Epitaxial Graphene

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Introduction to Graphene

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. The recent interest in Graphene has come from the success of attempting to grow or isolate graphene layers and the fact that we are beginning to learn more about its extraordinary electronic properties.
graphene – the wonder material

Electronic Properties
- Graphene is a gapless semiconductor exhibiting high electronic quality
- High charge carrier mobility
- Ballistic transport – no scattering; no energy loss
- Optically transparent, chemically inert and extremely conducting – used in optoelectronic devices (LCD screens)
- The electrons of graphene are massless Dirac fermions moving with speeds $10^6$ m/s
- Great tool for studying quantum electrodynamic phenomena like QHE;

Non-electronic Properties
- The thinnest and the strongest material – about 200 times stronger than steel
- Breaking strength – 40 N/m
- Thermal conductivity – 5000 W/mK
- It can be stretched elastically by about 20% (pliable) yet is brittle and breaks along lines of strain.
Future of Graphene

- Potential to replace Si in tiny integrated circuits
- Graphene based electronics - narrow graphene ribbons can be manipulated to control the band gap
- Graphene based Bio Sensors – Bio substances interacting with graphene layers cause large change in its properties
- Chemical sensing devices - quantum capacitance offers a low signal to noise ratio and allows for fine tuned resolution; doping can further lower capacitance
- OptoElectronics - optically transparent and extremely conducting and chemically inert - graphene based layers can replace ITO in LCD screens.
Growing Graphene at Gatech

Heating of 4H silicon carbide wafers in high vacuum conditions in specially designed induction furnace to drive off the silicon atoms. Both silicon and carbon terminated face used;
INSTRUMENTATION TECHNIQUES

- ATOMIC FORCE MICROSCOPY
- RAMAN SPECTROSCOPY
- ANGLE RESOLVED PHOTO EMISSION SPECTROSCOPY (ARPES)
- LOW ENERGY ELECTRON DIFFRACTION (LEED)
- QUANTUM HALL EFFECT
RAMAN SPECTROSCOPY

Raman Effect is the weak inelastic scattering of light by molecules named after the physicist Sir C.V.Raman.

C.V. Raman and K.S.Krishnan first discovered the scattering of light by molecules and Raman was awarded the Nobel Prize in 1930 for this discovery.

Raman Spectroscopy is a great tool in analyzing the Composition of matter and molecular structure. It is a non intrusive technique and though weak, powerful.
Importance of Raman Spectroscopy in Materials science

- Non destructive, fast and gives maximum structural and electronic information
- Ability to acquire vibrational data for many solids even under extreme conditions and output specific chemical identification
- Relatively easy and inexpensive to obtain raman spectrometers with the technological ease of producing laser sources
- Ability to look at and collect data for small samples of the order of micrometers
- Surface enhanced raman spectroscopy (SERS) and other techniques developed
Application of Raman Spectroscopy

Material Science- characterization of a wide variety of materials
Chemistry- Online monitoring of chemical reactions – by rapid sampling techniques, study of polymer structures
Nanotechnology- Study of carbonaceous materials – fullerenes, carbon nanotubes and graphene
Environmental Science- identification of harmful particulates in systems
Biology & Human System- study of human hair, bones and skin
Inspector Raman

- The Inspector Raman™ is a robust, portable Raman spectrometer that fits in your hand for analysis of solids, liquids, pastes, and slurries. This lightweight, dispersive spectrometer has no moving parts and may be used in any position. Raman spectroscopy offers the advantage of identifying various substances by their unique fingerprint, based on the chemical structure of the unknown, and can do so through walls of sealed bags, transparent bottles, flasks, vials, and ampoules without opening the container. Data is retrieved remotely with Bluetooth technology or USB with a laptop and NuSpec™ software. Spectral libraries are developed using DeltaNu's library development software for identification of unknown substances.

[Website Link](http://deltanu.com/inspector-raman)
Introduction to Raman Effect

Raman effect is a weak inelastic scattering process. When light falls on a substance, it interacts with the electron cloud of the molecule. The incident photon excites the electron into one of the virtual energy states created by the interaction. The electron then de-excites emitting a photon. Depending on the energy difference between the original state and the new state it returns to, the photon could either have lost or gained energy resulting in a shift in its frequency.

