TRANSPORT THROUGH GRAPHENE NANOCONSTRUCTIONS

A DISSERTATION
SUBMITTED TO THE DEPARTMENT OF PHYSICS
AND THE COMMITTEE ON GRADUATE STUDIES
OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Kathryn Todd
September 2009
UMI Number: 3382902

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

UMI Microform 3382902
Copyright 2009 by ProQuest LLC
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346
I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(David Goldhaber-Gordon)  Principal Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(Kathryn Moler)

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

(Malcolm Beasley)

Approved for the University Committee on Graduate Studies.
Abstract

Graphene is a recently-discovered material with remarkable physical properties, including high mechanical strength and thermal conductivity and the highest known room-temperature mobilities of any material. These properties make graphene an attractive candidate for next-generation high-frequency transistors, but extended sheets of graphene also display a non-zero minimum conductivity, making it impossible to fabricate transistors with high on-off ratios out of extended graphene sheets. However, the long narrow nanostructures known as graphene nanoribbons offer the possibility of high on-off ratios when used as transistors. Their properties were initially explained in terms of quantum confinement. We have fabricated and measured the transport properties of graphene nanoribbons of a variety of lengths, ranging from micron scales to very short constrictions tens of nanometers in length. We find that nanoribbons and constrictions of all lengths display transport properties consistent with the formation of quantum dots throughout the length of the ribbon. In very short constrictions, we measure transport consistent with the presence of only one or two quantum dots, with strong coupling to the bulk graphene leads. We present a model for formation of quantum dots in our constrictions due to background potential fluctuations in the presence of a confinement gap. Annealing experiments allow us to vary the density and arrangement of impurities in the vicinity of our ribbons; we find that annealing changes certain transport properties systematically in a manner consistent with our disorder-nucleated quantum dot model of transport.
Epigraph

Habe nun, ach! Philosophie,
Juristerey und Medicin,
Und leider auch Theologie!
Durchaus studirt, mit heißem Bemühn.
Da stehe ich nun, ich armer Thor!
Und bin so klug als ich zuvor;
Heiße Magister, heiße Doctor gar,
Und ziehe schon an die zehn Jahr,
Herauf, herab und quer und krumm,
Meine Schüler an der Nase herum —
Und sehe, daß wir nichts wissen können!
Das will mir schier das Herz verbrennen.
Zwar bin ich gescheidt, als alle die Laffen,
Doctoren, Magister, Schreiber und Pfaffen;
Mich plagen keine Scrupel noch Zweifel,
Fürchte mich weder vor Hölle noch Teufel —
Dafür ist mir auch alle Freud' entrissen,
Bilde mir nicht ein was rechts zu wissen,
Bilde mir nicht ein, ich könnte was lehren.
Die Menschen zu bessern und zu bekehren.
Auch hab' ich weder Gut noch Geld,
Noch Ehr' und Herrlichkeit der Welt.
Es möchte kein Hund so länger leben!
- Johann Wolfgang von Goethe, illustrating the perils of remaining in graduate school too long
Acknowledgements

My advisor, David Goldhaber-Gordon, took me into his lab several years into my Ph.D. Without his willingness to do so I would not have graduated. When I began working in his lab I didn't have a great deal of confidence in my ability to become a productive scientist. He, on the other hand, assumed as a matter of course that I would do good work in his lab, and his confidence was both reassuring and infectious. Over the three years I've spent in his lab, I've admired the creativity of his ideas, the care that he devotes to making sure that the results coming out of his lab are accurate, but most of all his concern for his students' development and well-being beyond their ability to generate results. I've been very lucky to have been his student.

I was also lucky early in my Ph.D. to have the chance to interact with and learn from the remarkable group of students who started the Manoharan lab. Laila Mattos, Gabriel Zeltzer, Mike Preiner, Brian Foster, Chris Moon, and Jason Randel taught me a great deal about UHV practices, mechanical design, programming and electronics, and helped me to feel at home at Stanford. When I joined the DGG lab, I benefited from the mentorship of the students in the lab at the time: Mark Topinka, Lindsay Moore, Hung-Tao Chou, Charis Quay, Ileana Rau, Andrei Garcia, Adam Sciambi, Alex Neuhausen, Joey Sulpizio, Mike Jura, and Mike Grobis all helped me learn where things were kept, how to use the equipment in the lab, and helped me brush up on my lithography skills. Sami Amasha, who joined the lab later on, spent hours patiently helping me understand quantum dot physics. I have also very much admired the way he exerts quiet leadership in the lab through his unfailing politeness, fairness, and concern for others. Markus König, who joined the scanning gate project in May 2008, has, along with Andrei Garcia, heroically battled against the ever-new problems with
the system and the added complexities of measuring an exposed-surface material like graphene. Matthias Baenninger, who joined the project more recently, has been fun to work with. Yang Bo, with whom I worked on the early stages of isolating graphene flakes, was an energetic and enthusiastic colleague. Nimrod Stander joined the lab just after I did, and his practicality and persistence were very helpful in the period when we were all working to get the graphene project off the ground. Benjamin Huard joined the graphene project in the fall of 2006. His energy and willingness to tackle complicated theory really raised the level of the game for all of us on the graphene project. Joey Sulpizio always had good ideas for solving the technical problems we encountered. Patrick Gallagher joined the graphene project to work on fabricating ribbons of controlled width and varying lengths; he worked diligently and creatively to develop a robust fabrication process, and when he had done so he applied the same care and intelligence to measuring his ribbons and interpreting the data. Over the past year and a half, I’ve enjoyed his humor, his skepticism and his energy; working with him has been one of the high points of my Ph.D.

I’ve benefited a great deal during my Ph.D. from the good advice of Kam Moler and Z. X. Shen. I’ve also benefited from interactions with a whole host of students from other labs: Ophir Auslander was always ready to listen to practice talks or to puzzle over my data with me. All of the inhabitants of the Moler and KGB labs were generous with their equipment and materials. The Brongersma and Mao lab students graciously helped me and the other members of the graphene group to use their Raman spectroscopy systems. Maria Wang, Fern Kundhikanjana, Keji Lai were fun and hard-working collaborators.

One of the great things about working in David’s group is the way he encourages his students to develop relationships with researchers from other institutions. I enjoyed collaborating with Micol Alemani and Kirill Bolotin, and benefited from discussions with Melinda Han, Kostya Novoselov, Michael Fuhrer, Gil Refael, Shaffique Adam, Enrico Rossi, Francoise Molitor and Christoph Stampfer.

I’m lucky to have had a great group of friends during my time at Stanford. Lindsay, Charis, Eran, Adam, Mark, Elene, Kalia, Doug, Shiv, Ramya, Vanessa, and Jit Kee helped me to celebrate triumphs and forget setbacks and to enjoy life outside the lab.
I’m also grateful for the support of my family. My mother, father, brother Sam, sister Lisa and nephews Ethan and Joshua listened patiently to my complaints and provided welcome distractions.

Finally, I’m deeply indebted to my husband Alex for his patience and good sense throughout my Ph.D. His constant conviction that this was something worth doing, and that I was capable of doing it well has sustained me over the last several years.
Contents

Abstract iv
Epigraph v
Acknowledgements vii

1 Survey of Graphene’s Electronic Properties 1
   1.1 Introduction ......................................................... 1
   1.2 Physical Structure and Band Structure .................................. 2
   1.3 Dirac Fermions ......................................................... 5
   1.4 Suppressed Backscattering and Klein Tunneling .......................... 6
   1.5 Conductance Properties ............................................... 7
   1.6 Quantum Hall Physics ............................................... 9
   1.7 Universal Conductance Fluctuations and Weak Localization .......... 10
   1.8 Graphene Nanoribbons ............................................. 14

2 Theories of Transport Through Graphene Nanostructures 15
   2.1 Introduction ............................................................. 15
   2.2 Edge-Dependent Theories ............................................ 17
   2.3 Confinement ............................................................ 18
   2.4 Quantum Dots Nucleated by Edge Roughness .......................... 19
   2.5 Anderson Localization .............................................. 19
   2.6 Bulk- Disorder Nucleated Quantum Dots ............................ 20
11.2 Graphene Constrictions as a Point or Collimated Particle Source 123
11.3 The Tip 123
  11.3.1 Multiple-Arm Geometries 124
  11.3.2 Magnetic Confinement 124
11.4 Mobilities Necessary to Image Particle Caustics 125
11.5 The Scanning Gate as a Probe Inside Graphene Nanostructures 126
  11.5.1 Localized states near a malformed constriction 126
  11.5.2 SGM images of a well-formed graphene constriction 127
  11.5.3 Graphene constriction with a metal particle 129
  11.5.4 Structures with many constrictions in parallel 131
11.6 Electrostatic Considerations 133
  11.6.1 The perils of tip set-downs 135
  11.6.2 Energizing the attocubes 135
  11.6.3 Imaging graphene flakes with tip deflection 137
11.7 Fabry-Perot-like oscillations 139
11.8 Summary 140

A Helium-3 Fridge Cold Finger 142

B Measurement Electronics 150

C Measurement Programs 152
  C.1 Introduction 152
  C.2 Conductance versus Back Gate Voltage Program 152
    C.2.1 Referenced by Conductance Versus Back Gate Voltage Program: gotoset2400 154
  C.3 Differential Conductance versus Two Voltages Program 155
    C.3.1 Referenced by the Differential Conductance Versus Two Voltages Script: NIgotoset 159
    C.3.2 Referenced by NIgotoset: NIselV 160
  C.4 Initializing the BiasDAC’s: startup 161
    C.4.1 Referenced by startup: beta6703 161
List of Tables

5.1 Long nanoribbon sets and their annealing histories .............. 50

6.1 Short constrictions and their properties ....................... 56
## List of Figures

1.1 graphene lattice structure ........................ 2
1.2 graphene unit cell .................................. 3
1.3 graphene Brillouin zone ......................... 4
1.4 graphene band structure ......................... 4
1.5 graphene band structure at low energies ..... 5
1.6 typical graphene conductance ................. 8
1.7 Landau level spacing in graphene and in a conventional 2DEG ... 10
1.8 Our etched Hall bar sample ................. 11
1.9 Hall conductance .................................. 11
1.10 Longitudinal resistance ...................... 12
1.11 Universal conductance fluctuations .......... 13

2.1 graphene nanoribbon transport characteristics ........... 16
2.2 armchair and zigzag edges .................... 17
2.3 a cartoon of quantum dot structures created by line edge roughness 19
2.4 STM imaging of puddle size and impurity location .......... 21
2.5 quantum dots from electron-hole puddles .......... 22

3.1 a non-conducting quantum dot ............... 24
3.2 a conducting quantum dot ................... 24
3.3 quantum dot conductance peaks .............. 27
3.4 Coulomb diamonds ................................. 30

4.1 circuit diagram of a parallel double-dot system .......... 33
6.10 conductance versus back and side gate voltages for sample 10-24-g
6.11 conductance map of constriction 10-24-g compared to locally gated bulk graphene
6.12 conductance versus back and side gate voltages for constriction 9-7-e
6.13 conductance versus back gate voltage for sample 9-7-e
6.14 conductance versus back gate voltage for sample 10-24-d
6.15 conductance versus back gate voltage for sample 10-24-g
6.16 differential conductance versus back gate and source-drain voltages for sample 10-24-g, March 2008 cooldown
6.17 differential conductance versus back gate and source-drain voltages for sample 10-24-g, June 2008 cooldown
6.18 differential conductance versus back gate and source-drain voltages for sample 9-7-e
6.19 differential conductance versus back gate and source-drain voltages for non-side-gated sample 4-8-p4
6.20 differential conductance versus back gate and source-drain voltages for sample 10-24-d
6.21 conductance peak fits, sample 1-17-a at 4 K
6.22 conductance peak fits, sample 1-17-a at 0.25 K
6.23 conductance versus back gate voltage for a wide range of temperatures, sample 10-24-g
6.24 conductance peak fits at 1.5 K, sample 10-24-g
6.25 conductance peak area versus temperature, sample 10-24-g
6.26 zero bias anomaly, sample 10-24-g
6.27 temperature dependence of zero bias conductance suppression, sample 10-24-g
6.28 power-law behavior of the zero bias anomaly, sample 10-24-g
6.29 temperature dependence of zero bias anomaly, sample 10-24-d
6.30 location of dI/dV versus bias cuts, sample 10-24-d
6.31 power-law behavior of the zero bias anomaly, sample 10-24-g
6.32 Fabry-Perot behavior in bulk graphene, sample 10-24-g at 250 mK
Chapter 1

Survey of Graphene’s Electronic Properties

1.1 Introduction

While graphene has been studied theoretically since 1946 [1] when it was used as a model system for understanding the electronic properties of graphite, and experienced renewed interest after the discovery of carbon nanotubes as a model system for understanding them [2], it was long believed that graphene could not exist in nature because of the thermodynamic instability of two-dimensional crystals [3, 4]. It was surprising, therefore, when Novoselov and collaborators isolated a single atomic layer of graphite, or graphene, on an SiO$_2$ surface in 2004 [5]. Since its discovery, graphene has flowered as a system that allows the study of effectively massless Dirac Fermions [6, 7] with exotic quantum Hall physics [6, 8] and scattering properties [9]. Its high mobility [10] and thermal conductivity [11], low spin-orbit coupling [12] and physical strength [13] have led to the exploration of many technological applications including MEMS devices [14], transparent electrodes [15], high-frequency transistors [16], and spin valves [17, 18, 19].

The worked discussed in this thesis deals primarily with the transport properties of graphene nanostructures, but in this chapter we survey the generic properties of graphene, highlighting its differences from other two-dimensional materials. Many
of the features of bulk graphene that we discuss have relevance to the properties of graphene nanostructures.

1.2 Physical Structure and Band Structure

Graphene is a single sheet of carbon atoms arranged in a hexagonal lattice, and is part of a family of sp² carbon constructs that includes nanotubes, buckyballs, and graphite. Graphene’s physical structure is illustrated in figure 1.1. The bond length in this structure is \( a_0 = 1.42 \text{Å} \). The graphene unit cell is illustrated in figure 1.2, with the primitive lattice vectors

\[
a_1 = \frac{a_0}{2}(3, \sqrt{3}), \quad a_2 = \frac{a_0}{2}(3, -\sqrt{3})
\]  

(1.1)

This unit cell gives rise to a Brillouin zone in reciprocal space that is also hexagonal. It is illustrated in figure 1.3, with the \( \Gamma \) point located at the center of the zone and the inequivalent \( K \) and \( K' \) points located at the corners. The reciprocal lattice
1.42 Å

Figure 1.2: Carbon atoms are depicted as blue spheres at the vertices of the hexagon. The bond length and one of the primitive lattice vectors are depicted.

vectors are

\[ b_1 = \frac{2\pi}{3a_0} (3, \sqrt{3}), a_2 = \frac{a_0}{2} (3, -\sqrt{3}) \]  \hspace{1cm} (1.2)

A band structure can be calculated based on this Brillouin zone and a nearest-neighbor hopping energy \( t \approx 2.8eV \) taking into account only nearest-neighbor hopping [1]:

\[ E_{\pm}(k) = \pm t \sqrt{3 + f(k)} \]  \hspace{1cm} (1.3)

A plot of the band structure is shown in figure 1.4. Several features of this band structure should be noted. The positive and negative energy portions of the band structure are identical: there is symmetry between electrons and holes. The electron and hole bands meet only at the K points of the Brillouin zone, and in the region near the K points the band structure is effectively linear.

In fact, if we limit ourselves to Fermi energies that are accessible in transport measurements via typical gate voltages, the band structure consists of isolated cones located at the K points of the Brillouin zone, only two of which are inequivalent. The band structure for energies less than 1 eV is shown in figure 1.5.
Figure 1.3: Blue circles are placed at the K and K' points of the Brillouin zone. The \( \Lambda \) and K points are labeled.

Figure 1.4: Graphene band structure in the extended zone scheme.
Figure 1.5: Low-energy graphene band structure: features with energy larger than 1 eV are not shown. At low energies the band structure consists of isolated cones at K-points.

1.3 Dirac Fermions

The low-energy excitations in this band structure obey the Dirac equation:

\[
-i\hbar v \begin{pmatrix} 0 & \delta_x - i\delta_y \\ \delta_x + i\delta_y & 0 \end{pmatrix} \begin{pmatrix} \Phi_A \\ \Phi_B \end{pmatrix} = E \begin{pmatrix} \Phi_A \\ \Phi_B \end{pmatrix} \]

(1.4)

where \(\Phi_A\) and \(\Phi_B\) are the amplitudes of the wavefunctions on the A and B sublattices, respectively. Because we consider only nearest-neighbor hopping events, the Hamiltonian couples A sublattice sites to B sublattice sites, but not to other A sublattice sites. In bilayer graphene, the stacking of the two planes provides a coupling mechanism between the two sublattices, and the charge carriers no longer behave as massless particles.

The Dirac equation has two equivalent sets of solutions, each at opposite corners of the Brillouin zone. These solutions \(\Phi_A\) and \(\Phi_B\) and \(\Phi'_A\) and \(\Phi'_B\) represent separate “valleys.”

Electric potentials do not couple the two valleys as long as they are smooth on the scale of the lattice spacing; thus valley polarization is a conserved quantity in
atomically ordered extended graphene sheets.

1.4 Suppressed Backscattering and Klein Tunneling

The behavior of Dirac Fermions incident on a potential barrier has a surprising quality; if the height of the potential barrier exceeds the particle's rest mass, a particle normally incident on the barrier can pass through with high probability. Particles are in fact forbidden from backscattering at the barrier because to do so would violate the conservation of chirality, the relationship between the particle's momentum and spin. Instead, the transmission takes place via electron-positron creation and annihilation events at the barrier edges [20, 21]. For electrons and positrons in vacuum Klein tunneling requires extremely high potential barriers because of the non-zero electron rest mass, and has never been observed experimentally. In graphene, however (in contrast to the vacuum and to other electronic materials) electrons and holes are effectively massless and (in contrast to other electronic materials) are symmetric particles. Electrons' or holes' sublattice identity (sometimes called pseudospin) in graphene is analogous in the context of the Dirac Hamiltonian that described electronic motion in graphene to electron spin in vacuum. Theoretical work on Klein tunneling in graphene was first published in 2006 [22]. In this phenomenon, electrons (or holes) normally incident on a high, wide barrier are forbidden from backscattering, because a sign change in the particle's momentum requires that it transition to the other branch of the band structure in order to preserve its identity as an electron (or hole). However, the electron (or hole) is able to tunnel through the barrier via opposite-momentum hole (or electron) states inside the barrier which are located on the same branch of the band structure. While in the vacuum this effect requires enormous potential drops over very short length scales, because the invariant Fermi velocity in graphene is 100 times smaller than the speed of light in vacuum and because the charge carriers in graphene are massless it is much easier to achieve Klein tunneling. For Klein tunneling to take place in graphene it is necessary that
the potential barrier be smooth on the length scale of the lattice spacing; otherwise intervalley scattering would break the preservation of pseudospin.

The transmission probability as a function of angle of incidence $\theta$ in the case of a potential step that is smooth both on the atomic scale and on the scale of the Fermi wavelength is calculated [23] as

$$w(\theta) = e^{-\pi(k_Fd)\sin^2\theta}$$

(1.5)

Note that in contrast to particles that impinge on the barrier at normal incidence, particles that are incident obliquely can be backscattered with some probability, because an oblique reflection does not involve a 180 degree change in the momentum.

1.5 Conductance Properties

The implications of this band structure and its associated scattering properties for conductance as a function of particle density are subtle. On one hand, the structure is gapless; on the other, there is vanishing density of states at the Fermi level. As we shall discuss in more detail later on, disorder, in conjunction with graphene’s peculiar scattering properties, plays an important role in its observed conductivity. However, even in the absence of disorder, it is predicted that graphene flakes would exhibit a non-zero minimum conductivity in the limit of zero density [24, 25]. This is in fact what is observed in every extended graphene sample that has been measured. In figure 1.6 we show typical conductance versus gate voltage (or, equivalently, carrier density) data from one of our bulk graphene samples.

This is a two-terminal measurement. Several features should be discussed. Note the sharp dip in conductance at close to zero volts on the back gate. This dip is common to all bulk graphene samples [26], and occurs at the point where the average charge density is equal to zero: the Dirac point. In this sample, it appears near zero gate voltage, but this need not be the case. It has been shown that the point of minimum conductivity moves away from zero volts with doping [27] and that the distance of the point of minimum conductivity from zero volts is correlated with
the mobility [28]. In the absence of Hall measurements to give a separate measure of particle density and four-terminal measurements to give an accurate value of the contactless resistance, the mobility of a graphene sheet can be estimated from two-terminal resistivity measurements alone by assuming that the contact resistances are small compared to the graphene sheet resistance near the Dirac point (a reasonable assumption in our samples, where the two-terminal resistances saturate at sub-kΩ values at high gate voltages and where the resistivities near the Dirac point are close to the typical value of ~6kΩ per square) and that the carrier density can be accurately estimated by modeling the graphene sheet and the back gate as a parallel plate capacitor whose charge is zero at the point of minimum conductivity:

$$n_{\text{carrier}} = \frac{\epsilon \epsilon_0 V}{ed}$$  \hspace{1cm} (1.6)

where $V$ is the distance in volts from the Dirac point, $\epsilon$ is the dielectric constant of the SiO$_2$ separating the highly-doped Si back gate and the graphene, which ranges between 3.9 and 4.5 for thermal oxide, and $d$ is the separation between the graphene and the back gate, typically 300 nm. The mobility can then be estimated, using
resistivities $\rho$ close to the Dirac point, as

$$\mu = \frac{1}{n_{\text{carrier}} e \rho}$$  \hspace{1cm} (1.7)

Two-terminal mobility estimates are practical for nanostructured samples, where it can be difficult to fit a full Hall or van der Pauw geometry on one side of the nanostructure. The asymmetry in the conductance across the Dirac point in the measurement shown in figure 1.6 is typical of two-terminal conductivity measurements in graphene, where regions of local doping by contact metals can give rise to a p–n junction for one sign of gate voltage that reduces the conductance into the contacts [29].

1.6 Quantum Hall Physics

The quantum Hall effect in two-dimensional electron gases (2DEGs) was experimentally discovered in 1980 in GaAs 2DEGs [30]. The discovery was surprising not because of the quantization of the Hall resistance at specific values of electron filling factor, but because that quantization persists over a range of filling factors wide enough to make it observable, with universal values of resistance unaffected by disorder or more generally by the properties of the particular semiconductor being measured. In fact, it is the presence of disorder (at low levels) that broadens the quantum Hall states enough to make them observable.

