Studies of bilayer and trilayer graphene

by

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Abstract

Graphene is a single 2-dimensional atomic layer of hexagonally packed carbon atoms. Graphene has a unique combination of thermal, mechanical, and electronic properties, making it a useful tool for learning new physics as well as a material with high potential for applications. Bilayer graphene (2LG) and trilayer graphene (3LG) share many of the interesting properties of its monolayer relative, but with several key differences. This thesis makes use of resonant Raman spectroscopy to characterize these systems and quantify their layer number as well as stacking order in different graphene flakes.

Three distinct graphitic systems were studied: bilayer graphene with Bernal stacking, and trilayer graphene with both Bernal and rhombohedral stacking. A number of back-gated bilayer and trilayer graphene devices were created via the method of mechanical exfoliation. The type of stacking and number of layers was confirmed using resonant Raman spectroscopy. Electron beam lithography was used in combination with a positive PMMA resist in order to pattern samples. Metal was then evaporated onto samples to create electrical contacts for use in gated measurements.

These samples, along with my procedure, will be used for future measurement by members of the Dresselhaus research group. These gated graphene devices will be used with gate-modulated resonant Raman spectroscopy (GMMRS) in order to explore the electron-phonon properties of AB 2LG, ABA 3LG, and ABC 3LG graphene.

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I have been very lucky to be able to enlist the help of so many great scientists. Javier Sanchez-Yamagishi for his pertinent advice on exfoliation, and Xu Zhang for his skills with metal evaporation and general advice, as well as helping me make samples when I was pressing up against my deadlines. Daniela Lopes Mafra took the time to help me understand some of the finer points of using the NPGS system in doing lithography. Britt Baugher, who I barely knew, spent two hours working with me to teach me how to take I-V measurements. Cosmi Lin gave me several samples to play around with. Patrick Boisvert trained me to use the CMSE SEM, and Dr. Shaoyan Chu allowed me to use it in the first place. Visiting graduate student Jenaina Soares helped me to make sense of some of my data. Read Schusky kept me abreast of current events as well as assisting me with a general administrative superiority. Lastly, I would like to thank my girlfriend for all her support and encouragement.

This process has been less of a learning curve and more of a learning cliff. However, I leave MIT with many lessons learnt about the value of punctuality, preparation, and hard work. I would not have been able to complete my work without the help of many good scientists. And once I struck a rhythm, I definitely began to enjoy experimental physics.
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Chapter 1

Introduction

1.1 Is Graphene Worth Studying?

Graphene is a single 2-dimensional atomic layer of hexagonally packed carbon atoms. Carbon can be packed into a 0D Buckminster fullerene, a 1D nanotube, 2D graphene, or 3D graphite. [1, 2, 3] Graphene can be transformed into any of these systems with the proper layer folding or stacking, as in Figure 1-1.

Graphene has a unique combination of thermal, mechanical, and electronic properties, making it a prime material for learning new physics. It has a breaking strength of $\sim 40\text{N/m}$, room temperature thermal conductivity $\sim 5000\text{W/m}$, and a carrier mobility $\mu$ of up to $15,000\text{cm}^2$. [5] It also has great potential to be used in diverse applications such as transistors, single-molecule gas detectors, integrated circuits, ultracapacitors, solar cells, and even as an anti-bacterial film. [6, 7, 8, 9, 10, 11, 12] Bilayer graphene (2LG) and trilayer graphene (3LG) share many of these properties, but with several key differences that will be discussed.

Although graphene has been theoretically studied for the past 60 or so years, it was thought to be experimentally impossible to realize monolayer graphene due to the Peierls instability of a 2D crystal lattice. [13, 14] Thermal fluctuations were believed to inevitably lead to physical dislocations and atomic movements within the lattice, causing the sheet to tear itself apart. This also seemed to be confirmed by repeated experiment. [15, 16] That is, until the Nobel Prize-winning experiments of A.K. Geim
and K.S. Novoselov [17] of 2004, who disproved the old theory with their creation of 2D materials.

There are several reasons why thermal fluctuations do not destroy the fragile graphene flakes. The relatively small size of flakes and the special strength of C-C interatomic bonding ensure that physical tears do not develop. [18, 19] In addition, a slight wrinkling of the 2D surface into the third dimension helps to minimize the effects of any thermally induced vibrations. [20, 21]

It has been shown that graphenes electronic properties rapidly approach those of graphite at greater than about 10 atomic layers. [22] Therefore, one can consider it a 2D crystal at anywhere between 1 and 10 layers. This agrees with experiment, as the screening length (a measure of the electric field screening by the electrons in a solid) of graphite is roughly atomic 2 layers; one can differentiate between the surface and the bulk of a sample with as few as 5 atomic layers. [23, 24]

Obviously some of these physical cases are simpler and more beneficial to study. Monolayer graphene has an unusual Dirac cone band structure at low energies, while bilayer graphene has a parabolic band but no band gap. Both monolayer and bilayer graphene have tunable electronic properties that may be controlled by different techniques. Because of this flexibility and tunability in their electronic structure,
both materials have great potential for use in nanoscale carbon-based electronics. [25, 26, 27, 28]

Trilayer graphene is not as well-studied, but has properties similar to those of 1LG and 2LG. In addition, although 2LG is typically only stacked in one way (AB-stacking or Bernal stacking), there are two ways to stack 3LG: ABA (Bernal stacking) or ABC (Rhombohedral stacking). A difference in stacking order amounts to a difference in the properties of the material. ABA-stacked is metallic with properties of both 1LG and 2LG, while ABC-stacked graphene has a tunable semiconducting bandgap. Lastly, turbostratic carbon contains layers that are haphazardly stacked and crumpled against each other. [29, 30]

1.2 Studying graphene with Raman spectroscopy

In 1928 Sir C.V. Raman experimentally verified the inelastic scattering of light in what became known as the Raman effect. [31] Raman spectroscopy relies upon the inelastic scattering of low-frequency monochromatic light to reveal information about the different vibrational and rotational modes of a system. [31, 32]

This vibrational information is specific to the chemical bonds and symmetries of different materials. For example, one can differentiate between the different forms of carbon by looking at these Raman “fingerprints.” More recently in 2006 it was shown that Raman spectroscopy can be used to quickly and simply determine the number of layers (up to 5) in a graphene sample. It can also be used to learn about different perturbational effects on phonon energies, [33, 34, 35, 36] or to estimate the doping of a sample. [37]

Resonant Raman spectroscopy can be used to learn about the specific vibrational and electronic properties of graphene systems. [38]

This thesis hopes to contribute to the understanding of the electron-phonon interactions of bilayer and trilayer graphene systems using Raman spectroscopy.


1.3 Goals of this thesis

My project uses two different graphitic systems. The first system is 2LG under a periodic external potential. Application of an external potential on the electronic structure of bilayer graphene shows that there is a critical value of the external potential below which new Dirac fermions are generated in the low-energy band structure, and above which a band gap is opened in the system. [39]

There are two major characteristics of importance: (1) Dirac-like electronic dispersion (i.e. Dirac fermions) is the main mechanism responsible for the unusual and outstanding features of graphene [26] and (2) the existence of band gaps through the system makes the material very attractive for use in electronic transistor-based devices [28]

A second system to be explored is 3LG under an external potential. Depending on the stacking order, 3LG will reveal different electronic and vibrational structures, which are still poorly explored.

These systems were to be studied using gate-modulated resonant Raman spectroscopy (GMRRS). By applying gate voltages in the 2LG and 3LG devices, one can modify their electronic structures with simultaneous observation of their vibrational properties (in other words, by observing the phonons of the system).

