ELECTRONIC BAND STRUCTURE EFFECTS IN MONOLAYER, BILAYER, AND HYBRID GRAPHENE STRUCTURES

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Abstract

Since its discovery in 2005, graphene has been the focus of intense theoretical and experimental study owing to its unique two-dimensional band structure and related electronic properties. In this thesis, we explore the electronic properties of graphene structures from several perspectives including the magnetoelectrical transport properties of monolayer graphene, gap engineering and measurements in bilayer graphene, and anomalous quantum oscillation in the monolayer-bilayer graphene hybrids. We also explored the device implications of our findings, and the application of some experimental techniques developed for the graphene work to the study of a complex oxide, Ca$_3$Ru$_2$O$_7$, exhibiting properties of strongly correlated electrons.

Graphene’s high mobility and ballistic transport over device length scales, make it suitable for numerous applications. However, two big challenges remain in the way: maintaining high mobility in fabricated devices, and engineering a band gap to make graphene compatible with logical electronics and various optical devices. We address the first challenge by experimentally evaluating mobilities in scalable monolayer graphene-based field effect transistors (FETs) and dielectric-covered Hall bars. We find that the mobility is limited in these devices, and is roughly inversely proportional to doping. By considering interaction of graphene’s Dirac fermions with with local charged impurities at the interface between graphene and the top-gate dielectric, we find that Coulomb scattering is responsible for degraded mobility.

Even in the cleanest devices, a band gap is still desirable for electronic applications of graphene. We address this challenge by probing the band structure of bilayer graphene, in which a field-tunable energy band gap has been theoretically proposed. We use planar tunneling spectroscopy of exfoliated bilayer graphene flakes demonstrate both measurement and control of the energy band gap. We find that both the Fermi level and electronic structure are highly sensitive to tunnel
bias-induced charging in these devices, an effect that is traditionally neglected in other materials. However, careful consideration of both these effects and non-ideal tunneling processes allows extraction of valuable information from the tunneling spectra. We compare the tunable insulating state to our transport studies of bilayer graphene-based FETs with similar dielectric environments. This work, as well as our work on top-gated monolayer-based devices, identifies the integration of graphene and a gate dielectric as being the next great challenge towards the realization of graphene-based electronics.

We also report the discovery of anomalous quantum oscillations in magnetotransport measurements of monolayer and bilayer graphene hybrids. In these graphene hybrid structures, the Fermi levels of either portion lock at their interface, and the greatly different energy scales of emergent Landau levels support strong charge imbalance. The nature the interface states are yet to be clarified.

Finally, we extend the techniques of device fabrication and measurement to exfoliated flakes of a layered material, Ca$_3$Ru$_2$O$_7$. This strongly correlated electronic system hosts a variety of exotic phenomena at low temperatures, which have been suggested to result from complex $d$-orbital interactions. We compare transport measurements of flakes to previous studies in bulk crystals, and explore the effects of tuning charge carrier density using an ionic liquid gate to induce densities several orders of magnitude greater than is possible with conventional dielectrics.
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Dedication

To my wife, Ashley. I will forever endeavor to offer you the level of support, encouragement, and selflessness that you have shown me over the first few of our many years together.
Introduction

Although its electronic structure has been theoretically considered since the middle of the 20th century[1, 2, 3], the recent inundation of graphene-related research followed the isolation of a single sheet of graphene exfoliated from bulk graphite onto insulating substrates in 2005[4], making graphene available for experimental study. Graphene research was immediately popular not only because its stability confirmed the preservation of solids in two dimensions (2D), which was previously thought threatened by thermal fluctuations[5, 6], but also because electrons follow a unique linear dispersion between energy and momentum, contrasting with the quadratic dispersion followed in a conventional 2D electron gas. This dispersion made electrons in graphene more comparable to relativistic particles, where the Fermi velocity is substituted for the speed of light in the Dirac equation. As a result, graphene research has revealed exciting, new electronic phenomena including an unconventional quantum Hall effect[7, 8, 9] and a complete suppression of back scattering[10] leading to proposed “Klein tunneling” of carriers through potential barriers[11].

Ballistic transport over device length scales[12, 13, 14] and evidence for ultrahigh mobilities[15] of carriers in graphene make the material attractive for electronic applications, building upon its flexibility, high mechanical strength[16], and scalable growth techniques[17, 18]. Already, high-frequency graphene-based field effect transistors (FETs) have been demonstrated[19, 20]. However, the performance of graphene-based FETs, as well as its role in potential electro-optical technologies, is challenged by the absence of an intrinsic energy band gap in graphene.
Such challenges can be met with bilayer graphene, in which attractive features like high carrier mobility are preserved. Bilayer graphene hosts an electronic structure that is very different from a monolayer, one that hosts not only another unconventional quantum Hall effect\cite{21, 22}, but also an energy band gap that is tunable by applying an interlayer bias\cite{23}. The insulating state has confirmed by angle-resolved photo-emission spectroscopy\cite{24} and infrared absorption experiments\cite{25, 26}. However, FET transport experiments\cite{27, 28, 29, 30, 31} have not yet demonstrated a truly insulating state.

Much of the work presented in this dissertation focuses on band structure-related phenomena, examined in the context of potential electronic applications. In Chap. 5, we explore the role of local charged impurity scatterers in the performance of FETs and Hall bar structures fabricated on epitaxially-grown monolayer graphene. To address the challenge of opening a band gap in graphene, we study the electronic structure revealed by planar tunnel junctions fabricated on bilayer graphene flakes in Chap. 6. In Chap. 7, our discovery of anomalous quantum oscillations in the magnetotransport of hybrid structures brings attention to the monolayer/bilayer interface that may exist in grown films or possible interface junctions. Finally, in Chap 8, we explore the strongly correlated electrons of Ca$_3$Ru$_2$O$_7$, where we seek to better understand of the role of $d$-orbital ordering in driving exotic phenomena by developing ionic liquid gating and surface-contacted transport in exfoliated flakes.
2.1 Monolayer graphene band structure

2.1.1 Tight-binding calculations of electronic band structure

The graphene monolayer is a two-dimensional honeycomb lattice of carbon atoms, shown in Fig. 2.1a. The unit cell of graphene contains two atoms, each from two inequivalent sublattices A and B, such that the nearest neighbors of each A (B) atom belong to the B (A) sublattice. We define $\mathbf{R}$ as the set of all points in the $x$-$y$ plane that make up the Bravais lattice for graphene. The lattice unit vectors, $a_1$ and $a_2$, which construct $\mathbf{R}$ ($R_{m,n} = ma_1 + na_2$, $m, n = 0, 1, 2, \ldots$), can be written as

$$
\begin{align*}
\vec{a}_1 &= \frac{a}{2}(3\hat{x} + \sqrt{3}\hat{y}), \\
\vec{a}_2 &= \frac{a}{2}(3\hat{x} - \sqrt{3}\hat{y}),
\end{align*}
$$

(2.1)

where $a$ is the spacing between adjacent atoms, equal to 1.42 Å[1]. In our tight-binding treatment of graphene, we consider electron hopping only between nearest neighbors, located at displacement vectors $\vec{\delta}_i$ from any A atom, given by
Figure 2.1. a) Honeycomb lattice of monolayer graphene. The unit cell contains two atoms, each members of sublattices A (blue) and B (red) separated by \( a \). The lattice unit vectors are \( \vec{a}_1 \) and \( \vec{a}_2 \), and the nearest neighbors of an A atom are located at \( \vec{\delta}_i \) with respect to that atom; b) Reciprocal lattice (green dots) of monolayer and bilayer graphene, with lattice vectors \( \vec{b}_1 \) and \( \vec{b}_2 \) labelled. The first Brillouin zone is outlined in red and the \( \Gamma \)- and \( K \)-points are marked.

\[
\begin{align*}
\vec{\delta}_1 &= \frac{a}{2}(\hat{x} + \sqrt{3}\hat{y}) \\
\vec{\delta}_2 &= \frac{a}{2}(\hat{x} - \sqrt{3}\hat{y}) \\
\vec{\delta}_3 &= -a\hat{x}
\end{align*}
\]

(2.2)

Given a nearest-neighbor hopping energy \( \gamma_0 \), we can construct the tight-binding Hamiltonian,

\[
\mathcal{H} = \gamma_0 \sum_{i,s} (c_{A,i,s}^\dagger c_{B,i,s} + \text{c.c.}),
\]

(2.3)

where \( c_{X,i,s} (c_{X,i,s}^\dagger) \) is the creation (annihilation) operator for an electron with spin \( s \) on an atom in sublattice \( X \) at position \( r_i \). Based on the fitting of optical transition experiments to tight-binding results for graphite, \( \gamma_0 \) has been determined to be \( \approx 2.9 \, \text{eV} \)\cite{1, 3, 32}. In order to proceed with the analysis, we must map out all
available electron states in reciprocal space. Such states are designated by their wavevector, $k$, and those states with the same periodicity as the real lattice belong to the set $K$ satisfying $e^{i(K\cdot R)} = 2\pi\nu$, $\nu = 0, 1, 2, \ldots$. Each reciprocal lattice point is therefore given by $k_i = nb_1 + mb_2$, where $b_1$ and $b_2$ are the reciprocal lattice vectors,

\[
\vec{b}_1 = \frac{2\pi}{3a}(\hat{x} + \sqrt{3}\hat{y}) \quad \text{(2.4)}
\]

\[
\vec{b}_2 = \frac{2\pi}{3a}(\hat{x} - \sqrt{3}\hat{y}).
\]

The hexagonal reciprocal lattice, with the first Brillouin zone highlighted in red, is shown in Fig. 2.1b. At the corners of the first Brillouin zone, there exist two inequivalent sets of the points, labelled $K$ and $K'$, which are each equivalent to points at to two other corners through reciprocal lattice vectors. These points, as labelled, are located at $k_{K,K'} = \frac{2\pi}{3a}(\hat{x} \pm \frac{1}{\sqrt{3}}\hat{y})$. Their importance will be made clear below. In the continuum limit, the part of the Hamiltonian in Eq. 2.3 that covers hopping from B to A, expressed as $H_{B\rightarrow A}$, can be reformulated:

\[
H_{B\rightarrow A}(\vec{k}) = \gamma_0 \sum_i e^{i(\vec{k}\cdot\vec{\delta}_i)}
\]

\[
= \gamma_0(e^{i(\frac{a}{2}k_x + \frac{\sqrt{3}}{2}k_y)} + e^{i(-\frac{a}{2}k_x - \frac{\sqrt{3}}{2}k_y)} + e^{i(-ak_x)})
\]

\[
= \gamma_0((2\cos(\frac{a\sqrt{3}}{2}k_y)\cos(\frac{a}{2}k_x) + \cos(ak_x)) + i(2\cos(\frac{a\sqrt{3}}{2}k_y)\sin(\frac{a}{2}k_x) - \sin(ak_x))).
\]

The conjugate of $H_{B\rightarrow A}$, $H_{A\rightarrow B}$, can be expressed trivially. The resulting energy dispersion, $\pm|E(\vec{k})|$, is plotted in Fig. 2.2a. The valence and conduction bands are shown to meet at each of the six corners (the $K$-points) of the first Brillouin zone. Since the Fermi level is located at those points, we solve for local dispersion for conducting electrons with the transformation with $\vec{k} \rightarrow k_K + \vec{k}$, for small $\vec{k}$:
Figure 2.2. Lowest energy bands of monolayer graphene determined by Eq. 2.5 for electron wavevector \( \vec{k} = k_x \hat{x} + k_y \hat{y} \). The valence and conduction bands meet at the corners of the first Brillouin zone and feature a linear dispersion following Eq. 2.7 in the text, blown up on the right.

\[
\mathcal{H}_{B-A}(k_K + \vec{k}) = \gamma_0 \sum_i e^{i((k_K + \vec{k}) \cdot \delta_i)} \\
= \gamma_0 (e^{i\frac{2\pi}{3}} e^{i(\frac{1}{2}k_x + \frac{a\sqrt{3}}{2}k_y)} + e^{i(\frac{1}{2}k_x - \frac{a\sqrt{3}}{2}k_y)} + e^{-i\frac{2\pi}{3}} e^{i(-ak_x)}) \\
\approx \gamma_0 \left( \frac{1}{2} + i \frac{\sqrt{3}}{2} \right)(1 + i \frac{a}{2} k_x)(1 + i \frac{a\sqrt{3}}{2} k_y) \\
+ \left( 1 + i \frac{a}{2} k_x \right)(1 - i \frac{a\sqrt{3}}{2} k_y) + \left( -\frac{1}{2} - i \frac{\sqrt{3}}{2} \right)(1 - iak_x) \\
\approx \frac{3}{4} \gamma_0 a(-\sqrt{3} + i)(k_x + ik_y).
\]

From here, we construct the two-component Hamiltonian in the basis of electron wavefunctions predominantly on the A or B site, \(|\psi>: \{\psi_A, \psi_B\}:

\[
\mathcal{H}_{B-A}(k_K + \vec{k}) = \gamma_0 \sum_i e^{i((k_K + \vec{k}) \cdot \delta_i)} \\
= \gamma_0 (e^{i\frac{2\pi}{3}} e^{i(\frac{1}{2}k_x + \frac{a\sqrt{3}}{2}k_y)} + e^{i(\frac{1}{2}k_x - \frac{a\sqrt{3}}{2}k_y)} + e^{-i\frac{2\pi}{3}} e^{i(-ak_x)}) \\
\approx \gamma_0 \left( \frac{1}{2} + i \frac{\sqrt{3}}{2} \right)(1 + i \frac{a}{2} k_x)(1 + i \frac{a\sqrt{3}}{2} k_y) \\
+ \left( 1 + i \frac{a}{2} k_x \right)(1 - i \frac{a\sqrt{3}}{2} k_y) + \left( -\frac{1}{2} - i \frac{\sqrt{3}}{2} \right)(1 - iak_x) \\
\approx \frac{3}{4} \gamma_0 a(-\sqrt{3} + i)(k_x + ik_y).
\]
$\Rightarrow \mathcal{H}(k_K + \vec{k}) = \hbar |v_F| \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$

$\Rightarrow E_{\pm}(k_K + \vec{k}) = \pm \hbar v_F |\vec{k}|$, (2.7)

where $|v_F| \equiv 3a\gamma_0/2\hbar \approx 1 \times 10^6$ m/s is the Fermi velocity. The matrix form of the Hamiltonian in Eq. 2.7 is in the basis of electron wavefunctions in the A or B sublattices, and the self-energy of each sublattice has been set to a reference equal to zero. The “Dirac cone” dispersion result, whose name is explained below, is highlighted in Fig. 2.2. The linear dispersion of low-energy electrons is what makes the graphene unique among electronic materials. Usually, low energy electrons in conducting materials follow a quadratic dispersion, $E(\vec{k}) = (\hbar k)^2/2m^*$, where $\hbar$ is Planck’s constant, $\hbar \vec{k}$ is the electron momentum $\vec{p}$, and $m^*$ is the effective mass within the crystal lattice. Electrons in such materials can be treated as a free electron gas with Fermi velocity $v_F = p/m^* = \sqrt{E/2m^*}$. In graphene, however, the Fermi velocity is independent of energy, leading to the interpretation of charge carriers in graphene as being “massless”. The result of Eq. 2.7 is of the same form as the Dirac equation governing relativistic electrons, but where the speed of light has been replaced with $v_F$. Graphene is thus a model system for studying relativistic quantum electrodynamics.

Given two inequivalent K-points contributing to a valley degeneracy of two, carriers in graphene have a total degeneracy of four including spin species. Assuming evenly spaced momentum states in reciprocal space, the total number of states $N$ up to Fermi wavevector $k_F$ in a sample of area $A$ is given by $N = 4A/(2\pi)^2 \pi k_F$. From the result of Eq. 2.7, the Fermi energy energy as a function of carrier density $n$ is then

$$E_F = \hbar v_F \sqrt{\pi n}. \hspace{1cm} (2.8)$$

Thus, in the linear regime, the density of states $N_{1LG} = dn/dE$ is

$$N_{1LG} = \frac{2}{\pi \hbar^2 v_F^2} E. \hspace{1cm} (2.9)$$
The approximation of a linear dispersion at the Fermi level in graphene is good up to 0.5 eV. Only above this value, at carrier density greater than \( 2 \times 10^{13} \text{ cm}^{-2} \), is there a significant deviation (>3%). Including the higher order terms (at least \( k_i^2 \)) in the derivation of Eq. 2.7 contributes to a trigonal warping of the Dirac cone at very low carrier densities[10]. However, these carrier densities are not typically realized in experiments due to the presence of charge inhomogeneity (see Sect. 2.3).

### 2.1.2 Finite magnetic field

In a perpendicular magnetic field \( H \), the density of electronic states in a two-dimensional electron gas (2DEG) splits into discrete Landau levels, each separated by a constant energy that scales linearly with field strength as \( E_j = \hbar \omega_c (j + \frac{1}{2}) \), where \( \omega_c = eH/m \) is the cyclotron frequency and \( j = 0,1,2, \ldots \). Each level’s electron degeneracy is equal to \( N_L = eH/\hbar \) multiplied by spin and valley degeneracy. The Hall conductance \( \sigma_{xy} \) in high quality 2DEGs has been shown to quantize to \( \sigma_{xy} = je^2/\hbar \), a phenomenon known as the quantum Hall effect[33, 34]. The quantization of \( \sigma_{xy} \) is associated with a vanishing of longitudinal conductance \( \sigma_{xx} \).

Monolayer graphene hosts a unconventional 2DEG - one with non-quadratic band structure. Owing to their linear dispersion, the electrons in a monolayer graphene show an unconventional integer quantum Hall effect[8, 9]. In this section, we derive the energy spectra in 1LG under an applied perpendicular magnetic field in order to better understand magnetoresistance oscillations presented in Sects. 5 and 7.

Under an applied magnetic field \( \vec{H} = H \hat{z} \), where \( \hat{z} \) points perpendicular to the graphene plane, the momentum \( \vec{p} \) of an electron is modified as \( \vec{p} \rightarrow \vec{p} + e \vec{A} \), where \( \vec{A} \) is the vector potential determined by \( \vec{H} = \nabla \times \vec{A} \), allowing freedom to choose any appropriate gauge. In the following, we choose the symmetric gauge, where \( \vec{A} = -\frac{H}{2} y \hat{x} + \frac{H}{2} x \hat{y} \). This choice modifies the momenta of Dirac fermions as:

\[
\begin{align*}
\hbar k \rightarrow & \ h \sum_i (k_i + \frac{e}{c} A_i) = \hbar k_x - \frac{eH}{2c} y + i(\hbar k_y + \frac{eH}{2c} x) \\
\hbar k^* \rightarrow & \ h \sum_i (k_i^* + \frac{e}{c} A_i) = \hbar k_x - \frac{eH}{2c} y - i(\hbar k_y + \frac{eH}{2c} x),
\end{align*}
\]  

(2.10)
where $e$ is the elementary charge and $c$ the speed of light. Employing the quantum mechanical definition of the momentum operator, $\vec{p} = \hbar \vec{k} = \frac{\hbar}{i} \partial_x$, and rearranging terms, we obtain

$$\begin{align*}
\hbar k &\to -i\hbar ((\partial_x - i\partial_y) - \frac{1}{2} \frac{eH}{\hbar c} (x + iy)) \\
\hbar k^* &\to -i\hbar ((\partial_x + i\partial_y) + \frac{1}{2} \frac{eH}{\hbar c} (x - iy)).
\end{align*}$$

(2.11)

Following Ref. [35], we define the complex variable $z = (x - iy)$. A derivative with respect to complex variable $z$ is, noting $\text{Re}[z] = \frac{z + z^*}{2}$ and $\text{Im}[z] = \frac{z - z^*}{2}i$, given by

$$\partial_z = \frac{\partial \text{Re}[z]}{\partial z} \partial_{\text{Re}[z]} + \frac{\partial \text{Im}[z]}{\partial z} \partial_{\text{Im}[z]} = \frac{1}{2} (\partial_x - i\partial_y).$$

This result, with a similar expression for $\partial_z^*$, reformulates Eq. 2.11:

$$\begin{align*}
\hbar k &\to i\hbar (\frac{1}{2\ell^2_B} z^* - 2\partial_z) \\
\hbar k^* &\to -i\hbar (\frac{1}{2\ell^2_B} z + 2\partial_{z^*}).
\end{align*}$$

(2.12)

where $\ell_B \equiv (\frac{\hbar c}{eH})^\frac{1}{2}$ is the magnetic length. The above expression is conveniently in terms of the operators:

$$\begin{align*}
a^\dagger &= \frac{1}{\sqrt{2}} (\frac{1}{2\ell^2_B} z^* - 2\ell_B \partial_z) \\
a &= \frac{1}{\sqrt{2}} (\frac{1}{2\ell^2_B} z + 2\ell_B \partial_{z^*}).
\end{align*}$$

The operator $a^\dagger a$ is Hermitian; we define it as the number operator, such that for an electron wavefunction $\psi_n$, $a^\dagger a |\psi_n\rangle = n |\psi_n\rangle$. Since $a^\dagger$ and $a$ follow the commutation rule $[a, a^\dagger] = 1$, but follows straightforwardly that $a^\dagger |\psi_n\rangle = \sqrt{n + 1} |\psi_{n+1}\rangle$ and $a |\psi_n\rangle = \sqrt{n} |\psi_{n-1}\rangle$. They are therefore raising and lowering operators where $n$ is the index. Expressed in terms of these operators, our momenta are
\[ h \hat{k} \rightarrow i \frac{\sqrt{2} \hbar}{\ell_B} a^\dagger \]  
\[ h \hat{k}^* \rightarrow -i \frac{\sqrt{2} \hbar}{\ell_B} a \]  
(2.13)

From Eq. 2.7, the Hamiltonian for finite magnetic field \( \vec{H} \) is:

\[ \mathcal{H}_{\vec{H}} = \frac{i \hbar v_F \sqrt{2}}{\ell_B} \begin{pmatrix} 0 & -a \\ a^\dagger & 0 \end{pmatrix} \]  
(2.14)

The eigenfunctions \( \psi \) of this Hamiltonian are expressed in terms of weighted, integer-indexed \((m,n)\) wavefunctions:

\[ \mathcal{H}_{\vec{H}} \psi = \frac{i \hbar v_F \sqrt{2}}{\ell_B} \begin{pmatrix} 0 & -a \\ a^\dagger & 0 \end{pmatrix} \begin{pmatrix} c_m |\psi_m\rangle \\ c_n |\psi_n\rangle \end{pmatrix} = E \begin{pmatrix} c_m |\psi_m\rangle \\ c_n |\psi_n\rangle \end{pmatrix} \]

Carrying out the above operations, we obtain:

\[ -\frac{i \hbar v_F \sqrt{2}}{\ell_B} c_n \sqrt{n} |\psi_{n-1}\rangle c_m E |\psi_m\rangle \]

\[ \frac{i \hbar v_F \sqrt{2}}{\ell_B} c_m \sqrt{m+1} |\psi_{m+1}\rangle c_n E |\psi_n\rangle. \]

We solve the above equations for the eigenstates of \( \mathcal{H} \) and \( E \):

\[ \psi = \frac{1}{\sqrt{2}} \begin{pmatrix} |\psi_{nLL}\rangle \\ |\psi_{nLL+1}\rangle \end{pmatrix}, \pm |E_{nLL}| = \pm v_F \sqrt{2eHn_{LL}/c}, \]
(2.15)

where \( n_{LL} = 0,1,2 \ldots \) The above expressions describe wavefunctions for electrons that populate discrete energy states, called Landau levels. The monolayer graphene energy spectrum differs from conventional 2DEGs in that each Landau level is not evenly spaced in energy, and that there exists a Landau level at zero energy. Quantized Hall conductivity can be observed experimentally by applying a perpendicular field and measuring Hall conductivity as magnetic field strength or carrier density is tuned by various means. The emergent Landau levels quantize the Hall conductivity at steps of \( \frac{g e^2}{h} \) as the carrier density becomes equal to integer multiples of the Landau level degeneracy \( N_L = gH/\phi_0 \)[34]. Here, \( g = 4 \) is the electron de-
generacy including double spin and double band (at the $K$- and $K'$-points), and
\[ \phi_0 = 4.14 \times 10^{-15} \text{ T m}^2 \] is the magnetic flux quantum. A comparison of Landau level spectra and Hall conductivity between a 2DEG, a graphene monolayer, and a graphene bilayer is shown in Fig. 2.2.2.

### 2.2 Bilayer graphene band structure

#### 2.2.1 Tight-binding calculations of electronic band structure

A graphene bilayer consists of two stacked monolayers. The natural stacking, and most energetically favorable, is Bernal stacking, shown in Fig. 2. In this arrangement, the two layers are separated by about 3.35 Å[1], with an A atom in the top layer directly above a B atom in the bottom layer. In this work, the A (B) atoms in the bottom layer are referred to as $A_1$ ($B_1$) atoms, and in the top layer as $A_2$ ($B_2$) atoms; the Bernal stacking is thus also called "$A_2 - B_1$" stacking. The bilayer graphene lattice is built two-dimensionally (only planar translations of a three-dimensional unit cell) by the same lattice vectors as in 1LG (Eq. 2.1), with four atoms per unit cell.

We investigate the electronic energy bands of bilayer graphene with a tight-binding approach. We can set up the tight-binding Hamiltonian by considering nearest neighbor hopping terms between $A_1, B_1, A_2,$ and $B_2$ atoms:

\[
H = \gamma_0 \sum_{i,s} (c_{A_1,i,s}^\dagger c_{B_1,i,s} + c_{A_2,i,s}^\dagger c_{B_2,i,s} + \text{c.c.}) \\
+ \gamma_1 \sum_{i,s} (c_{A_2,i,s}^\dagger c_{B_1,i,s} + \text{c.c.}) \\
+ \gamma_2 \sum_{i,s} (c_{A_1,i,s}^\dagger c_{B_2,i,s} + \text{c.c.}) \\
+ \gamma_3 \sum_{i,s} (c_{A_1,i,s}^\dagger c_{A_2,i,s} + \text{c.c.}) \\
+ \gamma_4 \sum_{i,s} (c_{B_1,i,s}^\dagger c_{B_2,i,s} + \text{c.c.})
\]

(2.16)
Figure 2.3. a) Drawing of several unit cells of bilayer graphene with representative atoms of the four sublattices labelled; b) Top-down view of the bilayer graphene lattice. Closed (open) circles refer to atoms in the bottom (top) layer, and blue (red) refers to the A (B) sublattice. The lattice vectors $\vec{a}_1$ and $\vec{a}_2$ are the same as in monolayer.

where $c_{X_{j,i,s}}^\dagger$ and $c_{X_{j,i,s}}$ are as defined in Sect. 2.1.1. The coefficient $\gamma_0$ is the in-plane hopping energy between $A - B$ atoms in each layer, $\gamma_1$ is the inter-plane hopping energy between the $A_2 - B_1$ atoms directly above/below each other, $\gamma_2$ is the inter-plane hopping energy between atoms $A_1$ and $B_1$ or $B_2$, $\gamma_3$ is the inter-plane hopping energy between atoms $A_1$ and $A_2$, and $\gamma_4$ is the inter-plane hopping between atoms $B_1$ and $B_2$.