Graphene’s unconventional band structure has a dramatic effect on its quantum Hall properties. In figure 1.7 we show a schematic adapted from Geim and Novoselov [31], contrasting the spacing of Landau levels in single-layer graphene to that in a conventional 2DEG. While the spacing in a conventional 2DEG has no dependence on energy, in single-layer graphene the first few levels are much more widely spaced than in a conventional 2DEG. This means that it is possible to observe the quantum Hall effect in these first few levels even at room temperature. Especially for larger densities, these first few levels are only accessible at very high magnetic fields [32].

Early in our work, we fabricated a sample to investigate quantum Hall physics, in part motivated by the need to confirm our AFM measurements indicating the presence
Figure 1.7: a) Landau level spacing in single-layer graphene and b) in a conventional 2DEG. Adapted from Geim and Novoselov.

of single-layer graphene. An optical micrograph of this device is shown in figure 1.8. Most of the flake is single-layer graphene as indicated by AFM measurements, with the exception of a thicker stripe running diagonally across the upper half of the flake, impinging on one of the contacts. We are careful not to measure longitudinal or Hall voltages using this contact.

In figure 1.9 we show the Hall conductance $\sigma_{xy}$ of this sample as a function of magnetic field measured at two gate voltages on opposite sides of, but at roughly equal distances from the Dirac point. At these low dopings, we are able to see clear quantum Hall plateaus at relatively low fields. The presence of plateaus at $0.5*4e^2/h$ is an unambiguous indication of transport through single-layer graphene.

1.7 Universal Conductance Fluctuations and Weak Localization

In figure 1.10 we show the longitudinal resistance of the same sample at low magnetic fields and at a variety of temperatures. There is a peak in the resistance at zero magnetic field that decreases in magnitude as the temperature increases. This is typical
CHAPTER 1. SURVEY OF GRAPHENE'S ELECTRONIC PROPERTIES

Figure 1.8: An etched Hall bar sample. Note the diagonal stripe of thicker material on the upper half of the flake.

Figure 1.9: Hall conductance at gate voltages close to zero doping. Note the plateaus at $0.5*4e^2/h$.
of weak localization behavior. The phenomenon of weak localization results from the existence of pairs of electron trajectories that originate and end at the same location that are related to each other by time-reversal symmetry. When time-reversal symmetry is not broken, these pairs of trajectories return to the origin with identical phases, and thus interfere constructively with each other. This constructive interference at a particle’s point of origin results in an increased sample resistivity. The presence of a magnetic field breaks time-reversal symmetry in general and the phase symmetry between clockwise and counterclockwise moving electrons in these paths in particular, suppressing constructive interference at the origin. When resistivity is measured as a function of magnetic field, a peak in the resistivity at zero magnetic field is observed; this is an experimental hallmark of weak localization. Phase coherence is a critical ingredient in weak localization: in the absence of phase coherence the interference effects leading to weak localization are washed out. Because of their typically long phase coherence lengths, graphene samples would be naively thought to exhibit robust weak localization. However, some experimental reports [33] suggest that weak localization is not always present in graphene. Variations between samples in the degree of weak localization (which is entirely absent in some samples, and quite strong in others) have been attributed to random local effective magnetic fields caused by ripples of the graphene surface [33]. Others [34] have suggested that strong
intervalley scattering is the necessary to observe weak localization in graphene, and that it can arise either from the rippling of the graphene sheet, from trigonal warping (at high electron densities) or from the presence of dislocation/antidislocation pairs.

Related to the phenomenon of weak localization is the topic of universal conductivity fluctuations. In figure 1.11 we show data from our Hall bar sample showing a conductance trace that fluctuates substantially (but reproducibly, in the sense that two separate measurements of the conductance at low temperature will register the exact same fluctuations) on top of its characteristic Dirac conductance at 0.4 K. As is apparent in the inset, these fluctuations smooth out when the temperature is raised to 7 K.

Anomalously large universal conductance fluctuations in graphene have been attributed to the absence of backscattering [35]. The same authors suggest that for weak disorder the variance of the conductance can exceed the value derived by Lee and collaborators for small metallic samples[36]. While the fluctuations we observe here are not substantially larger in variance than the standard $0.12(W/L)(2e^2/h)^2$, in
general universal conductance fluctuations in graphene samples complicate the measurement of other phenomena. Many published measurements are made at elevated temperatures (above 4 K) in order to present data uncontaminated by UCF’s.

1.8 Graphene Nanoribbons

Although graphene’s high mobility and thermal conductivity make it an attractive candidate for next-generation transistor technology, its non-zero minimum conductivity results in on-off ratios that are unacceptably low for all but very high-frequency applications. In 2007, however, it was shown experimentally that narrow strips of graphene with widths $\lesssim 100$ nm can exhibit a transport gap, displaying essentially zero conductivity for a range of electron densities and biases [37, 38]. Since then, graphene nanoribbons have been synthesized lithographically [39, 40], chemically [41, 42], and even with STM lithography [43], and with widths narrow enough to suppress conduction in the gap even at room temperature [44]. The work described in this thesis attempts to elucidate the origin of the transport gap in graphene nanoribbons.
Chapter 2

Theories of Transport Through Graphene Nanostructures

2.1 Introduction

The first measurements of transport across narrow ribbons of graphene [37, 38], known as graphene nanoribbons, revealed very different conductance properties than those observed in extended graphene sheets. In figure 2.1 we show a selection of those measurements. For narrow ribbons like those depicted here, conductance is suppressed by several orders of magnitude over a wide range of gate voltages and biases. The energy scale of the conductance suppression observed as a function of bias is measured for ribbons of a variety of widths, and found to vary inversely with the ribbon width.

In this chapter we discuss several theories that have been proposed to explain the transport properties of graphene nanoribbons. At the end of the chapter we will briefly mention our preferred model for graphene nanoribbon transport, which we will discuss in greater detail in chapter 7.
Figure 2.1: a) graphene nanoribbons fabricated by Han and collaborators, b) conductance across a 24 nm-wide ribbon as a function of gate voltage, showing a strong suppression of conductance over a range of gate voltages, and c) differential conductance across a 22 nm-wide ribbon as a function of gate voltage and bias. Differential conductance is suppressed in a broad diamond shape around zero bias and around approximately 75 V on the back gate. The yellow arrow marks the source-drain bias that they take to be the height of the gap. d) width dependence of the gap observed in bias as a function of ribbon width. Figure adapted from Han et al. [37].
CHAPTER 2. THEORIES OF TRANSPORT THROUGH GRAPHENE NANOSTRUCTURES

2.2 Edge-Dependent Theories

Even before the first experimental data on graphene nanoribbons was published, several papers appeared that predicted the existence of band gaps in graphene nanoribbon structures with specific edge configurations and ribbons widths [45, 46, 47, 48, 49]. The edge configuration predicted to produce a band gap is the “armchair” edge, depicted in figure 2.2 (a).

![Figure 2.2: A representation of a portion of a graphene sheet, with a) an armchair edge and b) a zigzag edge depicted in red. The lattice is viewed at a small angle from the normal.](image)

For such an edge, a band gap is expected for ribbons whose widths are other than $N_a = 3p + 2$ atoms wide [49]. Armchair-edged ribbons with widths $N_a = 3p + 2$ and ribbons with zigzag edges are expected to be metallic. Zigzag ribbons are additionally predicted to harbor highly conducting edge states with interesting magnetic properties [50, 46, 51] whose discussion is beyond the scope of this thesis. For armchair
ribbons, tight-binding and first principles calculations both show a gap whose size scales inversely with ribbon width [47, 49], similar to experimental findings [37, 38]. However, early experiments on etched graphene nanoribbons [37] showed that their transport properties did not depend on their orientation with respect to the material’s crystallographic axes, demonstrating that explanations of their properties that ascribed different behavior to different crystallographic edge orientations (in particular, armchair or zigzag edges) were not credible. Although there have been subsequent claims of fabrication of nanoribbons with atomically ordered edges [41, 52] they are not verified by TEM studies, dependence on crystallographic orientation or other transport signatures. We therefore look for explanations of graphene nanoribbon transport properties that do not rely on atomically ordered edges.

2.3 Confinement

Instead, in the first experimental paper published on graphene nanoribbons [37], quantum confinement was proposed as a mechanism for the gaps observed in transport through the ribbons. Confinement is consonant with the observed width-dependence of the gap, since the energy of the lowest-energy state of a Dirac Fermion in a box of width $w$ is

$$E_0 = \frac{h v_F}{2W}$$

Although the width dependence of the gaps observed by Han and collaborators was offset from this scaling as though the width were 0 when the measured width of the nanoribbon was $\approx 16$ nm, this was credibly explained by hypothesizing non-conducting “dead zones” at the edges as a result of lithographic line-edge roughness and atomic-scale roughness due to the oxygen plasma etch used to define the ribbon.

However, quantum confinement does not explain the length dependence of transport through graphene nanoribbons and constrictions or the presence of resonant features in the gap region that we observe in our ribbons and describe in more detail in chapter 5.
2.4 Quantum Dots Nucleated by Edge Roughness

Further proposals have included nucleation of quantum dots in graphene nanoribbons due to width variations caused by lithographic line edge roughness [53]. An illustration of this scenario is shown in figure 2.3. While this could explain the presence of the conductance resonances in and near the gap that we observe and describe in chapter 5 as well as their diamond-like shapes as a function of source-drain and gate voltages, it is not consonant with the changes we observe in conductance properties upon thermal cycling or annealing. Additionally, line edge roughness would be unlikely to give rise to the quantum dot behavior we observe in our short constrictions (described in chapter 6), where the constriction width is designed to systematically widen away from the constriction center, and where the dot sizes that we infer from our transport measurements are comparable to the constriction length.

![Figure 2.3: Adapted from Sols et al. [53].](image)

2.5 Anderson Localization

Two credible theories remain. One outlined by Evalsson et al. [54], separately by Mucciolo et al. [55], and later by Schubert et al. [56] hypothesizes that the atomically disordered edges created by the oxygen plasma etch process give rise to Anderson
localization within the ribbon. Simulations [55] based on edge disorder alone qualitatively reproduce the zero-bias shape of the transport gap as a function of gate voltage. However, Anderson localization cannot be expected to produce the Coulomb diamond-like features we observe in maps of dI/dV versus both gate and source-drain voltages. Diamond-like features are generically expected whenever conductance depends on the potential at a single point, as when electrons are localized in a quantum dot. In this scenario, the local potential is changed by both a gate modifying the Fermi energy by roughly similar amounts across the region of interest and the source-drain bias modifying the potential by a particular amount at the specific location of interest. Therefore at a local site gate voltage and source-drain bias produce qualitatively equivalent effects: local potential can be modified with either, and a diamond pattern results as one voltage is “traded” for another. Anderson localization, however, is an interference phenomenon: conductance depends on the potential across the set of locations located within a phase coherence length. Because of this, we do not expect Anderson localization phenomena to produce the diamond-like features inside nanoribbon gaps that we observe and describe in chapter 5. Instead, one might expect Anderson localization to produce several resonances at single specific Fermi energies, with no requirement (as in Coulomb blockade in a single-dot system) that they be regularly spaced.

2.6 Bulk-Disorder Nucleated Quantum Dots

Another hypothesis involves the presence of charge carrier density inhomogeneities in the graphene sheet, caused by variations in background potentials stemming from charged impurities either sitting on top of or immediately under the graphene or embedded in the oxide upon which the graphene sits. These inhomogeneities have been observed experimentally [57, 58] most recently and at highest resolution by Zhang and collaborators [58]. In figure 2.4 we show their data mapping the differential conductance dI/dV as a function of position; at low energies this quantity is proportional to variation in the local Dirac point. Because the variation in the local Dirac point gives rise to a variation in local charge carrier density, the spatial variation of dI/dV
is a proxy for the spatial variation of the charge density. Zhang and collaborators also present topographic data over the same spatial range (not shown in this thesis), and find that local height and curvature of the graphene sheet have no correlation with the local charge density. However, they are also able to map the locations of scattering centers by measuring quasiparticle interference patterns at gate voltages farther from the Dirac point. They find that the locations of scattering centers inferred from these measurements (shown in figure 2.4 as red crosses) do correlate with the local charge density.

Figure 2.4: A scanning tunneling microscopy measurement of dI/dV as a function of position at a gate voltage near the Dirac point (bias = -0.29 V, current = 25 pA, gate voltage = 15 V). The blue and yellow regions reflect the presence of electron and hole puddles, while the red crosses signify the location of charged impurities extracted from a complementary measurement. Adapted from Zhang and collaborators [58].

This measurement adds credibility to the evidence from transport measurements in the presence of varying densities of charged impurities [27] that that doping inhomogeneities in exfoliated graphene flakes on SiO₂ surfaces stem from the presence of a random landscape of charged impurities, and not from native ripples in the graphene sheet or from curvature in the sheet stemming from roughness in the underlying oxide.

This well-established local variation in charge carrier density is key to our model of transport through graphene nanoribbons. We believe that this variation, in conjunction with the presence of a small gap between the electron and hole bands, possibly
CHAPTER 2. THEORIES OF TRANSPORT THROUGH GRAPHENE NANOSTRUCTURES

induced by confinement, could give rise to isolated puddles of charge carriers that could act as quantum dots. To illustrate this idea, we show recent calculations by Enrico Rossi (figure 2.5) that simulate a realistic configuration of isolated charge puddles for experimentally relevant impurity concentrations and a small gap (6.5 meV) that is consistent with activation energies in recent experiments [59].

Figure 2.5: Quantum dots nucleated by electron-hole puddles and isolated from each other by a 6.5 meV confinement gap, at a) zero average electron density and b) 5.1 x 10^{11} cm^{-2}.

Related to, though not identical to this idea, is a proposal by Adam and collaborators that impurities in the bulk of graphene nanostructures can drive a metal-insulator transition [60].

Our model is discussed in greater detail in chapter 6 (dealing with our experimental results on long graphene nanoribbons) and in chapter 7.
Chapter 3

Introduction to Quantum Dots

Our data on long and short nanoribbons, described in chapters 5 and 6, has shown indications of being due to the presence of quantum dots located in our nanostructures. In this chapter we describe some basic properties of quantum dots that will be useful in interpreting our data.

A quantum dot is a small puddle of charge carriers isolated from reservoirs of free carriers (the leads) by tunnel barriers. Quantum dots have the property that a discrete energy is required to add an additional electron to the dot. This quantity is called the addition energy, and is equal to the difference in chemical potentials between the dot in its initial state and the dot with an additional electron on it:

\[ E_{\text{addition}} = \mu_{\text{dot}}(N+1) - \mu_{\text{dot}}(N) \] (3.1)

The chemical potential of the dot relative to the potentials of the leads can be manipulated by the application of a voltage to a nearby gate. When the chemical potential in the leads is less than the energy of the lowest unoccupied state in the dot, conduction through the dot cannot take place (in the limit of zero temperature). This circumstance is known as Coulomb blockade, and is illustrated diagramatically in figure 3.1. When the chemical potential in the leads is increased to equal the addition energy, electrons at the Fermi level in the leads can tunnel through the aligned level in the dot as in figure 3.2, and a peak in conductance results.
Figure 3.1: A cartoon representation of a non-conducting quantum dot. a) A cartoon of the spatial arrangement of the central puddle of electrons (the dot) arranged between the two leads. b) A representation of the dot and the leads in energy (the y axis) and one spatial dimension (the x axis). The chemical potential in the leads is not aligned with the first unoccupied level in the dot: the dot is in a non-conducting state.

Figure 3.2: A cartoon representation of a conducting quantum dot. The chemical potential in the leads is aligned with the first unoccupied level in the dot.
Two separate energy scales contribute to the total energy required to place a charge on the dot, and therefore indirectly to the addition energy. One is the level spacing: the energy difference between adjacent allowed states in the quantum well inside the tunnel barriers. The other is the charging energy: the Coulomb energy required to add an electron charge to a confined area already containing at least one electron charge. The energy required to add a particle to the dot is the sum of the charging energy and the level spacing. For a graphene dot the sum of these energies is

\[ E_{\text{add}} = \Delta E_{\text{total}} = v_F h / 2D + e^2 / C_{\text{tot}} \]  

(3.2)

where \( D \) is the dot diameter and \( C_{\text{tot}} \) is the total capacitance of the dot. While the exact value of the dot capacitance depends on the dot’s electrostatic environment, the value for an isolated disc is

\[ C \sim 2\varepsilon_0 (\varepsilon + 1) D \]  

(3.3)

leading to a charging energy

\[ E_{\text{charging}} = \frac{e^2}{2\varepsilon_0 (\varepsilon + 1) D} \]  

(3.4)

or approximately 100 meV for a 30 nm dot. The predicted level spacing for a dot of the same diameter is also on the order of 100 meV, although oblong shapes and the chaotic level statistics predicted for imperfect graphene quantum dots are expected to complicate this correspondence [61, 62].

One can therefore extract information about a quantum dot’s size from the measured charging energy, given an assumption about the dot’s geometry. In chapters 5 and 6 we present data on graphene nanostructures displaying quantum dot-like behavior; from these measurements we extract charging energies and infer dot sizes. We typically do not see clear signatures of level spacing; in the one case where we do the level spacing is (unsurprisingly) not consistent with that of a circular dot with non-chaotic level statistics.

As the chemical potential in the leads is swept relative to the energy levels in the
CHAPTER 3. INTRODUCTION TO QUANTUM DOTS

dot, the spacing of conductance peaks reproduces the pattern of $\Delta E_{\text{tot}}$ inside the dot, modulo a “lever arm” that takes into account the gate capacitance: the spacing of charging-adjusted energy levels inside the dot

$$\Delta E_{\text{tot}} = \Delta + e^2/C_{\text{total}}$$  \hspace{1cm} (3.5)

becomes

$$\Delta V_{\text{gate}} = \alpha \Delta + e^2/C_{\text{gate}}$$  \hspace{1cm} (3.6)

as measured by the spacing of conductance peaks as a function of gate voltage, where

$$\alpha = C_{\text{gate}}/C_{\text{total}}$$  \hspace{1cm} (3.7)

and can be determined from the shapes of the Coulomb diamonds.

3.1 Functional Form of Conductance Peaks

In the picture presented in the previous section, conductance through the dot occurs only when the chemical potential in the leads and the lowest unoccupied level in the dot are precisely aligned; conductance occurs at a vanishingly narrow range of energy at each alignment. In real measurements, finite temperatures and particle lifetimes broaden the points of finite conductance into peaks of finite width. This contrast between the naive picture of infinitely narrow conductance peaks and the experimental reality is illustrated in figure 3.3

The functional form expected for conductance peaks depends on the temperature relative to the intrinsic energy scales of the dot: when the temperature is much greater than the energy associated with the electron lifetime, temperature broadening is the dominant mechanism in determining the functional form of conductance peaks. In the classical regime, where temperature is much greater than the level spacing and therefore tunneling through the dot takes place though many energy levels at once,
CHAPTER 3. INTRODUCTION TO QUANTUM DOTS

Figure 3.3: a) A cartoon representation of the infinitely narrow conductance peaks expected from the alignment of the chemical potential in the leads with each energy level in the dot in turn. b) Conductance through one of our graphene nanostructures displaying quantum dot-like behavior as a function of gate voltage (a proxy for the chemical potential difference between the leads and the dot) at 4 K. Note the broadening of the conductance peaks.

the functional form of conductance peaks is

\[ G = e \frac{\Gamma^l \Gamma^r}{(\Gamma^l + \Gamma^r)} \frac{E^*}{kT} \sinh \left( \frac{E^*}{kT} \right) \]

(3.8)

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( E^* \) refers to the energy with respect to the center of the conductance peak, and \( \Gamma_r \) and \( \Gamma_l \) are the tunneling rates of particles between the dot and the right and left leads, respectively.

In the resonant tunneling regime, the temperature is still much greater than the energy scale associated with the particle lifetimes in the dot, but it is now much less than the level spacing within the dot. In this case, the functional form of conductance peaks is

\[ G = \frac{e^2}{4kT} \frac{\Gamma^l \Gamma^r}{(\Gamma^l + \Gamma^r)} \cosh^{-2} \left( \frac{E_p}{2kT} \right) \]

(3.9)

where the subscript \( p \) refers to the \( p \)th level inside the dot.

There is another limit to be considered, in which the lifetime of particles inside
the dot is the dominant mechanism influencing the peak lineshape. In the zero temperature limit, the conductance peaks obey a Lorentzian lineshape,

\[ G = A \frac{e^2}{h} \frac{\Gamma'}{\Gamma_0' + \Gamma' (E'/\hbar)^2 + (\Gamma'/2)^2} \]  

(3.10)

where \( E' \) is again the energy from the peak center, \( A \) is a constant and \( \Gamma \) is the total tunneling rate out of the dot, while at higher temperatures the peaks follow the (non-integrable) convolution of the Lorentzian and thermally-broadened lineshapes:

\[ G \approx A \frac{e^2}{h} \frac{1}{4kT} A \int \text{cosh}^{-2} \frac{E}{2kT} \frac{(\Gamma/2)/\pi}{(\Gamma/2)^2 + [(e\alpha V_{\text{gate}} - E_{\text{res}}) - E]^2} dE \]  

(3.11)

where \( E_{\text{res}} \) is the center of the conductance resonance, \( V_{\text{gate}} \) is the gate voltage, and \( \alpha \) is defined as in equation (3.7) [63].

By fitting measured conductance peaks to these functional forms, one can make inferences about the relationships between the energy scales associated with temperature, level spacing in the dot and particle lifetimes in the dot.

### 3.1.1 Temperature Dependence of Conductance Peaks

Given the functional form of conductance peaks in the resonant and classical regimes we can easily extract how the peak height and full-width at half-maximum (FWHM) should scale with temperature.

In the resonant tunneling regime, the FWHM of the conductance peaks scales with temperature as \( \approx 3.5 \) kT, while in the classical regime FWHM scales as \( \approx 4.4 \) kT. In the classical regime conductance peak amplitude is temperature independent, while in the resonant tunneling regime peak amplitude scales as \( 1/T \). In consequence, the area contained under the peak should remain constant with temperature in the resonant tunneling regime, while it should increase linearly in the classical regime.

