu$) of the samples. Depending on the device we were able to do 2, 3 or 4 terminal measurements. In the two and three terminal measurements, contact resistances make the mobility appear lower. To calculate the conductivity from the measured conductance we need the aspect ratio of the devices. As some devices were not rectangular, the aspect ratio was hard to determine and we used an underestimated value in our calculations. Those two factors make the measured mobility a lower bound of the actual mobility. The results for all samples are summarized in table 5.1. The
5.3. Mechanical cleaning with contact mode AFM

To remove the residues we scanned the samples in contact mode AFM with a constant force (Veeco OTR8-35 silicon nitride tip with a stiffness of 0.15 N/m). Hereby the tip is held in contact with the sample surface. We engaged the tip with the lowest force possible. When the tip made contact, we confirmed a reasonable set-point force with the help of a force distance measurement, discussed further below. Then we started scanning the sample with a rate of $0.5 - 1 \text{ Hz}$. Some samples were clean after the first pass. In most samples residues are gradually removed as is illustrated in Fig. 5.2a-c.

Tapping mode images taken after scanning in CM AFM show that we cleaned electronic measurements indicate that most of the devices were highly doped and had a relatively low mobility. Most likely residues on top of the graphene as seen in the AFM images induce doping and provide scattering centers that degrade the electronic quality. [81]

5.3 Mechnical cleaning with contact mode AFM

Figure 5.1: a) Tapping mode image of sample A after annealing at 440 $^\circ$C and contact mode scanning (both with a Veeco Nanoscope IIIa AFM). Only the part within the marked window was scanned with the CM AFM. We chose to show this device because it was much more contaminated than other devices before scanning, so that the effect of the CM AFM scan is easily visible. Wrinkles and some tears on the upper right side of the graphene are induced by the tip but were not observed in other devices. On the left and right of the bounding box, walls of deposited residue are visible. The contacts of the device are not visible in this image.

b) Backgate traces of sample B at room temperature in vacuum ($I_{bias} = 100 \text{ nA}$). The lower curve is before CM AFM imaging and the upper curve after. Using the geometric capacitance, we convert the backgate axis into carrier density. Then we extract the field effect mobility by fitting a straight line to the steepest part of the backgate trace:

$$\mu = \frac{t_{SiO_2}}{\varepsilon_{r,SiO_2} + t_{hBN}} \frac{d\sigma}{dV},$$

where $\varepsilon_{r,SiO_2} = 3.9$ and $\varepsilon_{r,hBN} = 3.0$, as calculated from Fig. 5.3. We extracted the thickness $t_{hBN}$ from TM AFM images of the devices.
Table 5.1: Results summary for four different samples (measurements in vacuum).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal T [°C]</th>
<th>Nr of passes</th>
<th>Scan force [nN]</th>
<th>Measure-Scan force</th>
<th>V&lt;sub&gt;np&lt;/sub&gt; before [V]</th>
<th>V&lt;sub&gt;np&lt;/sub&gt; after [V]</th>
<th>µ before [cm&lt;sup&gt;2&lt;/sup&gt;/Vs]</th>
<th>µ after [cm&lt;sup&gt;2&lt;/sup&gt;/Vs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>440</td>
<td>6</td>
<td>2.3</td>
<td>2-prb, RT</td>
<td>4</td>
<td>-7</td>
<td>3.4 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>8.9 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>A</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4-prb, 50mK</td>
<td>n.a.</td>
<td>-3</td>
<td>n.a.</td>
<td>3.6 × 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>B</td>
<td>360</td>
<td>1</td>
<td>-2.9</td>
<td>3-prb, RT</td>
<td>&gt;20</td>
<td>0</td>
<td>1.7 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>2.8 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>C</td>
<td>360</td>
<td>2</td>
<td>-4.6</td>
<td>3-prb, RT</td>
<td>&gt;20</td>
<td>1</td>
<td>2.6 × 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>9.2 × 10&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>D</td>
<td>360</td>
<td>5</td>
<td>-22</td>
<td>4-prb, RT</td>
<td>17</td>
<td>-1</td>
<td>2.7 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>6.7 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Figure 5.2: Snapshots of a cleaning sequence: CM AFM images a-c are the 1<sup>st</sup>, 4<sup>th</sup> and 12<sup>th</sup> pass of the CM AFM. Note in image b that residues get stuck to the fold in the graphene and are mostly removed in c. Only the fold in the hBN in image c stays covered in dirt. The diagonally running features indicated by the arrows are speckles of dirt that are pushed upwards every time the AFM tip passes. Image d shows an etched flake that is damaged after the 4<sup>th</sup> pass.
the graphene (Fig. 5.1a, inside marked window). The roughness is at most 0.2 nm, similar to the values measured before processing the devices. Further evidence that we removed residues from the graphene are the banks of deposits that are visible in Fig. 5.1a, exactly at the boundaries of the area that was scanned in contact mode.

After CM and TM AFM imaging we again recorded backgate traces at room temperature in vacuum (upper curve in Fig. 5.1a). Not only the mobility increased twofold, but also doping was reduced. For other samples we observed similar behavior (see table 5.1).

5.3.1 Double gated device

An attractive feature of mechanical cleaning is that it can be naturally followed by further sample processing. We fabricated sample A into a double gated bilayer device [28, 29]. With the same dry transfer method as mentioned before we stamped an hBN flake on sample A that will act as a topgate dielectric. We defined a topgate electrode across the flake and two voltage probes by e-beam lithography (lower left inset Fig. 5.3a). Resistance as function of the topgate and backgate voltages is plotted in Fig. 5.3a. The resistance peaks that run horizontally are caused by the regions next to the top gated region. The diagonal ridge shows the typical increase of resistance due to opening of a gap with increasing perpendicular electric field [28]. From the upper right inset we extract a (hole) mobility \( \mu \) of \( \sim 36,000 \text{ cm}^2/\text{Vs} \) at carrier density \( n \sim 5 \times 10^{10} \text{ cm}^{-2} \) (corrected for the change in slope due to the neutrality point around 17 V). This value is among the highest found in the literature for bilayer graphene devices, including suspended devices [12, 82, 83].

5.3.2 Discussions

We now turn to the mechanism by which CM AFM removes residues from the sample surface. Presumably the tip is plowing through a layer of physisorbed contaminants and thereby "brooms" the graphene clean, which means the interaction of the tip with the surface is larger than the interaction of the contaminants with the surface. We believe that removing residues is the main explanation for the improvement of the electronic quality of the graphene. In principle the CM AFM might also flatten the graphene, reducing ripples and thereby enhancing mobility. However, we observe no difference in the flatness of unrippled areas of graphene before fabrication (presumably equal to the state after lithography) and after mechanical cleaning.

The hBN substrate does appear to play a role in improving electronic quality. In Fig. 5.4 we show data on mechanical cleaning of a single layer graphene on a SiO\(_x\) sample. When comparing Fig. 5.4a and Fig. 5.4b and the zooms Fig. 5.4c and Fig. 5.4d, residues are clearly removed. The RMS roughness decreases from 850 pm to 330 pm after mechanical cleaning. Unfortunately the electronic quality did not significantly improve as shown in Fig. 5.4c. It is interesting to note that the RMS roughness of bare SiO\(_x\) (Fig. 5.4d) is 250 pm, which is lower than that of the graphene after mechanical cleaning. This observation might point to presence of contaminants below the graphene that can not be removed by mechanical cleaning. Two papers reported application of mechanical cleaning to single layer graphene samples on a SiO\(_x\) substrate [84, 85]. Lindvall et al. also applied the method to graphene on barium...
Figure 5.3: a) Measurements on a double gated bilayer graphene transistor fabricated out of sample A. The 4-probe resistance at $T = 50$ mK is plotted as a function of backgate and topgate voltage ($V_{bg}$ and $V_{tg}$ respectively). From the slope of the diagonal line we calculated the relative dielectric constant of the hBN to be 3.0 assuming a parallel plate capacitor model and $\epsilon_r, SiO_2 = 3.9$. The thickness of the bottom hBN flake was 14 nm and the top hBN flake 50 nm, values extracted from AFM images. Lowerleft inset: schematic of the device. Blue colored regions are hBN, green is bilayer graphene and yellow are the contacts and gate. Upperright inset: resistance as a function of $V_{bg}$ at $V_{tg} = -0.5$V. The dip at $V_{bg} \sim 17$V is caused by the uncovered graphene part. b) Force-distance curve of sample D, measured by holding the tip of the AFM in a fixed lateral position and approaching and retracting the tip in the vertical direction. While making these vertical movements, the deflection of the tip is recorded. Assuming that when the tip is in contact with the surface the tip deflects the same distance as the piezo moves, we can calibrate the deflection scale. With the spring constant of the tip we convert that deflection to a force. The horizontal axis has an arbitrary offset. The blue region indicates the range of forces that we used for cleaning the samples. Sample D was scanned at a force of $-22$ nN as indicated by the arrow. The illustrations picture the pulling and pushing regime.
5.3. Mechanical cleaning with contact mode AFM

Figure 5.4: AFM images of mechanical cleaning of a single layer graphene on SiO$_x$ sample. The scanning force was 0.3 nN. Panels a) and b) show TM AFM images before and after mechanical cleaning. The vertical scale of both images is 10 nm. c) Backgate sweeps before (black) and after (green) mechanical cleaning. The Dirac point shifted slightly towards 0 V and the mobility increased marginally as can be inferred from the increased slope. d)-f) Zooms of the areas indicated in panels a and b. The vertical scale of images d-f is 2.5 nm.

Strontium titanium oxide (BSTO) [85] In both papers the researchers observed an improvement in surface morphology, but electronic quality only improved for Lindvall et al. Their mobilities changed marginally, but residual doping was largely removed. For graphene on BSTO no electrical measurements were reported.

To gain more insight in the interplay of the surface and the CM AFM tip we took force-distance curves (Fig. 5.3b) in the area we scanned in contact mode. From these curves we can extract the force we were exerting on the sample during scanning, which ranged from $-22$ nN to $+2.3$ nN depending on the device. A positive force means the tip was pushing and a negative force that the tip was pulling on the surface. In pulling configuration the tip is held in contact by the Van der Waal’s interaction and adhesive forces due to water. The broad range of scanning forces that gave good results illustrates the robustness of the mechanical cleaning method. Lindvall et al. [85] use an even larger range of forces for mechanical cleaning. Tips with a stiffness of 15 N/m enable them to apply forces up to 180 nN. The researchers report that the morphology of graphene on SiO$_x$ changes drastically when using large forces. For small forces ($\sim 20$ nN) the graphene is almost atomically flat after mechanical cleaning. For large forces the graphene follows the roughness of the underlying SiO$_x$ layer after
mechanical cleaning. This implies that the tip pushes the graphene in closer contact with the surface. We also observe manipulation of the graphene morphology by the AFM tip. When we apply a large force on the tip, ripples in graphene on hBN can be partially flattened. One has to be careful here. Application of too large forces during mechanical cleaning can damage the graphene. In figure Fig. 5.2d we show a CM AFM image of a damaged graphene flake after scanning with a large force. Patches of suspended graphene are especially prone to rupture during mechanical cleaning. Another problem we encounter is that residues sometimes get stuck on edges and folds of graphene Fig. 5.2c. Even after thermal cleaning with a subsequent mechanical cleaning step the residues are not removed.

5.4 Conclusions

In summary, scanning bilayer graphene on hBN in CM AFM removes contaminants from the surface, reduces residual doping and significantly improves electronic mobility. A double gated bilayer graphene transistor which was mechanically cleaned in the fabrication process, showed mobilities up to 36,000 cm²/Vs at 50 mK, and opening of a bandgap. This illustrates the effectiveness and versatility of CM AFM for obtaining high-quality graphene devices. An interesting open question is the role of the substrate in the effectiveness of the mechanical cleaning method. For rough substrates like SiOₓ mechanical deformation of graphene and impurities below the graphene might limit the effect of mechanical cleaning on electronic quality. Most scanning probe studies of graphene require only absence of surface contaminants and not per se electronic quality improvement. For those studies mechanical cleaning is a very suitable cleaning method. AFM and scanning tunneling microscope (STM) setups in vacuum could benefit even more from mechanical cleaning as it can be applied in situ, avoiding subsequent contamination by molecules absorbed from the air. Recently cousins of graphene like MoS₂, TaS₂ and NbSe₂ have attracted lots of interest, largely because of their electronic properties. Most probably those two-dimensional materials will suffer from surface contamination as much as graphene does. Mechanical cleaning is likely to prove itself as an effective tool to remove surface contamination and improve electronic quality in this emerging field.
Bubbles and wrinkles in graphene on hBN

A.M. Goossens, T.A. Baart, L. Cantley K. Watanabe, T. Taniguchi, L.M.K. Vandersypen

Transferring graphene induces bubbles and wrinkles. We make this observation for bilayer graphene transferred to hexagonal boron nitride substrates. Annealing up to 600 °C after the transfer makes the small bubbles coalesce into the larger ones. This results in larger flat areas. We also report Raman measurements on the bubbles that indicate the bubbles are not strained. Moreover we manipulate the bubbles with an atomic force microscope tip. From our measurements we conclude that there is most likely a mixture of air and hydrocarbons inside the bubbles. Finally we observed that graphene sheets on hexagonal boron nitride can move. This movability facilitates strain release by bubble formation.
6.1 Introduction

Graphene is an atomically thin membrane. The nature of its sp$^2$ bonds makes this thin sheet much more susceptible to out-of-plane deformations than to in-plane deformations. Hence wrinkling of graphene acts as a very effective way to remove inhomogeneous in-plane elastic strain through out-of-plane buckling. This is observed in the form of undulations that are formed when graphene is exfoliated on rough SiO$_2$ substrates.\cite{78, 9} Recently developed techniques to grow large area graphene show out-of-plane buckling of the graphene.\cite{57, 88} Mismatch of thermal expansion between graphene and its host explains this buckling only partially. After growth the graphene needs to be transferred to another substrate. This transfer induces many out-of-plane deformations in graphene as well.\cite{89}

Graphene needs to be transferred for making layered heterostructures of graphene and hexagonal boron nitride (hBN) (see chapter 3).\cite{12} We observe that after transfer to hBN bubbles and wrinkles appear in the graphene. They can be even visible in optical microscope images as in Fig. 6.1a (the bubble is indicated with an arrow).\cite{90} Further inspection with tapping mode atomic force microscopy (TM AFM) shows many more smaller bubbles (Fig. 6.1b). A zoom on a typical bubble is shown in Fig. 6.1c. The bubble has a triangular geometry and a smooth surface without wrinkles. The width of bubbles is typically $w = 1\ \mu$m and their height $h = 100\ \text{nm}$.

Strain with trigonal symmetry applied to graphene induces a pseudo-magnetic field.\cite{91} Triangular bubbles have the right symmetry to cause this effect. The pseudo-magnetic field has been observed in bubbles formed in a graphene sheet on a platinum substrate.\cite{92} From an applications point of view the bubbles are not desirable. The yield of future large-area electronics made of graphene/hBN sandwiches will be too low when the issues with bubbles are not solved.\cite{93} Better understanding of their nature might help to discover possibilities to avoid them and provides interesting insights in the graphene/hBN heterostructure system. In this chapter we investigate methods to obtain large areas of graphene without bubbles. We also look into the origin of bubbles and explore their substance. We answer the questions if the graphene membrane that forms bubbles is still intact and whether it is strained. Furthermore we explore methods to manipulate the bubbles. Finally, the bubbles can teach us about the dynamics of graphene on hBN.

6.2 Larger flat areas and larger bubbles

Upon annealing the bubbles in graphene move position, deflate or inflate. In Fig. 6.3 we show TM AFM images of a bilayer graphene on hBN sample just after transfer and after 4 incremental annealing steps. After transfer (at room temperature) the graphene has many bubbles and wrinkles of up to 50 nm tall. After annealing at 200 °C some bubbles have disappeared and the size of the remaining bubbles increased. This effect was more dramatic after annealing at 600 °C. Some bubbles grew as tall as 700 nm. Annealing further at 800 °C only slightly changes the morphology. In Fig. 6.3 we show a scanning electron microscope (SEM) image of the large bubble in Fig. 6.3. Summarizing, the effect of annealing is that small bubbles coalesce into large bubbles that consequently grow even larger. The graphene sheet now has large flat
6.2. Larger flat areas and larger bubbles

areas where the graphene can be easily patterned in long Hall bars (1 \( \mu \)m wide and 10 \( \mu \)m long).

