Modulation of the Raman Spectra of Graphene by the Electric Field Effect

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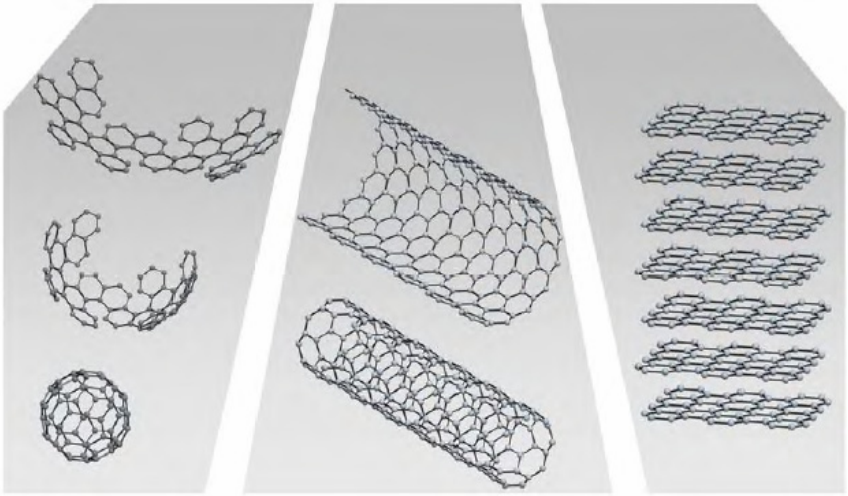
Abstract

We report success in modulating the electron-phonon interactions in graphene by means of the Electric Field Effect. There appeared a clear relationship between an applied gate voltage and both the energy and lifetime of scattered phonons in the lattice, with symmetry around the Dirac point. The data show that increased charge-carrier density results in higher-energy phonons with longer lifetimes.

Introduction

As you put pencil to paper and begin to write, you leave hundreds and thousands of graphene sheets behind. Graphene, a single atomic layer of carbon, is the building block of well-known graphite, as well as several other important structures. Stacked atop one another, these sheets become graphite. Rolled into a cylinder, a sheet is a carbon nanotube. Furled into a sphere, it becomes a buckyball.



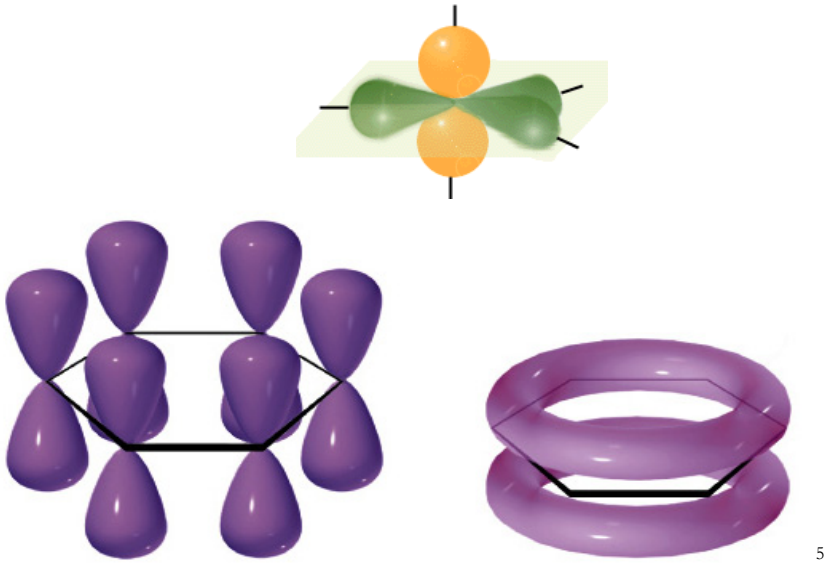
[1]

Figure 1: Graphene is the building block of buckyballs, carbon nanotubes, and graphite.

Graphene is a hexagonal lattice of carbon atoms. The four valence electrons on each carbon are distributed into an sp2 hybrid orbital, for bonding to the three other atoms, and the single remaining p orbital. This p-orbital extends perpendicularly out from the graphene sheet and forms π-bonds with the other p-orbitals on the other carbon atoms. Because this is occurring over the entirety of the graphene sheet, what results is essentially a 2-dimensional plane of charge-carriers. (See Fig. 2) It is because graphene acts almost like a 2-dimensional substance that it is so interesting. It is the first practical

[1] *The Rise of Graphene*, A.K. Geim and K.S. Novoselov

experimental stage upon which to test phenomena that have been theorized about 2-dimentional systems, such as the Klein Paradox[2] and *zitterbewegung*[3].[4]



[5]

Figure 2: An sp2 orbital, and the combination of the p_z orbitals in the lattice.

[2] The potential of particles in quantum mechanics to not be scattered by arbitrarily large barriers

[3] Jittery movements, which are proposed to occur in particles that obey the Dirac equation

[4] Geim

[5] Linus Pauling, *The Nature of the Chemical Bond*, 234-235

History

Only isolated in 2004, graphene is a relatively new material and, compared to its 'derivatives,' it is not well understood. For a long time, the existence of such 2-dimensional crystals was theorized, but it was always assumed that they would be unstable and impossible to isolate. Several reasons were given for this conclusion, the most prominent being that as the thickness of a film decreases, the possible atomic perturbations of its lattice due to thermodynamic phenomena grow relatively larger until they surpass the interatomic distances and essentially rip the film apart.[6] There had been studies on films that showed this to be essentially true – as thickness decreased, the film would break up.[7] To avoid this problem while attempting to fabricate such 2-dimensional crystals, experimenters would grow them on top of stable, 3-dimensional substrates. True isolation, they said, would be impossible.

Despite this, many people tried to isolate graphene in its own right. Common methods included chemical exfoliation and epitaxial growth. During chemical exfoliation, a sample of graphite would be intercalated to separate the layers, and then would be immersed in a chemical that would dissolve the intercalating molecules. The end result was a 'graphitic sludge' – certainly there were graphene sheets in it, but there was no way to separate them from one another. Epitaxial growth encountered similar problems, i.e. an inability to distinguish individual sheets, as well as the additional issue that the final product would be based on a metal substrate, completely invalidating any attempts to determine its conduction properties.[8]

However, despite all odds, graphene was isolated in 2004. These first graphene samples were prepared by "mechanical exfoliation" – peeling samples from a graphite crystal and then peeling thinner and thinner pieces from those samples. It is theorized that the reason these graphene sheets are not immediately torn apart by thermodynamic fluctuations is that they are

[6] Landau and Peierls, from Geim, references 11, 12, and 13
[7] Venables et al. and Evans et al., from Geim, references 15 and 16
[8] Geim

infinitesimally crumpled in the z-direction, causing them to be more stable than a simple flat sheet.[9] (See Fig 3)

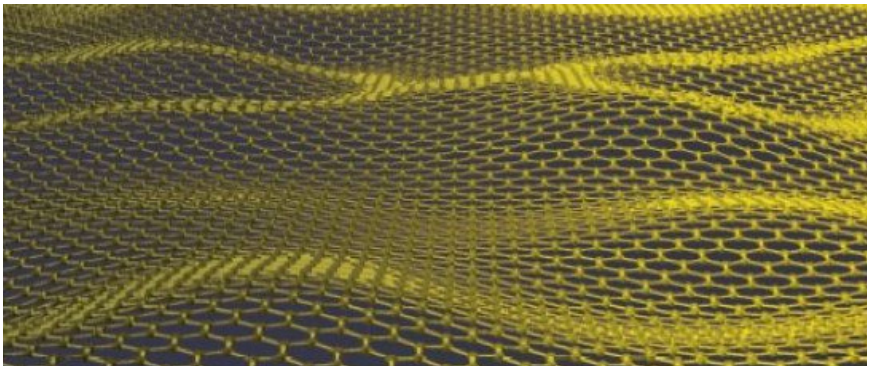


Figure 3: A potential for the solution of graphene's stability -- gentle crumpling of the sheets

Once this two-dimensional material was proven to exist by itself, it quickly became an object of great interest for scientists around the country. The number of articles containing the word *graphene* in their titles began to grow exponentially, with theoretical papers dominating over 90% of articles written. (See Fig. 4) The experimentalists, however, began trying to understand this new material they had been presented with, and were uncovering some peculiar results. The most interesting property that was uncovered and one that greatly fueled the growing interest in graphene was that it was essentially a "zero-gap semiconductor,"[10] which means there is no gap between the valence and conduction bands, making it very easy to control the conductivity using the Electric Field Effect. As tunable zero-gap semiconductors are very useful for the microchip business, graphene suddenly became an incredibly important material to understand.

