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SUBSTRATE-MEDIATED MODULATIONS OF GRAPHENE’S ELECTRONIC PROPERTIES

BY

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DISSEPTION

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Abstract

As a perfectly two-dimensional material graphene is exceptionally susceptible to its environment. In particular, the substrate used to support graphene can dramatically alter its electrical and mechanical properties. In this thesis we investigate the interactions between graphene and three distinct types of substrate. First we consider graphene on flexible substrates and the interaction between the strain induced by the substrate and graphene’s mechanical integrity. Next we consider ferroelectric substrates, the doping effect of the substrate polarization, and the effects of that polarization on polar adsorbates. Finally we consider topographically patterned substrates and the effects of local variations in strain and doping on the transport properties of graphene.

We explore these three topics using optical measurements, atomic force microscopy, and electrical transport measurements. We first find that graphene on flexible substrates undergoes partial mechanical failure when the substrate is stretched, but that graphene is robust to subsequent applications of strain provided the applied strain does not exceed the maximum strain previously applied. This result extends our understanding of graphene’s mechanical failure to the non-suspended case, and is directly applicable to technological applications which use graphene as a flexible conductor. We next find that ferroelectric substrates can affect the orientation of polar dopants adsorbed on graphene, and that different orientations contribute different degrees of doping. This result illuminates the subtleties of doping graphene via polarizable mediums. Finally, we find that local variations in doping can create quantum dot regions in graphene which are characterized by quasi-bound states rather than the fully bound states typically found in quantum dot systems. This result provides experimental verification of theoretical predictions and presents an experimental paradigm with which to further explore the interactions between local strain and doping and graphene’s electric properties. We discuss these findings in detail, and conclude by proposing future experiments which expand on the results presented here.
To my family

หนึ่งเลือนอย
Whenever anyone asks me for advice about graduate school the first thing I say is “Find a good advisor.” Nothing has a larger impact on your scientific growth, your professional development, and your quality of life as a graduate student than your advisor, and I have been incredibly fortunate to have had Nadya as mine. I’m leaving grad school as a competent scientist with both my sanity and my enthusiasm for physics intact, all of which is due to Nadya’s consistently upbeat attitude, generous mentorship, and supportive guidance. Not only that, I’ve also grown as a person during this time by having a meaningful life outside of lab. Many, many thanks to Nadya for creating an environment and offering perspective which made all of this possible.

Thanks to everyone in the group too – Nick who convinced me to come to UIUC and join the lab in the first place, Scott for showing me the ropes in the beginning, Serena and Clare for modeling the persistence it takes to graduate, Malcolm for always knowing how everything in the lab works, Jeff and Stephen for their Statler-and-Waldorf style commentary, Angela and Rita for commiserating about failed experiments, Sungjae, Joe, Yingjie, and Vincent for their advice from the other side, and Greg and Junseok for keeping things going.

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Last, and most importantly, thanks to my family and especially my wife (!) Nadha. I wouldn’t be where I am without all their love, support, and guidance. Thanks to Dad for sparking my love of science and physics in the first place, to Mom for all her support when things got tough, to Brother for his good advice these past few years, and to Nadha for being the best thing that ever happened to anyone in grad school.
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<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BOE</td>
<td>Buffered oxide etchant</td>
</tr>
<tr>
<td>CG</td>
<td>Coarse grained</td>
</tr>
<tr>
<td>CNP</td>
<td>Charge neutrality point</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DAQ</td>
<td>Data Acquisition (device)</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>hBN</td>
<td>Hexagonal boron nitride</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>iLO</td>
<td>in-plane, longitudinal optical (phonon mode)</td>
</tr>
<tr>
<td>iTO</td>
<td>in-plane, transverse optical (phonon mode)</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>KPFM</td>
<td>Kelvin probe force microscopy</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PFM</td>
<td>Piezoresponse force microscopy</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead zirconate titanate PbZr_{0.2}Ti_{0.8}O_{3}</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>SMU</td>
<td>Source-measure unit</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

God created the bulk; surfaces were invented by the devil.

Wolfgang Pauli

1.1 Motivation

If “surfaces were invented by the devil” then graphene might be the most infernal material known to mankind. As a perfectly two-dimensional crystal graphene is exceptionally susceptible to its environment: it adsorbs dopants at the first opportunity, it is both fantastically strong and extremely fragile, and it intimately pairs with any substrate it is placed upon. All in all graphene can be incredibly frustrating to work with as an experimentalist. At the same time, graphene displays an extraordinarily rich set of physical effects. Relativistic tunneling, mind-boggling strength and stiffness, effective magnetic fields an order of magnitude larger than what can otherwise be produced – all are present in graphene and accessible via the standard experimental methods of condensed matter physics. Graphene offers a small window with a remarkably large view into the workings of the universe.

The motivation for the experiments described in this thesis is to reconsider the fiendishness of graphene’s susceptibility to its environment. Rather than asking, “How does the environment distort the physics I’m trying to observe?” we ask, “What does the distortion tell me about the system, and how might we use this knowledge to advance science and technology?” In this spirit we explore three primary topics: graphene’s dependence on a substrate to preserve its mechanical integrity, graphene’s susceptibility to doping from both its substrate and its environment, and graphene’s response to local variations in mechanical strain and doping induced by a substrate.
1.2 Statement of thesis problem

In this thesis we report measurements of graphene’s electrical properties and mechanical integrity as a function of strain, doping, substrate topography, and substrate material. Our primary goal is to better understand how interactions between graphene and its substrate modulate the properties of graphene. In particular we address the following questions: First, how does the support of a flexible substrate affect the mechanical integrity and electrical resistance of graphene when the graphene is strained by stretching the flexible substrate? Second, what effect does a polarized ferroelectric substrate have on graphene, and how does the ferroelectric polarization interact with other dopants? And finally, how do local variations in strain and doping induced by substrate topography affect the electrical properties of graphene? We address these three question via optical, atomic force microscope, and electrical transport measurements of microfabricated graphene devices. The resulting data are analyzed within the framework of existing theory, and offer both experimental validation of theory and further insight into the physics of graphene’s interactions with its substrate.

1.3 Outline

The thesis is organized as follows: in Chapter 1 we motivate the work and state the thesis problem. In Chapter 2 we present background information about graphene and its properties. In Chapter 3 we summarize the relevant experimental techniques. In Chapter 4 we present the results of the experiments which comprise this thesis and discuss them in detail. Finally, in Chapter 5 we summarize our results and offer suggestions for future work.

The results of Chapter 4 are published in the following papers:


Chapter 2

Background

2.1 Introduction to graphene

Much of graphene’s interesting behavior comes from its unique, two-dimensional structure. Those properties of graphene which are relevant to the research comprising this thesis are summarized below; for a more complete description of graphene see one of the existing review articles [1, 2, 3]. Here I discuss graphene’s band structure and several relevant consequences, namely the massless Dirac fermion character of charge carriers in graphene, the unique variant of the quantum Hall effect these carriers give rise to, and the presence of Klein tunnelling. I also discuss the means and effects of doping and straining graphene. The latter discussion (of strain) includes a description of graphene’s mechanical properties as well as the optical signatures of lattice vibrations in graphene.

2.1.1 Band structure

As illustrated in Figure 2.1, graphene is composed of carbon atoms in a hexagonal lattice. The hexagonal lattice contains two interlaced triangular lattices, labelled A and B. Each individual sublattice has unit vectors $a_1$ and $a_2$. The Brillouin zone of graphene’s lattice is also illustrated in Figure 2.1, the corners, indicated by the labels $K$ and $K'$ are referred to as Dirac points for reasons described below. The band structure of graphene is shown in Figure 2.2; undoped graphene is a zero-gap semiconductor. This band structure is calculated using a simple tight-binding model, with a Hamiltonian (using units where $\hbar = 1$) [2]:

$$H = -t \sum_{\langle i,j \rangle, \sigma} (a^\dagger_{\sigma,i} b_{\sigma,j} + H.c.) - t' \sum_{\langle \langle i,j \rangle \rangle, \sigma} (a^\dagger_{\sigma,i} a_{\sigma,j} + b^\dagger_{\sigma,i} b_{\sigma,j} + H.c.)$$ (2.1)

where $t$ is the nearest neighbor hopping amplitude, $t'$ is the next nearest neighbor hopping amplitude, and $a_{\sigma,i}$ is the annihilation operator for an electron of pseudo-spin $\sigma$ at position $i$ on sublattice A. The Hermitian conjugate $a^\dagger$ gives the creation operator, and the $b$ operators are similarly defined for the B sublattice. This
Figure 2.1: The lattice structure of graphene and its Brillouin zone. Left: Graphene is composed of two interlaced triangular sublattices, labelled A and B. Each sublattice has unit vectors $a_1$ and $a_2$. Right: The Brillouin zone of graphene has several high symmetry points. In particular, the points $K$ and $K'$ are referred to as Dirac points. Adapted from [2].

Hamiltonian yields an energy spectrum of the form [2]:

$$E(k) = \pm t \sqrt{3 + f(k)} - t'f(k)$$

with

$$f(k) = 2 \cos \sqrt{3} k_y a + 4 \cos \frac{\sqrt{3}}{2} k_y a \cos \frac{3}{2} k_x a$$

which is plotted in Figure 2.2

2.1.2 Dirac fermions

In the low energy regions near the corners of the Brillouin zone the dispersion relation for graphene is approximately linear, as indicated in Figure 2.2. That is, for electrons or holes near these points,

$$E = \hbar v_F \sqrt{k_x^2 + k_y^2}$$

(2.3)

(where $\hbar$ is the reduced Planck’s constant and $k_x$ and $k_y$ are measured from the corner point). This has the same form as the energy of a massless, relativistic particle governed by the Dirac equation. These points are therefore called Dirac points, and in their vicinity the electrons behave as massless Dirac fermions. Each corner of the hexagonal Brillouin zone is related to two others by a reciprocal lattice vector, therefore two of the Dirac points, typically labelled $K$ and $K'$ are inequivalent.

The linear dispersion relation is not the only factor which ties transport in graphene to the Dirac equation; the two-component wave function of pseudoparticles in graphene is analogous to the spinor wavefunction used to describe spin $\frac{1}{2}$ particles in the Dirac equation [4]. In graphene the two components correspond to
the contributions to the pseudoparticle wavefunction from each of the two sublattices, whereas in quantum electrodynamics the spinor accounts for the spin up and spin down components of the wavefunction. The correspondence relies on the linkage of electron-like and hole-like states in graphene: in the vicinity of the Dirac point the positive-momentum, positive-charge states come from the same sublattice contribution as the negative-momentum, negative-charge states. This linkage between positive and negative energy and charge states is analogous to the charge conjugation symmetry present in quantum electrodynamics. This last point leads to the manifestation of Klein tunneling in graphene, as described below.

Note that there are two distinct two-fold degeneracies. The pseudospin degeneracy accounts for the geometric phase introduced by the hexagonal lattice of graphene. This is the degeneracy which causes the wavefunction of an electron in graphene to have two components. The valley degeneracy accounts for the fact that the Bravais lattice for graphene has a basis of two elements. This is the degeneracy that leads to the presence of two inequivalent Dirac points $K$ and $K'$. 

Near the $K$ and $K'$ points graphene is a zero-bandgap semiconductor and its transport properties are determined by the position of the Fermi level. When the Fermi level lies well within either of the bands graphene conducts, with a conductivity which is proportional to the number of carriers [5]. Conversely, when the Fermi level lies near the intersection of the two bands conductivity is suppressed, but does not reach zero. The latter point is due to the suppression of localization in systems governed by the Dirac equation. In the absence of localization effects the mean free path $l$ of charge carriers cannot be smaller than the wavelength $\lambda_F$ of the carrier [6]. Writing the conductivity in terms of the carrier wavelength

$$\sigma = ne\mu = \frac{e^2}{\hbar} \frac{l}{\lambda_F}$$

(2.4)
where \( n \) is the carrier density, \( e \) is the charge of an electron, \( \mu \) is the carrier mobility, and \( h \) is Planck’s constant we see that the conductivity \( \sigma \) cannot be less than \( e^2/h \).

### 2.1.3 Quantum Hall effect

Graphene displays a unique variant of the quantum Hall effect due to the massless, Dirac fermion nature of its charge carriers [7], [8]. In fact, the observation of graphene’s alternative manifestation of the quantum Hall effect provided one of the first experimental confirmations of the nature of charge carriers in graphene. In order to better emphasize the uniqueness of the quantum Hall effect in graphene we begin with a description of the standard quantum Hall effect.

In typical two-dimensional materials the application of a large magnetic field leads to a quantization of the allowed energy levels. These quantized energy states are called Landau levels, and for massive carriers the allowed energies are given by

\[
E = \hbar \omega_c (n + 1/2) \quad \text{with} \quad \omega_c = \frac{eB}{m^*}
\]  

(2.5)

where \( \omega_c \) is the cyclotron frequency, \( B \) is the applied magnetic field, and \( m^* \) is the effective mass of the carrier. Additionally, each of these energy levels is highly degenerate, having

\[
N = g_s \frac{eBA}{h} = g_s \frac{AB}{\Phi_0}
\]  

(2.6)

states per level, where \( A \) is the area of the device, \( g_s \) accounts for additional degeneracies in each state (for example, the spin and sublattice degeneracies in graphene), and \( \Phi_0 = h/e \) is the quantum of flux. The former result can be derived from a quantum mechanical treatment of the cyclotron orbits of particles in a magnetic field, while the latter can be calculated from the k-space density of allowed states. For a complete derivation see e.g. [9].

The resistivity of a two-dimensional device in a high magnetic field depends on the location of the Fermi level relative to these Landau level energy states. To calculate the resistivity we start from the Drude model for the motion of an electron of mass \( m \) and scattering time \( \tau \) in a magnetic field \( B \)

\[
m \frac{dv}{dt} = -eE - ev \times B - \frac{mv}{\tau}
\]  

(2.7)

and take the equilibrium solutions where \( dv/dt = 0 \). Substituting \( v = J/ne \) where \( J \) is the current density
and $n$ is the carrier density, and setting $\mathbf{B} = (0, 0, 1)$ allows us to rearrange Equation 2.7 as

$$\rho \mathbf{J} = \mathbf{E} \quad \text{with} \quad \rho = \frac{m}{ne^2 \tau} \begin{bmatrix} 1 & \omega_c \tau \\ \omega_c \tau & 1 \end{bmatrix}.$$  \hfill (2.8)

Thus we expect to find

$$\rho_{xx} = \frac{m}{ne^2 \tau} \quad \text{and} \quad \rho_{xy} = \frac{m}{ne^2 \tau} \omega_c \tau = \frac{B}{n}.$$  \hfill (2.9)

Both $\rho_{xx}$ and $\rho_{xy}$ depend on the position of the Fermi level $E_F$ relative to the Landau level energies. Considering first $\rho_{xx}$, when $E_F$ lies between Landau levels all available states are filled, and scattering is therefore strongly suppressed. When scattering is suppressed $\tau$ goes to infinity, and we expect $\rho_{xx}$ to go to zero. Conversely, when $E_F$ lies within a Landau level scattering is allowed, and we expect a finite value for $\rho_{xx}$. For $\rho_{xy}$, we recall that the degeneracy of each Landau level is given by Equation 2.6 and so the carrier density is given by $n = \nu g_s \frac{N}{\pi} = \nu g_s \frac{B}{\Phi_0}$ where $\nu$ is the number of Landau levels which are occupied. The magnetic field dependence of the density cancels and we’re left with $\rho_{xy} = \frac{1}{\nu g_s \tau \hbar}$, therefore we expect $\rho_{xy}$ to display plateaux, each at some whole number fraction of $\hbar/e^2$, where the steps coincide with the points when $E_F$ crosses through a Landau level energy. Finally, the conductivity and resistivity are related by $\rho = \sigma^{-1}$.

Following from the definition of $\rho$ in Equation 2.8 one can show that when $\rho_{xx} = 0$ (as is the case on the plateaux) then the Hall resistivity and Hall conductivity are related by $-\rho_{xy} = \frac{1}{\sigma_{xy}}$ so we expect to see plateaux in the Hall conductivity at $\nu g_s \frac{2}{\pi}$.

These features are most readily observed by sweeping the Fermi level through successive Landau level states, which can be accomplished by varying either the applied magnetic field or the carrier density. In the former case the Fermi level remains fixed while the allowed Landau level energies vary, while in the latter case the Fermi level is varied and the Landau level energies are constant. Both types of measurement are shown in Figure 2.3 the left-hand plot shows $\rho_{xx}$ and $\rho_{xy}$ as a function of the applied field for a non-graphene sample, while the right-hand plot shows $\rho_{xx}$ and $\sigma_{xy}$ as a function of carrier density for a graphene sample.

The quantum Hall effect as observed in graphene differs from the standard, integer QHE in two ways: the plateaux in $\sigma_{xy}$ are shifted by $2e^2/h$ and the sequence is uninterrupted as it passes through zero carrier density. Both differences stem from the massless character of graphene’s charge carriers. For massless particles in a magnetic field, such as the Dirac fermions in graphene, the energy quantization is [7],

$$E = \left[ 2 e \hbar c s^2 B \left( N + \frac{1}{2} \pm \frac{1}{2} \right) \right]^{1/2}.$$  \hfill (2.10)

where the sign of the last term depends on the pseudospin of the particle. This has two consequences: first,
Figure 2.3: Left: The quantum Hall effect in standard two-dimensional materials. Right: The quantum Hall effect in graphene. The Hall conductivity and longitudinal resistivity are plotted as a function of carrier concentration. Hall plateaux are present at $4e^2/h(N + 1/2)$, offset from the expected values by $2e^2/h$, and continue uninterrupted through zero concentration. Inset: Hall conductivity versus carrier concentration for bilayer graphene, showing the expected characteristics of the integer quantum Hall effect for comparison. Adapted from [10] and [7].

When $\pm \rightarrow -$ this quantization admits an $E = 0$ Landau level, which in turn causes the sequence of plateaux in the Hall conductivity to be uninterrupted as it passes through zero carrier density. Second, the $E = 0$ Landau level admits only those particles with ‘minus’ pseudospin (sublattice) polarization, therefore it is half as degenerate as all other Landau levels. This accounts for the $1/2$ offset in the locations of the Hall conductivity plateaux in graphene, $\sigma_{xy} = (4e^2/h)(N + 1/2)$.

An additional consequence of the masslessness of charge carriers in graphene is the persistence of quantum Hall effects to room temperature [11]. Considering again the energy quantization for Dirac fermions in a magnetic field quoted above, for $c^* = v_F \approx 10^6$ m s$^{-1}$ a 45 T field yields an energy gap of $\approx 2400$ K between the $N = 0$ and $N = \pm 1$ Landau levels, an order of magnitude greater than thermal fluctuations at room temperature. The high carrier concentration and temperature-independent carrier mobility also contribute to the robustness of the effect [11].

2.1.4 Klein tunneling

Another consequence of the ‘relativistic’ nature of carriers in graphene is the manifestation of Klein tunneling [12, 13, 14, 15, 16, 17]. Klein tunneling [18] is the counter-intuitive perfect transmission of massless, relativistic particles through a potential barrier. The effect was first proposed in 1929, however experimental tests of the theory remained elusive because it was impossible to produce relativistic particles in a transport measurement-type environment. The advent of graphene, and the relativistic nature of its charge carriers,
Figure 2.4: Left: Band structure of carriers in graphene incident on a potential barrier. The color (red / teal) of each line indicates the sublattice origin, i.e. pseudospin, of states at the specified energy and momentum. Notably, positive-momentum electron states have the same pseudospin as negative-momentum hole states. Right: Transmission probability as a function of angle of incidence. The red and blue curves correspond to different energies of the incident charge carrier. Adapted from [12].

provided a way to test the theory. Here I give a brief description of the theory, and summarize the relevant experimental results in graphene.