Due to time constraints, I was not able to use GMRRS to make measurements. However, I was able to create a number of gated bilayer and trilayer graphene samples, as well as an array in various stages of completion. These samples, along with my documentation of the procedure in this procedure, is a preparation for future measurement by members of the Dresselhaus research group.

1.4 Basic Outline

Chapter 2 will derive a basic model of graphene (in its one, two, and three-layer forms) as well as discuss some important electron-phonon properties. Chapter 3 will contain a theoretical discussion of Raman scattering as well as discussing its specific
use in graphene. Chapter 4 will discuss the fabrication of graphene devices, while Chapter 5 will discuss the types of measurements that were completed, and will also conclude the thesis.

Appendix A delineates the specific steps necessary to setting up the SEM and NPGS. Appendix B discusses the specific Raman apparatus used, as well as calibration steps.
Chapter 2

Graphene

Monolayer graphene is a semimetal without a bandgap and linear dispersion. Bilayer graphene is a semiconductor with a tunable bandgap and quadratic dispersion. Trilayer graphene can vary depending on the stacking order. The following sections will model 1LG, 2LG and 3LG, after which this thesis will focus on graphene’s phonon properties. [40, 41]

2.1 A model of monolayer graphene

Graphene is a hexagonal lattice of $sp^2$-hybridized carbon atoms. Carbon has 4 valence electrons. Three of the electrons form $\sigma$ bonds which hybridize to form the strong covalent $sp^2$ configuration, and the last electron is in a $2p_z$ orbital perpendicular to the 2D plane, and forms weaker delocalized $\pi$ electron states. The discussion of the single-layer model draws from references [5, 42].

In a hexagonal 2D lattice system, the locations of carbon atoms in a Cartesian coordinate system are given by the following primitive lattice vectors:

$$\vec{a}_1 = \sqrt{3}a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad \vec{a}_2 = \sqrt{3}a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)$$  \hspace{1cm} (2.1)

and basis vectors:

$$\vec{\delta}_1 = (0, 0) \quad \vec{\delta}_1 = a(1, 0)$$

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Figure 2-1: (a) The two different basis atoms each form their own sublattice in red and green. Primitive vectors are also shown. (b) Depiction of the real space of 1LG, with important points of symmetry labelled. Adapted from [41].

where $a = 1.42 \text{Å}$ is the carbon-carbon spacing. Figure 2-1 show the positions of the high-symmetry $\Gamma$, $K$, and $M$ points within real space, at the center, corner, and edge center of the hexagon, respectively.

The first Brillouin zone in graphene is also hexagonal, and is defined by the reciprocal lattice vectors:

\[
\vec{b}_1 = \frac{2\pi}{3a} (1, \sqrt{3}) \quad \vec{b}_2 = \frac{2\pi}{3a} (1, -\sqrt{3})
\]  

(2.2)

Each carbon atom has 4 valence electrons which can contribute to the bonding. The $p_z$ orbitals perpendicular to the lattice form delocalized $\pi$ electronic states, creating the valence and conduction bands. [5]

The band structure of graphene is well-approximated from a nearest-neighbor 2D tight-binding model. This ignores the $\sigma$ energy bands and treats only the $\pi$ bands, giving a good estimate of many of the 1LG properties. Following [22] we can calculate the tight-binding Hamiltonian:

\[
\mathcal{H} = \begin{pmatrix} \epsilon_{2p} & -\gamma_0 f(k) \\ -\gamma_0 f^*(k) & \epsilon_{2p} \end{pmatrix}
\]

where $\gamma_0$ is the nearest neighbor transfer integral between the two atoms of the basis, $\epsilon_{2p}$ is the atomic $2p$ orbital energy of an isolated carbon atom, and $f(k) = e^{i k_x a \sqrt{3}} + 2e^{-i k_x a / 2 \sqrt{3}} \cos(k_y a / 2)$. The nearest neighbor overlap integral matrix $\mathcal{S}$,
which yields information about the overlap of adjacent atomic wave functions, is given by:

$$S = \begin{pmatrix} 1 & sf(k) \\ sf^*(k) & 1 \end{pmatrix}$$

Solving the equation $\det(\mathcal{H} - ES)$ yields the eigenenergies and band structure:

$$E(\mathbf{k}) = \frac{\epsilon_2 \pm tw(\mathbf{k})}{1 \pm sw(\mathbf{k})}$$

where the + signs give the bonding $\pi$ band, and the - signs give the antibonding $\pi^*$ band, while $w(\mathbf{k})$ is given by $w(\mathbf{k}) = |f(\mathbf{k})|$, and $t$ is the negative of the nearest neighbor transfer integral by convention.

In monolayer graphene this leads to a Fermi energy that lies at the $K$ and $K'$ points, corresponding to the 6 corners of the first Brillouin zone (see Figure 2-2). The six points where graphene's valence and conduction bands meet are called the Dirac points. Near the Dirac point the conduction and valence bands are conical,
meaning that the electron energy $E$ depends linearly on the electron wave vector $\vec{k}$. We define $\vec{k'} = \vec{k} - \vec{K}$, where $\vec{K}$ is the wavevector from the $\Gamma$ point to the $K$ point in the Brillouin zone (refer to Figure 2-1(b)). Near the $K$ point ($|k'| << 1/a$), the dispersion is linear to first order:

$$E(k') = \frac{\sqrt{3}}{2} \gamma_0 a |k'|.$$  \hspace{1cm} (2.4)

In the above equation the energy is positive for the conduction band and negative for the valence band.

The Fermi velocity can be calculated from its definition to be $v_F = \frac{1}{h} \frac{dE}{dk} \approx 10^6$ m/s, which comes out to roughly 1/300 of the speed of light. The effective mass of an electron or hole at the Dirac point can be calculated to be massless: $m^* = \frac{1}{h^2} \frac{d^2E}{dk^2} = 0$ due to the linear bands.

The density of states $n(E)$ is given by

$$n(E) = \frac{g_s g_v}{2\pi(h\nu_F)^2} |E|$$ \hspace{1cm} (2.5)

where $g_s = 2$ is the spin degeneracy and $g_v = 2$ is the ”valley degeneracy” due to the symmetry of the $K$ and $K'$ points. This density of electronic states $n(E)$ determines the electrical transport properties.

2.2 A model for bilayer graphene

Bilayer graphene is most often found in the AB (or Bernal) stacking arrangement, where the second layer is shifted such that its atoms are centered over the centers of formed hexagons, as shown in Figure 2-3. In other words, there are two atoms per unit cell, in which the $A$ and $A'$ atoms are on top of one another and the $B$ atoms are over the centers of the hexagons on the next layer.