Small bubbles coalescing into large bubbles was also observed in graphene on Si\( \text{O}_x \) samples with intentionally created bubbles.\[94\] The authors of this paper assume that the bubbles are filled with gas and calculate their pressure for different sizes. The pressure in small bubbles is larger than in large bubbles. When the bubbles are connected via channels the pressure from the small bubbles can be released to the big bubbles. In graphene on Si\( \text{O}_x \) the channels are most likely percolation paths induced by an interplay of the roughness of Si\( \text{O}_x \) and heat. In perfect graphene on atomically flat hBN samples roughness is absent.\[95\] Thus transport of gas and/or other materials from one bubble to another needs to take place via a different channel than the roughness of the substrate. In the next paragraph we explore a possible mechanism for mass transport along graphene/hBN interfaces.

We think that channels formed by the wrinkles in graphene might be more efficient for material transport. Taking a closer look at the AFM image in Fig. 6.2c one can see that all bubbles are connected to other bubbles via wrinkles in the graphene. Other AFM images in this chapter also show this effect. Even in SEM images Fig. 6.3 the same observation can be made. In another study wrinkles in graphene are shown to behave as microchannels for water.\[89, 96\] Similarly, our wrinkles could transport

Figure 6.1: a) Optical microscope image (50x magnification) of a graphene flake on hBN after annealing at 400 °C. The blue flake is hBN and the graphene is the darker region on the hBN. The graphene also covers partly the Si\( \text{O}_x \). Note that the graphene has a monolayer, bilayer and multilayer region. The arrow indicates a large bubble and the bounding box the region where the TM AFM image in panel b is taken. b) TM AFM image of the region in the bounding box in panel a. The boundaries of the graphene are indicated by the yellow dashed line. The arrow indicates the large bubble also visible in panel a. c) TM AFM image of a typical bubble after annealing at 400 °C in three-dimensional representation.
material from the small bubbles to the large ones. We speculate that there is also solid material involved in the heat transport. Without supplied heat the bubbles do not move. Heat makes the solid material mobile. As the wrinkles also lead to the edges, material might leak away. Hence the total volume of the bubbles in a sheet of graphene is not preserved. We do not think material escaped through the graphene membrane as perfect graphene is impermeable to gases. In Raman spectroscopy on the graphene sheet after annealing at 800 °C the D-peak was absent, so no structural defects were induced.

6.3 Bubble strain and substance

Raman spectroscopy gives valuable information on strain and doping. Moreover it is sensitive to material below the graphene surface. We measured a Raman spectrum on a bubble and compared it to a spectrum next to that bubble (Fig. 6.4). The expected substrate peaks for silicon and hBN at 500 and 1370 cm$^{-1}$ are present in both spectra. It is also clear that we are dealing with bilayer graphene as can be inferred from the shoulder in the 2D-peak at 2700 cm$^{-1}$. A 2D' peak occurs at 3230 cm$^{-1}$. A D-peak (1350 cm$^{-1}$) is not visible, so the graphene is not damaged.

Comparing the two amplified, normalized (to the hBN peak) and background corrected sections of the spectra, we see that the G and 2D peaks have a larger intensity on the bubble. Also the ratio between the G and 2D peak is different for the two spectra. The 2D peak on the bubble seems to lack a clear shoulder. This observation is partly obscured by the noisiness of the spectrum on the bubble, so we cannot draw conclusions about whether the bilayer is still intact.

The position of the G-peak gives information about the strain and doping of the graphene. Strain red shifts ($\delta \omega_G / \delta \epsilon \sim -10.8 \text{ cm}^{-1} / \%$, $\delta \omega_G / \delta \epsilon \sim -31.7 \text{ cm}^{-1} / \%$ for uniaxial strain [68]) and doping of either sign blue shifts the position of the G-peak slightly ($\delta \omega_G / \delta |n| \sim +5 \text{ cm}^{-1} / 1 \cdot 10^{13} \text{ cm}^{-2}$, [69]). We measure for both spectra a G-
6.4 Manipulating bubbles: substance

Figure 6.3: Bubble development as a function of annealing temperature in a bilayer graphene on hBN sample. The z-scale is 700 nm for panels a-e. All the views have the same camera position. The lateral size of the AFM images is not equal. a) After transfer (room temperature), size 25 × 25 μm b) 200 °C, size 25.6 × 25.6 μm c) 400 °C, size 20 × 20 μm d) 600 °C, size 30 × 30 μm e) 800 °C, size 30 × 30 μm f) Scanning electron micrograph of the largest bubble after annealing at 800 °C. Note that the viewpoint is exactly opposite to the AFM images.

peak position of about 1585 cm$^{-1}$. This is 3 cm$^{-1}$ blue shifted from the pristine value for the G-peak and indicates residual doping of $|n| > 5 \cdot 10^{12}$. Residual doping levels much larger than $5 \cdot 10^{12}$ are unlikely so strain that compensates doping is unlikely. We conclude that the graphene in the bubble membrane is not strained.

When we compare the raw spectra we see the most striking difference: the large background signal that we measure on the bubble. This is most likely caused by residues underneath the bubble.

6.4 Manipulating bubbles: substance

In this section we explore different methods to manipulate the bubbles. Indenting the bubbles with an AFM tip can teach us about their substance. Furthermore, we tried to control the bubbles’ curvature with electrostatic forces and subjected them to pressure differences.

We manipulated the graphene bubbles with a contact mode atomic force microscope (CM AFM) tip. In Fig. 6.5, we show a TM AFM image of a typical bubble we find after annealing. After measuring force-distance curves (spring constant tip $k = 0.15$N/m) on this bubble its surface has changed considerably as we show in Fig. 6.5. From a smooth balloon anymore it turned into a rough mountain ridge. Moreover the bubble has grown laterally. The bubble is still as tall as before CM AFM
Figure 6.4: Raman spectrum on the bubble shown in Fig. 6.5a and next to that bubble in bilayer graphene on hBN. The sample was annealed at 400 °C. The sections amplified by a factor 10 have been corrected for background signal and are normalized to the hBN peak. See main text for the explanation of the peak labeling (BLG means bilayer graphene).

manipulation. Material in the surrounding area originating from the interface between graphene and hBN and on top of the graphene might have been accumulated in and on the bubble by mechanisms similar to mechanical cleaning (see chapter 5).

We indented the bubble in Fig. 6.5a with a stiffer AFM tip \( k = 26.1 \text{N/m} \) that enabled us to apply larger forces. This resulted in a popped bubble (Fig. 6.5b). There are only folded sheets of graphene and no residues left at the location of the bubble. We do not think that residues left underneath the bubble were removed with CM scanning. The CM image we took immediately after the bubble popped did not show typical horizontal lines and diagonal lines that occur when the CM tip is cleaning (Fig. 5.2a-c). While the bubble was still intact we took force-distance curves (Fig. 6.5c). In the horizontal part the tip approaches the surface and it exerts no force. In the linear part with finite slope the tip has come up against a non-deformable surface, thus the force is governed by Hooke’s law and the spring constant of the tip only. For the region in between the force increases non-linearly. From the shape of the curve we can deduce that the tip is pushing on a deforming and gradually stiffening surface. The non-linear region is exactly equal to the height of the bubble as can be seen from the inset (140 nm). Hence we can conclude that the tip pushes the bubble all the way to the substrate. Unless the residues are very soft, we can exclude the presence of a layer of residues underneath this bubble.

There are also bubbles that change shape but still look like a smooth balloon after AFM manipulation. The rectangular bubble in Fig. 6.5f was subjected to force-distance AFM measurements. The bubble changed shape during these measurements and became triangular as is visible in figure Fig. 6.5f. Strikingly, in Fig. 6.5k another bubble has appeared to the left of the original bubble. Not only CM AFM is strong enough to manipulate bubbles. In Fig. 6.5l we show a TM AFM image after 3 days of TM AFM scanning the area in Fig. 6.5l. The large bubble has entirely disappeared. On the spot of the large bubble, some residues are left indicated by the dashed circle. The graphene is still intact as we can infer from Raman mapping measurements.
6.4. Manipulating bubbles: substance

**Figure 6.5:**

a) TM AFM image of a bubble in bilayer graphene on hBN after annealing at 400 °C. The scalebar for both a and b is on the right.

b) TM AFM image of the same bubble as in figure b, but after taking force-distance curves.

c) TM AFM image (z-scale is 100 mV) of a bubble that is partly covered by a metal electrode. Along the green dashed line we took the profile in the inset of panel e. The spot on the linecut indicates where we measured the force-distance curve in figure e.

d) TM AFM image (z-scale is 100 mV) of the bubble in panel c after it popped while pressing on it with the AFM tip (k = 26.1 N/m).

e) Force-distance curves taken on the bubble in panel c (approach in black and retract in red). In the inset a profile along the bubble. The horizontal axis is the same for the force-distance and the profile.

f) TM AFM amplitude image (z-scale is 100 mV) with a rare rectangular bubble in a sheet of single layer graphene on hBN after annealing at 400 °C. The yellow dashed line indicates the edge of the graphene. The right side of the image is already scanned by contact mode AFM that also moved some residues visible as vertical banks of deposits.

g) TM AFM image (z-scale is 100 mV) after measuring force distance curves on the rectangular bubble in panel d.

h) TM AFM image (z-scale is 100 mV) after TM AFM scanning of the same area of the chip for 3 days.
Like in ref. [90] we tried to control the curvature of graphene bubbles with an 
electrostatic force. We contacted the samples and mounted them with connected back 
gate and ohmic contacts in the AFM. From a backgate sweep we determined that the 
samples were heavily hole-doped $n < -2 \times 10^{12} \text{ cm}^{-2}$ (the number density is positive for 
electrons and negative for holes). As a function of backgate voltages we measured the 
volume of the top half of the bubble. We did not observe consistent changes for 8 
different bubbles.

Another way to manipulate the bubbles is to cool them down to liquid nitrogen 
temperature. At those temperatures trapped air in bubbles would freeze out, the 
bubble would collapse and hopefully change morphology when the air evaporated 
again while warming up. We saw only a slight change in morphology of the bubbles 
after we did this experiment. A more successful experiment was done by storing a 
bubble for 3 months in vacuum. After this period the shape of the bubble entirely 
changed.

Summarizing this section we evaluate the substance of the different bubbles pre-
sented and the result of the manipulations. We think that in the bubble in Fig. 6.5a 
residues were accumulated. When the AFM tip was pressing the bubble the graphene 
membrane stuck to the residues and stayed in this position. The bubble in Fig. 6.5c 
does not contain residues. In panels f, g and h only the large bubble that disappears 
upon going from panel g to h, does contain residues. This is visible as a small heap 
in panel h indicated by the dashed circle. We did not manage to measure the change 
of curvature of the bubble by electrostatic forces. The influence of the AFM tip on 
the bubble might have obscured the effect. A non-invasive optical method as the re-
searchers in [90] used could have revealed the changes in curvature. Also a circular 
geometry of the bubbles might have been better for these manipulations.

6.5 Dynamics of graphene on hBN

In the introduction of this chapter we have mentioned that bubbles can act to 
release strain in the graphene sheet. From Raman measurements after annealing at 
400 °C we have learned that both the graphene in contact with the substrate and 
the graphene forming the bubble membrane are most likely not strained. This is in 
contradiction with Raman measurements on bubbles that are formed in graphene on 
SiO$_x$. [99] In this section we explain the discrepancy by strain release after the samples 
were annealed above 400 °C.

An unexpected side effect of annealing graphene on hBN is that graphene can move 
laterally and even form folds. The sample in Fig. 6.6 was annealed at 400 °C for 3 
hours. In Fig. 6.6a the position of the flake before annealing is shown and in Fig. 6.6b 
after annealing. We carefully overlayed the two images and it is very clear that the 
flake moved during annealing. A similar effect has been shown to occur for graphite 
on graphite and graphene on graphite microflakes [100]. The authors of this paper 
state that the energy of the system is lowered because of an increased Van der Waals 
(VdW) interaction of the two surfaces when they overlap more. In our sample the 
graphene was on very rough silicon oxide (much rougher than normal due to a long 
reactive ion etching process). This rough SiO$_x$ surface has less contact area with the 
graphene and hence lower VdW interactions, therefore it is favorable for the graphene
6.5. Dynamics of graphene on hBN

Figure 6.6: a) Optical microscope image of a bilayer graphene flake (outlined with the dashed green line) on top of a hBN flake (dark green). b) Volt-error tapping mode AFM picture after annealing at 400 °C. In green the position of the flake before annealing, in yellow the actual position of the flake. The boxes indicate where the tapping mode AFM scans of panel c and d are taken. c) Zoom in on the bubble that appeared after annealing. The z-scale of the picture is 10 nm. d) Zoom in on the double fold at the edge of the flake (z-scale is 3.5 nm). The profile plotted in white is taken along the dashed white line. To flatten the profile we fitted a linear function to the plateau between steps 3 and 4 and subtracted its values from the entire profile. In the inset the magnitude of the step heights for each profile is plotted. The color corresponds to the different steps and the # to the profile number.

to increase VdW interactions by retracting on the hBN.

Before annealing this sample there were no, or only small bubbles in the graphene as we can conclude from the optical microscope image Fig. 6.6a. After annealing a large bubble appeared in the middle of the graphene sheet (Fig. 6.6c). It has a width of about 1 µm and is 250 nm tall. When taking a closer look one notices features that originate from the three corners of the bubble. An AFM image of one of the features taken at the edge of the graphene sheet shows that it is a double fold of the graphene. By taking 48 linecuts as in the inset of Fig. 6.6d, we determined the step height and prove that the graphene is folded. The height of steps 1-4 was respectively $0.8 \pm 0.1$ nm, $0.7 \pm 0.1$ nm, $0.64 \pm 0.06$ nm and $1.33 \pm 0.07$ nm. Although the bilayer graphene sheets are not Bernal stacked on top of each other, the step height for 2 and 3 is within the error margins equal to the theoretical value of 0.68 nm for the thickness of bilayer graphene. Step number 4 is over a fold, so twice the value is expected and that is
what we find. Step number 1 is from hBN to bilayer graphene and the average value is slightly larger than for the graphene - graphene steps. However from the inset in Fig. 6.6d it is clear that most of the profiles for step 1 have a step height equal to the bilayer graphene - bilayer graphene step. The hBN - bilayer graphene interface is thus atomically sharp.

Summarizing, the graphene that we discussed in this section moved as a whole over its substrate during annealing. In the process of moving it formed a bubble and folds that start at the corner of the bubble. Most likely this bubble originated to release strain and is also strain free itself. From AFM measurements we extracted the width and height of the bubble. The strain in a bubble created by deforming a flat sheet of graphene into a bubble of this size is \( \epsilon = \frac{L - L_0}{L_0} \), where \( L_0 = w \) and \( L \) is the length of the arc after deformation that can be calculated knowing \( w \) and \( h \). For the bubble in Fig. 6.6c \( w = 1 \mu m \) and \( h = 250 \text{ nm} \). If the graphene sheet would not have moved, the strain would be as much as 15%. The strain for the bubble in the Raman experiment (Fig. 6.4) would be 4% with the same calculation. This strain should have been easily observed by a shift in G-peak position or have been compensated by a highly unlikely amount of residual doping. Hence we think that the graphene in the bubbles formed after annealing is not strained.

### 6.6 Conclusion

Upon transferring graphene on hBN bubbles appear. Annealing samples with graphene on hBN provides a good method to create large flat areas of graphene in atomically sharp contact with hBN. These areas are large enough to create devices like Hall bars and quantum dot channels. Raman spectroscopy and AFM indentation of the bubbles that appeared after annealing show that they contain most likely a combination of gas and solid material. Another argument for this hypothesis is that when graphene membranes are etched away by oxygen plasma etching, always some hard residues are left on the spot of the bubble. As the transfers are performed in air the gas must be air. The solid material consists most likely of hydrocarbon residues, leftovers from the transfer process. In ref. cross sectional TEM imaging and EDX analysis are done on graphene/hBN samples with bubbles. The authors report that bubbles are filled with material and with EDX they prove that the material is mainly hydrocarbons. This supports our observations on the substance of the bubbles.