Consider a massless, relativistic particle incident on a potential barrier. The particle’s wave function is governed by the Dirac equation; taking the motion to be in the $x$ direction we have

\[
(\sigma_x p + V) \psi = E_0 \psi, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad V = \begin{cases} 0, & x < 0 \\ V_0, & x > 0 \end{cases}
\]

where $\sigma_x$ is the Pauli matrix. We can write the wave function of a particle incident on the barrier in terms of the wave function in either region:

\[
\begin{align*}
\psi_1 &= A e^{ikx} |\uparrow\rangle + A' e^{-ikx} |\downarrow\rangle \\
\psi_2 &= B e^{iqx} |\uparrow\rangle
\end{align*}
\]

where $k = E_0 / \hbar$ and $q = (V_0 - E_0) / \hbar$. Note that $|\uparrow\rangle$ and $|\downarrow\rangle$ here refer to the pseudospin polarization, not the standard spin polarization. The polarization of each term in the wave function (incident $A$, reflected $A'$, and transmitted $B$) depends on the sublattice origin of the relevant branch of the dispersion relation, as illustrated in Figure 2.4: to the left of the barrier electrons with positive momentum have positive pseudospin, and vice versa. To the left of the barrier however the hole states with negative momentum have positive pseudospin. Continuity of the wave function requires

\[
9
\]
\[ |A|^2 = |B|^2 \]
\[ |A'|^2 = 0 \] (2.13)

and so we have perfect transmission and no reflection. Note that the analysis above is for normally incident carriers; a similar analysis for carriers incident at an angle \( \phi \) yields a transmission probability of

\[ T = \frac{\cos^2 \phi}{1 - \cos^2 (q_x D) \sin^2 \phi} \] (2.14)

where \( D \) is the width of the barrier and \( q_x \) is the x-component of the wavevector in the barrier region \([12]\); this angular dependence is shown in Figure 2.4.

Klein tunneling has been observed in graphene by both indirect \([15, 19]\) and direct \([17]\) measurements. Indirect measurements proceed by measuring transport across electrostatically defined potential barriers and comparing the observed resistance to theoretically expected values. This method shows qualitative signatures of Klein tunneling, however it is difficult to distinguish perfect from near-perfect transmission. The direct measurement proceeds by observing interference effects in transport across two separate potential barriers. This technique is sensitive to phase differences as well, and can thus conclusively demonstrate the presence of Klein tunneling.

### 2.2 Electrical effects in graphene

Graphene is eminently dopable. In fact, many of the most interesting experimental results involving graphene exploit the ease with which it can be doped; the ability to easily tune the carrier concentration, Fermi level, and even carrier species, and the ability to do so in finely defined spatial regions has exposed a host of interesting physics results. In this section I summarize previous work on methods of doping graphene.

#### 2.2.1 Electrostatic gating

The primary method by which graphene is doped is by capacitative coupling to an external gate electrode. As a voltage is applied between the graphene and the external gate, charge accumulates on both according to \( C = q/V \). By varying the applied voltage one can therefore vary the carrier concentration in graphene, and due to graphene’s distinct semi-metallic band structure, the carrier species as well. This is illustrated in Figure 2.5.

In addition to providing experimental control over the doping in a graphene device this technique can also be used to determine the intrinsic position of the Fermi level, i.e. the position of Fermi level in the
absence of gate-induced doping. The conductance of a graphene device is proportional to the carrier density, and thus should reach a minimum as the Fermi level passes through the charge neutrality point (CNP) where graphene’s valence and conduction bands touch. By measuring the conductance of a graphene device as a function of applied gate voltage and observing the gate voltage which corresponds to the minimum conductance one can determine how far, and in which direction, the Fermi level is from the charge neutrality point. This provides a basic characterization of the doping present in the device in the absence of any gate voltage, as shown in Figure 2.5.

### PN junctions

It is also possible to produce separate, distinctly doped regions in graphene devices through the use of multiple gate electrodes. An example device configuration is shown in Figure 2.6 [22]. In such devices the Fermi level can be tuned separately in each region by adjusting the relative gate voltages applied to each gate electrode. This in turn allows the device to be biased into p-n, n-p, n-n, or p-p junctions at will, where p- and n- indicate the species of the carrier in each region. Transport measurements on these devices display results similar to the conductance profile shown in Figure 2.5, however instead of a single minimum graphene p-n junction devices will show two distinct minima. This is because the charge neutrality points are offset in the two doping regions, and as the Fermi level is swept it passes through the two CNPs separately.

Graphene pn junctions display additional plateaux in quantum Hall measurements [22]. This is due to the dynamics of the circulating edge modes at the junction. The application of a large magnetic field produces circulating edge states in two-dimensional devices; in a sample which has separate regions containing p-
and n-type carriers the edge states will circulate in opposite directions (clockwise and counterclockwise) in the two regions because the carrier species is different. However, at the boundary between the two regions (i.e. at the pn junction) the edge states will propagate in the same direction as shown in Figure 2.6. This co-propagation facilitates mixing between the edge states of both regions, which modifies the conductance. In the case of perfect mixing between the edge states the expected conductance plateaux are given by

\[ g = \frac{|\nu_1||\nu_2|}{|\nu_1| + |\nu_2|} \times 2e^2/h. \]  

(2.15)

where \( \nu_1 \) and \( \nu_2 \) are the filling factors in the two regions.

**Quasi-bound states**

External gates can also be used to create one dimensional, quantum dot-like potential profiles in graphene, however the resulting electrical behavior differs from standard quantum dot dynamics. Here I begin with a description of standard quantum dot physics, and then elaborate on the different effects present in graphene.

A quantum dot is a one dimensional confined region in a conducting or semiconducting material where the confinement determines the character of electrical transport through the region. This confinement can be created electrostatically with spatially defined potential barriers, or physically by removing portions of the conducting material. Transport through quantum dots is governed by three energy scales: the energy of thermal fluctuations \( E = k_BT \), the Coulomb charging energy required to add a charge to the dot region \( E = e^2/C \), and the energy required to populate the next available quantum state in a confined region \( E = \Delta_{N+1} \). The thermal fluctuation energy \( E = k_BT \) is relevant only as a limit: it must be smaller than the other energy scales in order to observe the unique effects of the confinement.

When the energy of thermal fluctuations is small enough, transport through the quantum dot is deter-
Figure 2.7: Transport through a quantum dot depends on the energy of the next available state in relation to the chemical potentials in the electrical leads connected to the dot. When the energy of the next available state lies between the potentials of each lead (as in b) then carriers can tunnel from one lead into the quantum dot and then out to the other lead, yielding a high conductance. When the energy of the next available state does not lie between the potentials of the leads (as in a) then conductance is suppressed. The change in energy between quantum dot states depends on both the capacitive charging energy $E = e^2/C$ and the quantum mechanical energy associated with populating another state $E = \Delta_{N+1}$. Adapted from [23].

mined by the other two energy scales as shown in Figure 2.7. The relevant feature is the energy level of the next available quantum dot state in relation to the chemical potentials in the device’s electrical leads. When the energy of the next available quantum dot state lies between the chemical potentials of the leads charges can tunnel into and out of the dot and current can flow. When the energy of the next available state does not lie in between the chemical potentials of the leads conductance is suppressed. By sweeping the Fermi level using an external gate one can sweep the quantum dot energy levels, and thus measure their separation by observing the separation between conductance peaks.

As described above carriers in graphene display Klein tunneling, and thus cannot be completely confined by a potential barrier. To describe transport through an electrostatically defined graphene quantum dot the relevant model is thus a scattering, rather than a tunneling, process. Instead of tunneling into a confined region and then tunneling out, carriers incident on an electrostatic graphene quantum dot scatter off the quantum dot region, potentially exciting an internal state of the dot. These excited internal states are the quasibound states which characterize graphene quantum dots [24, 25, 26, 27, 28]. Note that the appearance of quasibound states is unique to electrostatically defined quantum dots; quantum dots defined by etching graphene display the dynamics described above.

The quasibound states can be understood either as drumhead-type excitations of the confined region [29], or alternatively as circulating carrier trajectories within the potential region which repeatedly collide with the barrier at non-normal incidence angles [30]. Recall that the manifestation of Klein tunneling depends on the angle at which carriers are incident on the potential boundary (see Figure 2.4); for angles far from 0 degrees transmission through the potential barrier is neither perfect (as in the Klein paradox)
Figure 2.8: Quasibound states in graphene quantum dots can be interpreted as excited modes of the confined region (left) or as circulating carrier trajectories (right). In either interpretation the permeability of the potential barrier accounts for the quasibound nature of the states: in the former interpretation the wavefunction does not decay exponentially outside the barrier, and in the latter interpretation the transmission probability is greater than zero for each collision with the boundary. Adapted from [29] and [30].

The transport properties of a graphene system containing an electrostatic quantum dot are governed by the mechanics of scattering between the continuous and discrete states present in the unbiased and quantum dot regions, respectively. Theoretical treatments of the problem [29, 30] proceed using the Mie formalism [31] for a wave scattering from a sphere and offer a description of the size and energy dependencies of transport. Briefly, forward scattering, and thus transport, is suppressed when the size of the quantum dot is small and when one of the quasibound states is excited at resonance, i.e. when the energy of the incident carrier matches the energy of a quasibound state. The suppression effect can be considered in terms of a Fano resonance [32]: the system contains both continuous and discrete states at the same energy; destructive interference between resonantly scattered and incident states causes the suppression.

These quasibound states have been considered analytically for a variety of confining potentials, e.g. for a confining potential of the form

$$V = -\left(\frac{x}{x_0}\right)^2 U/2$$  \hspace{1cm} (2.16)

the characteristic energy of the quasi-bound states is given by [25]

$$E = \frac{\hbar v_F}{\xi} \quad \text{with} \quad \xi = \left[\frac{\hbar v_F x_0^2}{U}\right]^{1/3}.$$  \hspace{1cm} (2.17)
2.2.2 Chemical adsorbates

Graphene can also be doped via chemical adsorbates. Both p- and n-type doping are possible using simple reagents: \( \text{NH}_3 \) and CO have been reported to produce n-type doping, while \( \text{H}_2\text{O} \) and \( \text{NO}_2 \) are known to produce p-type doping. The degree of chemical doping can be controlled by varying the exposure time as shown in Figure 2.9.

Doping by \( \text{H}_2\text{O} \) is particularly relevant experimentally because ambient water molecules will attach to graphene devices left in atmosphere. This produces p-doping in measurements performed in ambient conditions, though the precise mechanism behind the p-doping is a subject of continuing research. Generally the effect is understood to be caused by a combination of capacitive doping from the electric field of the \( \text{H}_2\text{O} \) dipole and charge transfer from the atomic species (H or O) or dangling bond closest to the graphene. When present, polar dopant molecules like \( \text{H}_2\text{O} \) add an additional degree of freedom to a graphene device. Different orientations of polar dopant molecules can contribute different amounts of doping; measurement processes which alter the polarization of the dopant molecule can thus induce additional dynamics in measurements.

In practice graphene is also often inadvertently (and undesirably) doped by the chemicals used in the fabrication process; such dopants usually produce p-type doping in the graphene and reduce the mobility of carriers. Efforts to remove unwanted chemical contaminants can be divided into two categories: annealing-based and solvent-based. The former category encompasses two main techniques, thermal and current annealing in vacuum. Current annealing requires that the graphene be suspended, and must be done cautiously so as not to destroy the sample. However, when successful current annealing produces samples of extraordinarily high quality, as measured by mobility (\( \sim 200,000 \) cm\(^2\) / V s); note that the high mobility is largely due to the suspension of the graphene, however the cleaning is an important step.

Thermal annealing in vacuum is also used to remove residual dopants from chemicals used in fabrication, in particular poly(methyl methacrylate) (PMMA). The technique has several drawbacks however. First, the temperatures required to completely remove PMMA residues are beyond what graphene can withstand. Lower temperatures do remove an appreciable portion of the PMMA residue, however the temperatures required to effectively remove residues (\( T > 300 \) K) also bring the graphene into closer contact with its substrate. For graphene on SiO\(_2\) substrates this closer contact induces significant p-doping and dramatically reduces the mobility of the graphene, effectively leaving the graphene in no better shape than it was to begin with.

Solvent-based cleaning techniques have reported significant success in removing residual dopants as shown in Figure 2.9. This efficacy comes at the cost of increased hazard to the researcher however; such
processes typically involve hazardous, volatile, and/or chlorinated solvents (e.g. HF).

### 2.2.3 Substrate effects in graphene

The substrate used to support graphene strongly affects electrical transport in the graphene. Scattering by surface phonons at the SiO$_2$ interface has been shown to limit the room temperature mobility of graphene [44]. Charge impurities can also create inhomogeneities in graphene’s local carrier density, which are thought to be responsible for the saturation of conductivity at low carrier densities [5]. Substrate features can also cause delamination of the graphene from the substrate; previous work has observed a snap-through transition for multilayer graphene on corrugated substrates [45] as well as the formation of network of wrinkle delaminations on a substrate decorated with silica nanoparticles [46].

Certain experiments, in an attempt to minimize the effect of the substrate have fabricated devices using suspended graphene [41], [47]. In a particularly noteworthy example, the authors of ref [41] observed carrier mobilities of up to 200,000 cm$^2$ V$^{-1}$ s$^{-1}$, an order of magnitude greater than the best results for graphene on silicon substrates, showing that the substrate can have a dramatic impact on graphene’s electrical properties. This particular example highlights the deleterious effect of scattering by SiO$_2$ phonons on graphene’s carrier mobility. Another technique used to isolate graphene from the effects of its substrate is encapsulation with hexagonal boron nitride (h-BN). Hexagonal boron nitride can be exfoliated in a manner similar to graphene; when produced this way few-layer samples have an atomically flat surface, large bandgap, and similar lattice constant to graphene. These properties combine to make it an ideal substrate for graphene: devices fabricated on or encapsulated with h-BN display drastically improved electronic properties compared
2.3 Mechanical effects in graphene

Graphene’s mechanical properties are nearly as exceptional as its electrical properties. It is incredibly strong: experimental results place its breaking strength at $42 \pm 4$ N m$^{-1}$ and its Young’s modulus at $1.0 \pm 0.1$ TPa making it the strongest material ever measured\cite{50}. Furthermore, when graphene is exposed to strain it displays a variety of unique effects. In this section I summarize previous work concerning these mechanical properties and strain-dependent effects.

2.3.1 Mechanical failure in brittle materials

Mechanical failure in brittle materials under global strain is governed by the competing energetics of lattice relaxation and surface creation\cite{51}. Creating or extending a crack in a material requires the creation of two new surfaces, each requiring some amount of surface energy. At the same time, cracks allow for the relaxation of strain in the lattice which releases elastic potential energy. As shown in Figure 2.10 the energies associated with the two effects scale differently with crack length: the surface energy is positive and linear while the elastic potential energy is negative and quadratic. Beyond a critical crack length $x_c$ the energy of the system is minimized by extending the crack indefinitely i.e. by total mechanical failure. The breaking strength of brittle materials therefore depends on the size and density of defects within the material in addition to
the intrinsic properties of the material [51]. For a material with Young’s modulus $E$, surface energy $\gamma$ and interatomic distance $r_0$ the breaking strength (for pristine and non-pristine samples) is given by

$$
\sigma_{\text{pristine}} = \sqrt{\frac{E \gamma}{r_0}}, \quad \sigma_{\text{with defect}} = \sqrt{\frac{E \gamma \rho}{4a r_0}}
$$

(2.18)

where $a$ is half the length of the defect and $\rho$ is the radius of curvature of the defect. Only in the limit of a perfect crystal does the breaking strength of a crystal approach the strength of its atomic bonds.

For brittle materials under global strain only two states obtain: stasis or total mechanical failure. This is the case for suspended graphene samples, where the strain is applied at the boundaries of the system. The situation is more complex when strain is applied to the sample locally rather than globally, as when graphene is supported by a flexible substrate. In this case partial mechanical failure is also possible. This is because when the strain is local a partial mechanical failure can relax the strain locally, reducing the amount of elastic potential energy released by a crack extension, and thus altering the energetic balance of the system so that crack propagation is no longer favorable.

2.3.2 Graphene’s Raman spectrum

As a two-dimensional material graphene’s mechanical properties are uniquely accessible via surface measurements. In particular, Raman spectroscopy is especially useful for characterizing graphene. Raman spectroscopy operates by illuminating a sample with a laser and measuring the spectrum of the scattered light. The inelastic scattering properties of a material depend on its internal degrees of freedom, so by observing the shift in frequency of the scattered light relative to the incident light one can gain information
about the internal states of the material. The strength of the interaction between the incident light and the material depends on the polarizability of the material. This is particularly relevant when considering the vibrational states in a system (e.g. phonons): oscillation modes which strongly vary the polarizability of the material will strongly couple to the incident light, and thus display high intensities in Raman measurements. Conversely, vibrational modes which do not vary the polarizability will not couple to the incident light and will not show up in Raman measurements.

The phonon dispersion and Raman spectrum of graphene are shown in Figure 2.11. Graphene has two atoms per unit cell and therefore has both optical and acoustic modes. Each mode is characterized by its axis of oscillation which can be in- or out-of-plane, and for the in-plane modes can be longitudinal or transverse relative to the C-C bond. Three primary peaks are apparent in the Raman spectrum, one (called the G peak) at approximately 1580 cm\(^{-1}\), another (alternately called the G\(^{\prime}\) or 2D peak) at approximately 2700 cm\(^{-1}\), and a third (called the D peak) at approximately 1350 cm\(^{-1}\).

Graphene’s G peak is due to scattering by iTO and iLO phonons at the Γ point: an incident photon scatters inelastically and creates an electron-hole pair, which then recombines into a phonon with zero momentum. The three optical modes have non-zero energy at zero momentum and are thus candidates for the emitted phonon, however the out-of-plane mode does not induce a change in the polarizability of the graphene and thus does not have an appreciable Raman intensity. The remaining iLO and iTO modes are degenerate at the Γ point, both having a frequency of 1582 cm\(^{-1}\), which corresponds to the frequency of the observed G peak.

The D and G\(^{\prime}\) (or 2D) peaks are due to second order scattering by iTO phonons near the K and K\(^{\prime}\) points. These processes are illustrated schematically in Figure 2.12. For the 2D peak, the scattering process involves two iTO photons: the first scatters an electron from a point near the electron K point to a point
Figure 2.13: Uniaxial strain opens a gap in graphene by merging the two Dirac points. Recall that graphene’s band structure is composed of two cosine type bands; increasing strain shifts the two bands away from each other, gradually shifting the Dirac point of the band structure away from the K point of the Brillouin zone. For large enough strain the bands cross and a gap opens.

near the K’ point, and the second scatters the electron back to the original K point where it recombines with a hole to emit the inelastically scattered photon. Each iTO phonon has a frequency of 1350 cm\(^{-1}\) near the K point, so the scattered photon’s frequency is shifted by approximately 2700 cm\(^{-1}\). The D peak is due to a similar process, except one of the iTO scattering steps is replaced by scattering from a defect. Recall that the two inequivalent K points stem from the two carbon atoms in graphene’s unit cell. A scatterer which acts only on a single atom of the unit cell (i.e. a defect in the lattice) can alter the phase of the carrier wavefunction on one sublattice relative to the other. This allows defects to alter the pseudo-spin of a carrier without changing it’s momentum or energy, thus scattering it from one K point to the other. In this case the incident photon is scattered inelastically by a single iTO phonon and the measured shift is 1350 cm\(^{-1}\).

### 2.3.3 Uniaxial strain

Several research groups have considered, both experimentally and theoretically, the effect of uniaxial strain on graphene. Uniaxial strain is predicted to open a gap in the band structure, either by itself at high (>20%) strains or in conjunction with a correlated scalar potential. In both cases the gap is a consequence of a shift in the position of the Dirac point of the band structure relative to the K point of the Brillouin zone. Recall that graphene’s band structure is given by the intersection of two cosine-like bands. Both strain and local scalar potentials reduce the amplitude of these cosine bands. As the amplitude of each band is reduced the point of intersection between the two shifts away from the K point, until at high strains the bands cross and a gap opens. This is illustrated schematically in Figure 2.13.

Experimental work following the latter approach measured the sheet resistivity of a graphene device patterned atop lithographically defined corrugations on a SiO\(_2\) substrate. In this case the periodic
potential comes from the periodic, substrate-induced doping in the regions not covered by the corrugations. The authors observed an increasing sheet resistivity with decreasing temperature; this behavior is indicative of a gap in the band structure, which the authors calculate to be approximately 200 meV.