[9] Ibid.
[10] Ibid.

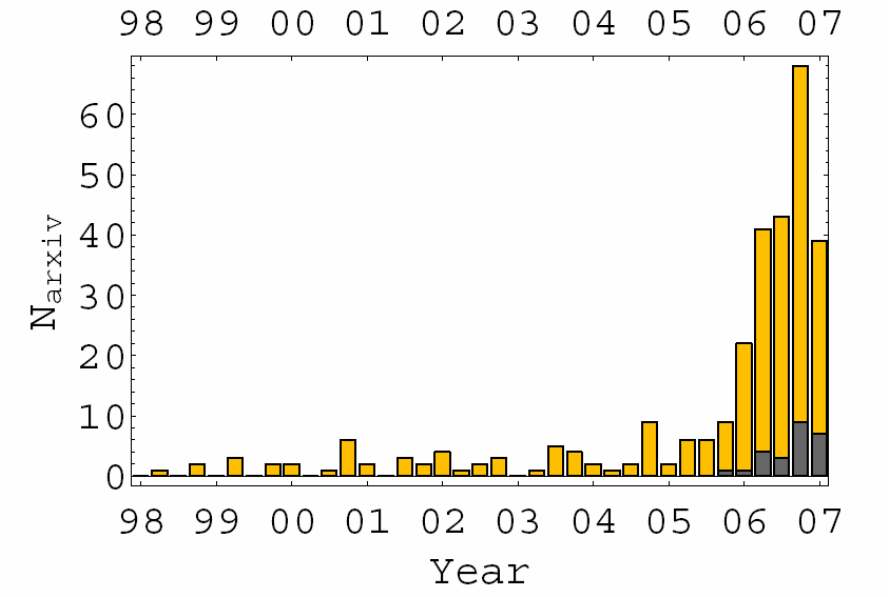


Figure 4: Number of articles in the condensed matter archive (xxx.lanl.gov/archive/cond-mat) containing the word 'graphene' in their title, by year. Yellow papers are theoretical, grey are experimental.

Fabrication

Impossible to see in a regular microscope because of its nearly-2-dimensional nature, the first samples of graphene were detected using Atomic Force Microscopy.[11] In these scans, a sheet of graphene appears as a small blip that is several Angstroms higher than the surface of the substrate, a number one can calculate from the electrostatic repulsion between graphene and the substrate atoms. (See Fig. 5) Determining the number of layers in a sample using this method can be problematic, however, because the distance at the interface between the graphene sample and the substrate can be between 0.5-1 nm, which, because the distance between two stacked sheets of graphene is usually approximately 3-4 Angstroms, can overshadow the number of layers in a sample.[12]

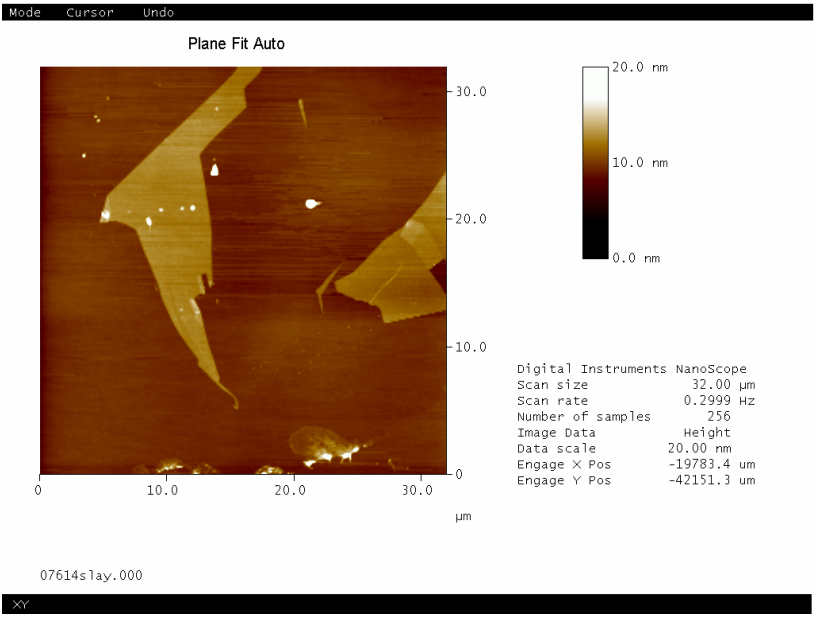


Figure 5: A graphene sample under the AFM.

[11] An Atomic Force Microscope measures the topography of a surface by means of an incredibly sharp-tipped cantilever that is affected by the forces at the surface of the material enough to give a relatively accurate picture.

[12] *Raman Spectrum of Graphene and Graphene Layers*, A.C. Ferrari, et al.

The methods of identifying graphene improved quite quickly from the original AFM detection. It was discovered that if placed on a silicon substrate with a very specific thickness of Silicon Oxide (SiO_2) in between, the graphene could be seen in an optical microscope. If the surface of the oxide on the wafer is consistent in its thickness, adding even a single atomic layer will change the thickness so that in an optical microscope, graphene shows up as a light purple/blue color. (See Fig. 6) This is because of iridescence, or the "soap-bubble effect", whereby different wavelengths of light that reflect off either the front or the back surface of a material interfere either constructively or destructively. This effectively cancels out some colors while making others more visible. A slight increase in the thickness of the substrate, in this case because of the presence of graphene, causes a different color to be most prominent. Because of the innate sensitivity of this system, the layer of silicon dioxide on top of the silicon wafer must be of a single, uniform width – the common practice is to use ~300 nm.

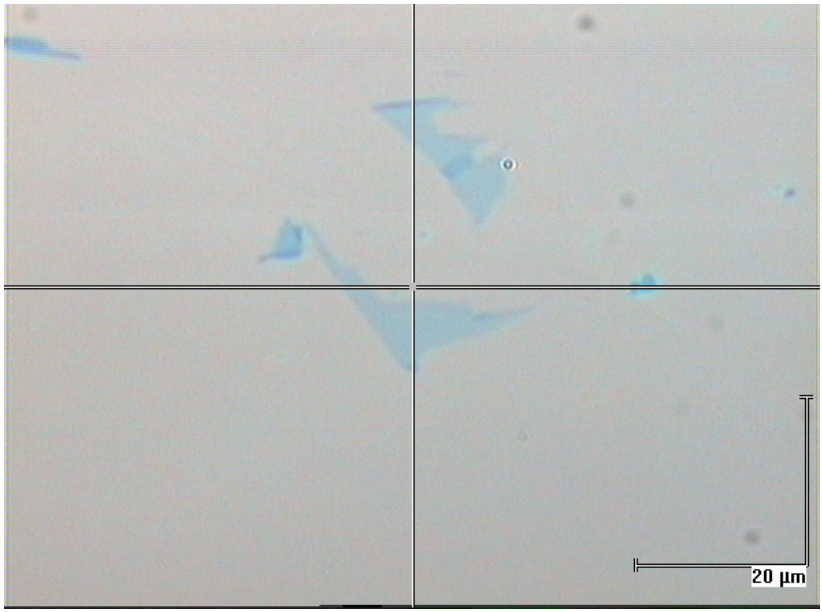


Figure 6: The same piece of graphene as Figure 5, this time as seen in an optical microscope.

Electric Properties

As graphene was discovered by a team of solid-state physicists, the first tests they ran were to determine what electrical behaviors it exhibited. The very first experimental article ever published on graphene explored the use of the Electric Field Effect (EFE) in the manipulation of graphene's conduction properties. The EFE is a process by which a material can be caused to conduct either better or worse, depending on a gate voltage that is applied. It works by forming essentially a capacitor, with the gate as one plate and the sample as the other. As more charge builds up on the gate, it induces more charge to flow in the sample. It was found that graphene is a "zero-gap semiconductor," a material that has no gap between the highest occupied level of electrons in the individual atoms (the valence band) and the level of energy necessary to dissociate the electron enough from the nucleus such that it can flow under an applied electric field (the conduction band. The lack of a gap between these two bands makes it very easy to excite electrons to a higher, conductive state by means of the EFE.[13]

The resistivity (ϱ) of graphene was measured as the gate voltage swept from negative to positive, and it was shown that at a specific voltage, it spikes sharply to several kilohms and then decreases to a few hundred in either direction of gate voltage. Looking at the conductivity ($\sigma = 1/\varrho$), it increases linearly on either side of the voltage that caused the spike in resistivity, where there is a minimum of conductivity, called the Dirac or neutrality point.[14] (See Fig. 7)

[13] *Electric Field Effect in Atomically Thin Carbon Films*, K.S. Novoselov, et al.
[14] Ibid.