Using these rules of thumb can sometimes allow us to experimentally distinguish between the two scenarios more easily than with detailed fits to peaks at a single temperature.
3.2 Differential Conductance

In addition to controlling the chemical potentials in both leads relative to the dot levels, we are also able to apply a source-drain bias that raises the chemical potential in one lead relative to the other. Consider a quantum dot in a state where the first unoccupied energy level in the dot is not aligned with the chemical potential in the leads, as in figure 3.1. Consider then applying a bias across the dot so that the chemical potential in one lead is higher than that in the other. When we apply a bias large enough so that the chemical potential in one of the leads is aligned with or above the first unoccupied level in the dot, conduction results. As we further increase the bias, the current through the dot should increase every time we include another unoccupied level within the bias.

In general, when applying bias, we measure the differential conductance $dI/dV_{sd}$, and so we expect to register the alignment of each level in the dot with the chemical potential in one of the leads as a spike in $dI/dV_{sd}$ rather than a plateau in $I$.

It is possible to measure differential conductance as a function of both gate voltage and source-drain bias at once. When such a measurement is performed on a single quantum dot, we expect to observe diamond-shaped lines of high differential conductance surrounded regions of suppressed differential conductance. This differential conductance pattern is illustrated in figure 3.4. The diamond width $\Delta V_{gate}$ reflects the quantity $\Delta E_{tot}$ described above, with factors that reflect the capacitance between the dot and the gate:

$$\Delta V_{gate} = e^2/C_{gate} + \alpha \Delta_{level} \tag{3.12}$$

where $\alpha$ is as defined above:

$$\alpha = C_{gate}/C_{total} \tag{3.13}$$

The height of the diamonds reflects only the charging energy:

$$V_{sd} = e^2/C_{total} \tag{3.14}$$

although additional lines running parallel to the first diamond border can reflect level spacing.
Figure 3.4: A cartoon representation the diamond-shaped conductance peaks (known as Coulomb diamonds) expected in differential conductance measurements as a function of both bias and gate voltage. The dotted line denotes zero bias.

The slopes of the diamond edges reflect the relative magnitudes of the capacitance to the source and to the drain.

### 3.3 Cotunneling

In the previous sections, we have discussed single-electron tunneling through quantum dots. There are also higher-order processes where two electrons tunnel simultaneously, known as cotunneling. When cotunneling events are considered, more complicated phenomena than those discussed above can result. Cotunneling can be inelastic (when the dot is left in an excited state, or when some other process is available to dissipate energy) or elastic. Cotunneling events are more common when the dot is well-coupled to the leads.

Observations of cotunneling do not play an important role in our data, nor is cotunneling prominent in our interpretation of our data. We mention the phenomenon here, though, because we observe features inside Coulomb diamonds measured in one of our constriction samples that are affected by source-drain bias but not by gate voltage; we speculate that these features may be due to inelastic cotunneling events.
in this particular sample.
Chapter 4

Electrostatics of Double Quantum Dot Systems

4.1 Introduction

The discussion in the previous chapter has given us a qualitative and quantitative framework for understanding transport through a single quantum dot. Unfortunately, for systems such as our graphene nanostructures where we hypothesize that quantum dots are nucleated by disorder, the number, size and external coupling of quantum dots are not well-controlled. While the preceding discussion of single quantum dot physics can give us qualitative insight into the behavior of more complicated multi-dot systems, we do not discuss in quantitative detail the most general case of \( n \) quantum dots located within a graphene nanostructure, instead referring the reader to the experimental and theoretical literature on the topic [64, 65, 66].

In this chapter, we consider the more analytically tractable case of conduction through a system of two quantum dots. A double dot system can conduct in parallel, where both dots are separately connected to source and drain leads, or in series, where electrons must pass through each dot in succession to pass from the source to the drain. In intentionally fabricated dots, it is simple to determine which situation is applicable: the location of gates and point contacts trivially determines the order of conduction. In quantum dots spontaneously formed in graphene nanoribbons, series
or parallel arrangement must be inferred from the system's conduction properties.

Figure 4.1: A schematic circuit diagram of a coupled double-dot system, with each dot coupled in parallel to the leads and to each gate.

The circuit diagram associated with a parallel double-dot system is shown in figure 4.1. Reservoirs of free electrons serve as the source and drain to the system and are coupled capacitively to dots 1 and 2 with capacitances $C_{1,2,S,D}$ and resistively via tunneling resistances $R_{1,2,S,D}$ to dots 1 and 2. The dots are also each coupled capacitively to the top gate and the back gate via capacitances $C_{1,2,T,B}$ and also to each other via the mutual capacitance $C_{1-2}$. Each dot can contain a variable number of charged particles $N_{1,2}$. The energetics of the double-dot system can be calculated electrostatically. The charge on each dot depends on the capacitances to other elements in the circuit and the voltages on those elements:

\[
Q_1 = C_{1-L}(V_1 - V_L) + C_{1-T}(V_1 - V_T) + C_{1-B}(V_1 - V_B) + C_{M}(V_1 - V_2) + C_{1-D}(V_1 - V_D)
\]

\[
Q_2 = C_{2-L}(V_2 - V_L) + C_{2-T}(V_2 - V_T) + C_{2-B}(V_2 - V_B) + C_{M}(V_2 - V_1) + C_{1-D}(V_1 - V_D)
\]
We simplify the situation by defining the total capacitance of each dot:

\[ C_1 = C_{1-L} + C_{1-T} + C_{1-B} + C_{1-D} + C_M \]  
\[ C_2 = C_{2-L} + C_{2-T} + C_{2-B} + C_{2-D} + C_M \]

Using the total capacitances of each dot, we can define the capacitance matrix

\[ C = \begin{pmatrix} C_1 & C_M \\ C_M & C_2 \end{pmatrix} \]  

Employing this simplification:

\[ \begin{pmatrix} Q_1 + C_{1-L}V_L + C_{1-T}V_T + C_{1-B}V_B + C_{1-D}V_D \\ Q_2 + C_{2-L}V_L + C_{2-T}V_T + C_{2-B}V_B + C_{2-D}V_D \end{pmatrix} = \begin{pmatrix} C_1 & -C_M \\ -C_M & C_2 \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} \]

and solving for the voltages on each dot:

\[ \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} = \frac{1}{C_1C_2 - C_M^2} \begin{pmatrix} C_2 & C_M \\ C_M & C_1 \end{pmatrix} \begin{pmatrix} Q_1 + C_{1-L}V_L + C_{1-T}V_T + C_{1-B}V_B + C_{1-D}V_D \\ Q_2 + C_{2-L}V_L + C_{2-T}V_T + C_{2-B}V_B + C_{2-D}V_D \end{pmatrix} \]

The electrostatic energy associated with a particular charge and voltage on each dot is

\[ U = \frac{1}{2}V \cdot CV \]

therefore, assuming the leads are grounded \((V_L = V_D = 0)\) and employing the typographical simplifications

\[ Q_{\text{equiv}1} = Q_1 + C_{1-T}V_T + C_{1-B}V_B \]
\[ Q_{\text{equiv}2} = Q_2 + C_{2-T}V_T + C_{2-B}V_B \]

\[ U(N_1, N_2) = \frac{1}{2(C_1C_2 - C_M^2)} (C_2Q_{\text{equiv}1}^2 + 2C_MQ_{\text{equiv}1}Q_{\text{equiv}2} + C_1Q_{\text{equiv}2}^2) \]
CHAPTER 4. ELECTROSTATICS OF DOUBLE QUANTUM DOT SYSTEMS

\[
\frac{1}{2(C_1 C_2 - C_M^2)} \left( C_2 (Q_1^2 + 2 Q_1 C_1 - T V_T + 2 Q_1 C_1 - B V_B) + C_1^2 - T V_T^2 + C_1^2 V_B^2 \right) \\
+ 2 C_M (Q_1 Q_2 + Q_1 C_2 - T V_T + Q_1 C_2 B V_B + Q_2 C_1 - T V_T + Q_2 C_1 - B V_B) \\
+ C_1 - T V_T C_2 - T V_T + C_1 - T V_T C_2 - B V_B + C_1 - B V_B C_2 - B V_B \right) \\
+ C_1 (Q_2^2 + 2 Q_2 C_2 - T V_T + 2 Q_2 C_2 - B V_B) \\
+ 2 C_2 - T V_T C_2 - B V_B + C_2^2 - T V_T^2 + C_2^2 V_B^2) \quad (4.12)
\]

and assuming that the charge on each dot

\[ N_i = \pm e N_i \quad (4.13) \]

for graphene dots and defining the quantities

\[ E_{C1} = e^2 \frac{C_2}{C_1 C_2 - C_M^2} \quad (4.14) \]

\[ E_{C1} = e^2 \frac{C_1}{C_1 C_2 - C_M^2} \quad (4.15) \]

and

\[ E_{CM} = e^2 \frac{C_M}{C_1 C_2 - C_M^2} \quad (4.16) \]

\[
U(N_1, N_2) = 1/2 N_1^2 E_{C1} + 1/2 N_2^2 E_{C2} + N_1 N_2 E_{CM} \\
\pm 1/e N_1 ((C_1 - T V_T + C_1 - B V_B) E_{C1} + (C_2 - T V_T + C_2 - B V_B) E_{CM}) \\
\pm 1/e N_2 ((C_2 - T V_T + C_2 - B V_B) E_{C2} + (C_1 - T V_T + C_1 - B V_B) E_{CM}) + \\
1/e^2 ((C_1 - T V_T + C_1 - B V_B)^2 E_{C1} + 2 (C_1 - T V_T + C_1 - B V_B) (C_2 - T V_T + C_2 - B V_B) E_{CM} \\
+ (C_2 - T V_T + C_2 - B V_B)^2 E_{C2}) \quad (4.17)
\]

Conduction through the double-dot system is possible when charge carriers can travel freely through the system. For a system of dots in series this occurs when the energy associated with an extra carrier on dot 1 is equal to that associated with an
extra carrier on dot 2, where both are equal to the energy associated with the original number of carriers:

\[ U(N_1, N_2) = U(N_1 + 1, N_2) = U(N_1, N_2 + 1) \]  
(4.18)

The sets of gate voltages where these three states are degenerate are called triple points.

This is the case when

\[ \frac{1}{2}(2N_1 + 1)E_{C1} + N_2E_{CM} \pm ((C_{1-T}V_T + C_{1-B}V_B)E_{C1} + (C_{2-T}V_T + C_{2-B}V_B)E_{CM}) = 0 \]  
(4.19)

and

\[ \frac{1}{2}(2N_2 + 1)E_{C2} + N_1E_{CM} \pm ((C_{2-T}V_T + C_{2-B}V_B)E_{C2} + (C_{1-T}V_T + C_{1-B}V_B)E_{CM}) = 0 \]  
(4.20)

Isolating one of the gate voltages

\[ V_T = \mp \frac{1}{C_{1-T}E_{C1} + C_{2-T}E_{CM}} \left( \frac{1}{2}(2N_1 + 1)E_{C1} + N_2E_{CM} + V_B(C_{1-B}E_{C1} + C_{2-B}E_{CM}) \right) \]  
(4.21)

and

\[ V_T = \mp \frac{1}{C_{2-T}E_{C2} + C_{1-T}E_{CM}} \left( \frac{1}{2}(2N_2 + 1)E_{C2} + N_1E_{CM} + V_B(C_{2-B}E_{C2} + C_{1-B}E_{CM}) \right) \]  
(4.22)

The mutual capacitance is the key quantity that makes the double-dot system different from two isolated dots. In the limit of very large mutual capacitance, the double-dot system behaves like a single quantum dot, while in the limit of vanishing mutual capacitance the double-dot system behaves like two isolated quantum dots. In the intermediate regime, lines of peak conductance form into hexagonal shapes like those shown in red in figure 4.2. This pattern stems from the fact that the charge on
each dot gives rise to a potential that affects the other dot; the charge on one of the
dots therefore depends not only on the total potential due to the two gate voltages
but also on the charge on the other dot. This result will be useful when we consider
our data on short nanoconstrictions in chapter 6.

Figure 4.2: Calculated conductance of a double-dot system as a function of two gates
that couple unequally to each dot. Parameters used in this calculation include a
ratio of charging energies of the two dots $\frac{E_1}{E_2} = 1/9$, a ratio of the gate couplings
$\frac{C_{1-1}}{C_{2-2}} = 20/9$, a ratio of gate cross-capacitances $\frac{C_{1-2}}{C_{2-1}} = 80$, and an energy associated
with the mutual capacitance between the dots of $E_M = 24E_1$. 
Chapter 5

Long Nanoribbons

5.1 Introduction

We originally began fabricating graphene nanoribbon devices as part of our efforts to make scanning gate measurements on graphene (described in chapter 11). However, early in this process we observed features in transport through our nanoribbons that were not consonant with contemporary models of graphene nanoribbon transport; these features made us realize that the graphene nanoribbons themselves were fruitful topics of investigation.

In this chapter we describe the results of our early measurements on long graphene nanoribbons that led us to suspect that quantum dot behavior might be responsible for the transport properties of our ribbons. Later in the chapter we describe measurements performed in collaboration with Patrick Gallagher that quantify our study by comparing graphene nanoribbons of well-controlled width and lengths that vary from 30 nm to 3 microns. We note that (particularly in the case of these later measurements) the designation of the ribbons described in this chapter as “long” is not so much a physical designation as an indication of fabrication geometry. The ribbons described in this chapter are made with a technique (described in chapter 9) capable of generating ribbons of more than a few hundred nanometers in length but also (in the case of our metal-mask fabrication protocol) very short ribbons of only a few tens of nanometers in length. The “short” nanoconstrictions described in the following
CHAPTER 5. LONG NANORIBBONS

chapter are distinguished from the ribbons described here by their fabrication geometry (described in chapter 10), which is not appropriate for generating constrictions of more than approximately 60 nanometers in length.

While there are several physical metrics that could be used to differentiate “long” from “short” constrictions, our interpretation of our data in terms of localization physics leads us to think of constrictions as “short” when the length scale of localization is comparable to the constriction length. As we will see, whether a ribbon is “short” or “long” according to this metric depends in part on the ribbon’s width, but by this metric all of the constrictions described in chapter 6 are short, though not all of the constrictions described in the latter sections of this chapter are long.

5.2 Transport Gap

Our first successfully fabricated long nanoribbon sample whose native Dirac point was accessible at obtainable gate voltages is shown in figure 5.1. Conductance was measured at 4 K across contacts separated by this constriction. A typical trace is shown in figure 5.2. Notice that the conductance is highly suppressed over a wide

Figure 5.1: An SEM micrograph of the 40 nm wide 200 nm long ribbon fabricated on chip 3-22-b. The red lines are guides to the eye outlining the areas where graphene has been removed via an oxygen plasma etch.
window of back gate voltage; when it begins to increase it does so via a series of spikes, gradually increasing in height up to the highly conducting regimes at large gate voltages away from the Dirac point. Following terminology which was introduced by Molitor et al. [67], we call the span in gate voltage of the region of suppressed conductance the transport gap.

We can also measure differential conductance as we simultaneously change the back gate voltage and the source-drain voltage. Representative data are shown in figure 5.3. There is a region of suppressed conductance centered on the Dirac point in gate voltage and on zero source-drain voltage. At this point we can introduce another kind of gap: the source-drain gap, which is the amount of source-drain voltage necessary to induce conduction across the nanoribbon. Because the span in source-drain bias of the region of suppressed conductance fluctuates rapidly as a function of gate voltage, we employ a smoothing procedure to numerically define the source-drain gap in cases where we wish to make quantitative comparisons between ribbons [68].

5.3 Coulomb Diamond Features

If we examine this region of suppressed conductance at higher resolution, we find that the irregularities seen in the large-scale differential conductance measurement
Figure 5.3: Differential conductance versus source-drain voltage and back gate voltage. Note the region of strongly suppressed conductance centered around zero source-drain bias and $\sim 15$ V back gate voltage.

actually resolve into a series of diamond-like features. This diamond-like geometry is consistent with the presence of quantum dots. From the geometry of these diamonds, we can learn several things about the quantum dot system they may reflect: within the transport gap, there is only one point at which conductance turns on at zero source-drain voltage. Most diamonds do not close at zero source-drain. This suggests that we may be observing conductance through several quantum dots in series. The slopes of each side of the diamond are roughly equal, which implies the dots are coupled roughly equally well to both the source and the drain leads. And the diamonds have a characteristic width, which given information about the electrostatics of the arrangement of conductors near the dot can give us information about the dot area.

Because the putative dots in this ribbon are separated from conducting graphene sheets on the other side of the etched region at a distances of $\approx 40$ nm, which is significantly less than the distance to the back gate of $\approx 300$ nm, I chose to model the quantum dot as a conducting island separated by a narrow strip of insulator from surrounding sea of conductor. Since the distance in the plane from the dot to the surrounding conductor is much less than the distance to the back gate, we can treat the insulating region as electrostatically insignificant and approximate this geometry
by a small area of parallel plate capacitor formed in conjunction with the back gate. Within this model, a range of areas for the dots under consideration can be calculated, which for this ribbon gives dot areas ranging from 860 to 1700 nm$^2$, with equivalent diameters (assuming roughly round dots, which is not necessarily the case) of 33 to 47 nm, roughly congruent with the ribbon width.

In figure 5.5 we show similar data from another long nanoribbon device, 10-24-a. In this higher-resolution data set we see both large Coulomb-diamond-like features several volts in width similar to those observed in 3-22-b and also many narrower features that may be due to larger quantum dots or Fabry-Perot physics occurring between the constriction and the leads (we will discuss this possibility in more detail in chapter 6). Unfortunately, this sample was measured in room 023, where we subsequently determined that spikes in the wall power associated with turning pumps on the evaporator on and off occurred with large enough amplitude and high enough frequency to damage our samples. We believe that one of these spikes occurred during our measurement of this sample, rendering the ribbon insulating. Because of this, further more detailed measurements of the characteristics of these narrow conductance spikes were not possible. However, we later observed similar narrow spikes in the long 30 nm-wide ribbons described in the following sections.
These observations, which are consistent with a model of several quantum dots in series, led us in two directions; the suggestions of quantum dot behavior observed in these long constrictions led us to investigate the transport properties of shorter graphene constrictions, described in the following chapter, in the hopes of isolating one or a few quantum dots inside the constriction. We also moved in the opposite direction, investigating the quantitative dependence of ribbon properties on their length—we describe this latter data set in the following section.

### 5.4 Quantitative Analysis of Gap Properties

In order to make more quantitative statements about the variation of ribbon properties with ribbon length, we developed a fabrication process that allowed us to make ribbons with standardized width (varying by less than the \( \sim 5 \text{ nm} \) resolution of the scanning electron microscope that we use to measure the ribbon width) and variable length. This fabrication process is described in section 9.4. These ribbons allow us to investigate the length dependence of conductance properties without contaminating our results with the known strong influence of width-dependence [37].
5.4.1 A Menagerie of Gaps

We begin by defining several energy scales that are relevant to the following discussion. We note that there is the possibility for semantic confusion between the term “gap” as it refers to a region of suppressed conductance and the term “gap” as it refers to the extent of that region in gate voltage, bias, or temperature. Nonetheless, we follow the standard used in the current literature [67, 40] and refer to both the region of suppressed conductance and its extent as “gaps.” In this section, the term is used to refer to the extent of the region of suppressed conductance.

The confinement gap is the energy of the lowest available state that we expect from Dirac Fermions confined in a box of the same width as the constriction:

\[ E_c = \frac{\hbar v_F}{2W} \]  

(5.1)

where \( v_F \) is the invariant Fermi velocity and \( W \) is the constriction width. In our model of transport through graphene nanostructures, described in chapter 7, the confinement gap plays an important role in isolating disorder-nucleated quantum dots from each other.

We measure the transport gap by quantifying the width of the region of suppressed conductance in gate voltage; in a model of quantum dots in series it is the Fermi energy required to fill the insulating regions throughout the ribbon; in the scenario depicted in figure 5.6 this would involve raising the Fermi level above or below the energy scale of the disorder.

We measure the source-drain gap by quantifying the bias required to turn on conduction in the center of the transport gap. It is more difficult to define this quantity in a model of quantum dots in series; for transport through a single dot it would be the charging energy of that dot. In a disordered multi-dot system the source-drain gap is a more complicated function of the charging energy of the smallest dot and the relative placement in energy space of each dot with respect to its neighbors. In the inelastic tunneling limit, it is the energy required to tilt the first unoccupied energy level of each dot above its neighbor, although even this simple picture is further complicated by electrostatic considerations having to do with the relative capacitance.
of the source and drain electrodes to dots in the middle of the ribbon and to dots at the ends of the ribbon.

The final relevant energy scale is the activation energy: it is the energy scale (in temperature) required to turn on conductance through the constriction, and is a reflection of the height of the energetic barrier separating one dot and the next. We do not perform the temperature-dependence measurements on these ribbons necessary to extract this quantity, but we do compare measurements of this quantity by others [59] to the quantities predicted by our model. In figure 5.6 we illustrate the meaning of the confinement and transport gaps in our model.

![Figure 5.6: The physical origin of the transport and confinement gaps in our model.](image)

### 5.4.2 Source Drain and Transport Gap Data

In order to quantitatively study the dependence of the magnitude of these gaps on different variables, it is important to develop a consistent way of extracting them from data sets such as that shown in figure 5.5.

To quantify the transport gap, we use the technique described by Molitor et al. [67], fitting lines to the roughly linear region of conductance increase on either side of the gap and taking the gap to be the distance between the points where they each intersect zero conductance. In figure 5.7 we show an example of one such fit. To quantify the source-drain gap, we first apply a smoothing routine over an 0.5 V range in back gate voltage to avoid identifying the source-drain gap with the very narrow spikes of suppressed differential conductance that rise far above the typical...
source-drain bias at which differential conductance turns on in the data set. After the smoothing, we identify the source-drain gap as the largest magnitude of bias for which conductance is suppressed below $5 \times 10^{-7}$ Siemens for both positive and negative bias. Both of these definitions break down for those very short ribbons that display no fully suppressed conductance, and both are arbitrary in the sense that different and equally consistent definitions could be chosen. However, applying a single standard across all of our data sets allows us to make meaningful comparisons among them. It has been alleged [67] that the transport and source-drain gaps are linearly related. Over our wide range of ribbon lengths, for our 30 nm-width ribbons, we do not find this to be the case. In figure 5.8 we show data from all of our metal-mask fabricated nanoribbon samples relating the transport gap for each sample to the source-drain gap. We do not find any systematic relationship between the two quantities. We show a plot relating the magnitude of the transport gap in a given ribbon to the ribbon’s length in figure 5.9. We find no correlation between the magnitude of the transport gap and the ribbon length. This is perhaps surprising, given our observation that short enough nanoribbons or constrictions display no transport gap. The source-drain gap, however, does appear to have a systematic dependence on ribbon length. In figure 5.10 we show the source-drain gap versus the ribbon length for all samples.
Figure 5.8: The measured source-drain gaps plotted against the corresponding transport gaps for all of our 30-nm wide ribbons.