2.3.4 Non-uniaxial strain

Theoretical [60, 61] and experimental [62, 63] results suggest that non-uniaxial strains in graphene have an effect similar to an applied magnetic field. From a theoretical perspective these strain-induced pseudomagnetic fields stem from a modification of the nearest and next nearest neighbor hopping amplitudes: as the lattice is strained the distances between lattice sites vary, and with them the relevant hopping amplitudes \( t \) and \( t' \). This effect can be modeled by introducing a gauge field vector potential [60]. Derivations of this correspondence proceed by considering the Hamiltonian which describes electron coupling to long-wavelength phonons (such phonons being essentially large scale deformations of the graphene lattice, i.e. strain). When the differential terms in this Hamiltonian are written in terms of the strain tensor (e.g. \( \partial_x R_x = u_{xx} \)) then it can be shown that the phonon-electron Hamiltonian is equivalent to a Hamiltonian for electrons in the presence of a vector potential \( \mathbf{A} \) under the condition

\[
\mathbf{A} = \frac{\beta}{a} \begin{pmatrix}
  u_{xx} - u_{yy} \\
  -2u_{xy}
\end{pmatrix}
\]  

(2.19)

where \( u_{ij} \) is the strain tensor and \( \beta = -\partial \ln t / \partial \ln a \) where \( t \) is the hopping amplitude and \( a \) is graphene’s lattice constant [60]. Magnetic fields also manifest as vector potentials in the Hamiltonian, hence the claim that non-uniform strains have an effect similar to that of a magnetic field.

A key requirement in generating pseudomagnetic fields is that the strain profile be anisotropic:

\[
\mathbf{B} = \nabla \times \mathbf{A} = \frac{\beta}{a} \left( \frac{\partial(-2u_{xy})}{\partial x} - \frac{\partial(u_{xx} - u_{yy})}{\partial y} \right).
\]  

(2.20)

To date experimental efforts have focused on creating anisotropic strain via nanobubble [62] or nanoridge [63] defects; using these types of samples field magnitudes up to 300 T have been reported. However defect-oriented experimental design schemes yield extremely small areas of graphene under strain, and as such the strain-related physics is only accessible through scanning tunneling microscopy (STM) measurements. Observing transport signatures of these pseudomagnetic fields was a primary motivation for the experiments on topographically patterned substrates described in Section 4.3; such high fields in conjunction with graphene’s high carrier concentration and mobility offer the potential to observe a zero field quantum Hall
effect. While the experiments described in this thesis did not display the desired signatures their results do suggest potential refinements for future work which are described in Section 5.2.
Chapter 3

Experimental Techniques

This thesis describes the results of experimental work, and while the experimental results comprise the bulk
of this work’s novelty a thorough record of the experimental methods employed to produce those results
is crucial for future reproducibility. In this chapter I present a summary of the fabrication, characteriza-
tion, and measurement techniques used in the course of this research.

3.1 Sample Fabrication

Sample fabrication is the primary task for experimental work on graphene devices, and can broadly be divided
into two subtasks: producing graphene and shaping it into useful geometries. In this section I present the
experimental techniques used to produce graphene and shape it into devices appropriate for optical and
electrical transport measurements.

3.1.1 Graphene synthesis and transfer

Mechanical exfoliation

There are two widely used methods used to produce graphene for experimental research: mechanical exfolia-
tion [64] and chemical vapor deposition (CVD) growth [65]. In mechanical exfoliation highly ordered pyrolitic
graphite is repeatedly cleaved, typically by attaching and then peeling off Scotch tape. After a succession
of such cleaving steps small regions of monolayer graphene are left attached to the Scotch tape, which are
then transferred to a silicon wafer having a 300nm thick layer of SiO$_2$. An optical interference effect caused
by the combination of the oxide layer and the graphene allows the graphene regions to be identified with
an optical microscope [66]. This process is illustrated schematically in Figure 3.1. Mechanical exfoliation
produces the highest quality graphene as measured by electron mobility; values up to 60,000 cm$^2$ V$^{-1}$ s$^{-1}$
have been reported [68]. However, the size of the resulting graphene flakes is limited, typically to tens of
square microns, and the transfer process precludes any alignment of graphene with pre-existing substrate
features.
CVD growth

In the CVD growth process a metal foil, usually nickel or copper, is placed in a vacuum furnace and heated while \( \text{H}_2 \) and \( \text{CH}_4 \) are introduced at controlled rates and for controlled times. Properly optimized growth recipes will yield uniform, monolayer graphene on top of the metal foil [65, 68, 69, 70]. For the precise recipes used to grow the graphene used in this research see Appendix A.

Unlike graphene produced by mechanical exfoliation, CVD graphene usually (though not always, see [71]) has multiple domains [72] which accounts for its lower quality, again as measured by electron mobility. Typical values for CVD graphene are in the \( 10^3 \) to \( 10^4 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) range [71]. From a practical perspective, the disadvantage of CVD graphene’s limited mobility is counter-balanced by the ease and volume of production via this method: while exfoliated graphene flakes are limited to tens of square microns, CVD graphene has been grown in 30 inch-wide films [73]. Larger graphene films allow for entire substrates to be covered, which in turn allows for device designs where graphene is deposited atop existing substrate features.

Wet transfer

Graphene grown on metal foils by chemical vapor deposition must be transferred to an insulating substrate before its electrical properties can be measured. This transfer is a critical step: if done poorly it has the potential to drastically alter the properties of the graphene, whether by destroying the mechanical integrity of the graphene or by introducing substantial electrical doping. Transferring graphene onto flexible or patterned substrates introduces additional complexities.
Figure 3.2: ‘Wet transfer’ of CVD graphene. Image adapted from [74]

The simplest transfer procedure is illustrated schematically in Figure 3.2 [65, 68, 69]. Copper foil with CVD graphene grown on top is coated with a thin, sacrificial layer of the polymer poly(methyl methacrylate) (PMMA) and then placed in a bath of 0.1M ammonium persulfate to etch away the metal. Once the metal is removed the PMMA-coated graphene remains floating on the surface of the solution. The ammonium persulfate solution is then flushed and replaced with de-ionized water. Finally the floating graphene / PMMA stack can be scooped onto the desired substrate, at which point the PMMA is removed using acetone.

This process is delicate, and in practice the quality of the transfer depends on several analog factors. First, the ammonium persulfate solution must be thoroughly replaced by de-ionized water; if traces of the original solution remain when the graphene is transferred to the target substrate then redeposited copper residue will be present between the graphene and the target substrate upon drying. Figure 3.3 shows a substrate contaminated by redeposited copper after graphene transfer. Second, the angle of the substrate relative to the surface during the scooping step must be close to ninety degrees. If the graphene is scooped at a shallow angle the graphene will trap a bubble of water beneath itself; as the water evaporates the graphene will wrinkle.

Copper transfer

The standard wet transfer procedure fails in cases where the graphene must be transferred to polymer substrates: the final acetone step which removes the sacrificial PMMA layer also damages the target substrate. In this case the transfer can be accomplished using a two-part process as illustrated in Figure 3.4 and adapted
Figure 3.3: SEM micrograph of a substrate contaminated by redeposited copper as a result of incomplete removal of the ammonium persulfate solution. The round debris are the copper; the regularly spaced pillars are the result of deliberate fabrication.

Figure 3.4: Schematic illustration of the process used to transfer graphene onto polymer substrates. First, using the standard wet transfer process graphene is transferred to an intermediate substrate coated in a thin layer of copper. Next the target substrate is mechanically pressed onto the intermediate substrate. The two substrates are then immersed in a chemical bath which etches the copper layer, leaving the graphene attached to the target, polymer substrate.
Figure 3.5: Graphene ripped in the vicinity of an array of pillars. The graphene was ripped by the surface tension of evaporating solvents. The dark rectangle in the middle of the ripped region is an artifact of surface charging from a previous SEM scan.

from \[75\]. First, using the standard wet transfer process graphene is transferred to an intermediate substrate coated in a thin layer of copper. Next the target substrate is mechanically pressed onto the intermediate substrate. The two substrates are then immersed in a chemical bath which etches the copper layer, leaving the graphene attached to the target, polymer substrate.

This transfer procedure also allows the creation of patterned graphene devices on polymer substrates. Typical lithographic processes do not work with flexible substrates, however when using this copper transfer procedure the graphene can be patterned on the rigid intermediate substrate. The final transfer onto the target substrate then produces patterned graphene on a flexible substrate.

**Critical point drying transfer**

Substrates having topographic features present another complication when transferring graphene. For such substrates the graphene will delaminate from the substrate in the vicinity of the vertical substrate features. When the sample is allowed to dry after the removal of the sacrificial PMMA layer, the surface tension of the evaporating solvent will tear the suspended graphene. Figure 3.5 shows a scanning electron microscope microgram of graphene torn by this mechanism.

The damaging effect of the evaporating solvent can be mitigated by performing the final drying step in a critical point drying apparatus. In this procedure graphene is transferred to the target substrate using the standard wet transfer process. However after the final acetone step to remove the sacrificial PMMA the substrate is transferred to the chamber of a critical point drying machine while still in liquid. The chamber is sealed, liquid CO\textsubscript{2} is introduced, and then the chamber is heated until the environment reaches a super-
critical phase. The chamber is flushed while in the super-critical state, then depressurized, thereby drying
the sample without ever exposing the suspended graphene to the surface tension of evaporating solvents.

3.1.2 Substrate patterning

Lithography

Once transferred to the desired substrate, graphene must be shaped into geometries appropriate for measure-
ments and contacted with metal leads; for both tasks the required patterns are defined using either photo- or
electron-beam lithography. Similarly, for devices where the substrate is modified lithography is used to define
the required profiles. Lithography is a standard experimental technique, and as such a complete description
of the principles behind its operation lies outside the scope of this thesis. However, certain aspects of the
fabrication used in this research required slight modifications to established lithography procedures. These
modifications are described conceptually below, for the exact processes used see Appendix A.

First, the flexible substrates used in this research are not amenable to standard lithography. In order to
produce graphene devices on such substrates the graphene must be patterned prior to being transferred to
the flexible substrate. The copper transfer procedure described above allows for this: after the first transfer
step the graphene can be patterned while on the intermediate, copper coated substrate. Once the graphene
is patterned the transfer process is completed, yielding patterned graphene on a flexible substrate.

Second, devices having suspended graphene (like those produced by the critical point drying method
described above) present an additional challenge: once graphene is freely suspended on the substrate no
further patterning can be done because applying a new layer of resist will destroy the graphene. To circumvent
this issue we pattern the graphene before it becomes free standing by using the same PMMA layer used to
transfer the graphene as a resist layer during an electron beam lithography step.

Deposition

A substantial fraction of the results in this thesis are the result of electrical transport measurements. Per-
forming transport measurements on graphene requires robust electrical contact between graphene and the
measurement apparatus; this contact is created by depositing metal leads atop the graphene using an elec-
tron beam evaporator. Metal deposition using an electron beam evaporator is also a standard experimental
technique so we again omit a detailed description of the technique. For the devices described here we use
gold leads along with a sticking layer made of either titanium or chromium; for the exact deposition recipes
used see Appendix A.
Reactive ion etching

Reactive ion etching (RIE) is the primary subtractive patterning technique used to fabricate our devices. We use RIE for two particular patterning tasks: first, to shape uniform sheets of CVD graphene into device geometries, and second to etch topographic features into SiO$_2$ substrates. Each etching task requires an appropriate chemistry; for graphene etching we use an O$_2$ plasma and for SiO$_2$ etching we use CHF$_3$. For the exact RIE processes used in this work see Appendix A.

3.2 Sample Characterization

The primary challenge of experimental condensed matter research, at least as measured by graduate student effort, lies in fabricating working devices. The fabrication techniques described above require finesse, skill, and a certain degree of luck – (especially when working with temperamental equipment). As such, a substantial fraction of the fabricated devices will fail to work. Characterizing the different failure modes of a given fabrication process – and thereby determining the optimal process parameters – is a crucial part of each research project. In this section several techniques which effectively characterize the quality and physical integrity of graphene and other fabricated device elements are described.

3.2.1 Atomic Force Microscopy

Atomic force microscopy (AFM) measurements offer an excellent way to verify the mechanical integrity of graphene. A complete description of the principles underlying the operation of an AFM lies beyond the scope of this thesis; here we offer a brief description of several of the primary modes of atomic force microscope operation which are used in this research. Atomic force microscopes can be operated in two primary modes: tapping and contact. In contact mode a sharp tip mounted on a cantilever is dragged across a surface, and the topography of the surface is measured by observing the deflection of a laser reflected off of the cantilever. Tapping mode proceeds similarly, however the tip is raised slightly above the surface and oscillated. In this mode both the amplitude and phase (relative to the driving force) of the tip’s oscillation are measured.

Phase measurements in tapping mode (i.e. measurements of the phase between the drive and response of an oscillating AFM tip) are particularly sensitive to the interaction of the AFM tip and the substrate. This sensitivity produces a high contrast in measurements that scan across two different materials, for example graphene and SiO$_2$. This contrast in turn makes it easy to observe rips in graphene and thereby investigate its mechanical integrity. Figure 3.6 illustrates this high contrast.

Conductive AFM tips enable a secondary set of measurement modes which probe electrical properties
of the sample. In piezoresponse force microscopy (PFM) mode, an AFM tip is placed in contact with the substrate and an AC bias is applied to the tip. For ferroelectric substrates the applied voltage will create a deformation in the substrate which can be measured by the deflection of the AFM cantilever. The deformation is proportional to the ferroelectric polarization; in particular opposite polarizations in the substrate will reverse the direction of the deformation, thereby changing the relative phase between the driving AC bias and the observed response by a factor of \(\pi\). By measuring the phase one can therefore measure the polarization of the substrate.

Conductive AFM tips can also be used to ‘write’ polarization domains in ferroelectric substrates. In this mode, a bias above the conducive voltage of the ferroelectric material is applied to the tip during a contact-mode scan. As the tip is scanned across the substrate the local voltage applied by the tip bias flips the substrate polarization and establishes a domain. Examples of PFM measurements and domain writing are shown in Figure 3.7.

Kelvin probe force microscopy is an AFM mode which probes the surface potential of a substrate. In KPFM mode, a conductive AFM tip is placed a constant distance above the substrate and an AC bias is applied to the tip. In this configuration the AFM tip and the substrate form a capacitor. The energy stored in a capacitor is proportional to the potential difference across the capacitor, which in this case is a function of both the applied AC bias and any DC offset between the tip and the substrate. If the AC bias is applied at the resonant frequency of the AFM cantilever the energy takes the form

\[
E = \frac{1}{2} C [V_{DC} + V_{AC} \sin(\omega_0 t)]^2 = \frac{1}{2} C [2V_{DC}V_{AC} \sin(\omega_0 t) - \frac{1}{2} V_{AC}^2 \cos(2\omega_0 t)] \tag{3.1}
\]
In this case the force on the cantilever (and thus the measured response) at the cantilever’s resonant frequency is proportional to the DC offset between the tip and the substrate. By scanning the tip across the substrate at a constant separation and observing the change in oscillation amplitude the potential difference between the tip and the substrate, and thereby the work function can be mapped over the whole substrate.

AFM measurements are well suited to flat sample geometries. For samples with topographic features however the measurements are limited by the sharpness of the AFM tip: AFM measurements are a convolution of the AFM tip shape and the substrate shape, and when the substrate is sharper than the AFM tip the finer details of the measurement will be washed out. This limitation is especially apparent on samples which have very sharp topographic features.

### 3.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is another useful characterization tool, especially for samples which have very sharp topographic features. SEM is a standard experimental technique and does not require any special adaptations for the devices described in this thesis, and so will not be described in detail here.

### 3.2.3 Raman Spectroscopy

**Characterizing graphene quality**

Raman spectroscopy is another characterization technique which is particularly useful for its ability to non-intrusively measure certain electrical properties of graphene. Pristine graphene has a well characterized Raman signature [76], and deviations from this signature can be used to measure the quality of the graphene.

Two features in graphene’s Raman signature are particularly relevant: first, the presence of a Raman peak near 1350 cm$^{-1}$ (referred to as the D peak) indicates that there are defects present in the graphene lattice which will reduce the electrical quality of the graphene. Second, the shapes and relative magnitudes of the
Figure 3.8: Raman spectra of mono- and multilayer graphene. As the number of layers increases the G peak (at 1600 cm$^{-1}$) intensity increases relative to the 2D peak (at 2700 cm$^{-1}$) and the shape of the 2D peak deviates from a Lorentzian. Adapted from [76].

Raman peaks at 1590 cm$^{-1}$ and 2600 cm$^{-1}$ (referred to as the G and 2D peaks, respectively) can be used to determine the number of graphene layers present in the sample: for high quality monolayer graphene the 2D peak should have a greater intensity than the G peak, and both peaks should be well approximated by a Lorentzian distribution. Figure 3.8 shows the change in the shape of the 2D peak with increasing graphene thickness.

Characterizing graphene strain and doping

When measuring strain-dependent effects in graphene quantifying the degree of strain present in the sample is a primary task. Raman spectroscopy is a useful tool for this task because it can non-invasively determine the strain present in graphene, however there are several complicating factors. Specifically, both strain and doping produce shifts in the G and 2D peak locations [77]; a measurement of either peak shift by itself is therefore insufficient to disentangle the competing effects of strain and doping. Below we describe the mechanisms by which strain and doping shift the Raman peaks, and how the two can be disentangled.

Applying strain to graphene modifies the positions of its Raman peaks by modifying the bond lengths in the graphene lattice. Longer bond distances lead to a softer lattice and lower energy phonons. This softening of graphene’s phonons creates a redshift in its Raman peak positions, which has been observed in many experimental studies [78, 79, 80, 81, 82, 83, 84]. These results provide a characterization of the expected Raman shift per unit strain, and can in principle be used to measure the strain in graphene. The situation is complicated however in the case where there is also a varying charge density in the graphene, which in practice is all the time.
Charge doping in graphene also produces shifts in graphene’s Raman spectra \[85, 86, 87, 88, 89\]. In the case of the G peak this is a consequence of renormalization caused by the coupling between zero-momentum iTO and iLO phonons and particle-hole excitations in graphene \[86, 87, 88\]. The number of electron-hole excitation states available in graphene depends on the Fermi level. Changing the charge doping shifts the Fermi level, thereby changing the number of available electron-hole states and thus the strength of the renormalization effect. The shift in the 2D peak is due to a similar renormalization effect, however the size of the shift is only \(\sim 10\%\) as big as it is for the G peak. The smaller shift stems from a smaller renormalization effect: the magnitude of the renormalization effect is inversely proportional to the energy of electron-hole excitations at the phonon wavevector \[80\], and the phonons responsible for the 2D peak have much larger wavevectors (and therefore corresponding electron-hole excitation energies) than those responsible for the G peak.

The two mechanisms (strain and doping) shift the locations of the two peaks by different relative amounts; the ratio

\[ r = \frac{\Delta \omega_{2D}}{\Delta \omega_G} \]

where \(\Delta \omega\) is the shift in the specified Raman peak, differs between the two mechanisms \[77\]. Experimental measurements \[83, 84, 90\] and theoretical \[78, 91\] results place the ratio for strain between 2.25 and 2.8 and the ratio for doping at approximately 0.75 \[77\]. Thus by plotting the Raman G and 2D peak positions against one another and comparing to the expected values for intrinsic, unstrained graphene one can decompose the peak shifts into components due to strain and doping \[77\]. This decomposition is shown in Figure 3.9.

Finally, Raman measurements can be used to measure spatial variations in the electronic quality and physical integrity of a graphene sample. By performing Raman measurements in a raster pattern across a region of interest one can map local variations in peak locations.

### 3.3 Data collection

Once a working device has been fabricated it must be measured. In practice, this entails two distinct tasks. First, the device must be placed in an environment appropriate for the desired measurement: i.e. the device must be cooled, or strained, or placed in vacuum depending on the effect which the measurement aims to observe. Second, the device must be coupled to the measurement instrumentation. In this section I describe the methods used to create the required environments, the equipment used to perform the measurements, and the various device configurations and independent variables used in the transport measurements described in this thesis.
Figure 3.9: Raman G and 2D peak locations for graphene. The black dashed line shows the ratio $r = \frac{\Delta \omega_{2D}}{\Delta \omega_G}$ expected for shifts due to strain, and the purple dashed line shows the ratio expected for shifts due to doping. The two lines intersect at the expected peak positions for undoped, unstrained graphene. By comparing measured Raman G and 2D peak positions to vectors corresponding to the black and purple lines one can determine the degree to which strain and doping, respectively, contribute to the observed shifts in peak positions. The data here show measurements of graphene both before (top right cluster) and after (bottom left cluster) annealing: the annealing step shifts the measurements along the doping axis, but preserves the distribution of strain values. Adapted from [77].
Figure 3.10: A custom sample stretching stage. Clamps at either end of the stage secure the ends of a flexible substrate. The rightmost clamp is mounted on rails and can be translated by turning a threaded rod, thereby stretching the substrate and applying strain to graphene devices fabricated on the substrate.