Raman measurements show that bubbles that appear after annealing are most likely unstrained. Initially, after transfer, the graphene is probably strained. This strain can be partly released by small bubbles coalescing into larger ones during annealing. A second method to release the graphene's strain is facilitated by its susceptibility to out-of-plane deformations and relatively weak interaction with the hBN substrate. During annealing graphene moves over the hBN surface and releases its strain in networks of bubbles, wrinkles and folds. The symmetry and dimensions of our bubbles are ideal to induce a modest but observable pseudo-magnetic field \( (B \sim 2 \text{ T}) \). However, our bubbles are unstrained and thus do not carry this pseudo-magnetic field. Transferred graphene sheets that are not annealed are better candidates for this effect to be observed.

Solving the problem of bubbles is an important step for devices with graphene
on hBN and other two-dimensional layered material stacks. Engineers will face the challenge of developing a transfer method that is residue free and prevents air and hydrocarbon residues to be trapped in small pockets between the graphene and hBN. In the paper by Bae et al. [102] no bubbles are observed after transfer of graphene on a PET substrate. This gives hope that roll-to-roll transfer is a good approach to fabricate bubble and wrinkle free graphene on hBN devices.
CHAPTER 7

Gate defined confinement in bilayer graphene - hexagonal boron nitride hybrid devices


We report on the fabrication and measurement of nanoscale devices that permit electrostatic confinement in bilayer graphene on a substrate. The graphene bilayer is sandwiched between hexagonal boron nitride bottom and top gate dielectrics. Top gates are patterned such that constrictions and islands can be electrostatically induced. The high quality of the devices becomes apparent from the smooth pinch-off characteristics of the constrictions at low temperature, with features indicative of conductance quantization. The islands exhibit clear Coulomb blockade and single-electron transport.

The content of this chapter is published in *Nano Letters* **12**, 4656 (2012).
7.1 Confinement in graphene

Confinement of charge carriers in graphene has been heavily investigated since graphene flakes on a substrate were first measured. Nanopatterning graphene into nanoribbons or small islands has been a widely used strategy for both zero- and one-dimensional confinement. Unfortunately, as a result of the etching process that is used for nanopatterning, the edges of the devices are very rough. This edge disorder, aggravated by substrate-induced disorder, leads to rather irregular device behaviour. For instance no quantized conductance was observed in etched constrictions, the transparency of barriers varied non-monotonously with gate voltage, no atom-like shell-filling has been observed in quantum dots and in many cases quantum dots fell apart into multiple islands.

Last year, suspended single layer graphene sheets narrowed by current induced heating showed quantized steps in conductance of $2e^2/h$ as the Fermi wavelength was varied. Presumably these constrictions were not only narrow but also short, as observed in recent transmission electron microscope measurements, reducing the effects of edge disorder. However, the formation of these constrictions is hard to control, making it difficult to reproduce these results. Clean ribbon edges can be obtained reproducibly by unzipping carbon nanotubes, and a well-behaved quantum dot formed in such a nanoribbon was recently reported. Barriers were formed at metal Schottky contacts, but such barriers are not tunable, limiting follow-up work. Moreover, as the ribbons are not obtained lithographically but are dispersed from solution, they face many of the limitations of the carbon nanotube they originate from.

The ideal device would confine charge carriers in the bulk, far from (disordered) edges, have well controlled tunnel barriers, and enjoy all the design freedom offered by lithography. All these requirements can be satisfied using patterned electrostatic gates, provided a band gap is present. This calls for the use of bilayer graphene rather than monolayer graphene, as in bilayers a band gap can be induced by an electric field perpendicular to the layers. An additional requirement for clean confinement is to minimize substrate-induced disorder. Substrate disorder can be eliminated in suspended devices with suspended top gates, as shown in recent work by Allen et al. However, it would be highly desirable to realize devices of comparable quality on a substrate, as this would facilitate integration of complex devices. Currently the cleanest gate dielectric available for graphene devices is hexagonal boron nitride (hBN), and mobilities reported on such substrates approach those of suspended devices.

Here we report on the first realization of electrostatic confinement devices in bilayer graphene on a substrate. The bilayer graphene is encapsulated in hBN top and bottom dielectrics via successive transfer steps. The devices have split top gates and a global back gate, which we bias so that a gap is opened in the graphene bilayer. The Fermi level is tuned inside the gap in the regions below the top gates so that they become insulating. We demonstrate the potential of this new device platform by confining charge carriers in one-dimensional channels and zero-dimensional islands.
7.2 Device fabrication

Schematic, optical and AFM images of the devices are shown in Fig. 7.1. We first deposit a 14 nm thick hBN flake by mechanical exfoliation on a silicon wafer coated with a silicon oxide (SiO$_2$) layer of thickness $t_{SiO_2} = 285$ nm. On top of the hBN we transfer a bilayer graphene flake ($\sim 22\mu m$ long and $\sim 3\mu m$ wide, its bilayer nature was confirmed by Raman spectroscopy) using a dry transfer method following the protocol of [12] (at a temperature of 100 °C to remove any water absorbed on the surface of the graphene and hBN flakes). The sample was subsequently annealed in an oven at 400 and 450 °C (Ar 2400 sccm, H$_2$ 700 sccm) to remove residues induced by the transfer process. Cr(5 nm)/Au(95 nm) electrodes are fabricated using electron-beam lithography (EBL). We annealed the samples again (same flow rate as the first annealing step, $T = 300, 350$ and $440$ °C) to remove fabrication residues. This did not give the desired sample quality. Hence we applied the recently developed mechanical cleaning technique [109] followed by dry transfer of a 50 nm thick hBN flake partly covering the bilayer graphene flake. This hBN flake will act as top gate dielectric.

In a two-step EBL process we deposited Cr/Au top gates. We defined several gate
patterns between the contacts on this flake and report here on two 'quantum dot' top gate structures, one with a lithographic diameter of 320 nm (device A) and one of 250 nm (device B). The separation between the top gates that together define a barrier is less than 30 nm. For device B, TG1 and TG2 were unintentionally connected.

This specific graphene sample was cooled down multiple times. The maximum field effect mobility measured at T=35 mK was \(\sim 36000 \text{ cm}^2/\text{Vs} \) (four-terminal configuration; both covered and uncovered graphene are in between the voltage probes, see Fig. 7.1c, so the measured mobility averages over both as well). The field effect mobility measured during the last cool-down was much lower (\(\sim 6000 \text{ cm}^2/\text{Vs} \), two-terminal configuration). Presumably this degradation of electronic quality was caused by deposition of amorphous carbon on the uncovered graphene induced by exposure to an electron beam during imaging in a scanning electron microscope. Nevertheless we expect that the graphene sandwiched in hBN retained high mobility.

### 7.3 One barrier: quantized conductance

We set the back gate to a large negative voltage and tune the top gate to a voltage that compensates for the doping induced by the back gate. For typical values \(V_{BG} = -50 \text{ V} \) and \(V_{TG} = 9 \text{ V} \) the displacement field is \(D \sim 0.6 \text{ V/nm} \), which translates into a theoretically predicted band gap of \(\sim 50 \text{ meV} \). As in earlier work, the transport gap is substantially smaller but still large enough to realize quantum confinement, as we will see.

In Fig. 7.2a we show a top gate trace at a large negative back gate voltage, taken at low temperature. Clearly visible is a region of suppressed conductance, with a minimum conductance of the order of a conductance quantum. The fact that conduction is not fully pinched off seems reasonable given the small induced band gap and the small dimensions of the gates near the constriction. Importantly, the top gate trace shows a remarkably clean transition region on the hole side. A somewhat less clean transition and lower conductance is seen on the electron side. This asymmetry can be expected since the leads are p-doped by the backgate, and a pnp-junction is formed on the electron side. The pnp-junction decreases the transparency of the device as the charge carriers have to Zener tunnel through the induced band gap. On the hole side the conductance suppression with top gate voltage is very smooth and well behaved. This is in strong contrast to similar top gate sweeps for graphene nanoribbons, which exhibit very irregular pinch-off characteristics when the Fermi energy is swept into the transport gap.

Zooming in on the steep flank of the pinch-off curve, we observe several plateaus in conductance, with a value that is independent of \(V_{BG} \) (Fig. 7.2b). The traces have been corrected for filter resistance, current amplifier input resistance and for a background resistance \(R_B \) consisting of contact resistance, Maxwell spreading resistance and graphene lead resistance. The background resistance is slightly dependent on back gate voltage. In Fig. 7.2b, for each value of \(V_{BG} \) we subtracted a value of \(R_B \) comparable to the two-terminal resistance \((R_{2T})\) of the graphene flake with all top gates at ground (see inset), fine tuning \(R_B \) such that the conductance \(G\) at the upper plateau is \(6e^2/h\) (other possible assignments are discussed in appendix B). The other two plateaus consequently appear at \(G = 4e^2/h\) and \(G = 2e^2/h\). The same
7.3. One barrier: quantized conductance

Figure 7.2: (a) Conductance (G) versus the voltage on TG1 and TG2 (device B, $T = 35 \text{ mK}$, $V_{bias} = 0.5 \text{ mV}$, $V_{bg} = -49.74 \text{ V}$). The other top gates of the device are set to 5 V, far from pinch-off, so that we are dealing with only one constriction. All measurements presented in this paper are conducted in two-terminal DC voltage bias configuration. The conductance has been corrected for filter resistance and current amplifier input resistance. In the inset we show cartoon of the bandstructure for pp’p and pnp measurement regimes. Solid lines indicate valence and conduction band edges and dashed line the position of the Fermi level. (b) Top gate traces for device B at back gate voltages from $-49.26 \text{ V}$ (leftmost) to $-49.74 \text{ V}$ (rightmost) in 10 equal steps ($V_{bias} = 0.5 \text{ mV}$, $T = 35 \text{ mK}$). The solid green line in the inset is the subtracted $R_B$. The dashed blue line is the two-terminal resistance of the graphene flake with all top gates at ground. (c) Channel width $W_n$ for modes $n = 1$, 2 and 3 for device A (blue triangles) and for two measurements on device B (green circles and squares). The widths are calculated in the square-well potential approximation $W = \frac{2}{\pi} \lambda_f$. The Fermi wavelength at the $n$-th plateau is estimated via $\lambda_f = \sqrt{\frac{2}{\pi \varepsilon_{TG} \Delta V_{TG,n} / e}}$, $\varepsilon_{TG}$ is the top gate capacitance per unit area, extracted from the slope of the position of the $\nu = 4$ plateau in top gate voltage against magnetic field (Fig. 7.3b). $\Delta V_{TG,n}$ is the difference between the top gate voltage in the middle of the $n$-th plateau and the top gate voltage at charge neutrality.
Chapter 7. Gate defined confinement in bilayer graphene - hexagonal boron nitride hybrid devices

Figure 7.3: (a) Conductance versus TG1 and TG2 voltage for device B at different magnetic fields (see legend, $T = 440$ mK, $V_{bias} = 150 \mu$V, $V_{bg} = -49.74$ V, $V_{PG}$ and $V_{T3G3} = 5$ V). The inset shows as a function of magnetic field the background resistances that we subtracted (solid green line) and the two-terminal resistance with all top gates at ground (dashed blue line, measured at $V_{bias} = 500 \mu$V). In the low field regime the background resistance was determined by aligning the plateaus near $G = 4e^2/h$ and in the high field regime by aligning the plateaus near $G = 8e^2/h$ (b) Extracted top gate voltages at the plateau centres versus magnetic field. By fitting a linear curve to the large field data we obtain $C_{TG1\&2} = \frac{4e^2}{h} \frac{dB}{dV_{TG,\nu=4}} \sim 1.04$ F/m$^2$. The value for $C_{TG1\&2}$ extracted from the $\nu = 8$ data is very similar.

sequence of steps was observed for device A (see the supplementary information Fig. 2b). In device B, a less well developed feature can be seen just below $G = 3e^2/h$, which does not appear in device A. This feature suggests that despite the encapsulation in hBN and the overall cleanliness of the pinch-off characteristics, there is some residual disorder. This analysis of the data suggests transport through two-fold degenerate one-dimensional ballistic channels and the formation of a quantum point contact.$^{[43, 44]}$

The $2e^2/h$ steps in conductance, also reported in ref. $^{[108]}$, are surprising given that there is both spin and valley degeneracy in bulk bilayer graphene, which would give $4e^2/h$ steps. What mechanism lifts the degeneracy is an open question that calls for further exploration. Increasing the temperature to 440 mK did not change the general behavior. Lowering the bias to 50 $\mu$V (lock-in measurement with an AC excitation of 10 $\mu$V) did not change the appearance of the plateaus either. Both a larger bias and a higher temperature smoothened out aperiodic conductance fluctuations, as can be expected.

We can estimate the width of the constriction from the position of the plateaus in top gate voltage with respect to the conductance minimum (Fig. 7.2). We see that as subbands become occupied, the width of the constriction increases from $W_1 \approx 90$ nm to $W_3 \approx 120$ nm for device A and from $W_1 \approx 80$ to $W_3 \approx 160$ nm for device B, which is characteristic of a smooth confining potential (with $W_n$ the constriction width for the $n$-th subband). The lithographically defined separation between the respective top gates was less than 30 nm for both devices. This implies that the channel extends below the top gates, which can be expected given the modest band gap induced underneath.
7.4 Two barriers: Coulomb blockade

When we induce two barriers by appropriate gate voltages, the device behaviour changes drastically. Fig. 7.4 shows a gate voltage scan of TG2 while TG1 and TG3 are also biased (device A). We see sharp conductance peaks separated by regions of strongly suppressed conductance, which is characteristic of Coulomb blockade. As expected for Coulomb peaks, their position on one gate voltage axis varies smoothly (linearly) when another gate voltage is swept (Fig. 7.5a). We note that the resistance in Coulomb blockade is orders of magnitude larger than the sum of the two barrier resistances, which saturates around $h/e^2$ (Fig. 7.2), indicating each gate couples to both barriers. Coulomb blockade is confirmed further by the diamond-shaped regions of suppressed conductance seen in a color plot of conductance versus gate voltage and bias voltage (Fig. 7.4b).

The Coulomb peak spacing exhibits a standard deviation of 1.4 mV, compared to an average peak spacing of 4 mV (device B). Irregular peak spacings can, in principle, originate from quantized level spacing contributions. However, no excited state
Chapter 7. Gate defined confinement in bilayer graphene - hexagonal boron nitride hybrid devices

Figure 7.5: (a) Current plotted in color scale versus the voltage applied to PG and TG3 (device B, \( V_{TG1&2} = 10.2548 \text{V}, V_{BG} = -49.38 \text{V} \) and \( V_{bias} = 50 \mu\text{V} \)). Occasionally shifts occur such as the one at \( V_{PG} \sim 10.4835 \text{ V} \), which we attribute to a rearrangement of background charges in the substrate. (b) Zoom-in on a conductance peak plotted on a logarithmic scale along with fits by a Lorentzian and hyperbolic cosine function (device B, \( V_{TG1&2} = 10.1907 \text{ V}, V_{PG} = 10.3880 \text{ V}, V_{BG} = -49.86 \text{ V} \) and \( V_{bias} = 50 \mu\text{V} \)). Fit formulas are

\[
G \propto \cosh^{-2} \left( \alpha \frac{V_{TG} - V_{TG,offset}}{2.5kT} \right) \quad \text{where} \quad \alpha = \frac{2E_c}{\Delta V_{TG}} \quad \text{(the factor 2.5 assumes temperature exceeds level spacing)}
\]

and

\[
G \propto \Gamma \left( \alpha \frac{V_{TG} - V_{TG,offset}}{\hbar} \right)^2 + \left( \Gamma / 2 \right)^2,
\]

where \( \Gamma \) is the coupling strength to the leads.

features are visible in the Coulomb diamonds so it is not clear that level spacing is responsible for the peak spacing variation. Instead the reason may be the breakdown of the constant-interaction model, for instance due to disorder-induced variations in the island size or position as charge carriers are added one by one, or a second island capacitively coupled to the main island.