Figure 5.9: The magnitude of the transport gap plotted versus the length of the nanoribbon.
The source-drain gap appears to continue to grow even for the longest ribbons we have fabricated.

![Figure 5.10: The magnitude of the source-drain gap plotted versus the length of the nanoribbon.](image)

We will discuss how these observations fit into our model of transport through graphene nanoribbons in chapter 7.

### 5.4.3 Annealing Experiments

As we will describe in further detail in chapter 7, our model for transport through graphene nanoribbons and constrictions involves quantum dots that are nucleated by a combination of background potential fluctuations caused by disorder in the vicinity of the ribbon and of the confinement gap of the ribbon. An important part of testing this model involves the ability to manipulate the arrangement of impurities that produces to the disordered background potential.

The charged impurities that lead to long-range Coulomb scattering can be located in any of three places: buried in top few nanometers of the oxide upon which the graphene sits, located on top of the oxide but underneath the graphene sheet, or sitting on top of the graphene sheet itself. While impurities buried in the oxide are mobile at room temperature, and can move at low temperature as a result of voltage...
shocks, we know of no way to reduce their density during transport measurements. However, it is possible to reduce the density of charged impurities sitting on top of the graphene sheet (and possibly between the graphene sheet and the oxide as well) by two methods: heating the entire chip containing the device in a hydrogen-containing atmosphere at 300 °C [69, 70, 71] and heating the graphene alone in vacuum by running a large current through it [72, 10]. It has been established by AFM [72] and STM [69] studies that both techniques reduce the density of impurities, including charged impurities, near the graphene. Whether this reduction occurs via evaporation, electromigration (in the case of current annealing of narrow ribbons that widen out into a broader graphene sheet), or chemical reactions (in the case of hydrogen annealing) is less well-understood. We have used both of these methods to change the impurity density in our graphene nanoribbons.

In table 5.1 we describe the annealing history of all of the ribbon sets described in the rest of this section. The total number of ribbons does not equal the number of ribbon sets: in general, each set contains multiple ribbons.

In figure 5.11 we show data detailing the changes of the source-drain and transport gaps upon annealing. In general, the transport gap shrinks upon annealing, while the source-drain gap sometimes shrinks and sometimes grows. In figure 5.12 we show data relating the magnitude of the transport gap in all of our samples to the distance of the gap's center from zero back gate voltage. This is an important relationship because in bulk samples it has been shown that the distance of the Dirac point from zero back gate voltage correlates with the magnitude of the background disorder potential [27]. In our ribbons too, the distance of center of the transport gap from zero back gate voltage clearly correlates with the gap's magnitude, lending credence to our assertion, discussed further in chapter 7, that the width of the transport gap is a reflection of the magnitude of the background disorder potential.

5.4.4 Calculating the temperature reached

It is important to calculate the temperature we reach when current-annealing our ribbons, in order to understand whether effects such as the edge-reconstruction observed
### Table 5.1: Long nanoribbon sets and their annealing histories

<table>
<thead>
<tr>
<th>Data set</th>
<th>Annealing History</th>
<th>Ribbon Lengths (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Not annealed; measured while immersed in liquid helium</td>
<td>1000, 1600, 2000</td>
</tr>
<tr>
<td>B</td>
<td>Not annealed; measured while immersed in liquid helium</td>
<td>500, 600, 800, 900</td>
</tr>
<tr>
<td>C1</td>
<td>Not annealed; measured while immersed in liquid helium</td>
<td>100, 500, 550, 750</td>
</tr>
<tr>
<td>C2</td>
<td>Removed from cryostat after C1, argon annealed at 300 °C, exposed to atmosphere, cooled and measured in vacuum</td>
<td>same as C1</td>
</tr>
<tr>
<td>C3</td>
<td>Warmed to RT after C2, current annealed at $3 \times 10^8$ A/cm, cooled and measured without breaking vacuum since C2</td>
<td>same as C1</td>
</tr>
<tr>
<td>D1</td>
<td>Not annealed; measured in xx</td>
<td>30, 1850, 3050</td>
</tr>
<tr>
<td>D2</td>
<td>Exposed to atmosphere after D1, current annealed at $5 \times 10^7$ A/cm, cooled and measured in vacuum</td>
<td>same as D1</td>
</tr>
<tr>
<td>D3</td>
<td>Warmed to RT after D2, current annealed at $3 \times 10^8$ A/cm, cooled and measured without breaking vacuum since D2</td>
<td>same as D1</td>
</tr>
<tr>
<td>E</td>
<td>Not annealed</td>
<td>40, 340, 1800, 2520</td>
</tr>
</tbody>
</table>
CHAPTER 5. LONG NANORIBBONS

Figure 5.11: The evolution of the transport and source-drain gaps with annealing. The short-dashed lines indicate rounds of current annealing performed in situ, while the wide-dashed line indicates hydrogen annealing followed by brief exposure to air before measurement in vacuum.

Figure 5.12: The magnitude of the transport gap plotted versus the distance of its center from zero back gate volts.
in graphitic nanoribbons at very high temperatures [73] are taking place.

Most elements of this calculation are straightforward; we know the dimensions of our nanoribbons, the current we are applying and the voltage drop occurring across the ribbon and the thermal conductivity of the graphene sheet and of the underlying substrate. The missing element is the thermal resistance of the graphene-substrate interface. Recently, Freitag et al. [74] made the first and (to this date) only measurement of the thermal conductance of the graphene-substrate interface for exfoliated graphene flakes placed on an SiO$_2$ surface. Spatially resolved Raman spectroscopy measurements on contacted graphene conducted during current annealing allow them to extract the thermal interface conductance between the graphene and the underlying oxide; they find $g_{gr-ox} = 2.4 \times 10^7$ W m$^{-2}$ K$^{-1}$; this is the thermal conductance of the graphene-oxide interface only, not including the thermal conductance of the underlying SiO$_2$ to the heavily doped Si underneath.

That quantity, for a nanoribbon with a thickness much less than the oxide thickness is given by

$$ g_{ox} = \frac{\pi k_{ox}}{\ln(8t_{ox}/\pi w)} $$

in analogy to the formula for a nanotube placed on oxide, with $k_{ox} = 4.7 \times 10^8$ W/m$^2$ K, yielding $g_{ox} = 1.3 \times 10^9$ W/m$^2$ K for our 300 nm oxide. The conductance of heat from the nanoribbon to the substrate is therefore limited by the nanoribbon-oxide interface.

Freitag et al. additionally find that radiative heat transfer out of the GNR removes an insignificant fraction of the heat from the GNR. Finally, they also extract the temperature dependence of graphene's thermal conductivity for temperatures above 350 K:

$$ \kappa_{gr}(T) = \frac{5000}{1 + 0.01(T - 350) mK} $$

In calculating the temperature reached in our ribbons, we use this data and following Murali et al. [75] calculate the temperature reached by a graphene nanoribbon
under Joule heating to be

$$T_{\text{anneal}} = T_0 + \frac{V_{\text{anneal}} I_{\text{anneal}}}{gL} \left[ 1 - \frac{1}{\cosh(L/2L_H)} \right]$$

(5.4)

where \(T_0\) is the temperature of the electrical leads (in our case roughly 300 K), \(L\) is the ribbon length, \(g\) is the thermal conductance of the ribbon to the substrate, and

$$L_H = \left( \frac{ak}{g} \right)^{1/2}$$

(5.5)

is the thermal healing length along the GNR, where \(a\) is the cross-sectional area of the graphene sheet (in our case the nanoribbon width multiplied by the graphene sheet thickness) and \(k\) is the thermal conductivity of the GNR itself.

This calculation is made for a slightly different geometry than ours: their nanoribbons extend from contact to contact, while ours end in regions of extended graphene, which are in turn contacted. However, by calculating the temperature reached in our ribbons as if they extended all the way from contact to contact, we can place an upper bound on the temperatures they can reach, since the thermal dissipation will be greater and the Joule heating less over the wide portions of the graphene near the contacts.

Given this information, we can calculate an upper limit for the temperature of our ribbons: for a typical ribbon where 3 V drops across 300 nm, with contacts spaced approximately 3 \(\mu\)m apart, the temperature of the ribbon must be less than 1280 K. This is comfortably below the SiO\(_2\) melting point of roughly 1950 K, which is consonant with the fact that we do not observe any melting of the substrate after annealing attempts. The SiO\(_2\) melting point is in turn well below the 2300 K which Jia and collaborators [73] believe marks the lower bound of temperatures at which their observed edge reconstruction takes place.

Finally, we consider the question of how this upper limit may vary for plausible variations of the graphene-substrate thermal conductance. Since Freitag and collaborators provide the only available data on the thermal conductivity of the graphene-substrate interface, we must look elsewhere to gain a sense of how much this quantity
might vary from sample to sample, or with the details of sample preparation. Carbon nanotubes on oxide surfaces constitute a similar system that can give us a sense of the likely variation in the thermal conductance of the graphene–oxide interface. Pop and collaborators [76] calculate the interface thermal conductances for carbon nanotubes on an SiO$_2$ surface based on measured breakdown voltages; their results for $g_{\text{nt-ox}}$ range from 0.14 to 0.20 W K$^{-1}$ m$^{-1}$ per nanotube length, a 50% variation. If we assume a similar level of variation for the thermal conductance of the graphene–oxide interface, and further assume that the value given by Freitag and collaborators is at the high end of the range, we calculate a maximum temperature of 2260 K.
Chapter 6

Short Constrictions

6.1 Introduction

Short nanoconstrictions are attractive because they offer the chance to investigate conduction through nanostructured graphene on length scales similar to or shorter than several physically interesting length scales, including the Fermi wavelength of electrons in the leads or the localization length of charge carriers inside the constriction. At gate voltages near the Dirac point (for instance, within 10 V) the Fermi wavelength of electrons in the leads (calculating charge carrier density based on a parallel plate capacitor model with the back gate)

\[ \lambda_F = \frac{2\sqrt{\pi ed}}{\sqrt{V \epsilon \epsilon_0}} \]  

(6.1)

(where \(d\) is the 300 nm oxide thickness, \(\epsilon\) is the permittivity of SiO\(_2\), and \(\epsilon_0\) is the permittivity of free space) becomes greater than \(\approx 40\) nm, which is a scale achievable by e-beam lithography techniques. Therefore for short constrictions and small gate voltages we can achieve Fermi wavelengths longer than the constriction length, and perhaps observe enhanced tunneling across the constriction. Of course, there is a practical limit to the Fermi wavelengths that can be reached experimentally; when the average carrier density becomes smaller than the variations in carrier density due to disorder the picture of a uniform Fermi wavelength is no longer valid. We choose
CHAPTER 6. SHORT CONSTRICTIONS

Table 6.1: Short constrictions and their properties

<table>
<thead>
<tr>
<th>sample name</th>
<th>width (nm)</th>
<th>length (nm)</th>
<th>flake mobility (cm²/Vs)</th>
<th>dot areas (nm²)</th>
<th>equiv. diam. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-17-a short</td>
<td>11</td>
<td>30</td>
<td>700</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>1-17-a long</td>
<td>15</td>
<td>60</td>
<td>700</td>
<td>300–900</td>
<td>20–34</td>
</tr>
<tr>
<td>10-24-g</td>
<td>35</td>
<td>60</td>
<td>3000</td>
<td>400–600</td>
<td>23–28</td>
</tr>
<tr>
<td>9-7-e</td>
<td>55</td>
<td>60</td>
<td>700</td>
<td>1600–7100</td>
<td>45–95</td>
</tr>
</tbody>
</table>

10 V as the gate voltage in the above calculation because this at this gate voltage the average carrier density is larger than typical density fluctuations even for rather low-mobility samples on oxide substrates. For very high-mobility or suspended samples, the experimentally achievable Fermi wavelengths are longer.

Furthermore, if, as our measurements on long nanoribbons suggest, localization of charge carriers into quantum dots is occurring on a lengths scale of tens of nanometers, fabricating constrictions on this length scale offers the possibility of isolating a single quantum dot or even making highly conducting constrictions that are shorter than the length scale on which charge carriers are confined.

Finally, the possibility of fabricating constrictions whose length is shorter than the mean free path of charge carriers in the graphene sheet offers the hope of observing behavior such as quantized conductance plateaus.

The fabrication of these constrictions is described in chapter 10. In table 6.1 we summarize the constrictions discussed in this chapter in terms of their widths, lengths, mobilities, and inferred dot areas and diameters (these last two quantities will be discussed in further detail in section 6.6). Each constriction’s width and length is determined from SEM micrographs taken after the conclusion of all transport measurements. Mobilities are measured between contacts that do not span the constriction by a method described in section 6.3.1.
6.2 Conductance Versus Back Gate Voltage

The differences between short constrictions and long nanoribbons become apparent upon making the first and simplest kind of measurement possible: conductance across the constriction versus back gate voltage.

In figure 6.1 we show conductance across our narrowest 60-nm long constriction on sample 1-17-a as a function of back gate voltage.

![Figure 6.1: Conductance across the 15 nm-wide by 60 nm-long constriction on 1-17-a versus back gate voltage at 4 K.](image)

This conductance trace differs from those of our long nanoribbons: while there is a region of gate voltage where conductance is suppressed on average and sometimes achieves values close to zero, inside of this region there are many conductance peaks. It is important to emphasize that this is an extremely narrow constriction: at 15 nm wide, one would expect a long nanoribbon to have a large transport gap of tens of volts.

In figure 6.2 we show data from another, shorter (11 nm wide and 30 nm long) constriction fabricated on the same flake as the constriction represented in figure 6.1. Despite being narrower, this shorter constriction displays much more open conductance. At no back gate voltage does the conductance approach zero. In fact, aside from the spiky features seen nearest the Dirac point, this conductance profile much
more closely resembles that of a sheet of bulk graphene than that of a nanoribbon.

Figure 6.2: Conductance across the 10 nm-wide by 30 nm-long constriction on 1-17-a versus back gate voltage at 4 K.

From this data alone, it is clear that constriction length is a critical factor in the conductance properties of graphene constrictions. On the length scales we are dealing with (where strong tunneling amplitudes across the constriction can be discounted), this observation rules out confinement alone as a credible explanation for the properties of graphene nanoribbons and constrictions.

### 6.3 Searching for quantized conductance

In measurements of the conductance through short constrictions fabricated on high-quality GaAs 2DEG's, steps in the conductance as a function of the ratio of the constriction width and the Fermi wavelength are observed. In figure 6.3 we show an example of such a measurement [77]. It is important to note that the gate voltage in this measurement is the voltage on the pair of split gates defining the quantum point contact, and primarily affects the constriction width (rather than the Fermi wavelength of particles inside the constriction). This is in contrast to the way in which such a measurement might be made in an etched graphene constriction, where the voltage would primarily affect the Fermi wavelength (through the particle density).
and could not change the constriction width. Nonetheless, the ratio of the constriction width and the Fermi wavelength can be varied in both cases.

Data such as that in figure 6.3 is interpreted in terms of the Landauer formalism [78, 79], where the conductance increases as each additional subband in the quantum point contact acts as an additional conductance channel. An important component in producing quantized conductance plateaus is the absence of inter-subband scattering. Also critical are mean free paths that exceed the constriction length: if particles have a high probability to scatter within the constriction, quantized conductance will not be observed.

In general, the extensive processing done on nanostructured graphene results in low final mobilities—less than 1000 cm$^2$/Vs in most of our samples (as measured across contacts not spanning the constriction). Few other researchers in the field publish their nanoribbon sample mobilities [37, 38, 80, 40, 67]. Those that do report mobilities of $\sim 200$ cm$^2$/Vs [44], comparable to (though slightly less than) ours. These mobilities produce mean free paths that are less than typical constriction lengths. However, we were able to fabricate one relatively high-mobility ($\sim 3000$ cm$^2$/Vs) constriction sample with a length of 60 nm and a width of 35 nm. Our method for determining
sample mobilities for constrictions such as this is discussed in section 6.3.1.

Figure 6.4: a) An SEM micrograph of the entire sample, showing the constriction and the contacts. The brightest features in the image are the metal contacts and gates, while the dark shape is the graphene flake. The apparent break in the gates defining the constriction at the upper edge of the flake is believed not to be shorting the two sides of the graphene together based on electrical measurements of the gate. b) A high-resolution image of the constriction region alone; the bright lines are the metallic gates that sit within the etched region defining the constriction. The small gap between them is the constriction.

Images of this sample (taken after the conclusion of our measurements) are shown in figure 6.4. While it appears from the image on the left that the flake actually has two parallel constrictions, we believe that the top break in the gates defining the constriction happened due to an electrostatic breakdown during measurement. In initial measurements, we were able to affect the conduction through the constriction with both side gates, and neither gate was shorted to the graphene on either side of the constriction. After the breakdown of one of the gates due to the application of a too-large voltage, voltage applied to that side gate did not affect the conductance properties of the constriction, and it was shorted to the graphene on one side of the constriction only. Because of these observations, we believe that this blown-out section is not shorting together the two sides of the graphene flake, and that the etch during the original fabrication processes was effective at removing the graphene under
this portion of the gate.

6.3.1 Calculating the flake mobility

![Graph showing conductance versus gate voltage](image)

Figure 6.5: Conductance versus back gate voltage of sample 10-24-g for two pins not separated by the constriction. The slope of the conductance trace at low gate voltages allows us to estimate the mobility.

In figure 6.5 we show the data from which we infer the mobility of this sample. The area comprised between the two measurement contacts is roughly one square, and so the conductivity is roughly equal to the conductance. From this data we can estimate the mobility as

\[
\mu = \frac{\sigma}{n e}
\]

(6.2)

where \(\sigma\) is the conductivity at some distance \(V\) (within the linearly increasing regime) from the Dirac point and \(n\) is the charge carrier density at that point, estimated via a parallel plate capacitor model:

\[
n = \frac{\varepsilon \varepsilon_0 V}{ed}
\]

(6.3)

where \(d\) is the 300 nm thickness of the SiO\(_2\) substrate, \(\varepsilon\) is the permittivity of SiO\(_2\), and \(\varepsilon_0\) is the permittivity of free space.

We have made careful measurements of conductance versus back and side gate voltages, looking for conductance plateaus that depended only on the total doping
inside the constriction. Data from these measurements are shown in figure 6.6. While

![Graph showing conductance versus side gate voltage for several values of back gate voltage for constriction 10-24-g.](image)

Figure 6.6: Conductance versus side gate voltage for several values of back gate voltage for constriction 10-24-g.

the data do show suggestive plateau-like features, they do not fall at integer multiples of $2e^2/h$, and they are complicated by the (reproducible) fluctuations layered over them. In the absence of other high-mobility samples and because of the marginal (at best) existence of plateaus in this data set, we chose to abandon the search for conductance plateaus in graphene constrictions. Since then, certain calculations have advanced the idea that conductance plateaus should be unobservable in all but the most nearly atomically ordered constrictions [55, 81]. While there is an experimental paper by Lin and coauthors that claims to observe conductance plateaus in graphene nanoribbons, [80] these plateaus do not occur at integer multiples of the conductance quantum, and they seem to be observed only at elevated temperatures (many 10's of K). Because of this, it seems likely that Lin et al are observing Coulomb blockade peaks that because of elevated temperatures resemble plateaus. Similar phenomena are seen in our elevated temperature data sets. In figure 6.7 we see that features clearly identifiable at lower temperature as conductance peaks superposed on a rising background at higher temperature broaden and come to resemble plateaus.
Figure 6.7: Green trace is relatively low temperature data at 6K, showing peaks in conductance superposed on a rising background. Red trace is taken at 20 K, where broadened peaks resemble plateaus.

6.4 Double Gate Measurements

In this section I will discuss one class of measurements that can be made on short constrictions fabricated with side gates: measurements of conductance versus two different gate voltages simultaneously. This technique allows us to control the potential in the constriction region separately from that in the graphene leads, an ability that is especially useful in very open constrictions where the conductance of the constriction is not much greater than that of the graphene leads. It also gives us the ability to address conductance features arising from within the constriction region with two gates that may couple to local features differently, an ability that has been useful to us in understanding transport through our very narrow constrictions.

6.4.1 Double gate measurements in very narrow constrictions

To begin I’ll present data from my narrowest short constriction, 1-17-a. In figure 6.8 conductance is shown versus both back gate and a single side gate voltages. Several features of this data set are worth noting. First, conductance is suppressed by many
orders of magnitude (note the log scale) for certain gate voltages. However, many conductance spikes are present throughout the "gapped" Dirac region (the diagonal stripe of suppressed average conductance running across the data set). Inside of the gapped region, the spikes are relatively narrow and straight, moving with the total energy inside the constriction region. Outside of the gapped region, the areas of high conductance are more geometrically complicated. In order to understand the nature of the conductance peaks outside this central region, we took a second data set at higher resolution concentrating on the transition region.

In figure 6.9 we show this higher-resolution data. At the upper right-hand corner of the data set, the simple conductance peaks characteristic of the Dirac region are still present. Occupying the bulk of the data set, however, are the more complicated high-conductance regions observed on the edges of the larger-scale data set in figure 6.8. A close examination of the high-resolution data reveals a rough hexagonal pattern of regions of suppressed conductance, broken up by several vertical and diagonal disruptions that we attribute to trapped charges moving around near the device causing abrupt changes in the effective voltage experienced by the constriction region. This pattern bears a resemblance to the behavior we would expect for the double-dot system described in chapter 3.