For the molecule to be Raman active, a change in the polarization potential of the molecule must happen on interaction with the photon and the amount of polarizability is related to the Raman scattering intensity. The Raman shift in wavelength is related to the vibrational and roational Energy levels of the sample.
Raman Scattering

When monochromatic light falls on a substance, the incident photon absorbed by the molecule can raise it to one of the virtual energy states created by the interaction of the laser with the electron cloud of the molecule. If the molecule deexcites back to the ground state, it reemits the photon of the same energy. This is completely elastic scattering involving no loss of energy and hence the scattered photon is the same frequency as the incident one. This is called as Rayleigh scattering which is what happens with most photons.

\[ h \nu = h \nu' \]
AntiStokes Region

However, a photon may cause the molecules to be excited to the virtual states and on deexcitation, the molecule can return to a lower energy level than where it started getting rid of the excess energy by giving it to the photon. The scattered photon is of greater energy and greater frequency than the incident photon and this part of the raman spectrum is referred to the antistokes region.

\[ h\nu + \Delta E = h\nu' \]
Stokes Region

The molecule on deexcitation may also return to a higher energy level that where it started, in which case it has absorbed some of the energy of the incident photon. The scattered photon hence will be of less energy and a lower frequency and this part of the raman spectrum is referred to as the Stoke’s region.

\[ h\nu - \Delta E = h\nu' \]
Raman and Infra Red

- While Raman and Infra Red spectroscopy both involve vibrational energy levels, they are governed by different selection rules.
- Infrared bands arise from an interaction between light and the oscillating dipole moment of a vibrating molecule. Raman bands arise from an oscillating induced dipole caused by light waves interacting with the polarizability ellipsoid of a vibrating molecule.
- Thus, Raman effect involves virtual energy states created by the interaction of laser with the electron and are dependent on the frequency of the laser source.
Raman Spectrometer

- Raman spectrometer uses a suitable wavelength laser as the source of photons because of their monochromatic nature and high flux and use a notch filter to cut out a narrow region centered on the laser frequency.
- The laser beam is directed to a small spot on the sample (1-100 mm dia) using the same optical microscope used for focusing and the Raman emissions from the spot are obtained.
- The emitted beam travels the same path as the visible light used for focusing; through the microscope optics into a spectrometer.
- The Raman emissions are separated from the Rayleigh component by filters or by a good spectrometer.
- Raman shifted radiation is detected with a charge-coupled device (CCD) detector, and a computer is used for data acquisition and curve fitting.

Components

- Optical confocal microscope
- Monochromator
- CCD detector
- Laser excitation source
Raman Spectrum of SiC

Intensity (a.u)

Raman shift (cm⁻¹)
Raman Spectrum of Graphene

- Raman spectrum of carbanaceous materials all show two peaks – G and D peak at 1560 and 1360 cm\(^{-1}\).
- However the position, intensity and shape of the peaks can distinguish between different types of materials like graphite, graphene, SWNT etc;
- The Raman Spectrum of graphene shows
  - G peak at 1580 cm\(^{-1}\)
  - 2D peak at 2700 cm\(^{-1}\)
Raman spectrum and graphene layers

- Monolayer graphene shows a single sharp 2d peak 4 times as intense as the G peak
- Graphene bilayers show a broader and upshifted 2D peak relative to monolayer; the 2d peak is of 4 components caused by interaction of graphene planes
- As the no. of layers increases, the 2D peak widens and G band intensity increases almost linearly with the no. of layers
- The substrate also affects the position and the intensity of the peaks.
- However, Raman spectrum also depends on Turbostraticity (rotational disorder stacking of layers)
- Doping
- Bond disorder
- Clustering of sp2 phase
- Presence of sp2 rings

The doublet structure of 2d peak can also be attributed to turbostraticity, which is generally observed with c terminated face samples.
Research Objective

- The graphitized samples show regions of contrast (refer fig) in big splotches that are spread randomly over the sample.
- The purpose of my research is to investigate what the contrast regions as seen in the optical microscope of the sample indicate and if they have any correlation to the thickness of graphene layers.
Research Objective

- The sample chosen was a patterned sample, so that region of study could be clearly identified by means of the markers. It is then possible to gather data about the same region by AFM, Raman and from the optical microscope and compare them.

- The patterning on the sample consists of five by five grid markers (refer fig) with spacing between the markers to be roughly about 50 micrometer. There were four such grids in the four corners and were identified by larger markers surrounding them.
Questions

- Do darker regions correspond to deeper regions in the sample?
- Can the contrast be explained in terms of the no. of graphene layers and hence the transparency of the sample at that point?
- Is the contrast just due to the topographical variations in the sample / thickness of substrate and hence the transparency?
- The Raman spectrum for graphene does show variations with difference in the no. of layers and literature studies reveal that it is possible to confirm the no. of layers from the Raman spectrum. However, in most cases the substrate has a contrast spectrum and is not Si C which is also transparent; this poses a problem.
- Raman spectrum signature also changes with doping – what sort of dopants could one expect in Si C and what are their characteristic Raman signatures?
- Do flakes or layers of graphene remain the same across the pleats developed as graphene flakes are formed?
- How can the average height or height of a region as measured from AFM images give an idea of the no. of graphene layers in the sample?
- Can the effects of substrate dopant effects be nullified by subtracting the Si C spectrum of the same wafer sample and studying the resulting graphene spectrum?
The plan- step 1