3.3.1 Sample environments

Uniaxial strain environments

Uniaxial strain can be applied to graphene devices by fabricating devices on a flexible substrate and then stretching the substrate. For the measurements described in this thesis this is accomplished through the use of the custom stretching stage shown in Figure 3.10. Clamps secure either end of a flexible substrate. The rightmost clamp is mounted on rails, and can be translated back and forth by means of a threaded rod. This threaded rod is attached to a stepper motor which precisely controls the angular position of the threaded rod rotation, and thus the lateral displacement of the second clamp. The position of the stepper motor is controlled by an Arduino-based microcontroller. At maximum extension this device is capable of applying up to three percent strain to substrates.

Vacuum environments

Vacuum environments are created by the mechanical evacuation of sealed chambers. For the experiments described in this thesis this is accomplished through the combined use of mechanical and turbomolecular pumps. When combined, these techniques are capable of producing vacuums in the $10^{-6}$ Torr range. For applications where the turbomolecular pumps are employed care must be taken to first produce a sufficiently low vacuum with the mechanical pump to avoid damaging the turbopump.

Cooled environments

Many of the effects described in this research are only visible at low temperatures; to perform the desired measurements the devices must be cooled to temperatures near or below 1 Kelvin. A complete description of
the operation of the cooling mechanisms used to produce low temperatures is beyond the scope of this report; here I give an overview of the cooling techniques employed in the course of this research. For measurements which only require temperatures in the 1 to 2 Kelvin range, evaporative cooling of $^4\text{He}$ is sufficient. In this case liquid $^4\text{He}$ is used to cool the sample environment to 4.2 Kelvin, then a vacuum is applied to the liquid $^4\text{He}$ which can lower temperatures to approximately 1.8 Kelvin. For measurements which require temperatures below 1.8 Kelvin we use evaporative cooling of $^3\text{He}$. This technique proceeds in two steps: first evaporative cooling of $^4\text{He}$ is used to produce temperatures around 2 Kelvin, then a second evaporative cooling step, this time using $^3\text{He}$ is used to reach temperatures around 250 mK.

### 3.3.2 Measurement equipment

When configuring equipment for electronic transport measurements there are two primary considerations: applying as clean a signal as possible to the device, and extracting as clean a signal as possible from the resulting noisy measurement. Different instruments have widely varying noise characteristics which can drastically affect both considerations, thus a careful consideration of the advantages and disadvantages of each piece of equipment is necessary. In this section I describe the relevant characteristics of the primary pieces of measurement instrumentation used in this research. For a more detailed description of each instrument see Appendix C.

**Keithley 2400 SMU** The Keithley 2400 Source-Measure Unit (SMU) is capable of sourcing and measuring voltage and current over a wide operating range. Its wide operating range makes it useful for preliminary explorations as well as for applying large gate voltages; for delicate measurements however other instruments have greater sensitivity.

**Stanford Research SR830** The SR830 is a lockin amplifier which provides excellent sensitivity even in noisy measurements. For measurements which are amenable to an AC bias the SR830 is the preferred measurement instrument. High resistance samples present a slight complication: the instrument can only source voltage so measurements requiring a current bias must pass the sourced voltage through a resistor which is large relative to the resistance of the sample.

**National Instruments DAQ** The National Instruments Data Acquisition Device (DAQ) is capable of precisely sourcing and measuring voltage and current over a limited operating range. The DAQ is ideal for experiments which require precise DC biases or measurements.

**Voltage and Current Preamplifiers** Preamplifiers can also be used to clean experimental signals. The experiments in this thesis used several different preamplifiers which were capable of applying various high- and low-pass filters to both current and voltage signals.
3.3.3 Transport measurements

This thesis is concerned with graphene’s electronic properties, and these properties are most readily observed via electrical transport measurements. There are a variety of factors which affect what information can be gained via transport measurements, from the arrangement of the electrical contacts on the device to the dependent variables which are varied in the course of the measurement. In this section I detail these factors, and describe their effects.

Electronic contact configuration

Graphene devices can be measured using a variety of contact geometries, the simplest of which is the two-point configuration shown in Figure 3.11, top left. In this configuration the device being measured is contacted once at either end, and then these two leads are used both to bias the device and measure the result. This configuration has the advantage of being simple to fabricate and measure, however this simplicity comes at the cost of accuracy. Contacts between an electrical lead and a graphene device will necessarily create a contact resistance; when a measurement is performed using the same leads which are used to bias the graphene the resulting signal is in fact a measurement of the device and the contact resistances in series.

To remove the confounding effect of contact resistances between the electrical leads and the graphene device one can perform measurements using a four-point configuration, illustrated in Figure 3.11, top right. This configuration employs two separate sets of leads, one set to bias the sample and a second set, placed in between the first set, to record the measurement. In this case no current flows through the measurement leads, and thus there is no voltage drop across their contact resistances and the resulting measurement reflects only the properties of the graphene device.

The contact configurations above are appropriate for measuring the longitudinal resistance, however it is also useful to measure the lateral (or Hall) resistance. This requires a third contact configuration which is commonly called a Hall bar and which is illustrated in Figure 3.11, bottom left. In this configuration a bias current is applied through the two leads at the end of the device and the voltage is measured between either the horizontal or the vertical set of leads; the former is equivalent to a four-point measurement of the longitudinal resistance while the latter measures the lateral (Hall) resistance.

A slight digression here on resistance vs resistivity: experimentally quantum Hall measurements measure the lateral and longitudinal voltage drop caused by a known bias current. The ratio of the measured voltage to the bias current gives the resistance \( R = V/I \). However, the quantity of interest is typically the resistivity \( \rho = E/J \) (where \( E \) is the electric field and \( J \) is the current density) because resistivity displays the precise quantization that is the hallmark of the Hall effect. Conveniently, in the lateral case the resistance \( R_{xy} \) is
equal to the resistivity $\rho_{xy}$. For a device of width $W$ we have

$$R_{xy} = \frac{V_y}{I_x} = \frac{WE_y}{WJ_x} = \frac{E_y}{J_x} = -\rho_{xy}$$

(3.2)

For the longitudinal case however we must account for the geometry of the sample: for a device of width $W$ and length $L$ we have

$$R_{xx} = \frac{V_x}{I_x} = \frac{LE_x}{WJ_x} = \alpha \rho_{xx}$$

(3.3)

where $\alpha = L/W$ is the aspect ratio of the device.

Finally, it is sometimes useful to measure the sheet resistance of a device in addition to its longitudinal and Hall resistances. This measurement requires another contact configuration which is illustrated in Figure 3.11 bottom right, and which is commonly called the van der Pauw configuration [92]. The sheet resistance cannot be measured directly in this configuration; it must be calculated using the results of two preliminary measurements. First, current is made to flow along one edge of the sample and the voltage drop is measured across the edge opposite to the current flow. The resulting current and voltage values can be used to calculate a resistance. The same measurement is then repeated using the two edges perpendicular to the original edges. The sheet resistance can then be calculated from the two resistance measurements by numerically solving...
the following equation:

$$e^{-\pi R_{\text{vertical}}/RS} + e^{-\pi R_{\text{horizontal}}/RS} = 1$$

\[ \text{(3.4)} \]

**Types of transport measurements**

The contact configurations described above are capable of measuring the resistance of a graphene device, however a single resistance measurement by itself is much less informative than a sequence of measurements taken as a function of some independent variable. For the graphene devices measured in the course of this research there are three particularly relevant independent variables: the bias voltage, gate voltage, and magnetic field. Here I describe the different types of transport measurements which can be performed by varying each of these variables independently or together, and what information each type of measurement provides.

**Gate sweeps**

Measuring the resistance of a graphene sample as a function of the applied gate voltage provides a basic characterization of the doping present in the graphene. For the devices described in this thesis the bottom surface of the chip on which the devices are fabricated serves as the gate. When a voltage is applied between the gate and the device the two form a capacitor, and the gate voltage serves to shift the Fermi level up or down, depending on the sign of the applied voltage. By sweeping the gate voltage one can therefore sweep the Fermi level through the charge neutrality point (the point where graphene’s conduction and valence bands touch). The point where the Fermi level crosses the charge neutrality point will appear as a maximum in the measured resistance, so by measuring resistance as a function of gate voltage one can determine the polarity and degree of doping in a graphene device. This point is often called the Dirac point. Gate sweeps can also be used to confirm the presence of regions with different doping levels in graphene (e.g. pn junctions): gate sweeps on such devices will show two distinct resistance maxima corresponding to the two offset charge neutrality points in the regions with different doping levels.

**Magnetic field sweeps**

Measurements of graphene’s resistance as a function of an applied magnetic field offer additional information about the graphene’s characteristics. In particular, such measurements can be used to determine the carrier density and mobility. The carrier density can be determined in multiple ways. First, one can measure the longitudinal resistance as a function of an applied, perpendicular field. At low fields the resistance will display Shubnikov-de Haas oscillations. As described in Chapter 2, the maxima of the oscillations are characterized by the equation $B_i = n \cdot h/2 \cdot e \cdot i$ where $i$ denotes the index of the oscillation and $n$ the carrier density. By plotting the inverse of the field maxima against their indices one can therefore extract
Figure 3.12: Resistance measurements of a graphene device as a function of gate voltage and magnetic field. An initial peak in resistance at the Dirac point evolves into Landau levels with increasing field.

the carrier density:

\[
\Delta \left( \frac{1}{B} \right) = \frac{1}{B_{i+1}} - \frac{1}{B_i} = \frac{2 \cdot e}{n \cdot h}.
\] (3.5)

This technique is useful for situations where the device is not in a Hall bar configuration. For devices which are configured as Hall bars the Hall voltage can also be used to determine the carrier density, as well as the carrier mobility.

As detailed in Chapter 2, the Hall resistance is given by \( \rho_{xy} = B/e \cdot n \). The carrier density can therefore be extracted from the measured Hall voltage via

\[
n = \left( e \frac{d\rho_{xy}}{dB} \right)^{-1} = \left( e \frac{dV_{xy}}{I \, dB} \right)^{-1}.
\] (3.6)

Armed with the carrier density and a measurement of the longitudinal resistance \( \rho_{xx} \), we can also compute the carrier mobility via

\[
\mu = \frac{1}{\rho_{xx} \cdot e \cdot n}.
\] (3.7)

Combining magnetic field and gate voltage sweeps into a single measurement offers a more complete picture of the behavior of a graphene device, as shown in Figure 3.12. In the figure we observe an initial resistance peak at the Dirac point, which evolves into several peaks corresponding to the formation of Landau levels as the applied magnetic field is increased. Examining the evolution and symmetry of oscillations in device measurements with increasing gate voltage or increasing magnetic field is a useful way to explore the physical origins of the oscillations. Often a single gate sweep or field sweep measurement can be rendered much more comprehensible by placing it in the context of a two dimensional plot like the one shown in
Coulomb blockade measurements

Measurements of graphene’s resistance as a function of both bias and gate voltage can be used to characterize confinement in the graphene. This is most useful in samples where the geometry of the graphene provides the confinement; recall from Chapter 2 that because electrons in graphene display Klein tunneling they cannot be confined by purely electrostatic means. For devices which provide spatial confinement, e.g. quantum dot-type devices, measurements of the differential conductance ($dI/dV$) will display a Coulomb blockade diamond pattern like the one shown in Figure 3.13. Regular oscillations (like those shown in Figure 3.13) indicate that the device is operating as a single electron transistor and therefore that the relevant energy scale is the charging energy of adding another electron the the quantum dot. For devices with spatially smaller confinement the oscillations will become irregular, indicating that the quantum mechanical energy associated with populating an additional state in a potential well is also relevant. This latter case is a consequence of the dispersion relation in graphene: the spacing between energy levels for massless carriers in a quantum box is much larger than for standard, massive carriers.

Coulomb blockade measurements are also useful for determining the capacitive lever arm of the back gate as shown in Figure 3.13. The ratio of the extent of the diamond along the bias axis divided by the extent along the gate axis gives $\alpha$, the capacitive lever arm. Knowing the lever arm is useful for relating changes in gate voltage to changes in the Fermi level in graphene:

$$\Delta E_F = e \cdot \alpha \cdot \Delta V_g. \quad (3.8)$$
Figure 3.13: Left: Differential conductance measurements as a function of gate and bias voltage in a graphene quantum dot device. The data display clear Coulomb blockade diamonds. Adapted from [93]. Right: The extent of the Coulomb diamond along the two axes can be used to determine the capacitive lever arm of the back gate $\alpha$. Adapted from [23].
Chapter 4

Results and Discussion

4.1 Rip formation in graphene on flexible substrates

In this section I present the results of research which examines the mechanical and electrical properties of graphene devices stretched on flexible elastomer substrates. Using atomic force microscopy, electrical transport measurements, and mechanics simulations, we show that micro-rips form in the graphene during the initial application of tensile strain; however subsequent applications of the same tensile strain elastically open and close the existing rips. Correspondingly, while the initial tensile strain degrades the devices' transport properties, subsequent strain-relaxation cycles affect transport only moderately, and in a largely reversible fashion, yielding robust electrical transport even after partial mechanical failure. Graphene's combination of superlative electronic properties, extreme flexibility, and robust functionality after partial mechanical failure is unique among conducting thin films and lends itself to a variety of promising future device applications; the new understanding provided here of when and how graphene rips can directly impact the design of novel graphene-based devices which are required to function under strain.

4.1.1 Introduction

Recent advances in graphene production \cite{54, 75, 94} – namely the ability to produce large area monolayer films by chemical vapor deposition – have enabled the fabrication of a variety of flexible, graphene-based electronic components, including transparent interconnects \cite{95}, high-performance capacitors \cite{96}, and transistors \cite{97}. The prospect of flexible and transparent graphene-based electronic devices suggested by these results raises an important question: are graphene's electrical properties and mechanical integrity robust under the strains graphene is likely to experience in such devices?

Pristine graphene has an exceptionally high breaking strength \cite{30}. This is due to the strong covalent bonding between the sp2 orbitals of its adjacent carbon atoms and the perfect crystallinity of pristine graphene samples. Despite its exceptional intrinsic mechanical strength graphene is still susceptible to mechanical failure. Several research groups have explored this topic, both experimentally \cite{98, 99, 100} and
theoretically \textsuperscript{101, 102, 103}. Several conclusions emerge from their work. First, graphene tears preferentially along its crystallographic axes, either along a zigzag or armchair edge (the two edge types are shown in Figure \textsuperscript{2.10}) depending on the angle between the applied strain and the lattice orientation \textsuperscript{104}. This experimental observation is justified theoretically by comparing the surface energy of zigzag and armchair edges to the potential energy stored in the lattice under a tensile load. As described in Section \textsuperscript{2.3.1} the dynamics of tear propagation depend on the energetics of surface creation and lattice relaxation. In graphene the degree of elastic potential energy relaxation depends on the angle between the applied stress and the crystal lattice, so different stress orientations produce rips along either zigzag or armchair edges.

Second, in polycrystalline samples tears do not propagate along grain boundaries in the crystal lattice, and such boundaries do not dramatically affect the mechanical strength of graphene. The latter point was initially the subject of debate, with several experimental results indicating that polycrystalline graphene samples were mechanically weaker than monocrystalline graphene samples \textsuperscript{98, 99}. However subsequent work \textsuperscript{100, 105} revealed that certain processing steps (namely exposure to ferric chloride and thermal baking in air) were responsible for most of the degradation in the mechanical strength.

In experimental settings graphene is rarely pristine and may therefore be susceptible to ripping at lower strains than its intrinsic strength would suggest. Previous work suggests that the presence of defects \textsuperscript{98, 100, 106, 107} adversely affects the breaking strength of suspended graphene. For practical applications however graphene is likely to be supported by a substrate; it is still relatively unknown under what strain conditions substrate-supported graphene rips, and how the electrical properties are then altered.

In this section I present the results of a research project in which we combine atomic force microscopy (AFM), coarse-grained mechanical simulations, and electrical transport measurements to study the effects of lateral strain on rips in graphene supported by a flexible substrate. We find that graphene adhered to a flexible substrate and then stretched laterally can develop small rips with only 1\% applied strain. However, even with ripping, the electrical properties remain relatively robust: introducing small rips slightly increases the resistance, but subsequent strain-relaxation cycles over the same strain range change transport only modestly, and in a largely reversible fashion. Such resilience is atypical for conducting thin films, which typically demonstrate rapid and irreversible device failure after the onset of rip formation \textsuperscript{108, 109}.

This new understanding of when and how graphene rips, and how its electrical properties are thereby altered is immediately applicable to the implementation and production of devices which include the graphene-based components mentioned above. Some applications, for instance frequency-tuned RC circuits (where the time constant of the device depends strongly on the resistance of the graphene components) using graphene capacitors and interconnects, would require careful consideration of what strains the device can withstand while keeping strain-induced variations in the electronic properties of graphene within the required spec-
4.1.2 Device configuration

Devices consisted of patterned graphene placed on flexible polydimethylsiloxane (PDMS) substrates. The devices were fabricated using a modified transfer printing process, similar to that described in Ref [54]. Single-layer graphene was grown using established chemical vapor deposition (CVD) techniques [111], and then transferred to a copper-coated silicon wafer where it was patterned using photolithography and reactive
ion etching. Next, a piece of PDMS was mechanically pressed onto the silicon wafer, and the copper was then etched to leave patterned graphene on the PDMS substrate. Raman spectroscopy was used to confirm the presence of graphene on the PDMS as shown in Figure 4.1; the shape of the Raman 2D peak, as well as subsequent AFM measurements verified the single-layer character of the graphene. Finally, shadow-mask evaporation was used to deposit Ti/Au contact pads. The device geometry is illustrated in Figure 4.1: a narrow graphene bridge connects two large graphene pads, each of which is covered with a Ti/Au contact pad. We studied 13 different devices having bridge aspect ratios ranging from 1.5:1 to 12:1 (length:width) and widths of 100, 50, and 25 µm. The data in this manuscript focuses on a device with a bridge width of 25 µm and an aspect ratio of 2:1. The data for all samples yielded similar qualitative results. Quantitative differences in transport data between different devices were uncorrelated with the bridge dimensions, and instead seemed to be dominated by pre-existing rips in the graphene, which are often introduced during the graphene transfer process.

AFM and transport measurements were performed while the PDMS substrate was mounted in a mechanical stretching stage, as shown in Figure 4.1. The substrate was clamped at either end, and then strained by turning the threaded rod, which laterally moves the sliding clamp along its guide rails. A mechanical stepper motor was used to control the stretching stage position to ensure reproducibility. Variable device positioning on the substrate as well as slight variations in substrate thickness preclude exact conversion between strain applied to the substrate and to the device, therefore ‘turns of the stretching stage control rod’ were used as the controlled variable. Each turn strains the substrate by approximately one percent, and we estimate that the strain applied to the graphene differs from that applied to the PDMS substrate by no more than ten percent. However, our conclusions are unaffected by this uncertainty, as variations in the magnitude of applied strain between devices only shift the strain axis of the data while preserving the observed trends. Optical observations indicated that the Ti/Au pad adhesion to the substrate was robust and did not slip during measurements. Transport measurements were performed by placing micro-manipulator probes in contact with the gold contact pads at each strain value, and AFM measurements were performed with an Asylum Research MFP-3D.

4.1.3 Rip formation under strain

Experimental results

Figures 4.2a-f show AFM phase images of graphene in the bridge region of a device at 0, 5, 0, 5, 10, and 0 percent strain applied along the horizontal axis of the images. Both rips and delaminations caused by wrinkles appear as a function of strain, and can be distinguished via AFM height data: Figures 4.2g and
Figure 4.2: (a-f) AFM phase measurements of graphene on a polymer substrate at approximately 0, 5, 0, 5, 10, and 0 percent strain (applied along the horizontal axis), as labeled. Rips are evident as light-gray, elongated vertical features. An example of a rip that opens and closes with applied strain is indicated by the dashed line. Dark spots present in each image are debris on the substrate surface; white halos surrounding some of the debris are indicative of graphene slightly delaminating from the substrate. Elongated horizontal features are strain-dependent wrinkles. (g) AFM phase and (h) height data. Variations in the height data distinguish between wrinkles and rips in the graphene, which have similar signatures in the phase data. The scanned area in each image is 25 $\mu$m$^2$. 
show that wrinkles have corresponding undulations in the height data (peaks and dips) while rips are indicated by a uniform depression (consistent with the substrate exposed between graphene regions). In Fig. 2, the vertical features are rips and the majority of the horizontal features are wrinkles.