This evidence for a change in the apparent number of dots (or alternatively a
dramatic increase in their coupling) as a function of the local potential of the constriction militates against the picture proposed by Sols et al. [53] where quantum dots inside a graphene nanoribbon are nucleated by line edge roughness in the lithography defining the ribbon’s edges, causing wider regions that are divided from each other by narrower necks. Such a configuration is outlined diagramatically in figure 2.3. While it is possible that one could begin to populate or separate from each other different edge-roughness-nucleated quantum dots as a function of gate voltage, such a scenario would be unlikely unless the dots were of widely different physical size, which is implausible given typical ribbon dimensions (10-100 nm) and line edge roughness dimensions (1-5 nm). Furthermore, the changes we observe in the apparent sizes and numbers of dots upon annealing or thermal cycling are also inconsistent with quantum dots nucleated by static line edge roughness.

6.4.2 Double gate measurements in wider constrictions

In wider short constrictions, measurements similar to those just described produce dramatically different results. In figure 6.10 we show data from a 35 nm-wide 60 nm-long constriction. Though a long nanoribbon of this width would be well-gapped, in this short constriction geometry the picture is very different. In this data set, the
conductance is never highly suppressed for any combination of gate voltages. Furthermore, instead of a broad region of highly suppressed conductance, this nanoconstriction displays a dip in conductance similar to the dip seen at the Dirac point in bulk graphene. Compare the characteristics of sample 10-24-g to those of the bulk sample depicted in figure 6.11 (b). In this figure a measurement of the resistance of a bulk graphene device versus both a local top gate voltage and a back gate voltage that affects the entire flake is shown next to the same data set presented in figure 6.10. In both the locally gated constriction and in the bulk graphene device there are two resistance peaks, one reflecting the Dirac point outside of the locally gated region that depends on back gate voltage alone, and one that moves with both the back gate and the local gate voltage that reflects the Dirac point in the locally gated region (note that in both of these geometries the back gate affects both the bulk flake energy and the energy of the locally gated region).

Incidentally, in both of these data sets, the slope of the resistance peak corresponding to the local region can give us information about the capacitance of the local gate to the sample; the slope of the conductance minimum due to the constriction region as a function of the back gate and the local gate voltages reveals the relative coupling of each gate to the constriction region. Since we have detailed knowledge of the back gate’s capacitance through its geometry and the relevant dielectric constants, we can
CHAPTER 6. SHORT CONSTRICTIONS

Figure 6.11: a) Resistance of side-gated graphene constriction 10-24-g as a function of both side gate voltage and back gate voltage. b) Resistance of a bulk graphene device as a function of both a local gate voltage and a back gate voltage. Resistance ranges from $1 \text{ K}\Omega$ (black) to $7 \text{ K}\Omega$ (white).

estimate the value of the local gate capacitance. The relative coupling of the side gate $V_{sg} = \beta V_{bg}$ ranges from $\beta \approx 10$ (sample 1-17-a) in the narrowest constriction to $\beta \approx 2$ (sample 9-7-d) in the widest. The variation of coupling with width makes sense, given that the wider the constriction becomes the farther the side gates are, on average, from a point inside the constriction. We will use these coupling factors later in estimating dot geometries.

If the constriction data in figure 6.11(a) differ from the bulk sample data in figure 6.11(b), it is in the features of the Dirac point associated with the local region: in the constriction sample this resistance peak is more diffuse, showing a number of peaklets or striations that move with the total energy in the constriction region. We observe these striations in other constriction samples as well.

In figure 6.12 we show a plot of the resistance of sample 9-7-e, a wider 55 nm wide 60 nm long constriction. While the coupling of the side gate to the constriction is much smaller, resulting in a different slope for the Dirac peak associated with the constriction, the striations characteristic of the constriction’s Dirac peak in 10-24-g are also present here.
6.5 Regularity of Conductance Peaks

These striations are also reflected in measurements of the conductance of these samples with respect to a single gate voltage. In certain samples, these fluctuations or conductance peaks are reproducible but do not occur with clear regularity, as in figure 6.13 and figure 6.14.

However, in our highest-mobility constriction sample, the conductance peaks (shown in figure 6.15) are more regular.

6.6 Differential Conductance Measurements

We can extend our study of the physics underlying these conductance peaks by applying a bias and making differential conductance measurements as a function of both gate voltage and bias.

In figure 6.16 we show data from our highest-mobility constriction taken in March of 2008. The regular conductance peaks observed in figure 6.15 appear here as regular Coulomb diamond-like features. The diamond height grows as the gate voltage nears the Dirac point.
Figure 6.13: Conductance of side-gated constriction 9-7-e as a function of back gate voltage only. Three different colored traces are taken as the gate voltage is ramped up to 50 V, down to -50 V, and up to 0 V again.

Figure 6.14: Conductance of side-gated constriction 10-24-d as a function of back gate voltage only. Data are taken at 4.3 K.
Figure 6.15: Conductance of side-gated constriction 10-24-g as a function of back gate voltage only. Data is taken at 6 K.

Figure 6.16: Sample 10-24-g measured in March 2008. T = 2 K.
This regularity is stable for weeks when the sample is kept below \( \sim 20 \) K in the fridge, but doesn't survive thermal cycling. In figure 6.17 we show data from a subsequent cooldown.

![Back gate voltage vs. source-drain voltage](image1.png)

**Figure 6.17:** Sample 10-24-g after thermal cycling. \( T = 0.25 \) K

A differential conductance map of sample 9-7-e shows a degree of regularity intermediate between that of sample 10-24-g pre- and post-thermal cycling: (figure 6.18).

![Side gate voltage vs. source-drain voltage](image2.png)

**Figure 6.18:** Sample 9-7-e. \( T = 4.2 \) K.

For each of these samples, we calculate the areas of quantum dots that might give
rise to the observed range of diamond widths using the parallel plate capacitor model described in section 5.3. The results of those calculations are summarized in table 6.1. Although the parallel plate capacitor model we use allows us to infer only dot areas, and not aspect ratios, we note equivalent diameters (assuming circular dots) in order to give a more intuitive sense of dot size.

Finally, we note that while among this selection of samples it is rare to observe the regularity of diamonds seen in 6.16, Coulomb-diamond like features nonetheless occur in each sample.

6.6.1 Short constrictions fabricated without side gates

There is an exception, though. In figure 6.19 we show differential conductance data from a constriction fabricated in the same way as the other short constrictions discussed in this chapter, except that the final steps where a dielectric and gate metal are deposited have not been undertaken. The differential conductance in this sample is qualitatively different from that of the metallized samples. Few to no Coulomb diamond-like features are present, and instead there are several streaks of suppressed conductance that are well-localized in Fermi level but persist for a wide range of bias voltages.

![Figure 6.19: Sample 4-8-p4. T = 4.5 K.](image-url)
Another example of this behavior is sample 10-24-d, whose differential conductance map is shown in figure 6.20. This sample was intended to be a side-gated sample, but during the sonication required for adequate liftoff of the dielectric (described more fully in chapter 10), the side gates broke and were lifted away for microns around the constriction region. In this data set, Coulomb diamond-like features are not readily identifiable.

We do not have a great deal of evidence that helps us to explain why short constrictions fabricated without side gates behave so differently. A few possibilities can be raised, though. Anderson localization in graphene nanostructures is expected to nucleate at the edges, because the missing atoms at the edge can provide potentials sharp on the scale of the lattice spacing, thus allowing transitions between the two branches of the band structure and breaking the suppression of backscattering found in bulk graphene. Our model for transport through graphene nanostructures, by contrast, involves charged impurities distributed over the whole surface of the nanostructure. In this model the edges are not privileged.

We expect the deposited dielectric and metallic side gates to have some effect on the nearby graphene, either through chemical modification and doping or through screening. It is likely that these effects are more important at the edges, in close proximity to the dielectric and the metal, than at the center of the constriction.

Figure 6.20: Sample 10-24-d. $T = 0.25\, \text{K}$.
We therefore hypothesize that the effect of the dielectric and gate metal is, through passivation or screening, to make the edges less important in the side-gated samples and to suppress Anderson localization effects in favor of quantum dot formation in the bulk of the ribbon or constriction due to background potential variation.

This supposition doesn’t explain why the behavior we see in long non-side gated nanoribbons seems to be better explained by quantum dot physics than Anderson localization. We can only hypothesize that in our relatively wide ribbons (w ≈ 30 nm) any Anderson localization taking place at the edges still permits the existence of a less-localized central channel in which we are able to observe quantum dot-like behavior.

### 6.7 Temperature Dependence

We have conducted measurements at multiple temperatures on a subset of our short constriction samples, and on a smaller number of samples we have been able to do controlled temperature-dependence measurements.

#### 6.7.1 Room Temperature Transport Measurements

Even in our narrowest short constrictions we observe no total suppression of conductance at room temperature. This is not surprising, as a room-temperature transport gap is observed only in the narrowest (w < 10 nm) long (l ≥ 200 nm) graphene nanoribbons [44].

#### 6.7.2 Temperature Dependence of Conductance Peaks

In this subsection we examine the temperature dependence of the conductance peaks that we observe to determine whether that dependence is consistent with transport through quantum dots.

We were able to make measurements at both 4.2 K in liquid helium and (briefly, before the breakdown of the sample) at 0.25 K in the helium-3 fridge on our narrowest constriction, 1-17-a. In figure 6.22 we show a narrow window of conductance
versus back gate voltage at 4 K, where we have fit a single conductance peak with functions corresponding to a lifetime-broadened (Lorentzian) peak and a temperature-broadened peak in the resonant tunneling regime. At this temperature and with this point resolution, it is impossible to single out one functional form as providing the better fit.

Data at 0.25 K were measured in the helium-3 fridge in a subsequent cooldown, so we cannot expect that conductance peaks will occur at the same voltages. In fact, at 0.25 K it was difficult to find a well-formed single conductance peak in our data set. Instead, we fit to a double-peak feature, as shown in figure 6.22.

At this lower temperature, the lifetime-broadened Lorentzian fit is clearly better than the temperature-broadened fit.

These two measurements taken together suggest that the temperature begins to exceed the energy associated with the particle lifetime for charge carriers in whatever state is responsible for the conduction properties of this constriction between 0.25 K and 4.2 K.

We can make more quantitative statements about our sample 10-24-g, thanks to more detailed temperature dependence data.

In figure 6.23 we show the complete data set for the zero-bias conductance of sample 10-24-g at temperatures ranging from 0.25 to 20 K, collected in a single
cooldown over a weeklong timescale. Several general features are worth noting. In general, the magnitude of the conductance increases with increasing temperature. However, this increase is most prominent off the conductance peaks: the value of peak conductance at low temperature is quite high. Second, the conductance traces become smoother as temperature increases. Third, the locations of conductance peaks are constant over this range of temperatures and timescales.

In figure 6.24 we show a representative fit to one of the conductance peaks in the data set of temperature-dependence measurements on sample 10-24-g. Because we do not have a large number of data points for each conductance peak, we can't place a high degree of certainty on the fits. At this temperature and with this degree of fitting certainty, it is not possible to distinguish between the Lorentzian fit and the \( \cosh^2 \) fit.

In figure 6.25 we show peak areas extracted from temperature-broadened resonant tunneling regime fits to the \( 6 \, V_{bg} \) peak at each temperature versus temperature. The kink in the relationship between peak area and temperature is indicative of a transition between the low-temperature regime where transport takes place through a single level inside the quantum dot to the classical regime where the thermal broadening exceeds the level spacing, and transport takes place through multiple levels at once. The temperature scale at which this occurs is more than an order of magnitude
CHAPTER 6. SHORT CONSTRICTIONS

Figure 6.23: Sample 10-24-g. Conductance versus back gate voltage for temperatures ranging from 0.25 K to 20 K.

Figure 6.24: Sample 10-24-g. T = 1.5 K. Fits to the 6 V conductance peak at one of a large collection of temperatures.
smaller than the expected \( \sim 100 \) meV level spacing in a dot of \( \sim 30 \) nm diameter, but much more similar to the \( \sim 1 \) meV level spacing that we observe in sample 1-17-a (the one device in which we measure clear indications of excited states).

### 6.8 Zero Bias Anomalies

In every sample we have measured, we have observed a suppression of differential conductance at zero bias that persists over all measured gate voltages. An example of this zero-bias suppression is shown in figure 6.26.

In certain samples we have made high-resolution measurements of differential conductance versus bias at a range of temperatures. In figure 6.27 we show these data for sample 10-24-g at 6.7 V on the back gate, which is in the middle of a Coulomb diamond region of suppressed conductance.

It is fruitful to plot this data on a log-log scale, as in figure 6.28. The conductance levels off at low biases, and the value of the bias at which the leveling first occurs is larger for the higher-temperature traces. The traces do not collapse onto a single curve when plotted, as in figure 6.28, as a function of \( eV/kT \). Each curve appears to have a similar slope in the higher-bias region, though, with a power-law exponent for
Figure 6.26: Sample 10-24-g. Suppression of differential conductance near zero bias persists over a wide range of back gate voltages.

Figure 6.27: Sample 10-24-g. Differential conductance versus bias for a range of temperatures. Each trace taken with 6.7 V on the back gate.
I vs. V of close to 1. This is similar to the prediction of Middleton and Wingreen for transport through a one-dimensional system of quantum dots with on-site interactions only [64].

\[ I \approx \left( \frac{e}{2RC_g} \right) v \]  

(6.4)

Figure 6.28: Sample 10-24-g. Differential conductance versus bias for a range of temperatures. Each trace taken with 6.7 V on the back gate.

The same power law behavior appears in the other sample on which we have made careful temperature-dependence measurements, 10-24-d. In figure 6.29 we show differential conductance versus bias for several temperatures with -25 V on the back gate, a location far from the Dirac point where conductance is not especially suppressed. In figure 6.30 we point out this location in the map of differential conductance versus bias and gate voltages.

When we plot the same data on a log-log scale, as in figure 6.31, we see a power-law dependence similar to that found in sample 10-24-g in the middle of a Coulomb diamond. Given the differences between these samples, this similarity is surprising. More data and more sophisticated analysis is needed to better understand the phenomenon giving rise to the zero-bias suppression of conductance in graphene nanostructures.
Figure 6.29: Sample 10-24-d. Differential conductance versus bias for a range of temperatures. Each trace taken with -25 V on the back gate, corresponding to a region far from the Dirac point, with no especially strong suppression of conductance.

Figure 6.30: Sample 10-24-d. Differential conductance versus bias and gate voltages at 250 mK. The arrow shows the location of the bias cuts shown in the preceding and following figures.
6.9 Fabry-Perot Behavior

Collections of phase–coherent electrons confined in a cavity exhibit resonances in their conductance due to interference effects—these are known as Fabry-Perot resonances. Bulk graphene is known to exhibit strong Fabry-Perot behavior because of its long phase coherence length [82]. Charge carriers in graphene can reflect off of contact–graphene interfaces, giving rise to Fabry-Perot interference effects in the cavity defined by the graphene edges and contacts. We see fluctuations similar to those observed by Miao and collaborators [82] in our samples between contacts not separated by a constriction. In figure 6.32 we show such data from sample 10-24-g.

In our short constriction samples we occasionally see small but reproducible conductance fluctuations occurring with a frequency in gate voltage much larger than that of the peaks that we attribute to Coulomb blockade physics. The apparent spacing of these features in gate voltage is compatible with spatial features that are much larger than the size of the constriction, on the order of microns. For this reason we speculate that they are due to Fabry-Perot oscillations in the graphene leads. To test this idea, we have investigated the temperature dependence of these fluctuations in comparison to the Fabry-Perot features we see on one side of the constriction. In
**Figure 6.32:** Sample 10-24-g. Differential conductance versus a small range of biases and gate voltages. This measurement is taken across contacts located on the same side of the constriction.

In figure 6.33 we show high-resolution data taken across the constriction showing the suppression of differential conductance near zero bias as well as circular features near -4.75 V on the back gate and at +/- 1 mV source-drain voltage that may be signatures of Fabry-Perot behavior in the leads.

In figure 6.34 we show similar data taken at 1.4 K. The circular features described above are largely blurred out. This occurs on a similar temperature scale to that at which Fabry-Perot oscillations in the graphene leads are substantially blurred (figure 6.35). On the basis of this limited and inconclusive evidence, we cannot rule out the possibility of the high-frequency (in gate voltage) and low-temperature features in our differential conductance maps being caused by something other than Fabry-Perot oscillations in the graphene leads. We can only suggest that Fabry-Perot oscillations in the leads are a plausible origin for these features.
Figure 6.33: Sample 10-24-g. Differential conductance versus a small range of biases and gate voltages. This measurement is taken across contacts located on opposite sides of the constriction, comprising areas of bulk graphene leads as well as the constriction itself.

Figure 6.34: Sample 10-24-g. Differential conductance versus a small range of biases and gate voltages. This measurement is taken across contacts located on opposite sides of the constriction, comprising areas of bulk graphene leads as well as the constriction itself.
Figure 6.35: Sample 10-24-g. Differential conductance versus a small range of biases and gate voltages. This measurement is taken across contacts located on the same side of the constriction.
Chapter 7

Our Model for Graphene Nanostructures

In the previous two chapters we have presented data showing conclusively that some type of localization is playing a role in transport through graphene nanostructures, along with evidence suggesting that this localization is associated with quantum dot formation in graphene nanostructures. In chapter 2 we outlined the state of the theoretical literature on transport through graphene nanoribbons. In this chapter we present the model we have developed to explain our data; this model is informed by data from many sources on the nature of disorder in the vicinity of graphene flakes.

Early transport measurements revealed fluctuations quantities such as Hall resistances and zero-field conductances of graphene flakes near (typically within 10 V of) the Dirac point [26]; as the doping was increased away from the Dirac point, these quantities varied more uniformly with gate voltage. We observed similar fluctuations in our early Hall measurements (see chapter 1 for more information); we found that it was desirable to make certain measurements with at least 10 V on the back gate in order to obtain clean data.

Work by the Yacoby lab [57] used a scanning single electron transistor (SET) to locally map density fluctuations with a 100 nm resolution. These measurements showed unequivocally that density fluctuations did exist in graphene flakes. Local probe measurements gave a fluctuation scale of $3.9 \times 10^{10}$ cm$^2$, although transport measurements...
of the broadening of Shubnikov-de Haas peaks suggested that the fluctuations were in fact occurring on shorter length scales than the resolution of the scanning SET, implying that they were also occurring on correspondingly larger density scales.

Most recently, STM measurements by the Crommie lab have mapped the energy and spatial scales of density fluctuations [58] with a resolution finer than the spatial scale of those fluctuations. This work also measured corrugations of the graphene sheet, and found no correlation between the height or curvature of the graphene sheet and the local density, reducing the credibility of models where density fluctuations stem from ripples or corrugations in the graphene sheet [83].

At this point, therefore, there is a strong consensus that density fluctuations exist in graphene sitting on SiO₂ substrates due to charged impurities located near the graphene sheet, and that the density fluctuations occur on length scales on the order of 10 nm and on density scales of a few times 10¹¹ cm⁻². We consider the question of what effect these fluctuations have inside a confined geometry such as a nanoribbon or nanoconstriction.

Although our measurements on constrictions of varying lengths have shown conclusively that confinement alone cannot explain the nature of the gap observed in graphene nanoribbon transport, we still expect the separation of graphene's continuous bands into discrete level structure to play some role. We hypothesize that the first allowed level for electrons is indeed split from the last allowed level for holes, but that the gap center is shifted to a different energy at each point in space, depending on the local potential. Because of this, we expect the bottom (top) of the electron (hole) band to follow a profile qualitatively similar to that shown in figure 7.1.

When we place a certain density of electrons in this potential, two scenarios are possible. If the Fermi level is placed in the hole band below the level of the variation in the disorder potential, or in the electron band above the level of the disorder potential, the ribbon is conductive, and the influence of the disorder and confinement potentials is minimal. However, when the Fermi level is placed within the energy range of the disorder plus confinement potentials as in figure 7.2, puddles of electrons and holes result, spatially separated from each other by the confinement gap.

In order to make an initial estimate as to whether this model was realistic given
CHAPTER 7. OUR MODEL FOR GRAPHENE NANOSTRUCTURES

Figure 7.1: A cartoon representation of fluctuations plus gap.

Figure 7.2: A cartoon representation of fluctuations plus gap.
For these realistic values, our crude calculation yields results similar to those we observe in our constrictions; in very narrow constrictions, we find a very small number of dots contained within a constriction that is otherwise completely empty of charge carriers. In wider constrictions, we find a constriction that is filled with a low density of charge carriers, except in a few locations surrounding puddles of charge carriers of the opposite sign.

Figure 7.3: a) mobility of 3000, 5 V from the Dirac point, 10 nm constriction width b) mobility of 3000, 10 V from the Dirac point, 30 nm wide constriction

7.0.1 Mobility and impurity density

For the calculations described here, it is necessary to have a measure of the density of charged impurities. In the absence of local probe techniques, we cannot make
measurements the charged impurity density in each of our samples; instead, we make transport measurements that allow us to estimate the sample mobility. Here we discuss experiments that establish the connection between these two quantities.

Measurements and calculations performed by the Fuhrer group at Maryland [84] showed that electron-phonon scattering negligibly affected the mean free path of charge carriers in graphene (consistent with observations that the mobility of a graphene flake is largely temperature-independent). Transport measurements on samples that were progressively doped with charged impurities by the same group showed that charged-impurity scattering could produce conductance profiles similar to those typically observed in graphene [27]. These measurements established a numerical relationship between mobility and charged impurity density:

\[ \mu = \frac{C e}{n_{imp}} \]  

where the constant \( C \) reflects the strength of the screened Coulomb potential, and is calculated by Hwang and collaborators [85] to be \( 5 \times 10^{15} \) (V s)\(^{-1}\).

### 7.0.2 Simulations

The details of the calculations are as follows:

We generate a set of random impurities at density per lattice site[86, 87, 9, 85] with a density given by equation (7.1), with strengths distributed uniformly over the energy interval \([-\delta, \delta]\) [35], where we choose [27] \( C = 5 \times 10^{15} \) and

\[ \delta = t \left( \frac{a}{\xi} \right)^2 \sqrt{\frac{K_0}{40.5 n_{imp} a_0^2}} \]  

where \( t \) is the nearest-neighbor hopping energy \( \approx 2.7 eV \), \( a_0 \) is the lattice constant, \( \xi \) is the screening length in the material, which we choose to be \( 4a_0 \) following Lewenkopf [88] and

\[ K_0 = \frac{2\lambda_F}{\pi \lambda_{mf}} \]  

The quantity \( \delta \) includes an assumption about the typical distance of impurities from
the graphene sheet $d$; here $d = 1$ nm.