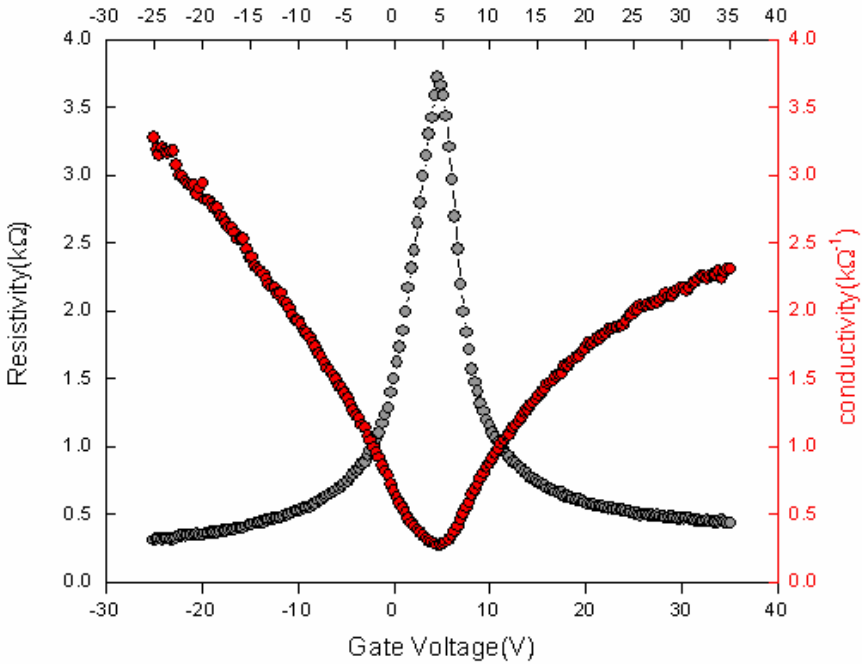


Figure 7: Graph of Conductivity and Resistivity vs. Gate voltage in graphene.

As mentioned before, graphene is a zero-gap semiconductor. Therefore, the Dirac point occurs when the highest filled energy state (the Fermi Energy) is at the very top of the valence band, i.e. there are no charge carriers free to conduct charge. This is easier to picture in reciprocal space, also called momentum-space, where the dimensions, instead of x, y, and z, are k_x, k_y, (momentum in the x and y directions, respectively) and energy. The hexagonal lattice shape and the fact that graphene is a single layer thick results in a very specific reciprocal lattice and energy spectrum. (See Fig. 8)

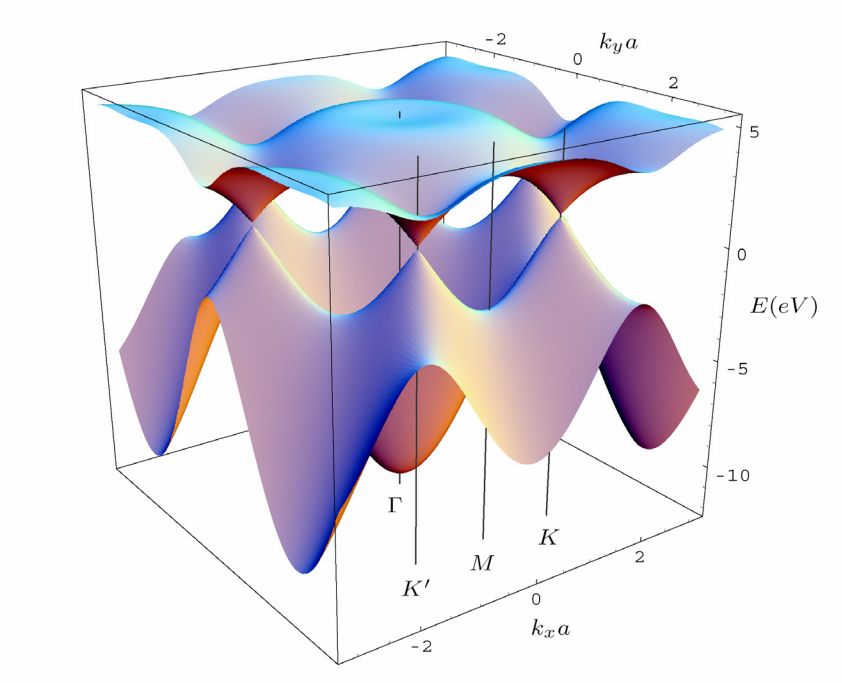


Figure 8: Graphene in reciprocal space. Each point where the lower boundary and upper boundary meet is an atom.

If one looks closely at the points corresponding to the atoms in real space, one finds that, unlike normal materials, which have an essentially quadratic relationship between energy and momentum ($k=mv$ and $E=\frac{1}{2}mv^2$), graphene has a perfectly conical spectrum. This is one the many properties that make the charge-carriers in graphene less like typical charge-carriers and more like relativistic particles, such as photons, for which energy and momentum are directly proportional. ($E=hc/\lambda$)

This cone, known as the Dirac cone, is helpful in visualizing the conduction properties of graphene. When the level of the Fermi Energy (the Fermi Level) is above the neutrality point, the sheet of graphene is conducting with electrons, and when it is below, the graphene is conducting with holes – the top and bottom cones can be seen as the conduction and valence bands respectively. (See Fig. 9)

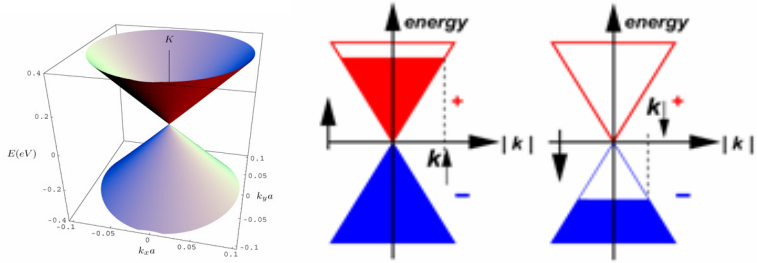


Figure 9: (left) The Dirac Cone, a close-up of the interface at the position of an atom in the lattice. This is the energy spectrum of each atom in the sheet. (right) How graphene conducts depends on the position of the Fermi Level.

Relating this back to the graphs of conductivity, on one side of the Dirac point, the graphene was conducting with holes and on the other, with electrons. It is at the Dirac point that the charge-carriers change type. Originally, the voltage at which the neutrality point occurs is a relatively high, positive voltage, which means that with no outside influence (i.e. at $V_g = 0$) graphene is a hole-conductor. However it was theorized that this was simply due to water absorbed from the air and indeed, by annealing the samples in a vacuum, it is possible to move the Dirac point to approximately 0 gate voltage. (See Fig. 7)[15]

At the neutrality point, however, the conductivity of the graphene samples did not approach zero. In fact, the minimum conductivity was approximately $4e^2/h$. This behavior can be explained by positing that graphene is a semi-conductor with small overlap between the valence and conduction bands in such a way that it can conduct with both electrons and holes at the Dirac Point. The amount of overlap between the two states was also calculated – it ranged between 4 and 20 meV for different samples. This is verified by Hall coefficient measurements that show a positive R_H growing exponentially on one side of the point and then a sharp decline at the bottom of the conductivity curve and then negative values exponentially approaching 0 on the right.[16]

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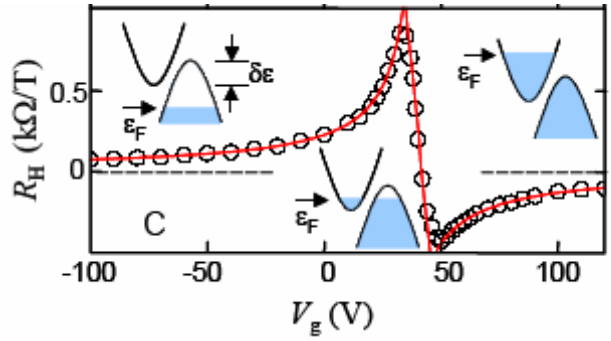
[15] Ibid.