The opening and closing of rips is clear in the Figure: the unstrained device (Fig. 4.2a) exhibits some small rips and defects. When the substrate is mechanically stretched (Fig. 4.2b) the existing rips widen and new rips form; when the applied strain is relaxed (Fig. 4.2c), pre-existing defects return to nearly their original condition and newly formed rips close. Subsequent strain-relaxation cycles over the same strain range re-open existing rips (Fig. 4.2d), but proceeding to a higher strain range forms new rips and widens pre-existing ones (Fig. 4.2e), which then close less completely when the strain is relaxed (Fig. 4.2f). The strain values at which we observe micro-rip formation are substantially lower than the reported fracture strength of graphene [50], however as described above the tensile strength of graphene is strongly susceptible to defects such as holes and tears [100].

We note that the reduced strength of the graphene devices here is not a result of the use of chemical vapor deposition-grown graphene. Although graphene produced by CVD is known to be polydomain, it has been shown that rips in graphene do not preferentially follow grain boundaries [100]. This is because, as described above, the dynamics of rip formation in graphene are governed by the competing effects of surface energy and lattice strain relaxation. Depending on the orientation of the applied strain, the most energetically favorable rip direction always lies along either the zigzag or armchair direction, even in the presence of grain boundaries [100]. Previous experimental results which indicated that grain boundaries adversely affect the strength of graphene [98, 99] were compromised by certain details of the fabrication procedures used to transfer the CVD graphene. In the case of this work we are limited by the fact that the fabrication procedures used to generate patterned graphene devices on polymer substrates routinely introduce rips and other defects in graphene, which accounts for the mechanical failure observed at low strain values.

**Simulation results**

To shed light on the underlying mechanism of the rip formation and evolution, our collaborators simulated rip formation and the subsequent elastic opening and closing of rips in graphene, via a coarse-grained (CG) modeling scheme [113]. The following description of simulation results describes their work. Given the prohibitive simulation expense to model rips of real size in experiments (microns in length), they simulated a scaled-down model of a graphene monolayer with a size of 24 nm by 200 nm (Fig. 4.3). Three pre-cracks of various sizes were introduced in the model (Fig. 4.3a) to mimic the pre-existing defects in the as-made sample. Each CG bead in the graphene interacts with a virtual substrate via a Lennard-Jones potential.
Figure 4.3: Coarse-grained simulations show the elastic opening and closing of rips during initial and subsequent tensile loading cycles, in good agreement with AFM measurements in Figure 2. The graphene region was simulated at 0, 5, 0, 5, 10, and 0 percent strain applied along the horizontal axis, as labeled. Values given in nm refer to the rip lengths. The vertical contraction of the graphene region at higher strain values is due to the Poisson effect.

\[ V_{gs}(r) = 4\varepsilon_{gs}\left(\frac{\sigma_{12}^{gs}}{\pi r^2} - \frac{\sigma_{6}^{gs}}{r}\right), \] where \( \varepsilon_{gs} = 0.01844 \text{ eV} \) and \( \sigma_{gs} = 0.29 \text{ nm} \), which gives rise to an adhesion energy around 0.044 eV/nm². In addition, the CG beads on the four outer edges of the simulation model were not allowed to slide relative to the substrate so that the tensile loading of the graphene can be applied by stretching the substrate along the horizontal direction, similar to the experimental setup.

As the applied tensile strain first increases to 5%, the stress concentration near the tips of the short middle crack (\( \sim 15.7 \) nm in length) becomes sufficiently high to cause the propagation of the short crack in both directions. As the crack extends the local lattice strain relaxes and elastic potential energy is released; this process continues until the energy released by the relaxation of the lattice strain is smaller than the surface energy required to extend the crack. As a result, the middle crack stops advancing at a length of \( \sim 40.1 \) nm (Fig. 4.3b). Upon unloading of the tensile strain the elongated middle crack closes, nearly fully recovering the original shape of the graphene (Fig. 4.3c); however, the atomic bond breaking in graphene during crack propagation is not reversible. Consequently, the graphene cannot fully recover its original mechanical integrity.

Further tensile loading up to 5% causes the cracks to reopen but further extension of the cracks is shown to be negligible (Fig. 4.3d), largely due to a lack of sufficient driving force for crack propagation. The crack previously extended to the point where the energy required to extend the crack was less than the energy
released by relaxing the lattice; re-establishing the same strain returns the graphene to the same energetic balance. The application of a tensile loading of 10% provides sufficient driving force to cause all three cracks to extend significantly. The crack propagation eventually saturates due to the same energetic balance argument as before (Fig. 4.3e). Upon unloading to zero strain, all newly formed cracks close, resulting in a graphene morphology nearly identical to its original shape (Fig. 4.3f), similar to the experimental observation (Fig. 4.2e to Fig. 4.2f).

Simulations also show the formation of delaminations and horizontal wrinkles in graphene upon tensile loading and the disappearance of such features upon unloading, which agrees with the experimental observations (Fig. 4.2). We attribute the formation of these delamination and wrinkle features to the combined effect of a mismatch in Poisson’s ratios between graphene and the PDMS substrate and the relatively weak graphene/PDMS interfacial bonding. Poisson’s ratio $\nu$ describes the extent to which, for a given material, a longitudinal strain creates a lateral compression: $\nu = -\Delta L/\Delta W$. In our devices the graphene is clamped to the PDMS at the ends by the evaporated contact pads so we expect both the PDMS and graphene to experience the same longitudinal strain $\Delta L$. However, the different Poisson ratios of the two materials cause the identical $\Delta L$ to produce non-identical changes in lateral strain. This mismatch in lateral compression, combined with the relatively weak adhesion between PDMS and graphene leads to the horizontal wrinkles.

The close agreement between the experimental observations and mechanics simulations yields two conclusions: first, pre-existing defects play a decisive role in the formation of rips in graphene. The concentration of stress near the edge of rips causes graphene to mechanically fail at lower strain values than its high intrinsic breaking strength would suggest, therefore when fabricating flexible graphene-based devices optimizing the mechanical integrity of the graphene is important not only to maximize the initial quality of the device but also its subsequent durability. Second, the generic nature of the simulations suggests that the first conclusion is generally applicable to thin membrane devices; while other thin films may not have the flexibility, transparency, and electronic properties of graphene the simulations suggest that their failure modes when supported by flexible substrates are similar.

### 4.1.4 Resistance changes under uniaxial strain

The behavior of the rips determines the electrical transport as a function of strain, as evident in Figure 4.4. Figure 4.4a demonstrates three important features of the data: first, during the initial application of strain (A to B in the Figure) the resistance increases (for this sample, by approximately 43 percent). Typical values for this initial increase in other devices ranged from 20 to 40 percent of the starting resistance. Second, the resistance of the device decreases as the applied strain is relaxed (from B to C) by 7 percent for this device,
Figure 4.4:  (a) Electrical resistance of a graphene device vs. applied tensile strain. The initial application of strain significantly increases the resistance while subsequent strain-relaxation cycles over the same strain range yield smaller, mostly reversible changes in the resistance. (b) Three consecutive strain-relaxation cycles (Cycles 3,4,5), showing largely reversible transport characteristics. Three arb. units correspond roughly to three percent applied strain.

and typically by between 6 and 14 percent. Finally, in subsequent strain-relaxation cycles over the same strain range the resistance changes only moderately, and in a largely reversible fashion.

The transport behavior can be explained by the opening and closing of rips: in the unstrained device, small rips largely determine the initial resistivity. The device’s resistance increases when the substrate is mechanically stretched, due to the widening of existing rips and formation of new ones; subsequent strain-relaxation cycles over the same strain range, which re-open and close existing rips, generate largely reversible changes in resistance. This reversibility is demonstrated in Figure 4.4b: data from the same device recorded during the third, fourth, and fifth strain-relaxation cycles are shown in green, blue, and red respectively. In each case the resistance changes by $\sim 14\%$ for $\sim 3\%$ applied strain, and returns to within 8% of its original value. Proceeding to a higher strain range forms new rips, consistent with a jump in resistance when the strain range is increased. This behavior – an increase in resistance with the initial application of tensile strain, followed by moderate and reversible changes in the resistance during subsequent strain-relaxation cycles over the same strain region – persists up to approximately 15% applied strain, at which point the devices become permanently non-conducting.

Previous experimental work has demonstrated reversible transport changes in strained graphene, either by depositing graphene on pre-strained substrates so as to create controlled crumpling [56] and buckling [115], by patterning complex interconnect geometries [75, 95], or by measuring transport across macroscopic graphene films [54, 94]. In comparison, this work demonstrates the continuing robustness of device functionality after partial mechanical failure. Such resilience is distinctly atypical for conducting thin films: similar studies
performed on tin-doped indium oxide (ITO) \cite{108} and zinc oxide \cite{109} reported rapid and irreversible device failure after the onset of rip formation. One potential explanation for graphene’s exceptional resilience is its morphological simplicity: as a two-dimensional membrane re-establishing electrical contact between two sides of a rip is as simple as overlaying two sheets of paper, while for typical three-dimensional thin films the process is more similar to fitting two halves of a snapped pencil back together.

4.1.5 Summary

In summary, we have observed the formation and subsequent evolution of micro-rips in graphene using atomic force microscopy. While an initial application of tensile strain introduces new mechanical defects, successive strain-relaxation cycles over the same strain range elastically open and close the existing rips. This behavior is a consequence of graphene’s two-dimensional character and the local nature of the applied strain. Mechanics simulations further reveal the underlying deformation and failure mechanisms of the graphene sample under initial and subsequent cyclic tensile loadings, which agree well with the AFM measurements. This mechanical effect has a corresponding electrical effect: the graphene’s transport properties are degraded by the initial application of strain, but show small, mostly reversible changes during ensuing strain-relaxation cycles.

Graphene’s combination of superlative electronic properties, extreme flexibility, and robust functionality after partial mechanical failure is unique among conducting thin films and lends itself to a variety of promising future device applications. For applications with stringent component requirements such as RC frequency filters or devices used for precise metrology the onset of rip formation and the subsequent variation in electrical properties described here are crucial design considerations. Similarly, the interplay between strain-dependent resistance increases and power consumption requirements may impose design limits on the use of graphene in next-generation flexible displays and touchscreens. If graphene is to be used in applied devices outside the laboratory a thorough understanding of when and how it will fail is essential. In this manuscript we present a detailed description of precisely this situation, with exciting implications for robust, graphene-based electronic devices.
4.2 Doping in graphene on ferroelectric substrates

In this section I report the results of a project where my collaborators and I performed electrical transport measurements on graphene p-n junctions formed via simple modifications to a PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) substrate, combined with a self-assembled layer of ambient environmental dopants. We show that the substrate configuration controls the local doping region, and that the p-n junction behavior can be controlled with a single gate. Finally, we show that the ferroelectric substrate induces a hysteresis in the environmental doping which can be utilized to activate and deactivate the doping, yielding an 'on-demand' p-n junction in graphene controlled by a single, universal backgate.

4.2.1 Introduction

As described in Section 2.2.1, p-n junctions in graphene have great potential for both fundamental research and commercial applications, and have been utilized to study the quantum Hall effect [22, 116, 117] and Klein tunneling [118, 119] as well as to fabricate flexible transistors [120]. Previous work on p-n junctions in graphene employed multiple electrostatic gates [19, 22, 116, 117, 118, 119, 121, 122, 123], charge transfer from the controlled deposition of chemical adsorbates [124, 125, 126, 127, 128, 129, 130], high current-induced charging of trap states in the substrate [131], or periodically poled ferroelectric substrates [132].

In this section we report the fabrication of p-n junctions in graphene deposited on a uniformly poled ferroelectric substrate. As described in Section 2.2.3 ferroelectric substrates produce doping in graphene devices, with additional dynamics in the presence of polar adsorbates. In this work we use the ferroelectric material lead zirconium titanate (PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\)) and simple substrate modifications – the evaporation of thin SiO\(_2\) films in some regions – to create local doping regions. We find that the PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) substrate modulates the doping effect of adsorbed dopants: devices are exposed to ambient conditions after fabrication whereupon experimental observations confirm both the presence of adsorbed dopants (likely primarily H\(_2\)O) and their enhanced doping effect on the PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) relative to the SiO\(_2\). Furthermore, we demonstrate that the PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) substrate induces a hysteresis in the environmental doping which can be used to activate and deactivate the doping via the application of large gate voltages. We employ this effect to create p-n junctions which can be reversibly transitioned between p-n junction and uniformly conducting configurations.

4.2.2 Doping via ferroelectric substrates

Ferroelectric substrates such as PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) (PZT) have been shown to vary carrier type and density in graphene with varying substrate polarizations [133], as seen in Figure 4.5. The electric field from the...
polarized ferroelectric substrate creates a local potential which dopes the graphene in a manner analogous to the doping created by the electric field of a back gate. The direction of the field produced by the substrate depends on the polarization of the ferroelectric, so different substrate polarizations can create different doping conditions. This effect is bidirectional: the application of a large bias to the graphene can also flip the polarization of underlying ferroelectric substrates. The strength of the electric field required to reverse the polarization of a ferroelectric material is called the coercive field. If the voltage applied to graphene on top of a ferroelectric produces an electric field greater than the coercive field it will reverse the polarization of the substrate.

Ferroelectric substrates display additional doping dynamics in the presence of polar adsorbates. As described above, the doping effect of polar adsorbates depends on their orientation. For ferroelectric substrates the polarization of the substrate can affect which orientation of adsorbates is energetically favorable, as shown in Figure 4.6. Notably, in certain cases the combined effect of substrate polarization and substrate geometry can create conditions where the polarization of adsorbed dopants is random, which effectively mitigates the doping effect of the adsorbates.

4.2.3 Device configuration

Devices consist of graphene micro-ribbons deposited on substrates which are partially covered by a thin layer of evaporated SiO$_2$, and contacted in a four-point geometry, as illustrated in Figures 4.7a-c. An SEM micrograph of a typical device is shown in the inset of Figure 4.7d. The devices are fabricated using standard lithography and deposition techniques on thin-film ferroelectric substrates. For the ferroelectric substrates, 120 nm thick (001)-oriented lead zirconium titanate (PbZr$_{0.2}$Ti$_{0.8}$O$_3$) films are prepared by pulsed-laser
Figure 4.6: It is energetically favorable for the polarization of adsorbed, polar dopant molecules to align with that of the substrate, however the molecular geometries of the substrate and dopant add additional constraints. Specifically, the separation between donor species in the substrate must match the separation between acceptor species (or dangling bonds) in the adsorbate, and vice versa in order for the adsorbate to have a stable orientation. In the example shown here H$_2$O has a stable orientation when down-polarized because the separation between the donor H atoms in the H$_2$O matches the separation between the acceptor O atoms in the substrate. In contrast, the up-polarization state does not have a stable orientation because the distance between the dangling bonds in H$_2$O does not match the separation between acceptor Ti atoms in the substrate. In contrast, ammonia is stable in either up- or down-polarized orientation because it has only a single dangling bond and therefore is not geometrically constrained by the spacing of the substrate Ti atoms. Adapted from [134]
deposition (PLD) on a strontium titanate (SrTiO$_3$) substrate coated with 20 nm of strontium ruthenate (SrRuO$_3$), following established procedures [135, 136]. For each substrate, an 80 nm-thick layer of SiO$_2$ is evaporated in small rectangular regions, with region widths ranging from 0.5 $\mu$m to 3 $\mu$m, as illustrated in Figs. 4.7a-c. CVD graphene is then transferred using standard wet transfer techniques [111], and patterned into ribbons spanning the deposited SiO$_2$ using photolithography and reactive ion etching. The graphene channel is 6 $\mu$m by 4 $\mu$m measured from the inner contacts. Control devices which span regions with no evaporated SiO$_2$ are also fabricated. Finally, Cr/Au (3 nm/20 nm) leads are deposited in a four-point measurement configuration. Raman spectroscopy is used to confirm the monolayer character and high quality of the graphene after fabrication; a representative spectra is shown in Figure 4.7d.

Transport measurements in air are performed using two Keithley 2400 SourceMeters. Measurements in vacuum are performed using an Agilent 4156C Semiconductor Parameter Analyzer. In both cases source-drain current is measured with a constant source-drain bias of 5 mV while the voltage applied to the backgate is swept. Gate leakage distorts transport results for gate voltages more positive than 1.5 V or more negative than -1 V, so gate voltages are limited to this range. Gate voltage sweep rates range from 10 mV/s to 100 mV/s; the data presented here are from sweeps at 100 mV/s. Slower sweep rates yield qualitatively similar results.
4.2.4 Variable local doping via substrate modifications

Figure 4.8a shows room temperature $I_{sd}$ vs $V_{\text{gate}}$ curves for devices having different widths of evaporated SiO$_2$ on a PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate. For the data shown here, the fraction of the graphene channel screened by evaporated SiO$_2$ ranges from 0% to 50% (corresponding to SiO$_2$ widths of 0 to 3 microns). Two features of the data are immediately apparent: first, for devices which span an evaporated SiO$_2$ region, the characteristic conductance minimum typically observed in graphene at the Dirac point is split into two distinct minima, one at the original Dirac point location and a second shifted to the right. This is apparent in the top and bottom curves of the Figure: the bottom curve, corresponding to a device with 0% screening, displays a single minimum, while the top curve, corresponding to a device with 50% screening, displays two pronounced minima. Second, the width of the evaporated SiO$_2$ region determines which of the two minima has a smaller absolute value. As the screening fraction is increased, ‘weight’ is transferred from the minimum at the original Dirac point location to the secondary minimum, and the depths of the two minima vary accordingly.

We attribute both of these effects to the presence of two different doping regions in the graphene, defined by the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate and the evaporated SiO$_2$.

The data can be understood by considering that as the gate voltage is swept from negative to positive, the Fermi level passes through the charge-neutrality point (CNP) of each graphene region separately. Taking the conductance to be linear with carrier density $\sigma \propto k_F \langle \tau \rangle \propto n$ and the carrier density to be linear with the thermally smeared energy difference between the Fermi level and the CNP, we model the conductance in the vicinity of the CNP as: $\rho^{-1} \propto n \propto 1 - e^{-\left(V_{\text{gate}} - \mu - \delta^2/2e^2 + \epsilon\right)}$ where the constant $\mu$ accounts for the extrinsic doping introduced by the fabrication process, $\delta \in \{0, 1\}$ describes the substrate-dependent doping, and $\epsilon$ accounts for the non-vanishing carrier density at the CNP. Assuming diffusive transport in the graphene, the relative weight of each separately doped region, and therefore the relative magnitude of the measured conductance minima, is determined by the fraction of the graphene channel which is screened:

$$I_{sd} \propto [\rho_{\text{scr.}} \times (\text{pct.}\text{scr.}) + \rho_{\text{non-scr.}} \times (\text{pct.}\text{non-scr.})]^{-1}$$  \hspace{1cm} (4.1)

This is simulated in Figure 4.8b which shows $I_{sd}$ vs $V_{\text{gate}}$ curves for screening fractions ranging from 0% to 75% and is in excellent agreement with our experimental data. We note that the simulations agree with our data for $\mu > 0$ and $\delta \geq 0$, which is consistent with the extrinsic p-doping typically observed in graphene devices fabricated on PbZr$_{0.2}$Ti$_{0.8}$O$_3$.

The substrate-selectivity of the doping in our devices suggests that the ambient dopants are polar H$_2$O molecules. Polar surface adsorbates have been shown to dramatically affect the electronic properties of complex oxide systems [137] as well as graphene [125, 134, 138]. The H$_2$O doping is substrate-selective because of
Figure 4.8: (a) $I_{sd}$ vs $V_{gate}$ curves (manually offset for clarity) for devices having different widths of evaporated SiO$_2$ on a PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate. The devices having evaporated SiO$_2$ show split Dirac points, and the relative dominance of the left and right Dirac points can be tuned by varying the evaporated SiO$_2$ width. (b) Simulations of transport across a graphene device having two different locally doped regions, as a function of applied gate voltage. The simulations show both Dirac point splitting and variations in left vs. right Dirac point dominance as a function of screening region width, consistent with the experimental data.
the unique ferroelectric nature of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate. Previous work [139, 140] has established the importance of the orbital structure of the adsorbate in determining the most energetically favorable orientation. For standard graphene devices on SiO$_2$ substrates, the structure of H$_2$O favors a uniform polarization throughout the range of applicable gate voltages. For graphene on ferroelectric substrates however, previous work [134] indicates that electrostatic effects of the remnant polarization and substrate lattice geometry can modulate the stability of the H$_2$O polarization as described in Section 2.2.3. Repeating the explanation here for convenience, it is energetically favorable for the polarization of the H$_2$O to match that of the substrate. However in the case where the physical spacing between donor atoms in the substrate is different than the spacing between acceptor atoms in the H$_2$O (or vice versa) the resulting polarization of the H$_2$O is unstable.