The relative magnitudes of the hopping energy coefficients have already been ordered from strongest to weakest. These values can be determined by matching the tight binding results for graphite to spectroscopic measurements of the band structure[1, 3, 32]. $\gamma_0$, by far the largest, $\approx 2.8$ eV, then $\gamma_1 \approx 0.35$ eV, $\gamma_2 \approx 0.3$ eV, and finally $\gamma_3$ and $\gamma_4 \approx 0.2$ eV. To simplify this tight-binding treatment, we respect all but the two weakest hopping terms, $\gamma_3$ and $\gamma_4$.

We are interested in the electronic band structure about the $K$-point in bilayer graphene. The reciprocal lattice is identical to that for monolayer (Fig. 2.1b, with lattice vectors given in Eq. 2.4. Again, as in monolayer, the valence and conduction bands of bilayer graphene meet at the six corners of the Brillouin zone,
the $K$- and $K'$-points. In the continuum limit, the components of the tight-binding Hamiltonian in Eq. 2.16 are reformulated about the $K$-point, $k_K = \frac{2\pi}{3a}(\hat{x} + \frac{1}{\sqrt{3}}\hat{y})$:

$$H_j = \gamma_j \sum_i e^{i((\vec{k} + \vec{k}) \cdot \vec{\delta}_i)} = \gamma_j \sum_i e^{i(\frac{2\pi}{3a} + k_x) \delta_{i,j,x} + (\frac{2\pi}{3\sqrt{3}a} + k_y) \delta_{i,j,y}}$$

(2.17)

where $\vec{\delta}_{i,j}$ are the positions of the nearest neighbors of a particular hopping and $\vec{k}$ is a small displacement from $\vec{k}_K$ in reciprocal space. Each term is evaluated separately, below.

- **$A_1$-$B_1$, $A_2$-$B_2$ hopping:** The in-plane nearest neighbor hopping problem is the same as in monolayer and is solved in Sect. 2.1.1. The result, applied here, is

$$\mathcal{H}_{A_i-B_i} = \hbar v_F (k_x - ik_y)$$

$$\mathcal{H}_{B_i-A_i} = \mathcal{H}^{*}_{A_i-B_i}$$

(2.18)

where $|v_F| \equiv \frac{2}{3}a\gamma_0$ is the Fermi velocity in monolayer graphene.

- **$A_2$-$B_1$ hopping:** This involves inter-plane hopping directly above or below to the neighbor, from below, located at $\vec{\delta} = \frac{c}{a}\hat{z}$. Therefore, the tight-binding contribution is trivially

$$H_{A2-B1} = H_{B1-A2} = \gamma_1.$$  

(2.19)

vspace5 mm

- **$A_1$-$B_2$ hopping:** Hopping between these atoms involves an inter-plane hop that is offset by the $\hat{x}$-reversed in-plane nearest neighbor vectors. Here, $\delta_i$ are given by

$$\vec{\delta}_{1,2} = \frac{a}{2}(-\hat{x} \pm \sqrt{3}\hat{y}) + \frac{c}{2}\hat{z}$$

$$\vec{\delta}_3 = a\hat{x} + \frac{c}{2}\hat{z}.$$  

These differ from $\delta_i$ in $B_1 - A_1$ and $B_2 - A_2$ hopping only by the addition of the $\frac{c}{2}\hat{z}$ term, of which the tight-binding Hamiltonian is independent (Eq. 2.17). Therefore, the results have similar form:
\[ H_{A_1-B_2} = -i \frac{3}{2} a \gamma_2 (k_x - i k_y) = \hbar (v_2 k)^* \]
\[ H_{B_2-A_1} = i \frac{3}{2} a \gamma_2 (k_x + i k_y) = \hbar v_2 k \]  

(2.20)

where \( |v_2| = \frac{3}{2} a \gamma_2 \) in the same spirit of \( v_F \).

Applying effective velocities as coefficients follows the work of E. McCann and V. Fal’ko [36], generally referred to as the Slonczewski-Weiss-McClure parametrization of Bernal-stacked graphite [2, 3]. Having derived the relevant contributions to the tight-binding Hamiltonian, we can now construct the Hamiltonian matrix in the basis of wavefunctions within each of the four sublattices. We again set the self energy of each wavefunction component to be a reference equal to zero. We also allow for a potential \( V \) between the two layers, applying \( +V/2 \) to the top and \( -V/2 \) to the bottom layer, which we can set to zero in a neutral, unbiased bilayer. Using the basis notation \( \psi : \{ \psi_{A_1}, \psi_{B_2}, \psi_{A_2}, \psi_{B_1} \} \), we have

\[
H = \begin{pmatrix}
  -V/2 & \hbar v_2 k & 0 & \hbar (v_f k)^* \\
  \hbar (v_2 k)^* & V/2 & \hbar v_f k & 0 \\
  0 & \hbar (v_f k)^* & V/2 & \gamma_1 \\
  \hbar v_f k & 0 & \gamma_1 & -V/2
\end{pmatrix}.
\]

(2.21)

We solve the energy eigenvalues of Eq. 2.21 from two perspectives. First, we directly compute the eigenvalues to reveal the general electronic band structure of bilayer graphene about the \( K \)-point. Second, we will zoom in to the low energy band to examine more closely the structure at the Fermi level.

We start from \( H|\psi\rangle = E|\psi\rangle \), and convert \( \vec{k} \) to complex polar coordinates: \( k = ke^{i\theta} \). The energy eigenvalues are:

\[
E_\pm^2 = \frac{\gamma_1^2}{2} + V^2 + (\hbar^2 v_F^2 + \frac{\hbar^2 v_2^2}{2})|k|^2 \\
\pm \sqrt{ \left( \frac{(\gamma_1^2 - \hbar^2 v_2^2|k|^2)^2}{4} + \hbar^2 v_F^2 |k|^2 (\gamma_1^2 + 4V^2 + \hbar^2 v_2^2 |k|^2) + 2\gamma_1 \hbar^3 v_2 v_F^2 |k|^3 \cos 3\phi \right)}.
\]

(2.22)
Figure 2.4. Energy bands of bilayer graphene calculated from Eq. 2.22 for a) interlayer bias $V = 0$, up to $|k| = 0.1$ Å$^{-1}$, b) $V = 0$, up to $|k| = 0.01$ Å$^{-1}$, c) $V = 100$ meV, up to $|k| = 0.1$ Å$^{-1}$, and d) $V = 100$ meV, up to $|k| = 0.05$ Å$^{-1}$.

Equation 2.22 defines four bands (two valence and two conduction) plotted in Fig. 2.4a for zero interlayer bias $V$. Simply by adding a second layer of graphene, the band structure has dramatically change from a linear dispersion to hyperbolic. Close to the Fermi energy the lowest two bands are roughly parabolic, but far away vary linearly. Zooming in at their intersection in Fig. 2.4b, tight-binding predicts a slight trigonal warping and band finite band overlap, which agrees with LDA calculations for bilayer graphene [37].

With finite interlayer bias $V$, an energy gap appears at the Fermi energy. The width of this bandgap is equal to $V$ at $k = 0$, and has a minimum value on the same order. The higher energy bands shift by $V/2$ but their form does not change significantly. The prospect of opening a bandgap by interlayer bias in bilayer graphene is very interesting from a devices perspective; by controlling the relative potentials (or charge concentration) of the top and bottom layer with a transverse electric field, one obtains a semiconductor with a tunable band gap that can be useful for a variety of transistor or photon absorption applications.

Electron transport in bilayer graphene is governed mostly by the low-energy band structure about the Fermi level at the K-point. From here on, we focus only the lower energy bands and the bandgap. Since Eq. 2.21 contains information about the higher energy bands as well, we use a Green’s function technique to construct a new Hamiltonian related only to $\psi_{A1}$ and $\psi_{B2}$, the lower band states[22].
This method is equivalent to eliminating components $\psi_A$ and $\psi_B$ by substitution between the four equations given by $H|\psi\rangle = E|\psi\rangle$ and Eq. 2.21[38]. We begin by splitting up the Hamiltonian into four quadrants, having the form

$$
H_{11} \equiv \begin{pmatrix} -V/2 & v_2k \\ (v_2k)^* & V/2 \end{pmatrix} \quad H_{12} \equiv \begin{pmatrix} 0 & (v_Fk)^* \\ v_Fk & 0 \end{pmatrix}
$$

$$
H_{21} = H_{12} \quad H_{22} \equiv \begin{pmatrix} V/2 & \gamma_1 \\ \gamma_1 & -V/2 \end{pmatrix}.
$$

We have

$$
H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}.
$$

(2.23)

We then define the Green’s function $G \equiv (H - E')^{-1}$, where $E'$ is small, and the 2 X 2 matrix component $G_{11,22} = (H_{11,22} - E')^{-1}$. It follows:

$$
(H - E')^{-1} = \begin{pmatrix} H_{11} - E' & H_{12} \\ H_{21} & H_{22} - E' \end{pmatrix}^{-1}
$$

$$
= \begin{pmatrix} G^{-1}_{11} & H_{12} \\ H_{21} & G^{-1}_{22} \end{pmatrix}^{-1} \equiv \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} = G.
$$

(2.24)

The element $G_{11}$ contains information only on the lowest energy band states, and is evaluated by performing the inverse shown above:

$$
G_{11} = \frac{G^{-1}_{22}}{G^{-1}_{11}G^{-1}_{22} - H_{12}H_{21}} = \frac{G_{11}}{G_{11}} \frac{G^{-1}_{22}}{G^{-1}_{11}G^{-1}_{22} - H_{12}H_{21}} \frac{G_{22}}{G_{22}}
$$

$$
= \frac{G_{11}}{1 - G_{11}H_{12}H_{21}G_{22}}.
$$

Inverting this result and adding $E'$ to both sides gives

$$
G^{-1}_{11} + E' = G^{-1}_{11} + E' - H_{12}G_{22}H_{21} = H_{11} - H_{12}G_{22}H_{21}.
$$

(2.25)
Evaluating Eq. 2.25 gives an effective 2 x 2 Hamiltonian \( \mathcal{H}_{A_1 - B_2} = G_{11}^{-1} + E' \) that describes the effective hopping between \( A_1 \) and \( B_2 \) atoms. We evaluate \( G_{22} \) for \( \gamma_1 \gg E', V \), which is reasonable at low energies. We obtain

\[
G_{22} = \frac{1}{E'^2 - V^2/4 - \gamma_1^2} \begin{pmatrix}
-V/2 - E' & -\gamma_1 \\
-\gamma_1 & V/2 - E'
\end{pmatrix}
\]

\[
\approx \frac{1}{\gamma_1^2} \begin{pmatrix}
V/2 + E' & \gamma_1 \\
\gamma_1 & -V/2 + E'
\end{pmatrix}
\]

and

\[
H_{12} G_{22} H_{21} = \frac{\hbar^2 v_F^2}{\gamma_1^2} \begin{pmatrix}
0 & k^* \\
k & 0
\end{pmatrix} \begin{pmatrix}
V/2 + E' & \gamma_1 \\
\gamma_1 & -V/2 + E'
\end{pmatrix} \begin{pmatrix}
0 & k^* \\
k & 0
\end{pmatrix} = \frac{\hbar^2 v_F^2}{\gamma_1} \begin{pmatrix}
0 & \gamma_1 k^2 (V/2 + E') \\
k^* & \gamma_1 k^2 (V/2 + E')
\end{pmatrix}.
\]

We have

\[
\therefore \mathcal{H}_{A_1 - B_2} \equiv G_{11}^{-1} + E' \approx \left( \frac{V}{2} (-1 + \frac{\hbar^2 v_F^2}{\gamma_1^2} |k|^2) \right) \left( \hbar v_2 k - \frac{\hbar^2 v_F^2}{\gamma_1} (k^*)^2 \right) \left( \frac{V}{2} \left( 1 - \frac{\hbar^2 v_F^2}{\gamma_1} |k|^2 \right) \right).
\]

In this simplified form, we can analyze the key features of the low-energy Hamiltonian. In an intermediate range of \( k \), slightly above the Fermi level, the terms of order \( k^2 \) dominate, and with zero interlayer bias, the Hamiltonian simplifies to

\[
\mathcal{H}_{A_1 - B_2}^0 = -\frac{\hbar^2}{2m} \begin{pmatrix}
0 & (k^*)^2 \\
k^2 & 0
\end{pmatrix},
\]

where \( m \equiv \frac{\gamma_1}{2v_F^2} \). The energy eigenvalues of this Hamiltonian are \( E_{\text{int.}}^0 = \pm \hbar^2 k^2/2m \), thus electrons in unbiased bilayer graphene behave as a free electron gas just above the Fermi level, whose density of states is constant with energy and equal to \( N_{2LG} = \pi \hbar^2/2m \). The Hamiltonian \( \mathcal{H}_{A_1 - B_2}^0 \) describes much of the transport phenomena in...
Figure 2.5. a) Cross section of the low energy band structure of bilayer graphene determined by the eigenvalues of Eq. 2.26 for zero applied bias $V$; b) Finite $V$ opens up an energy gap of minimum value $\Delta_{\text{min}}$; c) Calculated $\Delta_{\text{min}}$ vs. $V$; the dashed line is $V$.

bilayer graphene related to band structure, including its own anomalous quantum Hall effect, derived below. Including the linear $v_2$ term adds asymmetry and overlap to the bands, resulting in the trigonal warping that dominates low energy (Fig. 2.4b). Finally, including a finite $V$ shifts each band at $k = 0$ by $\pm V/2$, and adds an opposite quadratic dispersion contribution that gives the energy gap a minimum value slightly less than $V$. The relationship between minimum gap value $\Delta_{\text{min}}$ and $V$ is shown in Fig. 2.2.1. In this work, interlayer biases of $< 100$ meV are likely in experiment, where $\Delta_{\text{min}} \approx V$.

An interlayer bias can be controlled using external top and bottom electric field effect gates. However, our derivation did not take into account screening effects. At zero net carrier density, electrons and holes distribute unevenly between the top and bottom layer to minimize energy, and the resulting electric field screening is finite. When screening is taken into account, the energy gap opened in the density of states is equal to roughly 30% of the applied bias, depending on the dielectric constant of bilayer graphene[23, 39], and will certainly differ experimentally between samples with different levels of charge inhomogeneity.

2.2.2 Finite magnetic field

In a perpendicular magnetic field, bilayer graphene also exhibits an unconventional quantum Hall effect. While quadratic electron dispersion leads to the same spacing
between Landau levels as that of a 2DEG, its electrons are similar to monolayer in that they are chiral (low energy wavevectors are predominantly either on inequivalent A$_1$ or B$_2$ sites). Their chirality leads to two Landau levels forming at zero energy and a doubly-large Hall conductance step as the Fermi level is varied through zero[22, 21]. We derive the Landau level spectrum by following a similar procedure as that for monolayer in Sect. 2.1.2. We apply a perpendicular magnetic field $H$ and, using the symmetric gauge for the vector potential, we reformulate the low energy Hamiltonian in Eq. 2.27 with the magnetic field-modified momenta in terms of raising and lowering operators from Eq. 2.13:

$$\mathcal{H}_{A_1-B_2} = \frac{\hbar^2}{m\ell_B^2} \begin{pmatrix} 0 & (a)^2 \\ (a^\dagger)^2 & 0 \end{pmatrix}$$

$$= \hbar \omega_c \begin{pmatrix} 0 & (a)^2 \\ (a^\dagger)^2 & 0 \end{pmatrix},$$

(2.28)

where $\omega_c \equiv \frac{eH}{m}$ is the cyclotron frequency. The eigenfunctions $\psi$ can be expressed again as integer-indexed $(m,n)$ wavefunctions:

$$\mathcal{H}_{A_1-B_2} \psi = \hbar \omega_c \begin{pmatrix} 0 & (a)^2 \\ (a^\dagger)^2 & 0 \end{pmatrix} \begin{pmatrix} c_n |\psi_m\rangle \\ c_m |\psi_n\rangle \end{pmatrix} = E \begin{pmatrix} c_m |\psi_m\rangle \\ c_n |\psi_n\rangle \end{pmatrix}.$$

Carrying out the above operations, we obtain (see Sect. 2.1.2)

$$\hbar \omega_c (a)^2 c_n |\psi_n\rangle = \hbar \omega_c c_n \sqrt{n(n-1)} |\psi_{n-2}\rangle = c_m E |\psi_m\rangle$$

$$\hbar \omega_c (a^\dagger)^2 c_m |\psi_m\rangle = \hbar \omega_c c_m \sqrt{(m+1)(m+2)} |\psi_{m+2}\rangle = c_n E |\psi_n\rangle.$$

We solve these equations for the eigenstates of $\mathcal{H}$ and energy eigenvalues $E$:

$$\psi = \frac{1}{\sqrt{2}} \begin{pmatrix} |\psi_{n_{LL}-2}\rangle \\ |\psi_{n_{LL}}\rangle \end{pmatrix}, \pm |E_{n_{LL}}\rangle = \pm \hbar \omega_c \sqrt{n_{LL}(n_{LL}-1)},$$

(2.29)

where $n_{LL} = 0,1,2, \ldots$ is the Landau level index. The result differs from that of the conventional case where $E_{n_{LL}} \propto n_{LL}$, but their respective energy spacings both converge, for large $n_{LL}$, to $\hbar \omega_c$. It differs mostly due to the doubly degenerate
Figure 2.6. Sketch of the density of states (DOS) vs. energy $E$, with Landau levels represented by Gaussian peaks, and simulated Hall conductivity $\sigma_{xy}$ vs. carrier density $n$ for a) a conventional two-dimensional electron gas, b) monolayer graphene, c) bilayer graphene. Energy axes are scaled equally.

Landau level ($n_{LL} = 0, 1$) at zero energy, which can be observed as a jump in the Hall conductivity quantization by $8e^2/h$ as the Fermi level is varied through zero, rather than $4e^2/h$ through every other level.

We show in Fig. 2.2.2 a comparison of the quantum Hall effect in a conventional 2DEG and in bilayer graphene. As shown, the energy spacing between levels in 1LG is much greater than that of 2LG. For example, at $H = 8$ T, $E_{n_1} \approx (93 \text{ meV}) \sqrt{n_1}$ while $E_{n_2} \approx (12 \text{ meV}) \sqrt{n_2(n_2 - 1)}$, assuming for the latter $m = \frac{m_e}{2v_F} \approx 0.08m_e$. If the interlayer bias $V$ is finite, the degeneracy between states in either layer is broken. This causes the zero energy Landau level in bilayer graphene to split about zero and open an energy band gap. The measured Hall conductivity as a function of carrier density is then identical to that of a conventional 2DEG[23, 40].

2.3 Charged impurities

2.3.1 Doping and charge puddles

We seek to understand how the presence of charged impurities in the local environment of graphene affects charge carriers in graphene. These scatterers take the form of surface adsorbates or dangling bonds or local impurities in the substrate or top-gate dielectric. Following Ref. [41], we consider a density $n_i$ of only one species
of adsorbates located a distance \( d \) perpendicular to the graphene to simplify the treatment. We also assume that each impurity has net charge of \( e \), the charge of an electron. The random potential fluctuation induced at the graphene by such a density is given by

\[
(\delta V)^2 = n_i \int \frac{d^2 q}{(2\pi)^2} \left( \frac{V(\vec{q}, d)}{\epsilon(\vec{q})} \right)^2,
\]

where \( \vec{q} = \vec{k} - \vec{k}' \) is the transfer momentum due to a Coulomb interaction elastically scattering an electron in state \( \vec{k} \) to state \( \vec{k}' \), \( V(\vec{q}, d) \) is the Fourier transform of the Coulomb potential between \( n_i \) and the electrons in graphene, and \( \epsilon(\vec{q}) \) is the dielectric function of graphene. The Coulomb potential of a single impurity is expressed\[42\]

\[
V(\vec{q}, d) = \frac{e}{2\epsilon_l \epsilon_0} \frac{e^{-qd}}{|q|},
\]

where \( \epsilon_l \) is the dielectric constant of the local environment and \( \epsilon_0 \) the permittivity of free space. In the case two different local dielectrics with constants \( \epsilon_{l,1} \) and \( \epsilon_{l,2} \), such as for a substrate and top-gate dielectric or vacuum, a half-space approximation gives \( \epsilon_l = (\epsilon_{l,1} + \epsilon_{l,2})/2 \). The following approximation is used for \( \epsilon(\vec{q}) \):

\[
\epsilon(\vec{q}) = \begin{cases} 
1 + \frac{4k_F r_s}{q} & q < 2k_F, \\
1 + \pi r_s/2 & q < 2k_F,
\end{cases}
\]

\[
r_s = \frac{e^2}{4\pi \epsilon_l \epsilon_0 \hbar v_F}.
\]

The value \( r_s \) is a dimensionless coupling constant. Eq. 2.32 was found in Ref. [41] to be indistinguishable in its use from the complete random phase approximation (RPA) for \( \epsilon(\vec{q})\)[43]. The integral in Eq. 2.30 can then be analytically solved to obtain the result in Ref. [41]:

\[
(\delta V)^2 = n_i \frac{e^2}{2\epsilon_l \epsilon_0} \int \frac{d^2 q}{(2\pi)^2} \frac{e^{-2qd}}{q^2 \epsilon(\vec{q})^2} = 2\pi n_i \frac{e^2}{(4\pi \epsilon_l \epsilon_0)^2} C_0(r_s, a = 4k_F d),
\]

where \( C_0 \) is a constant depending on the dielectric function of the graphene.
\[
C_0(r_s, a) = -1 + \frac{4E_1[a]}{(2 + \pi r_s)^2} + \frac{2e^{-a r_s}}{1 + 2r_s} + (1 + 2r_s a) e^{2r_s} (E_1[2r_s a] - E_1[a(1 + 2r_s)]),
\]

Equation 2.33 gives the square amplitude of voltage fluctuations due to a charge impurity density \(n_i\). To relate this to the induced carrier density fluctuation amplitude \(n^*\) in graphene, we solve \(e^2(\delta V)^2 = E_F^2\), where \(E_F\) is the Fermi level in graphene given by Eq. 2.8, for carrier density \(n = n^*\):

\[
n^* = 2n_i \frac{e^4}{\hbar^2 v_F^2 (4\pi \epsilon_\text{r}\epsilon_0)^2} C_0(r_s, 4d\sqrt{\pi n^*}) = n_i(2r_s^2 C_0(r_s, 4d\sqrt{\pi n^*})).
\]  

Equation 2.34

The average shift in carrier density \(\bar{n}\) is equal to the added density at which the average potential \(\bar{V}\) is zero. The value of \(\bar{V}\) is estimated by impurity density divided by the density of states evaluated at the fluctuation amplitude[44]:

\[
\bar{V} = n_i \left(\frac{dn}{dE}\right)^{-1}_{n=n^*} = \frac{\sqrt{\pi}}{2} \hbar v_F \frac{n_i}{\sqrt{n^*}}.
\]

Equating \(e^2\bar{V}^2\) to \(E_F(\bar{n})^2\), we obtain

\[
\bar{n} = \frac{n_i^2}{4n^*}.
\]  

Equations 2.34 and 2.35 give the amplitude of carrier density fluctuations and the average doping level, respectively. In Table 2.1, we show calculated values for several experimentally relevant dielectric environments and impurity densities. Carrier density fluctuations have been resolved as “charge puddles” in graphene in previous scanning probe microscopy experiments on graphene supported by a substrate[45, 46, 47, 48]. In gated transport experiments, \(n\) varies linearly with applied gate voltage \(V_G\). Given a simple Drude model for conductivity \(\sigma \propto n\), one would naively expect that \(\sigma\) will also vary linearly as \(V_G\) charges the sample from electron to hole carriers, and furthermore \(n = 0\) when \(V_G = 0\). However, due to the presence of charged impurities, \(V_G\) must be tuned by \(\bar{V}_G\) to compensate \(\bar{n}\) and the fluctuations \(n^*\) give the minimum conductivity a finite value \(\sigma_{\text{min}}\) that roughly
Figure 2.7. Conductivity $\sigma$ vs. gate voltage $V_G$ and gate-induced carrier density $n_G$ in a field effect device fabricated on 1LG supported by 300 nm SiO$_2$. The significance of annotated values are discussed in the text. The blue dashed line marks the linear regime that follows the Drude model for constant carrier mobility. The value $n_G$ was calculated for 300 nm SiO$_2$ giving $n_G = (7.2 \times 10^{10} \text{ cm}^{-2} ) \times V_G$.

plateaus with voltage width $\Delta V_G$. Essentially, the fluctuations put a lower bound on carrier density at the “charge neutrality point”, such that although average $n = 0$, average $|n| \neq 0$. While $\sigma_{\text{min}}$ is discussed further below, an example the manifestation of $V_G$ and $\Delta V_G$ is shown in the transport of a field effect transistor prepared on 1LG in Fig. 2.7. For bilayer graphene, the effects of charged impurities are qualitatively similar, but weaker ($n^* \propto \sqrt{n_i}$) due to improved screening and a different electronic dispersion[49].

2.3.2 Scattering

Coulomb interactions with charged impurities in the local environment not only induce potential fluctuations in graphene, but also scatter carriers which, as a result, conduct less easily. With an applied electric field $\vec{E}$, the total current density $\vec{J}$ in a material is

$$\vec{J} = \sigma \vec{E},$$

(2.36)
Table 2.1. Theoretically calculated values of the coupling constant $r_s$, and charge puddle amplitude $n^*$ and doping level $\bar{n}$ for different impurity densities $n_i$, using Eqs. 2.34 and 2.35. Relevant half-space dielectrics are considered, where dielectrics constants for vacuum = 1, SiO$_2$ = 3.9, AlO$_x$ = 7.5 (amorphous), SiC = 9, and HfO$_2$ = 25. The impurity density was considered to be at a distance of 3 Å.

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<th>$r_s$</th>
<th>$n_i$</th>
<th>$n^*$</th>
<th>$\bar{n}$</th>
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<td></td>
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<td>30</td>
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<td>1000</td>
<td>430</td>
<td>580</td>
</tr>
</tbody>
</table>
where $\sigma$ is the electrical conductivity. A simple Drude model for conductivity expresses the conductivity of one species of charge carrier as

$$\sigma = \mu ne$$

(2.37)

where $\mu$ is the mobility, is a property of the conducting material, and is proportional to the mean free path of carriers. The mean free path can be expressed as the product of the Fermi velocity $v_F$ of the carrier and the relaxation time $\tau(\vec{k})$, the time between scattering events. Semi-classical theory of conduction in metals leads to an expression for two-dimensional conductivity in metals for a single band[50]:

$$\sigma^{(j)} = 2e^2 \int \frac{d^2k}{(2\pi)^2} \tau_j(\vec{k})v_j(\vec{k})v_j(\vec{k}) \left( \frac{\partial f}{\partial E} \right)_{E=E_j(\vec{k})}$$

(2.38)

where $j$ denotes the $j$th band and we integrate over all electron wavevectors $\vec{k}$. The factor of 2 takes into account spin degeneracy, $v_n(\vec{k})$ is the carrier velocity, and $f(E)$ is the Fermi function. In the case of graphene, the problem becomes fairly simplified. First, we have only two bands that contribute identically to conductivity. Second, the velocity of electrons graphene is constant for all $\vec{k}$ and is equal to $v_F$. To simplify things further, we evaluate at zero temperature $-\partial f/\partial E = \delta(E - E_F)$, where $\delta(E)$ is the Dirac-Delta function. Finite temperature will smear relevant energies on order $k_BT$, where $k_B$ is Boltzmann’s constant. In the zero temperature limit, only $\tau(k_F) = \tau$ is relevant, and we have

$$\sigma = \frac{e^2}{\pi^2} v_F^2 \int d^2k \delta(E - E_F) = \frac{2e^2}{\pi} \frac{E_F}{\hbar^2} \tau.$$  

(2.39)

The integral is performed simply by converting to polar coordinates and using $E(\vec{k}) = \hbar v_F k$. In order to evaluate how conductivity is affected by Coulomb scattering, we need to determine $\tau$. Using the Boltzmann equation for charge transport, $\tau$ is expressed[50]

$$\frac{1}{\tau(\vec{k})} = \sum_{\vec{k}'} T_{\vec{k} \rightarrow \vec{k}'}(1 - \cos \theta),$$

(2.40)

where $T_{\vec{k} \rightarrow \vec{k}'}$ is the probability per unit time that an electron with wavevector $\vec{k}$ is scattered to $\vec{k}'$, $\theta$ is the angle between $\vec{k}$ and $\vec{k}'$, and we sum over all $\vec{k}'$.  