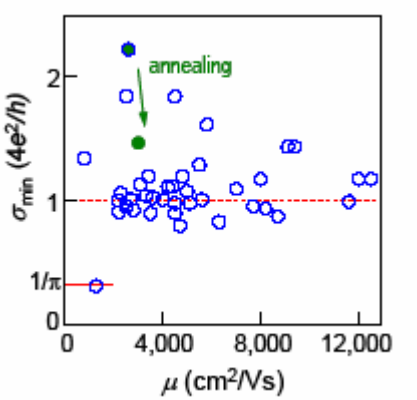
[16] The Hall coefficient is the ratio of the Hall voltage – a transverse voltage on a thin strip generated when a perpendicular magnetic field forces charge carriers to the



[17]

Figure 10: Hall resistance v. gate voltage

Strangely enough, the current theories predict that this neutrality-point-conductance should be $4e^2/h\pi$, fully $1/\pi$ of the current most-commonly observed values. This has come to be called "the mystery of the missing pie."[18]



[19]

Figure 11: Minimum conductivity measurements of different graphene samples. One sample with an anomalously large value was annealed at 400K and when tested again it's minimum had been reduced.

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sides of the strip – to the current times the magnetic field and divided by the thickness of the strip. In a semiconductor such as graphene, however, the one has to take two different charge carriers into account, and the form of the coefficient changes. For large fields, this is approximately $R_H = 1/e(p-n)$ where p and n are the concentrations of holes and electrons, respectively, and e is the electron charge.

[17] Novoselov

[18] Geim

[19] Ibid.

Though many materials before graphene have exhibited band-overlap behavior, up until this point, at low temperatures, every metallic system that has high resistivity has undergone a metal-insulator transition as concentrations approach zero. Due to weak localization, a quantum-mechanical correction to the predicted behavior of electrons[20], under these conditions, the resistivity of metallic materials vastly increases, causing them to become insulators. However, graphene showed either highly suppressed or completely absent magnetoresistance. It was theorized that this is because of tiny ripples in the graphene surface (See Fig. 3), which moves the Dirac point such that one is effectively putting the sample in a random magnetic field, but at this time there is no good way to be sure.[21]

Moving away from the Dirac point, graphene becomes as excellent conductor, for both kinds of charge-carriers. In fact, the concentrations of charge-carriers can reach as high as 10^{12}-10^{13} for reasonable gate voltages:

$$n = \frac{\varepsilon_0 \varepsilon V_g}{te}$$

ε_0 is the permittivity of free space, ε the permittivity of SiO_2, e is the charge on an electron and t is the thickness of the SiO_2 layer and Vg is the gate voltage. At a gate voltage of 100V, this gives a concentration of 7.2×10^{12}.

The mobilities (μ) of these charge-carriers, determined from magnetoresistance and EFE measurements, ranged up to approximately 15,000 cm^2/Vs at ambient conditions. [22]

[20] i.e. summing the probability amplitudes of instead of just the probabilities of their possible movements
[21] Morozov *et al.*, from Geim, reference 66
[22] Novoselov

Magnetoresistance: $\mu = \frac{R_H}{\rho}$ Electric Field Effect: $\mu = \frac{\sigma(V_g)}{en(V_g)}$

These values turned out to vary very little as a function of temperature, implying that the major limiting force for mobilities in graphene is defects in the crystal structure. Given this, it is clear that, as we are more able to produce better graphene films, these numbers will be able to drastically improve, and in fact, some experiments are now yielding mobilities of 100,000-200,000 cm^2/Vs[23] for graphene on a substrate and above that for suspended graphene.[24]

[23] *Carrier transport in 2D graphene layers*, Hwang, E. H. et al.
[24] *Ultrahigh electron mobility in suspended graphene,* Bolotin, K. I., et al.

Optical Properties

It was also noted that graphene has a very specific Raman spectroscopic signature. (See Fig. 12) Raman spectroscopy is a method used to determine certain molecular properties of a material. It is reliant on the inelastic (Raman) scattering of light. Most light scatters off a material elastically (Rayleigh scattering) such that the energy contained in each photon and therefore the frequency and wavelength, because $E = h\nu$ for light, is conserved. However, for every few million elastically scattered photons, there is approximately one that scatters inelastically due to a vibrational excitation in the material. These vibrations are called phonons and their frequency depends on the material itself.

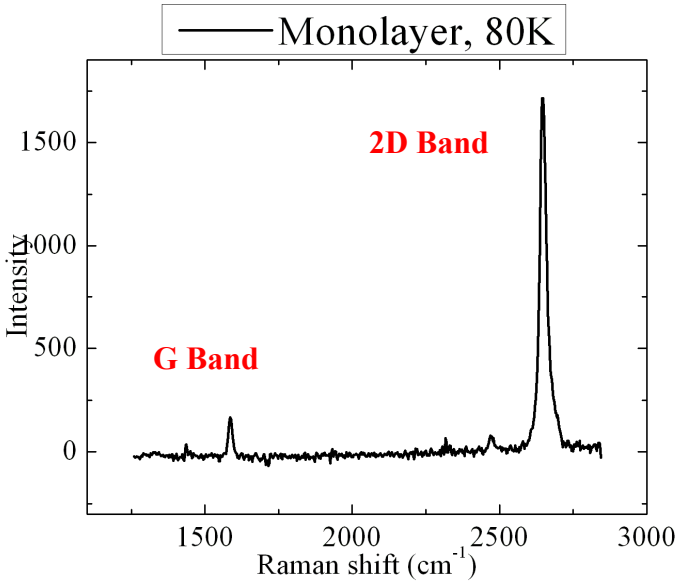

Figure 12: Typical Raman Spectrum of a Graphene monolayer.

In graphene, there are two atoms in the primitive cell.[25] These are called K and K' and alternate as one moves along the axis, i.e. all K atoms are

[25] You need two different carbon atoms to tessellate the entire sheet.

connected to only K' atoms, and all K' atoms are only connected to K atoms. (See Fig. 13) When a photon collides with an atom, it transfers its energy to an electron in the conduction band, which excites that electron up into a higher-energy state (the valence band). At some point, it will fall back down into its original state, emitting the extra energy in the form of a photon. If the electron manages to lose energy while excited usually by causing a phonon to propagate across the lattice, it will emit a photon of a different wavelength when it falls back down. This is the Raman shift.

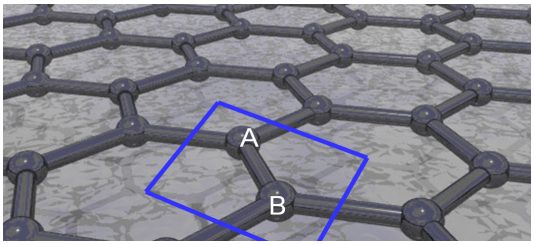

Figure 13: The primitive cell of graphene. Graphene's hexagonal lattice is actually made up of two separate sublattices, each populated solely by A (or K) or B (K') atoms.

Most Raman spectroscopy is done by reflecting a laser off the surface of a material and then collecting the scattered light and analyzing its frequency and wavelength. Experimentalists knew that graphite, the base material, had a distinctive peak at a Raman Shift of 1583 cm^{-1}, called the G-band (for Graphite), as well as several smaller peaks –most noticeable is one at ~2700 cm^{-1}, alternatively called the G' band, for being second most prominent; D' band, for being at approximately twice the energy of the D-band, a defect-induced band; or the 2D band, for the same reason as D'.

The G-band occurs when an incoming photon excites an electron to the conduction band where it scatters away a phonon and then relaxes back down, emitting a photon of a lower energy. The 2D band is a result of a photon-excited electron scattering a phonon to an adjacent lattice-point, which eventually, in order to conserve momentum, scatters a phonon back. This

phonon-scattering causes a loss of energy along the lattice, which shows up as a shift in the frequency of the finally-emitted photon.