• Identify regions of striking contrast in the sample by using the optical microscope in the Raman Spectrometer.
• Catalogue them by using the pattern markers.
• Collect Raman data for the identified regions of interest.
• Collect AFM data for the same regions of interest.
• Analyze and interpret both data to see if a meaningful conclusion can be arrived at.
Comparing optical image with the AFM image- the contrast features on the optical image are outlined on the AFM image too. The optical contrast correlates well with the height variation. 24c1-2,3,31

Ref: topright 2-4.ngc
Ref: 061600ca-cb
AFM image analysis- tr3_4

- The AFM image shows the same contrast as the optical image from Raman.
- Mean height in the lighter region: 110 nm
- Mean height in the smaller darker regions: 106 nm
- Height difference in the contrast regions: about 3 to 4 nm

There is a definite change in the intensity of the G peak between the lighter and darker regions. G peak drops in intensity in the lighter region. Small changes in the shape of the 2D peak. The color map seems to correlate well with the contrast in the afm image and the optical image.
AFM image lr1_1

Lower right grid 1_1  
Ref: 0624014e-4f.hdf

zoom in on contrast region  
06240150-51.hdf

zoom in on splotch  
06240152-53.hdf

Observations: Inside the splotch, lot of pleats were observed. Pleats are roughly 4 nm high. The height difference across the edges of the splotchy region is roughly about 4 – 5 nm.
Top left 4_4

Ref : 06140056-57.hdf

06140058-59.hdf

Height difference across the edges of contrast : 5-8 nm
Height difference across the hexagon : 5-9 nm
Sides of hexagon about 1600 nm
Pleats inside hexagon : about 4 nm height ; seem to be raised higher than the outside
# Raman spectrum tl4_4 (24c_33)

<table>
<thead>
<tr>
<th>Inside hexagon</th>
<th>Outside hexagon</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>High G peak; (6000-9000) 1D sometimes noticed and sometimes not; 2D peak is wide and less intense (1500)</td>
<td>G peak is sometimes low (4000) and sometimes high 1D is absent for the most part 2D is sometimes sharp and high (3500-5500) Sometimes wide and low (1500)</td>
<td>Right side of the splotch shows sharp 2D peak and low G peak</td>
</tr>
<tr>
<td>AFM</td>
<td>Optical</td>
<td>Raman</td>
</tr>
<tr>
<td>----------------------------</td>
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<td>---------------------</td>
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<tr>
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<td>Topleft 2_4.ngv</td>
<td>24c1_28</td>
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<td>96-97;( zoom)</td>
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<td>edge)</td>
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<tr>
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<td>zoom)</td>
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<td>51.hdf; 06240152-53.hdf;</td>
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<td>22bn_2.ngc</td>
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Step-1: Observations

• Analyzing the AFM images and comparing with the optical, I found that the dark regions correspond to deeper features on the surface in general.

• I looked to see if there was a significant change in height between contrast regions and it did not turn out to be consistent or anything that I understood as significant.

• There were usually pleats in the splotchy regions of the sample
Step-2:

Raman data for contrast regions

Identified the contrast regions and collected Raman data for different contrast points on the sample.
Corrected the spectrum with the SiC background spectrum to isolate the spectrum of graphene;
Obtained measurements of the Gpeak intensity, 2D peak intensity, position and bandwidth.
Analyzed the data to form histograms for the darker and lighter regions to look for trends.
Step-3 comparing xps and optical image

Obtained the images of xps from Jeremy and compared it with the corresponding Optical image. Looked for matching contrast patterns with the patterns for carbon and oxygen from the xps images and could not find any correlation between the two.

Had efm images taken on the same region of the sample by John to look for any patterns /changes involving local fields or electron charge and could not find anything significant.

Obtained the Raman data for random points in the same region, however could not find anything significant to correlate with the presence of oxygen.
Step- 4

- Obtained a thicker sample (24AE- thickness 12.271 Å) and recorded the Raman spectrum of contrast regions.

Collected the data for the Gpeak intensity and the 2D peak intensity, position and bandwidth and analyzed the data in histograms.

Have the graphene layers etched off on one half of the sample by the graphene team and then record the Raman spectrum after etching (to be completed...)
Conclusions

- The darker regions are certainly deeper, however the difference in height between contrast regions seem to be more related to the surface features than to the thickness of graphene.
- The contrast cannot be just due to the difference in thickness of graphene and more experimentation needs to be done to find out
Future work

- Perform SKPM scanning Kelvin probe microscopy to determine work function changes on patterned samples and then analyze the Raman data for the same regions.
- Obtain samples which have been characterized in terms of graphene layers by other instrumentation techniques and obtain the Raman data and correlate the two.
- Obtain a sample of larger thickness and obtain Raman data focusing on different depths including the interface to see if there are any changes at the same point.
Lesson Plan - Polarization

Key Concepts:

Nature of electromagnetic waves
Polarization of Transverse waves
Polarization by reflection – Brewster’s law
Testing Polarized light
Malus Law
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