In the devices described here, it is likely that the interaction between the remnant polarization of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate and the H$_2$O molecules sufficiently alters the energetics of different H$_2$O orientations as to destroy the stability of the H$_2$O polarization, and thus create less-polarized regions. This hypothesis is in agreement with data collected from similar devices fabricated on non-ferroelectric substrates, shown in Figure 4.9. Such devices show a well-understood hysteresis associated with charge trapping in the substrate [36] but display none of the characteristic Dirac point splitting associated with different doping regions. In these control devices the entire substrate is SiO$_2$; the absence of p-n junction-type transport signatures supports the conclusion that the variable doping behavior observed above is due to the effect of the ferroelectric substrate.
4.2.5 Hysteresis in local doping

The gate-voltage dependence of the H$_2$O polarization configurations on PbZr$_{0.2}$Ti$_{0.8}$O$_3$ vs SiO$_2$ leads to hysteresis in the devices. This can be seen in Figure 4.10a, which shows $I_{sd}$ vs $V_{gate}$ curves for forward and reverse gate sweeps performed on the same devices as measured in Fig. 4.8a. A pronounced hysteresis between forward and reverse gate sweeps is apparent. As in Fig. 4.8a, devices spanning a region of evaporated SiO$_2$ display two distinct minima during forward sweeps, while a control device having no SiO$_2$ displays a single minimum. However, all devices display a single minimum during reverse gate sweeps. We note that the gate voltages applied here remain below the coercive voltage of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film (the voltage required to reverse the polarization of the ferroelectric substrate), therefore ferroelectric switching is not a possible cause of the observed hysteresis. Ferroelectric switching has been shown to produce similar behavior [141], however in this work gate voltages above the coercive voltage of the film are experimentally inaccessible due to large gate leakage in our devices.

In order to understand how the hysteresis is related to the different H$_2$O polarization configurations on the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ as compared to the evaporated SiO$_2$, it is instructive to consider the gate voltages at which the various minima appear. For example, for the 17% screened curve in Fig. 4.10a, the red arrows point out two minima on the forward sweep (at 0.6 V and 1.1 V) and one minimum on the reverse sweep (at 0.9 V). These can be compared to the position of the Dirac point in vacuum at 0.6 V (see Fig. 4.11). The minimum on the forward sweep at 0.6 V occurs at the same gate voltage as the vacuum Dirac point, implying that it corresponds to a region of the graphene without a net polarization in the adsorbed H$_2$O. The remaining minima occur at voltages larger than the Dirac point (0.9 V and 1.1 V) and thus correspond to regions of the graphene on which the adsorbed H$_2$O is polarized and produces p-doping. Polarized H$_2$O typically produces p-doping in graphene, though the precise mechanism is the subject of continuing research [35, 36, 37, 38, 139]. We identify the forward-sweep minimum at 0.6 V as corresponding to graphene on the non-screened PbZr$_{0.2}$Ti$_{0.8}$O$_3$ region. This is supported by the fact that all devices demonstrate a minimum at 0.6 V, independent of different SiO$_2$ screening fractions. In contrast, the minimum indicated by the rightmost arrow (e.g. at 1.1 V for the 17% screened device) corresponds to graphene on the evaporated SiO$_2$ region, as evidenced by its evolution with increasing SiO$_2$ screening fraction.

4.2.6 Polar adsorbates as local dopants

We conclude that the application of a negative gate voltage destroys the net polarization of adsorbed H$_2$O on PbZr$_{0.2}$Ti$_{0.8}$O$_3$, but preserves a net polarization on the SiO$_2$-screened regions. This creates different local doping levels and thus a p-n junction. A positive gate voltage establishes a net polarization in both
Figure 4.10: (a) $I_{sd}$ vs $V_{gate}$ curves (manually offset for clarity) for forward (light) and reverse (dark) gate voltage sweeps. Representative minima locations are indicated by the vertical arrows. (b) H$_2$O polarization by device region, as prepared by positive and negative gate voltages. For negative gate voltages, H$_2$O on the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ region is unpolarized, and H$_2$O on the SiO$_2$ region is polarized. For positive gate voltages both regions have a net polarization. (c) Simulated carrier density vs. applied gate voltage. The onset of H$_2$O polarization is indicated by grey shading. Inset: simulated conductance vs. applied gate voltage. (d) A schematic illustration of the H$_2$O doping hysteresis with applied gate voltage; arrows indicate the direction of the gate voltage sweep.
regions, and thus a uniform channel with no p-n junction, as depicted in Figure 4.10. This interpretation is further corroborated by the different widths of the forward and reverse minima for the control (0% screened) device, as evident in Fig. 4.10a. This difference can be explained by considering that conductance is linear with carrier density [5], so the width of the conductance minimum at the Dirac point is determined by the slope of the carrier density vs. gate voltage curve. Typically the slope is constant, determined by the gate capacitance. However, for our devices the onset of H₂O dipole doping introduces a nonlinearity in the regime where the adsorbed H₂O transitions from unpolarized to polarized; this is shown schematically in Fig. 4.10c. The polarized H₂O in our devices p-dopes the graphene, so the onset of its doping contribution temporarily reduces the slope of the carrier density vs. gate voltage curve, broadening the conductance minimum. During reverse sweeps, the transition from polarized to unpolarized H₂O occurs far from the CNP, so the width of the conductance minimum is unaffected. The hysteresis in H₂O polarization is illustrated schematically in Figure 4.10d. Experimentally, the polarization hysteresis displays a dependence on both the magnitude of the applied gate voltage and the duration of its application, which prevents an exact determination of the gate voltages required to establish or destroy the H₂O polarization.

The hysteresis of the H₂O polarization on PbZr₀.₂Ti₀.₈O₃ substrates adds an ‘on/off’ switching element to the p-n behavior. Specifically, we can selectively transition the device into and out of the p-n junction configuration through the application of large positive and negative gate voltages. The initial application of a large positive gate voltages establishes a uniform polarization across the device, yielding a unipolar conducting channel, while a large negative gate voltage destabilizes the polarization on regions supported by PbZr₀.₂Ti₀.₈O₃. In the latter case the different H₂O polarizations create separate locally doped regions, and thus a p-n junction. This ‘on/off’ switching is different than the standard gate induced switching observed in p-n junctions, for example from p-n to p⁺-p. By comparison, in our devices the same applied gate voltage can generate either a p-n junction or a uniformly doped channel, depending on the H₂O polarization condition.

The ferroelectric nature of the PbZr₀.₂Ti₀.₈O₃ substrate might suggest that the residual electric field from the substrate polarization dopes the regions of graphene in direct contact with the substrate [133, 142], but has less effect in the graphene regions screened by evaporated SiO₂. Similarly, graphene-ferroelectric interfaces are known to have complex interfacial charge trap dynamics which can generate similar transport signatures [141]. However, both explanations are precluded by several further experimental observations. First, the Dirac point splitting effect disappears when the devices are measured in vacuum. Figure 4.11 shows $I_{sd}$ vs $V_{gate}$ curves for the same devices measured at $5 \times 10^{-6}$ Torr but otherwise under conditions identical to those of Figure 4.8a. All devices show a single minimum, independent of evaporated SiO₂ width or gate sweep rate. Second, leaving the devices in ambient conditions overnight recovers the splitting effect. The observed behavior is consistent with an ambient dopant mechanism, i.e., the substrate-selective formation of
a self-assembled layer of dopant molecules. In vacuum, dopant molecules desorb from the surface leaving all regions of the graphene identically doped. Leaving the device in ambient conditions allows the dopant layer to reassemble, thereby re-establishing the separately doped regions.

The absence of Dirac point splitting in vacuum measurements also eliminates differences in gate capacitance as a dominant source of the splitting effect. The screened and non-screened regions of the device have different gate thicknesses and dielectric constants, which might suggest that the application of the same gate voltage would generate different doping levels in each region, and hence the transport behavior we observe. However, any capacitative differences between the regions are static, depending only on the geometry of the device, while the Dirac point splitting effect is dynamic, disappearing in vacuum. Capacitance-based explanations are further ruled out by the nearly identical Dirac point locations observed in all devices under vacuum. In particular, the similarity of data under vacuum from the control device (having no evaporated SiO$_2$), and from the devices which do span an evaporated SiO$_2$ region confirms that gate capacitance differences between the two regions are not the primary cause of the Dirac point splitting effect.

We note that the vacuum-dependence of our results requires that the ambient dopant molecules be present on top of the graphene rather than trapped between the graphene and the substrate. Pristine monolayer graphene is impermeable to atomic and molecular species [143], therefore the brief application of a moderate vacuum would be insufficient to remove any molecules trapped underneath the graphene. This in turn requires that the substrate-dependent localization of the ambient dopants occurs through the graphene; similar behavior has been previously reported elsewhere [35, 125, 144, 145].

4.2.7 Summary

In summary, we have fabricated a controllable p-n junction in graphene on a ferroelectric substrate. We employ simple substrate modifications to define local doping regions, where the doping is accomplished through the substrate-selective formation of a self-assembled layer of ambient doping molecules. Alternative explanations for the local doping effect are ruled out, and the dynamics of the ambient doping suggest that it is due to polar H$_2$O molecules. Finally, the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ substrate creates a hysteresis in the ambient doping effect which can be used to controllably bias the device into and out of a p-n junction configuration, using a single, universal backgate.
Figure 4.11: Offset $I_{sd}$ vs $V_{gate}$ curves for devices measured in vacuum. The Dirac point splitting effect disappears in vacuum, but can be recovered by leaving the device in ambient conditions overnight.
4.3 Transport in graphene on strain array substrates

In this section I describe a research project which examined electrical transport in graphene devices fabricated on substrates having arrays of topographic features. Engineered substrates offer an avenue towards graphene devices with tunable properties. In particular, substrates which apply strain to graphene can expose unique behavior. However, existing options for fabricating strain-inducing substrates do not create devices which are suitable for electrical transport measurements. Here I describe the fabrication of substrates which induce strain in graphene via controlled local adhesion and delamination; analysis of these devices offers a better understanding of how to controllably strain graphene using topographic substrates. The technique is first developed using flexible, polymer substrates and then extended to substrates made from silicon wafers which are suitable for transport measurements. We report both optical and transport measurements of graphene devices fabricated on these substrates showing characteristics induced by the substrate feature arrays.

4.3.1 Introduction

Engineered substrates present a practical method to locally tune graphene’s properties [146, 147], as described in Sections 2.3.3 and 2.3.4. There are a variety of avenues by which substrates can modulate graphene’s properties: previous work has employed substrate topography [148], electrostatic charge injection [149], substrate lattice mis-match [147], and ferroelectric polarization [150] to achieve a range of modifications to graphene’s properties.

Of the various substrate engineering techniques, applying strain via substrate topography is particularly interesting because of the large effect strain has on graphene’s electrical properties [146, 151, 152]. To date however, the techniques used to produce strain in graphene are either not tunable [152] or not amenable to performing electrical transport measurements on graphene [78, 79, 148, 153]. Here we demonstrate the fabrication of engineered arrays of strain-generating features. The process is first developed using flexible, polymer substrates which are used to explore the origin of the generated strain as well as methods with which to control it. The polymer substrates elucidate the tunable dynamics of straining graphene via patterned substrates, but they are unsuitable for transport measurements. We next develop similar devices on SiO$_2$ wafer substrates; these substrates are both suitable for transport measurements and capable of applying tunable strain. Finally, we report optical and transport measurements of devices on the SiO$_2$ wafer substrates which display characteristics induced by the patterned substrate.
Figure 4.12: (A) 3D AFM rendering of a pyramid array fabricated on a PDMS surface. (B) AFM phase image demonstrating the contrast in an area with and without graphene (dark gray and light gray, respectively). (C) Profile trace of a PDMS pyramid from AFM height data before and after depositing monolayer graphene. The flexibility of the substrate and the rigidity of graphene combine to make deformations of the substrate more energetically favorable than delamination.

4.3.2 Strain engineering via substrate topography

We begin by exploring the mechanical response of monolayer graphene deposited on substrates patterned with arrays of mesoscale triangular pyramids. We systematically study the morphology of graphene for pyramid arrays having different spacing, symmetry, and surface rigidity by atomic force microscopy (AFM) and Raman spectroscopy, and we find that the adhesion of graphene to the substrate – and hence the strain experienced by the graphene – can be controlled by changing the array aspect ratio and/or the topological arrangement of pyramids in the array.

Figure 4.12A shows a representative AFM micrograph of a pyramid array formed in polydimethylsiloxane (PDMS). Pyramid arrays were fabricated by defining molds using nanoindentation: a polycarbonate surface was nanoindented using a Berkovich or square corner styled tip to leave arrays of pyramid-shaped indentations. The molds were casted with PDMS – a polymer that becomes flexible and rubbery after curing – to produce samples. Graphene was synthesized using standard CVD techniques for growth on a copper foil [65] and was transferred onto pyramid arrays using previously reported wet transfer techniques [75].

Figures 4.12B and 4.12C show that graphene on PDMS both adheres conformally to and flattens the topographic features. This flattening effect reflects the competing energetics of deforming the substrate and relaxing the strain associated with graphene’s conformal adhesion to the topography. As shown in Figure
Figure 4.13: Pyramidal flattening factor as a function of strain array spacing. Larger spacings produce smaller flattening effects, reflecting the reduced strain present in sparsely spaced arrays. The relation between strain and spacing highlights the tunable nature of this experimental paradigm.

4.13, the degree to which the substrate is flattened decreases with increasing array spacing. Flattening occurs to minimize strain in graphene; the decrease in flattening with increasing spacing demonstrates that more sparsely spaced arrays produce less strain, i.e. that strain in graphene can be systematically varied as a function of array spacing. This demonstrates the tunable character of strain generated by patterned, topographic substrates.

The compliant nature of flexible, polymer substrates limits the amount of strain which can be applied via substrate features, so we next consider similar devices with enhanced rigidity. Specifically, we prepare identical PDMS substrates and then apply a coating of 5 nm Ti followed by 50 nm SiO$_2$. For rigid substrates the behavior of the graphene is determined by the competing energetics of graphene’s surface adhesion and strain relaxation. As shown in Figure 4.14 the resulting behavior depends on both the symmetry and aspect ratio of the strain array. Square arrays display conformal adhesion for all experimentally accessible aspect ratios, down to $\lambda/H = 3$ where $\lambda$ is the array spacing and $H$ is the height of the pyramid features. For triangular arrays, in contrast, graphene adheres conformally for aspect ratios $\lambda/H \geq 7$, partially de-adheres for aspect ratios $\lambda/H \approx 5$, and de-adheres everywhere except at the tip of the pyramid for aspect ratios $\lambda/H \approx 3$. This demonstrates that the adhesion behavior in our devices is determined by the aspect ratio of the array, in agreement with theoretical predictions [154, 155].

Finally, we examine the strain in these partially delaminated devices using Raman spectroscopy. As discussed in Section 2.3.2 we expect strain to produce shifts in the Raman peak locations. Here we measure the location of the Raman 2D peak for graphene devices on our strain array substrates. The results are presented in Figure 4.15 for graphene which adheres conformally to the substrate (as is the case on the square array) we observe no meaningful shift in the Raman 2D peak location compared to its location on flat substrates. For delaminated graphene (as on the triangular arrays with $\lambda/H < 5$) however we observe a distinct blueshift. The different behavior of square and triangular lattices of the same aspect ratio again
Figure 4.14: AFM images of rigid, pyramidal strain arrays before (top) and after (middle) the deposition of graphene; line traces across a pyramid are shown in the bottom row. The aspect ratios of the arrays are, from left to right, 3, 7, 5, 3. The adhesion behavior of graphene depends on both the symmetry and the aspect ratio of strain array substrates. For square arrays (A) graphene adheres conformally for aspect ratios as low as $\lambda/H = 3$. For triangular arrays graphene adheres conformally for aspect ratios $\lambda/H \geq 7$ (B), partially de-adheres for aspect ratios $\lambda/H \approx 5$ (C), and de-adheres everywhere except at the tip of the pyramid for aspect ratios $\lambda/H \approx 3$ (D).

Figure 4.15: Raman measurements of the 2D peak in graphene display shifts associated with strain when the graphene is delaminated. For pyramidal substrate features, the 2D peak shifts upward compared its location on flat substrates. The upward shift indicates a stiffening of the lattice, which corresponds to compressive strain.
confirms that the arrangement of topographic features can controllably create strain in graphene.

The increase in peak location indicates a stiffening of the lattice, which corresponds to compressive strain. We attribute this to the region of graphene which remains pinned to the tip of the pyramid. In the regime where graphene partially delaminates from the pyramids, areas that remain pinned to the pyramid accumulate compression to enable the delamination of graphene. We emphasize that the strain present in graphene is a consequence of the competition between adhesion and delamination; cases where the graphene is either conformal or entirely delaminated display no signs of strain.

These studies demonstrate controllable strain in graphene generated via patterned substrates, however the polymer substrates used here are not suitable for transport measurements (especially at low temperatures). Next we consider similar patterned substrates fabricated on standard SiO$_2$ wafers which are suitable for transport measurements.

### 4.3.3 Device configuration for transport measurements

The process used to create strain features on SiO$_2$ substrates is illustrated schematically in Figures 4.16A-D. First an array of copper circles is deposited, using standard electron-beam lithography and evaporation techniques, on a silicon chip covered with a 1000 nm layer of thermal oxide. The thick oxide layer is necessary
Figure 4.17: SEM micrographs of substrates prepared by this method. (A) SiO$_2$ pillars before the BOE etch. The scale bar is 1µm. (B) After the BOE dip the SiO$_2$ pillars are sharpened into cones with a tip diameter of less than 10 nm. The scale bar is 1 µm. Inset: A single sharpened cone. The scale bar is 100 nm. (C) For tight array spacings the graphene is suspended on the pointed tips of the substrate features. Here the substrate is visible through rips in the graphene. The scale bar is 500 nm. (D) After transfer the graphene is patterned in a Hall bar geometry. The six triangular features are Ti/Au electrical leads. The scale bar is 20 µm.
because subsequent etching steps remove several hundred nanometers of oxide, which would completely strip
the oxide layer of a chip with the standard 300 nm of SiO$_2$. The deposited copper is then used as a mask in
a reactive ion etching (RIE) step to produce cylindrical pillars in the SiO$_2$ layer. For the devices described
here the etch was performed in a PlasmaLab Freon RIE at 35 mtorr for 10 minutes using 100 W of incident
power and 70 sccm of CF$_4$. The RIE etch time and the diameter of the deposited copper mask circles
together define the aspect ratio of the resulting pillars; note that the aspect ratio of the pillar $r/H$, where
$H$ is the height of the pillar and $r$ is its radius, is distinct from the aspect ratio of the array $\lambda/H$. For
these devices we use a diameter of 100 nm, and the 10 minute etch time gives a height of approximately 200
nm. Devices were fabricated with array spacings ranging from 250 nm to 750 nm, corresponding to array
aspect ratios from 5:4 to 15:4. The range of aspect ratios is informed by the experiments on pyramidal strain
arrays described above: our goal is to apply strain, which is present when graphene is partially delaminated.
The patterned substrates produced in this section are square arrays, so we fabricate arrays having aspect
ratios $\lambda/H \leq 3$ corresponding to the range where delamination is expected to occur. After the etch, the
copper mask is removed by immersing the chip in a 0.1M solution of ammonium persulfate for several hours.
Finally, the chip is dipped in buffered oxide etchant (6:1 40% NH$_4$F : 49% HF) to sharpen the SiO$_2$ pillars
produced during the RIE step into pointed, conical shapes. The BOE dip time is an important parameter
which depends on the initial diameter of the pillars; for the the devices described here BOE was found to
etch the tip of the pillars at a constant rate of approximately 2 nm/s.

Graphene devices are fabricated on substrates prepared by this method using the process shown in Figures
4.16E-F. First Ti/Au (5 nm/30 nm) leads and contact pads are defined and deposited using electron-beam
lithography and evaporation. Next, a monolayer of graphene is grown using established chemical vapor
deposition techniques [111]. The graphene is then transferred to the patterned substrate using standard
polymer-assisted wet-transfer techniques [70]. The same polymer layer used to transfer the graphene is then
used as a resist in an electron-beam lithography step. Next the exposed graphene is removed using a reactive
ion etch (100 W, 50 mtorr, 20 sccm O$_2$, 30 s), yielding graphene in a Hall bar configuration. Finally the
remaining polymer resist is dissolved in acetone and the chip is dried in a critical point drying apparatus.