The D-band is similar in that the original electron scatters a phonon, but a defect in the crystal lattice causes the second lattice-point to not scatter a phonon back, and the electron eventually falls back down to its original energy state in the second atom. This is why the 2D band has twice the shift of the D band – there are twice as many phonon-energy-transfers involved and therefore twice as much energy is lost. (See Fig. 12)

Given the well-known Raman properties of graphite, it wasn't long before they began to test graphene sheets for a similar peak. What they found is that the regular peak that appears in graphite (the G-peak) is noticeable smaller in graphene and the 2D-peak is far more intense, especially in single-layer graphene. As the number of layers increases, the sizes of the two bands begin to assume the proportions of those in graphite. It was noticed that the 2D peak seemed to be made of four separate waveforms that, as the number of layers increases, spread out from a common center. This gives different types of graphene – up to about tri- or quadri-layer – very specific and identifiable Raman spectra.[26] Simply taking a Raman spectrum is a much faster and has a greater throughput than AFM, which requires a great deal of time and is not necessarily conclusive, as the gap between a sheet of graphene and the substrate can vary. Suddenly, Raman spectroscopy became the best way to identify and determine the number of layers in possible graphene samples.

[26] Ferrari

Modern Methods

Despite the incredible amount of interest in it, the methods for producing graphene have hardly improved. Though it is a significant part of the research being done now, the current method is little changed from the original. In our lab, and this seems to be the favored method in most other labs, we use a sample of Highly-Ordered Pyrolytic Graphite (HOPG) and apply a length of scotch tape and then remove it, taking with the tape a certain amount of graphite. The graphite on the tape is then thinned by pressing the tape to itself repeatedly, until a sufficient thinness is reached. At this point, the tape is applied to a silicon wafer with ~300um SiO2 on top, and when it is removed, some graphene has hopefully been transferred to the wafer.

Finding the graphene, on the other hand, is rather more time-consuming. As there are yet no good automated methods for scanning the silicon wafer for possible graphene pieces, a person has to scan each wafer individually in an optical microscope, looking for the incredibly faint, blue-purple color that indicates a possible monolayer graphene sample. Then, when samples have been noted, they can be tested using Raman spectroscopy to determine what kind of graphene sample it is.

Our Experiment

The purpose of this experiment is to take Raman data of graphene at low temperatures while sweeping a back gate from a negative to a positive voltage. We should end up with a three-dimensional graph showing how the various distinctive Raman-shift spikes of graphene evolve with a changing gate voltage.

By changing the gate voltage, one changes the concentrations of charge carriers available to conduct with and therefore, the Fermi level. The height of the Fermi level affects how electrons can be excited – a photon with only enough energy to excite an electron to a state that is below the Fermi level, and therefore one that is occupied, will not be able to – and therefore the way electrons and phonons interact. This causes a change in the appearance of the Raman spectrum. Understanding the changes that occur is invaluable information when trying to understand the properties of the phonons in graphene.[27]

It is worthwhile to note that the entire process described above is that for the excitement of electrons. However, because graphene exhibits what is called the ambipolar electric field effect, it applies exactly oppositely for holes. After all, when an electron is exited, it is as if a hole is created in the valence band, which is where holes conduct. Graphene conducts identically with both electrons and holes, and therefore the two types of charge-carriers should behave similarly with respect to phonons.

[27] *Electrochemically Top Gated Graphene: Monitoring Dopants by Raman Scattering*, A. Das et al.

Procedure

The first step in any process is to find a sample of graphene. This is done just as in the Introduction, with a strip of Scotch Tape and a graphite crystal, repeatedly peeled until a sufficient thinness is acquired. The tape is then pressed to a silicon wafer with 300μm of SiO2 on top and quickly removed. This can be done on multiple samples at once, but one must be careful not to drop the wafers onto a potentially dirty surface. The samples are then loaded onto a microscope slide and examined in an optical microscope. The wafers we use are n-doped silicon to support later back gating. They also have a crosshair pattern etched into the SiO2 such that if one believes one has found a potential graphene sample of the desired thickness, one can map out its location with relative accuracy.

This is of great help in the next stage, where the wafers possibly containing graphene are tested by means of Raman spectroscopy and the pieces of 'graphene' must be located again. (When the entire wafer is approximately 1cm square and a piece of graphene can be approximately 10μm a side, it can be relatively difficult to find a piece again without use of the crosshairs. If the Raman spectrum is indicative of the type of graphene one is looking for (in fact, not all of the research is being done on monolayer graphene – bilayer graphene is nearly as popular) the sample is usually then contacted so that one may run a voltage across it.

To contact such a tiny piece of material, one first covers the entire wafer with a photoresistive chemical. This is done by putting it into a spinner, which holds it in place with a vacuum and spins it incredibly quickly (we set it at 3,000 rpm). While it is spinning, one places a drop of PMMA (Polymethyl methacrylate, also known as acrylic or Plexiglass) which spreads over the wafer due to centrifugal force. After several (approximately 30) seconds, when it has spread to an appropriate thickness, it is taken out of the spinner and baked (in a 100° oven for about five minutes) to solidify the PMMA. The photoresist is

then etched with an electron-beam microscope in the shape that you want your contact.

From there, the etched samples are placed in a thermal evaporator and coated with whatever metal has been selected to be the contact. Ideally, one wants to achieve an Ohmic contact, i.e. when one creates a circuit from the first contact, through the substrate, and into the second contact, the measured current should be directly proportional to the given voltage ($V=IR$ and $J=\sigma E$). In this case, the graph should simply be a straight line passing through the origin. After trying several different metal combinations, the best contact we found was a layer of approximately 5μm of Chromium and then a 50 μm layer of Gold. Once contacted, the samples were rinsed with Acetone which dissolved the photoresist under the metal to remove all the evaporated material except for where the contact was etched in. The graphene samples we had consistently stayed in place during the contacting process unless a sonicator was used to dissolve the photoresist, in which case the graphene would occasionally be ripped from under the contacts.

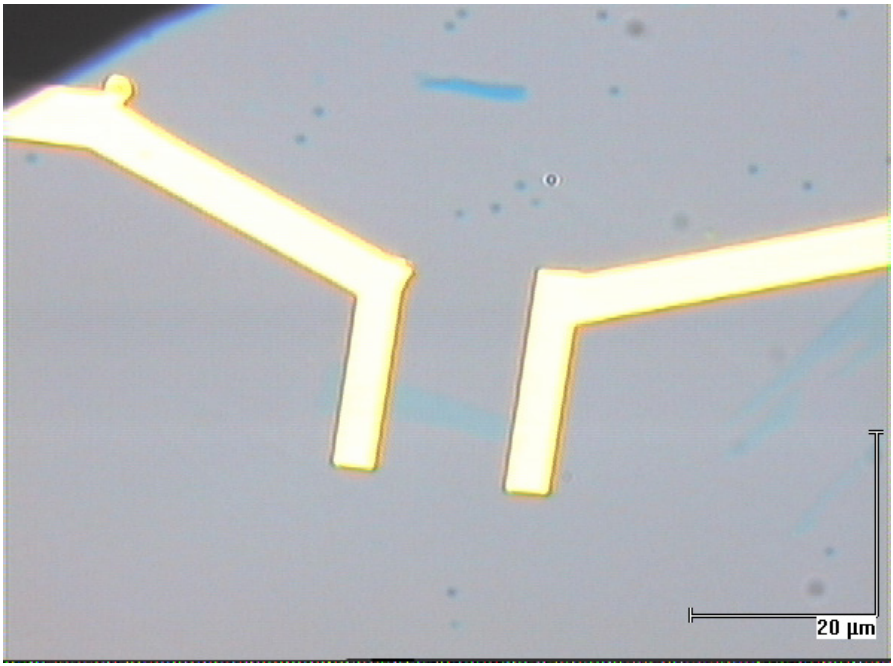

Figure 14: A contacted piece of graphene.

Also necessary is a back gate, and it is simply easier to use the silicon of the wafer as the back gate than to manufacture one. We used n-doped silicon, which is almost entirely silicon except for a few extra atoms that, taking the place of a silicon atom in the wafer, add extra available electrons to conduct. A layer of photoresist is applied to the wafer and then a pattern is etched out of it. The photoresist is then solidified and the wafer can be put into the Reactive Ion Etcher or an etching chemical to etch through the oxide layer. This is also how the crosshairs are etched in. If one uses an etcher that is part of a thermal evaporator, one can immediately plate the back contact so as to avoid any buildup of natural oxide on top of the silicon. Otherwise, one must hurry to put the samples into an evaporator and pump it down to low pressure to avoid this excess oxide. Once it has been back-contacted, the sample can be attached to a stage and the contacts) are wire-bonded using thin aluminum bonding wire to small metal plates on the stage which can be soldered to the wires that lead to the rest of the circuit.