Bilayer graphene also exhibits many interesting properties. It does not have a linear electronic dispersion like 1LG, but instead has a zero gap parabolic band. [45] Bilayer graphene also has a shifted quantum Hall effect, [46] and one can open up
Bilayer

Figure 2-3: Bilayer graphene can be found in two different stacking arrangements, but Bernal stacking (depicted here) is most common. Adapted from [44]

a bandgap by applying a perpendicular electric field, where the magnitude of the voltage difference can determine the size of the gap. [47, 48, 49, 50]

The nearest-neighbor tight-binding Hamiltonian can be calculated to be:

\[
\mathcal{H}_{\text{bilayer}} = \begin{pmatrix}
0 & \gamma_0 f(k) & \gamma_1 & \gamma_4 f^*(k) \\
\gamma_0 f^*(k) & 0 & \gamma_4 f^*(k) & \gamma_3 f(k) \\
\gamma_1 & \gamma_4 f(k) & 0 & \gamma_0 f^*(k) \\
\gamma_4 f(k) & \gamma_3 f^*(k) & \gamma_0 f^*(k) & 0
\end{pmatrix}
\]

There are now 4 different tight-binding overlap parameters to be calculated, which now include interactions between layers. These parameters are labeled in Figure 2-3. Diagonalizing the Hamiltonian yields the band structure of bilayer graphene. In contrast to 1LG’s single valence and conduction bands, 2LG has two valence and two conduction bands. The linear dispersion near the \( K(K') \) points has also been replaced by a more traditional parabolic dispersion relation.
2.3 A model for trilayer graphene

As might be expected from the previous models, trilayer graphene has three valence and three conduction bands. While monolayer graphene and bilayer graphene have linear and quadratic dispersions, respectively, the electronic structure of trilayer graphene varies depending on its stacking order, giving rise to more complex properties. [44]

With Bernal stacking (see Figure 2-4) the electronic structure consists of overlapping linear and quadratic bands, containing properties of both 1LG and 2LG. With rhombohedral or ABC stacking (again, refer to Figure 2-4) one finds a cubic dispersion. [30]

One of the notable characteristics of bilayer graphene is the ability to open up a bandgap by applying a perpendicular electric field. Research has shown that while ABA-stacked trilayer graphene remains metallic at all field strengths, ABC-stacked 3LG has a tunable semiconducting band gap, similar to that of bilayer graphene. [29]

The nearest-neighbor tight-binding Hamiltonian has also been calculated, and has the form of a diagonalizable 6x6 matrix, discussed extensively in the references [51, 52, 53].
2.4 Graphene phonon structure

One cannot interpret Raman spectra without an understanding of graphene's phonon dispersion.

We may first model the phonon dispersion by realizing that ion core movement is very small, and considering their positions to be fixed at equilibrium. Later on, one can tack on additional considerations to the model.

In our first approximation there are \(3N\) phonon phonon dispersion branches in a material with \(N\) atoms per unit cell. 1LG thus has 6 branches, of which three are acoustic (A) modes and three optical (O) modes. These modes can also be classified as longitudinal (L), meaning that the vibrations are parallel to the lattice, or transverse (T), meaning that the vibrations are perpendicular to the lattice. Lastly, the transverse vibrational modes can be classified as out-of-plane (o) or in-plane (i). Altogether, in the highly symmetric \(\Gamma M\) and \(\Gamma K\) directions, the modes are called: \(LO, iTO, oTO, LA, iTA,\) and \(oTA\) phonon modes. The resultant phonon dispersion relations are shown in Figure 2-5. Graphene's phonon structure is explained in more
detail in the next chapter on Raman spectroscopy.
Chapter 3

Raman Spectroscopy

Raman spectroscopy is the use of the inelastic scattering of light in order to measure the properties of materials. This experimentally simple and nondestructive technique has evolved into one of the most important tools in the arsenal of modern nanoscience. Much of the following chapter is adapted from references [5, 32, 56].

Raman spectroscopy has been used for the last four decades in studying graphitic materials such as carbon fibers, glassy carbon, nano graphite ribbons, fullerenes, nanotubes, and graphene. For $sp^2$ hybridized carbon materials such as graphene, Raman spectroscopy helps us to learn about chemical impurities, densities, electronic energy structure, edge structure, and phonon vibrational states, among other things.

It is important to realize that the spectra from different systems are all unique, a "fingerprint" identifying each specific material.

3.1 Theory of Raman Scattering

In 1923 Adolf Smekal predicted the inelastic scattering of light. Independently, this was experimentally verified in 1928 by Sir C.V. Raman together with K.S. Krishnan. They used sunlight and a narrow band filter to create monochromatic light. When this light passed through a subsequent filter meant to block this frequency, this meant that a small amount of the light had changed frequency. [31] The frequency change in this case was due to phonons.
Figure 3-1: Three different types of light-matter interactions. In Rayleigh scattering, there is no energy exchanged between the photon and material (elastic scattering). In Raman scattering, electrons that are excited to a virtual energy state fall back to a different vibrational state, creating (Stokes process) or destroying (anti-Stokes process) a phonon. (Adapted from reference [57].)

Raman scattering is a two-photon event. Incoming radiation interacts with polarizable molecules to create an induced dipole moment, and the subsequent radiation emitted by this induced dipole moment causes both Rayleigh and Raman scattering. Elastic Rayleigh scattering involves emission of light at the frequency of the incident radiation, while inelastic Raman radiation's frequency is shifted to account for a gain or loss of vibrational energy in the molecule. In other words, Raman scattering causes the emission or absorption of a phonon. If the particle gains vibrational energy it is called Stokes (S) Raman scattering, observed as a lowering of the frequency of the scattered light. If the particle loses vibrational energy it is called anti-Stokes (aS) Raman scattering, and the scattered light is upshifted in frequency. (See Figure 3-1.) Phonons are bosons, and the probability to create or destroy one is determined by the Bose-Einstein distribution. The probability for Stokes and anti-Stokes differs because the first process increases the number of phonons by one, while the second process decreases it. The intensity ratio between the $S$ and $aS$ signals is given by $I_S/I_{aS} \sim e^{E_\theta/kB T}$, meaning that the Stokes signal is typically stronger, and the one that we experimentalists usually care about.
Figure 3-2: Phonon modes at the $\Gamma$ and $K/K'$ symmetry points of the Brillouin zone; i/o stands for in-plane or out-of-plane; T/L stands for transverse/longitudinal; A/O stands for acoustic/optical. Different modes and combinations of modes create different peaks in Raman spectra. (Adapted from reference [5])

In a Raman scattering process, the photon shakes electrons. The inelastic scattering by phonons happens because the ability of the photon to shake the electrons is different at different locations within the crystal. This "shakeability" is determined by the polarizability of the material. The different types of phonon modes seen in graphene are shown in Figure 3-2.

### 3.1.1 Plot of spectra

The Raman spectrum refers to a plot of scattered intensity $I_S$ as a function of $(E_{\text{laser}} - E_{\text{Stokes}})$. Peaks will be seen at positive and negative phonon energies. In Stokes scattering laser energy is down-shifted and particle energy is upshifted, creating the peaks on the positive side of the spectrum. In anti-Stokes scattering laser energy is up-shifted and particle energy is down-shifted, creating the peaks on the negative side of the spectrum.

Phonon excitations can be approximated as classical damped harmonic oscillators, and the shape of each Raman peak looks like the response of a driven damped
harmonic oscillator, which is best described by a Lorentzian curve. In certain cases the lineshape can differ from a simple Lorentzian. For example, when a feature is composed of several phonon contributions, the shape is determined by a convolution of different Lorentzian curves. And when an electron-phonon interaction takes place, there is an additional broadening of the peak and distortion of the lineshape called the Kohn anomaly, best approximated by a Raman lineshape called the Breit-Wigner-Fano lineshape (discussed in detail in [58]).

The energy of Raman peaks is usually given in units of cm\(^{-1}\), where 1\(\text{cm}^{-1}\) is the energy of a photon with wavelength \(2\pi\text{cm}\). This convention is also supported by the fact that many Raman spectrometers have an accuracy down to 1\(\text{cm}^{-1}\).