The critical point drying is necessary because for certain array spacings the graphene remains suspended
between strain features, and when the device is allowed to dry in air the surface tension of the evaporating
solvent tears the suspended graphene. Figure 4.17 shows scanning electron microscope (SEM) micrographs
of substrates and graphene devices produced by this process.
Figure 4.18: Raman peak positions for graphene on micropatterned and flat substrates. (A-B) Raman G and 2D peak positions extracted from a raster scan of graphene on patterned and flat substrates for array spacings from 300 nm to 700 nm. The data for the flat substrates is collected separately for each device to account for the varying residual doping present in each sample. (C) Raman G peak position vs. 2D peak position for graphene on a flat substrate and a 700 nm-spaced patterned substrate. The black dashed line shows the ratio $rac{\Delta \omega_{2D}}{\Delta \omega_G}$ expected for shifts due to strain, and the purple dotted line shows the ratio expected for shifts due to doping. The two lines intersect at the expected peak positions for undoped, unstrained graphene.

4.3.4 Optical measurements of strain

Optical measurements of graphene devices fabricated on substrates prepared by the process described above confirm the presence of strain. Raman measurements are collected in a raster pattern across a 20 $\mu$m $\times$ 20 $\mu$m area with a measurement spot size of 350 nm. At each raster point the Raman G and 2D peak positions are extracted [76]. Figures 4.18A and 4.18B summarize the extracted positions of the Raman G and 2D peaks, respectively, for graphene on patterned and flat substrates.

Both the G and 2D peaks of graphene on the patterned substrates display shifted peak positions relative to graphene on a flat substrate. This shift increases with increasing array spacing and displays a qualitative jump for spacings above 600 nm. We attribute this jump to a snap-through transition [153, 156] in the adhesion of the graphene to the substrate: for spacings below 600 nm the graphene is suspended in the entire patterned region, while for spacings above 600 nm the graphene adheres to the substrate except in the immediate vicinity of a patterned pillar. The partial delamination present in the sparse array samples produces strain in the graphene which generates the shifted Raman peak positions.

We note that for these devices we observe a redshift in the Raman peak location, rather than the blueshift observed for the pyramid samples above. We attribute this to the drastically different aspect ratios of the PDMS pyramids compared to the SiO$_2$ pillars. The pyramids have an aspect ratio of approximately 10. Near
their tips the SiO$_2$ pillars have a radius on the order of 10 nm, giving them an aspect ratio of approximately 0.05. The redshift in the pyramid experiment is attributed to the compression of graphene conformally adhered to the tip of the pyramid; the SiO$_2$ pillars are so sharp that they do not have an appreciable area over which graphene adheres conformally. For the SiO$_2$ pillars the dominant strain contribution stems from the frustrated adhesion in the vicinity of the pillars. However, despite the opposite sign of the Raman shift in the two experiments the underlying source of strain in both cases is the competition between adhesion and delamination.

As described in Section 3.2.3, doping from charge impurities in the substrate is also known to shift Raman peak positions in graphene [68, 85]. SiO$_2$ substrates in particular are known to dope graphene, therefore it is possible that the shift in Raman peak positions is due to variable doping from the substrate caused by the local delaminations. This explanation can be ruled out by examining the relative shifts of the G and 2D peaks. The ratio

$$r = \frac{\Delta \omega_{2D}}{\Delta \omega_G}$$

(4.2)

(where $\Delta \omega$ is the shift in a Raman peak position relative to its intrinsic value) differs between the two mechanisms [77]. Experimental measurements [83, 84, 90] and theoretical results [78, 91] place the ratio for strain between 2.25 and 2.8 and the ratio for doping at approximately 0.75 [77]. Figure 4.18C shows the extracted Raman G and 2D peak positions for a representative patterned sample having a spacing of 700 nm, along with lines corresponding to $r_{\text{strain}}$ (dashed) and $r_{\text{doping}}$ (dotted). The difference between the patterned substrate and flat graphene samples lies along $r_{\text{strain}}$ thus we attribute the shifted peak positions to the effect of strain in the graphene.

4.3.5 Magneto-transport measurements of quasi-bound states

We next perform low-temperature transport measurements on these devices. However, the behavior we observe is not caused the strain dependent effects we set out to observe. Rather, the local delaminations alter the gate capacitance and create local variations in the electrostatic potential. Fortuitously, transport measurements across local variations in the electrostatic potential are also experimentally fruitful. In the following we examine the current case of transport through electrostatically defined graphene quantum dots; in Section 5.2 we propose two new experiments which expand on these results to disentangle the local variations in strain and doping, with the intent of observing the strain-dependent physics that originally motivated this work.

Figures 4.19A and 4.19B show the results of magneto-transport measurements performed at 250 mK on a 750 nm-spaced patterned device and a flat control device, respectively. The Dirac point for both devices
Figure 4.19: Longitudinal resistance $R_{xx}$ of a graphene device fabricated on (A) a 750nm-spaced patterned substrate and (B) a flat substrate as a function of gate voltage and magnetic field. The color scale is measured in kΩ. (C) The same data as in (A) with a linear background $R_{\text{background}} = mV_g + b$ subtracted. (D) The potential profile created by the local delamination of the graphene. In the delamination regions the vacuum layer alters the gate capacitance, and thus creates local variations in the potential. In order to compare our results to theoretical predictions we model the potential as a parabola of height $U$ and half-width at half-maximum $x_0$. 
is located at approximately 40 V; this reflects both the residual doping from the fabrication process as well as the reduced gate capacitance of the thicker-than-normal SiO$_2$ dielectric layer. Qualitative differences between the patterned and flat devices are apparent: the unstrained control device displays the onset of a typical Landau level fan pattern [157], however the patterned device displays several resistance maxima not present in the control device. Figure 4.19C shows the same data as Figure 4.19A with a linear background $R_{\text{background}} = mV_g + b$ subtracted; several additional local maxima are visible in the low gate voltage region.

We attribute these features to the presence of local variations in the electrostatic potential induced by the patterned substrate. In the vicinity of each pillar the graphene is locally delaminated; this delamination alters the effective gate capacitance by including a region of vacuum in series with the SiO$_2$ dielectric layer. The local variation in the gate capacitance creates a corresponding variation in the potential, effectively creating a circular potential barrier, e.g. a quantum dot. This is illustrated schematically in Figure 4.19D. Carriers in graphene cannot be confined electrostatically: as massless particles governed by the Dirac equation (in the low energy limit) they display Klein tunneling [12, 17]. However, as described in Section 2.2.1 previous work has shown that circular potential barriers can create pseudo-bound states in graphene [25, 26, 29, 158, 159]. We attribute the transport behavior of our devices to resonant scattering off of pseudo-bound states in the quantum dots defined by the local delamination regions. We note that the spacing of the array, and thus the delamination regions is greater than the coherence length in this sample, so the behavior is not due to superlattice or Fabry-Pérot resonance effects.

This analysis is corroborated by both the energy and field scales of the features we observe in our data. Considering first the field scale, previous work [29] has shown that the scattering properties of quantum dots in graphene depend on the size of the dot: for small dots forward scattering is strongly suppressed while large dots can focus carriers and enhance conductivity. These size dynamics stem from the interaction of the incident plane wave and the excited wavefunction within the quantum dot. In the limit where the quantum dot is much smaller than the relevant length scale of the incident wave the quantum dot can be treated as a zero-dimensional region subject to quantized excitations. In contrast, the case where the quantum dot is of a similar size to the length scale of the incident wave is dominated by the internal dynamics of the wave within the quantum dot region. In this latter case the system behaves analogously to an optical system, with the incident particle wavefunction refracting and then interfering with the original wave [160].

In the presence of a magnetic field, we take the cyclotron radius to be the relevant length scale:

$$r_c = \frac{v_F m^*}{eB} = \frac{\hbar \sqrt{n\pi}}{eB}.$$  \hspace{1cm} (4.3)

We take the cyclotron radius as the relevant length scale because when $r_c$ is comparable to the size of the
quantum dot region the incident carrier is no longer well approximated by a plane wave. The transport
dynamics of a system containing quasi-bound states depend on the interference between the incident plane
wave and the reflected or refracted wave. When the incident wave is not a plane wave the interference
effects, and thus the transport behavior, will differ from the expected behavior. In our experiment, where
the cyclotron radius is the relevant length scale, the quantum dot is ‘small’ at low fields (because \( r_c \) is large)
and ‘large’ at high fields (because \( r_c \) is small); we therefore expect suppressed conductance at low fields and
enhanced conductance at high fields. For our devices, with a carrier density of \( 10^{11} \) cm\(^{-2} \) and a field of 1 T
corresponding the the field at which the transport features disappear, we find a cyclotron radius of 40 nm
and thus a characteristic length of 80 nm. This is in excellent agreement with the 100 nm diameter of the
patterned pillars and the resulting local delamination regions.

Next we consider the agreement between theoretical predictions and our observations in the energy scale;
the goal in the following section is to relate the observed gate voltage spacing between resistance maxima to
the spacing between the energy levels of quasi-bound states. We start with the gate voltage spacing; features
in the transport data are spaced approximately 5V apart. The change in the Fermi energy in graphene for
a given change in gate voltage is given by

\[
\Delta E_F = e \cdot \alpha \cdot \Delta V_g \tag{4.4}
\]

where \( \alpha = C_{bg}/C_Q \) is the capacitive lever arm of the back-gate. The capacitance of the backgate \( C_{bg} \) is
that of a SiO\(_2\) parallel plate capacitor with an area of 20 \( \mu \)m\(^2\) and a separation \( d \) of 500nm. The quantum
capacitance of the graphene sheet is given by \( C_Q = \frac{e^2}{\hbar v_F} \) \[161\] (in the low temperature limit where
\( E_F \gg kT \)). The density of states \( \rho \) is in turn given by \[2\]

\[
\rho(E) = \frac{g_sg_v A_c}{2\pi (\hbar v_F)^2} |E| \tag{4.5}
\]

where \( A_c \) is the area of one unit cell in graphene, \( g_s = g_v = 2 \) are the spin and valley degeneracy factors, and
\( v_F = 1 \times 10^6 \) m/s is the Fermi velocity in graphene. Calculating a value for \( \rho \) (and thus \( C_Q \) and ultimately
\( \Delta E_F \)) requires that we know the Fermi energy; we can extract a value for the Fermi energy from the sheet
carrier density via

\[
n(E_F) = \int_0^\infty \rho(E)f(E)dE \tag{4.6}
\]

where \( f(E) = (1 + \exp[(E - E_F)/kT])^{-1} \) is the Fermi-Dirac distribution. For a carrier density of \( 10^{11} \) cm\(^{-2} \)
this gives a Fermi energy of 37 meV, a quantum capacitance of 2.6 pF, and thus an energy scale for the
observed transport features of approximately 40 meV. Next we relate this experimental value to theoretical
predictions.

For a parabolic potential of the form $V = -(x/x_0)^2U/2$ theoretical results [25] give the following expression for the energy scale of the quasi-bound states:

$$E = \frac{\hbar v F}{\xi} \text{ with } \xi = \left(\frac{\hbar v F x_0^2}{U}\right)^{1/3}. \tag{4.7}$$

As shown in Figure 4.19D, the potential profile in our devices is defined by the local delamination of graphene in the vicinity of the SiO$_2$ pillars. Approximating the potential profile in our devices as parabolic in order to use the theoretical prediction for the energy scale of the quasi-bound states, we take $x_0 = 25$nm to be half the radius of the strain features, and $U$ to be the change in potential created by the locally varying gate capacitance

$$U = e \cdot V_g \cdot (\alpha_{\text{pillar}} - \alpha_{\text{flat}}). \tag{4.8}$$

The capacitive lever arm for the flat region $\alpha_{\text{flat}}$ remains the same as above, and we model the capacitance of the pillar region as cylinder of air in series with the SiO$_2$ substrate. The cylinder of air has radius $x_0$ and height 100nm, where the latter figure is half the height of the patterned features on the substrate. Taking $V_g = 22.5$V as the midpoint of the region of interest we find a predicted energy scale of 57 meV. This is in good agreement with our experimental results: the energy spacing extracted from our experimental features (40 meV) closely matches the theoretically predicted spacing of energy levels (57 meV) of the quasi-bound states for a quantum dot potential which approximates our experimental system.

We note that the energy scale of the quasi-bound states depends on the height of the potential barrier as $E \propto U^{1/3}$. In our experimental configuration the height of the potential barrier depends in turn on the magnitude of the applied gate voltage as $U \propto V_g$. The gate voltage in our measurements varies by a factor of two in the region of interest, and so we expect the theoretically predicted energy scale to vary by a factor of $2^{1/3}$ over the course of the measurement.

### 4.3.6 Summary

In summary, we describe a fabrication procedure for producing graphene devices on substrates having an array of strain-generating features and we report experimental signatures caused by these features. We find that the spacing of the patterned features determines the adhesion behavior of the graphene, and that for large spacings the partial delamination creates strain in the graphene which we observe using optical measurements. Finally, we find that magneto-transport measurements display features consistent with the presence of a locally varying potential, which we attribute to the variable gate capacitance induced by the
local graphene delamination. In particular, we observe transport signatures consistent with the presence of quasi-bound states in the quantum dot region defined by the local delamination regions. Through careful considerations of the array spacing and pillar height this technique can be adapted to regimes where either the quantum dot or strain dependent dynamics dominate, thereby offering a novel method to study both quasi-bound states and strain effects in graphene.
Chapter 5

Summary and conclusions

In this section I give a summary of the primary research results of this thesis and offer experimental extensions which build on the foundations established here.

5.1 Summary of results

In Section 4.1, we observed the formation and subsequent evolution of micro-rips in graphene using atomic force microscopy. While an initial application of tensile strain introduced new mechanical defects, successive strain-relaxation cycles over the same strain range elastically opened and closed the existing rips. Mechanics simulations further revealed the underlying deformation and failure mechanisms of the graphene sample under initial and subsequent cyclic tensile loadings, which agreed well with the AFM measurements. This mechanical effect had a corresponding electrical effect: the graphene’s transport properties were degraded by the initial application of strain, but showed small, mostly reversible changes during ensuing strain-relaxation cycles. This project provided insight into graphene’s failure modes when supported by a flexible substrate, how such failures differed from the well studied failure of suspended graphene, and finally how the transport properties of graphene degrade under mechanical strain and partial mechanical failure.

In Section 4.2, we fabricated a controllable p-n junction in graphene on a ferroelectric substrate. We employed simple substrate modifications to define local doping regions, where the doping was accomplished through the substrate-selective formation of a self-assembled layer of ambient doping molecules. Alternative explanations for the local doping effect were ruled out, and the dynamics of the ambient doping suggested that it was due to polar H\textsubscript{2}O molecules. Finally, the PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} substrate created a hysteresis in the ambient doping effect which could be used to controllably bias the device into and out of a p-n junction configuration, using a single, universal backgate. This project elucidated the role of ferroelectric polarization in the stability of polar dopants on graphene, and how the orientation of such dopants modulates their doping effect.

In Section 4.3, we described a fabrication procedure for producing graphene devices on substrates having an array of strain-generating features and we reported experimental signatures caused by these strain-
generating features. We found that the spacing of the patterned features determines the adhesion behavior of the graphene, and that for large spacings the partial delamination created strain in the graphene which we observed using optical measurements. Finally, we found that magneto-transport measurements displayed features consistent with the presence of a locally varying potential, which we attributed to the variable gate capacitance induced by the local graphene delamination. In particular, we observed transport signatures consistent with the presence of quasi-bound states in the quantum dot region defined by the local delamination regions. This project offered a preliminary experimental observation of quasi-bound states in electrostatically defined quantum dots.

5.2 Future work

Part of the appeal of experimental research is that every answer begets a new question. The work described in this thesis addresses certain aspects of graphene’s interactions with substrates, and how those interactions modify graphene’s properties, but each conclusion generates new potential avenues for exploration. Below I propose two new experiments which build on the most experimentally promising elements of the work described in this thesis.

5.2.1 Quasi-bound states in a single graphene quantum dot

The results of Section 4.3.5 provide a preliminary observation of quasi-bound states in electrostatically defined graphene quantum dots, however a precise interpretation of the data is complicated by certain factors in the sample design. In particular, the presence of an array of quantum dot regions rather than a single dot, the conical shape of the potential profile, and the semi-uncontrollable delamination dependence of the dot region make it difficult to quantitatively compare experimental results to theoretical predictions. Here I propose an experiment to perform transport measurements on an electrostatically defined graphene quantum dot device in a manner which closely mimics situations which have been treated theoretically.

Proposed devices

The proposed device geometry is illustrated in Figure 5.1: devices consist of a graphene channel contacted in a Hall bar configuration, which spans a single evaporated disk of SiO$_2$. Different devices on a single chip have different disk radii, and each chip includes at least one control device having no evaporated SiO$_2$ disk. The width of the graphene channel is twice the diameter of the largest evaporated disk. Such devices should be able to be made using standard wet-transfer techniques, without requiring the use of critical point drying. Additionally, the controlled deposition of additional SiO$_2$ on a substrate of known thickness (in contrast to
Figure 5.1: Proposed device geometry for experiments measuring transport signatures of quasi-bound states in an electrostatically defined graphene quantum dot. Graphene is patterned in a Hall bar shape atop a single SiO$_2$ pillar and contacted with Au leads.

the etching processes used in the experiment of Section 4.3.5) should allow for more precise determination of the gate capacitance.

**Proposed measurements**

The relevant experimental results can be collected via low temperature transport measurements. Specifically, sweeps of longitudinal resistivity $\rho_{xx}$ as a function of gate voltage will display signatures of quasi-bound states if such behavior is present in the proposed devices. These measurements can be performed using an SR830 lockin amplifier to measure the signal, a Keithley 2400 to provide the gate voltage, and optionally a voltage preamplifier like the PAR 113 to clean the resulting signal.

Coulomb blockade-type measurements of differential conductance $dI/dV$ as a function of both dc source-drain bias and gate voltage could also serve to emphasize the difference between quantum dot behavior in graphene and other two dimensional materials. These measurements can be performed with a Keithley 2400 for gating and a National Instruments DAQ for supplying the source-drain bias, as well as for measuring the current (optionally using a current preamplifier).

**Proposed analysis**

The collected resistivity data will be analyzed in terms of scattering from quasi-bound states in the quantum dot region defined by the evaporated SiO$_2$; as in the current work the quantum dot potential is established by the different gate capacitances in the two regions. Transport through such devices is predicted to display a Fano resonance when the Fermi energy of carriers in the flat graphene matches the energy of a quasi-bound state in the dot. This resonance will manifest as an increase in the device resistivity; by correlating the gate voltages at which the resistivity displays a maximum with the theoretically predicted energy levels of the quasi-bound states this experiment will provide a direct observation of quasi-bound states in graphene.
5.2.2 Psuedo-magnetic field effects in strain array substrates

Observing pseudo-magnetic field effects in transport measurements was the original motivation for the project described in Section 4.3. Experimentally the behavior of the devices was dominated by the scattering mechanics of the quantum dot regions produced by the local delamination of the graphene, and so ultimately we were unable to observe pseudo-magnetic field effects. However, in addition to the observation of quasi-bound state dynamics, the experiment also provided a better understanding of how strain is generated in such strain array-type devices: contrary to our expectations the dominant contribution to the strain stems from the competition between surface adhesion and delamination, rather than from conformal adhesion to the sharp tips of the pillars. Here I propose an experiment which employs this understanding to produce similar devices for which strain (rather than scattering from quantum dots) will be the dominant effect.

Proposed devices

The proposed device geometry is illustrated in Figure 5.2. Devices consist of a graphene channel contacted in a Hall bar configuration, which sits atop a strain array substrate. The strain array in these devices is both shorter and more densely packed than previously. Referencing previous work [153] on the snap-through transition in graphene, the pitch of the strain array is chosen to maximize the density of strain features (pillars) while still ensuring that the graphene remains adhered to the substrate between features. As local (but not global) delamination is the dominant factor leading to strain in these devices increasing the density of the local delaminations will increase the effective strain applied to the graphene. At the same time, minimizing the height of the strain features will reduce the capacitive difference between delaminated and adhered regions, and thus minimize the formation of quantum dot type potential profiles. The absence of large suspended regions of graphene should also dramatically improve the yield of these devices, compared to previous efforts.
Proposed measurements

This experiment requires low temperature magneto-transport measurements. Measurements of the longitudinal and Hall resistivity ($\rho_{xx}$ and $\rho_{xy}$) as a function of both gate voltage and applied magnetic field will display pseudo-magnetic field effects if any are present in the system. These measurements can be performed using two SR830 lockin amplifiers (one for longitudinal and one for Hall resistivity so that both can be measured simultaneously) and a Keithley 2400 to provide the gate voltage.