We determine the scattering probability using Fermi’s golden rule for interactions with an impurity density $n_i$:

$$T_{\vec{k} \rightarrow \vec{k}'} = n_i \frac{2\pi}{\hbar} \left| \langle \vec{k}' | \mathcal{H}' | \vec{k} \rangle \right| ^2 \delta(E(\vec{k}) - E(\vec{k}')) ,$$

(2.41)

where $\mathcal{H}'$ is the Hamiltonian specific to the interaction. The Hamiltonian term is similar to the Coulomb potential in Eq. 2.31, with the following modification:

$$\left| \langle \vec{k}' | \mathcal{H}' | \vec{k} \rangle \right|^2 = \frac{e^2}{(2\epsilon_i\epsilon_0)^2} \frac{e^{-2qd}}{q^2\epsilon(\vec{q})^2} \frac{1 + \cos \theta}{2} ,$$

(2.42)

where $\vec{q} = \vec{k} - \vec{k}' = 2k_F \sin \theta$ can be shown geometrically at the Fermi level, and the $\theta$-dependent term reflects the prohibited back-scattering due to pseudo-spin conservation in graphene[10, 51]. We plug the expressions above into Eq. 2.40, and convert the sum into an integral over $\vec{k}$:

$$\frac{1}{\tau(\vec{k})} = \frac{\pi n_i}{2\hbar} \frac{e^2}{(4\pi\epsilon_0)^2} \int d^2q \frac{e^{-2qd}}{q^2\epsilon(\vec{q})^2} (1 - \cos \theta)^2 \delta(E(\vec{k}) - E(\vec{k}')) .$$

(2.43)

The integral in Eq. 2.43 can be solved exactly using the approximation Eq. 2.32. After plugging the result into Eq. 2.39, and using Eq. 2.8 to convert $E_F$ to $n$, the following result from Ref. [41] for conductivity is obtained:

$$\sigma = \frac{e^2}{h} \frac{n}{n_i G[2r_s]} ,$$

(2.44)

$$\frac{G[x]}{x^2} = \frac{\pi}{4} + 3x - \frac{3\pi x^2}{2} + \frac{x(3x^2 - 2 \arccos 1/x)}{\sqrt{x^2 - 1}}.$$ 

With Eq. 2.44, we determine $r_s$ for specific dielectrics, and can calculate theoretical $\mu = \sigma/ne$ as a function of impurity density. In Fig. 2.8, we show the dependence of $\mu$ on $n_i$ for several experimentally relevant dielectric environments. In uniform graphene on typical substrates, charged impurity scattering is by far the dominant scattering mechanism at low temperatures, as phonon interactions are negligible[52]. However, in highly disordered graphene, short-range scattering such as that from lattice dislocations must be taken into account, and can easily by the primary source mobility degradation[53, 54]. For multiple sources of scat-
Figure 2.8. Theoretically calculated inverse mobility $\mu^{-1}$ vs. impurity density $n_i$ from charged impurity scattering, as determined by Eqs. 2.44 and 2.37. Different combinations of half-space dielectrics are considered as labeled, where dielectrics constants for vacuum = 1, SiO$_2$ = 3.9, AlO$_x$ = 7.5 (amorphous), SiC = 9, and HfO$_2$ = 25.

Matthiessen’s rule can be applied in the relaxation time approximation, which gives $\tau^{-1} = \sum_i^{-1}$, summing up over all distinguishable scattering events types. Within this work, most of the graphene is within the non-disordered limit, such that the relaxation time for impurity scattering $\tau_{CIS} \ll \tau_i$ for all $i$. 
Chapter 3

Device preparation

In this chapter, we first describe the design of all electronic devices. The measurements of these are presented in the remainder of the thesis. We will cover specific details of the fabrication of these devices.

3.1 Device design

3.1.1 Electrical transport with field effect gating

We rely on electrical transport measurements to study many signatures of the electronic density of states in graphene. Four-point measurements, involving four separate electrical connections to the sample, are ideal as they ignore contributions by the electrical contacts themselves. However, two- and three-point measurements are also conducted regularly; in these devices, varying carrier density allows us to account for contact resistance, whose response is negligible. We tune carrier density and the Fermi level in samples by using electric field effect gating. By applying a voltage between an electrode in contact with the sample and an electrode separated from the sample by a dielectric, the sample is charged capacitively with two dimensional carrier density \( n \) (electrons per unit area), where

\[
    n = \frac{\varepsilon \varepsilon_0}{ed} V_G, \tag{3.1}
\]

where \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) the permittivity of free space, \( e \) the elementary charge, \( d \) the thickness of the dielectric, and \( V_G \) the applied gate voltage. In this
work, the positive polarity of $V_G$ is applied on the electrode away from the sample, such that positive $V_G$ charges the sample with electrons. For graphene gated through 300 nm silicon dioxide ($\epsilon = 3.9$), which is typical for substrate-supported flakes in this work, one volt of $V_G$ charges the graphene with $7.2 \times 10^{10}$ electrons cm$^{-2}$.

Important details are revealed by measuring the electrical resistance response $R$ to tuning the Fermi level in graphene. In both monolayer and bilayer graphene, as the carrier density is tuned to zero the electronic density of states vanishes and resistance peaks. Thus, by tuning voltage such that the resistance is maximized, we learn the extrinsic carrier density in our samples, which can be induced by local impurities and disorder. By tuning the carrier density through zero, we can study both hole and electron transport which feature roughly symmetric conductivities. Conductivity $\sigma = 1/R$ for a single carrier species in a two-dimensional system is given by the expression\[50\]

$$\sigma = \mu |n| e, \quad (3.2)$$

where $\mu$ is the “mobility” of charge carriers in the sample. It is related to scattering caused by interactions with disorder (see Sect. 2.3), and is often used as a measure of sample quality. In the Drude model, $\mu$ is proportional to the mean free path of an electron between scattering events. Experimentally, $\mu$ can be evaluated by field effect; we combine Eqs. 3.1 and 3.2 to obtain

$$\mu_{FE} = \frac{d \sigma}{\epsilon \epsilon_0 \frac{d}{dV_G}}, \quad (3.3)$$

where the subscript “FE” distinguishes it as having been measured by field effect. Thus, by varying $V_G$ and measuring $\sigma$, we calculate $\mu$ from the slope.

### 3.1.2 Hall bar structures

We use the classical Hall effect to measure charge carrier density and to determine, independently of field effect, carrier mobility. We turn on a finite magnetic field $H$ perpendicular to the sample and apply a current $I$ in one direction. The magnetic field curves electron and hole paths by a Lorentz force perpendicular to the direction of current and charge builds up on the edge of the sample. The charging
continues until the resulting Coulomb field perpendicular to the direction of \( I \) is large enough that the electric force on a charge carrier cancels the Lorentz force. That is, \( eV_{xy}/w = ev_d H \), where \( V_{xy} \) is the transverse voltage drop across the sample, \( w \) is the width of the sample, and \( v_d \) is the charge carrier drift velocity. Given \( I = enwv_d \) in two dimensions, we define the Hall coefficient \( R_H \):

\[
R_H^1 = \frac{V_{xy}}{IH} = (en_H)^{-1},
\]

(3.4)

where the superscript “1” notes a single carrier species, and the subscript \( H \) on \( n \) refers to it having been determined by Hall effect. The sign of \( R_H \) is distinguished for holes or electrons. For two carriers, the derivation of \( R_H \) follows the same strategy, and some algebra nets the following result:

\[
R_H^2 = \frac{V_{xy}}{IH} = \frac{n_h \mu_h^2 - n_e \mu_e^2}{e(n_h \mu_h + n_e \mu_e)},
\]

(3.5)

where \( \mu_{e,h}, n_{e,h} \) are electron and hole mobilities and carrier densities, respectively. In the single carrier limit, the mobility is determined by measuring conductivity at \( H = 0 \), and calculating

\[
\mu_H = \frac{\sigma}{ne} = \sigma |R_H|,
\]

(3.6)

where the subscript “H” distinguishes it as having been measured by Hall effect. In experiment, voltage leads contact the sides of a sample to measure \( V_{xy} \) in finite \( H \) and applied \( I \). Since there is likely to be some spatial offset parallel to the direction of current, it is good practice to measure \( V_{xy} \) at both positive and negative fields, and halve the difference. This subtracts off a longitudinal portion that should be even with \( H \). In this work, \( R_H \) is typically measured by holding \( I \) constant and sweeping \( H \). We then calculate \( R_H \) from the slope of \( V_{xy}(H) \) to ensure linearity. In gated experiments, a top gate electrode is deposited to cover the whole sample (separated by a dielectric), and a voltage \( V_G \) is applied between it and one current lead. Current \( I \) is kept low enough to keep the voltage drop along the sample to <1 meV, negligible compared to \( V_G \), in order to avoid non-uniform gating.
3.1.3 Planar tunnel junctions

Planar tunneling spectroscopy is useful in directly measuring the electronic density of states of a sample. The details of the technique are described in Sect. 6.3. For the purposes of this section, a planar tunnel junction requires at least one electronic contact to the sample, and another contact - the tunneling probe - separated from the sample only by a thin insulating layer. This insulating tunnel barrier must be thin enough to support a measurable tunneling current (tunneling probability drops exponentially with thickness), but thick enough to prevent pinholes from shorting the junction, which might be present due to inevitable non-uniformity. In practice, the thickness is typically between 2 and 4 nm.

3.2 Device fabrication procedures

We performed much of the device processing described in this section at the Pennsylvania State University Materials Research Institute Nanofabrication Laboratory (PSU Nanofab), featuring a class 10-100 cleanroom facility, is part of the National Nanofabrication Infrastructure Network. Some work, as noted, was performed at the PSU Materials Characterization Laboratory. All other device preparation and characterization was performed within Ying Liu’s laboratory.

3.3 Tools for micromanipulation

Simple tools for precise under-the-microscope manipulation were fabricated for many experimental techniques and processing steps. These tools were generally a bare gold wire, an insulated copper wire, or a tungsten STM tip (in order of increasing stiffness) attached with GE varnish to the wooden end of a cotton-tip applicator (Puritan®). Examples of usage was in the scratching removal of conducting film, precise movement of quartz filaments on a substrate, and surgery of large flakes to isolate a desirable portion.
3.4 Mechanical exfoliation of flakes from bulk crystals

The mechanical exfoliation of atomically thin flakes from bulk, layered crystals was pioneered by the work of Novoselov et al.[55], who first deposited flakes of material including graphite, boron nitride (BN), molybdenum diselenide (MoSe$_2$), niobium diselenide (NbSe$_2$), and BISCO (Bi$_2$Sr$_2$CaCu$_2$O$_x$) onto silicon/silicon dioxide (Si/SiO$_2$) substrates. Depending on the crystal quality and strength of interlayer bonding, single crystals down a single unit cell thickness can be isolated for study. From high quality bulk graphite, such flakes exceeding 50 microns in the planar dimension can be deposited on a clean substrate using only adhesive tape. Requiring only several minutes training and several hours practice for regular success, flake preparation is a highly cost-effective technique. While the discussion below focuses specifically on the exfoliation of graphene flakes, many of the details can be generalized for other layered materials.

In this study, the substrate of choice for deposition of graphene flakes was 300 nm SiO$_2$ thermally grown on degenerately doped N-type Si (with phosphorous dopants). The Si/SiO$_2$ wafers were purchased from Si-Tech, Inc.. This choice of substrate offers several important advantages for graphene studies. First, as-purchased wafers are well-polished, featuring a roughness below 0.2 nm. The smooth surface facilitates the adhesion by van der Waals forces and prevents significant corrugations in atomically smooth flakes. Second, silicon wafers feature strong crystalline order and can thus be easily cleaved (with the assistance of a diamond tipped scribe) into chips of desirable size. Third, the doped Si and SiO$_2$ can be employed as a back gate electrode and high quality dielectric, respectively, in experiments where the electronic gating of a flake on the stack is needed. Finally, 300 nm of SiO$_2$ offers near peak optical contrast of graphene flakes on the substrate background[56], simplifying their identification with an optical microscope.

Properly preparing the Si/SiO$_2$ substrate is crucial for obtaining high yield graphene flake production. Wafers are coated with a protective layer (typically Shipley 1805 or 3012 photoresist) and diced into square chips between 5 and 10 mm on a side. Each chip is then subjected to the following cleaning process, which in this work was performed at the PSU Nanofab: 1) Sonicate in acetone
for 1 minute to remove the resist; 2) Transfer to isopropyl alcohol and soak for 1 minute to remove acetone residue; 3) Dry with nitrogen gun and transfer to Nano-Strip™ (Cyantek Corp.) heated to ≈50° C or freshly prepared Piranha etch (3:1 concentrated sulfuric acid to 30% hydrogen peroxide) for 20 min to remove all organic residue. Extreme safety precautions should be excercised in this step, as the solutions involved are highly acidic; 4) Transfer to a dry container and spray with deionized water, then transfer to a deionized water bath; 5) Sonicate in fresh acetone for 1 minute, which may act to react with residue from step 3; 6) Transfer to fresh isopropyl alcohol for 1 minute; 7) Dry with nitrogen gun. Confirm that the surface is free of debris and visible residue that would make the adhesion of graphene flakes difficult.

The acidic solutions used in step 3 above are known to hydroxylate to the SiO₂ surface. Hydroxyl ions (OH⁻) attach and form silanol groups at the surface, making it hydrophilic. Based on experience, the process also facilitates the adhesion of thin graphene flakes, as higher yields and larger flakes were produced more frequently by the exfoliation method discussed below once this process was introduced. The improvement is most likely due to the improved removal of organics, making the SiO₂ more receptive to flakes.

The successful mechanical exfoliation of flakes is dependent on the quality of the bulk graphite source. Our graphene production process was developed using highly ordered pyrolytic graphite provided by SPI® Supplies (Grade SPI-1). However, while this graphite features very high c-axis order, we found that flake graphite produced by Asbury Carbons (Grade 3763) featured much higher order in the basal plane, so that production yielded flakes of much larger area. The second graphite source is also much cheaper, since samples of this graphite, typically sold in great bulk quantity for industrial lubrication purposes, can be obtained without much difficulty or cost. General graphite quality can be checked by eye under optical microscope, where highly reflective domains (indicative of atomic smoothness) larger than the desired flake area and zero discoloration from impurities can be confirmed.

The mechanical exfoliation of flakes from bulk graphite is performed with the use of adhesive tape. It is most desirable to use a tape with just enough glue to cleave graphite, as excess glue from such tapes as 3M Scotch® Magic Tape
can leave too much residue on the substrate and hinder subsequent processing. Powder-free latex or nitrile gloves should be worn and a clean work environment maintained during the following procedure: 1) Unroll a considerable length (>10 cm) of tape and place it glue-side up, though held down at one end, on a workbench; 2) Choose a piece of graphite with clean tweezers and place it on the tape, near one end (Fig. 3.1a); 3) Pick up the tape and fold it in on itself, making the edge of the fold as close to the graphite piece as possible. After pressing both sides of the tape on the graphite well to ensure good adhesion, pull the tape apart, slowly (≈ 1 mm/s) through the graphite, leaving behind two mirrored, freshly cleaved graphite surfaces; 4) Repeat step 3 several times by folding at different angles to create a dense pattern of freshly cleaved graphite, being careful to limit graphite-to-graphite contact that might damage each surface (Fig. 3.1b). An ideal folding sequence would be to cleave first along a fold 45° to the tape edge, and then at 90° to produce a 2x2 pattern, repeating again for 4x4, and so on; 5) Once the pattern covers the width of the tape, cleave further along the length of the tape towards
the other end. The goal is to obtain a dense area of graphite that has lots its sheen, which is a sign that it has become very thin. It is likely that these thin cleaves yield better flakes because they conform more easily to the substrate’s surface during the next step; 6) Once satisfied with thin graphite coverage on the tape, place the tape graphite-side-down onto the surface of a prepared substrate (Fig. 3.1c). It is useful to affix the substrate to a glass slide beforehand, and to use the rest of the tape’s length to hold it in place on the glass slide; 7) Using plastic tweezers, or other firm but flexible tool, apply light pressure to the top of the tape on the substrate. The pressure should be slightly stronger than the weight of the tool, to prevent shredding of the graphite underneath. Using smooth, circular motions, massage the tape onto the substrate for roughly 3 minutes. This time should be adjusted depending on the pressure applied and the yield results; 8) Holding down the substrate with tweezers or the glass slide by hand, slowly peel the tape off of the substrate (≈ 1 mm/s). A slower peel helps the glue more easily return to the tape and not the substrate, and reduces graphite shredding. The substrate should appear slightly spotty with graphite deposition, but remain highly reflective (little glue residue) elsewhere (Fig. 3.1d). The substrate is now ready for examination by optical microscopy.

Our source material for Ca$_3$Ru$_2$O$_7$ flakes were bulk crystals grown using a floating-zone method by Dr. Zhiqiang Mao at Tulane University. Although crystals cleave more readily parallel to the $ab$-plane, each layer is still fairly well bonded along the $c$-axis, thus atomically thin flakes could not be obtained by the mechanical exfoliation technique described above. Ca$_3$Ru$_2$O$_7$ flakes were prepared by cleaving a crystal repeatedly over an SiO$_2$ substrate with a razor blade. This results in the substrate being covered with a high density of flakes of a variety of sizes. Desirable flakes had a thickness of several hundred nanometers (along the $c$-axis) and a lateral size of 10-50 µm, and were chosen from the rest based on our ability to focus both the flake’s and substrate’s surfaces within a sub-micron depth of view field of our optical microscope. We transfer a desirable flake (an example is shown in Fig. 3.15a) to a fresh substrate by picking it up with static electricity on the end of a wire tool (see Sect. 3.3), so as to make use of multiple flakes from each cleavage.
3.5 Identification of graphene and other flakes

3.5.1 Optical microscopy

The identification of single atomic layers of graphene isolated as described above is possible due to the optical contrast between thin flakes and the underlying substrate. This fascinating result is due to both an increased optical path of impinging light and graphene’s finite opacity[56]. The contrast is quantized by layer, such that flakes up to about 10 layers can be easily distinguished from one another. Above that thickness, flakes become more reflective and difficult to distinguish. By combining optical contrast with techniques (described below) to confirm actual thickness, one can learn a color code to identify flakes immediately with only optical microscopy.

To search for thin flakes, substrates with deposited graphite should be scanned using an optical microscope with a translating stage. For all optical microscopy in this work, we used a Nikon model LV150 microscope equipped with 100x, 50x, and 10x objectives. A large working distance on the 50x and 10x (≈ 8 mm on the latter) was arranged so that various surgical methods could be performed. Images were captured with a Nikon Ds-Fi1 camera. While this work only employed white illumination, the contrast of flakes can also be enhanced with a filter; green light provides the highest contrast for our substrate[56]. Following the procedure in the above section, the substrate should be covered with a variety of graphite flakes (Fig. 3.1e). The trick to inexperienced searching for flakes is to locate the faintest objects of regular shape; exfoliated graphene usually tears along one termination over many microns, resulting in sharp corners and straight edges (Fig. 3.2a). With enough coverage, many thicknesses will be deposited (Fig. 3.2b), so the faintest flake should be a monolayer. In some cases, flakes can be found with partially overlapping layers, allowing easy association of color code with layer thickness, as shown in the “staircase” flake in Fig. 3.2c.

3.5.2 Atomic force microscopy

Surface topography can be studied with approximately 1 Å vertical and 10 Å lateral resolution with atomic force microscopy (AFM). We used a Digital Instruments


Figure 3.2. Optical images of a) a bilayer graphene flake with dashed lines emphasizing regular shape, b) graphene flakes of various thicknesses, and c) a "graphene staircase" emphasizing the quantized contrast due to layer overlap. Numbers refer to atomic layer thickness. All flakes are supported on a SiO$_2$ substrate, and all image are contrast-enhanced.

MultiMode AFM in “non-contact tapping mode,” to avoid damaging our samples. The probe was equipped with phosphorous-doped Si tips with a quoted tip radius of 8 nm, provided by Veeco. Flakes with partially overlapping layers provide opportunity to measure atomic thickness. In Fig. 3.5.2a, an AFM image of a “staircase” graphene flake is shown with each thickness labeled. The height difference between graphene steps is always measured as a multiple of 3.4 Å - the interlayer spacing for graphite. However, the step from the SiO$_2$ substrate to single layer graphene is somewhat variable between samples. In Fig. 3.5.2, an AFM image a 1LG flake on SiO$_2$ is shown, where the measured height difference across the step is 13 Å. Typically, we see this step range between 5-15 Å, and is likely due to substrate adsorbates (e.g. water, glue) beneath the graphene. Because of this uncertainty, AFM is mainly useful for measuring interlayer steps and residue from processing on the surface of flakes. In order to confirm absolute thickness, other techniques are required.

### 3.5.3 Raman microscopy

Raman spectroscopy measures inelastic scattering events of single-wavelength photons with phonons in a sample. In crystalline samples, the technique is highly useful in determining not only vibrational modes in the lattice, but also band structure...
Figure 3.3. Atomic force microscopy image of a) a multilayered graphene flake and b) a monolayer graphene flake supported on an SiO$_2$ substrate.

details through the interaction of excited electrons with phonons. Traditionally requiring only a laser excitation source and monochrometer, the technique can be combined with a confocal microscope and a translational stage, allowing high resolution spatial scans of a materials surface. We used a WITec CRM200 Confocal Raman microscope with an excitation wavelength of 488 nm and spot size of $\approx 250$ nm. Measurements were performed at the Penn State Materials Characterization Laboratory (MCL).

The Raman spectrum of graphene is shown with prominent peak locations labeled conventionally in Fig. 3.4b. Within this range, the prominent Raman excitation peaks of the substrate, present due to the finite penetration depth of the laser light, appear at Raman shifts outside this range. The D peak at 1350 cm$^{-1}$, also known as the “disorder peak”, corresponds to an in-plane optical phonon mode and defect scattering event that is only active in crystals of “finite” size[57]. It is prominent only in highly polycrystalline graphite or disordered graphene, and is not typically observed in exfoliated flakes like that in Fig. 3.4. The G peak at 1580 cm$^{-1}$ is due to a longitudinal optical mode, and is prominent for all graphite thicknesses, as is the G* peak at 2350 cm$^{-1}$, which arises from two contributions: a doubly resonant transverse optical mode[58] and a combination of a longitudinal acoustic and transverse optical mode[59].
Figure 3.4. a) Optical image (contrast-enhanced) of a multi-layered graphene flake on SiO$_2$. The circles denote where the Raman spectra in (c) were taken, coded by color. The dashed box indicates the area scanned in (d); b) Raman spectra of monolayer graphene with each peak labeled conventionally. See text for details; c) Raman spectra of the 2D peaks in monolayer and bilayer graphene. Black lines are fitted Lorentzian curves. In 2LG, four Lorentzians (shown as green curves) sum to the fit; d) Raman topography map of the full width at half maximum (FWHM) of the 2D peak for the graphene flake in (a), showing regions of 1LG (blue), 2LG (red), and SiO$_2$ (black).
The 2D peak at 2690 cm\(^{-1}\) is particularly important for this work, since its shape and height are dependent on graphene thickness and distinguish between mono- and bilayer graphene. In fact, the 2D peak can be used to distinguish layer thickness up to about five layers, but only the thinnest two will be discussed here. The 2D peak is called such because it is the second order of the D peak, and arises due to the interaction of an electron, excited from the valence to conduction band by the incident laser, with two phonons of equal and opposite momentum[60]. The band structure of 1LG (Sect. 2.1.1) is such that the excited electron can only scatter from one Dirac cone to another and back, resulting in a narrow peak that can be fit to with a single Lorentzian (Fig. 3.4c). The band structure of 2LG (Sect. 2.2.1), however, hosts two bands at the relevant energies, allowing four possible electron-phonon interactions, resulting in four Raman peaks spaced very closely. The 2D peak in 2LG can therefore be fit with the sum of four Lorentzians (Fig. 3.4c). The shape, width, and even height (the 2D/G peak height ratio is \(\approx 2.4\) in 1LG, \(\approx 1.3\) in 2LG) of the 2D peak can therefore be used to distinguish 1LG from 2LG easily.

With a translational stage, a two-dimensional map can be constructed to characterize the spatial variance of Raman-resolvable features. For example, Fig. 3.4d shows such a Raman topography map of an area of the flake in Fig. 3.4a, where the value of the 2D peak width resolves a sharp transition between 1LG and 2LG. Other properties that can be gleaned from 2D and G peak variation include local strain[61] and doping[62]. Strain, in particular, which distorts band structure, was resolved topographically in this work by tracking shifts in the 2D peak position. In Ref. [63], we reported results of Raman topography experiments in graphene grown epitaxially on SiC, revealing strain inhomogeneity and areas of free-standing graphene.

### 3.5.4 Scanning electron microscopy

Scanning electron microscopy was performed on the Leo 1530 Field Emission Scanning Electron Microscope (FE-SEM) at the PSU Nanofab and on the FEI NanoSEM 630 FESEM at the MCL. Although graphene films are almost entirely transparent to emitted electrons (contrast is provided mostly by differing amounts
of contaminants between the graphene and substrate), this technique was generally useful in resolving 10 nm-scale features of our devices including adhesive tape glue residues and deposited film granules. FESEM was most useful in resolving grain formation in the deposited AlO$_x$ tunnel barrier, due to the high contrast between insulating grains and conductive graphene.

### 3.6 Device fabrication using a quartz filament as a shadow mask

Simple two-lead electrical junctions can be fabricated with the use of a quartz filament shadow mask[64]. This technique offers two main advantages. First, sub-micron-width devices can be prepared without the use of photo- or e-beam lithography, which may include organics and solvents that pose a threat to device performance. Second, from the isolation of a sample on an insulating substrate, fabrication of the junction can be completed in a matter of hours. While samples of many different geometries can be considered, it is here applied to micron-scale graphene flakes.

Quartz filaments were drawn from molten quartz rods, based on previous work in our lab[65]. The ends of two 1/8”-diameter rods are melted in the flame of an oxygen-acetylene welding torch (typically, acetylene is ignited and the flow of oxygen is regulated to increase heat). After being brought into contact by hand, the two molten ends are pulled quickly away from each other. With practice, this results in ultrathin drawn-out filaments whose observation is aided by bright, focused lighting. These filaments are then captured between the arms of a U-shaped slide and separated from the rods. The slide facilitates transfer of the filament to a desired substrate, particularly when the substrate is small enough to fit within the slide’s arms. Once the filament is captured onto the substrate surface by static forces, it can be cut at either end (with either a razor blade or tweezer edge) and the slide removed.