From the Coulomb diamonds and peak spacing we can obtain information on the dimensions and location of the island. For the dataset of Fig. 7.4b (device A), the addition energy \( E_{add} \) is \( 0.35 \pm 0.02 \text{ meV} \). When we neglect orbital energies, \( E_{add} = 2E_c \), where \( E_c \) is the charging energy. Using \( E_c = \frac{q^2}{2C} \), we can calculate the total capacitance of the dot, \( C_\Sigma = 0.46 \pm 0.03 \text{ fF} \). From the slope of the Coulomb diamond edges, we find that \( C_\Sigma \) is dominated by the source and drain capacitances \( (C_s = 0.10 \pm 0.024 \text{ fF}, C_d = 0.30 \pm 0.033 \text{ fF}) \), which makes it difficult to estimate the island size from \( E_{add} \) and \( C_\Sigma \).

Instead, we compare the measured top gate capacitances with top gate capacitances simulated using a 3D Poisson equation solver (Ansoft Maxwell). From the average Coulomb peak spacing \( \Delta V_{TG2} \) we extract a capacitance \( C_{TG2} \sim 45 \text{ aF} \). \( C_{TG3}, C_{TG1} \) and \( C_{PG} \) are comparable. The calculated capacitance between a circular island of 320 nm in diameter and a metal plate with a 320 nm hole, 50 nm above the island, is 40 aF, about as large as each measured top gate capacitance by itself. We thus infer that the island is formed in the central region uncovered by the top gates and extends underneath all the gates. This is consistent with the quantum point contacts extending underneath the split gates as discussed above (see also [108]). Presumably lateral confinement is less tight in these devices than in GaAs split gate devices, due to the much smaller band gap.

Finally, we investigate whether the dot is weakly or strongly tunnel coupled to the leads by inspecting the line shape of the Coulomb peaks at low bias voltage.
In Fig. 7.5b, we overlay on the data a fit by a hyperbolic cosine function and by a Lorentzian function. The former fits the data much better, indicating that the dot is in the weakly coupled regime, where temperature determines the linewidth rather than tunnel coupling to the reservoirs. Doing the same analysis for 50 peaks we find that they are consistently in the weakly coupled regime. We extract an electron temperature of 69 ± 14 mK.

7.5 Conclusion

Concluding, we developed a new bilayer graphene device platform for electrostatic confinement based on hBN top and bottom gate dielectrics. Transport through a single-barrier device shows clean pinch-off characteristics with signs of conductance quantization. In double-barrier devices clear Coulomb blockade is observed. These first results invite further development of this new platform. The question can be addressed how electron-electron interactions, electron-phonon interactions, and spin and valley lifetimes in graphene are modified by the confinement. Moreover, this double-gated device structure can be used to explore the nature of the electric field induced bandgap in clean bilayer graphene and the broken symmetry states at zero magnetic and electric field. Further development of this technology by adding local bottom gates will open the way to create topological confinement in bilayer graphene.
Anomalous insulating state in bilayer graphene sandwiched in hBN


We report on an anomalous insulating state in bilayer graphene sandwiched in between hexagonal boron nitride flakes. This state can be lifted by applying a perpendicular displacement field of $\sim \pm 140$ mV/nm to the bilayer graphene. Moreover there is a finite intrinsic electric field of about $\sim |60|$ mV/nm present in the hexagonal boron nitride / bilayer graphene / hexagonal boron nitride system. We discuss several explanations for the observed effects: interactions, strain and Moiré pattern formation.
Chapter 8. Anomalous insulating state in bilayer graphene sandwiched in hBN

8.1 Introduction

Bilayer graphene is a special two-dimensional system. It is gapless like single layer graphene, but its charge carriers are massive due to the parabolic dispersion relation. By applying a transverse displacement field the layer symmetry breaks and a band gap opens. The magnitude of the band gap increases with displacement field. This band gap induces an insulating state that was observed in electrical transport measurements. Also in the absence of an external displacement field a gap can be opened in bilayer graphene by applying mechanical strain to both layers.

Recently an insulating state at zero electric and magnetic field has been observed in suspended bilayer graphene samples. The effect is interpreted as a manifestation of gap opening due to charge carrier interactions that occur in high electronic quality samples.

In this chapter we report on insulating state measurements in high quality bilayer graphene sandwiched between hexagonal boron nitride (hBN) flakes. By applying a transverse electric field the conventional layer symmetry breaking induced band gap opens. Moreover, we observed a finite intrinsic electric field in the system and an anomalous insulating state that lifts by applying a finite transverse electric field.

8.2 Fabrication

The anomalous insulating state was observed in two different samples. Sample 1 was made by depositing a bilayer graphene on hBN \( d_{hBN,bottom} = 16 \text{ nm} \), on a p++ Si wafer with \( d_{SiO_x} = 285 \text{ nm} \) thermal silicon oxide (SiO\(_x\)) with the standard dry transfer technique (see chapter 5). After the transfer we annealed the sample at 400 °C and defined 100 nm thick Cr/Au contacts with electron beam lithography (EBL), followed by electron beam (e-beam) evaporation and lift-off. With EBL and oxygen plasma etching we carved out a channel of 1 \( \mu \text{m} \) wide and 4.7 \( \mu \text{m} \) long. We annealed the sample in air at 305 °C to remove a film of residue that was left on the chip after etching. Then the sample was subjected to another annealing step in forming gas at 330 °C and a mechanical cleaning step. We transferred another hBN flake \( (d_{hBN,top} = 20 \text{ nm}) \) on top of the graphene channel to serve as top gate dielectric. Then we defined 15 nm thick Cr/Au top gates with EBL and electron beam evaporation and finished the sample by connecting the top gates with 100 nm thick Cr/Au leads. An optical microscope picture of the device is shown in Fig. 8.1a. An AFM picture of the top gate structure used for measurements is in Fig. 8.1b. Sample 1 has a mobility of at least 10,000 cm\(^2\) V\(^{-1}\)s\(^{-1}\) at \( T = 35 \text{ mK} \). This is a lower bound because the measurement was performed in 2 terminal geometry with a contact resistance of at least 10 kΩ. Sample 2 has undergone similar processing steps as sample 1. On top of the SiO\(_x\) was a 20 nm Al\(_2\)O\(_3\) layer deposited by atomic layer deposition to prevent back gate leakage. The bottom hBN is 35 nm thick, the top gate hBN is 50.5 nm thick and the graphene channel was 1.3 \( \mu \text{m} \) wide and 13.5 \( \mu \text{m} \) long. The cleaning steps after the contacts were finished differ from the steps taken for sample 1. Sample 2 underwent a mechanical cleaning step, annealing at 300 °C and another mechanical cleaning step. The mobility of the sample at \( T= 4 \text{ K} \) was \( \sim 17,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \).
8.3 Anomalous insulating state

Figure 8.1: a) Optical microscope image at 100x magnification of sample 1. The large blue area is the top gate flake. The flake covers everything including the contacts. The arrows indicate the position of the graphene channel. There are two ‘quantum dot’ top gate structures in this device. The yellow lines are contacts and gates. Note that there is also a hall bar device next to the channel. b) TM AFM voltage error image of the upper top gate structure in panel a. The z-scale is 100 mV. c) Optical microscope image at 100x magnification of sample 2. The yellow area in the middle is the top gate hBN flake that covers almost the entire graphene channel indicated by the arrows. On top of the contacts the flake has a different color due to different interference. The light blue area is the bottom hBN flake. The yellow lines are contacts and gates. There are two ‘quantum dot’ top gate structures in this device. d) TM AFM voltage error image of the lower top gate structure in panel c. The z-scale is 100 mV.

\[ \text{cm}^2 \, \text{V}^{-1} \text{s}^{-1} \], measured in 4 terminal geometry DC with \( I_{\text{bias}} = 50 \text{nA} \). Note that the top gate flake does not entirely encapsulate the graphene channel: underneath the hBN top gate dielectric the electronic mobility might be much higher.

8.3 Anomalous insulating state

In Fig. 8.2a, we show a measurement at \( T = 35 \text{ mK} \) of resistance as a function of top gate and back gate voltage for sample 1. The diagonal ridge is where the charge carrier density goes to 0. In Fig. 8.2b, we show a linecut along this diagonal. The axis is converted to displacement field induced by back gate and top gate:

\[
D_{\text{gates}}/\epsilon_0 = V_{BG}/(\frac{d_{\text{SiOx}}}{\epsilon_{r, \text{SiOx}}} + \frac{d_{\text{hBN, bottom}}}{\epsilon_{r, \text{hBN}}}) + \epsilon_{r, \text{hBN}} V_{TG}/d_{\text{hBN, top}}. \tag{8.1}
\]
Figure 8.2: Measurements for the 'quantum dot' device in Fig. 8.1c and d. a) Resistance against back gate and the voltage on all top gates (2-terminal measurement, \( V_{\text{bias}} = 1 \) mV, \( T = 35 \) mK). The data has been corrected for the influence of the regions uncovered by the top gate. This is done by subtracting the resistance measured at \( V_{TGS} = 2V \) for positive \( V_{BG} \) and at \( V_{TGS} = -2V \) for negative \( V_{BG} \). b) Linecut along the charge carrier density neutral diagonal. c) Zoom-in on the peak at 0 displacement field (2-terminal measurement, \( V_{\text{bias}} = 1 \) mV, \( T = 35 \) mK). This plot has not been corrected for background resistance. The dashed pink and blue lines are the linecuts shown in panel d. d) Linecuts at \( V_{TG} = 4.1 \) V (pink) and \( V_{TG} = 9.0 \) V (blue) in panel c.

\( \varepsilon_{r,\text{SiO}_x} = 3.9 \) and \( \varepsilon_{r,\text{hBN}} = 3.0 \), extracted from Fig. 8.2a). We assumed parallel plate capacitors for this calculation.

The increase of resistance with displacement field due to broken layer symmetry is apparent at large field values. Surprisingly, a peak with a resistance that can be as large as 80 kΩ appears at \( V_{BG} = 4.1 \) V and \( V_{TG} = -0.55 \) V. The peak crosses over at \( \sim \pm 140 \) mV/nm (relative to the center of the peak) to the broken layer symmetry regime. In Fig. 8.2c we zoom in on the large peak. The FWHM in density is 3.2 \( \cdot 10^{10} \) cm\(^{-2}\). Assuming the parabolic dispersion relation of bilayer graphene (\( \hbar^2k^2/2m^* \), \( m^* = \gamma_1/2v^2 = 0.035m_0 \) [123]) we convert the width into an energy scale of 1.1 meV. We did not investigate this sample more as the insulating state suddenly disappeared after a sweep of the back gate over a range of 20 V.

In sample 2 we observed the same anomalous insulating state at 4 K. In Fig. 8.3a we show a measurement of the resistance as a function of back gate and top gate voltage. As expected the resistance increases when the displacement field increases. In a later measurement, Fig. 8.3b, a peak of about 40 kΩ occurs along the diagonal, centered at \( V_{BG} = -12.7 \) V and \( V_{TG} = 2.45 \) V. The peak disappears at a displacement field
8.3. Anomalous insulating state

Figure 8.3: Measurements for sample 2. We use the same labeling for the gates as in Fig. 8.1. a) Resistance against back gate and the voltage on all top gates (4-terminal measurement, \(I_{\text{bias}} = 50\, \text{nA}, 0.7\, \text{K} < T < 4\, \text{K}\)). The data has been corrected for the influence of the regions uncovered by the top gate. This is done by subtracting the resistance at \(V_{TG} = 3.5\, \text{V}\) for positive \(V_{BG}\) and at \(V_{TG} = -3.5\, \text{V}\) for negative \(V_{BG}\). b) Differential resistance against back gate voltage and the voltage on top gates TG1 and TG2 (4-terminal lock-in measurement, \(I_{\text{exc}} = 2\, \text{nA}, T = 4\, \text{K}, V_{TG3} = V_{TG4} = 0\, \text{V}\)). The data has been corrected for the influence of the regions uncovered by the top gate. c) Differential resistance against back gate voltage and the voltage on top gates TG1 and TG2 (4-terminal lock-in measurement, \(I_{\text{exc}} = 2\, \text{nA}, T = 4\, \text{K}, V_{TG3} = V_{TG4} = 0\, \text{V}\)). The data has not been corrected for the influence of the regions uncovered by the top gate. d) Plot of conductance against perpendicular electric field and density adapted from ref. [120] for comparison. (\(T = 300\, \text{mK}, \text{scale bar unit is } \mu\text{S}\))

of \(\sim 140 \text{ mV/nm}\) (for the calculation we used a similar equation to equation [8.1] with values \(\epsilon_{r, SiO_x} = 3.9\) and \(\epsilon_{r, hBN} = 3.9\), extracted from Fig. 8.3). This value could not be extracted unambiguously because the layer symmetry breaking is not visible in the gate range of Fig. 8.3b. Moreover, the diagonal line is not entirely straight. The full width half maximum of the peak is \(3.4 \cdot 10^{10}\, \text{cm}^{-2}\). This width converts into an energy scale of \(1.2\, \text{meV}\). After a sweep of the magnetic field to \(10\, \text{T}\) the anomalous insulating state disappeared or shifted. The data in Fig. 8.3 is the result. It shows in the negative back gate direction the expected increase in resistance with displacement field. In the positive back gate direction there is no increase in resistance. We have observed the disappearance of the band gap opening in one displacement field direction in other double gated bilayer graphene devices. Currently we do not understand this
Chapter 8. Anomalous insulating state in bilayer graphene sandwiched in hBN

In two samples we have observed an anomalous insulating state at small displacement fields and low charge carrier densities. The data in Fig. 8.2a and Fig. 8.3 are very similar to measurements in double gated suspended bilayer graphene devices. For comparison we inserted a typical measurement that shows an insulating state at low density and displacement field (Fig. 8.3b). In the paper by Weitz et al. a crossover field of 20 mV/nm and a maximum resistance of 30 kΩ at T = 100 mK were observed. In suspended bilayer graphene the displacement field is the same as the electric field as dielectrics are absent. In the paper by Velasco Jr. et al. the crossover field was 15 mV/nm and the maximum resistance 50 kΩ at T = 300 mK. From temperature dependent measurements and transport spectroscopy a gap of ~2 meV was extracted. In different experiments on suspended graphene, with only a back gate present, transport spectroscopy revealed a gap of 2.5 meV and temperature dependent measurements a thermal activation gap of 0.33 meV. The observed effects are interpreted as interactions between charge carriers that forces them in a broken symmetry state. These broken symmetry states are characterized by an order parameter. When the order parameter is in the bilayer graphene plane a gapless nematic phase is predicted. However, when this order parameter is out of plane a gap spontaneously opens. In this case there are four non-trivially different states: quantum anomalous hall, quantum spin hall, layer antiferromagnetic and charge layer polarized (quantum valley hall) state. The first three states involve no net layer charge polarization so are most likely to be the ground state. It is still debated which of the three states describes the measurements in the literature best. In section 8.5 we will compare our measurements to the literature on these special broken symmetry states.

8.4 Bias spectroscopy and magnetic field dependence

We further investigate the anomalous insulating state by performing bias spectroscopy on sample 2. In Fig. 8.4 we see a clear differential resistance peak in the bias dependence for $D/\epsilon_0 = 0$. With increasing displacement field the peak broadens and diminishes. The maximum differential resistance is 25 kΩ which is lower than for the measurement in Fig. 8.3b. We do not have an explanation for this decrease. An interesting feature develops for negative displacement fields. The peak in resistance splits into two. The same effect can be observed in the measurements of Freitag et al. shown in Fig. 8.4c. The feature remains to be explained. We did not record the voltage the current source supplied to the sample, so we cannot convert the current bias axis to an energy axis. When we compare these spectroscopic measurements to refs. and we note that our data lacks a shoulder.

In Fig. 8.5 we show bias spectroscopy sweeps for parallel magnetic fields from 0 T to 10 T in a small displacement field of 6.3 mV/nm. There is no magnetic field dependence except for a small increase with field near zero source-drain bias. This is in agreement with ref. However, in a small decrease in resistance was observed for increasing parallel field.
8.5 Discussion and outlook

Summarizing, we have observed an anomalous insulating state with resistances of 25-80 kΩ for displacement fields lower than $|140| \text{ mV/nm}$ and carrier densities less than $|4| \cdot 10^{10} \text{ cm}^{-2}$. From nonlinearities in spectroscopic measurements we can deduce...
that the state has a gap-like nature. In a parallel magnetic field the behaviour of the system did not change significantly. To our knowledge there have been no earlier reports of this behaviour for bilayer graphene sandwiched in between hBN flakes.