We calculate the local potential at every point on our mesh due to the presence of all of the charged impurities, and then employ a crude method that neglects electron interaction effects to get a rough measure of the local density at each point $r$ due to the charged impurities and Fermi energy due to the overall back gate voltage:

$$n_e(r) = \text{sign}(E_F + r_s V(r)) \left( \frac{E_F + V(r) r_s}{h v_F} \right)^2$$

(7.4)

where $r_s$ is the coupling constant on the SiO$_2$ substrate: $r_s = 0.8$ [89]. Finally, we set the density to zero whenever

$$|E_F + V(r) r_s| \leq E_{gap}$$

(7.5)

where $E_{gap} = h v_F \frac{\pi}{w}$ and $w$ is the width of the constriction. This results in constrictions completely empty of charge carriers except at the locations of largest $V(r)$ for low Fermi energies or narrow constrictions, and constrictions where small regions of charge carriers are isolated from a conducting sea by small annuli empty of charge carriers for higher Fermi energies and wider constrictions.

We recognize, however, that electron-electron interactions should modify this picture qualitatively and quantitatively. To better understand whether our model continues to be plausible when these interactions are considered, we collaborated with Enrico Rossi at the University of Maryland to produce calculations of electron densities in the presence of a random impurity potential and a confinement gap, including Coulomb and exchange interactions within the Thomas–Fermi–Dirac formalism. In figure 7.4 we show his calculations for two average electron densities. For the confinement gap, he uses 6.5 meV, based on unpublished activation energies measured by Han and collaborators [59]. This value is smaller than straightforward calculations of expected confinement gaps based on ribbon geometries.

These simulations qualitatively reproduce the features we infer from our transport measurements on nanoribbons and nanoconstrictions; charge puddles with dimensions of 20–30 nm are separated by narrow insulating regions. As the average charge carrier
density grows, the puddles merge into each other, eventually leaving only conducting regions over a certain length scale.

### 7.0.3 Electrostatic Considerations

Of particular importance in understanding how the source-drain gap scales with ribbon length is the question of how strongly a given region in the ribbon is capacitively coupled to the gate versus the source and drain leads. Broadly speaking, we expect the capacitive coupling to the leads to be dominant for short ribbon lengths, while for longer ribbons we expect the capacitance to the gate to become relatively more important: for long enough ribbons, we expect the energy of a dot in the middle of the ribbon not to be affected by the source-drain voltage. If this were the case, one would observe a saturation of the source-drain gap as ribbon length grew much longer than the distance to the gate. This scenario is shown for the unrealistic case of a single dot located in the middle of the ribbon in figure 7.5. In point of fact, we do not observe such a saturation, even when the ribbon length approaches 3 μm, or 10 times the distance to the back gate. However, the scenario presented in figure 7.5 is not realistic: in long ribbons we observe data consistent with many dots in series. A
more accurate scenario, with many dots distributed along the length of the ribbon, is shown in figure 7.6. We expect that the presence of a series of quantum dots through-

out the ribbon should dramatically increase the capacitance of the dot in the middle of the ribbon to the leads, increasing the ribbon length that would be necessary to achieve a saturation of the source-drain gap.
Chapter 8

Graphene Preparation Techniques

All of the measurements described in this thesis were made on exfoliated graphene flakes. In this chapter I will discuss the preparation of these flakes starting from graphite crystallites and ending with a contacted sample. In the following two chapters, I will discuss the preparation of graphene nanostructures on such samples.

8.1 Preparation of Substrates

Following [26] we prepared 300 nm of thermal oxide on heavily n-Arsenic doped ($\rho < 0.005\Omega \cdot \text{cm}$) Si wafers purchased from Silicon Quest [90]. After stripping the native oxide and cleaning the wafers according to the Stanford Nanofabrication Facility (SNF) protocols, we grew $\sim 300$ nm of thermal oxide in the Tylan oxidation furnaces (actual oxide thicknesses ranged from 285 to 310 nm from batch to batch; it was possible to identify single-layer graphene on all of these wafers). Early wafers were treated with between 10 and 15 minutes of wet oxidation using program WET1100, where the oxidation time was determined by oxidizing a single wafer, measuring the oxide thickness with SNF's Nanospec ellipsometer, extracting the wafer doping via the thermal oxide thickness calculator at http://www.lelandstanfordjunior.com/, and using the calculated doping to grow the desired thickness of thermal oxide, which is generally correct to within 10 nm and varies by $\approx 6$ nm over the extent of the wafer. Later samples were fabricated on wafers prepared with between 4 and 5 hours of dry
oxidation (depending on the doping of the wafer batch) using program DRY1100A (including a 1 hour high-temperature annealing step). Joey Sulpizio has conducted measurements of breakdown voltage on both wet- and dry-oxidized wafers, and has found that dry oxidation results in a higher breakdown voltage for thick oxides such as ours; in all cases breakdown voltages were greater than 150 V across our \( \sim 300 \) nm oxides.

Following oxidation, we patterned alignment grids across entire 4’’ wafers using the Quintel mask aligner, Shipley 1813 photoresist and Microposit CD-30 developer, and a photomask designed in L-Edit and fabricated by Delta Mask (http://www.deltamask.nl/). Following spinning resist at 5krpm for 40 seconds, we utilize a pre-exposure bake at 115 °C for 3 minutes to minimize problems with resist peeling during development; it is important that the wafer make good thermal contact to the hot plate during this bake, otherwise the photoresist will not adhere to the wafer during development. Exposures on the Quintel were calculated based on the UV power, so that the product of the power and the time was similar to 50 mJ/cm\(^2\). Development time was based on development of a test wafer, and varied between 30 seconds and 1 minute. After a postbake at 110 °C for 45 seconds, Ti/Au was evaporated onto the grid. Because of metal degradation by a subsequent piranha clean, metal thicknesses of greater than 50 nm were preferred for ease of subsequent SEM alignment steps.

After spinning a protective layer of resist, wafers are sent to Micro Dicing Technology in Sunnyvale (http://www.microdicingtechnology.com/pages/776811/index.htm) for dicing into 5 mm chips, which is more time and cost-efficient than using the wafer dicing equipment available in SNF. After a sonication in warm acetone and an isopropanol rinse to remove resist residue, chips are exposed to a final cleaning process. Early on we used an oxygen plasma descum for this step, but later we switched to using a 3:1 sulfuric acid:hydrogen peroxide piranha clean for 5-10 minutes to remove organic contaminants from the surface shortly before depositing graphene.
CHAPTER 8. GRAPHENE PREPARATION TECHNIQUES

8.2 Mechanical Exfoliation of Graphite

After experimenting with several varieties of tape, including water-soluble wavesoldering tape, we successfully produced single-layer graphene flakes with Blue Nitto SPV224LB Surface Protection Tape from Permacel and with red Scotch Transparent Tape. Although it is difficult to control for variation in other variables, anecdotally we find that Scotch tape results in larger flakes on average, while blue Nitto tape offers the advantage of having an adhesive that dissolves in acetone.

We have deposited graphene made from both natural graphite provided to us by the Geim lab and from highly oriented pyrolytic graphite (HOPG) purchased from SPI. It is possible to make large flakes (of up to a few tens of microns across) and achieve high flake densities (of up to ~ 4 flakes per 5 x 5 mm chip) using both of these starting materials (although we believe we observe an slight anticorrelation between flake size and the density of single-layer flakes on a chip). We have also obtained natural graphite from Asbury Graphite Mills. Both "vein" and "flake" graphites are available. The sample of vein graphite we obtained did not flake readily into graphite crystallites. Superior Graphite Mills is another supplier of natural graphite. At the time of our contact with them, they required a large minimum order quantity.

When depositing graphite, we begin by placing a low density (roughly 5-9) of small (millimeter-scale) graphite crystallites onto a freshly exposed 1 to 2" long section of "red" scotch tape. The spatial arrangement of the crystallites on the tape is not critical (though it is desirable that they not be all in the same spot), because we subsequently fold the tape 10-12 times, trying to achieve an even coverage of powdery graphite crystallites over the tape surface. Without allowing the tape to spend unnecessary time exposed to air, we then apply the tape to freshly piranha-cleaned chips and press hard with the gloved thumb for 2-3 seconds. We then carefully peel the tape off the chip and place the chip into a container for later inspection.

We have also experimented with Jimmy Williams' hot chip method, where tape is applied to a chip heated on the hot plate and the chip/tape combination is exposed to continued heat for several minutes, but we find that this method often creates a thick residue of tape mastic on the chips that makes further processing on nearby
graphene flakes difficult.

When we have produced several chips coated in graphite crystallites, we begin the visual inspection process. Under the brightest possible illumination, and at 20x magnification, we scan over the entire chip to find light purple flakes that may be single-layer graphene. When we find a good candidate flake at 20x magnification, we take a photo at 150x magnification, under which the flake's shape and thickness is easier to ascertain. If the flake continues to look like a promising candidate under 150x magnification, we take a photograph at 20x magnification to help locate the flake on the chip for future processing.

Next we begin the e-beam lithography process to make electrical contact to the flake by spinning on an e-beam resist. To maximize liftoff quality, we choose a layer of MMA, spun at 4Krpm and baked at 160 °C for 4 minutes, followed by a 1 minute cooldown of the chip and the spinning of 950K PMMA, baked at 160 °C for 2 minutes.

We spin the resist early in the fabrication process because occasionally flakes fold or float away when surrounded by the liquid of the resist droplet, and by spinning resist early we avoid spending a great deal of time on flakes that may disappear. Fortunately, our preferred method of layer determination works well on flakes that are buried beneath a resist layer.

After spinning, we inventory the flakes on the chip again and take additional 150x photos to document whether they have folded or floated away.

8.3 Determination of Layer Number

Until early 2007, we had no access to Raman spectroscopy equipment, and therefore had to rely on AFM measurements to determine layer number in our graphene samples. We found AFM to be a barely-adequate tool for this characterization. It is necessary to have very clean graphene and substrate surfaces in order to make an unambiguous measurement of layer number, but there is another problem as well. Under normal atmospheric conditions, graphene sits not directly on the oxide substrate but on a thin layer of adsorbed water. The thickness of this layer seems to vary both from sample to sample and from day to day, causing the step size from
the substrate to the first layer to vary between 0.5 and 1.3 nm. By baking the chip at temperatures above 100 °C immediately before measurement, we can often reduce the thickness of the layer of adsorbed water; if we can measure a substrate–graphene step size that is unambiguously less than 1.0 nm (twice the graphene–graphene step size) then we can have confidence that we have identified a single layer.

In the summer of 2006 we also attempted to use SNF’s Zygo white light interferometer to measure the thickness of thin graphitic flakes. This technique was of limited utility because the graphene introduces a phase shift into the reflected light that makes it appear that the graphene thickness is negative; at this time we did not have access to other reliable and fast-throughput techniques that would allow us to calibrate the correspondence between real and measured thicknesses in this instrument.

Luckily, following work by Ferrari and collaborators [91] and Graf and collaborators [92] we have found that Raman spectroscopy is a fast and robust means of determining graphene layer number. We are able to do Raman spectroscopy on graphene flakes through the resist layer after spinning. While scanning Raman spectroscopy is helpful for creating maps of flakes that can point up details like folds or tears that may not be readily apparent in optical micrographs, single-point Raman spectroscopy is adequate (in conjunction with indications of layer thickness provided by flake color) for identifying single-layer graphene flakes. We have found the quickest indication of single-layer graphene to be the width of the 2D peak occurring at roughly 2700 cm⁻¹. A peak with a full width at half maximum of roughly 30 cm⁻¹, which can be fit by a single Lorentzian, is indicative of single-layer graphene. The width of this peak in single layer graphene is easily distinguished from its width in bilayer graphene, where the FWHM is roughly 60 cm⁻¹. In figure 8.1 we show a map of the width of the 2D peak taken across a typical flake, showing both single-layer and thicker regions. We also show a higher-resolution trace of the Raman spectrum centered around the 2D peak, from which the peak full width at half maximum can be ascertained.

While Raman spectroscopy can identify single-layer flakes incontrovertibly, it is a surprising fact that a well-trained eye can be very nearly as accurate. As others have found as well, after having the opportunity to compare my judgements about
Figure 8.1: a) Map of the 2D peak width across a graphitic flake, showing clearly the difference between the single layer portion on the lower right and the thicker portion on the upper right. b) The portion of the Raman spectrum centered on the 2D peak for the thin portion of this flake, showing the peak width. c) A typical Raman 2D peak for a bilayer graphene sample. Note that the peak full-width at half-maximum is roughly twice as large.
graphene layer number to Raman data for a few batches of candidate flakes, it was extremely rare for me to find that a flake I had optically identified as single-layer was not, although it was more common to judge a flake that was in fact single-layer to be thicker, especially for larger flakes.

8.4 Making Electrical Contact

After spinning on resist and confirming by Raman spectroscopy that a flake has a substantial single-layer portion, we begin designing a pattern of contacts to the flake. The design process begins with an optical micrograph of the flake area that includes all four adjacent photolithographically patterned alignment marks. We then use the paint-bucket tool in Adobe Photoshop to outline the alignment marks, and the line tool to outline the flake in a color (such as bright blue) that isn’t present in the original photo. We then use select color range to select only these elements, and save this selection as a new document. We invert this document so that the background is white and the foreground black, change the format from multichannel to grayscale, and finally save the file as a .jpg. At this point, we can convert the .jpg to a .gds file using LinkCAD. We can then import the .gds file into LEdit, rescale the elements so that there is a 50 micron spacing between alignment marks, and begin designing a pattern of contacts to the flake.

Several considerations are relevant in the contact design. The precision with which we’re able to perform alignment in the initial contact write (using the photolithographically patterned marks) is not typically better than 400 nm. Therefore to have a high degree of certainty that we will make good contact to the flake, we generally design at least 500 nm of overlap between the contacts and the flake. On the other hand, for the contacts to be minimally invasive [29] and to take up as little as possible of the flake area, we try to locate them as near the edge of the flake as possible. In order to determine the flake mobility, we try to locate at least two and preferably four contacts on the same side of any future nanostructure, and if there are thicker portions of the flake we design the contacts such that they span only single-layer regions. We route the contacts on the sample to large 120 micron square
bonding pads. This size allows for several rebonding attempts if necessary, while still allowing us to place many pads within our e-beam system's largest write field. We place the connectors between the sample and these pads carefully to avoid shorts between them via any large graphite crystals present on the surface, or breakages due to running over a thick crystal.

When we have designed a satisfactory pattern in LEdit, we separately export the inner contact pattern, the outer contact pattern, and the inner and outer alignment mark patterns to .gds files and transfer them to the NPGS system, where we convert them to .dc2 files. Problems with the conversion process result when the file sizes are too large, which can happen when the pattern files contain too many artifacts of features from the original photographs. The alignment patterns must be converted to a format compatible with the NPGS system: the marks themselves are converted to unbroken lines, which signify a line, while they are outlined with windows delineated by boxes made from dashed lines, signifying the border of an area. Alignment and pattern files are then integrated into one run file directing the writing of inner contacts and another the writing of outer contacts. Point and line spacings of approximately 20 nm are chosen for small features such as the inner contacts, while large line and point spacings of 100 nm are chosen for the outer contacts. Doses of 260-290 μC/cm$^2$ at an acceleration voltage of 30 kV are used using our group's FEI SEM with the attached Nabitity Pattern Generation System (NPGS), where we vary the dose slightly depending on the size of the features.

After exposure, the chip is developed in a 3:1 mixture of isopropanol and methylisobutylketone for 40 seconds. At this point, the pattern where PMMA has been removed is visible in the optical microscope. The flake can be easily seen underneath the PMMA pattern, and so alignment of the contact pattern to the flake can be checked. If the pattern is satisfactory, we go on to evaporate metal onto the contact pattern. For standard devices, a sticking layer of 5 nm of Ti followed by 25 nm of Au is used.

If the pattern is well designed, with no areas that are intended to be free of metal enclosed within metallized areas, liftoff is relatively easy; most unwanted metal lifts off with a short soak in acetone and a few squirts from the acetone bottle. More stubborn liftoffs require several minutes immersion in hot or boiling acetone at temperatures
above 110 °C on the hot plate or even short (> 5 second) bursts of sonication, which generally do not harm graphene samples for short sonication times.

After successful liftoff, a pattern delineating a nanostructure can be designed and written on the flake. For isolated nanostructures fabricated with the PMMA process on graphene, a single layer of 950K PMMA provides the best resolution, but for nanostructures requiring metal deposition and liftoff we use a bilayer of 495K PMMA/950K PMMA.

8.5 Fabrication of Nanostructures

In the absence of high-quality dose correction software, we design our nanostructure patterns to compensate for proximity effects. In the case of the side-gated geometry (described in chapter 10), for instance, we never specify a constriction width of less than 40 nm in our CAD files, relying on a slight overdose to provide us with a (narrower) variable-width gap. Doses are sensitively dependent on PMMA thickness and other factors that vary from write to write, but generally area doses of 120 to 150 μC/cm² and line doses from 300 to 450 pC/cm in the Stanford Nanofabrication Facility’s Raith e-beam system are appropriate. Using this method, gaps between lines as small as 10 nm can be fabricated, although fabricating a specified width on demand is difficult with the process and equipment we used.

The work in this thesis deals with two types of nanostructures. One, the side-gated geometry, is described in detail in chapter 10. The other, which we use for the fabrication of long nanoribbons with exposed surfaces, is described in chapter 9.

8.6 Packaging

When all nanofabrication on the chip is concluded and the chip has undergone liftoff or the dissolution of the etch mask, we attach the chip to a chip carrier and make electrical contact from the chip carrier to the bond pads on the chip by wirebonding. Before wirebonding, the chip must be firmly attached to the surface of the chip carrier. We use a highly concentrated solution of PMMA in anisole to glue the chip to the
carrier. This technique results in a bond that is stable through temperature cycling and yet can be broken with mechanical pressure or dissolved in acetone. After curing at 80 C for 30 minutes or more, the epoxy is stable enough to permit ultrasonic wirebonding. During the bonding process, we observe a number of precautions to protect the graphene device from large abrupt voltage changes which can destroy the device. First it is necessary to use a wirebonder whose critical surfaces are all well electrically connected to each other. Second, it is important to use relatively low power to make the bond. Powers near 350 mW are sufficient for us to make strong bonds without damaging the sample. Third, we begin the bonding process with every pad on the chip carrier shorted to its neighbors with wirebonds, in order to compensate for the sometimes imperfect grounding through the backside of the pins. Fourth, we always make the first bond to the back gate, which then serves as a ground plane for the other pins on the device. If there are local gates on the device, we bond these most fragile pins last, after making contact to larger regions of the graphene flake. Relatively low heat on the sample, roughly 77 °C, facilitates the making of good bonds.

When the bonded sample is photographed and the pinout is indexed, it is ready for measurement.

8.7 ESD Issues

Once bonded to a chip carrier, graphene samples (particularly nanostructured samples) are extremely susceptible to damage from uncontrolled static voltages. In addition to the precautions during wirebonding described above, we take great care during the measurement process to ground the pins in the cryostat when inserting or removing samples or when measurement is not in progress. We also store our bonded samples in static-dissipative boxes, and use ungloved hands, metal tweezers and grounding straps when handling them. These precautions are not necessary before wirebonding because the pre-bonded device on the chip surface is well isolated from static voltages.
Chapter 9

Long Nanoribbon Fabrication

9.1 Introduction

The first graphene nanostructures I fabricated were long graphene nanoribbons, inspired by the goal of creating a source of collimated charge carriers in graphene for use in scanning gate measurements. Because of this goal, I chose not to fabricate the ribbons with HSQ, a negative e-beam resist that can achieve narrow linewidths of 10–20 nm, but that when developed leaves a difficult-to-remove SiO₂ etch mask on the surface of the ribbon. Because of the desirability of having ribbons whose surfaces are exposed for scanning gate work, I began developing a process to fabricate long graphene nanoribbons with an easy-to-remove PMMA etch mask.

9.2 Fabrication with PMMA Etch Masks

Because graphene nanostructures were expected to be vulnerable to peel-up and breakage under sonication or even immersion in solvent, I chose to fabricate metallic contacts to the graphene flake before patterning the nanostructure. This process order both exploited the ability of the contacts to pin down the flake in subsequent processing steps to protect it from floating away and protected the vulnerable nanostructure from the trauma of further processing steps. After preparing a graphene flake and patterning contacts to it in the manner described in chapter 8, I typically
spun a layer of 950K PMMA to pattern an etch mask for the long nanoribbon(s). Because the long nanoribbon geometry cannot be written as a single-pixel line with

Figure 9.1: a) Typical etch pattern used for long nanoribbon samples such as 3-22-b, patterned with area doses in a PMMA etch mask. b) Later etch pattern made with line doses written in a PMMA etch mask, used for many scanning gate samples.

a positive resist system like PMMA, more complicated geometries are required to produce a narrow ribbon of uniform width. Two typical geometries are shown in figure 9.1. Several factors are relevant to determining the appropriate electron dose to use in making these devices. The presence of the graphene flake requires a much larger dose relative to bare SiO$_2$; it is hard to say precisely why this is. In general, the electron dose required on a conducting substrate can be increased over that required on an insulating substrate because charge is more efficiently conducted away from the location at which the beam is pointed, or it can be reduced because of the damping of charging effects that can cause electrons to be deflected from their target. The presence of metallic contacts in the area also affects the dose to a lesser degree. Because of these factors it is best to determine the appropriate line and area doses via a test write on a contacted graphene flake similar to the flake of interest. Dose arrays show a wide process window, so if the SEM is stable a single dose determination can serve for several subsequent writes. Because of the lack of dose stability (sometimes during
a single write) for small features in our group’s Nabit/FEI e-beam system documented over a period of several months in the summer and fall of 2007, I switched to using SNF’s Raith e-beam system for nanostructured patterns in the winter of 2008. While there is some indication that subsequent maintenance has improved the dose stability of the DGG lab e-beam system, I was reluctant to modify a working process to switch back to a system that in any case has natively inferior resolution. Typical line and area doses used for etch writes on the Raith system ranged between 300-450 pC/cm for line doses and \(\sim 150 \mu\text{C/cm}^2\) for area doses. I typically used 10 kV acceleration voltages for side-gated samples and 20 kV acceleration voltages for long nanoribbon samples, and didn’t find a great deal of difference between the two acceleration voltages in terms of the dose required. The line doses in particular were sensitively dependent on the thickness of the PMMA film, and drifted over time as our stock of PMMA become more concentrated through solvent evaporation. A typical device produced with a PMMA etch mask is depicted in figure 9.2.