The technique described above can be used to prepare filaments of any desired diameter, with practice, down to about 500 nm reliably. Filaments with diameters below 2 microns are desirable for use in well defined shadow-masking, as these
Figure 3.5. a) Optical image (contrast enhanced) of a bilayer graphene flake with a 2 micron-wide quartz filament lying overtop; b) Schematic of the two-point transport junction fabrication employing the filament as a shadow mask; c) Optical image of a completed two-point electrical transport junctions on the same flake as in (a).

Filaments are highly flexible and conform to the surface well. Flexible filaments are also desirable since manual manipulation is usually necessary to align the filament with the sample. Manipulation was typically performed with wire and tungsten tip tools (Sect. 3.3). Once the filament is aligned overtop the sample, as shown in Fig. 3.5a, most of the substrate is typically masked off with teflon tape resulting in only two exposed regions, separated by the filament.

In these experiments, two types of devices were prepared using the masking technique described above - two-point electrical transport junctions and planar tunnel junctions - and are distinguished by the film deposition technique that follows (see Sect. 3.7 for deposition details). Two-point transport junctions are prepared by depositing a conducting film directly onto the substrate (Fig. 3.5b). The filament, acting as a shadow mask, is then lifted, leaving behind a completed junction (Fig. 3.5c). Planar tunnel junctions are prepared by taking advantage of the cylindrical geometry of the filament and applying two film depositions (Fig. 3.6). The first film deposition is that of the tunnel barrier material (see Sect. 3.7.2) and is made at angle to the perpendicular, typically between 30 and 60 degrees. Any final preparations of the tunnel barrier (usually film oxidation) are then conducted. A second deposition, the tunnel probe material, is made at the opposite angle, producing an asymmetric junction with electrical contact on one side, and tunneling contact on the other. The completed device features a tunnel
Figure 3.6. Planar tunnel junction fabrication using a quartz filament as a shadow mask; a) Schematic of the first angled deposition of the tunnel barrier film; b) A second deposition at the opposite angle forms a tunnel junction on one side and electrical contact at the other; c) Atomic force microscopy image of a completed junction, showing height differences that confirm the desired structure.

barrier in electrical series with a portion of the sample. While a rotator could be rigged within the system to allow subsequent depositions without venting the chamber to air, devices in this work were manually rotated after air ventilation.

3.7 Film deposition

3.7.1 Metals

To make electronic contact to samples and lay films to be oxidized in various devices, metals including gold (Au), aluminum (Al), and titanium (Ti) were deposited by thermal or electron beam evaporation. Deposited metallic interconnects were typically Au, which is an excellent conductor of electricity and is highly resistant to corrosion. While Au offered fairly good electronic contact to graphene ($\approx 10-100 \ \Omega \ \mu m^2$), we found that an intermediate layer of Ti not only improved graphene contact ($\approx 1-10 \ \Omega \ \mu m^2$), but also improved adhesion of the metallic film to the SiO$_2$, making for a sturdier device.

The deposition of metallic contacts in photolithographically defined devices were performed in a Kurt Lesker Thermal and Electron Beam Evaporator within the PSU Nanofab. This evaporator features both a roughing pump and cryo-pump.
Samples were taped onto a 6 inch wafer mount using Kapton tape and held at a throw distance of $\approx 24$ inches. When angled depositions were needed, samples were affixed to an aluminum plate bent at $30^\circ$, which was then screwed into the wafer mount. Contacts were made by depositing $50 \, \AA$ Ti followed by $250 \, \AA$ Au. The Ti layer was deposited typically at a chamber pressure of $\approx 7.5 \times 10^{-7}$ Torr at a rate of 1-2 $\AA$/s. When deposited on the chamber walls, Ti acts as an excellent “getter” of gases, allowing Au to be subsequently evaporated at $\approx 7.5 \times 10^{-7}$ Torr at a rate of 1-2 $\AA$/s, as well. Absolute thickness was measured with a quartz crystal monitor (QCM).

Metallic contacts in lithography-free electronic transport devices and planar tunnel junctions, as well as tunneling probe electrodes in all planar tunnel junctions, were deposited in a custom-built thermal evaporator within our laboratory. Room temperature pressures of $10^{-6}$ Torr were reached with a mechanical pump and liquid nitrogen-cooled diffusion pump. Source metals were evaporated by joule-heating a tungsten (W) boat. Samples were mounted onto glass slides and hung on a ceiling assembly across a throw distance of $\approx 9$ inches. When angled depositions were needed, the slides were attached to an installed rotator motor held at a fixed angle of $30^\circ$. The system was not equipped to evaporate Ti; only Au was used for metallic contacts, and was deposited to a thickness of $250 \, \AA$ at a rate of 1-4 $\AA$/s and at a deposition pressure of $\approx 2 \times 10^{-6}$ Torr. Absolute thickness was measured with a QCM.

### 3.7.2 Tunnel barrier

It was desired within this work for our tunnel barrier to be electronically insulating yet thin enough to yield a measurable tunneling current. The strategy was to deposit a thin, uniform seed layer of Al and allow it to oxidize before capping it with a tunneling electrode, based the success of such films in resolving superconducting energy gaps[66]. The first planar tunnel junctions were fabricated according to the lithography-free design described in Sect. 3.6. The thin Al films were made within the custom thermal evaporator described in Sect. 3.7.1, by evaporating 15-20 $\AA$ Al, at a rate of 1-3 $\AA$/s, directly onto filament-masked graphene flakes held at an angle of $30^\circ$ with the chamber ceiling. Heating aluminum up to melting temperatures
Figure 3.7. a) Schematic of a monolayer graphene transport device measured during b) the deposition of 2 nm aluminum and c-d) subsequent oxidation in a pure oxygen atmosphere up to 20 hours; e) Resistance $R$ vs. gate voltage $V_G$ in the device at different times during oxidation, as noted. At “final”, the film had oxidized for 20 hours and the oxygen atmosphere was pumped out.

It tended to raise chamber pressures above $10^{-5}$ Torr, so that repeated heating and pumping was performed to achieve desired deposition rates at pressures $<5\times10^{-6}$. Once deposited, the chamber was allowed to cool then vented near 1 atm with pure oxygen ($O_2$) to oxidize the film. The chamber was then vented fully with nitrogen ($N_2$) and introduced to air briefly while the samples were manually rotated so that the other side of the filament was facing the source (see Fig. 3.6). The system was then pumped down and tunneling electrode deposited.

Since local charged impurities (such as a non-oxidized Al grain) induce charge inhomogeneity in graphene (Sect. 2.3), it was necessary to ensure that the Al film was fully oxidized. In order to determine the necessary time scale, we measured transport in a back gated 1LG flake while the aluminum was oxidizing in $O_2$ in the vacuum chamber, via electrical feedthroughs. By tracking the back gate voltage at which the resistance maximum was observed, we could determine the residual carrier density induced by non-oxidized aluminum. Based on the results shown in Fig. 3.7, it was determined that Al seed layers be left in $O_2$ for a day (or
Figure 3.8. a) Resistance $R$ vs. temperature $T$ in a planar tunnel junction prepared by the filament method on a niobium diselenide flake, showing a superconducting resistance drop at the critical temperature $T_c$ of the flake. Resistance does not drop to zero because of the tunneling portion in series. Inset: Schematic of the device; b) Tunneling conductance $dI/dV_B$ vs. bias voltage $V_B$ in the same device, measuring the superconducting energy gap $\Delta$. Device fabrication and measurements were performed by Neal Staley.

≈20 hours) before the subsequent electrode metal deposition. In order to test the alumina $\text{AlO}_x$ films as a tunnel barrier, we made a planar tunnel junction on a thin flake of $\text{NbSe}_2$ in place of graphene deposited as the contact and tunneling electrode. Using a liquid helium dip probe (Sect. 4.4), we cooled the device below the critical temperature of $\text{NbSe}_2$ ($T_c \approx 7$ K) and measured a suppression in the tunneling conductance with a width equal to four times the superconducting energy gap (Fig. 3.8). This was likely due to the formation of two tunnel junctions in series due to early, insufficiently angled film depositions. However, the quality of the tunnel junction for measuring the density of states was confirmed. Tunnel barriers prepared in this fashion were used in lithography-free 2LG planar tunnel junctions, whose measurements are described in Sect. 6.5.

While some of the early planar tunnel junctions did show tunneling behavior, results were inconsistent among all samples. Based on experience, ideal tunneling resistance was between 8 and 20 k$\Omega \mu$m$^2$. Many less resistive devices suggested electrical shorts through the tunnel barrier through likely pinholes. In those samples
in which gateable features in the tunneling conductance were observed, a strong “V”-shaped tunneling background made their analysis very difficult. The background resembled a two-step tunneling mechanism[67, 68] (see Sect. 6.5), which suggested that our AlO$_x$ film was made up of grains that hosted non-oxidized Al cores. AFM images of the AlO$_x$ (Fig. 3.9a) film confirmed that the film was not uniform but very grainy, and not ideal for tunneling experiments. We explored the possibility of depositing a more uniform AlO$_x$ film via atomic layer deposition, but graphene resisted growth for reasons discussed in Sect. 3.7.3. We resolved to make several improvements to our initial process to improve film uniformity.

Returning to our Al deposition, we reasoned that the uniformity of the deposited Al layer may be affected by adsorbates on the surface after exfoliation, and the high thermal energy of Al atoms. In the latter consideration, incident Al atoms with high thermal energy are only loosely adsorbed on the graphene surface. They diffuse on the surface until they exchange enough energy to rest stably on the surface or find other Al adatoms with which to bind and form grains[69]. By cooling the graphene to 77 K, we can provide more efficient heat exchange. To address these two issues, we installed a resistive heater on the back of the sample holder to bake off adsorbates under vacuum, and flowed liquid nitrogen through a circulation conduit on the ceiling of the chamber during Al deposition. The process was further improved by implementing a photolithography-based process that removed the need to expose the film to air before the second deposition. After oxidation, some nitrogen gas (N$_2$) was introduced into the chamber to mix with the O$_2$ and reduce the chance of ignition with the mechanical pump oil before pumping the chamber again.

After these improvements were made, films grown on graphene from 2 nm deposited Al showed increased uniformity. Based on analysis of the AFM images shown in Fig. 3.9a and c, average film roughness was reduced from $\approx$8 to 4.5 Å, and average grain diameter was reduced from $\approx$12 ± 19 nm to $\approx$3.1 ± 4.8 nm. Although SEM images in these films do show less than complete coverage (Fig. 3.9d), the “V”-shaped tunneling conductance background in completed devices was reduced substantially. Tunnel barriers prepared in this fashion were used in photolithography-based 2LG planar tunnel junctions, whose measurements are described in Sect. 6.6.
Figure 3.9. a) Atomic force microscopy (AFM) image of 2 nm alumina (AlO$_x$) grown on graphene from aluminum (Al) deposited at 300 K; b) AFM image of atomic layer deposited growth of single crystal alumina (Al$_2$O$_3$) on graphene supported by a silicon dioxide substrate. Inset: Side-view growth schematic; c) AFM image of 2 nm AlO$_x$ grown on graphene from Al deposited at 77 K; d) Scanning electron microscopy image of the same film as in (c).
3.7.3 Atomic layer deposition of dielectrics

For use in top-gated graphene field effect transistors (FETs) fabricated at Penn State University (Sect. 6.7), thick dielectrics were prepared by atomic layer deposition (ALD). We used a Cambridge Savannah™ 200 Atomic Layer Deposition Tool within the PSU Nanofab. The ALD process deposits single crystalline oxide monolayers by successive cycles. Within each cycle, the sample is coated with water, which reacts chemically reacts with a precursor (trimethylaluminum, Al(CH₃)₃ for Al₂O₃) to grow a uniform, crystalline oxide monolayer. Graphene’s hydrophobicity makes it incompatible with this process. In Fig. 3.9d, we show an AFM image of the poor Al₂O₃ growth by ALD at 90° C, preferentially on the SiO₂ substrate and on the edges and possible defects in graphene, where dangling bonds accept water adsorbates more easily. ALD growth, therefore, can be an excellent tool for highlighting defects in graphene films. In fact, successful growth of oxides by ALD requires pretreatment of the surface with ozone to create defects[70, 71, 72] or functionalization[73, 74] compatible with water. For our top-gated FET dielectric, we employed our thin film tunnel barrier (Sect. 3.7.2) as a seed layer for growth. ALD was performed at 150° C, which was calibrated for 0.9 Å per cycle of Al₂O₃, to deposit 50 nm.

3.8 Etching

Chemical etching was performed to remove undesired metallic or dielectric films from devices, primarily during the fabrication of planar tunnel junction devices by photolithography (see below). To remove Au films, we used Transene Gold Etchant TFA (primarily potassium iodide) in a concentration of 1:10 water (H₂O); the etch rate was ≈13 Å/s. Titanium films are resistant to this solution. Thin AlOₓ films (≤2 nm) were removed during photoresist development by Microposit MF® CD-26 Developer (primarily tetramethylammonium hydroxide); exposure to etchant was on the order of 10 seconds. Thicker films of AlOₓ were etched away with 10:1 H₂O to sodium hydroxide; the etch rate was ≈50 nm per minute. Photoresist and related organic residues were removed using a variety of N-methylpyrrolidone (NMP)-based solvents including Microposit Remover 1165, MicroChem Remover
PG, and DuPont EKC 830®. Since NMP-based solvents were found to etch thin AlO\(_x\) films, MicroChem EBR PG (primarily dioxolane propylene glycol methyl ether) was used to remove photoresist when AlO\(_x\) etching was undesirable.

We remove photoresist residue from the surface of Ca\(_3\)Ru\(_2\)O\(_7\) flakes with a short oxygen plasma descum within a PlasmaTherm 720 Reactive Ion Etch system at the PSU Nanofab. Our descum consists of three etches at 100mTorr O\(_2\) stabilized with 15 sccm flow, for 10 seconds at a voltage of 250 V d. c. (≈ 100 W).

### 3.9 Photolithography and Metallization

Photolithographical processes were developed in order to fabricate device structures more complicated than two-point junctions. The technique takes advantage of thin, photosensitive polymer films. Portions of these films that are exposed to ultraviolet light dissolve more readily (or, in the case of negative photoresist, less readily) in particular solvents, due to photon-activated breaking of polymer chains. By aligning patterned shadow masks to a resist-covered substrate, one can use this technique to obtain a physical image of that pattern. This is typically followed by metal/insulator film deposition or etching of the substrate, and finally the remaining resist is removed to leave the structure behind. Using contact photolithography, where the mask is brought into direct contact with the photoresist, we achieved well-defined, three micron-width features consistently, and down to two micron-width features in the most successful devices. Photolithography was used to fabricate top-gated Hall bars (Sects. 5.4 and 8.2), planar tunnel junctions (Sect. 6.6), dual gated 2LG field effect transistors. Details and examples of the masks used in this work are shown in Sect. 3.3.

All photolithographical processing was performed at the PSU Nanofab, using a Karl Suss MA/BA6 Contact Aligner, according to the following general procedure: 1) If preparing devices on a small flake, document its location on a wafer chip by sketch or optical images; 2) Spin photoresist onto a static wafer chip and soft-bake, according to the recipes shown in Table 3.1. We found more uniform photoresist films could be achieved by using larger wafer chips; square chips between 6 and 8 mm on a side were fairly standard; 3) If using a bilayer resist stack, spin on and soft-bake the second layer. In this work, we typically used a lift-off resist (LOR) as
Figure 3.10. a) Schematic of our photolithography process for transport devices: 1) Sample is deposited onto a Si/SiO$_2$ substrate; 2) Photoresist is spun onto the wafer; 3) Photoresist is selectively exposed and developed; 4) Pattern is metallized; 5) Resist/metal stack is lifted off by resist remover; b) Optical image of a completed transport device.

an underlayer, which is undercut isotropically by the developing solvent, improving lift-off performance after metals depositon; 4) Affix the wafer to a contact aligner chuck. These chucks typically hold wafer by vacuum, but small wafers can be affixed with double sided adhesive tape on top of plastic film to seal the vacuum; 5) Remove edge beads at the corners of the wafer chip that would prevent hard contact during exposure. Scraping with a razor blade and blowing off resist dust with compressed air is sufficient; 6) Locate the flake and align the mask pattern. Because graphene is difficult to contrast from the substrate in the aligner’s microscope, good documentation from step 1 combined with a scaled transparency image of the mask pattern is highly useful in precision alignments; 7) Expose the pattern according to the recipes shown in Table 3.1, followed by a post-exposure bake if necessary; 8) Develop the pattern in Microposit MF® CD-26 Developer for 1 minute, soak in water for 1 minute, then blow dry; 9) Confirm pattern under a red filtered optical microscope, and develop longer if necessary.

Even after development, there is typically some organic residue leftover on the exposed surface. We used short, low power oxygen plasma (see Sect. 3.8) to descum the surface of Ca$_3$Ru$_2$O$_7$ flakes before metal deposition. However, such a physical etch will remove graphene just as easily as any organic. Therefore, no additional cleaning was performed between photolithography and depositing metals for electrical contact to graphene. After metal deposition, lift-off was performed in a bath
Figure 3.11. a) Schematic of our photolithography process for planar tunnel junctions: 1) Tunnel barrier (AlO$_x$ and tunneling probe metal (Au) are grown/deposited onto the substrate-supported sample; 2) Photoresist (PR) is spun onto the stack and patterned; 3) The Au film is chemically etched away; 4) Second photoresist is spun and patterned. The developer (CD-26) etches the AlO$_x$; 5) The pattern is metallized and lift-off is performed; b) Optical image of a completed tunneling device.

of Microposit Remover 1165 warmed to roughly 40°C. Lift-off of AZ nLOF 202, a negative resist, was performed with MicroChem EBR PG, within which AlO$_x$ is not etched. Sonication is not recommended to assist lift-off, as it can wrinkle, tear, or displace flakes. Instead, directing solvent currents with a pipette is sufficient for removing a LOR/resist stack. For the smallest and most crowded features, we perform lift-off in a shallow dish to allow monitoring of lift-off progress under an optical microscope. Remover 1165 is soluble in water and IPA, so that upon complete lift-off, we transfer the wafer to either bath before blowing dry. In Figs. 3.10 and 3.11, we show schematically our general process for fabricating transport and tunneling devices, respectively, using photolithographical techniques.

### 3.10 Photolithography masks

We designed our mask patterns using Lasi7, a free integrated circuit design software program authored by Dr. David E. Boyce. Soda-lime masks were fabricated by and purchased from Microtronics, Inc.. In Fig. 3.12, we show examples of photomask patterns for transport and tunneling devices. The colored portions show clear on the mask, and different colors refer to separate mask patterns in multi-step
Table 3.1. Photolithography recipes; Thicknesses are quoted for a spin speed of 4000 rpm for one minute, (excluding AZ nLOF 2020). Exposure times are quoted for an 8 mW/cm² @ 365 nm lamp (Ushio USH-350DS). Parameters may need to be tuned on occasion, due to variations in lamp intensity. All resists are positive unless otherwise noted. PEB = Post-exposure bake.

<table>
<thead>
<tr>
<th>Resist name</th>
<th>Thickness (µm)</th>
<th>Soft-bake</th>
<th>Exposure time (s)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shipley 3012</td>
<td>1.2</td>
<td>90° C, 1 min.</td>
<td>6.9 s</td>
<td>PEB: 1 min. @ 115° C</td>
</tr>
<tr>
<td>Shipley 1805</td>
<td>0.5</td>
<td>115° C, 1 min.</td>
<td>2.3 s</td>
<td>Most successful resist for small features</td>
</tr>
<tr>
<td>Shipley 1813</td>
<td>1.3</td>
<td>115° C, 1 min.</td>
<td>4 s</td>
<td>Slightly overexposed</td>
</tr>
<tr>
<td>AZ nLOF 2020</td>
<td>1.7</td>
<td>110° C, 75 s</td>
<td>4 s</td>
<td>Negative; PEB: 75 s @ 110° C</td>
</tr>
<tr>
<td>MicroChem LOR2A/5A</td>
<td>2/5</td>
<td>190° C, n/a</td>
<td>4 min.</td>
<td>5A requires ≈ 2 min. developing time</td>
</tr>
</tbody>
</table>

processes. On the soda-lime mask, these patterns tended to be separated by about 1 cm, or roughly the size of a wafer chip.

3.11 Ultrahigh carrier density gating techniques

As will be seen in the following chapters, the ability to tune the Fermi level in graphene by electrostatic gating is extremely useful in probing and understanding its electronic properties from the context of the size of its Fermi surface. We would like to extend this technique to Ca₃Ru₂O₇ flakes, whose Fermi surface is subject to orbital ordering effects at low temperature. However, since the carrier density is so high (≈ 10¹³-10¹⁵ cm⁻² per bilayer at low temperatures[75]), gating through our traditional SiO₂ substrate does not change carrier density significantly. We therefore adapt polymer electrolytic[76] and ionic liquid[77] gating techniques, which are capable of inducing up to 10¹⁵ cm⁻² charge carriers[78].

These techniques employ ions in a liquid. When an electric field is applied between two submerged electrodes, the liquid segregates and ions align at the
Figure 3.12. a) Photomask layout for an 8-lead transport device and alignment features; b) Zoomed-in display of (a); c) Photomask layout showing two separate layers for a planar tunnel junction. The tunneling probe is red and the contacts are blue. Alignment features common to both layers are purple; d) Zoomed-in display of (c).

surfaces of either electrode. These ions draw charge at each surface, forming what is called an electrical double layer (EDL), which is effectively a sub-nanometer gap capacitor[79]. EDL gating has an advantage over chemical doping in that it is capable of inducing comparable carrier densities without added disorder.

A few experimental concerns for both polymer electrolytes and ionic liquids are
as follows: First, chemical reaction with the sample is a very real concern at both voltage polarities. Samples should be monitored at the full range of applied voltage, as higher voltages are more likely to cause an electrochemical reaction. Gating should be performed at the lowest possible temperatures while the solution is still liquid to slow down possible reactions. Second, charging is not instantaneous, particularly at low temperatures; after applying a voltage, gate current should be monitored to allow enough time for complete charging (≈ 20 minutes in a typical device). Third, the presence of impurities such as water causes gating hysteresis and non-reproducibility for measurements[80]. Water can be reduced by baking off adsorbed water at 100° C prior to deposition of the liquid, and heating and pumping on the device within the measurement system.

3.11.1 Polymer electrolyte

Polymer electrolytes are made by dissolving a salt into a liquid polymer. We used the salt lithium perchlorate (LiClO$_4$, although potassium perchlorate can be substituted) dissolved in polyethylene glycol (PEG), which has a melting point of 39° C. Effective gating is achieved with molar ratios of LiClO$_4$ to PEG between 1/100 and 1/20. The weight ratio is easily calculated as 2.4077 multiplied by the desired molar ratio. The polymer electrolyte is prepared with the following recipe: 1) Melt ≈ 2 cc PEG wax; 2) Weigh and add LiClO$_4$ powder, mixing with 1-2 cc methanol at 80° C to assist dissolution; 3) Let sit at room temperature and allow methanol to evaporate. The mixture should solidify into a wax. Once prepared, the electrolyte is highly water absorbent, and will gelatinize/liquify in ambient conditions after about fifteen minutes in air. Water can be removed by heating to 100° C and pumping. The electrolyte is employed in a device by melting at 80° C and dripping it onto coplanar electrodes, where one electrode is the sample to be measured. A device schematic is shown in Fig. 3.14, where the melted PEG:LiClO$_4$ would substitute the ionic liquid. Changes in gate voltage are made with the device held at 80° C. We used polymer electrolytes to develop our EDL gating technique in early experiments. We confirmed huge carrier density shifts in mono- and bilayer graphene, and detected surprising changes to the low-temperature insulating state in Ca$_3$Ru$_2$O$_7$. However, we found polymer electrolytes
to have a high probability of damaging samples by thermal expansion/contraction. Because of this and the electrolyte’s more complicated preparation, we transitioned smoothly to ionic liquids, which were used for all data presented in Chap. 8.

### 3.11.2 Ionic Liquids

An ionic liquid is a salt that is liquid at room temperature due to the weak ionic character of its large molecular ions. We use N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI), which we purchased from Kanto Corporation (see Fig. 3.13). DEME-TFSI has a freezing point at around 210 K[81]. Devices are prepared by first heating the sample to 100° C to remove adsorbed water, and then dripping the ionic liquid by syringe onto coplanar electrodes, shown schematically in Fig. 3.14a. Changes in gate voltage are applied with the sample held at 220 K. To test and calibrate gating, we prepared a Hall bar on monolayer graphene gated by DEME-TFSI. In Fig. 3.14b, measurements show a carrier density sweep of $\approx 10^{14}$ cm$^{-2}$. We found that for Ca$_3$Ru$_2$O$_7$ and Ca$_2$RuO$_4$, chemical reactions occur between DEME-TFSI and the sample and/or photoresist somewhere between 2.5 and 4 V for the electrode geometry shown in Fig. 3.15e, although a careful study was not performed.
3.12 Surface-contacted flakes

Due to the relatively large thickness and high conductivity of Ca₃Ru₂O₇ flakes ($\rho_{ab} \approx 10 \, \Omega \, \mu m$), it was desirable to electrically contact only the surface in order to measure effects of ionic liquid gating. Here, we are taking advantage of the material’s anisotropic resistivity ($\rho_c > 1000 \rho_{ab}$ at low temperatures)[82]). We therefore designed a photolithographical process to achieve that goal, with the following recipe: 1) Spin on thick photoresist and photolithographically pattern a sufficiently large window exposing only the flake’s surface (Fig. 3.15b). Thick resist is desirable to cover the flake - Shipley 1813/1827 can be spun to thicknesses > 2 $\mu m$; 2) Hard-bake the resist to be resistant to further UV exposure and solvents. This step takes a bit of engineering, also to ensure that resist does not flow substantially during hard-baking; 3) Using a bilayer photoresist stack and careful alignment, pattern the electrical contacts. In this work, we use a Hall bar geometry. It is useful to acquire and consult optical images at each step of this process to help with alignment; 4) Perform an oxygen plasma descum of the resulting pattern; 5) Deposit metal contacts (Ti/Au, preferably) with two metal evaporations at op-
Figure 3.15. a) Optical image of a Ca$_3$Ru$_2$O$_7$ flake supported on a Si/SiO$_2$ substrate; b) Optical image of a window defined photolithographically to expose only the surface of the flake, after hard-baking the remaining resist. Contours of height variation in the photoresist are visible; c) Optical image of a completed Hall bar device, where electrical contacts are made only to the flake's surface; d) Side-view schematic of a completed device; e) Optical image of most of the completed pattern for a coplanar, ionic liquid-gated Hall bar. The black dashed lines outline the area shown in (c). The blue dashed lines indicate the desired size of an ionic liquid drop.

posite angles, to ensure continuity of the film over the large hard-baked photoresist step; 5) Lift-off and perform a second descum of the exposed surface Ca$_3$Ru$_2$O$_7$ (Fig. 3.15c).

A schematic and optical image of a completed device, the latter showing two potential local gate electrodes, is shown in Fig. 3.15d-e. A desirable size of ionic liquid drop is also annotated - the effective area of the gate electrode is preferably larger than the effective area of the sample and electrical contacts to maximize induced carrier density per volt applied. The most difficult step in this process is engineering a uniform window layer; non-uniformities in the as-spun film are amplified by hard-baking. From our experience, the photoresist should be at least twice as thick as the flake.
Measurement techniques

Electrical measurements of micron-scale devices with control of temperature and magnetic field were used extensively in this thesis research. For experiments in high-resolution tunneling, quantum Hall effect, and Ca$_3$Ru$_2$O$_{7}$ transitions, low temperature techniques with control down to 1.8 K are demanded. In this chapter, we describe how devices are wired, cleaned, cooled, and measured.