The FWHM in charge carrier density for both samples is less than $4 \cdot 10^{10}$ cm$^{-2}$. Thus the effect will be less visible in samples with large electron hole puddle fluctuations such as bilayer graphene on SiO$_x$. These low charge carrier densities also mean that the origin of the anomalous insulating state has to be explained by the low energy electronic band structure of bilayer graphene. Now we will discuss different scenarios that could explain our observations.

A first observation in both samples is that the anomalous insulating state peak does not center around $D_{\text{gates}}/\epsilon_0 = 0$ (see Fig. 8.2b and Fig. 8.3b). For sample 1 it is displaced to $D_{\text{gates}}/\epsilon_0 = D_{\text{off}}/\epsilon_0 = \sim 60$ mV/nm and for sample 2 to $D_{\text{gates}}/\epsilon_0 = D_{\text{off}}/\epsilon_0 = \sim -60$ mV/nm. Moreover, the residual doping of the samples is zero as can be inferred from the diagonal going through $V_{TG}, V_{BG} \sim 0$. The analysis in section 2.3 and Fig. 2.3 leads us to the conclusion that both samples have a finite intrinsic electric field built into the device. On top of this effect there is the anomalous insulating state that can be lifted with external fields of either polarity.

First we try to explain the finite intrinsic electric field. An external displacement field induced by two layers of oppositely charged impurities such as in Fig. 2.4f could explain the displacement of the center of the peak to finite field. The fact that our samples have a high electronic quality rules out the possibility that the external displacement field is induced by charged impurities. The presence of those impurities would significantly reduce charge carrier mobility. Moreover the measured charge density inhomogeneity is much lower than what is expected from charged impurities that induce a field of 60 mV/nm. We estimate that the charged impurities induce a charge carrier inhomogeneity of roughly the same magnitude as the charged impurity density. A field of 60 mV/nm converts to a charged impurity density of $\sim 3 \cdot 10^{11}$ cm$^{-2}$. The measured charge inhomogeneity of our samples is on the order of $10^{10}$ cm$^{-2}$ which is more than an order of magnitude lower. An alternative explanation would be homogeneous strain. Homogeneous strain with different strengths applied to each layer of bernal stacked bilayer graphene generates transverse electric fields across the two layers and opens a band gap. Our samples consist of bilayer graphene sandwiched in between hBN flakes with most likely different crystal orientations. The lattice mismatch between graphene and hBN is approximately 1.8% [127]. When all the carbon atoms would align on the boron and nitrogen atoms, an anisotropic homogeneous strain on each layer would be present. A simple estimate of the potential difference of the two layers by calculating $c_0 \cdot D_{\text{off}} = 0.335 \cdot 60 \sim 20$ mV is in agreement with the potential difference reported in ref. [117] for a strain of 1%. Raman spectroscopy might detect whether strain is present in the bilayer spectrum. Another method to detect strain is surface probe microscopy: deeper analysis of scanning tunneling microscopy measurements might prove that monolayer graphene on hBN is slightly strained. Here we would like to note that in these scanning tunneling measurements no band gap in monolayer graphene was found to open due to the commensurate alignment of the sublattices with the boron and nitrogen atoms in the substrate.

From now we focus on the anomalous insulating state. The general behaviour of our samples as a function of displacement field and carrier density is very similar to
measurements in suspended bilayer graphene where a spontaneous gap was observed that was interpreted as a many body interaction effect. The values of maximum resistance are in the same ballpark as references [114, 120, 121]. The data on sample 2 shows a maximum resistance of $\sim \frac{h}{e^2}$, so we cannot exclude the formation of an edge channel. [120, 121] The carrier density regime for which the effect appears in our measurements is larger than the $< 10^{10}$ cm$^{-2}$ values reported in literature. [114, 130] According to ref. [130] a density of $1.42 \cdot 10^{10}$ cm$^{-2}$ is even an upper limit depending only on the interaction strength. A measure of the interaction strength is the Wigner-Seitz radius. It gives the ratio of the average Coulomb energy ($E_C$) and Fermi energy ($E_F$): 

$$r_s = \frac{E_C}{E_F} = \frac{e^2}{\hbar^2 \pi n / 2m^*}, \quad (8.2)$$

where $r_{cc}$ is the average distance between charge carriers in the system: $r_{cc} = 1/\sqrt{\pi n}$.

The interaction strength is inversely proportional to the relative dielectric constant of the system. For our samples the graphene is embedded in hBN so the effective dielectric constant felt by the charge carriers is larger and hence the interaction strength is expected to be reduced. Thus we expect interaction effects to be only visible at even lower densities than for suspended samples. Another difference with the literature is the magnitude of the displacement field that breaks the insulating state. It is an order of magnitude larger for our samples.

Another explanation for the anomalous insulating state would be layers of oppositely charged impurities in bottom and top gate dielectric that change sign in different regions of the dielectrics (see Fig. 5.5b). [41] In other words, the sign of the displacement field ($D_{imp}$) depends on the position in the graphene layer. $D_{gates}$ of either sign then diminishes the net field over the graphene ($D_{GR}$) in half of the regions and increases $D_{GR}$ in the other half. Modeling the system with parallel resistors gives a total sample resistance that is lower for increasing $D_{gates}$ (when $D_{gates} < D_{imp}$). For $D_{gates} > D_{imp}$ a band gap with the same sign opens in all regions. Charged impurities are most likely not the the cause of this alternating electric field, again because the charge density inhomogeneity in our samples is too low (see reasoning above). Still the model with charged impurities provides a useful intuitive picture for the possible explanations we are going to describe in the next two paragraphs.

The first scenario we would like to focus on is the case of inhomogeneous strain. Homogeneous strain causes a transverse electric field in one direction. We speculate that inhomogeneous strain can generate fields in both directions. Recently Gorbachev et al. reported Coulomb drag measurements on two layers of graphene with a hBN spacer in between. [132] Explaining their observations, the authors speculate that their charge inhomogeneity (e-h puddles) has a predominantly non-electrostatic origin, that is, due to random strain. [133] For a distance between the two graphene layers that is much smaller than the e-h puddle diameter, the Coulomb interaction is much larger than the strain energy and anticorrelations between e-h puddles in different layers appear. That is, e(h)-puddles in one layer appear on top of h(e) puddles in the other. The samples of Gorbachev et al. are very much like our samples in the sense that the two single layers of graphene are in randomly oriented contact with a different hBN...
surface. Hence our samples might also exhibit e-h puddles due to random strain in different layers that would induce an electric field and thus induce a band gap. Unlike in the homogeneous strain case, this electric field would be alternating in sign.

As a last scenario, we propose the formation of a Moiré pattern as the cause of the anomalous insulating state. In ref. [134] a Moiré pattern is observed when a single layer of graphene is placed on top of hBN with a finite orientation angle between the two crystals. This Moiré is essentially a periodic potential. Our bilayer graphene is sandwiched in between two differently oriented hBN flakes, so two different Moiré patterns will be induced. It is very likely that areas in one layer with a positive induced potential occur on top of areas in the other layer with a negative induced potential. Consequently the sign of the electric field will alternate.

We have presented several scenarios for the anomalous insulating state: interaction effects, strain and Moiré pattern formation. At present we cannot rule out any of the explanations. We must stress that the effect we observed was fragile. In sample 1 it disappeared after sweeping the gates and in sample 2 it appeared after warming up from 20 mK to 4 K and suddenly disappeared after sweeping the magnetic field. When a stable sample is found further measurements can be done to pin down the nature of the anomalous insulating state. Temperature dependence and behaviour in perpendicular magnetic field are most needed at this stage. Temperature dependence would give insight in the energy scale of the insulating state. The behaviour in parallel magnetic field could give more information on possible many body interaction effects. To explore the strain and Moiré scenarios a local spectroscopy experiment like in refs. [41, 134] could prove very useful.
CHAPTER 9

Reflection and Outlook

The purpose of this chapter is to put the work presented in this thesis in a broader perspective. I will briefly review the work and reflect on the steps I took to realize my goals. On the way I will compare my results with the rest of the field and make recommendations for follow-up experiments in the near future. The last part I devote to explain my view on the far future of confinement in graphene and graphene research in general.

In the introduction I formulated the goal of this thesis as follows: I want to study the properties of confined quasiparticles in bilayer graphene (BLG). To reach this goal I first needed to make a device that confines quasiparticles.

9.1 Device platform

Making a confinement device in bilayer graphene required to accomplish three milestones: 1) create a bandgap in graphene 2) realize devices with the required electronic quality 3) create a confined region by using electrostatic gates.

Opening a gap in graphene can be realized in two practical ways: size confinement (i.e. nanopatterning) or applying a transverse electric field to bilayer graphene. Nanopatterning graphene has proven to be a very fruitful approach. Nanopatterned graphene nanoribbons and quantum dots have been studied intensively and generated many interesting insights in low dimensional graphene systems. A good review on transport in graphene nanostructures on SiO$_2$ is written by T. Ihn et al.[135] I regard the experiments of J. Güttinger et al. that observed spin states and signs of the electron-hole crossover in an etched graphene dot as the top achievements in this field.[17, 136] Unfortunately due to edge roughness the device behaviour was rather irregular. Even when the nanopatterned graphene devices were made on clean hBN substrates their behaviour was dominated by edge-roughness induced puddles.[137] Unzipping a carbon nanotube into a graphene nanoribbon proved to be a better strategy to obtain clean edges and a device based on this technique showed two-fold shell filling.[106] The first observation of quantized conductance in graphene was realized in a suspended graphene sheet that was narrowed to a width for
which \( k_F W \sim 1 \). I opted for the approach that allows more design flexibility and device tunability: bilayer graphene with a band gap induced by an external electric field. In chapter 2 I describe the underlying physical mechanism and in chapter 3 how this can be converted in device designs for quantum point contacts and quantum dots. In chapter 4 I reproduce the results of J. Oostinga et al. and prove that the induced band gap leads to an insulating state in bilayer graphene. My data is very comparable to ref. [28] so transport in these double gated SiO\(_x\)/BLG/SiO\(_x\) is most likely governed by midgap states. I reached milestone 1.

From the data on doping and mobility in chapter 4 and the considerations on device design in section 3.2 I had to conclude that we would not observe quantized conductance in a SiO\(_x\)/BLG/SiO\(_x\) split gate device. An electrostatic SiO\(_x\)/BLG/SiO\(_x\) quantum dot would have more chance of success as the carriers are confined very locally. We tried this approach but failed. The electron-hole puddles were probably too small (\( \sim 20 \text{ nm} \)) so that a proper barrier could not be formed. Measurements by S. Dröscher et al. showed that replacing one of the dielectrics with a clean dielectric such as hBN or vacuum is not enough to increase the quality of electrostatic confinement devices. It was necessary to move away from SiO\(_x\) to reach milestone 2.

In 2009 I developed a recipe for fabricating double gated suspended bilayer graphene devices in the group of Prof. dr. P. Kim at Columbia university (see Fig. 1.1). Initial measurements were disappointing mainly because of a leaking suspended top gate. However, Allen et al. proved that the suspended device technology can be successful to create confinement in bilayer graphene. From my trials I learned that in practice measurement of suspended devices is difficult. A low-yield current annealing step is necessary to obtain high electronic quality in suspended devices. Moreover suspended devices are prone to collapse due to electrostatic forces induced by the gates. These two disadvantages together with the fact that the suspended graphene platform would severely reduce design freedom pushed me to adopt a new approach: sandwiching graphene in between hBN flakes. Chapter 5 describes the transfer technique that was necessary to make these devices. In chapter 6 I describe and analyse the bubbles and wrinkles that occur after transferring bilayer graphene on top of an hBN flake. For the confinement devices that we were going to make, the bubbles and wrinkles were not limiting. It was the cleanliness of the graphene. It was impossible for us to obtain clean graphene by annealing or chemical cleaning methods after the contacts to graphene were fabricated. I developed a new and effective cleaning technique, named mechanical cleaning, to clean graphene on hBN devices. This was the key to obtain high mobility, low doping bilayer graphene: milestone 2 accomplished.

Chapter 7 describes how I reached milestone 3. I observed signs of electrostatic confinement induced quantized conductance in steps of \( 2e^2/h \) and Coulomb blockade. Having reached milestone 3 gives me the opportunity to evaluate the choices that I made in reaching milestones 1 and 2. First I want to ask the question if electrostatic confinement proved to be better than size confinement. Both a nanopatterned one-dimensional channel and electrostatic one-dimensional channels (supplementary of ref. 108 and chapter 7) showed quantized conductance in steps of \( 2e^2/h \) with roughly similar data quality (similar number of steps observed, crossover to QHE). In our electrostatically defined QPC’s we were not able to perform proper spectroscopic measurements (which was possible in the nanopatterned channel), since the
insulating regions underneath the split gates start conducting at higher bias. For the measurements on the quantum dot device we are still far behind the mature field of nanopatterned quantum dots. The only confinement effect observed in electrostatic confinement devices is Coulomb blockade ([108] and chapter 7). Concluding, at this stage of research electrostatic confinement has not proven to be better than size confinement.

On the road towards milestone 2 I chose for a hBN/BLG/hBN sandwich over suspended bilayer graphene. I already motivated this by mentioning the cumbersome processing and handling of suspended devices. Comparing our results to those of Allen et al. we cannot judge which platform provided better results. Current electrostatic devices show switching events due to nearby charges or coupled nearby dots accidentally formed underneath the gates ([108] and chapter 7). The barriers still show resonances as well. Finally, confinement is weak so the dots are large (∼400 nm) and the dots did not show orbital confinement.

I have to assess the future potential of our device platform to make a fair final judgement. For that I will first evaluate how current limitations can be overcome. The instabilities in device operation and weak confinement are problems that can be solved. A larger induced band gap will eliminate dots underneath the gates and will remove resonances in the barriers. Moreover a larger gap will decrease the size of the dot and thus give stronger confinement. A larger gap is feasible since a recent explorative experiment showed that depositing a layer of atomic layer deposition Al₂O₃ on top of the SiOₓ layer helps avoiding gate leakage. Before we were always limited by gate leakage at displacement fields of ∼ 0.6 V/nm. Still I want to take improvements a step further and propose a dramatically new device design. For future electrostatic bilayer graphene devices it is best to vertically flip the device geometry. We start out with a Si/SiOₓ wafer. On top of this wafer we deposit the fine gates (with QPC and quantum dot structures) and transfer an hBN flake. Then we transfer the bilayer graphene and fabricate ohmic contacts. We encapsulate the device with another hBN flake and deposit a global gate over the entire device. The improvements will be twofold. First the dielectrics will be of high quality as they consist of just hBN flakes without the unstable, leaky SiOₓ layer underneath. Second it will improve the yield in fabrication as the critical step of fabricating the fine gates will be done first.

Now I have come to the point where I want to make a final recommendation on which platform to use. I have argued that the limitations of the electrostatic confinement hBN/BLG/hBN can be overcome by adopting a vertically flipped device design. The advantage of the flexibility of our platform we have already proven by measuring both quantized conductance and a quantum dot with one set of gates (see Fig. 3.1b,c). The potential of our platform is great because we can easily scale up our system to more quantum dots. In principle we can adopt all device structures and measurements on GaAs 2DEG lateral quantum dots for our platform. I would advise all research groups to take up hBN/BLG/hBN electrostatic confinement devices for future quantum confinement measurements in graphene.
9.2 Confinement of bilayer graphene quasiparticles

What did we learn about the properties of confined quasiparticles in graphene? First I will discuss the quasiparticles that flow through a one-dimensional quantum point contact. As described in chapter 7, we observed signs of quantized conductance in steps of $2e^2/h$. This is surprising as the degeneracy of bilayer graphene is fourfold. This observation calls for further exploration. The first question to be answered is if the spin or valley degeneracy is broken. For a device designed to answer this question I recommend to use dedicated QPC split gate structures to avoid resonances caused by nearby gates. The split gates should be farther away at their apexes so that more modes fit in the channel and more steps in conductance can be observed. It is also highly desirable to have two voltage probes located close to the one-dimensional channel to minimize background resistance. A first follow-up measurement is to reproduce quantized conductance and investigate how a parallel magnetic field affects the behaviour of the QPCs. In the supplementary information of [108], steps of $1e^2/h$ occur in QPC data in a parallel magnetic field. This suggests that the valley degeneracy was lifted in zero magnetic field. When it is known which degree of freedom has a broken symmetry in our device, the physical mechanism behind the splitting needs to be found.