Proposed analysis

The magneto-transport data will be analyzed in terms of the quantum Hall effect. The quantum Hall effect in graphene is well understood; deviations from typical behavior would provide strong indications of pseudo-magnetic effects. In particular, asymmetries between different field directions, as well as unexpected peaks or plateaux at zero applied field, along with the evolution of such features with increasing field are the primary experimental signatures of interest.
Appendices
Appendix A

Device Fabrication Procedures

A.1 Growing CVD graphene

Begin with 99.999% pure copper foil (Alfa Aesar part #10950) cut into squares which are approximately 2 cm × 2 cm. Place at most three such squares of copper foil in a quartz boat, and slide the boat to the middle of the CVD oven. It is important to accurately center the foil in the furnace so that the temperature at the foil is as close as possible to the temperature set by the furnace, which is measured at the center. Seal the CVD tube, and pump on it for 20 minutes. Confirm that the the H₂ flow rate is set to to 17 sccm and the CH₄ flow rate is set to 60 sccm, then turn off the CH₄ (but leave the H₂ flowing). Set the CVD oven to 1000 C, close the lid, and wait for the system to reach 1000 C. Once the system is at 1000 C allow the copper foil to anneal for one hour. Next turn on the CH₄ flow. Exactly 20 minutes after turning on the CH₄ open the CVD oven and allow the system to cool. Once the system reaches 200 C turn off both gases. Finally, once the system reaches 100 C shut off the pump and remove the quartz boat from the CVD oven. After removing the copper foil pieces, spin coat PMMA 950 A4 at 3000 rpm, 1000 rpm / s acceleration for 30 seconds. Allow the PMMA to dry in air without baking (ideally overnight) and then RIE the non-PMMA coated side with 20 sccm O₂, 100 W at 200 mTorr for 60 seconds.

A.2 Graphene on flexible substrates

The devices were fabricated using a modified transfer printing process, similar to that described in Ref [54]. Single-layer graphene was grown using established chemical vapor deposition (CVD) techniques [111], and then transferred to a copper-coated silicon wafer where it was patterned using photolithography and reactive ion etching. Next, a piece of PDMS was mechanically pressed onto the silicon wafer, and the copper was then etched to leave patterned graphene on the PDMS substrate [75]. Raman spectroscopy was used to confirm the presence of graphene on the PDMS: the shape of the Raman 2D peak [112] along with subsequent AFM measurements verified the single-layer character of the graphene. Finally, shadow-mask evaporation was used to deposit Ti/Au contact pads.
A.3 Graphene on ferroelectric substrates

Substrates were prepared by pulsed-laser deposition: strontium titanate (SrTiO$_3$) substrates were first coated with 20 nm of strontium ruthenate (SrRuO$_3$) followed by 120 nm of (001)-oriented lead zirconium titanate (PbZr$_{0.2}$Ti$_{0.8}$O$_3$). The details of the substrate fabrication are discussed in Refs. [135, 136]. For each substrate, 80 nm of SiO$_2$ was evaporated in small rectangular regions defined by conventional photolithography. CVD graphene was then transferred onto the substrate using standard wet-transfer techniques as discussed in [111]. Photolithography was used to define graphene channels which spanned the evaporated SiO$_2$ regions; the remainder of the graphene was removed by oxygen plasma etching (60 seconds, 100 W, 200 mtorr, 20 sccm O$_2$). Finally, electrical leads were defined in a four-point measurement configuration using photolithography, and 20 nm of gold was deposited by electron-beam evaporation with a 3 nm sticking layer of titanium.

A.4 Graphene on strain array substrates

First an array of copper circles is deposited, using standard electron-beam lithography and evaporation techniques, on a silicon chip covered with a 1000 nm layer of thermal oxide. The thick oxide layer is necessary because subsequent etching steps remove several hundred nanometers of oxide, which would completely strip the oxide layer of a chip with the standard 300 nm of SiO$_2$. The deposited copper is then used as a mask in a reactive ion etching (RIE) step to produce cylindrical pillars in the SiO$_2$ layer. For the devices described here the etch was performed in a PlasmaLab Freon RIE at 35 mtorr for 10 minutes using 100 W of incident power and 70 sccm of CF$_4$. The RIE etch time and the diameter of the deposited copper mask circles together define the aspect ratio of the resulting pillars. For these devices we use a diameter of 100 nm, and the 10 minute etch time gives a height of approximately 200 nm. After the etch, the copper mask is removed by immersing the chip in a 0.1M solution of ammonium persulfate for several hours. Finally, the chip is dipped in buffered oxide etchant (6:1 40% NH$_4$F : 49% HF) to sharpen the SiO$_2$ pillars produced during the RIE step into pointed, conical shapes. The BOE dip time is an important parameter which depends on the initial diameter of the pillars; for the devices described here BOE was found to etch the tip of the pillars at a constant rate of approximately 2 nm/s.

Graphene devices are fabricated on substrates prepared by this method using a modified wet-transfer process. First Ti/Au (5 nm/30 nm) leads and contact pads are defined and deposited using electron-beam lithography and evaporation. Next, a monolayer of graphene is grown using established chemical vapor deposition techniques [111]. The graphene is then transferred to the strain array substrate using standard polymer-assisted wet-transfer techniques [70]. The same polymer layer used to transfer the graphene is then
used as a resist in an electron-beam lithography step. Next the exposed graphene is removed using a reactive ion etch (100 W, 50 mtorr, 20 sccm O₂, 30 s), yielding graphene in a Hall bar configuration. Finally the remaining polymer resist is dissolved in acetone and the chip is dried in a critical point drying apparatus. The critical point drying is necessary because for certain array spacings the graphene remains suspended between strain features, and when the device is allowed to dry in air the surface tension of the evaporating solvent tears the suspended graphene.
Appendix B

Python Measurement Code

During the course of this research I became frustrated with the existing instrument control programs our lab used to perform measurements. Most of this frustration stemmed from what I perceived to be shortcomings in LabVIEW, the programming language in which they were implemented. Briefly, these shortcomings are as follows:

1. **Code modification and reuse:** LabVIEW is a graphical programming language: programs are ‘written’ by connecting boxes representing functions and variables with ‘wires’ which pass input and output values. This paradigm makes it nearly impossible to modify an existing program of any complexity. To understand the logical flow of the program one must trace the paths and connections of upwards of 100 wires, each with multiple forks and branches; see Figure B.1 for an example. The result of this is that any existing code can only be used to perform the exact same measurement for which it was created; to perform an only slightly different measurement one must create an entirely new program, or invest an equivalent amount of time in debugging changes to an existing program.

2. **Commenting and versioning:** LabVIEW does not have robust options for commenting or versioning code. The lack of commenting exacerbates the difficulty of understanding an existing program, and the lack of version control makes it difficult to incrementally develop a program. Taken together these shortcomings also require that all meta-information about the program must be stored in the program file name, leading to program names like ‘gate_sweep_keithley_sr830_jeffs_edit_v3_new_B_usethisone.vi’.

3. **Version incompatibility:** New versions of LabVIEW are released yearly, however each new version breaks backwards compatibility. This causes many, many headaches when trying to run measurement programs inherited from previous students in the lab, or when trying to run a new program on a workstation with an earlier version of LabVIEW installed.

Given these frustrations, the obvious question is “Why use LabVIEW at all?” “Instrument drivers” is the short answer. Nearly every conceivable lab instrument provides drivers which allow the instrument

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1 'Versioning' refers to the process of tracking changes between sequential versions of some code. For example, the Track Changes functionality in Microsoft Office is used to version text documents.
Figure B.1: A portion of a LabVIEW program. The boxes are functions and variables, and the wires pass input and output values between the functions.
to communicate with LabVIEW. The primary barrier to writing instrument control programs in languages other than LabVIEW is the absence of instrument drivers in those languages.

B.1 Instrument Drivers

In order to address these issues I wrote drivers in the Python programming language for most of the instruments in our lab. These drivers can be found at https://github.com/masonlab/labdrivers and their usage is documented at http://labdrivers.readthedocs.io/en/latest/. In the rest of this section I describe the process used to create these drivers.

B.1.1 Writing new drivers

The purpose of an instrument driver is to facilitate communication between an instrument and a computer. Each instrument has a fixed set of commands it accepts, and a fixed set of outputs it will provide upon request. The task when writing a driver is to provide a convenient way to send commands and retrieve the relevant data. Most instruments provide a complete list of the commands they accept, often at the end of their instruction manual. These commands are not convenient for human use however, they are typically short and obscure (“*IDN?” or “*RST” for example). The task is to write a set of Python functions with simple, meaningful names which pass the appropriate command to the instrument (for example “get_instrument_id” or “reset_instrument”). For convenience, these functions can then be collected in a Python class to group all the functions for a particular instrument.

The majority of the instruments in our lab communicate with a computer using the National Instruments VISA standard. This standard describes how commands (like *RST) get translated into a format interpretable by the instrument. Conveniently, there is already a Python library called PyVISA which implements this standard. In practice, this means we can pass a command to the PyVISA library, and the library will handle the low-level work of passing that command to the instrument in a format it understands. Writing a Python instrument driver is thus a three step process:

1. Enumerate the commands which the instrument accepts

2. Write a python function to pass each instrument command to PyVISA

3. Collect the python functions into a class

Below I demonstrate this process for a single command.
FIGURE B.2: An excerpt from the manual of the SR830 lock-in amplifier which details one of the commands which the SR830 will accept from a computer.

**Enumerate commands the instrument accepts**

In this example I will write a partial instrument driver for the SR830 lock-in amplifier. The first step is to find a listing of the commands which the instrument accepts; for the SR830 such a list can be found at the end of the instrument’s instruction manual. An excerpt is shown in Figure B.2. This portion of the manual describes two commands: passing `FREQ?` to the instrument queries the current frequency, and passing `FREQ X` where `X` is some number sets the instrument frequency to that number.

**Write a python function for each command**

The next step is to write a python function which passes this command to the instrument. To do this we use the existing PyVISA [link](#) library in python. This library facilitates communication between computers and instruments which communicate using the VISA standard, which in practice is most instruments. Most of this communication is done using a python class from the PyVISA library called `GPIBInstrument`. This class has two relevant methods: `write()` and `query()`. The first passes a command to the instrument, and the second passes a command and retrieves the response. The general approach here is to create an instance of the `GPIBInstrument` class and then call `write()` and `query()` with appropriate arguments.

Below I demonstrate how to create an instance of the `GPIBInstrument` class for an instrument having a GPIB address of 14. Note that this tutorial closely follows the PyVISA documentation, available at the link given above.

```python
import visa

GPIB_addr = 14

rm = visa.ResourceManager()
my_instrument = rm.open_resource('GPIB0::{}::INSTR'.format(GPIB_addr))
```

We can now use this instance of the `GPIBInstrument` class to communicate with our SR830. In this case we will write two functions, one for each of the commands we enumerated above. Note that both commands require the existence of the `my_instrument` variable which we created in the previous code block.
def set_frequency(my_instrument, freq):
    my_instrument.write('FREQ {}'.format(freq))

def get_frequency(my_instrument):
    return my_instrument.query('FREQ?')

Now we can use the functions defined above to get or set the frequency of the SR830.

Collect the functions into a class

The final step is to collect the functions for a given instrument into a python class for that instrument. The rationale here is that collecting functions into a class allows us to more logically track multiple instruments. This grouping can be accomplished as follows:

class SR830():
    def __init__(self, GPIB_addr):
        self.instrument = rm.open_resource('GPIB0::{}::INSTR'.format(GPIB_addr))

    def set_frequency(self, freq):
        self.instrument.write('FREQ {}'.format(freq))

    def get_frequency(self):
        return self.instrument.query('FREQ?')

The code above uses the standard python class definition syntax; for an explanation of that syntax see the python documentation.

B.1.2 Wrapping existing drivers

The process described above requires that the instrument can be controlled using the VISA standard. For instruments where this is not the case, another option is to ‘wrap’ existing drivers which are written in other languages. The practical implementation is more complex, but this wrapping process is logically similar to the VISA-based process:

1. Enumerate the commands which the other driver accepts

2. Write a python function to invoke each command in the existing driver

3. Collect the python functions into a class

Instead of passing commands to the PyVISA library we invoke commands in the existing driver, but otherwise the process of creating a Python driver is the same.
The difficulty of wrapping other drivers mostly lies in figuring out how to run commands from another programming language (the language that the original driver was written for) from within Python. The method required to do this depends on the language of the original driver, however there are often existing Python libraries to facilitate this task. A complete accounting of these existing libraries is beyond the scope of this thesis, and in fact would likely be immediately out of date; the motivated reader is encouraged to Google around. For examples of drivers created by this process see the drivers for the National Instruments BNC-2100 DAQ (link) and the Quantum Design PPMS DynaCool (link).

B.2 Example measurement programs

These drivers are meant to be used interactively, ideally in the Jupyter notebook environment (link). Briefly, Jupyter is a browser based programming environment. The central feature of Jupyter is the use of ‘notebooks’ which combine text, plotting capabilities, and code. The labdrivers project contains several example Jupyter notebooks for common measurements, which are available here. A subset of those examples are reproduced here as examples of how the drivers can be used.

B.2.1 IV-sweep example

This example performs a IV-sweep measurement using the DAQ to both source the voltage and measure the current.

```python
import numpy as np
import matplotlib.pyplot as plt
from labdrivers.ni import bnc2110

daq = bnc2110('Dev1')

# define some parameters
v_min = -10E-3
v_max = 30E-3
v_step = 1E-3

voltages = np.arange(v_min, v_max, v_step)
readings = []

for volt in voltages:
    # set the DAQ output
    daq.setVoltageOutput('ao1', volt)

    # take a measurement
    data_pt = daq.readCurrentInput('ai1')

    readings.append(data_pt)
```

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# plot the results
plt.plot(voltages, readings)
plt.xlabel('Volts')
plt.ylabel('Amps')

B.2.2 Coulomb blockade measurement example

This example performs a two dimensional sweep of longitudinal resistance as a function of both gate voltage and source drain bias. The measurement uses an SR830 to measure the resistance, a National Instruments DAQ to supply to bias voltage, and a Keithley 2400 to supply the gate voltage.

```python
import numpy as np
import pandas as pd
import matplotlib.pyplot as plt
from labdrivers.ni import bnc2110
from labdrivers.srs import sr830
from labdrivers.keithley import keithley2400

# define some parameters
vgate_min = 20
vgate_max = 50
vgate_step = 0.5
sleep_time = 0.05
vbias_min = -10E-3
vbias_max = 10E-3
vbias_step = 0.5E-3

gate_lines = np.arange(vgate_min, vgate_max, vgate_step)
bias_lines = np.arange(vbias_min, vbias_max, vbias_step)

# make data frames w vbias as columns, vg as index
lockin_x_2d = pd.DataFrame(columns=bias_lines, index=gate_lines)
lockin_y_2d = pd.DataFrame(columns=bias_lines, index=gate_lines)

# for temporarily storing each 1d gate sweep
lockin_x = []
lockin_y = []

for vbias in bias_lines:
    # connect to the instruments
dac = bnc2110('Dev1')
lockin = sr830(8)
gate_keithley = keithley2400(20)

    # configure the gate keithley
gate_keithley.setMeasure('current')
gate_keithley.setSourceDC('voltage')
```

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gate_keithley.setCompliance('current', 0.5E-6)

# turn the outputs on
gate_keithley.rampOutputOn(vgate_min, 0.5)
time.sleep(3)

# set s-d bias to vbias
dac.setVoltageOutput('ao1', vbias)

lockin_tuples = []

# do the gate sweep
for volts in gate_lines:
    # set the keithley output, then take a measurement
gate_keithley.setSourceDC('voltage', volts)
    lockin_tuples.append(lockin.getSnapshot(1,2))

    # sleep so that the gate doesn’t sweep too fast
time.sleep(sleep_time)

# unpack [(x1, y1), (x2, y2), (x3, y3), ...]
# to [x1, x2, x3, ...] and [y1, y2, y3, ...]
lockin_x, lockin_y = zip(*lockin_tuples)

lockin_x_2d[vbias] = lockin_x
lockin_y_2d[vbias] = lockin_y

# to keep track of where we are in the scan
print('V_bias: {:.3e}'.format(vbias))

# turn the keithley output off
gate_keithley.rampOutputOff(vgate_max, 0.5)

# save the data to file
lockin_x_2d.to_csv('path/to/save x', index=True)
lockin_y_2d.to_csv('path/to/save y', index=True)
Appendix C

Measurement instrumentation

C.1 Keithley 2400 SMU

The Keithley 2400 is a source-measure unit (SMU) capable of sourcing both current and voltage, and simultaneously measuring either current, voltage, or resistance. Its primary advantage is its wide operational range: it can source and measure up to 1 A in current mode, or 200 V in voltage mode. The Keithley 2400’s wide operational range comes at the expense of precision; Figure C.1A shows the measured output of a Keithley 2400 set to source 1 V, along with a similarly configured BNC2110 DAQ. The Keithley’s output fluctuates by up to 0.5% of the specified output value. The Keithley’s precision can be improved by setting the ‘Range’ parameter of the input and output: using the smallest range which still encompasses all the required values will provide the best precision.

In practice, the Keithley 2400 is most useful for preliminary sample characterization (i.e. determining if a device conducts, and if so approximately what its resistance is) and for applying gate voltages. In the first case, the Keithley is useful because it can be manually configured by using the buttons on its face; for simple ‘Does the device conduct or not?’-type measurements this is often the most convenient option. The Keithley 2400 is also particularly well suited to the latter use case: effectively gating graphene samples often requires gate voltages in the tens of volts, and the precise value of the supplied voltage is typically less critical for gating than for other applications.

C.2 National Instruments Multifunction Data Acquisition Device (DAQ)

The National Instruments Multifunction Data Acquisition Device (DAQ) is a source-measure unit mounted on a PCI card. The PCI card must be physically installed in a computer, at which point it can be connected to an external connector block (e.g. the NI BNC-2110) which provides BNC connectors. Measurements using the DAQ must use instrument control programs installed on the computer which makes it less suitable
Figure C.1: Top: The voltage output of a Keithley 2400 SMU and a National Instruments BNC2110 Digital to Analog Converter measured over 10 seconds. Both were set to source 1 V. Middle: The output of a Keithley 2400 SMU before and after being passed through three different voltage pre-amplifiers. Bottom: The same data as above with only the amplified signals shown.
for quick, one-of measurements.

The DAQ makes the opposite trade-offs as the Keithley: it provides high precision sourcing and measurement in a limited operational range. The DAQ can source and measure voltages from -10 V to 10 V. However, within this limited range the DAQ is more precise than the Keithley as seen in Figure C.1A. The DAQ is particularly useful for applications which require high precision, for example providing the bias voltage in an I-V sweep or in a $V_{\text{gate}}$ vs $V_{\text{bias}}$ Coulomb blockade-type scan.

C.3 Stanford Research System SR830

The SR830 is a lock-in amplifier. Lock-in amplifiers operate by applying an AC drive to a device, measuring the resulting signal, and then multiplying the original drive and resulting signal and integrating over time. Because sinusoidal functions at different frequencies are orthogonal, the multiplication of the original drive and resulting signal and the subsequent integration combine to filter out components of the measured signal which are not at the same frequency as the original drive. Since most noise components will not be at the same frequency as the drive this technique is particularly effective at extracting a desired signal from a noisy measurement.

In practice the SR830 is the preferred instrument for measuring resistance, provided the particular measurement is amenable to an AC bias. Additionally, the SR830 can only provide a voltage output; for applications which require a current bias the output of the SR830 must be passed through a large resistor to convert the voltage to a current. ‘Large’ in this case means ‘large enough that the resistance of the device being measured in series does not appreciably change the total resistance of the circuit’.

C.4 Voltage and current preamplifiers

Voltage and current preamplifiers are useful for amplifying and filtering signals. Current preamplifiers are also useful for converting current signals into voltage signals. Figure C.1B demonstrates the filtering capabilities of a voltage preamplifier: it shows the output of a Keithley 2400 before and after being passed through several different preamplifiers (the raw Keithley signal has been rescaled to allow for direct comparison). All three preamplifiers drastically improve the cleanliness of the signal. Figure C.1C compares the performance of the three preamplifiers; The PAR 113 provedes the best performance, while the SRS 560 and ITHACO provide good accuracy at the expense of precision, and vice versa.
Bibliography


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