4.1 Protection of devices

When handling and measuring micron-scale devices, it is absolutely necessary to prevent electrical shocks through devices caused by static charge build up. Such shocks can occur when a device electrode is put in contact with a large charge reservoir. If another contact is connected to ground, there is a risk of sudden charge flow through the device that could fry the sample or weaker contacts. When handling these devices, it is then important to short large charge reservoirs (including humans and experimental systems) to ground before contacting the sample. To this end, grounding straps should be worn while manipulating the device contacts, and only reliable, well-grounded tools should be used. It is also important to provide alternate current pathways while the sample is not being measured. This can be done with a low resistance electrical short either at the sample level with gold/copper wire, or at the instrument level with BNC cabling. Other equipment, including ionizing fans, humidifiers, and grounded floor mats, can be employed to reduce the risk of electrical shocks.
4.2 Minimizing contact resistance

Devices prepared by quartz filament masking or photolithography have electronic pad sizes that are \( \approx 0.2 - 1 \) mm in scale. It is necessary to make electrical connections to a larger header that can be interfaced with measurement systems. In this work, connections at the pads were made by wirebond or silver epoxy. In Fig. 4.1, we show a schematic of the finished sample/header layout, and each part is described below.

Manual wirebonding of 1 mil Au wire purchased from Alfa Aesar\textsuperscript{®} was performed with a Kulicke & Soffa Industries, Inc., model 4123 wire bonder installed with a ceramic wedge bonder tip purchased from DeWeyl Tool Co., Inc.. The technique works by applying pressure and ultrasonic power to a wire at the bonding site (a metallic pad), followed by free spooling of the wire during manual translation to a second site where another bond is made and wire torn. Wirebonding has the advantage of being a very clean method for making strong electrical contacts. Its disadvantages include potential damage to the substrate, and the requirement that the contact pads be very well-adhered to the substrate/header. A film of 5 nm Ti plus \( \geq 40 \) nm Au on a SiO\(_2\) substrate was found to work well. A copper (Cu) square, 1 cm to a side, is a useful header for wirebonding. Cu pads can be well-adhered (through cigarette paper to insulate electronically) with GE Varnish on the edges.
of the header, and the substrate adhered to the center (also isolated electronically). Variable parameters for wirebonding are applied force, applied power, and duration. These parameters tend to vary from device to device, and require both coarse and fine tuning starting from low values each session. However, there are two very important preparations that should be made before attempting wirebonding. One, be sure that the substrate is strongly fixed to the header that is strongly fixed to the stage (with clamps), such the substrate does not move at all when a force is applied by the wedge tip. Two, before making bonds, rotate the stage such that the bond locations are aligned with the spooling direction of the wire to minimize bending. Additional tips can be found in the manual accompanying the bonder.

Batches of Ag epoxy were prepared from Epoxy® Technologies E4110 resin and hardener, mixed at a ratio of 10:1 by weight, respectively. Viscosity in a good mix should be such that whipped peaks can be drawn by a thin tool. The success of Ag epoxy relies first on whether it makes good electrical contact to the pads, but then completely on the dexterity and attention of the user to the epoxy volume and guidance of the application tool. A wire tool (Sect. 3.3) with 2 mil wire is recommended for application. The best results were obtained by preparing the header ahead of time, with Au wire (to be connected to device pads) connected to stronger Cu wire by Ag Epoxy on the edges of the header. Quartz wafer chips, several millimeters larger than the substrate, serve as good headers because they are thermally conductive and electronically insulating, but also because quartz wafers are cheap and dice easily. After attaching the device substrate to the center of the header, the Au wire can be manipulated and bent with tweezers to physically touch the device pads. This facilitates the application of Ag epoxy, because the wire will wick the flow to the pad and form a small but strong connection. Epoxy dots will typically take \( \approx 5 \) hours to cure at room temperature. To reduce cure time, and also to reduce the spread of resin and hardener that flows preferentially along the leads towards the device, a hot plate set to 130° C will stop hardener flow in several minutes, and cure the leads sufficiently in roughly one hour.

In both techniques, Au wire connects a device pad to the header, from where one end of a stronger Cu wire extends (which itself is connected strongly to the header by tin solder on a Cu pad or by Ag epoxy on quartz). The Cu wire used in this work was 2 mil and insulated, purchased from the California Fine Wire
Company. The insulation can be easily stripped by light scraping with a razor blade. This setup allows the header to be easily transferred to a cryostat sample block or PPMS puck where only the stronger Cu wire is manipulated and tin soldered to the measurement apparatus.

4.3 Graphene cleaning

Over the years, we have tried and put into use a combination of different methods to clean graphene of adsorbates like water from atmosphere and organic residue from photolithography. Prior to deposition of a top gate dielectric for top-gated devices in Sect. 6.7, photolithographically processed graphene devices were annealed at 300°C in an Ar/H\textsubscript{2} atmosphere for 1 hour (at higher flowrates than our meters could measure, \(\gg 83\) sccm Ar and 400 sccm H\textsubscript{2}), which has been shown to be highly successfully in burning off organic residue\cite{83}. If the cryostat is properly equipped, bare graphene to be measured should be heated to 100°C and the chamber continuously evacuated to remove water on the top surface. Another \textit{in situ} cleaning method is current annealing\cite{84}, which involves ramping current density across a device to on the order 1 mA/\(\mu\)m, where power densities upwards of 15 kW/cm\(^2\) heats the graphene locally to temperatures >500 K\cite{85}. The success of this technique should be weighed with the risk of frying a device, particularly if contacts are poor.

4.4 Low temperature techniques

The electronic measurements of devices reported in this work were performed between 400 and 1.8 K using cryogenic refrigeration techniques. While the lowest temperatures were preferred to observe quantum Hall behavior in our graphene hybrid structures (Chap. 7), to improve energy resolution in tunnel junctions, and explore low-temperature transitions in Ca\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}, most transport and tunneling measurements of graphene presented in Chaps. 5 and 6 were conducted between 5 and 10 K to reduce the amplitude of universal conductance fluctuations\cite{86}.
4.4.1 Dip probe

The dip probe is the simplest method of reaching “low” temperatures. Our custom-built probe consists of a brass sample stage on the end of a stainless steel rod, with electronic leads wired between the stage and a breakout at the other end. Samples are loaded onto the stage and dipped directly into a liquid helium (LHe) dewar. Temperature is measured with a Cernox thermometer provided by Lakeshore Cryotronics, Inc., and temperature control is limited to closing the proximity of the sample to the LHe surface. While this technique does offer the advantage of quick characterization and sure thermal anchoring to 4.2 K, it lacks good temperature control and water condensation is likely upon sample retrieval.

4.4.2 1K pot

Lower temperatures can be reached by manipulating the He phase diagram. By pumping on LHe, higher temperature He is pumped away as gas and the liquid temperature can be reduced to about 1.2 K. We cool our samples using this technique by thermally connecting a pumped reservoir of He (the 1K pot) to the sample stage, and isolating the stage from warmer environment with vacuum. We use a recycled He-3 refrigerator provided by RMC Cryosystems, whose He-3 has been removed, and whose sample stage is thermally anchored to the 1K pot. Temperature is monitored with a Cernox thermometer, and controlled using resistive heaters tied to the stage governed with a Conductus LTC-20 temperature controller. A superconducting magnet controlled by an Oxford IPS 120-10 Power Supply is installed in the dewar, capable of fields up to ±8 T. Lithography-free planar tunnel junctions (Sect. 6.5) and graphene hybrid structures (Chap. 7) were cooled and measured in this system.

4.4.3 Physical Property Measurement System

For many measurements at all temperatures between 1.8 and 400 K, we rely on the Physical Property Measurement System (PPMS) built by Quantum Design, Inc.. This system regulates the flow of pumped helium vapor along around a sample space that is well thermally isolated from the LHe supply bath so that a large range of temperatures is available without too much consumption of LHe. It is
equipped with superconducting magnet with a maximum field of ±9 T, and a cryopump to lower heat exchange within the chamber and improve pumppout of potential sample adsorbates. The PPMS is useful for quick characterization, since single samples (up to 12 leads) are soldered onto pucks and loaded in from the top, and temperature can be ramped at a rate of 10 K/min. The system is particularly useful in ionic liquid gating experiments, where temperature must be raised above the liquid’s freezing point (≈210 K) between every gate voltage change. Epitaxial graphene devices (Sect. 5), lithography-based planar tunnel junctions and FETs (Sect. 6.6), and Ca$_3$Ru$_2$O$_7$ flake devices (Sect. 8) were cooled and measured in this system.

### 4.5 Electrical transport and planar tunneling measurements

In all cryogenic measurement systems, electronic leads run from the sample stage to a breakout outside. While the PPMS was purchased pre-installed with its own current sources and voltmeters, we built our own breakout box for complete custom control and to allow for voltage sources that are impossible with the PPMS as purchased. The breakout box adapts the PPMS’ multi-lead LEMO connector to individual BNC outputs, and each line is interrupted by a radio-frequency filter to reduce broadcast noise between input and output. We use Low Pass LC Filter Modules purchased from Coilcraft (p.n. P7LP-304L), featuring 3 dB attenuation at 0.30 MHz, 78 dB attenuation at 1 MHz, and 65 dB attenuation at 10 MHz. Each filter is mounted on an easily accessed breadboard within the box for easy modification. Meters and sources connect to our breakout boxes with BNC cabling. Voltage meters used in this work include the Keithley 2002, 2182, and 182. Current sources include the Keithley 220 and 6221. Our primary voltage source for electrostatic gating was the Keithley 2400. A combination of the 2182 and 6221 was found to produce the lowest instrument noise. Instruments are routinely checked for good grounding, as broken shorts to ground produced excessive voltage noise.

Both electronic transport and tunneling measurements are performed by ap-
plying a d.c. current and measuring the voltage response. The only exception is the measurement of epitaxial graphene field effect transistor IV curves, where bias voltage is applied and output current measured by the Keithley 2400. Tunneling conductance $dI/dV$ is numerically calculated. Gate voltage is applied with positive voltage polarity on the back gate, so that a positive (negative) gate voltage charges the sample with electrons (holes). Gate leakage is monitored with the Keithley 2400 with a sensitivity of 1 nA. Large, fast changes in gate voltage were found to fry early devices; a safe ramp rate of 0.2 V/s was implemented for all gate voltage changes.

### 4.6 Data acquisition

The data presented in this work was acquired digitally. Communication is supported by the General Purpose Interface Bus (GPIB, IEEE-488) between a computer (Macintosh or PC) and our instruments. A GPIB Bus Isolator/Expander (National Instruments model GPIB-120A) isolates noisier instruments (including the computer) while remaining transparent for data communication. Automated measurements are programmed in National Instruments’ Labview, a graphical computing environment designed for laboratory data acquisition. While we write most of the subroutines used, we acquire some of the instrument level communication subroutines from the instrument manufacturer, most notably temperature and magnetic field control of the PPMS.

### 4.7 Numerical simulations

Various numerical simulations, data processing, and a many different calculations were performed with Wolfram Mathematica and Mathworks MATLAB, including coding in MUPad as part of the Symbolic Math Toolbox add-on.
5.1 Introduction

It is of interest whether the properties that make graphene so attractive for technological application, such as high room temperature carrier mobility, can be preserved after device fabrication. Many proposed applications require both the growth of scalable films and the integration of graphene and a top-gate dielectric. At the time of this work, two techniques hold genuine promise of producing high quality, scalable films useful for application. The first method is by sublimation of silicon (Si) from the surface of Si-face silicon carbide (SiC) wafers, which leaves behind nearly uniform, restructured single atomic layers on an insulating substrate[17]. The second is by chemical vapor deposition on metallic substrates such as nickel[87] or copper[18], which is capable of producing very high quality graphene that can be easily damaged when transferred to insulating substrates. We studied devices prepared on epitaxial graphene (EG) grown by the first method.

While much work has been done to evaluate the underlying SiC substrate as a source of strain inhomogeneity[88] and charged impurities[89] that scatter charge carriers, the role of the overlaying dielectric in top-gated devices has been relatively
unexplored. In this chapter, we investigate the effect of a deposited top-gate dielectric on the performance of graphene-based field effect transistors (FETs), and on the characteristics of dielectric-covered Hall bars to more carefully scrutinize its influence on carrier density and mobility. We published some of the results in this chapter in reference [90].

5.2 Device description

Our monolayer graphene films were grown at the Naval Research Laboratories in a controlled argon (Ar) environment on the Si-face of 6H-SiC wafers[91]. The grown films were both electron- and hole-doped, with carrier mobilities between 1,000 and 10,000 cm²/Vs[92]. Both FET and Hall bar structures were patterned by photolithography at HRL Laboratories. The graphene was selectively etched with a low power oxygen plasma, and electrical leads were a titanium/platinum/gold stack. A top gate dielectric of 35 nm silicon dioxide (SiO₂) was deposited by e-gun evaporation for use in FETs and to cover some of the Hall bars. This EG/dielectric combination was used previously in the development of high-performance EG-based FETs, which demonstrated record (at the time) peak transconductance of 600 mS/mm[20]. Capacitor arrays confirmed that the dielectric constant of the top-dielectric was 3.9, close to that of bulk SiO₂. Ideal capacitance is then rated at 0.99 F/m², drawing to the channel $6.2 \times 10^{11}$ cm⁻² electrons per volt of gate-source voltage. However, as discussed below, the actual device capacitance was found to be far from ideal. Leakage rates were less than 1 nA/µm during all measurements.

5.3 Epitaxial graphene FETs

The goal of work presented in this chapter is to understand the role of the top-gate dielectric in limiting the performance of EG-based devices. We begin by evaluating the transport in FETs at room temperature. In Fig. 5.1a we show a typical FET of channel width $\approx 11$ µm and length 5 µm. The gate electrodes do not span the entire channel, so ungated graphene adds to the contact resistance. A typical conductivity $\sigma$ vs. gate-source voltage $V_{GS}$ is shown in Fig. 5.1b. A
Figure 5.1. a) Schematic of a field effect transistor (FET) device fabricated on epitaxial graphene; b) Scanning electron microscopy image of a typical graphene FET with source (S), drain (D), and gate (G) labeled. Monolayer graphene is outlined by dashed lines; b) Conductivity $\sigma$ vs. gate voltage $V_{GS}$. Field effect mobility $\mu_{FE}$ of electrons is calculated from the slope of the dashed line, and is high relative to state-of-the-art silicon-based devices ($\approx 1,000 \text{ cm}^2/\text{Vs}$), but low compared to exfoliated graphene flake-based devices ($\approx 10,000 \text{ cm}^2/\text{Vs}$).

Conductivity minimum observed at $V_{GS} \approx -1 \text{ V}$ suggests that the graphene is initially electron doped, as are all FET devices measured, at $\approx 6.2 \times 10^{11} \text{ cm}^{-2}$ assuming ideal capacitance. Conductivity shows the expected linear response with $V_{GS}$ at low voltages. The deviation beyond $\pm 1.5 \text{ V}$ on $V_{GS}$ is likely due to a voltage dependent reduction on the gate capacitance. Past $\pm 2 \text{ V}$, gate leakage in many devices becomes substantial, and past $\pm 3 \text{ V}$ quickly becomes too high for the graphene or contacts to withstand. Field effect mobility $\mu_{FE}$ is extracted from the slope of $\sigma$ vs. $V_{GS}$ on the “electron” side, and is typically between 2,000 and 4,000 cm$^2$/Vs assuming ideal capacitance (a “hero” device with abnormally high $\mu_{FE}$ is shown in Fig. 5.1). While these values are higher than those found in silicon-based FETs, they are still fairly low by graphene standards; flakes supported on SiO$_2$ typically feature mobilities between 4,000 and 20,000 cm$^2$/Vs$[93]$. The saturation of current at large applied bias voltages is a desirable feature of FET transport; drain current that is independent of some range of bias voltage supports consistent on/off performance. Saturation occurs in gapped materials because the bias across the sample changes the potential between the channel and gate electrode such that a carrier-depleted portion emerges at the drain, and the total current is “pinched-off”. Graphene does not host and energy band gap, thus...
the bias-induced carrier depletion has a different effect. In Fig. 5.2a, we show IV curves (drain-source current $I_{DS}$ vs. drain-source voltage $V_{DS}$) for the same device shown in Fig. 5.1. We observe a temporary saturation-like “kink” that occurs at a $V_{GS}$-dependent bias threshold, observed at lower bias when the gate voltage brings conductivity towards its minimum value. Beyond the threshold, ohmic behavior returns. This is expected in graphene; as depicted in Fig. 5.2b, at some threshold voltage, the potential between the gate and the graphene at the drain is such that the carriers are depleted to the conductivity minimum (channel potential $V_{ch.} = 0$), bottlenecking the current. At higher biases, however, the graphene at the drain becomes hole-doped, and the average conductivity increases. While such behavior would be unexpected in conventional semiconductor PN junctions, carriers in graphene are fairly immune to large potential variations[11, 12]. We can reproduce this effect with simple numerical simulations of $I_{DS}$ vs. $V_{DS}$, treating the graphene channel as a one dimensional series of resistors. The value of each resistor is calculated from the field effect mobility and the local carrier density determined by the potential difference between the gate and that point in the series. A comparison of our simulations and performance from the same device, measured at small steps of $V_{GS}$ to highlight the kink, is shown in Fig. 5.2c-d. This effect has been previously observed in top-gated graphene flake-based FETs[94], and the bias-induced variation of potential along a graphene channel was previously observed directly from thermal measurements of the local Fermi level[85]. This effect may be unavoidable in monolayer graphene. Therefore, gapped bilayer graphene may be more suitable for logical electronics.

Our measurements of EG-based FETs find comparatively low field effect mobilities, which leads to very poor maximum $I_{ON}/I_{OFF}$ ratios (≈6 in the device in Fig. 5.1). However, we need a better tool than FET statistics to better understand the mechanisms that limit carrier mobility in graphene-based devices. We turn to Hall bar structures covered by the same dielectric, which allows us to more carefully characterize carrier density and mobility in related devices.
Figure 5.2. a) Drain-source current $I_{DS}$ vs. voltage $V_{DS}$ at different gate-source gate voltages $V_{GS}$ in the same device as in Fig. 5.1; b) Schematic of device with voltage profile along the channel of the device with an applied $V_{DS}$. When a voltage drop across the channel sets the potential at the drain to $V_m$ (top), where the Fermi level is set to the conductivity minimum, $I_{DS}$ is temporarily saturated. At higher $V_{DS}$, the low conductivity point moves towards the source (bottom), but the average conductivity increases, resulting in the upswing of $I_{DS}$; c) $I_{DS}$ vs. $V_{DS}$ in the same device as (a) but with smaller $V_{GS}$ steps to highlight kink; d) Numerical simulations of $I_{DS}$ vs. $V_{DS}$ using the model proposed in (b) (further details in the text).
5.4 Top-gated Hall bars

As discussed in the Sect. 3.1.2, Hall bar structures allow us to measure the density and mobility of charge carriers in graphene away from the charge neutrality point. We show in Fig. 5.3a a Hall bar fabricated on EG and covered with SiO$_2$. On some Hall bars, we also deposited a top-gate electrode to tune the carrier density as in our FETs. We show in Fig. 5.3b the Hall coefficient $R_H$ and longitudinal conductivity $\sigma_{xx}$ as a function of gate voltage $V_{GS}$ in a typical gated Hall bar. When $V_G$ minimizes $\sigma_{xx}$, $R_H$ shows very interesting behavior. Away from the charge neutrality point (CNP), the graphene is essentially single carrier where $R_H$ diverges as $V_G$ approaches the CNP, according to Eq. 3.4. Close to the CNP, potential variations induce hole and electron puddles throughout the film. In this regime, a two carrier model is more appropriate as $R_H$ vanishes at the CNP. By plotting the calculated Hall carrier density $n_H = 1/eR_H$, as in Fig. 5.3c, we can estimate the approximate amplitude of charge fluctuations as the value at which we observe a deviation from linear variation, and is $\approx 3 \times 10^{12}$ cm$^{-2}$ in EG Hall 1. The corresponding Hall mobility $\mu_H$ maximizes to 2,600 cm$^2$/Vs.

In all devices measured, there is a large discrepancy in the carrier density and mobility as measured by either Hall or field effect methods. Assuming ideal capacitance, field effect mobilities (carrier densities) are generally more than order of magnitude larger (smaller) than when measured by Hall effect. The discrepancy is understood when the top-gate capacitance is calculated from $dn_H/dV_G$, which suggests a value of 18 times higher than ideal in EG Hall 1. This detail suggests the possibility of a large density of charge traps at the graphene-dielectric interface that act like parallel nano-gap capacitors, which is further supported by the effects of varying temperature.

Hall carrier density and mobility in dielectric-covered EG Hall structures have a strong dependence dependence on temperature $T$, as shown for many devices in Fig. 5.4a-b. It is expected that $\mu_H$ increase slightly with decreasing temperature as phonons freeze out. However, the behavior of $n_H$ is contrary to what is expected in intrinsic graphene, whose carrier density depends only on extrinsic factors. The change in top-gate dielectric capacitance with temperature further highlights problems with the dielectric. In Fig. 5.4c we show $\sigma_{xx}$ vs. $V_G$ for both sweep directions.
Figure 5.3. a) Optical image of an epitaxial graphene Hall bar covered by 35 nm SiO$_2$. Dashed lines outline the monolayer graphene. Colored arrows refer to the direction of voltage measured for plots (b)-(d) in a similar Hall bar where a top-gate electrode covered both Hall crosses; b) Hall coefficient $R_H$ and longitudinal conductivity $\sigma_{xx}$ vs. gate voltage $V_G$; c) Hall effect carrier density ($n_H = 1/eR_H$) vs. $V_G$; d) Hall effect mobility ($\mu_H = |\sigma R_H|$) vs. $V_G$. 
Figure 5.4. a) Hall effect carrier density $n_H$ vs. temperature $T$ in many SiO$_2$-covered EG Hall bars, differentiated by color; b) Hall effect mobility $\mu_H$ vs. temperature $T$ for the same devices shown in (a) with color preserved; c) Longitudinal conductivity $\sigma_{xx}$ vs. top-gate voltage $V_G$ in a gated EG Hall bar at $T = 300$ K and 1.8 K. Arrows indicate sweep directions.

of $V_G$ at $T = 300$ K and 1.8 K. At 300 K, the response is history dependent, and the location of the CNP, supported by $R_H$ measurements, suggests an initial electron doping of $1.2 \times 10^{13}$ cm$^{-2}$. After cooling the sample down to 1.8 K while holding $V_G = 0$, $\sigma_{xx}$ is very weakly $V_G$-dependent, and $R_H$ measurements suggest that the capacitance decreased by $\approx 40$ times its value at 300 K. Furthermore, the carrier density can be changed substantially by warming to 300 K, varying $V_G$ to a new value, and cooling while that voltage is held. This is caused by a large density of charge traps at the graphene-dielectric interface. Each charge trap is either an impurity or dangling SiO$_2$ bond which has a particular ionization energy and a higher probability of ionization at 300 K. At 1.8 K, these traps freeze out and the effective dielectric constant approaches ideal. Therefore, Hall mobility is much closer to the true carrier mobility than field effect mobility in these devices.

Ionized charge traps and impurities in the dielectric act as Coulomb scatterers for carriers in graphene, and impose charge inhomogeneity through potential fluctuations throughout the film[41, 46]. One signature of charge inhomogeneity is in magnetoresistance measurements at low temperature. We show in Fig. 5.5 transverse ($R_{xy}$) and longitudinal ($R_{xx}$) resistances as a function of applied perpendicular magnetic field $H$ in a single EG-based Hall structure. At low temperatures and finite $H$, the emergence of Landau levels in graphene leads to dips in $R_{xx}$ as $H$
is ramped. However, in Hall crosses that are adjacent to the longitudinal portion, oscillations and plateau formations in \( R_{xy} \) do not line up with dips in \( R_{xx} \), nor do we observe plateaus forming at the expected quantization \( R_{xy,n_{LL}}^{-1} = 4\frac{e^2}{h}(n_{LL} + \frac{1}{2}) \), where \( e \) is the elementary charge, \( h \) is Planck’s constant, and \( n_{LL} = 0,1,2, ... \) the Landau level index. The agreement on \( R_{xy} \) measured in two Hall crosses on the same Hall bar at low \( H \), but not high, suggest that while the average carrier density is roughly equal, they each feature greatly different levels of inhomogeneity.

To support that the charge inhomogeneity is not dominantly associated with the underlying SiC substrate, we performed Raman topography on the Hall cross junctions of SiO\(_2\)-covered EG-based Hall structures. Graphene grown on the Si-face is SiC is separated from the SiC by a carbon-rich buffer layer that is covalently bonded to the substrate[89], making it electronically interactive, but doping the overlaying graphene with \( 10^{12} - 10^{13} \) cm\(^{-2} \) charge carriers. The inhomogeneity associated with this doping is \( \approx 10\% \) variation, as revealed by previous Kelvin probe microscopy measurements[95]. Coupling to the buffer layer also requires the
graphene lattice to stretch by about 8%[89], thus stronger strain and higher carrier density should be correlated. As discussed in Sect. 3.5.3, Raman topography of the 2D peak in graphene can be used to reveal strain variation. As shown in Fig. 5.6a, planar strain causes 2D peak shift (by $\approx 10 \text{ cm}^{-1}$) and broaden[61]; the effect of carrier density is much weaker[96]. In Fig. 5.6b-c we show Raman topographical
maps of the 2D peak position in two Hall crosses from different devices, and in Fig. 5.6d we show related histograms. The surprising result is that the device with a larger area of strained graphene features a lower $n_H$, and maps of many devices confirmed no correlation between $n_H$ and average strain. This supports the argument that the doping and inhomogeneity thereof in our devices is related to the deposited SiO$_2$ dielectric and not the substrate.

The presence of charged impurities and traps at the interface between graphene and the top-gate dielectric adversely affects the mobility of charge carriers through Coulomb scattering. In Sect. 2.3, we showed that the inverse of mobility $\mu^{-1}$ is linearly proportional to the density of Coulomb scatterers, and the potential that they induce draws a local residual concentration of charge carriers in the graphene that is proportional to their density. We show in Fig. 5.7a $\mu^{-1}_H$ vs. $n_H$ from the many SiO$_2$-covered EG-based Hall bars measured in this study. The data includes measurements at different temperatures between 2 and 300 K, with lower temperature measurements tending towards $n_H$. While $n_H$ and $\mu_H$ both vary with temperature, the relationship between the two does not, suggesting that phonons play a negligible role.

We also include in Fig. 5.7 trend lines following theoretical predictions based on the work of Adam et al.[41] and derived in Sect. 2.3 for the relevant relationship, where $n_H$ is set equal to the residual carrier density induced by Coulomb scatterers. We include trends for charged impurities located at an average distance of 3Å perpendicular to the graphene, and assuming half-space dielectric combinations of SiO$_2$/SiC and SiO$_2$/vacuum. The latter, when offset in $n_H$ by $8 \times 10^{11}$ cm$^{-2}$ to account for the contribution of substrate-induced initial doping, fits very well to the data. The better fit of this model over the SiO$_2$/SiC combination suggests that the electrostatic role of SiC is very weak, and that the underlying buffer layer, with an uncertain effective dielectric constant, provides electrostatics no better than vacuum.