Now I turn to reflect on the dot data. From the data on Coulomb blockade we have learned that the dot extends underneath the top gates. This is due to the small band gap that the gates have induced. Because of a small band gap the evanescent tail of the wave function can extend far in the gapped region. As we did not observe excited states, we could not extract other specific properties of bilayer graphene quasiparticles in quantum dots. The dot measured in chapter 7 had a diameter not larger than 400 nm. This diameter corresponds to a predicted level spacing of $\sim 30 \mu eV$ based on a constant bulk density of states. The smaller dot measured in chapter 7 has a larger predicted level spacing that is $\leq \sim 100 \mu eV$. As the addition energy observed was $\sim 300 \mu eV$ it is surprising that we did not observe the excited states given that the electron temperature was $\sim 72$ mK and we measured in the weakly coupled dot regime. In the paper by Allen et al. [108] no excited states were observed either. The question arises how the level spacing could decrease. An explanation could be the opening of the band gap in bilayer graphene. At the band edge an enhanced density of states occurs. As our dots are most likely operated in the low density regime, we are dealing with states at the band edge. The level spacing is in a first approximation inversely proportional to the density of states. A solution to this problem is counterintuitive: make a larger quantum dot gate design and measure with a larger back gate voltage. A larger dot will decrease the compensating action of the top gates so that the quasiparticle density in the middle of the dot is dominated by the back gate. Operating the dot with a larger back gate voltage has two positive consequences. First the band gap will be larger so the dot extends less in the low density area underneath the gates. Second the dot will be more doped and consequently operate away from the band edge in the constant density of states regime. S. Dröscher suggests in chapter 8 of her thesis to measure the stability diagram of the bilayer graphene quantum as a function of displacement field and density. The effect of the non-constant level spacing would be visible as a change in slope of the
Coulomb peak lines as a function of displacement field and density. Note that for nanopatterned bilayer graphene confinement devices the situation is different. They do not require a gap induced by layer symmetry breaking so the density of states in the material is constant and hence the level spacing is constant. In ref. [147] this constant level spacing was beautifully observed in a nanopatterned bilayer graphene double quantum dot.

The bipolar nature of the quasiparticles in bilayer graphene quantum dots still has to be observed. Similar to measurements in other small band gap systems as carbon nanotubes and InSb nanowires the stability diagram will show both electron and hole Coulomb-peak lines. From the distance in energy between the last electron Coulomb peak line and the last hole line the band gap can be extracted. Measuring the stability diagram as a function of density and displacement field should show the opening of the band gap and allow for quantification of the size of the gap as a function of displacement field. As this measurement probes local properties it would help to shed light on the discrepancy in observed gap size between transport measurements and optical measurements. For these measurements we have already adapted the quantum dot design in section 3.2b with a stronger coupling plunger gate as we show in Fig. 9.1.

In quantum dots the degeneracy of bilayer graphene quasiparticles can be observed in the so-called quantum dot shell filling. For a four-fold degeneracy this will show in a bias versus gate voltage measurement as one large diamond followed by three small diamonds that reflect the orbital filling with three more electrons before the next orbital has to be filled. Clean shell filling has never been observed in a bilayer graphene dot. The first signs of the degrees of freedom of bilayer graphene quasiparticles in a quantum dot were observed by Volk et al. [147] in a bilayer graphene double dot system. They measured interdot transition energy splittings on the order of the Zeeman splitting. The shifts occurred with a slope of $\pm 0.1 \text{ meV/T}$ corresponding to a g-factor of $\sim 2$. Here arises another possibility to explore a special feature of bilayer graphene. It is theoretically predicted that the Zeeman-splitting in bilayer graphene can be tuned by the interlayer potential difference. For a difference of 60 meV the g-factor increases to $\sim 8$. To conclude this section I would like to mention that measurements on the degrees of freedom of quasiparticles in a quantum dot can also help to interpret the quantized conductance steps of $2e^2/h$.

### 9.3 Bilayer graphene research

In the previous section I discussed electrostatic confinement measurements in bilayer graphene. I reflected on what I learned about the nature of the quasiparticles and I discussed natural follow-up experiments. Hopefully these experiments will be carried out in the near future. The outcome of the measurements will naturally pose new questions and guide the experiments on bilayer graphene confinement devices towards new discoveries. There are several directions that deserve to be actively pursued. 1) Investigate how the electron-phonon coupling in bilayer graphene is different in zero dimensions from two dimensions. 2) Measure the spin lifetime in a bilayer graphene quantum dot. With quantum information processing and spintronics as motivating applications it would be very useful to see that spin lifetimes in a quantum
dot are much longer than in two-dimensional bulk graphene. I should note here that the spinful nuclei of the boron and nitrogen atoms can be of detrimental influence on the spin lifetimes. 3) Investigate how the valley degree of freedom can be controlled independently from the spin degree of freedom. For making a spin/valley qubit it is necessary to lift respectively the valley/spin degeneracy.\[151\] In carbon nanotubes the two valleys lead to electronic orbits that encircle the nanotube circumference in a clockwise and anticlockwise fashion.\[152\] Hence the valley degree of freedom can be broken by a parallel magnetic field to the tube. In flat graphene there is not such a straightforward method. However, in ref. \[142\] the authors predict that a perpendicular magnetic field to a bilayer graphene dot with smooth boundaries can controllably lift the valley degeneracy.

Zooming out from the confinement measurements, I think it is valuable to investigate the band gap opening in bilayer graphene. In bilayer graphene on SiO$_x$ the band gap is contaminated with mid gap states that limit the strength of the insulating state. It was expected that a cleaner substrate would lead to fewer midgap states. However, our results on hBN/BLG/hBN sandwiches do not show a much better insulating state. The non-linearities in bias dependence still occur around $\sim 100 \mu$eV. An explanation could be the observation that the two layers of bilayer graphene can connect and form one continuous, but folded single layer graphene sheet.\[153, 154\] This could generate a conduction path parallel to the insulating regions underneath the gates. There are predictions about topological edge states at the physical edges in bilayer graphene.\[155\] Although measurements in a Corbino geometry on SiO$_x$ showed that these edge states are not existent they might become relevant in our clean devices.\[74\] Topological one-dimensional states are an interesting property of bilayer graphene. They are predicted to occur when two regions with an induced band gap of opposite sign meet.\[115, 116\] It is possible to make a device with bottom and top split gates to induce this effect. In the light of chapter \[8\] it is possible that these states occur when the theory of an alternating gap is true.

The subfield of double gated (confinement) devices in bilayer graphene can generate many insights in the rich physics of bilayer graphene. With the implementation of
the hBN encapsulation the insights can also contribute to the general understanding of
the interaction of bilayer graphene with hBN. The preliminary data in chapter might
be explained to be an effect of a Moiré pattern or strain induced by the encapsulating
hBN flakes. From a broader perspective our results on transfer methods, mechanical
cleaning and confinement devices contribute to the emerging field of heterostructures
of layered two-dimensional systems. The advent of high quality chemical vapor depo-
sition grown graphene layers and recently also the first reports on large area growth
of hBN further increase the promise of these systems.


[16] K. S. Novoselov et al. “Unconventional quantum Hall effect and Berry’s phase of $2\pi$ in bilayer graphene”. In: Nat. Phys. 2.3 (2006), pp. 177–180. DOI: 10.1038/nphys245


[33] Y. Zhang et al. “Experimental observation of the quantum Hall effect and Berry’s phase in graphene”. In: Nature 438.7065 (2005), pp. 201–204. DOI: 10.1038/nature04235


[57] Y. Zhang et al. “Origin of spatial charge inhomogeneity in graphene”. In: Nat. Phys. 5.10 (2009), pp. 722–726. DOI: 10.1038/nphys1365


[84] R. Jalilian et al. “Scanning gate microscopy on graphene: charge inhomo-
geneity and extrinsic doping”. In: Nanotechnology 22 (2011), p. 295705. DOI: 10.1088/0957-4484/22/29/295705
force microscope”. In: Journal of Applied Physics 111.6 (2012), pp. 064904–
064904–4. DOI: 10.1063/1.3695451
scanning probe microscopy based on quartz tuning fork force sensors”. In: Nan-
technology 21 (2010), p. 145702. DOI: 10.1088/0957-4484/21/14/145702
[87] X. Li et al. “Large-Area Synthesis of High-Quality and Uniform Graphene
Films on Copper Foils”. In: Science 324.5932 (2009), pp. 1312–1314. DOI:
10.1126/science.1171245
[88] W. Zhu et al. “Structure and Electronic Transport in Graphene Wrinkles”. In:
Nano Lett. 12.7 (2012), pp. 3431–3436. DOI: 10.1021/nl300563h
[89] V. E. Calado et al. “Formation and control of wrinkles in graphene by the
103116–3. DOI: 10.1063/1.4751982
quantum Hall effect in graphene by strain engineering”. In: Nat. Phys. 6.1
(2010), pp. 30–33.
in Graphene Nanobubbles”. In: Science 329.5991 (2010), pp. 544–547. DOI:
10.1126/science.1191700
[93] F. Bonaccorso et al. “Production, Processing and Placement of Graphene and
Transport under Graphene Films”. In: Nano Lett. 9.1 (2009), pp. 332–337.
DOI: 10.1021/nl803087x
[95] S. J. Haigh et al. “Cross-sectional imaging of individual layers and buried inter-
faces of graphene-based heterostructures and superlattices”. In: Nature
[97] S. Reich et al. “Resonant Raman scattering in cubic and hexagonal boron ni-
Strain: Bubbles and Balloons”. In: Nano Lett. 12.2 (2012), pp. 617–621. DOI:
10.1021/nl203359n
Bibliography


[111] Other choices of $R_B$ compatible with $R_{2T}$ gave either unphysical results, such as negative resistances, or quantized conductance values that we consider highly unlikely, such as plateaus at 8, 5 and 2 times $e^2/h$. Subtracting a parallel conductance of $e^2/h$, the value of the minimum conductance in the measurement gave an unlikely conductance plateau at $e^2/h$.


APPENDIX A

Guide for fabricating double gated hBN/bilayer graphene/hBN

This appendix provides details about the procedures for making devices described in chapter 3. The devices in chapters 4, 5, 7 and 8 are fabricated with this method. The chapter will hopefully serve as a step-by-step guide for reproduction of the devices. Moreover it contains comments on what can go wrong.

A.1 Substrate preparation and obtaining graphene and hBN flakes

In this section we will discuss the two different substrates we need for our devices. First a Si/SiO$_x$ substrate and second a Si substrate covered with a stack of AQS and PMMA. In the second part of the section we discuss mechanical exfoliation for the dry transfer method.

Recipe for making a Si/SiO$_x$ substrate for backgated graphene devices

1. Clean a heavily doped Si wafer with 285 nm SiO$_x$ in piranha (150 mL 40% $H_2SO_4$ and 50 mL 30% $H_2O_2$) for $\sim$ 10'.
2. Deposit 20 nm Al$_2$O$_3$ with atomic layer deposition to prevent back gate leakage.
3. Make W markers and bonding pads (Cr/Au layers will degrade at 500 °C annealing) with sputtering, electron beam lithography (EBL) (Vistec EBPG5000+ HR) and reactive ion etching (RIE). The RIE makes the substrate quite rough, so another hard material that can be processed with EBL and lift-off would be better.
4. Dice the substrate in $\sim$ 7 x $\sim$ 4 mm pieces (markerfield is 4 x 3 mm).
5. Clean the substrate in piranha.

This section is based on the appendix in the Master thesis of T.A. Baart, http://repository.tudelft.nl/view/ir/uuid:24179af7-d2f0-40d8-838b-512528d67ed6/
Appendix A. Guide for fabricating double gated hBN/bilayer graphene/hBN

6. Deposit hBN flakes and anneal the chips at 500 °C as described in section A.3 to remove residues.

Recipe for a Si chip covered with ±50 nm Aquasave (AQS) and ±390 nm PMMA A6 950k for transferring graphene

1. Put 2.5 cm x 2.5 cm Si chips in acetone and ultrasound for approximately 3’ to wash away remaining polymer residues. We reuse these silicon substrates.
2. Repeat with isopropanol.
3. Rinse with distilled water to wash away remaining AQS residues.
4. Clean the chips further in piranha for at least 15 minutes.
5. Rinse with distilled water.
6. Dry the chips using the nitrogen-pistol.
7. Spin Aquasave for 5” at 500 RPM and 55” at 2000 RPM (thickness ± 50 nm).
8. Spin PMMA A6 950k for 5” at 500 RPM and 55” at 6000 RPM (thickness ± 390 nm).
9. Bake for 1-2’ at 140°C.

Mechanical exfoliation of graphene and hBN

Mechanical exfoliation works in the same way for graphene and hBN. In both cases you start with a ‘master-piece’ of tape containing many graphite flakes or hBN crystals. Here we describe the procedure for Si/AQS/PMMA substrates. For hard Si/SiO$_x$ substrates the procedure can be easily extracted.

1. Take a new piece of blue Nitto tape and put this on top of the master-piece of tape. Rub against both pieces of tape for half a minute and pull the pieces apart. Continue with the new piece of tape.
2. Make a plastic frame that fits the chip you are going to use. The plastic we use is 0.5 mm thick Lexan that we obtained from Stout Perspex Rotterdam (brand name Makrofol). Lexan is a form of polycarbonate and it is certified to withstand temperatures up to 120 °C, but in practice 180 °C is not a problem. The dimensions of the frame should be such that there is a (square) hole inside that is 4-6 mm smaller in width than the actual chip (to ensure enough double sided tape can attach to the PMMA-layer). Around the hole should be ±1 cm of plastic to ensure the window can float in water. Sand the piece of plastic so that it cannot accidently rupture the PMMA-film with any sharp sides. Clean the plastic frame with ethanol and next IPA (acetone will make the Lexan crack).
3. Heat the chip to 100°C for 1-2’ so that any remaining water molecules can evaporate.
4. Position the Lexan frame on the chip and put the piece of tape on top of that. Be careful not to move the tape after it has hit the PMMA; in that case the PMMA will rupture.
A.2. Dry transfer of graphene on top of hBN

5. Press the tape softly with your finger to make it touch the whole chip. Next rub it gently with the handle of a screwdriver for 2.5’. Do not apply any pressure, just let the weight of the screwdriver do its task. If you rub for too long, glue from the Nitto tape might remain on the chip.

6. Now comes the most difficult part: taking the piece of tape off without rupturing the PMMA-film. For this you need a rectangular piece of plastic that just fits inside the square hole. You gently grab the piece of tape and under an angle of almost 90 degrees with the chip you slowly pull it off, whilst exerting pressure on the tape that is still on the chip with a rectangular piece of plastic.

7. After this step you can start searching suitable flakes.

8. In the case of bilayer graphene we always check the bilayer nature with the Raman spectrometer.

**A.2 Dry transfer of graphene on top of hBN**

We attach the Lexan frame to the chip as follows:

1. Put double-sided tape on the inner edges of the frame; the pieces of tape were approx. 4 mm wide.

2. Attach the plastic frame to the chip and place the structure in DI water so that the frame floats (graphene side up, so that the graphene does not get in contact with water)

3. Next the Aquasave will dissolve in \( \sim 30' \) and the chip will be released leaving a layer of PMMA such as shown in Fig. 3.6. If the chip does not release by itself you can gently take the plastic frame out of the water and move the Si chip with a tweezer slightly sideways. Now you put the structure back in the DI water: the Si chip will sink to the bottom.

4. Attach the frame with PMMA to a glass slide that is fixed in a micromanipulator. The glass slide has a hole that fits a conical metal piece that has another hole in the middle. This hole is used to look through when aligning. The graphene flake needs to be in the middle of the hole of the metal piece.

5. Put the target Si/SiO\(_x\) substrate with hBN flakes on the heater that is on the microscope table. Rotate the chip with your tweezers to get the relative orientation of the hBN with respect to the graphene flake right.

6. Mark the position of the hBN with the help of the microscope camera on the computer screen and bring the hBN out of focus (microscope table down).