The stage is a circular piece of oxygen-free copper, into which have been drilled holes that allow it to mount properly in the microscope. On the mount is a sample, the contacts and back gate of which are wire-bonded to a set of metal contacts (isolated from the copper). Soldered to these contacts are wires that connect back to the circuit. Also on the mount are two dissipative resistors (39Ω and 47 Ω) in parallel, attached with varnish-inundated cigarette paper (which electrically isolates the resistors, but provides an excellent thermal link) to act as heaters. There is also a Ruthenium-Oxide resistor attached with cigarette paper, which works as a thermometer (because it has regular resistance changes with regard to temperature).

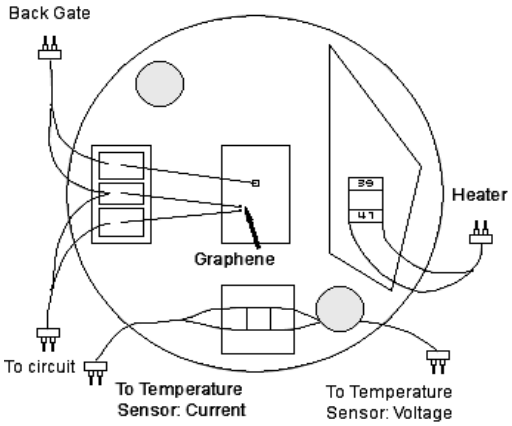

Figure 15: Our Sample Mount

Set-up

We used an Attocube Cryogenic Microscope. It is set up so that a laser, traveling down the microscope, is focused onto the sample, and the reflected light come back up, is collected through a beam-splitter by a spectrometer, and then the light is analyzed. The entire microscope is put into a cryogenic dewar which will then be filled with liquid nitrogen. The microscope is actually in an isolated chamber, so that there is no interference with the sample. Underneath the sample are three piezoelectric[28] motors to move it in the x, y, and z directions so that the correct part of the sample can be focused on.

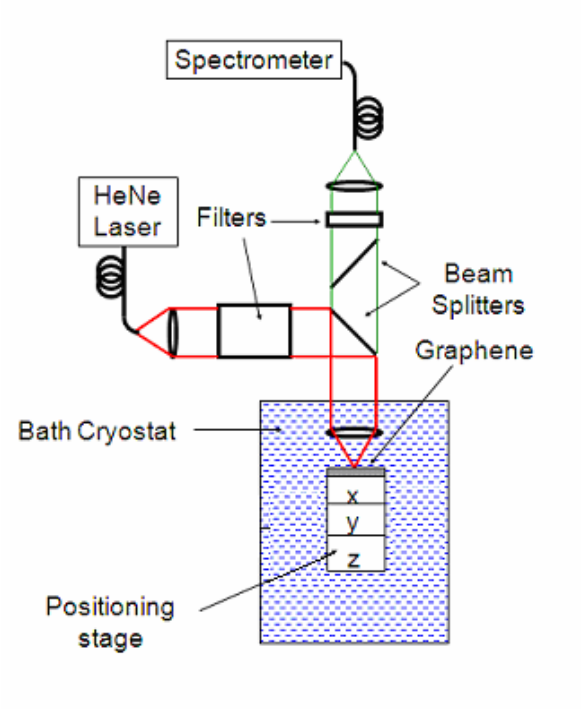

Figure 16: Our microscope set-up.

To take our Raman spectra, we used a Helium-Neon laser that outputs light of wavelength 632.8nm. The circuit is set up as in Fig. 17.

[28] Materials that produce a potential difference when put under stress or strain. This also works in the reverse, as in these motors, where an applied voltage causes movement.

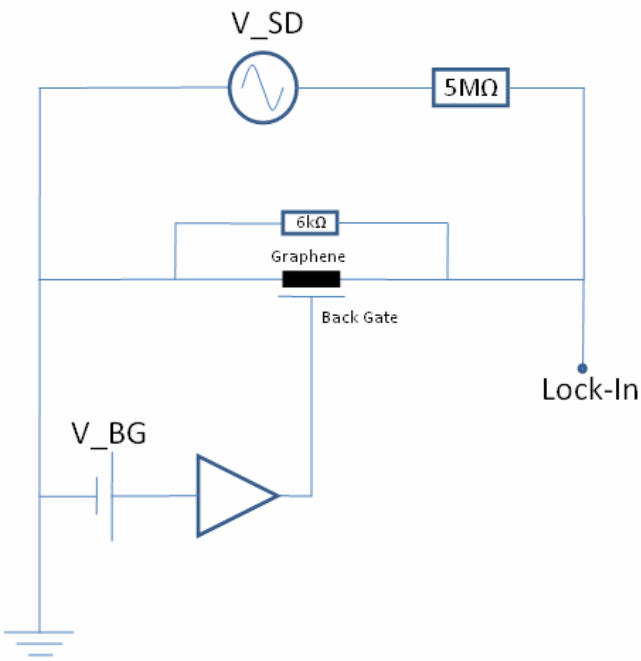

Figure 17: Our Circuit. The only important piece to this experiment is the Back Gate. The Source-Drain Voltage, Lock-In, and 5 MegaOhm resistor are for taking resistivity and conductivity curves.

Before taking spectra, the first thing we needed to do was cool down the cryostat to 77K. This is done by filling the dewar with liquid nitrogen and pumping out the thermal isolation chamber. This keeps the heat from the outside world from penetrating to the walls of the dewar. Then, after sealing the microscope into the sample chamber, we opened the valve between the vacuum of the isolation chamber and the sample chamber, and slowly brought the sample chamber to a near vacuum as well.

To create a better thermal link between the sample and the liquid nitrogen, we injected a small amount of an exchange gas – in our case, Helium – into the sample chamber. This gas would allow energy to pass more easily from the sample to the cryostat and back without the risk of residues from regular air. After this, we could begin to take spectra.

To achieve our desired results, we first took several Raman spectra of the sample while the back gate was off. Then, we incrementally increased the gate and took a spectrum each time. Each scan was run for 8 minutes.

Results and Analysis

Primary Testing

The first piece of data we looked at was the silicon line. This peak is a natural peak due to the properties of silicon. It is used to determine how well the microscope is collecting the light off the sample.

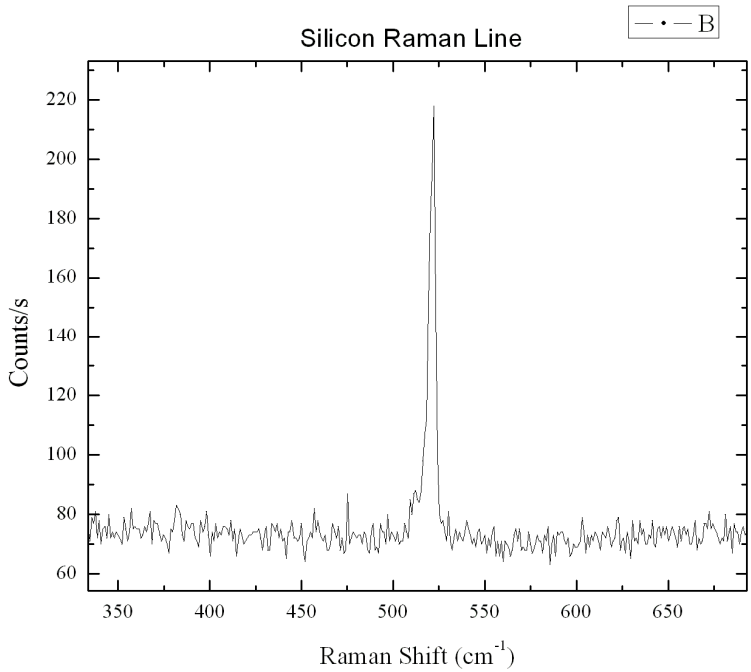

Figure 18: The Raman line of Silicon.

The units on the Y-axis of a Raman spectrum are arbitrary units, sometimes referred to as counts – the number of photons detected with this wavelength shift. As this spectrum was taken over a single-second interval, the units of the Y-axis can be classified as counts/s.