Measurements from two bare EG-based Hall structures, also at different temperatures between 2 and 300 K, are plotted in Fig. 5.7a and do not follow the theoretical predictions outlined above. These devices exhibit a much higher $\mu_H$ for a given $n_H$. Improved local electrostatics are not likely the reason; although total charge neutrality must be conserved, the source of donated electrons may
be passivated by other means. The dependence of \( n_H \) in the same bare devices is shown in Fig. 5.7b along with that of two representative SiO\(_2\)-covered devices for comparison. The small temperature dependence of \( n_H \) on temperature is likely due to adsorbate doping, and possibly due to varying substrate interactions - graphene and SiC feature opposing thermal expansion coefficients. While the strong temperature dependence of doping in SiO\(_2\)-covered devices does not follow simple thermally activated behavior, the activation barrier may vary with temperature. In its entirety, Fig. 5.7 confirms that charge traps and impurities in the top-gate dielectric are the source for the dominant doping of dielectric-covered EG Hall bars, and the of carriers mobility is limited primarily by Coulomb scattering.

The above picture can be examined further by reducing sample size. The inconsistency between \( R_{xy} \) measured in two Hall crosses 10 \( \mu \)m apart (Fig. 5.5) suggests that the spatial charge inhomogeneity is on the scale of a micron. If the
device is reduced in size to include fewer puddles, $\mu_H$ and $n_H$ should improve. This may explain why FET devices ($\approx 5 \times 10^3 \mu m$) generally featured mobilities several times higher than in the larger Hall devices ($\approx 10 \times 30 \mu m$). We measured one smaller top-gated Hall bar structure ($\approx 5 \times 10^3 \mu m$), shown in Fig. 5.8a, which featured single carrier type behavior down to a $n_H = 5 \times 10^{11} \text{cm}^{-2}$, roughly an order of magnitude better than in larger devices. While holding the gate voltage just outside the charge puddle onset, we cooled this device down to 1.8 K, then varied $V_G$ at low temperature, where the dielectric behaves more ideally so that larger voltage without leakage is possible. We show in Fig. 5.8c its magnetoresistive behavior at 1.8 K, where $\mu_H \approx 5,000 \text{ cm}^2/\text{Vs}$. The Hall resistance clearly plateaus at the expected quantization for the $n_{LL} = 1$ Landau level filling at $H > 2.5 \text{ T}$. Observation of the quantum Hall effect is a hallmark of graphene quality, and in graphene grown on the Si-face of SiC has only been observed recently as growth uniformity has improved[97, 98, 99]. In the quantum Hall regime, we expect that the longitudinal resistance $R_{xx}$ vanish. However, as shown in Fig. 5.8c, we observe only saturation to a minimum, which suggests that the longitudinal portion may be more disordered than the transverse portion. The observations of vanishing $R_{xx}$ in the quantum Hall regime in Si-face EG has only been reported in graphene
without a deposited top-gate dielectric\cite{98}. By varying carrier density with $V_G$, we show that the onset of the $n_{LL} = 1$ quantization can be shifted, as expected. We can also tune the carrier density below the puddle regime, where quantization of both holes and electrons to $\pm h/2e^2$ results in an intermediate average value of resistance, depending on the ratio of electron puddles to hole puddles. It is reasonable to assume that by pushing both FET and Hall bar structures to smaller dimensions, quality and performance can be improved even further.

In this section, we have only discussed one source of scattering. Additional sources of scattering contribute according to Matthiessen’s rule: $\mu^{-1} = \sum_i \mu_i^{-1}$. The independence of the relationship between $\mu_H$ and $n_H$ with temperature in dielectric-covered graphene, as shown in Fig. 5.7a, suggests that phonon scattering plays a very limited role, in agreement with other studies\cite{100}. Theoretical studies of short-range scattering due to vacancies treated as localized barriers of infinite potential suggest a highly non-linear relationship between $\mu$ and $n$\cite{53}. While it has been suggested that graphene vacancies can lead to lattice deformation and Coulomb-like long-range scattering interactions\cite{101}, such scattering would not be associated with the induced doping that we observe. While electron-phonon interactions and short-range scattering may play a stronger role in bare graphene, as evidenced in Fig. 5.7a, charged impurity scattering is most clearly the dominant source of scattering in dielectric-covered graphene.

5.5 Conclusion

Our studies of electrical transport in EG-based FETs and dielectric-covered Hall bars propose that charged impurities located at the interface between graphene and the deposited dielectric dominate scattering in electronic transport. Through Coulomb interactions, they impose potential variations throughout the device channel and severely limit carrier mobility. When ionized, impurities act as local charge traps evidenced by a strongly temperature-dependent gate capacitance in FET devices. We showed that carrier mobility and inhomogeneity as measured by Hall effect were greatly improved by reducing the size of devices towards the scale of spatial inhomogeneity, which also facilitated observation of the quantum Hall effect. Therefore, integration of graphene and a top-gate dielectric must be seriously
addressed for gated graphene electronics to be realized. In considering top-gated electronics, a poor dielectric interface will bottleneck device performance. As for graphene’s potential for logical electronic applications, even with improved carrier mobilities, a finite minimum conductivity results in an inability to turn current off. Poor $I_{ON}/I_{OFF}$ and non-ideal current saturation characteristics demand an energy band gap.
Chapter 6

Bilayer graphene - Band gap engineering

6.1 Introduction

While monolayer graphene’s high carrier mobility, among other properties, make it attractive for practical applications, its lack of an intrinsic energy band gap preclude it from playing an effective role in many related technologies, including logical field effect transistors (FETs). Although engineering a gap in monolayer graphene has been underway through quantum confinement in graphene nanoribbons[102] or chemical modification[103], related devices have so far shown poor carrier mobility and, in the case of the former, poor control of graphene edge states. However, bilayer graphene (2LG), which features comparable carrier mobility and an interlayer electric field-tunable band gap (see Sect. 2.2.1), may offer a pathway for such technologies. Opening a gap in 2LG has been previously demonstrated by angle-resolved photoemission spectroscopy of top-doped bilayer graphene[24] and infrared absorption in dual-gated FETs[25, 26]. However, thermally activated transport studies[27, 28, 29, 30, 31] suggest that variable range hopping-like transport mechanisms dominate at low temperatures. The disorder discussed in the last chapter induces energy gap and Fermi level variations[104], as well as localized states that provide tunneling channels[29], that undermine true gapped transport. Disorder can be reduced by suspending graphene[15, 14] or by using single crystal
boron nitride flakes as a gate\cite{105}, but neither technique has been shown to be compatible with a scalable technology.

We use planar tunneling spectroscopy (Sect. 6.3) to probe electronic density of states (DOS) in 2LG flakes, employing a thin film dielectric and FET-like design to allow direct comparison with transport in FETs fabricated with similar dielectric environments. We use exfoliated flakes not only because the growth of scalable, uniform 2LG has not yet been demonstrated, but also because the exfoliation onto a back gate-ready substrate, in conjunction with a top-gate, facilitates the application of an interlayer electric field. Our work was first motivated to use a planar tunnel junction on 2LG to both control and directly measure its energy band gap. However, bilayer graphene’s low carrier density and electric-field dependent electronic structure make it very sensitive to tunneling bias induced charging, which is ignored in traditional tunnel junctions. When looking to correlate tunneling conductance fluctuations with band structure features, one other complication is the presence of fluctuations due to quantum interference effects. To address these, we begin this chapter by briefly discussing studies of conductance fluctuations in 2LG. We then present results of planar tunneling measurements of the energy gap in biased bilayer graphene.

6.2 Conductance fluctuations

In a mesoscopic sample, which due to its size lacks self averaging of its properties, disorder can cause quantum interference of its charge carriers, which produce conductance fluctuations (CF) in low temperature electrical transport\cite{106, 107}. They can be observed by tuning the Fermi level with gate voltage $V_G$, or by ramping magnetic field $H$. In the latter case, $H$ varies the charge carrier’s wavefunction, which is well correlated within the dephasing length, $L_\phi$. Whenever the magnetic flux through an area defined by $L_\phi$ is an integer multiple of the flux quantum $\phi_0$, the carrier’s phase is shifted by $2\pi$ and the resulting interference causes a change in conductance. Within the weakly disordered regime ($k_Fl \gg 1$, where $k_F$ is the Fermi wavevector and $l$ the mean free path of a charge carrier), CF are on the order of $e^2/h$, independent of sample size or level of disorder, and so are referred to as universal conductance fluctuations\cite{106, 107}. CF have been studied theo-
Figure 6.1. a) Conductivity $G$ vs. gate voltage $V_G$ in an electrical transport device fabricated on disordered bilayer graphene; b) Background-subtracted conductance fluctuations $\Delta G$ vs. $V_G$ showing back-to-back measurements; c) $\Delta G$ vs. magnetic field $H$ at different constant $V_G$ as labeled; d) $\Delta G$ vs. $H$ at different constant temperatures $T$ as labeled.

Theoretically in both monolayer graphene (1LG)[108, 109] and 2LG[110]. In 1LG, CF have been previously reported in both mechanically exfolated flakes[111] and films grown epitaxially on SiC[112]. We reported observations of CF suppression near the charge neutrality point in 2LG and trilayer graphene flakes in Ref. [86]. In this section, we present studies of CF in 2LG flakes.

In Fig. 6.1a, we show conductance $G$ vs. $V_G$ in a disordered 2LG electrical transport device, fabricated with a quartz filament shadow mask (see Sect. 3.6). Observation of a minimum $G$ at $V_G = 65$ V suggests that the device is hole-doped, presumable by adsorbed water from atmosphere. Large CF are also observed far from the charge neutrality point (CNP), and are shown in Fig. 6.1b after subtracting off a piecewise polynomial background. Back-to-back measurements prove that the large fluctuations are reproducible, thus intrinsic to the sample rather than
measurement noise. With application of $H$ perpendicular to the sample, periodic CF are clearly discerned in magnetoconductance in Fig. 6.1c. Here, a polynomial background $G_{bgd} = G_0 + a|H| + bB^2$ has been subtracted off, where the linear term corresponds to a slight density gradient in the samples[113] and the quadratic term corresponds to classical magnetoconductance. A conductance dip centered about $H = 0$ corresponds to weak localization effects, a common phenomenon in disordered graphene[111]. Periodic CF in $H$, symmetric about $H = 0$ and of order $e^2/h$, feature stronger amplitudes far away from the CNP. Close to the CNP, they are suppressed. Fluctuations are also suppressed with increasing temperature, as shown in Fig. 6.1d, and in the most disordered samples persist up to 40 K. From the period of oscillations $\Delta H$, the value of $L_\phi$ can be estimated using $\Delta H \approx L_\phi^2/\phi_0$, and decreases from $\approx 200$ to 87 nm as temperature increases from 1.4 to 40 K.

The suppression of CF near the CNP is not fully understood. In Ref. [86], we proposed two possible scenarios. First, we proposed that the edge states of 2LG, which are one-dimensional and would not feature quantum interference with the opposite edge, may dominate conductance as the minimum conductivity is approached. However, this is not too likely, as the bulk of the 2LG would still be highly conductive, and minimum conductivity in graphene is independent of sample size at the mesoscopic scale. A second scenario, which is more likely, is that the electronic inhomogeneity in substrate-supported graphene, discussed in Sect. 2.3 and the last chapter, are responsible for CF suppression. Near the CNP, in the “charged puddle” regime, graphene features spatially varying areas of electron and hole puddles due to Coulomb interactions with charged impurities. Phase coherence may be lost as carriers cross the boundary between puddles, reducing $L_\phi$. This may be why only larger period CF are observed in the magnetoconductance near the CNP in Fig. 6.1c. A recent study of CF in 1LG electrical transport reported that $L_\phi$ decreases roughly linearly as $V_G$ approaches the CNP[114].

Flakes presented in this chapter and Chap. 7 feature considerably less disorder than those in our CF studies, due to improved graphite source material. However, CF are still finite at the lowest temperatures. Most of the following tunneling and magnetoconductance measurements were performed at 10 K, to suppress CF to negligible amplitudes, while retaining strong signals from other phenomena.
6.3 Planar tunneling in measurement-sensitive materials

Having been originally developed to measure superconductor energy gaps[66], planar tunneling spectroscopy can also be used to explore features in the density of states in semiconductors and other materials[115]. The technique relies on quantum tunneling of electrons through an insulating barrier separating the sample and a metallic probe. Since the probability of electron tunneling decreases exponentially with barrier thickness, in experiments the barrier is usually an insulating film of nanometer thickness. Typically, the chemical potentials of sample and probe will disagree and cause an electric potential difference between the two sides. If the potential difference between them is enforced to be zero through a connected circuit, charge transfer will align the Fermi levels in the respective materials at the tunnel junction.

When a bias $V_B$ is applied between the sample and probe, as shown in Fig. 6.2, electron tunneling occurs between filled electronic states on one side and empty states on the other. Therefore, the total tunneling current $I$ can be evaluated[115]:

$$I \propto \int_{-\infty}^{\infty} T(E)N_P(E)f(E)N_S(E-eV_B)(1-f(E-eV_B))dE,$$

(6.1)

where $N_P(E)$ is the DOS in the tunneling probe, $N_S(E)$ is the DOS in the sample, $T(E)$ is the tunneling matrix for electrons of energy $E$, and $f(E)$ is the Fermi function. Neglecting voltage distortion of the tunnel barrier, we treat $T(E)$ as a constant. Assuming also constant $N_P(E)$, the above integral becomes, at zero temperature,

$$I \propto \int_{\mu}^{\mu+eV_B} N_S(E)dE.$$

(6.2)

where $\mu$ is the Fermi energy ($= 0$ at the charge neutrality point). It should be noted that Eq. 6.2 was derived for zero temperature, such that $f(E)$ can be approximated to the mirror of the Heaviside function. Finite temperature $T$ complicates the functional derivation, but the qualitative result is a “smearing” of relevant $E$ by roughly $k_BT$, where $k_B$ is the Boltzmann constant. Taking the first derivative with
Figure 6.2. a) Schematic of a generic planar tunnel junction with bias $V_B$ applied across the tunnel barrier (shaded); b) Energy diagram of a biased planar tunnel junction between a metallic probe with constant density of states $N_P(E)$ and a sample with non-trivial density of states $N_S(E)$. Arrows indicate electron tunneling occurring between filled states on one side and empty states on the other; c) A small change in bias $\delta V_B$ increases the tunneling current by a small amount (blue sliver) roughly proportional to $N_S(\mu + eV_B)$, where $\mu$ is the Fermi level in the sample.

For $V_B$, assuming that both $\mu$ and $N_S(E)$ are independent of $V_B$, gives the tunneling conductance,

$$\frac{dI}{dV_B} \propto N_S(\mu + eV_B). \quad (6.3)$$

The result above, shown graphically in Fig. 6.2c, is typically a sufficient approximation for samples that are either metals, most semiconductors, or superconductors, due to high carrier densities in these materials. Tunneling spectroscopy is not useful for measurements of wide-band semiconductors or insulators, since relevant biases would need to be much larger than a regime where $T(E)$ can be treated as constant or even larger than the dielectric breakdown of the tunnel barrier [115]. If the sample is a low-carrier density semi-metal or narrow-band semiconductor, then the approximations that led to Eq. 6.3 are no longer valid. In these materials, the capacitive charging (Fig. 6.3a) due to an applied bias is not negligible, making the Fermi level $V_B$-dependent. Furthermore, in some materials, $N_S(eV)$ varies with an applied electric field $D$. Given these considerations, the derivative
Figure 6.3. a) Reproduction of Fig. 6.2a, showing the capacitive charging and electric field \( \vec{D} \) induced by a tunneling bias \( V_B \); b) Reproduction of Fig. 6.2c for a sample whose Fermi level and density of states \( N_S(E) \) are bias-dependent. A small change in bias \( \delta V_B \) increases the current by a contribution roughly proportional to \( N_S(\mu_0 + eV_B) \) (blue sliver), a contribution roughly proportional to \( N_S(\mu_0) \) (orange sliver), and a contribution due to the change \( N_S(E) \) at energies between \( \mu_0 \) and \( \mu_0 + eV_B \) (green line), where \( \mu_0 \) is the Fermi level in the sample with applied bias \( V_B \).

of Eq. 6.2 must be taken using the Leibniz rule\[116\] for the general case:

\[
\frac{dI}{dV_B} \propto (1 - \zeta) N_S(\mu + eV_B) + \zeta N_S(\mu) + \frac{1}{e} \int_{\mu}^{\mu + eV_B} \frac{\partial N_S(E)}{\partial V_B} dE, \tag{6.4}
\]

where \( \zeta = -(1/e)d\mu/dV_B \) represents the bias-induced charging discussed above and is positive for the positive polarity of \( V_B \) on the sample. The physical origins of the three terms above are shown schematically in Fig. 6.3b. Eq. 6.4 must be used to analyze tunneling spectra obtained from bilayer graphene, which features both low carrier densities and an energy band gap that is tunable with interlayer bias.

6.4 Tunneling bias effects and the band gap

Our planar tunnel junctions are fabricated on 2LG flakes supported on a Si/SiO\(_2\) substrate so that we can capacitively back-gate the sample during tunneling measurements. The tunnel junction also acts to top-gate the sample through our 2 nm
Figure 6.4. a) Schematic of a back-gated, planar tunneling device prepared on bilayer graphene (blue); b) Energy diagrams at the tunnel junction between the tunneling probe and an initially gapped bilayer graphene for zero applied bias $V_B$, where the graphene is initially charge neutral ($n_0 + \frac{C_{BG} V_{BG}}{e} = 0$), c) electron doped ($n_0 + \frac{C_{BG} V_{BG}}{e} > 0$), and d) hole doped ($n_0 + \frac{C_{BG} V_{BG}}{e} < 0$).

Alumina ($\text{AlO}_x$) tunnel barrier. A schematic of the dual gated structure is shown in Fig. 6.4. The voltage polarities are set up such that the total carrier density $n_{\text{tot.}}$ and displacement field $D$ are given by

$$n_{\text{tot.}} = \frac{1}{e} (C_{BG} V_{BG} - C_{TB} V_B) + n_0,$$

$$D = \frac{1}{2\epsilon_0} (C_{BG} V_{BG} + C_{TB} V_B) + D_0,$$

where $e$ is the elementary charge, $\epsilon_0$ the free space permittivity, $C_{BG}$ the back-gate capacitance, $V_{BG}$ the applied the back-gate voltage, $C_{TB}$ the tunnel barrier capacitance, $V_B$ the tunneling bias, and $n_0$ and $D_0$ the initial charge carrier density and field, respectively, due to initial conditions. The terms $n_0$ and $D_0$ depend on the relative work functions between graphene and the tunneling probe and doping induced by local impurities, and can vary between samples. Energy diagrams at the tunnel junction are shown in Fig. 6.4b–d for different initial conditions and applied $V_G$, assuming the 2LG is finitely gapped.

In a typical tunneling spectroscopy experiment, the carrier density of the sample is very high ($n_0 \gg 0$), so that an applied bias $V_B$ does not significantly charge the sample. In 2LG, we must consider that $V_B$ varies not only the Fermi level, but also
Figure 6.5. Energy diagrams at a tunnel junction prepared on gapped bilayer graphene for finite bias $V_B$, given a) an initially charge neutral and b) an initially electron doped graphene. Qualitative results are shown for both polarities of $V_B$, and for the cases of both a positive and negative initial displacement field ($D_0 + C_{BG}V_{BG}/2\varepsilon_0$) perpendicular to the bilayer. Red dashed lines mark the Fermi level in 2LG, which shifts with finite $V_B$ due to charging. Cartoons of the expected tunneling conductance $dI/dV_B$ vs. $V_B$ for each case, where gray dashed lines indicate where the band edges are sampled.
the electronic structure. In Fig. 6.5, we show schematics of the effects of $V_B$ on the energy diagrams for zero and initial negative electron density and for both signs of the initial displacement field. The case of initial positive electron density would be similar to that of negative, only mirrored about the charge neutrality point (CNP). As qualitatively shown, the tunneling spectra as $V_B$ is swept is sensitive to $n_0$, $D_0$ and $V_{BG}$.

The tunneling conductance $dI/dV_B$ in junctions prepared on 2LG follows the general form of the expression for tunneling conductance (Eq. 6.4), derived and discussed in Sect. 6.3:

$$
\frac{dI}{dV_B} \propto (1 - \zeta)N_{2LG}(\mu + eV_B) + \zeta N_{2LG}(\mu) + \frac{1}{e} \int_{\mu}^{\mu+eV_B} \partial N_{2LG}(E) \frac{\partial V_{BG}}{\partial V_B} dE, \quad (6.7)
$$

where $N_{2LG}(E)$ is the DOS of 2LG, $\mu$ is the Fermi level, and $\zeta = -(1/e)d\mu/dV_B$ is related to the bias induced charging and is positive for our polarity of $V_B$. We estimate the value of $\zeta$ by reformulating it to $\zeta = -(1/e)(d\mu/dn)(dn/dV_B)$, where $n$ is the carrier density. The expression $d\mu/dn$ is related to the electronic compressibility of 2LG, and $dn/dV_B$ the capacitance of the tunnel barrier. The former does vary in 2LG with Fermi level, particularly at the edge of and within the energy band gap[117, 118, 119]. However, charge inhomogeneity can prevent its value from varying significantly[120]. We can use our tunneling spectra to evaluate $d\mu/dn$ by determining the bias $V_{BG}^0$ at which the CNP is sampled, which gives $\mu = -eV_B$, calculating $n$ from Eq. 6.5. We then use $V_{BG}$ to vary $n$ independently and calculate $d\mu/dn$.

We use Eq. 6.7 to perform numerical simulations of tunneling spectra in order to relate spectrum features that we observe experimentally to an electronic structure that varies with applied bias. We calculate $N_{2LG}(E)$ numerically using results from tight-binding theory (Sect. 2.2.1), assuming that the band gap $\Delta$ follows the simple dependence

$$
\Delta = aD + \Delta_n, \quad (6.8)
$$
Figure 6.6. Numerical simulation of tunneling conductance $dI/dV_B$ (red) and its derivative (blue) $v$s. tunneling bias $V_B$ in a bilayer graphene tunnel junction. Calculations are based on Eq. 6.7 assuming zero carrier density at $V_B = 0$, a constant back gate voltage, and a zero bias energy band gap $\Delta(V_B = 0) = 30$ meV.

where $a$ is a constant and $\Delta_n$ is a correction at finite carrier density that includes charge distribution and screening effects[22, 39]. While $a$ does vary with $n_{tot.}$, self-consistent tight-binding calculations[23, 39] suggest that it does not vary by more than 1% for experimentally relevant $n_{tot.}$. To simplify our numerical simulations, we consider the case of $V_{BG}$ set such that $\mu$, $n_{tot.} = 0$ at $V_B = V_B^0 = 0$, shown schematically in Fig. 6.5a. Here, $\Delta_n \approx 0$ for small $V_B$, and is ignored. We show in Fig. 6.6 the results of our simulation for initial $\Delta(V_B = 0) = 30$ meV and $\zeta = 0.2$. We assume that 300 nm SiO$_2$ ($\epsilon = 3.9$) determines $C_{BG}$ and that 2 nm amorphous AlO$_x$ determines $C_{TB}$. We apply a Gaussian smoothing of $N_{2LG}(E)$ at each point with width $\approx 5$ meV to account for thermal smearing and the likelihood of tunneling through multiple channels into a charge-inhomogeneous film.

As shown in Fig. 6.6, the large peaks in simulated $dI/dV_B$ are due to the sampling of the band edges in 2LG and are contributed by the first term in Eq. 6.7. The width between these peaks is proportional to the band gap, and is roughly equal to $\Delta/(1 + \zeta)$. Another peak located roughly at $V_B = -50$ meV is due to the contribution of the second term in Eq. 6.7 - when the Fermi level is shifting through a band edge. The third term in Eq. 6.7 produces asymmetry in the peak heights, but does not affect their position substantially. We fit prominent features of our simulated $dI/dV_B$, as well as the numerically calculated second derivative (Fig. 6.6) to relevant experimental spectra, which returns the energy band gap.
Figure 6.7. a) Junction resistance $R$ vs. back-gate voltage $V_{BG}$ in a bilayer graphene planar tunnel junction prepared by the filament technique. Arrows correspond to locations of tunneling spectra measured and shown in (b) at $V_{BG} = 0$ and in (c) at $V_{BG} = -51$ V.

This gives a measure by which to relate the bias-width between the prominent peaks in $dI/dV_B$ to the energy band gap at arbitrary $V_{BG}$ and $V_{BG}^0$. Our fitting also determines the coefficient $a$, with which we can estimate $\Delta_n$ from Eq. 6.8 and $\Delta$ measured at finite carrier density.

6.5 Filament-based planar tunnel junctions

Our early planar tunnel junctions were fabricated on 2LG flakes using the filament shadow mask method outlined in Sect. 3.6 in order to prevent sample damage inherent to photolithographical processing and to fabricate devices quickly[64]. The growth of the tunnel barrier used in the device presented in this section was performed as described in Sect. 3.7.2 using the original technique, before improvements were made. These devices feature a transport portion in series with the tunnel junction. Since graphene resistance is typically between 1 and 10 kΩs per square for experimentally relevant charge carrier densities, the voltage drop across the transport portion is on the same order as that across the junction. For a fixed current, then, the junction acts as a large contact resistance. We show in Fig. 6.7a the total device resistance $R$ vs. $V_{BG}$ in one device. The position of the resistance maximum suggests that the 2LG Fermi level can be shifted to the vicinity of the CNP at $V_{BG} \approx -55$ V. It should be noted that the average Fermi level in the trans-
Figure 6.8. Tunneling spectra (smoothed and relatively shifted) $dI/dV'_B$ vs. device bias $V'_B$ in a bilayer graphene planar tunnel junction prepared by filament masking, at temperature $T = 10$ K (same device as in Fig. 6.7). Spectra are shown for back gate voltages $V_{BG}$ from -56 to -48 V at steps of 1 V.

Port portion may disagree slightly with that involved in electron tunneling, due to the differing environment above the 2LG. In the device discussed in this section, we relabel the bias $V'_B$ because the actual tunneling bias $V_B$ is significantly less, due to the voltage drop across the transport portion.

We show in Fig. 6.2b the tunneling spectrum measured in the same device...
with $V_{BG} = 0$, measured at $T = 10$ K. The spectrum shows a very strong “V”-shaped background that, upon further measurements, was observed to be static with changing $V_{BG}$. We also observe small features at low bias that shift with $V_{BG}$. When $V_{BG}$ is tuned near the transport portion’s CNP, a large suppression in the tunneling conductance appears at low bias. This is the largest feature observed in the tunneling spectra of this device. At $V_{BG} = -51$ V (Fig. 6.2c), the suppression is characterized by a flat, featureless conductance of width $\approx 50$ meV, and two bounding conductance peaks, which suggests that it is related to an energy band gap in 2LG.

The evolution of the suppression is shown at 1 V steps of $V_{BG}$ in Fig. 6.3. With the help of dashed lines, we track features related to the suppression in the spectra. A positive shift in $V_{BG}$ raises the Fermi level in the 2LG, such that common features will be observed at more negative biases, as shown. Other sharp features appear to emerge within the suppression, such as the peak observed at $(V_{BG}, V'_B) = (-48 \text{ V}, -20 \text{ mV})$, which may be due to parallel tunneling into a portion of 2LG with an unequal Fermi level. This interpretation raises the possibility of a strongly charge-inhomogenous graphene film and a non-uniform tunnel barrier.