7. Bring the graphene in focus and move it with the micromanipulator screws to the right position.

8. Heat the substrate to 105 °C and check the alignment.

9. Bring the graphene and hBN in contact.
Appendix A. Guide for fabricating double gated hBN/bilayer graphene/hBN

10. Heat to 140 °C for ~ 10' to promote adhesion between PMMA/graphene and SiO_x/hBN.

11. Slowly cool down the system and dissolve the PMMA on top of the graphene with acetone. Rinse the chip in IPA and blow dry.

Remarks for performing transfers

- Check the position of your flake with respect to the frame. Ideally the flakes should be at least 4 mm away from the sides of your frame.

- To ensure that the plastic frame does not touch the heater during the transfer (and thereby leading to misalignment), one should put the chip on a small piece (1x1 cm) of metal approx. 3 mm high.

- The metal piece in the microscope glass usually contains a lot of residues from previous transfers as can be easily seen in the microscope. Putting the microscope glass in a sonicator is not an option as this will break the glass. Leaving the glass in acetone for too long will dissolve the stycast (used to glue the metal piece to the glass). It is therefore better to clean the inside of the sphere with a thin clean screwdriver and tissues with acetone.

- It is best to align the whole system at room temperature and get the orientation of the chip right. Next, move the microscope table down (with the heater and chip on it) and start heating to the desired temperature. When the temperature has been reached wait for another 2-4 minutes to make sure the whole system is thermally equilibrated. Now restore the microscope back just under the plastic window and do little adjustments to realign.

- Take your time for the alignment. You will need to change the focus of the microscope from the chip to the flake being transferred quite often to ensure that vertical movements do not induce lateral movements. The absolute height changes made while changing focus from one substrate to the other were approximately 2-5 mm to make sure the chip and flake do not hit each other by mistake. Check the alignment at least 3 times by focussing on the chip and back to the graphene/hBN flake again; if nothing changed during this time you can be quite sure it will all work out. It is really worth the effort.

Problems encountered during transfers

Several problems have been encountered during the transfer procedures. Problems include:

1. The PMMA-film is not so strong and if not treated carefully (e.g. moving the microscope glass when it is already attached to the plastic window) it will break. After some ‘training’ in transferring this problem occurs less often. Otherwise solutions would be to increase the thickness of the PMMA (keeping in mind the contrast values) or using round plastic windows instead of square ones to support the PMMA-film.

2. If the substrate with hBN touches the plastic window when you bring the PMMA-film close to the hBN misalignment will be the result.
A.3 Annealing at 400 °C

To clean the graphene from transfer residues we annealed for 3 hours at 400 °C in forming gas environment. Here we describe how the annealing was performed.

1. Put a very clean quartz glass tube (be very careful with other people using the tube to avoid contamination) and a quartz glass boat for the samples in a tube oven (1” Lindberg Blue M). Do not connect the tube to the argon and hydrogen cylinder. Heat the oven to 900 °C. Once it has reached this temperature, leave it there for at least 15’ to burn away any contaminations inside the tube.

2. Attach the argon and hydrogen cylinder in the correct way and let argon flow at 2.4 L/min for 5’ to remove any oxygen inside the tube. Next also open the hydrogen at 0.7 L/min and leave this open for another 5 min.

3. Close the hydrogen valve and keep the argon open. Set the oven to room temperature, open the lid, and let it cool down.

4. Once cooled down, do not close the argon valve and open one side of the tube. Place the samples, close the lid and flush again for 5’ with argon gas (2.4 L/min). Open the hydrogen cylinder and set the flow to 0.7 L/min.

5. Set the ramp rate of the oven to 5-10 °C min$^{-1}$ and set the temperature to 400 °C and leave it warming up.

6. Anneal for approximately 3 hours at the setpoint temperature.

7. Change the setpoint temperature to 0 °C and let the samples cool down with the lid closed to ensure slow cooling and as little thermal stress as possible.

8. Once room temperature has been reached close the hydrogen cylinder and 5 min. later also close the argon cylinder. Remove your samples.

9. Take an AFM image of the graphene flake to check its position, the position of wrinkles/bubbles and its cleanliness.

A.4 Pattern contacts with EBL

1. Make a design for the contacts in Designcad with the help of the AFM and optical images of the sample. Make sure that there is enough space for the top gate hBN flake. A flake of $\sim 40$ nm follows a step of $\sim 100$ nm in about 1 µm.

2. Spin PMMA 495k a6 for 5” at 500 RPM and 55” at 6000 RPM and bake for 1’ at 140 °C. Spin PMMA 950k a3 for 5” at 500 RPM and 55” at 6000 RPM and bake for 1’ at 140 °C.

3. Write the pattern using EBL. The typical dose for fine structures ($\sim 300$ nm) is 1400 µC cm$^{-2}$.

4. Develop in MIBK:IPA (1:3) for 2’ and rinse in IPA for 30 s.
Appendix A. Guide for fabricating double gated hBN/bilayer graphene/hBN

5. Inspect the structures with the optical microscope.

6. Evaporate with an e-beam evaporator 1 nm Cr and 99 nm Au (thickness depends on the thickness of the bottom hBN flake). We had many problems with broken contacts at low temperature, so the contacts need improvement. A stack of Cr/Pd/Au might help against diffusion of Cr into the Au.

7. Do lift-off in warm (60 min) or cold (over night) acetone. A stir magnet improves lift off. A syringe with sharp needle helps to squirt away sticking gold films.

8. Rinse the sample in IPA and blow dry.

A.5 Etch graphene into channel

For electrostatic confinement devices we would like to limit parallel conduction as much as possible. Therefore we etch the graphene into a channel of about 1 µm. The etching also enables us to deterministically place the device in the best spot on the graphene flake. Doing so we avoid transport through bubbles, wrinkles and other mobility degrading features.

1. Spin PMMA 495k a6 for 5” at 500 RPM and 55” at 4500 RPM (∼ 300 nm) and bake at 140 °C for 1 min.

2. Write pattern at a dose of 1300 µC cm$^{-2}$.

3. Develop in MIBK:IPA (1:3) for 2 min. and rinse in IPA for 30 s. Inspect the pattern.

4. Preclean the RIE etcher with an oxygen plasma for 2 hours at 250 W and at an oxygen flow of 25 sccm.

5. Etch the sample with an oxygen flow of 25 sccm for 40 s at 20 W at 4 µbar. This removes the graphene layers and also a couple of nm hBN.

6. Wash away the PMMA etch mask with acetone and rinse in IPA.
   We had problems with a thin film that was left after etching. Precleaning of the etching chamber and putting the sample vertically in the acetone and for 5 s in low power ultrasound might help avoiding the formation of this thin film.

A.6 Mechanical cleaning of graphene

At this point the residues from contact fabrication need to be removed. In our lab annealing did not work at this stage so we developed a new method to clean the graphene as is described in chapter 5.

1. Mount a CM AFM tip in the AFM.

2. Load the sample and place the tip just next to the region to be cleaned
A.7. Dry transfer of top gate hBN flake on graphene

3. Lower the tip and measure a force distance curve. Set the force to \( \sim 0 \) N.
4. Move the tip to the region to be cleaned and start scanning.
   
   It is best to scan slowly (\( \leq 1 \) Hz) windows of 4 \( \mu \text{m} \times 4 \) \( \mu \text{m} \) at once. Sometimes the area is clean after one pass, sometimes more than 15 passes are needed.

A.7 Dry transfer of top gate hBN flake on graphene

This procedure is roughly the same as in A.2. The same hints apply as given, but some extra remarks can be made.

1. Exfoliate a hBN flake with PDMS stamps on a Si/AQS/PMMA substrate.
2. Identify suitable hBN flakes and characterize their cleanliness with the AFM.
3. Perform the transfer as described in A.2.
   
   • Think carefully about the orientation of the top hBN-flake with the sample. Not all orientations will be able to follow the shape of the contacts easily. You can really think of this system as a blanket falling down.
   
   • If you misalign in this step and by accident withdraw the plastic frame including the PMMA film you have a high risk of rupturing your graphene. The PMMA-film tends to stick really well to the graphene and hBN-flakes; so if it (instead of the hBN top flake) gets in contact with your graphene it is best to not get it off mechanically (by withdrawing) but just stop and dissolve the PMMA with acetone. Then check in the AFM and if everything is still fine: redo this transfer step.

A.8 Annealing at 250 °C

Anneal the samples as described in A.3 but now at 250 °C to clean the last residues and enhance the adhesion of the hBN top flake to the graphene. We use a lower temperature to avoid degradation of the contacts.

A.9 Pattern top gates with EBL

The top gate structures need to be very fine. Hence the metal cannot be thicker than 15 nm. As the thickness of the hBN/graphene/hBN stack (\( d_{\text{stack}} \)) for our devices is larger than 60 nm we need to do a two step lithography process for the top gates. One step to define the fine gates and one step to connect them to the bonding pads.

1. Spin PMMA 950k a3 for 5” at 500 RPM and 55” at 3000 RPM (\( \sim 130 \) nm, thickness should \( > 2 \cdot d_{\text{stack}} \)) and bake at 175 °C for 30 min.
2. Write pattern at a dose of 1100 or 1300 \( \mu \text{C cm}^{-2} \), depending on the structure.
3. Develop in MIBK:IPA (1:3) for 2’ and rinse in IPA for 30 s. Inspect the pattern.
4. Evaporate 1 nm Cr at 0.5 Å/s and 4 nm Au at 0.5 Å/s and 10 nm Au at 1 Å/s
5. Perform lift-off in warm acetone (50 °C) with a stir magnet.
6. Make an AFM image of the fine gates.
7. Follow the same steps as described in A.4 to fabricate the gate structures that connect the fine gates to the bonding pads. Choose $d_{metal} \geq 2 \cdot d_{stack}$.

A.10 Package and bond the device

Nanofabrication is now finished and we are ready to load the chip in the measurement setup.

1. Glue the chip in a 32-pin PLCC chip carrier with silver paint to make an electrical backgate connection.
2. Bond wires from the chip carrier to the sample (Al-wire).
3. Load the chip carrier in the measurement setup.

Bonding is a delicate task. We found out that for thin layers ($\sim 100$ nm) of metal bonding is very different from industrial bonding. In industry relatively thick bonding pads are used ($\sim 1 \mu$m) and hence it is advised to use metals that have are equally soft as the bond wires. In our case soft pads (f.e. Au) turn out to be too soft: often the pad just rips off while bonding. Hard metals like Pd, W and NbTiN work best. To avoiding back gate leakage, use a bond power as low as possible (at a bond force of 18 g).
APPENDIX B

Background resistance subtraction and alternatives for qpc conductance data

The main paper presents top gate traces for a constriction in device B after subtraction of a background resistance resulting in conductance plateaus at 6, 4 and 2 $e^2/h$. There are different scenarios possible for subtraction of a background series resistance and/or a parallel conductance, as was discussed in chapter 7. In figure B.1 we show top gate traces for various scenarios for two typical data sets. On the left are the data for device A and on the right the data for device B (Fig. 7.2b in 7).

(a) Top gate traces (raw data) for device A at backgate voltages from $-49.26$ V (left most) V to $-49.74$ V (right most) in 10 equal steps of $-48$ mV ($V_{bias} = 0.5$ mV, $T = 35$ mK and $V_{TG2} = 7$ V).

(b) Data of panel (a) after subtracting a background resistance (see inset) to put the upper plateau at $6e^2/h$. Note that the background resistance is much lower than in fig. 2b of the main paper. This is because the graphene leads were damaged in between measuring device A and B.

(c) Data of panel (a) after subtracting a background resistance (see inset) to put the upper plateau at $8e^2/h$.

(d) Data of panel (a) after first subtracting a parallel conductance (see inset) to put the conductance minimum at 0, and next subtracting a background resistance (see inset) in series with the device to put the upper plateau at $8e^2/h$.

(e) Top gate traces for device B (raw data, same as figure 2b in the main paper) at back gate voltages from $-49.26$ V (leftmost) to $-49.74$ V (rightmost) in 10 equal steps of $-48$ mV ($V_{bias} = 0.5$ mV, $T = 35$ mK).

(f) Data of panel (e) after subtracting a background resistance (see inset) to put the upper plateau at $6e^2/h$.

(g) Data of panel (e) after subtracting a background resistance (see inset) to put the upper plateau at $8e^2/h$.

(h) Data of figure (e) after first subtracting a parallel conductance (see inset) to put the conductance minimum at 0, and next subtracting a background resistance (see inset) in series with the device to put the upper plateau at $8e^2/h$.

All traces have been corrected for a known filter resistance of 5 kOhm and current
amplifier input impedance of 2.1 kOhm. Also in the raw data of figure 2 these resistances are already subtracted since they are extrinsic to the device. The background resistance consists of a contact resistance, graphene lead resistance and Maxwell spreading resistance. From 4 terminal measurements at high density we can estimate that the contact resistance is in the order of 1 kOhm. The Maxwell spreading resistance is approximately $\pi^{-1} \rho \ln(W_{\text{flake}}/l)$ where $\rho$ is the resistivity of the graphene, $W_{\text{flake}}$ the width of the flake and $l$ the mean free path. As the resistivity of the high mobility graphene around the point contact is relatively low, this term is in the order of a few hundred Ohms. The rest of the background resistance is made up of the graphene leads from the metal contact to the point contact.
Figure B.1
Acknowledgements

Nobel Prize winner Andre Geim calls graphene the new disruptive technology. I believe the fascinating material will change the lives of many people in the near future. Graphene has already been disruptive to my life. The decision to work on graphene made a lot of impact on me. Here I would like to thank everyone that contributed to this impact.

At the end of my master’s thesis I decided to work on graphene. When I attended a talk from the Quantum Transport group in Delft about controlling single electrons I decided to move from Groningen to Delft to work with Lieven Vandersypen. Lieven, it was a great experience to work with such an excellent scientist as you are. The support you gave is something every PhD student would wish. You taught me about physics, supervising students, fighting for small and big milestones and countless other skills. I enjoyed working with you a lot, I want to especially mention the writing process on our two papers. Above all, I am grateful for the focus that you gave me by teaching me that I should always look for my inner motivation and set clear goals based on that motivation.

Whenever I meet researchers from other labs, they ask me if the Quantum Transport group is really the factory of great science that they think it is. Personally I did not have the feeling that QT is a factory. True, the size of QT is like a small company, but a small company can only make one product. QT hosts over 50 intrinsically motivated scientists that work together in small teams producing and fundamentally understanding the basic building blocks of quantum computing. I am very grateful to all scientists that ever worked for QT to have created and still create this fantastic atmosphere. Especially I would like to mention Hans Mooij who is the true God Father of the QT family. Leo Kouwenhoven, Ad Verbruggen, Ronald Hanson, Val Zwiller and Leo DiCarlo thank you for preserving, guiding and developing the QT spirit so well.

The graphene team has a special position in QT. Sometimes it was as if we would better fit in the non-existing group ‘We are almost in the Quantum transport regime, but we first have to clean the graphene’. All of us: Lan Liu, Amelia Barreiro, Mihai Popinciuc, Victor Calado, Shou En Zhu, Srijit Goswami and Lieven Vandersypen developed state of the art graphene technology and researched the fundamental physics of graphene. I am very proud of our results and I want to thank you for so much helpful advice, good times and bonding my samples. During my project I supervised several students. Angelo Maggiti, Tim ‘Fred’ Baart and Stefanie Driessen did their master’s project with me. Aldo Kingma his bachelor’s project and Lauren Cantley her summer internship. You all proved to be very valuable, it was very special to
work together with you. Graphene is naturally a multidisciplinary subject. I had contact with many inspiring scientists. I would like to thank Sangeetha Hari, Kees Hagen, Gregory Schneider, Andres Castellanos Gomez and Gary Steele from the Delft University of Technology, Anton Akhmerov and Maria Medvedeva from the University of Leiden, Bart van Wees, Paul Zomer, Marcos Guimarães and Niko Tombros from the University of Groningen, Kiril Bolotin, Andrea Young, Inanc Meric and Cory Dean from Columbia University New York and Javier Sanchez-Yamagishi and Pablo Jarillo-Herrero from MIT for their enthusiastic input and support to my project. Here I want to mention that I owe a lot to Philip Kim who generously offered me a spot in his group at Columbia University to learn about suspended graphene. Moreover during my stay he gave me all the support I needed. I am very grateful to Lieven for supporting me to go to the group of Philip Kim.