### 3.1.2 Resonance Raman scattering

Typically Raman spectra only contain information about phonons, and are independent of the laser excitation energy. However, when the laser energy \(E_{\text{laser}}\) matches optically allowed electronic transitions, such as the gap between the valence and conduction bands of a semiconductor \(E_g\), the Raman signal gets much stronger through a process called resonant Raman scattering (RRS). The intensity in this case increases by about a factor of 1000. One also obtains resonant Raman scattering if the scattered laser light \(E_{\text{laser}}\pm E_q\) (+ for Stokes and − for anti-Stokes scattering, where \(E_q\) is the phonon energy) is equal to the transition energy \(E_g\).

The resonance condition is particularly important in the study of nanomaterials. Since the Raman signal from nanomaterials is usually very small due to the small sample size, RRS allows provides a method of using Raman spectroscopy to study materials such as graphene and other nanocarbon materials. Figure 3-3 depicts several different resonant Raman processes.

### 3.1.3 First and higher-order Raman processes

The order of a Raman process is determined by the number of phonons created. The most common is first-order Stokes Raman scattering, where an incident photon creates
Figure 3-3: Shown are (a) one-phonon first-order, (b) one-phonon second-order, and (c) two-phonon second-order resonance Raman processes. The top row show resonance conditions for incident photons. The bottom row show resonance conditions for scattered photons. The solid circles are resonance points. (Adapted from reference [5])

a low-momentum phonon \( (q \approx 0) \) in the crystal. Second, third, or higher-order Raman processes which involve more phonons reveal more interesting information about electron, phonon, and electron-phonon interactions by making wavevector-dependent study possible. Figure 3-3 depicts several resonant Raman processes of first and second order.

### 3.1.4 Quantum description of Raman scattering

In order to have a quantitative model of Raman processes, one must call on quantum mechanics, specifically time-dependent perturbation theory. This is especially important to understanding resonance Raman scattering, which is responsible for several important phonon processes in graphene. The theory of Raman scattering is discussed in greater detail in [5, 59].

### 3.1.5 Group theory

The selection rules governing Raman scattering are derived from group theory. Group theory is a branch of mathematics which, in its application to physics, translates complex symmetry principles to simple linear algebra. A true grasp of Raman processes involves an understanding of group theory. However, in the interest of time, this
thesis will not attempt a group theoretical treatment of Raman scattering, but refer the reader to several useful references [5, 59] and quote results.

3.2 Raman processes in graphene

In monolayer graphene the most recognizable features in the Raman spectrum are the $G$ band at 1582 cm$^{-1}$ as well as the $G'$ band (2700 cm$^{-1}$). There is also a smaller peak near 2400 cm$^{-1}$ called $G^*$. Lastly, with a disordered or unclean sample, or at the edges, one can also see several disorder-induced peaks, $D$ and $D'$ bands at about 1350 cm$^{-1}$ and 1620 cm$^{-1}$ respectively. These are all shown in Figure 3-4, found using a laser excitation of 2.41 eV.

3.2.1 G band in graphene

The $G$ band is present around 1580 cm$^{-1}$. It is caused by the in-plane C-C bond stretching mode, which creates both the in-plane transverse optical (iTO) phonon as well as the longitudinal optical (LO) phonon (refer to Figure 3-2 for a diagram). Due to the strong covalent bonding between carbon atoms and their small mass, the $G$ band has a relatively high frequency compared to other materials, and one can easily measure shifts in the peak frequency $\omega_G$. Perturbations to the $G$ band can be time-independent, such as strain caused by mechanically deforming the sheet of atoms, or time-dependent, such as the effects of temperature and gate voltage on the electron-phonon coupling. The $G$ band can thus be used to probe the effects of different modifications made to graphene.

Normally the iTO and LO modes are doubly degenerate at the $\Gamma$ point of the Brillouin zone. However, when there is a physical strain to break the hexagonal symmetry of the graphene lattice, then that degeneracy splits, and one may observe a splitting in the frequency contributions of the two modes. The relatively high frequency means that small amounts of mechanical stress will result in large observable effects in the Raman spectra.

To understand temperature and doping-dependent effects one must understand
Figure 3-4: (a) and (b) depict the Raman spectrum from clean and defective 1LG, respectively, with important features labeled. Note the presence of additional disorder-induced $D$ and $D'$ bands in (b). (Adapted from reference [32])
Figure 3-5: The differences between the adiabatic and non-adiabatic cases are shown in this depiction of the $\pi$ band structure near the $K$ point of graphene's Brillouin zone. In order to more clearly show the effects of the approximation, the figures show electron doped graphene, so that the Fermi energy (in gray) lies above the normal zero point. (a) A doped graphene crystal. The Dirac point is still at the $K$ point, and the circular Fermi surface is centered at the $K$ point. (b) Conduction and valence bands in the presence of a phonon distortion. In the adiabatic approximation the Dirac points are shifted, but the Fermi surface has the same shape and follows the displacement of the carbon atoms. (c) In the non-adiabatic case, the electrons do not have time to relax and follow the instantaneous ground state. The Fermi surface is unchanged and does not follow the shifting of the Dirac cone. The electron energy is increased. (Adapted from reference [5])

The underlying physics of electron-phonon coupling. This is because the adiabatic, or Born-Oppenheimer approximation, is no longer valid, and el-ph interactions change both the electron energies (in a Peierls-like effect) and the phonon energies (causing a Kohn anomaly, or a discontinuity of the phonon dispersion). Instead, perturbation theory must be used to describe these time-dependent effects. [37, 60, 61, 62, 63, 64] See Figure 3-5 for an illustration of the basic differences involved in the adiabatic and non-adiabatic cases.
3.2.2 General considerations for calculating Raman spectra in graphene

The calculation of Raman spectra requires a lot of computation. To calculate the non-resonant Raman intensity, one needs the electronic energy band structure and phonon dispersion relations. One can use what is called bond-polarization theory to do this. [42] However, in order to describe differences between the one, two, and three-layer graphene, one must be able to understand and calculate resonance Raman intensities. Properties such as the electron-photon and electron-phonon interactions are then needed.

One can begin to approximate many useful properties of the Raman spectra via the tight-binding model. Software has been developed which makes use of this model to calculate Raman spectra. A general overview of tight-binding methods can be found in [65], while sp$^2$-nanocarbon specific information can be found in [5]. This thesis has also attempted a basic description of graphene's band structure earlier in Chapter 2.

3.2.3 The $G'$ band and double resonance in graphene

The $G'$ band is a second-order two-phonon process with a spectral feature between 2500-2800cm$^{-1}$. It has a dispersive dependence on the laser excitation energy ($\omega_{G'} = \omega_{G'}(E_{laser})$), and is one of several examples of higher-order Raman spectra.

The $G'$ band in particular is related to a phonon near the $K$ point in graphene. It comes from two $iTO$ phonons with opposite momentum in the highest optical branch near the $K$ point. The $G'$ band is strongly dependent on perturbations to the phonon and electronic structure of the material. Its shape, location, and intensity can thus be used to differentiate between the different types of graphene, which have different electronic structures depending on the number of layers and type of stacking.

It is useful to note that the $G'$ band is also called the $2D$ band in much of the graphene literature. This thesis adopts the convention of [5] for reasons of clarity. For one, the $D$ and $D'$ bands refer to defect-induced features, while the $G'$ band is not
created by defects. Secondly, 2D is an abbreviation of “two-dimensional”. Therefore we will refer only to the G' band.

The two-phonon process can be modeled quantum mechanically using fourth-order perturbation theory. The creation of the G' peak involves four virtual energy transitions. Double resonance, which couples phonon wave vectors to the electronic structure, enhances the Raman intensity of a two-phonon process. A photon incident on 1LG, a zero-gap semiconductor, will always excite an electron from the valence band to the conduction band.