Further evidence that this suppression is related to an energy gap is supplied by the application of a perpendicular magnetic field $H$. We reproduce the zero-field spectrum at $V_{BG} = -51$ V along with a spectrum measured at $H = 8$ T in Fig. 6.9a. At finite field, two conductance peaks appear at the edges of the suppression. This effect is consistent with the emergence of Landau levels in gapped bilayer graphene (Sect. 2.2.2), which corresponds to an enhanced density of states at the valence and conduction band edges as the 2LG is transitioning into a quantum Hall regime. By mapping the position of these peaks with changing $V_{BG}$ in Fig. 6.9b, we support that these emergent features are in fact signals from the density of states that follow the evolution of the suppression at zero field.

Several complications make quantitative analysis of the gap-like feature in filament-fabricated devices difficult. Features that dominate at low bias drown beyond $V_B \approx 40$ meV in the overwhelming “V”-background. Therefore, only a small range of $V_{BG}$ can by studied for a single feature. The “V”-shaped background is consistent with a two-step tunneling process that was explored by Giaever et al. in tunnel junctions between Al electrodes grown intentionally with metallic
tin particles embedded in the barrier[68, 67]. The tunneling process is described by intermediate charging of metallic particles with a distribution of capacitances. Tunneling current increases as electrons overcome a threshold voltage equal to $(e/2C) + V_D$, where $e/C$ is the charging energy of a single metallic particle and $V_D$ is a randomly varying offset between the Fermi level of the electrode and the highest filled electron level in the metallic particle. Following this model, metallic particles on the order of 30-40 Å in diameter embedded in our tunnel barrier could be responsible for the background we observe. This suggested, confirmed later by atomic force microscopy measurements (Sect. 3.7.2), that our tunnel barrier was composed of AlO$_x$ grains hosting non-oxidized Al cores. Therefore, we identified improvement in barrier uniformity as a route to diminishing the background conductance. Furthermore, a significant voltage drop across the transport portion of the sample requires that we subtract it from $V_B'$ in order to obtain the true tunnel bias. Since we have no independent measurement of that voltage drop which is itself $V_{BG}$-dependent, working it into our analysis would be difficult.
6.6 Photolithography-based planar tunnel junctions

As described in Sect. 3.7.2, improvements were made to the uniformity of the tunnel barrier. We also redesigned our planar tunnel junction fabrication with a photolithography-based process (Sect. 3.9) that would not only preserve the pristine quality of the graphene into which we were tunneling, but also removing a contribution from transport. The latter was done by patterning contact leads on either side of the junction, allowing us to bias current through one side and measure the voltage drop, purely across the junction, on the other.

In Fig. 6.10, we show tunneling spectra in one device fabricated with our photolithography process and improved tunnel barrier, measured at $T = 10$ K and at different set $V_{BG}$ as labeled. The most notable evolution of tunneling spectra is an overall “rocking” as $V_{BG}$ is swept to more positive values, from low differential conductivity at positive bias and high at negative, to high at positive and low at negative. This is consistent with the 2LG being initially hole-doped at zero $V_{BG}$, thus a low density of states is probed at energies higher than the 2LG Fermi level, and the Fermi level increases with $V_{BG}$, as expected. Bias-symmetric background conductance, observed prominently in the filament-based devices, plays a much weaker role in this device. It is, however, still finite, and likely explains the local minimum observed at zero-bias in low $V_{BG}$ spectra.

It is also clear that spectra obtained at higher $V_{BG}$ are generally broader those at lower, related to the junction resistance increasing with $V_{BG}$ for a given bias current. As a result, spectra at higher $V_{BG}$ are not anti-symmetric to those at lower $V_{BG}$ (ignoring the changing gap width), contrary to what is expected in an ideal device. This is likely related to the relatively low tunneling resistance found in this sample; it is likely that current through this junction includes pinhole shorts, making the total resistance $V_{BG}$- and $V_{B}$-dependent due to a varying work-function mismatch between Au and 2LG.

The most interesting feature in the spectra of Fig. 6.10 is a wide suppression bounded by two peaks that is strongest when centered at zero bias, at $V_{BG} \approx 30$ V. This feature can be tracked for a large range of gate voltages, and gray dashed lines have been added to roughly track the bounding peaks. Its shape and variability
Figure 6.10. Tunneling spectra (smoothed and relatively shifted) $dI/dV_B$ vs. bias $V_B$ in a bilayer graphene planar tunnel junction prepared by photolithography, at temperature $T = 10$ K. Spectra are shown for back gate voltages $V_{BG}$ as annotated. Dashed gray lines roughly track a large conductance suppression.

with total electric field is highly suggestive of a gap in the density of states. Its depth does weaken with larger magnitudes of bias voltages, which is likely due to the still-present role of background conductance.

One complication is a small “bump” that shows up at small, positive bias, most apparent when within the center of the gap. Due to the similar location of this
Figure 6.11. Tunneling spectra (smoothed and relatively shifted) in another bilayer graphene planar tunnel junction prepared by the photolithography, at temperature $T = 10$ K. Spectra are shown different back gate voltages $V_{BG}$ as annotated. Dashed gray lines indicate static features in the spectra.

“bump” at most gate voltages, it is likely a result of inelastic electronic tunneling, described by phonon generation in the tunnel junction that is independent of the Fermi level in the sample[115]. Such features are observed in other devices; in Fig. 6.11, we show tunneling spectra in a second lithography-defined planar tunnel junction. In this device, the “V”-shaped background is prominent, and the spectra
Figure 6.12. a) Tunneling spectra $dI/dV_B$ vs. bias $V_B$ at back-gate voltage $V_{BG} = 28$ V measured at temperature $T = 10$ K for the same device in Fig. 6.10; b) Numerically simulated tunneling spectra determined by Eq. 6.7, with parameters determined by a fit of $d^2I/dV_B^2$ in (c) and (d); c) Calculated first derivative of tunneling conductance $d^2I/dV_B^2$ vs. $V_B$; d) Numerical simulation of $d^2I/dV_B^2$ vs. $V_B$, whose strongest peaks have been fit to those of (c). Band edges, as sampled by tunneling spectroscopy, are annotated.

also reveals several small peaks in the conductance that are fixed with $V_{BG}$. Each peak has a partner at equal and opposite bias, as expected in phonon-assisted tunneling.

In Fig. 6.12a, tunneling spectra with $V_{BG} = 28$ V for the device in Fig. 6.10 are plotted. This particular spectrum was chosen because the slopes of the tunneling conductance at high positive and negative bias are most similar, suggesting that the charge neutrality point is roughly centered at $V_B = 0$, assuming a symmetric background. Comparing with our numerical simulation of the tunneling spectra from Sect. 6.4 in Fig. 6.10b, we find several similarities, but the simulation hardly provides a reasonable fit. Since the simulation was calculated purely on the DOS in 2LG, it does not include a conductance background. If the background is roughly linear, we render it to a constant by performing the second derivative of current with respect to bias voltage, $d^2I/dV_B^2$. We compare numerically calculated $d^2I/dV_B^2$ in both experiment and simulation in Fig. 6.12c-d, the latter determined by fitting
Figure 6.13. Bias $V_B^0$ at which $\mu + V_B^0 = 0$ vs. total charge carrier density $n_{tot}$. The slope of the dashed line approximates $d\mu/dn$, which is used to determine the bias induced charging factor $\zeta$ (see text) for the fit in Fig. 6.12.

the most prominent peaks of $d^2I/dV_B^2$ to those of the former, and by determining, as described below, the bias-induced charging factor $\zeta$ discussed in Sect. 6.4. We find that the spectra compare much more favorably this way.

The fit shown in Fig. 6.12c-d provides a scale by which to relate the positions of prominent peaks in experimental $d^2I/dV_B^2$ back to the numerically determined band gap $\Delta$, and also to $V_B^0$, the bias at which the CNP is probed, for arbitrary $V_B$. The latter is found closer to the valence band edge signal than that of the conductance band edge due to the variability of $\Delta$ with $V_B$. In Fig. 6.13, we plot $V_B^0$ vs. $n_{tot}$ determined by Eq. 6.5 in the same device. The relationship gives a direct determination of $d\mu/dn$ in our device, which is used to determine $\zeta$. While there is likely some nonlinear variation, the trend suggests that assuming a constant $d\mu/dn$ is within uncertainty of our measurements. We find a value of $d\mu/dn \approx 97 \ \text{Å}^2 \text{eV}$, which gives $\zeta \approx 0.2$. This roughly translates to a feature in the tunneling spectra appearing at a bias energy that is 25% greater than the actual energy above the Fermi level in the DOS at $V_B = 0$. Therefore, the actual $\Delta$ is $\approx 80\%$ of the width of the measured conductance suppression for a given $V_{BG}$ and $V_B^0$.

We show in Fig. 6.14 $\Delta$ determined as described above vs. perpendicular electric field $D$ from Eq. 6.6 in the same device, where $n_{tot}$ has been labeled
Figure 6.14. Measured energy band gap $\Delta$ vs. perpendicular displacement field $D$ in the device in Fig. 6.10. Marker color refers to total charge carrier density $n_{tot}$. The dashed line follows the linear dependence of $\Delta$ on $D$ according to $\Delta = aD + \Delta_n$ (Eq. 6.8) with $\Delta_n = 0$ and $a$ determined by the fit in Fig. 6.12. Inset: $\Delta_n$ vs. $n_{tot}$.

by color. Both $D$ and $n_{tot}$ are determined using $V_{BG}$ and $V_B^0$ from each spectrum. Although many more spectra were measured than are represented in this plot, gaps in the data exist where the signals of the conduction and valence band edges cross zero bias, where interference with the symmetric tunneling conductance background complicate the tracking of such features. We find a roughly monotonic increase whose magnitude agrees with previous infrared absorption and transport experiments[25, 31]. By subtracting off the linear dependence of $\Delta$ on $D$, determined by the fit in Fig. 6.12, we obtain the correction $\Delta_n$ for finite $n_{tot}$, shown in the inset of Fig. 6.14. The trend suggests little variation for hole doping but substantial increase with electron doping. Previous calculations[39] agree with the behavior for electron doping, but predict also a substantial decrease at large hole doping.

Possibly the most important assumption in our determination of $\Delta$ is the approximation of constant $d\mu/dn$ with $n_{tot}$. This value is related to the quantum capacitance and is well known to vary in 2LG, particularly as the DOS varies strongly near the energy gap[117, 118, 119]. Charge inhomogeneity smears the
variance, such that constant $d\mu/dn$ is a sufficient approximation, at least among relevant values of $\Delta$.

### 6.7 Dual-gated field effect transistors

In order to confirm the creation of an insulating state in 2LG, we also fabricated top- and bottom-gated FETs, using our traditional SiO$_2$ back-gate and employing the alumina tunnel barrier used in tunnel junctions as a seed layer for atomic layer deposition (ALD) growth of 50 nm Al$_2$O$_3$ for the top-gate dielectric. In this geometry, shown in Fig. 6.15a, the total carrier density $n_{tot.}$ and perpendicular electric field $D$ can be expressed, as analogs to Eqs. 6.5 and 6.6, as

$$n_{tot.} = \frac{1}{e}(C_{BG}V_{BG} - C_{TG}V_{TG}) + n_0, \quad (6.9)$$

$$D = \frac{1}{2\epsilon_0}(C_{BG}V_{BG} + C_{TG}V_{TG}) + D_0, , \quad (6.10)$$

where $C_{TG}$ is the top-gate dielectric capacitance and $V_{TG}$ the top-gate voltage. If a truly insulating state is opened, and Fermi level is tuned to the center of the energy gap to maximize resistance, then the resistance $R_{max}$ of the 2LG can be expressed as

$$R_{max} \propto e^{\frac{-\Delta}{k_B T}} \quad (6.11)$$

where $k_B$ is Boltzmann’s constant. We expect that as $\Delta \propto D$ is increased, $R_{max}$ as well as the ratio of maximum to minimum resistance $(\sigma_{On}/\sigma_{Off})$ will increase. By holding $V_{BG}$ constant while sweeping $V_{TG}$, we tune the Fermi level through the gap, and show in Fig. 6.15b-d for two devices that this is indeed the case. However, the increase in both $R_{max}$ and $\sigma_{On}/\sigma_{Off}$ is much smaller than expected; an exponential increase of $R_{max}$ is not observed in our FETs.

Further details are revealed by the temperature dependence of resistance. From Eq. 6.11, we expect that $R_{max}$ vary exponentially with inverse temperature $T^{-1}$. We show in Fig. 6.16a that this may be true only at high temperatures. The implied energy gap, shown in Fig. 6.16b, increases monotonically but very weakly
Figure 6.15. a) Schematic of the device showing positions of the current source $I$ and voltage probes $V$; b) Square resistance $R_{\square}$ vs. back-gate voltage $V_{BG}$ for different top-gate voltages $V_{TG}$, measured at temperature $T = 4$ K, for a dual-gated bilayer graphene field effect transistor; c) $R_{\square}$ vs. $V_{BG}$ for different $V_{TG}$, measured at $T = 300$ K, for another device; d) On/off conductivity ratio $\sigma_{On}/\sigma_{Off}$ vs. perpendicular electric field $D$ (Eq. 6.10) for the device in (c). The ratio is calculated for maximum and minimum measured conductivities measured for each $V_{TG}$ in (c).
Figure 6.16. a) Maximum resistance $R_{\text{max}}$ vs. inverse temperature $T^{-1}$ at different top-gate voltages $V_{TG}$ for the device in Fig. 6.15. Inset: Energy band gap $\Delta$, determined by simple thermal activation fits at high temperature, vs. perpendicular displacement field $D$. Marker colors correspond to $V_{TG}$ labeled in the main panel.

with $D$. In the case of one FET, such a model can only be fit for $T > 220$ K. This is consistent with previous measurements of gapped 2LG [27, 28, 29, 30, 31], where transport more closely resembled variable range hopping or conduction through dense, localized quantum well states. In two-dimensions, variable range hopping gives $\log R_{\text{max}} \propto T^{-1/3}$, and while that model certainly provides a better fit for our data at low temperatures, the fit is not strong enough to suggest that it is the sole mechanism. Previous numerical calculations [104] propose that even moderate densities of local charged impurities produce charge inhomogeneity strong enough to place the Fermi level in the conduction or valence band for significant portions of 2LG. Based on those results, the impurity densities suggested by the initial residual doping in our devices are more than enough to result in the percolating, charge puddle-jumping current paths proposed by Rossi and das Sarma [104].
6.8 Conclusion

We have measured a tunable band gap in the bilayer graphene DOS, and have demonstrated that engineering of the graphene/dielectric interface is required if top-gated, 2LG-based electronics are to be fully realized in applications. By fitting numerical simulations of tunneling spectra to our experimental results, we show that the gap increases with applied perpendicular electric field, as expected from previous theory and infrared absorption and transport experiments. Although we measured only a maximum gap in one device of $\approx 80$ meV, that is the limit only of the applicable field before breakdown in our particular device. Through surface engineering of the substrate and high-$k$ dielectric integration, much greater gaps are possible, but likely limited $\sim 10^2$ meV. In order to relate the insulating state measured by planar tunneling to transport in 2LG, we fabricated and measured dual-gated FETs featuring a similar dielectric environment, using the tunnel barrier deposition as a seed layer for ALD growth of alumina. Our transport studies of these devices suggest that although we can increase the energy gap with an applied electric field, the insulating state is very dirty. It is likely that the Coulomb fields of charged impurities in the local dielectric environment not only spatially vary the energy gap, but also the Fermi level such that although the average Fermi level is set to the middle of the gap, significant portions of the graphene feature a Fermi level sitting in the conduction or valence bands. Thus, electronic transport can be described by a percolating “puddle-hopping” model, and not as true electronic insulation.

Our studies of planar tunneling spectroscopy on graphene show that these experiments are difficult for several reasons. First, in low carrier density materials like graphene, the application of a bias across a thin tunnel barrier varies the Fermi level significantly. In these materials, the conventional approximation that the tunneling conductance is proportional to the DOS in the sample is not valid. One needs to take into account the additional tunneling current into states near the changing Fermi level. Bilayer graphene is a special case where the effect of a variable DOS due to finite electric fields also needs to be considered. The model that we developed for simulations of tunneling in bilayer graphene will be useful in future tunneling experiments of other low-dimensional materials, a field that has
been growing since the mechanical cleavage and isolation of layered crystals was first shown possible [55]. Second, the surface of graphene is fairly non-welcoming of thin, insulating tunnel barriers, leading to film non-uniformity and background conductance in the tunneling spectra. We find that even if barrier uniformity is improved, conductance features caused by inelastic tunneling via phonon interactions can also muddle the spectra. However, with careful attention given to these issues, valuable information about the density of states can be obtained from materials like bilayer graphene.
Chapter 7

Hybrid graphene structures - Anomalous quantum oscillations

7.1 Introduction

While both mono- and bilayer graphene have each received a great deal of individual attention, the interface between the two has received much less. Such an interface occurs when one of the layers in bilayer graphene terminates abruptly, resulting in an atomic step and a 1LG/2LG hybrid structure. The graphene hybrid is a new material system worthy of study from a number of different angles. First, since the 1LG/2LG interface occurs in both natural graphite flakes and grown films, it is useful to study the emergent electronic states at this interface, given that theoretical studies of the electronic edge states in either 1LG[121, 122, 123, 124] or 2LG[125] have been useful in understanding electron transport in both graphene nanoribbons and graphene tuned insulating by the quantum Hall effect. Second, theoretical studies of the hybrid interface have propose unconfirmed phenomena including asymmetric charge redistribution [126], enhanced local density of states in the top layer of 2LG[123], and anisotropic and energy-dependent transmission of electrons through the step[127, 128]. A prediction of the extension of zero-energy interface states into 1LG when 2LG is gapped[129], which would enhance conductivity of the 1LG portion, proposes a hybrid-based nano-scale switching device. Third, because of the slight difference in work function and/or selective doping, planar p-n junctions result at the hybrid interface under proper conditions. While
p-n junctions produced by locally gating 1LG have been studied in a number of experiments [12, 130, 131], such a junction in a hybrid structure has received only little attention. In one experiment, Fermi level mismatch between 1LG and 2LG was shown to produce a photothermoelectric effect in a device fabricated to measure transport across rather than along the interface[132].

We are particularly interested in the physics of the interface in the presence of a large perpendicular magnetic field. As derived in Sects. 2.1.2 and 2.2.2, in the presence of finite magnetic field $\vec{H}$, electrons in both 1LG and 2LG fall into unique sets of Landau levels whose energies are given by

\begin{align}
E_{n_1} &= v_F \sqrt{2e\hbar n_1} \\
E_{n_2} &= \hbar \omega_c \sqrt{n_2(n_2-1)},
\end{align}

for 1LG and 2LG, respectively, where $v_F$ is the Fermi velocity in graphene, $e$ the fundamental charge, $\hbar$ Planck’s constant, $\omega_c$ the cyclotron frequency, and $n_1$, $n_2 = 0, 1, 2, \ldots$ are Landau level indices. At the interface of a graphene hybrid, unique sets of hybridized Landau levels, smoothly varying from 1LG to 2LG, depending on the top-layer termination, have been theoretically predicted[133]. In the case of an armchair boundary, Ref. [133] predicts an enhanced density of states for electrons in the top layer of 2LG at the interface at specific energies, suggesting a magnetic field-tunable interlayer bias and band gap. As discussed at the end of Sect. 2.2.2, at low index, the spectra of 1LG features levels that are spaced much greater than those in the spectra of 2LG. Such a large disagreement in electron energy scales for a given carrier density would suggest interesting interplay at the 1LG/2LG step. In this chapter, we present studies of magnetotransport parallel to the interface in two flavors of graphene hybrid structures. We published much of the results presented here in reference [134].

### 7.2 Bulk hybrdis

We classify a bulk hybrid as a sample featuring large areas of contiguous 1LG and 2LG. Such structures can be found commonly in bulk graphite exfoliation, but
patterned etching may be required to isolate a sample from thicker layers for device preparation. Rarely, such a hybrid flake is readily cleaved from graphite, and an example is shown in Fig. 7.1. Two-point transport junctions were prepared using a quartz filament shadow mask (Sect. 3.6) such that each gold contact terminates the interface edge, which would therefore be roughly parallel to a bias current.

Using the Si/SiO$_2$ substrate as a back-gate to tune carrier density $n_e$, we show in Fig. 7.2a the conductivity $\sigma$ vs. gate voltage $V_G$ in the device shown in Fig. 7.1, measured at temperature $T = 10$ K. The value of $V_G \approx -18$V needed to reach the charge neutrality point (CNP) and measure a resistance minimum suggests that this device is initially electron doped, which may be caused by gold atoms on the surface that diffuse underneath the filament during deposition. With zero magnetic field, $\sigma$ vs. $V_G$ in hybrid flakes are indistinguishable from uniform few-layer graphene flakes, assuming that both portions are doped equally. Asymmetric carrier mobilities (6,000 cm$^2$/Vs for electrons and 1,500 for holes in the flake in Fig. 7.2), which are typical in either uniform or hybrid flake devices, might be due to imbalanced carrier injection from graphene electrodes doped strongly by the
Figure 7.2. a) Conductivity $\sigma$ vs. gate voltage $V_G$ measured at 10 K in the bulk hybrid shown in Fig. 7.1. Dashed lines indicate linear fits used to extract field effect mobilities shown for each carrier type within the plot; b) Resistance $R$ vs. perpendicular magnetic field $H$ in the same device, at different set $V_G$ as labeled. Inset: Background-subtracted resistance $\Delta R$ vs. $H^{-1}$ at $V_G = 20$ V.

With the application of increasing perpendicular magnetic field $H$, we observe the emergence of Shubnikov-de Haas oscillations (SdHOs) in the otherwise classical $R \propto H^2$ magnetoresistance as Landau levels emerge in the density of states (DOS). As shown in Fig. 7.2b, the SdHOs are $V_G$-dependent, which is expected since tuning carrier density varies the Landau level occupation. Since each Landau level is populated with $N_L = 4H/\phi_0$ electrons, where $\phi_0$ is the flux quantum, we expect fluctuations in resistance as $H$ increases and levels are depopulated, thus a constant frequency of SdHOs in $H^{-1}$. In the inset of Fig. 7.2b, we show $R(H^{-1})$ at $V_G = 20$ V with the classical magnetoresistance background substracted. The few oscillations available do not encourage a reliable Fourier transform, but the data appears irregular, such that a single frequency model would not fit.

The reason for such an irregular trend in $R(H^{-1})$ is made clear in Fig. 7.3. By holding $H$ constant, we vary $V_G$ to tune carrier density linearly and populate/depopulate Landau levels, which should induce SdHOs of constant frequency in $V_G$. This strategy allows us to see many more oscillations due to the benefit
Figure 7.3. a) Resistance $R$ vs. gate voltage $V_G$ at different set magnetic fields $H$ as labeled in a bulk hybrid device; b) Background-subtracted conductance fluctuations $\Delta \sigma$ vs. $V_G$ in the same device. Dashed lines annotate two sets of periodic conductance peaks with a period equal to 8.3 V, expected for both mono- and bilayer graphene. Black arrows mark unexpected peaks; c) Fan diagram describing the values of $(V_G, H)$ where conductance peaks are found. Color refers to the source of each set of peaks.

of increased amplitude at higher $H$. These sweeps are shown in the same sample in Fig. 7.3a. While the expected regular oscillations are immediately apparent, a closer look reveals a second set of oscillations of smaller amplitude, visible, for example, as small resistance dips halfway between the large, regular dips at $H = 8$ T. By plotting $\sigma$ rather than resistance, and subtracting off a linear background extending from the CNP at $V_G = -18$ V, we show these fluctuations at $H = 6$ T in Fig. 7.3b. At this field, the filling factor in both 1LG and 2LG is $N_L^{6T} \approx 6 \times 10^{11}$ cm$^{-2}$, giving oscillations with period $\Delta V_G = 8.3$ V. We annotate two sets of oscillations, peak-to-peak: one set that occurs roughly at integer multiples of gate voltage from the CNP, and one at half plus integer multiples from a slightly shifted CNP. This is exactly what we’d expect for separate contributions from 1LG and 2LG. The $n_1 = 0$ Landau level in 1LG gives it an odd filling factor, and the doubly degenerate $n_2 = 0,1$ Landau level in 2LG gives even.

The short and wide geometry of our samples results in conductance peaks as $V_G$ shifts the Fermi level through DOS peaks at each Landau level[136], thus the
set with a conductance peak at the CNP belongs to 1LG. In the set for 2LG, we note peaks on either side of the CNP separated by one filling factor. This suggests that the double degeneracy of the \( n_2 = 0,1 \) level has been broken by asymmetric doping between the top and bottom layer in 2LG, and that the material is finitely gapped[23, 40]. Given an initial doping level of \( 1.3 \times 10^{12} \text{ cm}^{-2} \) determined by \( V_G = -18 \text{ V} \) achieving charge neutrality, the gap is likely on the order of 10 meV. The positions in \( V_G \) of each set of conductance peaks are given for magnetic field magnitudes at which they are discernible in Fig. 7.3c, producing a “fan diagram” extending from the CNP. The expected positions, \( V_{LL}^{i,m} \), of the middle of each indexed Landau level are given by

\[
V_{i,m}^{LL} = V_{i}^{CNP} + N_L \frac{\partial V_G}{\partial n_e} (i + \iota) = V_{i}^{CNP} + 4 \frac{H}{\phi_0} \frac{\partial V_G}{\partial n} (i + \iota),
\]  

where \( i = 0,1,2, \ldots \) is the Landau level index, \( \iota = 0 \) for 1LG and 1 for 2LG, and \( V_{i}^{CNP} \) is the value of \( V_G \) at which CNP is found in either 1LG or 2LG. The CNP of 2LG is slightly shifted (\(<1 \text{ V}\)) from that of 1LG, due to a slight doping difference between the two. The shift could either be due to a slight difference in affinity for adsorbed dopants (such as water), or due to the slightly increased Coulomb screening available in 2LG. Eq. 7.3 is also plotted in Fig. 7.3c, and fits the data nicely.

Our studies of SdHOs as they relate to the emergence of Landau level in bulk hybrids suggest that the sample behaves as we’d expect from two separated, parallel channels of 1LG and 2LG. While we do expect a charge imbalance effects at the interface due to mismatched Fermi energy in finite magnetic field, the related signal in magnetotransport is not well discernible. We do observe several unexpected conductance peaks that do not appear to belong to either the 1LG or 2LG set. These are marked by black arrows and triangles in Fig. 7.3b-c, and can make the determination of nearby 2LG peaks difficult. While these may be related to the states at the interface, they do not show with enough prominence to learn much about their nature. Since bulk hybrid magnetotransport appears to be dominated by transport along the edges of the entire sample (either 1LG or 2LG), it would be useful to measure hybrids where the interface is located at the edge, as in our “edge hybrids”, presented below.
Figure 7.4. a-b) Optical images of two edge hybrid graphene flakes with quartz filaments lying atop to serve as shadow masks during gold contact deposition; c) Atomic force microscopy image of the device fabricated on the flake in (b), taken after low-temperature measurements were performed.