Pleased with the results of this preliminary test, we moved on to the 2D band. After aligning the microscope to collect light at the proper frequency, we took several spectra of this band:

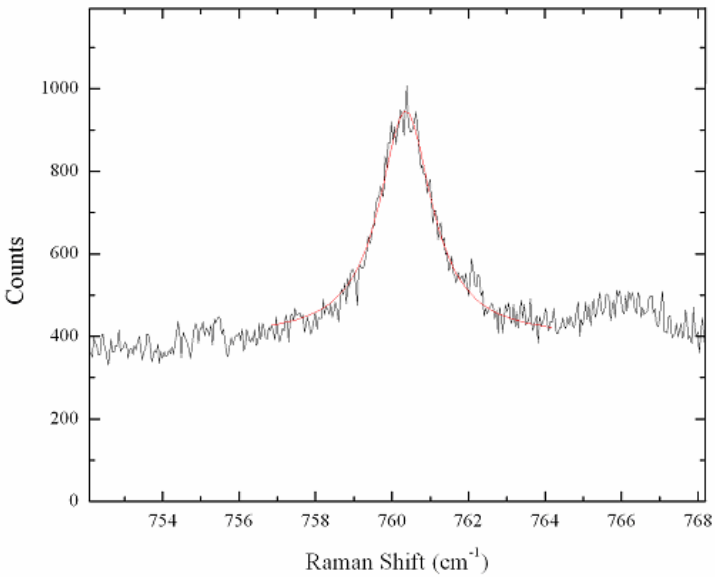

Figure 19: The 2D band in graphene. The Lorentizan function approximating its shape is shown in red.

Its smooth, symmetrical shape is indicative of a monolayer graphene sheet. Of the three bands, this is the most intense peak. It is also worthwhile to note the Lorentzian shape of the peak, as shown by the close relationship with the Lorentzian approximation.

First Attempts

After the 2D band, we realigned the microscope to look at the spectrum near 700 cm^{-1}, where the D and G bands are. After taking a few neutral spectra of these two bands (See Fig. 20), as well as a spectrum of the background silicon so that it could later be subtracted from the graphs to show just the spectrum of graphene, (See Fig. 21) we started using the gate voltage.

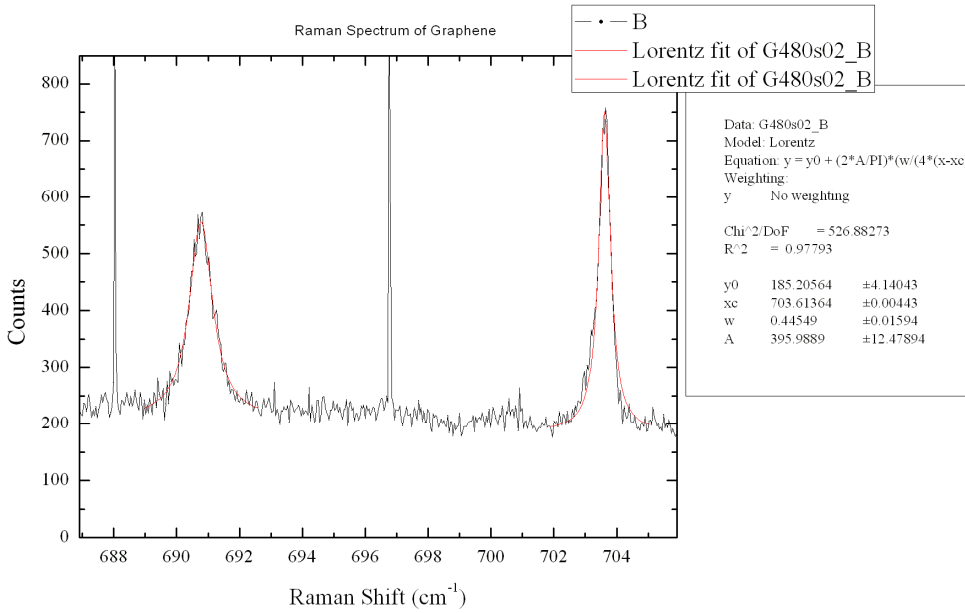

Figure 20: The D and G bands, respectively, in graphene. Both of these also have a Lorentzian shape.

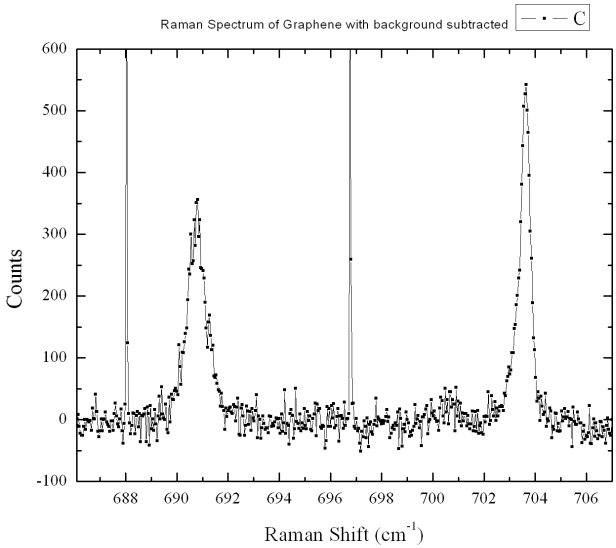

Figure 21: The D and G bands in graphene with the background spectra removed.

Strange, thin peaks appeared at random locations, but as they were by no means permanent and would disappear or move with every new scan, it is acceptable to simply call them anomalies and ignore them.

We took several scans with different gate voltages: at -60V, -20V, and +20V. Put together with the neutral sample gives us an excellent opportunity to compare them:

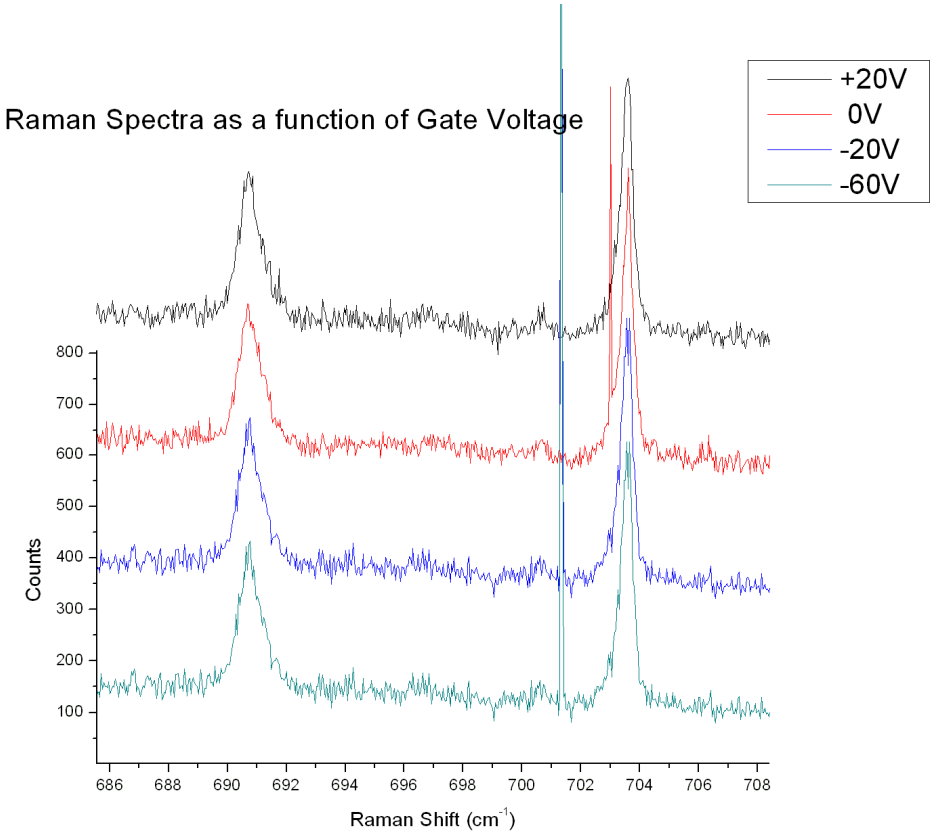

Figure 22: D and G bands of graphene at varying voltages.

The surprising result here is that nothing seems to have changed with the varying gate voltage. Though there is a documented correlation between Vg and the shape of the peaks, no such deformations to the G and D bands are seen here, even at large negative voltages.

Second Attempts

After checking the system one more time and re-running the experiment, we obtained a new set of data more consistent with prior experiments. (See Fig.'s 23-25) Here it is clear that the change in the concentrations of charge carriers is having an effect on the phonons excited by the Raman Spectra.