An electron-hole pair is created, corresponding to the a→b transition in Figure
3.6(a). This excited electron is scattered by emitting a phonon of momentum $\mathbf{q}$ (b→c) in what is called intervalley scattering, connecting the $K$ and $K'$ points. (See Figure 3-3(c).) A second electron-phonon scattering event creates a phonon of momentum $-\mathbf{q}$ moving in the opposite direction to the original valley. And lastly, there is recombination of the electron-hole pair to create a scattered outgoing photon. Conservation of energy leads to double resonance. [66] Double resonance may also occur with intra-valley scattering, which creates different DR features in the Raman spectrum of graphene. The creation of the $G'$ band, however, is dependent on intervalley scattering. [32]

One consequence of the DR phenomenon is that the locations of the $G'$ and $D$ bands within the Raman spectrum also shift with changing laser energy. The phonons are effectively coupled with momenta near the $K$-point. This also explains why $2LG$, which has a steeper dispersion relation, contains a larger shift in the band peak with increasing energy than $1LG$. [67, 68] Figure 3-9 depicts the upshifting of the $G'$ band location with increasing laser excitation energy.

### 3.2.4 Dependence of the $G'$ band on the number of graphene layers

One can distinguish between the different types of graphene using resonance Raman scattering. Since the electronic structure changes with the number of layers, the differences can be seen most clearly in double resonance features such as the $G'$ band, which depend on the electronic structure. The first-order $G$ peak and second-order $D$ peak also vary for monolayer and bilayer graphene. [66] It is the $G'$ band, however, that can be used as the accurate identifier of layer number, especially between the two types of trilayer graphene. Bilayer graphene has two valence and two conduction bands, and its $G'$ band is actually composed of four separate peaks from four different scattering events, seen in Figure 3-8. These peaks are caused by electronic interactions between the $\pi$ and $\pi^*$ bonds between graphene planes. According to Density Functional Theory (DFT), of the four possible transitions, the ones shown in
Figure 3-7: These are plots of the $G'$ band at $E_{laser} = 2.41\, eV$ for graphene, ranging from 1LG to ordered (HOPG) and disordered (turbostratic) graphite. (Adapted from reference [5])

3-6(b) are the strongest, and correspond to 4 different phonon processes. The strong dispersion relation of 2LG means that the slightly different wave vectors correspond to appreciable frequency differences in the Raman spectrum, as seen in [66]. These can be fit by four Lorentzian curves, an example of which is seen in Figures 3-7(b) and 3-9. [38]

Adding layers adds more possible scattering processes. Trilayer graphene has three valence and three conduction bands, and 15 possible scattering events. Since the separation in frequency is very small for some of these events, the $G'$ band of the 3LG is well-fitted by six Lorentzians. As the number of layers further increases, the structure of the $G'$ band actually is simplified as the number of allowed DR processes
Figure 3-8: There are four possible scattering processes that combine to create the overall $G'$ band that one sees in bilayer graphene. (Adapted from reference [5])

goes to infinity, and the electron and phonon dispersion becomes three-dimensional. The changing of the $G'$ band with layer number is discussed further in [69].

One can use the $G'$ peak to differentiate between the two different types of trilayer graphene. ABC-stacked graphene's $G'$ band is less symmetric, has a more prominent shoulder feature and sharper peak, and is generally broader when compared to ABA-stacked graphene. (See Figure 3-10). [70]

The presence of unique identifiers in graphene’s Raman spectrum, coupled with non-destructive methods and relative speed of use, mean that Raman spectroscopy is a highly suitable method of determining the number of graphene layers. [66]

### 3.2.5 Summary of Raman spectroscopy on graphene systems

Most of the high-intensity Raman features of graphene can be related to phonons at the high-symmetry $\Gamma$ or $K/K'$ points of the Brillouin zone. The $G$ band is a signature of all $sp^2$ carbon materials and is observed at around $1585\text{cm}^{-1}$. It is a combination of the $iTO$ and $LO$ phonons which are degenerate at the $\Gamma$ point. The $G$ band is highly sensitive to changes in temperature, mechanical deformation of the hexagonal lattice, and doping.
Figure 3-9: Components of the $G'$ band in 2LG at two different laser excitation wavelengths. Note the upshift of the peak at higher laser excitation energy, which is larger than the upshift seen in 1LG. (Adapted from reference [66])
Figure 3-10: The 2D Raman band in ABA (red) and ABC (green) 3LG, at 4 different laser excitation levels. Note the shift in the peak with excitation energy, similar to 1LG and 2LG. (Adapted from reference [70])

The $G'$ band is another signature $sp^2$ Raman band, composed of one or several peaks and located in the range 2500-2800cm$^{-1}$. It is a result of a two-phonon double resonance Raman process. At a laser excitation energy $E_{laser} = 2.41$eV, the frequency is $\omega_{G'} \approx 2700$cm$^{-1}$. However, the frequency increases with increasing laser energy, and the dispersion will vary somewhat depending on the structure of the nanocarbon material in question. Measurement of the $G'$ band is a reliable method of counting the number of graphene layers. In 1LG the $G'$ band is larger relative to the $G$ band, while in AB-stacked 2LG the $G'$ band is much-reduced relative to the $G$ band. It is also sensitive to doping.
Chapter 4

Graphene Device Fabrication

Much of the following procedure relies on the meticulous work of past scientists. [41, 17]

The great thing about creating devices using graphene is that one can rely on tried-and-true lithography methods used in industry with silicon-based electronics. An electron beam is scanned over the graphene sample in a computer-generated pattern to selectively expose a layer of resist that was deposited onto the substrate. The exposed resist is developed in a solution to reveal a patterned surface. Metal is evaporated onto the pattern to create electrical contacts, completing the device.

There are several methods of graphene production. The method of micromechanical cleavage popularized by Geim and Novoselov has been found to yield the highest-quality crystals. [17] Essentially it is the use of Scotch tape on graphite. Exfoliation onto a specific thickness of silicon dioxide allows for the optical imaging of single atomic layers, as the presence of graphene changes the interference condition of the light passing through silicon dioxide and reflecting off of the silicon substrate. [41] Mechanical exfoliation is a reliable way of obtaining electronic-quality graphene samples. Highly oriented pyrolytic graphite (HOPG) was used with the exfoliation method detailed in other references. [17, 41]

The substrate used was p-doped silicon with a 300nm layer of SiO₂, in approximately 10x10mm pieces. The substrates were first cleaned with acetone and isopropanol alcohol (IPA) for 30 seconds each and blown dry with compressed nitrogen.
before graphene deposition using the tools in Figure 4-2. Exfoliation was completed as shown in Figure 4-4. The samples were exposed to light under a UV lamp (UVO-Cleaner Model 42 shown in Figure 4-1) for 10 minutes, which acted to create a concentration of ozone to etch away small organic particles.

After the exfoliation of graphene onto the chips using methods detailed in ??, inspection was performed using an Axio Zeiss optical microscope in Prof. Pablo Jarillo-Herreros clean room in 13-2023. Flakes were found using the 20x objective, with pictures taken at 20x and 100x in order to map the placement of possible 2LG and 3LG sites. The lower-left corner was chosen as an origin so that one could assign an (X,Y) position to each flake, facilitating subsequent localization of the sample. [71, 72]

The number of layers in different flakes was validated with a measurement of the Raman profile of each flake using a Raman spectrometer (see Chapter 5 and the Appendix B for more information on how this was accomplished).
Figure 4-3: The optical microscope in Prof. Jarillo-Herrero's lab in 13-2023 with camera attached. The digital readout allowed for quick and easy mapping of flake location.