7.3 Edge hybrids

We define an edge hybrid as a graphene structure that is mostly 2LG but whose edges are single layer. The step from 2LG to 1LG must occur close enough to the edge that the interface states extend all the way to the edge, a length that can be roughly estimated to be on the order of the screening length in graphene, or on the order of the width graphene nanoribbons that feature transport different than that of bulk graphene. This places the width of the 1LG portion in edge hybrids to be less than 200 nm. In this geometry, if the 2LG portion is driven insulating by finite magnetic field, magnetotransport will be dominated by current along 1LG/2LG interface. We show in Fig. 7.4a-b images of two edge hybrid devices with filaments placed to indicate the two-terminal division before gold contact deposition. Atomic force microscopy (AFM) scans, performed after low temperature measurements to avoid damaging the device, indicate the existence of 1LG at the edge of average width less than 200 nm. Like our bulk hybrids devices, two-point transport devices were fabricated with gold contacts by filament shadow-masking. Schematics of two completed devices are shown in Figs. 7.5a and 7.6a.

The conductivities of edge hybrids respond to $V_G$ similarly to uniform flakes and bulk hybrids. Sweeps of $\sigma$ vs. $V_G$ for two edge hybrids are shown in Figs. 7.5b and 7.6b. By bringing the Fermi level to the CNP with $V_G$, conductivity minima
Table 7.1. Field-effect mobilities for electrons ($\mu_e$) and holes ($\mu_h$) for the devices presented in this chapter. Measurements were performed at 10 K for the bulk hybrid, and 1.6 K for the edge hybrid. Variable-temperature measurements indicate negligible change in mobility with temperature in this range.

<table>
<thead>
<tr>
<th>Device</th>
<th>$\mu_e$ (cm$^2$/Vs)</th>
<th>$\mu_h$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk hybrid</td>
<td>6,000</td>
<td>1,500</td>
</tr>
<tr>
<td>Edge hybrid 1</td>
<td>1,000-2,500</td>
<td>4,500</td>
</tr>
<tr>
<td>Edge hybrid 2</td>
<td>2,200</td>
<td>1,700</td>
</tr>
</tbody>
</table>

again suggest strong initial electron doping. The edge hybrids that we measured did show relatively low conductivities, which may indicate higher levels of disorder. Hole and electron mobilities, in comparison to the bulk hybrid from the previous section, are shown in Table 7.1. Application of finite $H$, however, reveals very different behavior.

In Fig. 7.5c, we show $R$ vs. $V_G$ in one edge hybrid with different values of applied $H$ held constant for each sweep. Close to the CNP, we note very weak SdHOs at high fields. However, a positive change of $V_G$ eventually reveals sudden strong oscillations in resistance that persist for several periods. The oscillations then abate as before, and rise again at further positive changes in $V_G$. The oscillation suppression is associated with an overall increase in conductance. The regions of suppressed oscillations exist for ranges of $V_G$ that are dependent on $H$, but we have labelled them based on their evolution with the integer $j$. It is also important to note that these regions are not specific to Landau level index, since indices that show a weak oscillation in one field show up strong in another. The same behavior is shown in another edge hybrid in Fig. 7.6c, only with weaker conductance fluctuations.

Since conductance peaks (resistance dips) appear on either side of the CNP in both samples, and the transport portion is again wide and short[136], we claim that the regular oscillations belong to 2LG. This is no surprise, since the samples are mostly 2LG. We do not see the additional set of regular oscillations belonging to 1LG that appeared in bulk hybrids. Assuming that the regions of enhanced conductance may be related to the 1LG edges, we track their positions and plot them against the value $\sqrt{jH}$ in Fig. 7.7. The linear relationship recalls Eq. 7.1, where the energy of a Landau level in 1LG is proportional to $\sqrt{jH}$, where $j = n_1$. 
Figure 7.5. a) Schematic of a two-point transport device fabricated on an edge hybrid; b) Conductivity $\sigma$ vs. gate voltage $V_G$ in the device. Dashed lines denote linear fits used to extract mobilities for Table 7.1; c) Resistance $R$ vs. $V_G$ for constant applied magnetic fields (from bottom to top) $H = 0, 2, 4, 5, 6, 7, \text{ and } 8 \text{ T}$. Dashed lines track oscillation suppression regions labeled by values of $j$.

Figure 7.6. a) Schematic of a two-point transport device fabricated on another edge hybrid; b) Conductivity $\sigma$ vs. gate voltage $V_G$ in the device. Dashed lines denote linear fits used to extract mobilities for Table 7.1; c) Resistance $R$ vs. $V_G$ for constant applied magnetic fields (from bottom to top) $H = 0, 4, 5, 6, 7, \text{ and } 8 \text{ T}$. Dashed lines track oscillation suppression regions labeled by values of $j$. 
Figure 7.7. Gate voltage at which the center of the region of enhanced conductivity and oscillation suppression is observed, shifted from that at which the charge neutral point is observed, $V_{G}^{supp.} - V_{G}^{CNP}$ vs. $\sqrt{JH}$, where $j$ is the integer label of the suppression region as shown in Figs. 7.6c and 7.6c, and $H$ is the applied magnetic field in units of Tesla. Error bars span the width of the region, and a dashed line emphasizes the linear relationship.

The observations outlined above are consistent with the following physical interpretation. We propose that, at the 1LG/2LG interface, the Fermi levels of the two are locked. This is due to the greatly differing energy scales of Landau levels in 1LG and 2LG. For a given carrier density, electrons in the highest occupied Landau levels in 1LG will be at higher energies than those in 2LG, and will flow to 1LG when placed in contact to minimize their energy. The 2LG makes up a large portion of the sample, and acts as a charge reservoir such that the Fermi level change with $V_G$ is not significantly greater than that expected without the charge transfer. The locked Fermi levels enforce that, as $V_G$ is ramped, Landau levels in 1LG are only filled when levels in 2LG of the same energy are filled. Since levels in 2LG are roughly evenly spaced in energy and each level has equal population, $V_G$ is approximately proportional to energy in quantized steps, which explains the linear relationship observed in Fig. 7.7.

With this model in mind, we have $V_G \propto E$ and $\Delta \sigma \propto DOS$. We can simulate the conductivity fluctuations in such a device by calculating the DOS as a func-
Figure 7.8. a) Sketch of the density of states contribution of Landau levels in mono- and bilayer graphene vs. Fermi energy $E_F$, represented by Gaussian peaks of arbitrary width; b) Simulated conductance fluctuations $\Delta \sigma$ determined by the sum of the two spectra in (a); c) Background subtracted conductance $\Delta \sigma$ vs. gate voltage $V_G$ in an edge hybrid measured at magnetic field $H = 5$ T. For comparison, the energy scale in (b) has been matched appropriately with $V_G$ in (c) based on the spacing between and carrier populations of energy levels.

tion of energy $E$, representing each Landau level as a simple Gaussian peak, and superimposing them. This is shown in Fig. 7.8a-b. The simulation matches the experimentally observed $\Delta \sigma$ well, assuming that the DOS of 1LG levels is described by significantly wider Gaussians. The sharpness of SdHOs will decrease with increasing disorder, since electrons in cyclotron orbits will have a higher probability of scattering and delocalizing. The width of the contribution will also increase with
charge inhomogeneity. It is reasonable to assume that the edges of the flake will host more charge donor/acceptor adsorbates, inducing some spread of the Fermi level as electrons in 1LG equilibrate with the Fermi level mismatches at both the edge and the interface.

We are able to observe such unusual phenomenon because of the existence of the hybrid interface at the edge of the sample, suggesting that the interface is fairly well ignored in bulk hybrids. The locking of Fermi levels relies on substantial charge transfer between 1LG and 2LG, and at $H = 5$ T was observed to be at most $5 \times 10^{12}$ cm$^{-2}$ (roughly equal to $10N_L$) just below the filling of $n_1 = 1$. As mentioned earlier, the charge imbalance must exist over a distance roughly equal to the screening length in graphene, which has been theoretically estimated to be between 10 and 100 nm\[137, 138\], but is certainly dependent on $n_e$ in the sample and the level of disorder. A spatially sensitive measurement tool, such as a scanning tunneling microscope, would be able to measure not only the width of the charge imbalance regime, but also the theoretically predicted hybridized Landau level spectra that are theoretically predicted to exist at the interface\[133\].

7.4 Conclusions

Our magnetotransport studies of graphene hybrid structures have revealed interesting physics at the 1LG and 2LG interface. In bulk hybrids, magnetotransport appears to be dominated by the edges of the entire sample - either 1LG or 2LG - and the role of the interface is subtle at best. In edge hybrids, however, the location of the hybrid interface is at the edges of the sample, allowing us to measure its effect on transport. In zero magnetic field, transport in either flavor of hybrid is indistinguishable from 1LG or 2LG, since it is dominated by the bulk. However, in finite magnetic field, magnetotransport in edge hybrids suggests that the Fermi level of 1LG is locked to that of 2LG, resulting in the discovery of anomalous quantum oscillations. These take form of enhanced conductance and suppressed Shubnikov-de Haas oscillations only for the filling of 2LG Landau levels whose energies match those in 1LG. Such a phenomenon requires substantial charge transfer across the interface from the thin 1LG edge, and is likely limited to a width on the order of $<100$ nm.
The interface between 1LG/2LG in graphene hybrid structures is a fairly unique electronic system, because it features a relatively clean and smooth transition between two materials with very different band structures, and vastly different Landau level energy scales with the application of a magnetic field. Further study of graphene hybrids is likely to reveal interesting physics, where we expect unique interface states to emerge from the mixing of inequivalent chiral states.
Flakes of the complex oxide
Ca$_3$Ru$_2$O$_7$ - An ionic liquid gating study

8.1 Introduction

The successful exfoliation of graphene flakes from bulk graphite and transfer to a substrate for experimental study encouraged the extension of that technique to other layered materials[55]. One group of layered materials is the transition metal oxides, which have been of significant interest since the discovery of high temperature superconductivity in the cuprates. In these systems, charge, spin, and/or orbital interactions may be responsible for many exotic physical phenomena including superconductivity, colossal magnetoresistance, and metal-insulator transitions[139]. This behavior is in contrast to the two-dimensional electronic systems of few-layer graphene, whose band structures are determined sufficiently by crystalline structure interaction with single particles.

In this chapter, we present electronic measurements of exfoliated flakes of the correlated electron system Ca$_3$Ru$_2$O$_7$, a bilayered ruthenate which was discovered to exhibit rich structural, antiferromagnetic (AFM) ordering, and insulating transitions at low temperatures[140]. In the ruthenates, the Ru atoms of the ruthenates are surrounded by six oxygen ions, making up RuO octahedra, as shown in Fig.
8.1a. The valence $d$-orbitals (Fig. 8.1b) not directed along RuO bonds are energetically favorable, thus the $d$-orbitals are split degenerately between two $e_g$ and three lower energy $t_{2g}$ orbitals[139]. In the case of calcium ruthenates, the small Ca ions distort the octohedra orthorhombically, and tilt them primarily into the $ac$-plane and slightly into the $ab$-plane[141]. In Ca$_3$Ru$_2$O$_7$, the tilting of the octahedra and extension of Ru orbitals are such that Hund’s rules determine it to be energetically favorable that all four valence electrons of Ru fill the $t_{2g}$ orbitals, and the $e_g$ are empty[142]. This unusual population distribution has been theoretically explained by the emergence of an orbital ordered state supported by a combination of lattice and Coulomb interactions[143]. Reducing temperature or increasing pressure compresses the $c$-axis lattice parameter, and the associated distortion of the octahedra lowers the energy of $d_{xy}$ orbitals relative to $d_{yz}$ and $d_{zx}$. The resulting orbital repopulation is associated with the complex phase phenomena observed in Ca$_3$Ru$_2$O$_7$[142] at low temperatures. These phases include ferromagnetic ordering within the $ab$-plane and antiferromagnetic ordering along the $c$-axis below 56 K[144], and a structural transition associated with a metal-nonmetal transition at 48 K[145]. The $t_{2g}$ orbitals are associated with strong spin-orbit coupling[139]; it is predicted that the ground state of $t_{2g}$ ruthenates can be tuned and long range
orbital ordering can be demolished by the application of magnetic field\[146\]. As a result, the structural, magnetic, and electrical transport properties show strong anisotropy with magnetic field\[147\]. Since the different phases of \(\text{Ca}_3\text{Ru}_2\text{O}_7\) are very close in free energy, they can be tuned by temperatures, magnetic fields, and pressures\[148\] attainable in the laboratory. The tuning of these phases by varying orbital population through charge injection or depletion, which would directly identify their origin to be orbital ordering-driven, has not yet been demonstrated.

We tune charge carrier density in \(\text{Ca}_3\text{Ru}_2\text{O}_7\) using an ionic liquid gating (see Sect. 3.11). The technique has been previously used to tune phenomena in insulating transition metal oxides. Superconductivity was discovered in insulating \(\text{KTaO}_3\)[149] by gating beyond \(3 \times 10^{14} \text{ cm}^{-2}\), and in \(\text{YBCO}\)[150] the superconducting critical temperature was pushed to zero by depleting a comparable density. EDL gating has also confirmed carrier-mediation of ferromagnetic ordering in \(\text{Ti}_{0.96}\text{Co}_{0.10}\text{O}_2\)[151]. Developing a challenging process to tune and measure the surface properties in \(\text{Ca}_3\text{Ru}_2\text{O}_7\) flakes is useful not only in exploring the fundamentally interesting orbital ordering physics behind these transitions, but also in opening a new direction of physics research on the formation and manipulation of a two-dimensional electron gas on the surface of a correlated material.

\section{8.2 Surface-contacted Hall bars with an ionic liquid gate}

We chose a Hall bar geometry for our measurements of \(\text{Ca}_3\text{Ru}_2\text{O}_7\) flakes in order to measure both transport and Hall coefficient as a function of applied gate voltage. Although leads are placed along the \(ab\)-plane, finite \(c\)-axis resistance leads to the signal containing contributions from both \(ab\)- and \(c\)-axis transport. We show in Fig. 8.2a resistance \(R\) vs. temperature \(T\) in two flakes that represent two types of flake transport. “Type A” flakes, which are the most common, feature a resistance that is roughly linearly proportional to temperature above \(\approx 60\) K. Lowering \(T\), at 56 K an AFM ordering transition coincides with a drop in resistance[144, 152], followed by a discontinuous jump in resistance at 49 K that is associated with first order structural transition[145] and metal-nonmetal transition. In the AFM
regime, spins align ferromagnetically within each layer and antiferromagnetically between layers[144]. Transport remains insulating-like until a new metallic phase below 8 K. In “Type B” flakes, $R$ vs. $T$ is similar save for a distinction below 33 K, when the transport transitions to a metallic phase that continues, interrupted only by an “elbow” between 15 and 10 K, to lowest temperatures. This behavior has

Figure 8.2. a) Resistance $R$ vs. temperature $T$ in two $\text{Ca}_3\text{Ru}_2\text{O}_7$ flake Hall bar devices. Specific temperatures annotate major transport transitions discussed in the text; b) Derivative of $R$ with respect to $T$ $dR/dT$ vs. $T$ in flake A1 from (a); c) $dR/dT$ vs. $T$ in flake A1 from (a).
been interpreted as a transition to a quasi-two-dimensional, spin-polarized metallic state in Ca$_3$Ru$_2$O$_7$, observed previously in bulk $ab$-axis transport[153]. We also show $dR/dT$ vs. $T$ for both types of flakes, which highlights that that concavity transitions in $R$ are actually identical. The derivative with $T$ will be useful below in detecting small changes with applied gate voltage. The behavior that we observe in flakes agrees well with what was previously measured in bulk crystals, although the differences observed between A and B flakes are fairly identical to those observed between $c$- and $ab$-axis transport[153, 82]. It is likely that our devices feature variability between respective contributions, which may depend on slight differences in effective contact separation, and probably less on variations in interlayer coupling within the source crystal.

With finite magnetic field $H$ applied parallel to the $c$-axis, $R$ in both types feature slight negative magnetoresistance between the AFM transition at 56 K and the 33 K transition and larger positive magnetoresistance below 33 K (Figs. 8.3a and c). It is possible that the slight negative magnetoresistance is associated with a small but finite field parallel to the $ab$-axis, which has been previously observed to reduce $ab$-axis resistivity due to increased spin-polarization within each ferromagnetic layer. We observe the positive magnetoresistance to be much stronger in B flakes than in A, which is consistent with a picture of a stronger, more metallic $ab$-axis contribution in the former. At least at low fields, non-metallic $c$-axis magnetoresistivity is fairly small with $H//c$, consistent with observations in bulk[153]. We did not observe the positive magnetoresistance to follow classical magnetoresistance $R \propto T^2$. Instead, we observe something closer to a linear relationship even at low $H$, which has been previously suggested[82] to be associated with a Fermi surface with a very small radius of curvature[154]. This result is consistent with angle resolved photoemission spectroscopy (ARPES) measurements of the Fermi surface in Ca$_3$Ru$_2$O$_7$, which confirmed a nested Fermi surface composed of small electron and hole pockets[155].

We also show in Fig. 8.3b and d the Hall coefficient $R_H$ vs. $T$ for the same devices. The strong increase in $R_H$ magnitude below 40 K and “elbow” feature at $\approx 20$ K agree with previous measurements in bulk Ca$_3$Ru$_2$O$_7$[75]. These results are consistent with the transition to a much-reduced Fermi surface[155]. The “elbow” may be associated with the metallic transition in $ab$-transport below 33
Figure 8.3. a) Resistance $R$ vs. temperature $T$ in a Type A Ca$_3$Ru$_2$O$_7$ flake device for different magnetic fields $H$ parallel to the $c$-axis; b) Hall coefficient $R_H$ vs. $T$ in the same flake, measured at $|H| = 3$ T; c) $R$ vs. $T$ in a Type B flake device for different $H$ parallel to the $c$-axis; d) $R_H$ vs. $T$ in the same flake, measured at $|H| = 3$ T.

K, though its emergence at $\approx 20$ K is not fully understood. The disagreement between both types at lowest temperatures is surprising; $R_H$ with $H//c$ should only feature contributions from the $ab$-plane. However, many measurements of flakes suggest similar inconsistencies at lowest temperatures, and may be related to disorder, which would play a more prominent role at the lowest carrier densities.
Figure 8.4. a) Resistance $R$ vs. magnetic field $H$ applied parallel to the $c$-axis, measured at temperature $T = 2$ K in a Type A $\text{Ca}_3\text{Ru}_2\text{O}_7$ flake device; b) Even and odd responses of $R$ vs. $H$ from (a); c) Resistance fluctuation $\Delta R$ vs. $H^{-1}$ in the same device; d) $\Delta R$ vs. $H^{-1}$ in another device, measured at different $T$.

(thus lowest temperatures).

At high magnetic fields, we observe quantum oscillations in the resistance in the metallic regime below 10 K. In Fig. 8.4a-b, we show $R$ vs. $H$ in one Type A device whose magnetoresistance featured an especially large transverse contribution, which is odd in $H$, and fluctuations at high $H$. By separating the even
and odd portions of $R$, we note stronger fluctuations in the even (longitudinal) portion than in the odd (transverse). We also show in Fig. 8.4b that the longitudinal magnetoresistance is linear with $H$ at low values, as discussed above. After subtracting off a resistance background, we show that the fluctuations are periodic with $H^{-1}$ in Fig. 8.4c, classifying them as Shubnikov-de Haas oscillations (SdHOs). A Fourier transform of the oscillations in this and other Type A flakes suggest a single frequency of $\approx 43$ T. The size of the Fermi surface $\mathcal{A}$ can be calculated from the SdHO period $\Delta H^{-1}$ according to the de Haas-van Alphen equation:

$$\Delta H^{-1} = \frac{2\pi e}{\hbar \mathcal{A}}.$$  \hspace{1cm} (8.1)

Using the lattice parameters from Ref. [145], this implies a Fermi surface that is roughly 0.3% of the 1st Brillouin zone, in close agreement with previous studies of SdHOs in bulk[156, 153, 82] and ARPES measurements[155]. Although previous studies report multiple oscillations that may be associated with out-of-plane dispersion effects[156, 82], noise and lower maximum $H$ restrict us to observe one set confidently. Observation of oscillations with such a large frequency is a testament to the quality of these crystals, as it corresponds to a very large cyclotron orbit free of scattering. We note that oscillations were not observed in Type B flakes, which may indicate that the surface signal is strong in Type B; the surface, which is likely to feature more disorder than bulk, may not support oscillations of such a large real space cyclotron orbit.

The application of a gate voltage $V_G$ across an ionic liquid does not change transport substantially in Type A flake devices. As shown in Fig. 8.5, the effect of an applied gate voltage is to induce slightly more strongly insulating behavior below the structural transition temperature $T_{c^{str.}} = 56$ K. There is also no apparent effect on the SdHO frequency or amplitude. It is likely that in the Type A flakes, where $c$-axis transport dominates, the $ab$-plane surface signal is very weak. The increased insulating behavior may be due to increased disorder from thermal cycling and electrochemical reaction.

In the Type B flake from Fig. 8.2, the effect of an applied gate voltage is a lot stronger. Since $ab$-axis transport dominates transport in this flake, we expect, given surface-contact, the surface contribution to be stronger than in Type A. As shown in Fig. 8.6a, the most apparent effect is an increased conductance
**Figure 8.5.** a) Resistance $R$ vs. temperature $T$ in a Type A flake device at zero and finite applied gate voltage $V_G$; b) Derivative of $R$ with respect to $T$ $dR/dT$ vs. $T$ calculated from (a); c) Resistance fluctuation $\Delta R$ vs. inverse magnetic field $H^{-1}$ at zero and finite $V_G$.

**Figure 8.6.** a) Resistance $R$ vs. temperature $T$ in a Type B flake device at zero and finite applied gate voltage $V_G$; b) Derivative of $R$ with respect to $T$ $dR/dT$ vs. $T$ calculated from (a); c) Same plot as in (b), but zoomed in on the structural and magnetic ordering transitions.

at temperatures below $T_{c}^{str}$. Since the conductance increases more strongly as temperature decreases, this is consistent with an added electron density that becomes more significant as the Fermi surface shrinks. The increase in conductivity suggests an increase in carrier density by $\approx 20\%$ at 2 K. Comparing that to previous bulk measurements[153], and assuming that we are gating only the top few layers, 20% would require a gated density on the order of $10^{14}$ cm$^{-2}$, which is reasonable for ionic liquid gating. By looking closely at $dR/dT$ in Fig. 8.6b-c, we observe an apparent shift of $T_{c}^{str}$ and the AFM ordering temperature $T_{c}^{AFM}$ to
higher temperatures ($\approx 2$ K), which is a remarkable result. In the case of $T_{c}^{\text{str}}$, we see an shift from 51 K to 52.5 K of the point of most negative slope. This shift may imply successful tuning of the orbital ground state, which is predicted to be responsible for magnetic ordering in the layered ruthenates[146]. Previous studies of electrical transport in Ca$_3$Ru$_2$O$_7$ under pressure suggest that the structural and AFM ordering transitions are linked[148], possibly through orbital ordering. Tuning the structural and magnetic ordering transitions by carrier density alone would directly confirm that these phenomena are driven by orbital ordering.

Although a large range of gate voltages were applied for many samples, mostly of Type A, we found too many inconsistencies and non-reproducibility that can be likely attributed to increasing disorder after thermal cycling and possible electrochemical reaction. Therefore, for Ca$_3$Ru$_2$O$_7$, we feel that only the first applied gate voltage may be trusted, which is why, for the samples presented in Figs. 8.5 and 8.6, we apply 3 V immediately to check for a strong effect, and ignore further changes in $V_G$.

8.3 Conclusions

The most important result of this work is that we developed a process to prepare surface-contacted devices on micron-scale, exfoliated flakes for polymer electrolytic and ionic liquid gated transport studies. Such a technique is useful for the studies of the layered transition metal oxides, as it provides an opportunity to explore orbital physics in highly correlated electronic systems with potentially less disorder than in bulk crystals. We employed this process to Ca$_3$Ru$_2$O$_7$ flakes and confirmed, in agreement with bulk crystal studies, large changes in $dR/dT$ associated with magnetic ordering and structural transitions, a metal-non-metal transition below 48 K, a transition to a metallic state below 33 K in some flakes, and metallic regime below 8 K in all flakes. We also observed quantum oscillations in the magnetoresistance in the low temperature metallic regime. Although we were only able to observe reasonable gating effects and a possible shift of the structural and magnetic ordering transition temperatures in one sample, the positive result is encouraging for further studies of this and related materials. It should be noted that Ca$_3$Ru$_2$O$_7$ is a particularly difficult material to test the effects of ionic liquid
gating, given the relatively high conductivity of the bulk crystal. Nevertheless, our preliminary results in Type B samples do suggest a positive result, and encourage further experiments.
Conclusions

In this work, we began by showing that the interaction between graphene’s Dirac fermions and Coulomb scatterers in the local dielectric environment predominantly degrades performance of top-gated devices fabricated on scalable graphene. Although the interface could be engineered for better integration, many proposed applications require an energy band gap in the material. We work to exploit the remarkable change in band structure with the addition of a second layer, where an energy gap in the density of states can be opened by electric field effect. We confirm this effect with planar tunneling spectroscopy only after careful considerations of bias-induced charging and electric fields on the Fermi level and band structure. We stress that these considerations are absolutely necessary for the understanding tunneling spectroscopy in low carrier density, two-dimensional materials. Our transport measurements of bilayer graphene-based field effect transistors suggest that the insulating state is deteriorated by same impurity interactions encountered in monolayer graphene devices. It is certain that serious material engineering of the graphene/dielectric interface is crucial for the realization of top-gated graphene technologies.

We also explored a new material system - graphene hybrid structures - featuring a juxtaposition of the two unique band structures of monolayer and bilayer graphene. We expect that interesting and new electronic states result from their mixing, and show the role of these states in magnetotransport, where very different energy scales of emergent Landau levels encourage charge transfer and locking of respective Fermi levels across several hundred nanometers. Graphene hybrid struc-
tures present an opportunity to explore charge imbalance junctions, including \( p-n \) junctions, in a material where the crystal lattice transition is perfectly smooth, at least in one layer.

After seven years of intense research in the graphene community, electronic structure is fairly well understood in both monolayer and bilayer graphene. The intrinsic properties of both materials make them very attractive for a number of practical technologies, but whether or not graphene will establish such a presence is a matter of materials engineering, and will require extreme impurity control.

Finally, we performed ionic liquid gated electrical transport studies of the strongly correlated material \( \text{Ca}_3\text{Ru}_2\text{O}_7 \). The process that we developed to contact only the surface of gated flakes and our preliminary results encourage the ability to tune surface properties in this and related materials. In the context of this work, tuning charge carrier density and Fermi surface size allows us to explore the role of orbital ordering in magnetic, structural, and metal-insulator transitions in the transition metal oxides.
Bibliography


Vita

Conor Puls

Conor Puls was born August 10, 1984, and raised in Columbia, Maryland (with a short stint in Virginia Beach) to William and Kathleen Puls. His parents stoked his interest in all things natural from bugs on the ground to stars in the sky, and encouraged his academic successes. His brother Brendan and sister Kasey were equal sources of both support and competition. Conor attended Haverford College in 2002, where he found delight in experimental research as well love in fellow student Ashley Emmons. He received his B.S. in Physics with minors in Mathematics and Astronomy, having performed research on granular flow with Dr. Jery Gollub. He pursued research under the direction of Dr. Ying Liu while a student Penn State University, beginning in 2006. Conor and Ashley were married on July 24, 2010.

Academic Publications:

Conor Puls and Ying Liu, Planar tunneling measurements of the energy gap in biased bilayer graphene, in preparation.