Stichting fundamenteel onderzoek der materie (FOM) generously provided the funding for my research. I want to thank them also for being such a caring employer. Besides Yuki Nakagawa, Angele Fontijn, Dominque Meijer and Marja Plas, I would like to thank Bram van der Enden, Jelle Haanstra and Remco Roeleveld for their support of QT and my project. I am very grateful to Raymond Schouten for his informative help with the many electronics problems and for developing such a fantastic measurement setup as the IVVI rack. Aad Poot is the mechanics workshop technician that always looks very friendly but also friendly mills sample mounts in any shape. The support staff in the clean room was of invaluable help in my project. Thanks for all your support!

A PhD project is in fact of short duration. When I visit Quantum Transport in 5 years from now I will see many new faces. The constant renewal of people working in QT guarantees a constant inflow of very interesting individuals. It is a truly great experience to work in an environment with so many smart and driven people. Sometimes so driven that they forget to put their dirty mugs in the dish washer and rely on my feeling for responsibility. The upside is that when something has to happen, it will happen in QT. Even when the snow is melting, quantum transport puts on their skis (and leopard print underwear) to go for a good descent in the Swiss Alps. Our sense for bars with a twist is legendary so in Delft we end a PhD party in bar De Klok where the most handsome guys in the group are being courted by mature gay men. As a last statement to advertise QT I can recommend the group to any local disco with deteriorating customer numbers. We will liven up your place and your turnover. Thank you so much QT!

Graphene changed my life. The friends that I made during the period I worked on graphene changed my life even more. Dear friends, I hope you share and keep on sharing with me the beautiful memories I describe in this paragraph. We enjoyed great experiences in New York where we explored Columbia University, International House NYC, Bukharian Jewish restaurants, the MOMA and Carnegie Hall in search for Doutzen Kroes. When I came back from New York I submersed myself in the Nerd House and the Nieuwelaan. Dear Nieuwelaners, fellow-nerds, thank you for letting me develop into a graphene nerd! To counterbalance the graphene overdose we played and went to many concerts together. It was amazing listening to Tsjaiakovski in the Concertgebouw by the Concertgebouw orchestra, singing Mare Liberum with Krashna Musika in Hamburg and dancing Balkan Swing in the basement of De Koornbeurs. Music is relaxation for the mind and sports is relaxation for the body so I joined the
rowing club in Delft where I enjoyed many hours on the water, even with the spin qubit / graphene team peaceably together in one boat. My first slopes on the skis I experienced together with the great Winterberg ski team. The summer after the same team miraculously transformed itself into a sun seeking Sicily mob. Later I went to another Mediterranean island, Corsica, for a graphene conference where we celebrated the Nobel Prize win with the winner himself: Sir Kostya Novoselov.

I am very grateful to Marius and Miriam, my parents, to have infected me with an explorative attitude. Marius, you showed me that around every corner there are immensely interesting subtleties to be discovered. Miriam, you made me realize that persistence is a very important prerequisite to be able to explore. Aart, Rob and Wim, dear brothers, it is very inspiring to see you living the life that you chose. It is wonderful you made choices based on your own motivation. Inner motivation is very important, but the seed for this motivation is crucial. The seed for my decision to pursue a PhD project in this specific direction was planted by Wilbert. Many interesting discussions about biology, recumbent bikes, electronics and physics guided me into the direction of semiconductor physics and eventually graphene. Dankjewel Wilbert. Now graphene has put the seed for the motivation in the near future of my life. Apart from the success of graphene technology, the material has already proven to be positively disruptive!

Stijn Goossens
Delft, 2013
Graphene is an atomically thin layer of carbon atoms ordered in a hexagonal lattice. Since its isolation in 2004 it has attracted enormous attention and many amazing properties of graphene were discovered. To name a few of them: graphene is a gapless semiconductor, it absorbs only 2% of light, it is 10 times stronger than steel and it is impermeable to any gas. The research on graphene has paved the way for a new research field on two dimensional layered structures. Graphene is a member of a large family of atomically thin two-dimensional materials. Combining these different materials by stacking them opens virtually limitless possibilities for new devices.

The most simple stack is a Bernal stacked structure of two layers of graphene: bilayer graphene (BLG). Bilayer graphene is also a two dimensional material and inherits many of the special properties of monolayer graphene. The electronic structure of bilayer graphene has many charming properties. First of all the quasiparticles are chiral and secondly they are fourfold degenerate. As bilayer graphene does not possess a band gap, conduction can be switched from electron to hole conduction. In this thesis we aim to investigate these fundamental properties of quasiparticles in bilayer graphene. We do this by confining them to one-dimensional and zero-dimensional structures: quantum point contacts and quantum dots.

Nanopatterning graphene in nanoribbons and small islands has been a successful strategy for one-dimensional and zero-dimensional confinement. Unfortunately, as a result of the etching process that is used for nanopatterning, the edges of the devices are very rough. This edge disorder, aggravated by substrate-induced disorder, leads to rather irregular device behaviour. The alternative is to confine the carriers in graphene electrostatically. Electrostatic confinement requires a band gap. In bilayer graphene, a band gap can be opened by applying a perpendicular electric field.

In this thesis we show that an insulating state can be created in bilayer graphene by opening a band gap by applying a perpendicular electric field with the help of bottom and top gates. Moreover we pattern the top gate into a split gate geometry that can electrostatically induce a narrow conduction channel. We can pinch off the channel, but no signs of ballistic transport in the channel are observed.

The absence of ballistic transport has two causes. Number one is the detrimental effect of the silicon oxide dielectrics of the double gated devices. The solution is sandwiching graphene between hexagonal boron nitride (hBN) flakes. hBN is a member of the family of two dimensional layered materials. The basic structure is a honeycomb lattice, with boron and nitrogen atoms replacing the carbon atoms. The flatness and perfect crystal structure of the hBN flakes result in a substantial
Summary

increase of the electronic quality of our graphene devices. Cause number two is contamination of graphene due to residues from nanofabrication. This contamination often introduces background doping and reduces charge carrier mobility. For samples of high electronic quality, post-lithography cleaning treatments are therefore needed. We report that mechanical cleaning based on contact mode atomic force microscopy removes residues and significantly improves the electronic properties. A mechanically cleaned dual-gated bilayer graphene transistor with hexagonal boron nitride dielectrics exhibited a mobility of $\sim 36,000 \text{ cm}^2/\text{Vs}$ at low temperatures.

Fabrication of bilayer graphene sandwiched in between hBN dielectrics involves a transfer of graphene on top of the hBN flake. This transfer easily induces bubbles and wrinkles in the graphene. Annealing up to $600 \degree \text{C}$ after the transfer makes the small bubbles coalesce into the larger ones. This results in larger flat areas. We also report Raman spectroscopy measurements on the bubbles that indicate the bubbles are not strained. Moreover we manipulate the bubbles with an atomic force microscope tip. From our measurements we conclude that there is most likely a mixture of air and hydrocarbons inside the bubbles. Finally we observed that graphene sheets on hexagonal boron nitride can move. This movability facilitates strain release by bubble formation.

Our key result is the fabrication and measurement of nanoscale devices that permit electrostatic confinement in bilayer graphene for the first time on a substrate. The graphene bilayer is sandwiched between hBN bottom and top gate dielectrics. Top gates are patterned such that constrictions and islands can be electrostatically induced. The high quality of the devices becomes apparent from the smooth pinch-off characteristics of the constrictions at low temperature, with features indicative of conductance quantization. The islands exhibit clear Coulomb blockade and single-electron transport.

Unexpected is the observation of an anomalous insulating state in bilayer graphene sandwiched in between hBN flakes. This state can be lifted by applying a perpendicular displacement field to the bilayer graphene. Moreover there is a finite intrinsic electric field present in the hBN / BLG / hBN system.

Concluding, we show one-dimensional and zero-dimensional confinement of quasi-particles in bilayer graphene. Unexpectedly we observe a twofold in stead of a fourfold degeneracy in the conductance quantization. Follow-up research is needed to explain this degeneracy lifting. In the zero-dimensional confinement regime we measure Coulomb blockade. Physics related directly to bilayer graphene quasiparticles confined to zero dimensions such as fourfold shell filling and the electron hole crossover still has to be measured. From a broader perspective, our results on transfer methods, mechanical cleaning and confinement devices contribute to the emerging field of heterostructures of layered two-dimensional systems. The advent of high quality chemical vapor deposition grown graphene layers and recently also the first reports on large area growth of hBN further increase the promise of these systems.
Samenvatting

Grafeen is een atomair dunne laag koolstofatomen die zijn geordend in een hexagonaal rooster. Sinds de isolatie van het materiaal in 2004 heeft het enorm veel aandacht getrokken en zijn veel verbazingwekkende eigenschappen van grafeen ontdekt. Om er een paar te noemen: grafeen is een halfgeleider zonder bandkloof, absorbeert slechts 2 % van het licht, is 10 keer sterker dan staal en is ondoorgringoerbaar voor gassen. Het onderzoek naar grafeen heeft de weg geplaveid voor een nieuw onderzoeksveld dat zich bezig houdt met twee-dimensionale, gelaagde structuren. Grafeen is lid van een grote familie atomair dunne twee-dimensionale materialen. Het combineren van deze materialen door ze te stapelen geeft ondenkbaar veel mogelijkheden voor nieuwe devices. De meest eenvoudige stapel is een Bernal gestapelde structuur van twee lagen grafeen: bilaag grafeen (BLG). Bilaag grafeen is ook een twee-dimensionaal materiaal en erfz veel van de speciale eigenschappen van grafeen. De elektronische structuur van bilaag grafeen heeft veel charmante eigenschappen. Ten eerste zijn de quasideeltjes chiraal en ten tweede zijn ze viervoudig ontaard. Omdat bilaag grafeen geen bandkloof heeft, kan de geleiding van elektronen- naar gatengeleiding geschakeld worden. In dit proefschrift mikten we erop de fundamentele eigenschappen van quasideeltjes in bilaag grafeen te onderzoeken. Dit doen we door ze op te sluiten in één-dimensionale en nul-dimensionale structuren: kwantum puntcontacten en kwantum dots. Het nano-structureren van grafeen in nanoreepjes en kleine eilandjes is een succesvolle strategie gebleken om één-dimensionale en nul-dimensionale opsluiting te verwezenlijken. Helaas zijn als gevolg van het etsproces dat gebruikt wordt voor het nano-structureren, de randen van deze structuren zeer ruw. Die wanorde in de randen, versterkt door wanorde in het substraat, zorgt voor onregelmatig gedrag van de nanostructuren. Het alternatief is om ladingsdragers in grafeen elektrostatisch op te sluiten. Voor elektrostatische opsluiting is een bandkloof nodig. In bilaag grafeen kan een bandkloof geopend worden door een loodrecht elektrisch veld aan te brengen.

In dit proefschrift laten we zien dat een isolerende toestand in bilaag grafeen gecreëerd kan worden door een bandkloof te openen met de hulp van ‘gates’ onder en boven het grafeen. Daarnaast structureren we de ‘gates’ in een gesplitte geometrie waarmee we elektrostatisch een smal kanaal kunnen induceren. Dit kanaal kunnen we afknippen, maar we zien geen tekenen van ballistisch transport. De afwezigheid van ballistisch transport heeft twee oorzaken. Oorzaak n is het nadelige effect van de silicium oxide dielectrica van de apparaatjes met twee ‘gates’. De oplossing is het plaatsen van grafeen tussen twee plakken hexagonaal boor nitride (hBN) die als dielectricum werken. Dit hBN is net als grafeen lid van de familie van twee-dimensionale,
gelaagde structuren. De basisstructuur is een honingraatrooster, met boor- en stikstofatomen die de koolstofatomen vervangen. De vlakheid en de perfecte kristalstructuur van de hBN plakken zorgt voor een substantiële verhoging van de elektronische kwaliteit van onze grafeen apparaten. Oorzaken twee is verontreiniging van het grafeen door overblijfselen van de nanofabricage. Deze overblijfselen veroorzaken vaak achtergrondstoring en verlagen de mobiliteit. Voor monsters met een hoge elektronische kwaliteit zijn daarom post-lithografische schoonmaakbehandelingen nodig. We laten zien dat mechanisch schoonmaken, gebaseerd op atoomkrachtmicroscopie, overblijfselen verwijdert en de elektronische eigenschappen significant verbetert. Een mechanisch schoongemaakte bilaag grafeen transistor met hBN dielectrica laat een mobiliteit zien van $\sim 36,000 \, \text{cm}^2/\text{Vs}$ bij lage temperatuur.

Voor het plaatsen van een bilaag grafeen tussen twee hBN dielectrica is een transfer nodig van een grafeen plak bovenop een hBN plak. Deze transfer veroorzaakt gemakkelijk bubbels en rimpels in het grafeen. De stapel van grafeen en hBN na de transfer langdurig verwarmen tot een temperatuur van $600 \, ^\circ \text{C}$ zorgt ervoor dat de kleine bubbels samengaan met de grotere. Dit resulteert in grotere vlakke gebieden. We doen ook verslag van Raman spectroscopie metingen op de bubbels die een indicatie geven dat het grafeen in de bubbels niet opgerekt is. Daarnaast manipuleren we de bubbels met een atoomkrachtmicroscooptip. Uit onze metingen concluderen we dat de bubbels hoogstwaarschijnlijk een samenstelling van lucht en koolwaterstoffen bevatten. Tot slot observeren we dat grafeenplakken op hBN kunnen bewegen. Deze beweegbaarheid vergemakkelijkt de relaxatie van rek in de bubbels.

Ons belangrijkste resultaat is de fabricage en meting van apparaten op de nanoschaal die voor het eerst elektrostatische opsluiting in bilaag grafeen op een substraat mogelijk maken. Het grafeen is geplaatst tussen twee hBN plakken. De gates die bovenop zitten, zijn gestructureerd zodat constricties en eilanden elektrostatisch genduceerd kunnen worden. De hoge kwaliteit van de apparaten wordt duidelijk door de gladde afknijpingscurves van de constricties bij lage temperatuur. In die curves zien we tekenen van geleidingskwantisatie. Het eiland laat duidelijk Coulomb-blokkaade en transport van enkele elektronen zien.

Onverwacht is de waarneming van een ongewone isolerende toestand in bilaag grafeen dat geplaatst is tussen twee hBN flakken. Deze toestand kan opgeheven worden door een loodrecht elektrisch veld aan te brengen over het bilaag grafeen. Daarnaast is er een eindig intrinsiek elektrisch veld aanwezig in het hBN/BLG/hBN systeem.

Concluderend laten we één- en nul-dimensionale opsluiting van quasideeltjes in bilaag grafeen zien. Onverwacht nemen we een tweevoudige ontaarding in plaats van viervoudige ontaarding in de geleidingskwantisatie waar. Vervolgonderzoek is nodig om deze ontaardingsopeffing uit te leggen. In het nul-dimensionale opsluitingsregime meten we Coulomb blokkade. Natuurkundige verschijnselen die direct gerelateerd zijn aan quasideeltjes in bilaag grafeen die opgesloten zijn in nul-dimensies, zoals viervoudige schilopvulling en de elektron-gat overgang, moeten nog waargenomen worden. Vanuit een breder perspectief gezien dragen onze resultaten op het gebied van transfermethoden, mechanisch schoonmaken en opsluitingsapparaten bij aan het opkomende veld van heterostructuren van gelaagde, twee-dimensionale materialen. De komst van hoge kwaliteit chemische dampdepositie gegroeide grafeen lagen, en recentelijk ook de eerste publicaties over groei van hBN op grote schaal vergroot de belofte van deze systemen verder.
Curriculum Vitae

Stijn Goossens

March 17, 1985
Born in Lichtenvoorde, The Netherlands.

Education

1997–2003
High School
VWO - Gymnasium, SG Het Assink, Haaksbergen, The Netherlands

2003–2006
B.Sc. Applied Physics
University of Groningen, Groningen, The Netherlands

2006–2008
M.Sc. Nanoscience (cum laude)
University of Groningen, Groningen, The Netherlands
Graduation research in the group of prof. P.W.M. Blom

2008–2013
Ph.D. research
Delft University of Technology, Delft, The Netherlands
under supervision of prof. dr. ir. L. M. K. Vandersypen
subject: quantum transport in graphene