Figure 4-4: (a), (b) Mechanical cleavage of graphite into thinner and thinner layers. (c) Finally, the resulting material is deposited onto a clean SiO$_2$ substrate, and (d) one may search for graphene flakes using an optical microscope. Adapted from [32].
After this measurement it was time for electron-beam lithography. In the case of this thesis, polymethyl methacrylate (PMMA) was used as a positive resist. In a positive resist, it is the exposed areas that dissolve after development. The JEOL 5910 scanning electron microscope (SEM) in 13-1015 was used in doing the lithography.

I used a 4% (by volume) PMMA solution in anisole to create the resist layer. Prior to the spin-coating step, the sample was heated for 5 minutes at 75°C on a hotplate in order to remove any molecules (e.g. water) adsorbed to the surface (see Figure 4-6). Three drops of solution were applied via pipette to each ~1cm² sample. The sample was then spin-coated at 4000rpm (see Figure 4-5). Afterwards it was baked for an additional 5 minutes at the same temperature. This combination of procedures give an overall coating thickness of ~200nm.

The dose and energy of electrons is picked so as to penetrate through only part of the polymer layer (see Appendix A for specific parameters used). At an accelerating voltage of 10keV, one was able to distinguish features underneath the thin film of PMMA and to adequately expose the sample.

In the first lithography step, a set of marker patterns are exposed by the e-beam. After development, these could be used to align the sample to create contacts in the correct location. Each pattern consisted of a 1mm² grid with the letters A-D at each respective corner. 16 smaller markers within this square were labeled with the two
Figure 4-6: The hotplate used to heat the samples to remove excess water and dry PMMA.

Figure 4-7: The marker pattern created in DesignCAD and exposed using an SEM.
letters which were most closely associated with the location (AA, CD, etc.) and an array of even smaller dots were evenly spaced between these. (See Figure 4-7.)

The development was completed using a solution of 1 part methyl isobutyl ketone (MIBK) to 1 part IPA. Each sample was immersed for 15 seconds in the MIBK/IPA solution and rinsed for 10 seconds in IPA. It was then blow-dried using compressed nitrogen gas.

A conductive material such as SiO\(_2\) can easily be seen under both the optical microscope and the SEM (Figure 4-8(a)), and one could use the markers, as well as original mapping information, in order to precisely find the location of graphene flakes using the SEM.

The use and design of the device and marker patterns are described in detail in Appendix A. Each device consisted of two larger square contacts, with a lead going to each end of the graphene flake. The procedure to etch the device pattern was the same as that used to create the markers, though in this case the pattern had to be aligned with the already-etched markers. (See Figure 4-8(b)(c)(d))

The next step was to evaporate metal contacts into the pattern. Evaporation of a Ti/Pd/Au metal combination was deposited with the help of graduate student Xu Zhang in the Microsystems Technology Laboratories (MTL) facility. The overall thickness of metal was 46nm, with 1nm Ti, 20nm Pd, and 25nm Au.

After metal evaporation, acetone and IPA rinses were used for liftoff of the remaining PMMA, ideally leaving only the metal-covered pattern. Annealing of the sample at 75\(^\circ\)C was used to remove residual PMMA. (See Figure 4-8(e))

### 4.1 Fabrication challenges

#### 4.1.1 Weak adhesion of graphene to substrate

The bonding between graphene layers is relatively weak, and bonding to other materials is also often weak. [32] A too-thick layer of evaporated metal will stress the film and cause it to peel back. This also pulls up the graphene flake underneath,
Figure 4-8: The fabrication of a graphene device from start to finish: (a) A flake is located and optically imaged. (b) A marker pattern is created in DesignCAD and exposed using an SEM. (c) Another image is taken with both the flake and markers after development. (d) The image of the flake with markers is used to design a two-terminal device, also using DesignCAD. (e) The image after SEM patterning and development. Note the unwanted crossover of the leads onto two different flakes. (f) The finished device after metal evaporation and liftoff of PMMA.
destroying the sample. Metal directly in contact with SiO₂ does not peel due to the stronger intermolecular forces between titanium and silicon dioxide.

The solution is to evaporate thinner layers of material, such as 46nm that was used. I relied upon the meticulous research done by Nezich, as well as the advice of postdoctoral associate Paulo Araujo and the hard work of graduate student Xu Zhang to prevent these types of mistakes.

4.1.2 Lithography

There were a number of issues that arose in the steps involved with e-beam lithography. For example, if the sample was overexposed with the e-beam when writing the markers, development would reveal letters with a much poorer resolution, where the edges are “fuzzy”. (See Figure 4-9).

This means that any pattern design made on the basis of these marker locations would be misaligned with respect to the graphene flake, and likely not form contact on either side of the flake. (See Figure 4-10).
4.1.3 Spin-coater vacuum system

The spin-coater (see Figure 4-5) was a relatively simple machine to use. It relied on a rubber O-ring to form a vacuum seal on each silicon chip. However, if the O-ring contained any PMMA residue, or was too small, or too large, then the vacuum would not be sufficient. The sample would reach up to 4000rpm before being shot off, and typically lost for ever (as it would stick immediately to a PMMA-encrusted surface).

4.1.4 Use of samples with pre-made marker patterns

Due to time constraints and the repeated failure of necessary equipment such as the optical microscope and SEM, it was necessary to create several devices via an alternative procedure. Xu Zhang and Cosmi Lin were instrumental in helping me to complete these.

Cosmi provided SiO$_2$-covered silicon chips with a previously evaporated marker pattern. These chips were then exfoliated, mapped using the optical microscope, and measured using Raman spectroscopy. Xu then helped me to perform lithography and pattern the devices.
Chapter 5

Measurements using simple gated graphene devices

5.1 Raman measurements and verification of flake layer number

Raman measurements were carried out to characterize the graphene flakes. Focus was placed on the $G'$ band as the indicator of the number of layers and stacking order, as related in Chapter 3.

Bilayer graphene has a very noticeable shoulder feature on the $G'$ band of the Raman spectra. (See Figure 5-2.) Figure 3-7 is a good comparison between bilayer and trilayer graphene.

As was previously mentioned, trilayer graphene has three valence and three conduction bands, and 15 possible scattering events. [5] The small separation in frequency means that the Raman spectrum of 3LG is well-fitted by six Lorentzians. The $G'$ band of ABA trilayer graphene has a defined shoulder (see Figures 3-10 and 5-3) similar to bilayer graphene, especially in comparison to ABC trilayer graphene, which is in general more symmetric. [70]

The Raman spectra for four different working bilayer and trilayer devices reproduced in the following pages.
Figure 5-1: Raman spectra of 4 different graphene devices on two chips, taken with a 2.33eV laser. The names refer to specific samples and flake locations.

Figure 5-2: The same spectra, looking more closely at the $G'$ bands.
Figure 5-3: Example of ABA-stacked 3LG, fit with 6 Lorentzian curves, taken with one of my samples. Plot courtesy of Jenaina Soares.

Figure 5-4: Example of ABC-stacked 3LG, fit with 6 Lorentzian curves. Courtesy of Jenaina Soares.
This section features two more examples of trilayer graphene taken using my samples, with an example of both ABA and ABC stacking, as well as a third figure comparing the two different flakes. (Figures 5-3, 5-4, and 5-5 respectively.)