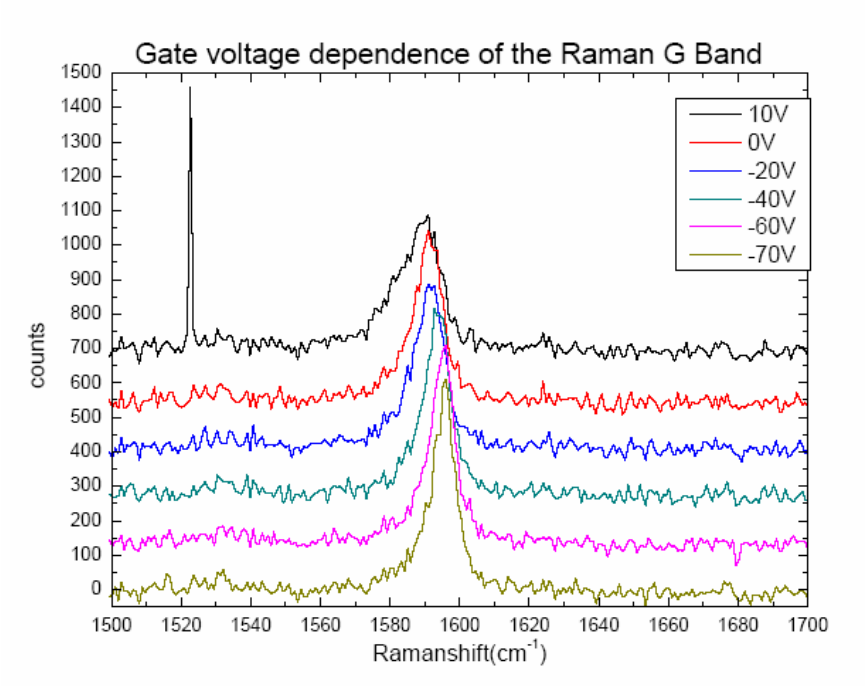

Figure 23: The changing G-band of graphene with a changing gate voltage.

To be able to quantify these results, we took measurements of the position of the peak as well as the width of the peak with respect to the gate voltage. This is simply an easier way to look at the data presented in Fig. 23:

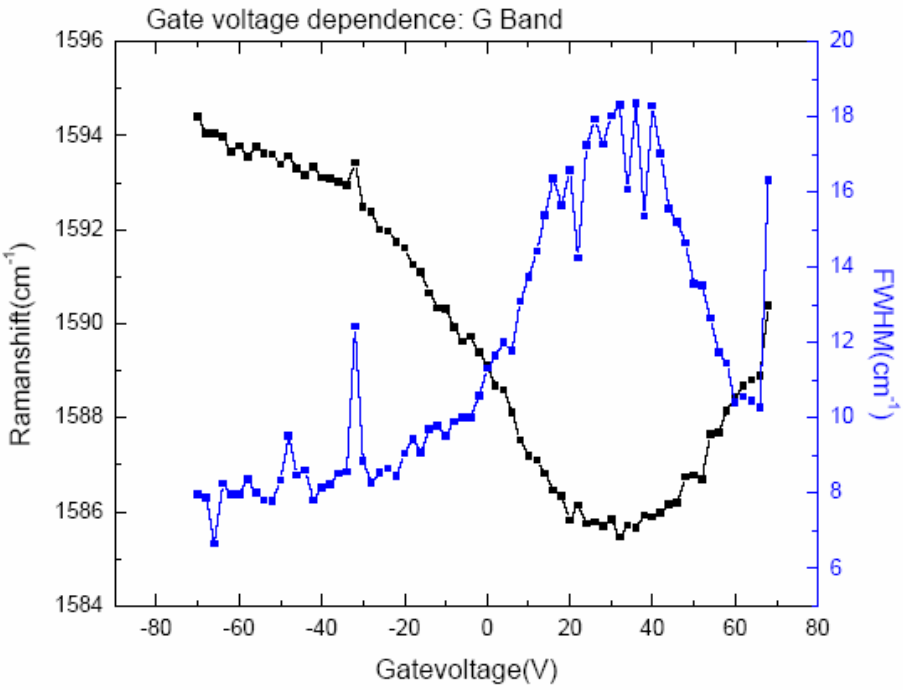

Figure 24: The Raman shift and Full Width at Half Maximum of the G band with respect to gate voltage.

We repeated this part with the 2D band, to observe the effects on this electron-phonon interaction:

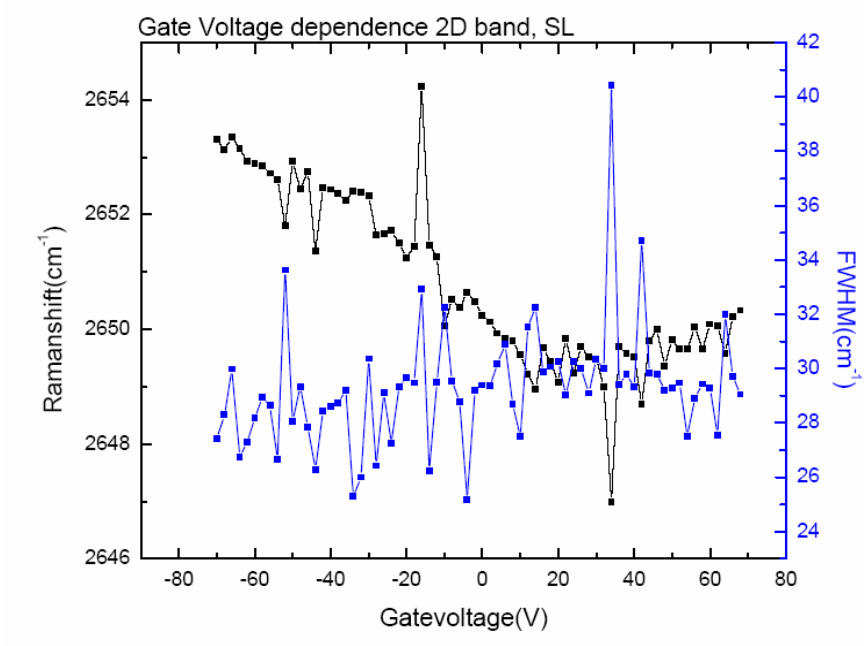

Figure 25: Raman Shift and Full Width at Half Maximum of the 2D band in graphene with respect to gate voltage.

Looking at this second set of data, one can see the obvious effect a gate voltage has on the Raman spectrum of graphene. Because applying a gate voltage causes more charge carriers to fill the conduction band, the Fermi energy increases. Looking at the Dirac cone, it is obvious to see that it will be harder for a photon to excite a photon to an unfilled location when the unfilled space is smaller and only in the higher-energy portions of the cone.

Because the Raman shift is proportional to energy change, and the width of a peak is inversely proportional to the lifetime of the phonon described therein[29], one can look at Fig.'s 24 and 25 as plotting both phonon energy and lifetime versus the gate voltage. The line of symmetry that appears in both at approximately 30V is clearly the Dirac point.

In the G band, the energy of the phonons decreases until it reaches a minimum value at the Dirac point. The FWHM, however, does exactly the

[29] *Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene*, Jun Yan, et al.

opposite, and reaches a maximum at the neutrality point. This tells us that higher concentrations of charge carriers lead to higher-frequency phonons, which is indicative of a stiffening of the lattice. It also indicates that the same relationship holds for phonon lifetime; the more charge carriers, the longer the phonon propagates.

Looking at the 2D band, we see a very similar pattern – the Raman shift reaches a minimum and the FWHM reaches a maximum at the Dirac point. This is not surprising because even though the two bands are caused by separate phonons, the relationship between charge-carrier density and electron-phonon coupling should not change.

It is interesting to see that the changes due to gate voltage in the 2D band are far less than those in the G band. This, it is theorized, is because the electron-hole transitions that occur in the 2D band – an electron being excited to the conduction band and then relaxing back down – have a higher energy than those in the G band. Therefore, it exhibits a weaker response to EFE-caused changes.[30]

[30] Ibid.

Conclusions

Although originally, we were left with a strange set of results, after a second attempt, this experiment yielded some worthwhile data. The first, anomalous results seem to have been the result of a mechanical or electric error, somewhere in the circuit. Although one tries to constantly check that all parts are working properly, it is possible that there is a break somewhere in the circuit that caused the gate to not work properly.

By looking at the second set of data, we were able to discern a relationship between the gate voltage applied and the Raman signature of graphene. It is clear that electron-phonon interactions can be influenced by charge-carrier densities, and that at low densities the lattice undergoes a certain amount of hardening. Much work still is required, but we are closer to understanding the properties graphene under the influence of the Electric Field Effect

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