Figure 9.2: a) An SEM micrograph of a typical isolated graphene nanoribbon produced with a PMMA mask. Yellow lines outline the area that has been removed by the etch process; the red arrow points to the constriction through which charge carriers must flow to traverse the sample. b) A representation of the cross-sectional structure of the device. The central block of graphene diagrammed in this cross-section corresponds to the constriction pointed out with the red arrow in part (a).
9.3 Unsuccessful strategies

Because of the difficulties involved with making a long uniform line etch mask in a positive resist environment, I invested some time in attempting to find a high-resolution negative resist that could be easily removed after the etching process. Several candidates were rejected out of hand for not having sufficient resolution to make reliably gapped nanoribbons: for instance, SAL-601 and MA-N 2403. I ordered and characterized Allresist’s AR-N 7500 negative e-beam resist. AR-N 7500 promises sub-30 nm resolution, good dry etch resistance and easy stripping in acetone. The resist’s drawbacks include light sensitivity (it must be handled like photoresist) and the fact that it chemically attacks graphene. Figure 9.3 shows an SEM micrograph of a portion of a graphene flake that has been processed with AR-N 7500 resist. Though the extent of the damage varies from sample to sample, it seems not to be attributable to etch-through of the resist, but to the the activity of the resist itself. In transport measurements, these samples are characterized by very large resistances or initially large conductances that drop irreversibly to zero at some point. Figure 9.4 shows an example of such a measurement. Initially there is a high value of conductance, but at approximately 30 V on the back gate the conductance drops precipitously to a small value and never recovers.

Figure 9.3: SEM image of graphene that has been attacked by AR-N 7500 resist
Figure 9.4: (a) The initial sweep up in gate voltage from 0 to 50V. (b) The sweep back down to 0 V. Note the difference in conductance scales.

9.4 Metal Mask Fabrication

In order to create ribbons of standardized width, a different and more reproducible negative process was needed. Because of our difficulties with finding an adequate negative resist system, Patrick Gallagher and I together developed a metal mask technique for fabricating ribbons whose width is based on the reproducible linewidth of a single pixel line written in PMMA. In this process, a graphene flake is first contacted with Ti/Au contacts far from the region to be nanostructured. A single layer of 950K PMMA is spun on, and a single pixel line longer than the eventual length of the nanoribbon is written using the Raith e-beam system. 15 nm of Ti is then evaporated onto the PMMA mask, and liftoff is performed. A second layer (~ 50 nm thick) of 950K of PMMA is spun onto the sample, and a window the length of the desired nanoribbon is written on the flake, exposing the Ti line and the surrounding graphene, leaving the contact region protected. In figure 9.5 we show a false-color image depicting the locations of the PMMA and metal etch mask on a real ribbon.
sample.

![Figure 9.5: A hybrid cartoon-SEM micrograph detailing the process by which our metal-mask ribbons are fabricated. We begin with the contacted graphene flake (depicted in light gray). The Ti metal mask (red) is added, covering the region that will become the ribbon. In a subsequent write, a PMMA mask (green) is written over the areas of graphene near the contacts that we wish to retain.]

The exposed graphene is then etched away with oxygen plasma for 8 seconds, leaving graphene under both the Ti line and the PMMA near the contacts. The PMMA mask is then removed in acetone, and the Ti line etched away using a 30% solution of HCl at 85 °C. At the end of the process, a 30-nm width exposed graphene nanoribbon is obtained, merging into exposed graphene leads which are in turn contacted by Ti/Au contacts. In figure 9.6 we show the sample after the removal of the PMMA and Ti masks.

9.4.1 Equivalence of ribbons fabricated with the metal mask technique

It is important to learn whether ribbons fabricated by this method are equivalent to ribbons patterned with PMMA etch masks.

One piece of evidence that suggests that the metal-mask and the PMMA mask methods are equivalent is the similar conductance properties of the two kinds of
Figure 9.6: An SEM micrograph of a completed metal-mask ribbon device; the graphene areas in figure 9.5 that were unprotected by either Ti metal or PMMA have been etched away with oxygen plasma, and the Ti metal and PMMA masks have been removed.

ribbons. In bulk samples that have been covered in titanium which has subsequently been removed by etching, we have not observed significant changes in the conductance properties other than a typical reduction in the mobility similar to what we observe in other samples that have undergone two rounds of processing.

Another piece of evidence is the response of these ribbons to thermal annealing. If the quantum dot behavior we observe in our metal-mask graphene nanoribbons were due to the presence of small particles of titanium, we would not expect our thermal annealing, which we think likely does not heat our graphene ribbons to the 1960 K melting point of titanium, to rearrange the putative system of dots. As we argue in section 5.4.4, 1960 K is at the extreme high end of plausible temperatures reached by annealing.

Finally, we have performed scanning Auger measurements on samples on which we have evaporated and then etched off titanium. We describe these measurements in the following section.
9.4.2 Auger measurements

Auger electron spectroscopy (AES) yields information about the elemental content of a surface by recording the energies of electrons emitted from the outer shells of atoms as a result of shell to core transitions caused by the removal of a core electron from the atom by an energetic incident electron. Based on the energy of the ejected electrons, it is possible to identify the element from which they are emitted. AES is therefore an effective tool for identifying the elemental composition of a sample surface. The penetration depth of the incident electron beam varies based on its energy and on the material comprising the surface, but is typically less than a few nanometers.

In figure 9.7 we show a typical differentiated Auger spectrum (actually, a set of four Auger spectra centered around the peak locations for silicon, oxygen, carbon and titanium) from a sample that has been prepared with titanium deposited in a diffraction grating pattern, then exposed to the same etch process used for our metal-mask ribbon samples. The spectrum at the energy where the titanium peak is expected is difficult to distinguish from noise, and the percentage of titanium on the sample surface (under the assumption that the surface is composed only of silicon, oxygen, titanium and carbon) is 0.3 %. In figure 9.8 we show a typical differentiated Auger spectrum taken on a region of the surface of a sample that has been exposed to the same processing described above far from any deposited titanium or graphene flake. Again, the titanium “peak” is indistinguishable from noise, and the calculated percentage of titanium on the sample surface is similar to that of the sample where titanium has been deposited: 0.4 % in each case. The high percentages of carbon in both cases are due to the deposition of amorphous carbon by the electron beam as the spectra are taken. Both spectra above are taken with 10 cycles of averaging for a narrow window of energies around each Auger peak, thus maximizing the signal for each peak while minimizing the total exposure time. We do not find that a more distinct titanium peak develops for higher numbers of averaged cycles: rather, the magnitude of the carbon peak grows as more carbon is deposited onto the surface. For as many as 500 cycles of averaging, the carbon percentage grows to as large as 67 %, but the silicon peak does not disappear, indicating that we are still measuring the surface of the chip underneath the deposited carbon.
Figure 9.7: A differentiated Auger spectrum taken on a region of a test thin graphite flake covered with a titanium diffraction grating pattern and subsequently etched using the same process used with our metal-mask ribbon samples. The differentiated Auger peaks from left to right are due to the presence of: C, Ti, O, Si. The larger the peak amplitude, the greater the quantity of that element on the surface. The percentages in the upper corner quantify the amounts of each element present, based on the assumption that these four elements comprise all of the material on the surface.
Figure 9.8: A differentiated Auger spectrum taken on a region of oxide on our test sample surface that has not been coated with titanium. The differentiated Auger peaks from left to right are due to the presence of: C, Ti, O, Si. The larger the peak amplitude, the greater the quantity of that element on the surface. The percentages in the upper corner quantify the amounts of each element present, based on the assumption that these four elements comprise all of the material on the surface.
These Auger measurements show that the density of titanium left on our graphene ribbon devices after the removal of the etch mask is no larger than that on a portion of the chip surface that has never been coated with titanium; for this reason, as well as the others outlined previously, we believe that our titanium etch mask technique produces ribbons whose transport behaviors are not modified by titanium residues.
Chapter 10

Fabrication of Graphene Nanoconstrictions

In this chapter I describe the fabrication process for our short graphene nanoconstrictions.

10.1 Short Constriction Geometry

In figure 10.1 we show a schematic of the structure of our short side-gated constrictions.

To fabricate this structure, we draw two lines in a bilayer of 495K/950K PMMA with a narrow gap between them that will become the constriction region. After development, the PMMA remaining outside these lines serves as an etch mask for a short (7-10 second) oxygen plasma etch performed at a power of 65W, a pressure of 100 mTorr, and an oxygen flow rate of 20 sccm. This step removes the graphene within the lines that we have patterned lithographically. Without removing the PMMA mask, we then grow an approximately 4 nm layer of alumina by atomic layer deposition, and on top of this dielectric we deposit 5 nm of Ti followed by 10 nm of Au. We then soak the sample in acetone to lift off the unwanted metal coating the device outside of the patterned region.

In figure 10.2 we show an SEM micrograph of a graphene flake that has been
Figure 10.1: Schematic of a side-gated constriction sample: a) the sample geometry viewed from above. The white region represents the graphene flake, while in the dark regions on either side graphene has been etched away, a 4 nm layer of alumina has been deposited by atomic layer deposition, and gate metal has been deposited. Note that the color scale in this diagram is the opposite of what one sees in SEM micrographs, where metal appears bright and graphene appears dark. b) The sample geometry viewed in cross section.
prepared by this method with two nanoscale constrictions. The central region of the flake, between the two constrictions, is contacted by two contacts.

Figure 10.2: SEM micrograph of sample 1-17-a, showing the entire flake, including both constrictions, visible in this image as the metallic lines extending across the whole flake.

At this scale it is impossible to see the breaks in the gates that define the constrictions through which transport takes place. In figure 10.3 we show two higher-resolution SEM micrographs of each constriction region. These two constrictions are each between 10 and 15 nm in width. The constriction shown on the left has been fabricated with a triple line pattern to yield a 60 nm long nanostructure, while the constriction on the right has been fabricated with a single line to yield a 30 nm long structure.

### 10.1.1 Liftoff Problems

Liftoff on these alumina-coated samples is generally difficult, requiring long periods of immersion in boiling acetone and even brief sonication to clear the chip of unwanted metal and alumina. When sonication is required, sometimes the delicate nanostructure is destroyed, contributing to the low yields in fabrication of these samples. 10-24-d is an example of a side-gated sample that was broken by sonication.
Figure 10.3: SEM micrographs of a) the righthand 60 nm long constriction on sample 1-17-a, and b) the lefthand 30 nm long constriction. Images have been rotated to display the constrictions horizontally.

In figure 10.4 we show an AFM phase image of this flake in its entirety: the region where the side gates have broken far from the constriction region is circled in red.

In figure 10.5 we show a high-resolution image of the constriction region of this sample.

10.2 Non-Side Gated Samples

In the course of our measurements we became interested in the effect of our metal gates and the underlying dielectric on the conduction properties of our short constriction samples. We therefore began to fabricate samples in the side-gated geometry, but with the processing steps where the alumina and metal are deposited skipped. Such a sample is shown in figure 10.6.
CHAPTER 10. FABRICATION OF GRAPHENE NANOCONSTRICIONS

Figure 10.4: AFM phase image of sample 10-24-d, showing the contacts, side gates, and the region (circled in red) where the gates broke during processing.

Figure 10.5: AFM phase image of sample 10-24-d, in the constriction region. Either because the sample topography is complicated or possibly because of contamination of the AFM tip it is difficult to identify the borders of the constriction with certainty: two plausible choices are shown as red lines and dashed black lines. For either of these borders, the constriction is less than $\sim 50$ nm in width.
Figure 10.6: AFM phase image of non-side-gated sample 4-8-p4, zoomed in on the constriction region.
Chapter 11

Samples for the Scanning Gate System

11.1 Introduction

Graphene is predicted to have exotic scattering properties due to the Klein physics of its charge carriers [22, 9], and some experimental work has yielded evidence in favor of this prediction in the context of scattering off engineered potential barriers. Magnetotransport measurements on locally-gated graphene have yielded data in agreement with the predictions of Klein tunneling theory [93], and zero field resistance measurements on locally gated samples have shown differences between the resistance of ballistic and diffusive p–n [94] and full p–n–p [95] junctions consistent with Klein tunneling as well. However, a more direct measurement of graphene’s scattering properties is desirable—in particular, a technique that could elucidate how charge carriers in graphene scatter off of random disorder potentials (and not just large engineered potential barriers) would shed a great deal of light on how charge transport occurs in graphene.

Such a technique has been developed and employed to study scattering and local transport in GaAs two-dimensional electron gas (2DEG) systems [96, 97, 98]. In this technique, known as scanning gate microscopy, a scanning tip whose position and voltage are precisely controllable is deployed above a 2DEG. The tip acts on the
2DEG as a local gate, and for an appropriate tip voltage the 2DEG below can be completely depleted. Electrons in the 2DEG impinging on this depleted region are efficiently backscattered. Before measurement, the 2DEG is patterned with a narrow constriction defined by a split gate; electrons must pass through this constriction to get from the injection contact to the extraction contact. The conductance between these contacts (the transconductance) is recorded as the tip is scanned over the sample. Electrons emitted from the constriction and incident on the tip potential are backscattered; often this backscattering will send an electron back through the constriction, reducing the transconductance for that tip position. If the tip is placed at a position where no electrons emitted from the constriction are incident on the tip, the transconductance is unchanged. A map of the change in transconductance versus tip position can therefore reveal the trajectories through the 2DEG that particles emitted from the constriction take. These trajectories are called electron caustics. Some of the concepts discussed in this paragraph are illustrated in figure 11.1.

In GaAs 2DEG's it is believed that the paths that electrons take through the material are a result of the sum of a long series of small-angle scattering events [97]. Because the nature of scattering in graphene is expected to be quite different from that in GaAs 2DEGs, it is anticipated that scanning gate measurements on graphene will yield significantly different results.

A number of technical obstacles exist to performing measurements on graphene in a scanning gate system. First, because charge carriers in graphene can travel through potential barriers, creating a point source for charge carriers with a pair of electrostatic gates, as in GaAs scanning gate samples, is not possible. For the same reason, charge carriers are not expected to be efficiently backscattered by the electrostatic voltage on a scanning tip. Finally, as we learned during our preliminary measurements, exquisite control of the tip voltage and height is necessary to prevent electrostatic damage to graphene nanostructures during measurement. We describe our progress towards solving these difficulties below.
Figure 11.1: An SGM image mapping electron caustics through a GaAs 2DEG. The black shape at the bottom denotes the location of the split gate. The change in transconductance versus tip position maps the paths that electrons take through the 2DEG. The mean free path $l$ of electrons in the 2DEG is noted. Adapted from [98].
11.2 Graphene Constrictions as a Point or Colli-mated Particle Source

To solve the problem of producing a point source of charge carriers in graphene, we began fabricating nanoribbons and nanoconstrictions. Although this solution does not provide the same tunability as quantum point contacts in GaAs/AlGaAs heterostructures do, it allows us to produce a sample where charge carriers are emitted from (and can potentially be directed back through) a single place in the sample.

11.3 The Tip

There are more options available to solve the problem of scattering from the tip. The simplest option is simply to use an unmodified electrostatic tip: although charge carriers normally incident on the tip potential are not expected to be backscattered, because the tip potential should have a roughly circular profile carriers on parallel and nearby trajectories can be backscattered.

11.3.1 Multiple-Arm Geometries

Another option is to use an electrostatic tip in conjunction with a multi-arm collector geometry in order to collect carriers that are scattered from the tip in a variety of directions. We illustrate this situation diagramatically in figure 11.2.

11.3.2 Magnetic Confinement

Finally, we have considered the possibility of creating efficient backscattering by a magnetic tip. 1 T would be a very large magnetic field to produce on a sample surface with a magnetic tip. Still, even at this large field the cyclotron radius

\[ r_c = \frac{\hbar k_F}{eB} \]

(11.1)
11.4 Mobilities Necessary to Image Particle Caustics

Setting aside for the moment these problems with efficient backscattering, in order to measure particle caustics in graphene the momentum relaxation length must be longer than a realistic distance between the constriction and the scanning tip. For many of our nanostructured devices, momentum relaxation lengths are smaller than 30 nm; even in the highest-mobility samples fabricated on SiO₂ substrates momentum relaxation lengths are only about 300 nm. In an effort to obtain devices with longer momentum relaxation lengths, we entered into a collaboration with Kirill Bolotin in the Kim group to fabricate (non-nanostructured) suspended graphene devices with contact geometries and alignment marks suitable for scanning. In figure 11.3 we show
an AFM image taken by Kirill Bolotin of a flake fabricated by our group with a contact geometry suitable for scanning and with an alignment grid (protected from etching by a PMMA film) and suspended by the Kim lab. We have not yet imaged this sample.

Figure 11.3: AFM image of a suspended sample for scanning.

in the SGM, pending resolution of the problems of poorly controlled tip heights and voltages that we believe would prove more even certainly fatal to suspended samples than to our standard samples.

11.5 The Scanning Gate as a Probe Inside Graphene Nanostructures

Because of the difficulties described above, we have not yet succeeded in imaging particle caustics in graphene. However, we have found that the scanning gate system is a useful probe of localized states inside graphene nanostructures. This work was performed in collaboration with Markus König and Andrei Garcia; I fabricated the samples and Markus and Andrei operated the scanning gate system, and we discussed the interpretation of the data together. The remainder of this chapter will focus strongly on the sample fabrication, with data from the scanning gate system used to illustrate our conclusions about the samples. More detailed analysis of the SGM data
will likely appear in Andrei Garcia’s thesis.

Early on we concluded that relatively wide constrictions \((w > 50 \text{ nm})\) were preferable for these measurements because for samples with very wide transport gaps it was difficult to move the constriction between conducting and non-conducting states with the voltages we were able to apply to our tip. An example of such a constriction is shown in figure 11.4.

![AFM height image of sample 2-11-f flake HH. The constriction is located inside of the red box. Constriction width is approximately 60 nm.](image)

Figure 11.4: AFM height image of sample 2-11-f flake HH. The constriction is located inside of the red box. Constriction width is approximately 60 nm.

### 11.5.1 Localized states near a malformed constriction

Sample 2-11-f OS was measured in two different incarnations. The initial nanostructure fabricated on this flake was written at too low a dose to be etched properly: we hypothesize that the etch on this flake extended not much farther than the areas etched far from the constriction region.

In figure 11.5 we show an SGM image of the center of the flake 2-11-f OS. In the central portion of the image, nearer to the lefthand contacts there are a number
of concentric ring-like features. Their ring-like character will be easier to discern in the higher-resolution SGM image in figure 11.6. These ring features are centered at approximately the transition between the area and line doses in the original etch pattern. While the ring features appear at a broad range of back gate and tip voltages, they are most pronounced when the back gate voltage is 10 V (figure 11.6). The centers of the rings can be pinpointed to within 10 nm, and the distance between subsequent rings changes with tip height and voltage in the way that one might expect if the effect of the tip were to charge a localized state located at the center of the ring. This is similar to results from scanning gate studies on carbon nanotubes and quantum dots [99, 100].

Later we reprocessed sample flake 2-11-f OS with another etch: figure 11.7 shows this constriction.
Figure 11.6: Higher resolution SGM image of the lefthand set of rings with 10 V on the back gate and 10 V on the tip.

Figure 11.7: Sample 2-11-f flake OS, zoom in on a small region. This constriction is approximately 50 nm in width.
11.5.2 SGM images of a well-formed graphene constriction

After the measurements described above we took greater care to make sure that samples for measurement in the SGM contained well-formed nanostructures. Our confidence in our preliminary AFM images to reveal any nanostructure on the graphene also increased with more experience. In figure 11.8 we show an example of a well-formed constriction sample that we made and, for a short time, measured in the SGM. Unfortunately, this sample was the victim of an electrostatic breakdown event that shortened its life. In figure 11.9 we show transport and SGM images detailing the conductance before and after this event and the SGM data on the damaged sample.

Figure 11.8: AFM image of sample 8-11-e flake MR. Constriction is approximately 65 nm wide and 850 nm long.

11.5.3 Graphene constriction with a metal particle

8-11-e IR was another originally well-formed constriction sample that was unintentionally modified during measurement. During our measurement of sample 8-11-e IR, we believe a collision between the tip and one of the contacts resulted in metal
Figure 11.9: a) Conductance versus back gate voltage across constriction 8-11-e MR, in units of $2e^2/h$, before scans. b) Conductance traces immediately before and after breakdown event. c) Conductance after the breakdown event. Location of the gap has changed. d) SGM image of the constriction region after the breakdown event. Although the conductance is small, periodic features parallel to the constriction can be seen.
particles being sprayed across the sample, including one that landed on top of the constriction. Before the measurement, AFM images of the sample showed unblemished contacts and a flake surface free of foreign objects: after the measurement, AFM images showed a crater in one of the contacts (figure 11.11) and ~50 nm diameter particles scattered over the flake, including on inside the constriction (figure 11.10 (a)). Scanning gate images of this device show resonances that appear to run parallel to the constriction, like those we observe in other constriction samples, convolved with a rounded feature that appears to be centered on the location of the particle inside the constriction. These resonances are present at a variety of back gate voltages near the gap edge (where the smaller tip voltage is capable of moving the underlying region in and out of the gap) and at back gate voltages farther from the gap as well.

Figure 11.10: a) AFM image of sample 8-11-e flake IR after scanning gate measurement, showing both the constriction and a series of metal particles that fell on the flake as a result of a collision between the tip and the contacts. b) A scanning gate image of the sample with the back gate placed at a value near the constriction's gap. c) A scanning gate image of the sample with the back gate positioned well outside the gap.

11.5.4 Structures with many constrictions in parallel

With sample 1-2-1a flake Al we experimented with fabricating many constrictions in parallel on the same flake. Because of the high failure rate of constrictions inside the scanning gate system, we hoped that such parallel fabrication would allow us to take data for longer periods of time before thermally cycling, or even that the many
parallel paths to each contact through the many constrictions could alleviate some of the problems with sample breakdown observed over and over in other devices. In figure 11.12 we show an AFM phase image of the entire flake 1-2-1 a Al, showing the many parallel constrictions, each spaced about 1 \( \mu \text{m} \) apart. In figure 11.13 we show a high-resolution AFM image allowing us to roughly identify the width of a single constriction. Scanning measurements on sample 1-2-1 a Al are shown in figure 11.14. Rings centered on some (though not all) of the constrictions can be seen. Unfortunately, rings from different constrictions interfere too much to permit detailed analysis, as the tip used in this measurement produces a long-range potential, coupling strongly to features that are 1 \( \mu \text{m} \) or more away. This should be ameliorated in the future by using coaxially-shielded tips under development by Nahid Harjee in a collaboration between the Goldhaber-Gordon and Pruitt groups. Until then, though, we will avoid parallel-constriction samples such as this one, in order to produce more easily interpretable data.