5.2 I-V measurements

One can induce charges in graphene by applying a potential difference between graphene and the p-doped silicon substrate. This creates a parallel plate capacitor, as in Figure 5-6, with one plate the graphene flake (with a gold contact), and the other plate the silicon substrate. The 300nm layer of SiO₂ acts as the dielectric medium. The capacitance of the parallel plate capacitor will vary depending on the gate voltage that is applied between them. The two gold contacts on either end of the graphene flake act as a Source and Drain for electrical current, allowing induced charge carriers to move. Thus one can make measurements of resistance, and plot I-V (current versus voltage) curves for specific graphene devices. [17, 32]

The induced surface charge density \( n(V_g) \) can be calculated using a simple model used in [17], and given by the equation below:

\[
    n(V_g) = \frac{\epsilon_0 \epsilon V_g}{t \epsilon}
\]

where \( \epsilon \) and \( \epsilon_0 \) are the permittivities of free space and SiO₂, \( V_g \) is the gate voltage, \( t \)
Figure 5-6: Diagram of graphene device. (Adapted from reference [32])

Figure 5-7: Four-probe station at left, with lock-in amplifier and power sources on right.

is the thickness of the SiO\textsubscript{2} dielectric (300nm), and $e$ is the electron charge.

If one can calculate the conductivity $\sigma$ as a function of the gate voltage, then one can use this to calculate the carrier mobility $\mu$, using $\sigma = n(V_g)e\mu$. Quoted values of $\mu$ are given using the minimum of the conductivity curve, so that $\sigma_{\text{min}} = \varepsilon_0eV_{g\text{min}}/t$. The results for several devices are given in Table 5.1.

These electrical measurements were made purely to demonstrate the successful manufacture of graphene devices. The setup measured the Drain-Source voltage $V_{ds}$ as a function of changing Gate voltage $V_g$. Sweeps were made from -25-100V for $V_g$. A lock-in amplifier was used as a source of low-frequency AC voltage through a 1M$\Omega$ resistor. The lock-in amplifier filters out much of the background noise, making for a cleaner signal.

The devices were given a constant current. A 1V source and 1 M$\Omega$ resistor yielded
Figure 5-8: Four different curves for each sample, plotting conductance between the source and drain leads as a function of the back gate voltage. Minima occur at the neutrality point and are marked by vertical lines.

a 1μA of current. One could therefore convert the voltage output into resistance $R_{ds}$ via Ohm’s Law and plot that as a function of the back Gate voltage. Converting to conductance $G$ is as simple as inverting the resistance.

To convert the resistance $R$ into sheet resistance $R_s$, one must have a knowledge of the relative length and width of the graphene flake, as seen in the following equation:

$$\rho = \frac{RA}{L} = \frac{RWt}{L} = R_s t \rightarrow R_s = \frac{R}{L}$$

where $\rho$ is the resistivity, $A$ the area, $W$ the width of a flake, $t$ the thickness, and $L$ the length along which charge flows.

I approximated the ratio $W/L$ of my flakes using optical images (one can also use an AFM for greater precision), and could use this to create plots of sheet resistance versus gate voltage. Analogous to bulk resistance, I could invert the quantity to obtain sheet conductance. Using Equation 5.2, I could also make a plot of conductivity versus Gate voltage, shown in Figure 5-8.

These values for $\mu$ are within the ranges predicted and verified by multiple groups. [17]
### Table 5.1: Results from Gate Voltage Sweeps

<table>
<thead>
<tr>
<th>Flake Name</th>
<th>$V_g$ [V]</th>
<th>$\mu$ [cm$^2$/V·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cs2(7.12,18.33)</td>
<td>44</td>
<td>$4.4 \times 10^4$</td>
</tr>
<tr>
<td>cs2(5.81,15.63)</td>
<td>28</td>
<td>$1.8 \times 10^4$</td>
</tr>
<tr>
<td>P(2.4,1.86)</td>
<td>84</td>
<td>$4.0 \times 10^3$</td>
</tr>
<tr>
<td>P(6.63,8.21)</td>
<td>59</td>
<td>$1.2 \times 10^4$</td>
</tr>
</tbody>
</table>

### 5.3 Conclusion

Graphene’s potential as a research tool and for a myriad of applications has led to a high volume of patents and papers, and a significant amount of funding. Only this year for example, the European Union allocated 1,000,000,000 Euros towards graphene research. It seemed sensible to spend time doing graphene-based research as an undergraduate in such a booming field of research.

A Bachelor’s thesis strives to make some advancement to the body of scientific research. Additionally, however, and I would argue more importantly, it is a tool to demonstrate to undergraduates the necessary depth and complexity of a doctoral thesis. I was able to successfully create simple bilayer and trilayer graphene transistors, and measure both Raman spectra and gated I-V curves to ensure that devices were working as planned. In addition to learning extensively about the physics of graphene and Raman processes, I learned how to create high-quality graphene flakes, locate them, and determine useful properties using Raman spectroscopy. I also learned how to perform and analyze gated measurements.

The use of bilayer graphene (2LG) and trilayer graphene (3LG) share many of the interesting properties of its monolayer relative, but with several key differences. This thesis made use of resonant Raman spectroscopy to characterize these systems and quantify layer number as well as stacking order in different graphene flakes. Although only four devices were measured, 18 additional silicon samples are in various stages of preparation. However, due to the repeated failure of necessary equipment such as the SEM, optical microscopes, and stage control of the Raman spectrometer, they have not yet been completed. Other lasers that might have been used (in order to measure dispersion relations, for example) were also in a state of disrepair during the
course of the year.

All of my devices, and those in various steps of completion, will be used in future measurements by members of the Dresselhaus research group. My documented procedure will be helpful in this pursuit. The gated graphene devices will be used with gate-modulated resonant Raman spectroscopy (GMMRS) in order to explore the electron-phonon properties of AB 2LG, ABA 3LG, and ABC 3LG graphene.
Appendix A

Scanning Electron Microscope (SEM) and Nanometer Pattern Generation System (NPGS) Setup

A.0.1 Overview

The JEOL 5910 was the SEM of choice for this thesis. The SEM is coupled with a computerized Nanometer Pattern Generation System (NPGS) which are both housed in the CMSE Electron Microscopy Shared Experimental Facilities in room 13-1015.

SEM instruction was provided by Patrick Boisvert, a Technical Associate in the CMSE. Training is required prior to the use of the facility. NPGS instruction was provided by Paulo Araujo.

In 13-1015 there are two computers, one dedicated to running the SEM, the other for the NPGS. A switch changes control of the SEMs motorized beam to the NPGS, allowing one to easily expose a certain pattern using the e-beam.

The steps for lithography were as follows:

1. Prepare the chip

2. Design the pattern

3. Prepare the NPGS and SEM
Figure A-1: The SEM is at the left, with the NPGS system controlled by the computer at the right.

4. “Writing the pattern

5. Process the chip

Several of these steps, such as (1), (4), and (5), have been already described. (2) involves the use of DesignCAD 16 Express, a copy of which was obtained from Javier Sanchez-Yamagishi in Prof. Pablo Jarillo-Herreros group. (3) involves sample loading and calibration for the SEM and formatting of the run files in the NPGS.

A.0.2 Pattern design

Designing the patterns in DesignCAD required certain parameters for compatibility with the NPGS program.

Patterns are in micrometers.

Different portions of the pattern can be placed in different layers, colors and line types. One can stipulate a different NPGS procedure for each layer or line type. Dashed lines told the NPGS to expose, while solid lines signified that the e-beam should ignore them.