The scanning gate system began to experience electrical problems with the piezo
Figure 11.12: Sample 1-2-1a flake Al.

Figure 11.13: AFM phase image of sample 1-2-1a flake Al, zoom in on a small region. Constrictions vary in width around 60 to 100 nm, are spaced 1 micron apart.
Figure 11.14: a) AFM image of flake 1-2-1 a Al with the constrictions locations highlighted in black and the scanning window superposed in white. b) Scanning gate data within that window. The color scale represents a conductance change of approximately $0.2 \times 2e^2/h$ measured between the contacts.
positioning system soon after this measurement was done, necessitating a long period of maintenance, and we have not yet revisited these measurements.

11.6 Electrostatic Considerations

Adding the apparatus associated with making scanning probe measurements, including the presence of a tip with a possible potential differences of volts with respect to the very nearby graphene surface and the presence of high-voltage piezo scanners near to the electrostatically sensitive graphene nanostructures presented a number of problems.

11.6.1 The perils of tip set-downs

One of the greatest difficulties we encountered in making scanning measurements on graphene nanostructures was their extreme sensitivity to poorly controlled tip voltage and height. We found that a tip touching down on the surface at a potential that was not precisely the same (within a few mV) as the potential on the flake almost always resulted in the nanostructure becoming non-conducting. Avoiding setting the tip down on the sample surface or on the contacts is the best way to prevent these events, but this strategy is complicated by the fact that voltages applied to the back gate tended to pull the tip into the sample in a way we only began to understand several months into our measurements. In figure 11.15 we show an AFM image of the entire flake 9-6-1 i before its insertion into the scanning gate system. Even at this resolution it is possible to see the (relatively wide) nanoconstrictions fabricated in parallel on the flake.

Figure 11.16 shows one of the nanoconstrictions in close-up.

After insertion into the scanning gate an event occurred which resulted in the sample losing conductivity across the constrictions. AFM images after this event are shown in figure 11.17 (the whole flake) and in figure 11.18 (a single constriction). The narrow isthmuses of graphene connecting the two sides of the flake have been burned away in a manner typical of ESD events.
Figure 11.15: Sample 9-6-1-i before measurement in the scanning gate system. Constrictions range from approximately 80 to 100 nm in width.
Figure 11.16: Sample 9-6-1-i, zoom in on a small region. Constriction is approximately 90 nm in width.

Figure 11.17: Sample 9-6-1-i after measurement in the scanning gate system. Every constriction has been burned away.
Figure 11.18: Sample 9-6-1-i after measurement in the scanning gate system, zoom in on one of the former constriction regions.

This was a recurring pattern with many samples.

11.6.2 Energizing the attocubes

In the SGM system, fine positioning of the tip within the micron-scale scan field is done with x, y, and z piezos. Although the voltages on these piezos can be large, they are smoothly varying, and do not seem to affect the transport properties of graphene samples.

Coarse positioning in the system, however, is done with devices manufactured by Attocube, in which piezo voltages are ramped very quickly to produce coarse motion with a stick-slip technique. We found that moving the scan field by energizing the attocubes always affected the transport properties of the graphene devices; fluctuations observed in conductivity measurements would change, and patterns seen in SGM scans would also be rearranged. Because of this, we tried whenever possible to choose a scan window at the beginning of our cooldown and do all measurements
11.6.3 Imaging graphene flakes with tip deflection

Using the scanning gate system in AFM mode relies on voltages generated by the deflection of a piezoelectric cantilever to measure the tip height; this technique is less sensitive to the tip deflection than the optical interferometry used in most AFMs. The native height sensitivity of the scanning gate AFM does not allow us to image very small step heights like those at the edges of graphene flakes, which means that in general we must infer the position of the flake from images of the thicker contacts. However, we found that there is a crude means of imaging the outline of a graphene flake in the scanning gate system; in figure 11.19 we show images of the tip deflection signal for a selection of back gate voltages, ramping down from 0 V on the back gate to -60 V, then back to 0 V for sample 9-7-d OM. As the back gate voltage becomes larger, the tip deflection signal differential from the flake to the bare gate oxide increases, and the flake outline becomes clearer. As the gate voltage is ramped back to 0 V, a substantial hysteretic effect is observed. We hypothesize that the change in tip deflection over the flake arises from screening of the back gate voltage by the (grounded) flake. We suspect that the hysteretic behavior does not arise wholly from the back gate voltage, since we see similar hysteresis as a function of tip height.

11.7 Fabry-Perot-like oscillations

In figure 11.20 we show data from our sample 2-11-f OS where we scan the tip between a pair of contacts that are not separated by a nanostructure. In this region we see features that may correspond to Fabry-Perot oscillations between the contacts. The features seen here differ from those shown in figure 11.6 in that the circular patterns here do not form closed rings centered around a single point, but intermesh with each other. These features are not unique to this sample: we see wave-like patterns between contacts on every sample we have imaged.
Figure 11.19: Tip deflection vs position at a tip height of 100 nm for back gate voltages of a) 0 V, b) -40 V, c) -60 V, d) -40 V again, e) -60 V again and f) 0 V again on sample 9-7-d OM. In the color scale blue corresponds to the tip being pushed away from the surface, while red signifies the tip being pulled toward the surface, with total changes in tip deflection less than 4 nm.

11.8 Summary

To conclude this chapter, we briefly summarize the points that may be useful to anyone trying to make SGM measurements on graphene in the future.

The narrowest, most highly gapped nanostructures do not make good scanning gate samples, because of the difficulty in moving the nanostructure in and out of the conducting regime with the limited tip voltage.

Detailed AFM imaging of samples before measurement in the SGM is invaluable.

Well-controlled tip voltage and height is necessary to make scanning gate measurements on graphene: unintentional tip set-downs at uncontrolled voltages will almost always destroy nanostructured graphene samples, as will tip crashes on the exposed graphene surface. It is important to note that voltages on the back gate will cause changes in tip deflection that vary above the graphene and the oxide surface. At small tip heights, these deflections can cause tip crashes.

Tips that do not create long-range potentials on the surface are necessary to make meaningful measurements sample with many nanostructures in parallel.
Figure 11.20: SGM image centered on the area between two contacts, sample 2-11-f OS.
Appendix A

Helium-3 Fridge Cold Finger

In the following pages I show the engineering drawings for the cold finger I designed for the helium-3 fridge used in many of the experiments described in this thesis. The design was based on a cold finger designed by Sergey Frolov Josh Folk’s group, and on input from Lindsay Moore. The purpose of the perpendicular wrap rods is to aid in wrapping the wiring around the central rod of the cold finger for good thermal sinking and to allow bidirectional wrapping that avoids voltage fluctuations in the wiring due to inductive coupling to magnetic fields: after the wiring is wrapped in a spiral around the central rod all the way to the wrap rod, it is doubled around the wrap rod, allowing it to be wrapped up the central rod in the other direction. The three resistor plates each contain one 100 Ω nonmagnetic resistor per wire (the replacements for these resistors are the non-magnetic brass solder capped Vishay ERL and ERC resistors). These resistors, in conjunction with the parasitic capacitance of the wiring, form low-pass RC filters that reduce the amount of high frequency noise reaching the sample. Locating the resistors at low temperatures quenches the thermal noise these resistors would add to the circuit at room temperature. The central rod was initially designed to be cryogenically press-fit into the top plate: when this was determined to be too difficult the physics shop hard-soldered it instead. This seems to have had little adverse effect on its thermal properties: the thermometers on the helium-3 pot and on the chip carrier are in good agreement for those temperatures at which they are both functional (between 1.4 and 6.7 K). After fabrication and welding,
the entire assembly was gold-plated (without the standard nickel sticking layer, to preserve the cold-finger’s non-magnetic properties). Future designers should note that gold-plating adds a surprising amount of thickness to the outer dimensions, and this should be taken into account when considering tolerances. The engineering drawings do not show holes drilled and bent tubes soldered into bottom of the radiation shield can ex post facto in order to provide effective venting of the can at vacuum.
Figure A.1: The entire cold finger assembly.
Figure A.2: Top plate in the cold finger assembly: bolts to helium-3 pot.
Figure A.3: Plates used in the cold finger assembly for mounting resistors in filtering system and for radiation shielding.
Figure A.4: Copper rod leading from the top plate to the socket.
Figure A.5: Perpendicular rods to aid in wrapping wiring.
Figure A.6: Radiation shield for the cold finger assembly.
Appendix B

Measurement Electronics

Our requirements for electronics for measuring graphene devices are relatively straightforward. We need to apply large (up to 100 V) but stable voltages to the back gate, and smaller and concomitantly more stable voltages to side gates and graphene contacts. We need to make low-noise measurements at low temperatures, and we need to monitor leakage currents in real time in order to prevent breakdown events.

In order to achieve the low noise necessary to make low-temperature measurements, we use a lock-in detector, most often the SRS830 and the PAR124A. The SRS lock-in offers the option of interfacing with the data acquisition program directly via GPIB, thus bypassing any additional noise and delay by an auxiliary digital multimeter (DMM), but the using the digital SRS requires more attention to the high dynamic range and low noise options—choosing incorrectly for one’s signal level can result in spurious digital binning of the signal.

To supply large voltages to our back gate, we preferred the Keithley2400. It is capable of sourcing voltages of up to 210 V, and thus allows us to avoid daisy-chaining multiple voltage sources together. On the 210 V setting, it has a resolution of 5 mV, which is adequate for all but the finest back gate sweeps. It automatically measures the leakage current as it supplies a voltages, which makes it ideal for anticipating oxide breakdown events or avoiding sample destruction during current annealing. The Keithley allows the user to set a maximum leakage current, which the instrument will not exceed.
To supply voltages to the more delicate side gates, we sometimes used the Keithley 2400 and sometimes the Yokogawa 7651. While the Yokogawa offers finer output voltage resolution, it also puts out a large voltage spike upon initialization, and does not offer the Keithley's useful leakage-current measurement and regulation features.

We also used power supplies from Valhalla early in our measurements, but abandoned them when we encountered a failure mode where they would drop to zero voltage output unpredictably, even when used on a manual setting.

When making initial measurements on a new sample, we prefer to apply a voltage bias, so as not to apply large or unpredictable voltages across the sample should any contact resistances be large. Later, if we wish to do four-wire measurements, we use current bias.
Appendix C

Measurement Programs

C.1 Introduction

In this appendix I present the Matlab code used to make the measurements described in this thesis. Each of these programs is meant to be used with low-frequency excitations (below \( \sim 100 \) Hz) and with adder boxes and filters appropriate for those frequencies. In all cases programs are adapted from earlier versions of code written by Silvia Luscher, Lindsay Moore, and Hung-Tao Chou. Certain improvements in the code were suggested by Patrick Gallagher.

C.2 Conductance versus Back Gate Voltage Program

Reproduced below is the measurement program used to collect data on the conductance of a device versus a voltage on the back gate. The leakage current is also monitored. This program can also be used for annealing of graphene devices: in this case a much smaller Keithley output voltage is used to apply a bias across the device for Joule heating, and the current across the device is measured in place of the leakage current.

```matlab
%*********************************************************************
```
function DATA = keithleysweep\_plotleak(vs, ve, nosteps, delay, k2400, a34401A\_current, voltnowt);

vrange = ve-vs; \% Output voltage range.
voltout = vs*1.0 + [0:nosteps]*(vrange/nosteps); \% Vector of output voltages.
bias = 27e-6; \% AC signal coming from lock-in after voltage divider
sens = 2e-3; \% lock-in sensitivity
Ithaco = 1e-6; \% current pre-amp sensitivity
krate = 0.001; \% ramp rate of the Keithley voltage source
e = 1.6e-19;
h = 6.6e-34;
GO = 2*e^2/h;
\% Go to starting gate voltage.
gotoset2400(krate,vs,k2400)
pause(1)
\% Begin ramping gate voltage.
for i = 1:length(voltout)
    voltnow = voltout(i);
gotoset2400(krate, voltnow, k2400);
pause(delay);
fprintf(a34401A\_current,['INIT']);
fprintf(a34401A\_current,'FETC?');
current\_voltage = str2num(fscanf(a34401A\_current));
R = bias/(current\_voltage*sens.*Ithaco/(10));
G = 1./(R*GO);
[V,I] = read2400(voltnow,k2400);
leak = I;
DATA(i,:) = [voltnow R G leak voltnowt];
\% Plot each data point as it is taken.
if i == 1
    TempFig = figure;
upperplot = subplot (211);
lineone = line(DATA(i,1), DATA(i,3));
set(lineone,'Color','k','LineStyle','-','Marker','.',
'MarkerSize',2,'MarkerEdgeColor','r');
xlabel('Applied Voltage (V)');
ylabel('Conductance (2e^-2/h)'); drawnow; hold on;
lowerplot = subplot (212);
linetwo = line(DATA(i,1),DATA(i,4));
set(linetwo,'Color','r','LineStyle','-','Marker','.',
'MarkerSize',2,'MarkerEdgeColor','r');
xlabel('Applied Voltage (V)');
ylabel('Leakage Current (A)'); drawnow; hold on;
else
    set(lineone,'XData',DATA(:,1),'YData',DATA(:,3)); drawnow;
    set(linetwo,'XData',DATA(:,1),'YData',DATA(:,4)); drawnow;
end
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

C.2.1 Referenced by Conductance Versus Back Gate Voltage
Program: gotoset2400

Reproduced below is the function gotoset2400 called by the function keithleysweep.plotleak.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

function gotoset2400(step,setpoint,k2400)
fprintf(k2400,['READ?']);
temp = [str2num(fscanf(k2400))];
    volt=temp(1);
    if (setpoint-volt>0)
        step=abs(step);
else step=-abs(step);
end
while abs(setpoint-volt)> abs(1.1 *step)
    volt=volt+step;
    fprintf(k2400, ['SOUR:VOLT ' num2str(volt)]);
    pause(0.01);
end
fprintf(k2400, ['SOUR:VOLT ' num2str(setpoint)]);

%********************************************************************************

C.3 Differential Conductance versus Two Voltages Program

Reproduced here is the program I used generically to apply two voltages, one potentially large (up to ±210 V) and one limited to ±15 V by the maximum output of the National Instruments digital to analog converter (DAC) on the measurement computer attached to the helium-3 fridge. The program can be adapted to use either voltage as the fast axis: the version shown here uses the large voltage as the fast axis. The program can also be used to apply two gate voltages: a large one on the back gate and a small one on a side gate. Additional channels can be added to sweep another voltage or a magnetic field.

%********************************************************************************

%last mod 2-4-08 KT sweeps a single dac channel
sens = 20e-3; %lockin sensitivity
vbias = .27e-3; %correct for imperfect voltage divider
Ithaco = 1e-6; %current preamp sensitivity
e = 1.6e-19;
h = 6.626e-34;
G0 = 2*(e^2)/h;
folder = '\20090126\'; %change this variable each day
APPENDIX C. MEASUREMENT PROGRAMS

10-24-d in 8 out 4 across constriction, ch0 = 101*Vsd, Vbg = 15, T = 5.5K, 27 microV AC excit, gate pin 23 grounded but shorted pin 6 open, 77Hz freq 300ms time const;

filename = '10-24-d-%04d-%02d-%02d-%02d.%02d.%02d.mat'; %change this with each sample to organize data output

titre = 'across constriction nonlinear G';
GQPCtitle= 'G across constriction 10-24-d
-%04d-%02d-%02d-%02d.%02d.%02d.jpg';
numaverage =5; %averages queries of DMM's
Vsd = -0.020:0.0005:0.020; %the real source-drain voltage, after adder box. Middle number is the step size.
ch0=101*Vsd; %the output of the DACs applying this voltage, before the adder box

Vbg = -5:0.1:35; %back gate voltage series. Middle number is the step size.
[ch0,Vbg] = meshgrid(ch0,Vbg); %generates a 2D array of source-drain and back gate voltages

ch2=(zeros(number, steps));
%go to starting voltages
gotoset2400(0.0005,Vbg(1,1),k2400);
[NIData]=NIGotoset(ch0(1,1),0,NIData,NI6703,NIcalibration);
% Generating the filename
c = fix(clock)
fname = sprintf(filename, c(l), c(2), c(3), c(4), c(5), c(6)); %generate time and date filename

thisdir = pwd;
fnamen=[thisdir,folder,fname];

%*******************************************************************************
% Initialize the GPIB connections
% % Set parameters for DMM measuring conductance with set range and resolution.
resi = 0.00001*10;  % Resolution is fast 4 digit. See p.54-57 of Agilent 34401A manual.
fprintf(a34401A_current, ['CONF:VOLT:DC 10, ' num2str(resi)]);

% Starting the run
pause(3)

% Initialize Arrays
[number,steps] = size(chO);  % calculates the length of the array in each dimension
up = zeros(number,steps);
Gup = zeros(number,steps);
timelog = zeros(number,steps);
% Tnow = zeros(number,steps);
tic;
for m=1:number
% set back gate
gotoset2400(0.0005,Vbg(m,1),k2400);
if mod(m,2) == 1;
[NIdata]=NIgotoset(chO(m,1),0,NIdata,NI6703,NIcalibration);
else
[NIdata]=NIgotoset(chO(m,steps),0,NIdata,NI6703,NIcalibration);
end
pause(2);
if mod(m,2) == 1;
for n=1:steps
[NIdata]=NIgotoset(chO(m,n),0,NIdata,NI6703,NIcalibration);
pause(0.1)
end
% Read from the DMM and average the results
A=zeros(1,numaverage);
for p=1:numaverage
fprintf(a34401A_current,'INIT');
fprintf(a34401A_current,'FETC?');
A(p) = str2num(fscanf(a34401A_current)); %read from DMM
end
R = vbias/(mean(A)*sens*Ithaco/10); %transfer volt value in number
G = 1./(G0.*R);
up(m,n)=R;
Gup(m,n)=G;
t=toc;
timelog(m,n) = t;
% Echo the present voltage settings to the screen
[chO(m,n) Vbg(m,n)];
end
else
for n=1:steps
[NIdata]=NIgotoset(ch0(m,steps+1-n),0,NIdata,NI6703,NIcalibration);
pause(0.1)
% Read from the DMM and average the results
A=zeros(1,numaverage);
for p=1:numaverage
fprintf(a34401A_current,'INIT');
fprintf(a34401A_current,'FETC?');
A(p) = str2num(fscanf(a34401A_current)); %read from DMM
end
R = vbias/(mean(A)*sens*Ithaco/10); %transfer volt value in number
G = 1./(G0.*R);
up(m.steps+1-n)=R;
Gup(m.steps+1-n)=G;
t=toc;
timelog(m,n) = t;
APPENDIX C. MEASUREMENT PROGRAMS

% Echo the present voltage settings to the screen
[ch0(m,steps+1-n) Vbg(m,steps+1-n)];
end
end
figure(45), hold on, plot(ch0(:,),Gup(,:))
end
Rup=up;
% Store the final data
data.Vsg = ch0;
data.Vbg = Vbg;
data.R = Rup;
data.G = Gup;
data.time = timelog;
% Saving the file
save(fnamen, 'ch0','Vbg', 'Rup', 'description', 'titre', 'data');
% Reseting the BiasDACs and the Keithley
gotoset2400(0.001,0,k2400);
[NIdata]=NIgotoset(0,0,NIdata,NI6703,NIcalibration);

C.3.1 Referenced by the Differential Conductance Versus Two Voltages Script: NIgotoset

The function NIgotoset smoothly ramps to a given voltage on the BiasDAC’s and returns the variable [NIdata] as a record of the current BiasDAC voltages.

function [NIdata]=NIgotoset(ziel,channel,NIdata,NI6703,Nicalibration);

% sets a voltage in with smooth speed ... NIdata is defined as a global variable
start=NIdata(channel+1);
startpum=polyval(NIcalibration(channel+1).p,start);
if startpum < ziel
    V=[startpum:0.001:ziel];
end
if startpum > ziel
    V=[startpum:-0.002:ziel];
end
if startpum==ziel;
    V=[];
end;

if length(V) > 0
    for i=1:length(V)
        [NIdata]=NIsetV(V(i),channel,NIdata,NI6703,NIcalibration);
        pause(0.06) %was 0.02
    end
else
end

[NIdata]=NIsetV(ziel,channel,NIdata,NI6703,NIcalibration);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%***************

C.3.2 Referenced by NIgotoset: NIsetV

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%***************

function [data]=NIsetV(V,channo,data,NI6703,NIcalibration);
y=polyval(NIcalibration(channo+1).p,V);
APPENDIX C. MEASUREMENT PROGRAMS

out=checkvoltage(channo,V);
if out==0
  data(channo+1)=y;
  putsample(NI6703,data);
end
if out==-1
  'voltage out of range'
end

C.4 Initializing the BiasDAC’s: startupp

The script startupp must be run before running any other program that addresses
the BiasDAC voltages in order to initialize the variable NIcalibration

beta6703
load NIcalibration

C.4.1 Referenced by startupp: beta6703

beta6703

nofchannels=5
% Simple program for the 6703.

% Create analog output object.
NI6703 = analogoutput('nidaq',1);
addchannel(NI6703,0:nofchannels-1);
% Create channels
%NI6703ch = addchannel(NI6703,0:15,1:16,{‘out0’,‘out1’,
‘out2’,‘out3’,‘out4’,‘out5’,‘out6’,‘out7’,‘out8’,‘out9’,
‘out10’,‘out11’,‘out12’,‘out13’,‘out14’,‘out15’})

% Set sample rate and check.
% set(NI6703,’SampleRate’,0);
% get(NI6703,’SampleRate’);

% Set trigger type.
% set(NI6703,’TriggerType’,’Manual’);

% Create data vector, initialise with zeroes.
NIdata = zeros(1,nofchannels);
putsample(NI6703,NIdata);
Bibliography


BIBLIOGRAPHY


BIBLIOGRAPHY