After the markers were made, a picture was taken with the light microscope, and it could be loaded into DesignCAD. It was overlaid onto the marker .dcd file, allowing
one to design a set of contacts in a .cad file for each sample.

Within the pattern files, a set of alignment markers was designed in order to align it with the previous markers. It was also given a different layer than the pattern for the contacts to specify a different method of exposure (the former along the edges to mark something, and the latter with an area dose to expose the underlying substrate.

**A.0.3 NPGS Setup**

The right-most computer (Figure A-1) was turned on (user name and password are both NPGS) or restarted if already on, in order to prevent extra bugs in the software. The computer then undergoes an automatic calibration, which can be run twice.

The NPGS program was opened, and a New Project created. Marker and pattern .dcd files, prepared using DesignCAD, were loaded via a flash memory drive and copied into the Project Files folder of the program. Each file was opened in DesignCAD and saved as a .dc2 (NPGS-compatible) file. It was also necessary to create a run file which would actually create markers and patterns.

In the case of the pattern run files, it was necessary to use one “entity for alignment and a second for the pattern-making. Each could then be given different parameters. In the Alignment entity, layers not containing alignment marks were skipped, and the same held true for the Pattern entity. It was very important that the magnification for each layer was set to be the same as that of the SEM. When finished editing, one can hit “Process Run File in order to begin writing to the chip.

Here is a listing of the important parameters and instructions for each entity, first listing those for alignment:

- Magnification = Largest possible that matches with all others
- Measured beamcurrent = 120pA
- Center-to-center distance = 40
- Linespace = 40 (This value will also adjust itself depending on other parameters)
- Dwell = 2
For the pattern entity:

- Magnification = Largest possible that matches with all others
- Measured beamcurrent = 120pA
- Center-to-center distance = 40
- Linespace = 40
- Coarse Marks Area Dose = 150
- Fine Marks Area Dose = 190

Lastly, it was important to use a specific feature of the CAD file as the origin, or \((0,0)\) point. This origin is also used by the e-beam when writing, and so it is important to center the e-beam on that same feature using the SEM stage control. However, if the area taken up by the pattern is too large, such that the e-beam’s field of view cannot reach it without moving the stage, then choosing an origin close to the center of the pattern will reduce these issues. For example, I chose a marker that was near my pattern, that would already be easily seen.

A.0.4 SEM Setup

A larger aperture increases the maximum beam current.

Parameters:

- Accelerating voltage: 10kV
- Aperture: second slot
- Spot Size: 10 when observing 39 when writing
- Working Distance: 15mm
- Magnification: x80 or x150
A specialized grabber was used to handle the circular metallic sample holder. I use a carbon tape to hold silicon chips in place onto the sample holder.

These settings corresponded to a writing beam current of 120pA.

The size of the beam current is important for determining the needed dose in writing patterns. The spotsize (which affects the beam current directly) was changed when looking at a grounded conducting surface on the sample holder far from the sample. It was adjusted until the correct current was reached.

In general the procedure for PMMA-layered samples was:

1. Log onto the CORAL CMSE reservation software to engage the SEM.
2. Vent the sample chamber.
3. Apply carbon tape to a sample holder, and firmly stick samples.
4. Record the orientation of samples on the holder.
5. Load the sample holder.

6. Evacuate the chamber.

7. Set aperture, accelerating voltage, spot size, sample holder type, working distance, sample height.

8. Turn off Scan Rotation setting

9. Focus the sample, correct astigmatism, focus again, use OL Wobbler.

10. Find correct spot size for the required beam current

11. Locate and mark locations of chip origins (rotations might be necessary to keep samples aligned as in the original optical microscope mapping)

A.0.5 Writing Pattern

The SEM controls are used to move to the correct sample location, and the NPGS controls are used to process the run file and write the pattern. Since the correct spot size must be set on the SEM before switching over control to the NPGS, it is important to turn on beam blanking beforehand, which shuts off the beam and prevents overexposure. The following is the general procedure that was followed:

1. The sample is moved using SEM controls

2. Beam blanking enabled

3. Spot size increased

4. Adjust magnification to that of NPGS run file

5. SEM-to-NPGS switch flipped

6. Process Run File on NPGS computer, while simultaneously turning off Beam Blanking
7. If there is an alignment entity, the system will pause the beam after scanning the markers and display an image of the scan, allowing one to shift the sample to better match the alignment marks.

8. After changing any necessary parameters, proceed with the pattern-writing.

9. Blank beam after completion of pattern.
Appendix B

Using and calibrating the Raman apparatus

The process of calibration was a painful one to learn, involving many small steps meant to prevent the crashing of the software. I have tried to list them below, with appropriate notes along the way.

If the laser path is not aligned, then only those that are already experienced should be allowed to adjust the optics. (Paulo Araujo and Xi Ling are two researchers who come to mind.)

1. Turn on the water cooling system (Figure B-1).

2. Turn on the 2.41eV laser by switching the key to "on", opening the shutter, and setting the power to 0.10 Watts.

3. Turn on the optical microscope’s light source. (Figure B-2)

4. Switch to the x10 objective

5. Load an unneeded silicon chip into the microscope.

6. Execute the program “Quickfix” a few times on the computer. Leave it open.

7. Open FocusTest10
Figure B-1: Water-based system used to cool laser.

Figure B-2: Optical microscope used in the Raman lab, capable of taking pictures at 10x or 100x magnification.
8. Click on "Operate" tab and switch the program to "Run" mode.

9. Open the YAWCam camera software, making sure to deny the software update. If the camera is not cooperating, turn off the computer, unplug and replug the USB camera, and turn it back on (this tends to resolve the issue).

10. Carefully push the metal sliding bar into the microscope to allow laser light to strike the sample.

11. Set “Focus” time to 500ms, and click the button so it lights up green.

12. Go into the “Settings” tab, and click “Binning”

13. Move the two horizontal bars so that they bound the top edge of the signal. Press ”Return” to reach the main menu again (do NOT make the mistake of closing the window, which may cause the software to crash).

14. Set an acquiring time to however long you wish to acquire data (such as 5s).

15. Select naphthalene as a calibration sample.

16. Remove the black card blocking the calibration samples, and physically rotate the holder until the signal is maximized on the screen.

17. At this point turn off all lights in the room and press “Calibrate”.

Figure B-3: The general layout of the Raman laboratory in 6C-048. The optics allow for different lasers to be used with minimal changes to the setup, although all but one were in repair at the time this thesis was being completed. Below (not shown) is the housing to turn on the Coherent Innova laser used in Raman spectroscopy, which has an energy of 2.33eV
18. The system will return a series of peaks, which can be matched with a sample Raman spectrum of naphthalene saved on the computer (on the right screen).

19. Fit the peaks until one obtains a low RMS error. Press “Return” to go back to the main menu.

20. Reblock the calibration samples.

After the calibration, one can load samples, physically align them so that they origin matches the origin chosen on the original optical microscope, and begin taking measurements. Once a sample was found using the camera view, one could switch from the 10x objective to the 100x objective. To ensure that the laser was focused, pull the metal rod out partway, so that some of the green laser light reaches the sample, but one can still see the flake location. By adjusting the focus, one will see a red dot, hopefully at the location of the plastic arrow taped to the computer screen. At this point the laser is properly focused, and one can push the rod in completely in order to take a measurement.

It is also important to note that the two optical microscopes that were used contained electronic stages which were differently calibrated. They measured position in different units, and defined positive “X” and “Y” differently.

Once the calibration and adjustment of coordinate system was completed, however, Raman spectroscopy tended to be extremely fast and efficient.
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