Metrology for Emerging Materials, Devices, and Structures: Graphene as an Example

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Outline

• Characterization and Metrology
• Physical Properties of Graphene
• Optical Microscopy
• LEEM
• LEED
• HR-TEM
• Electrical Characterization
• Overriding Themes
Characterization and Metrology: Themes

• Nano-Scale and Quantum Phenomena

• Familiar Methods show a “new light”

• New Methods always help

• Advancements still Required
Properties of Graphene

• High Mobility
  ~ 100,000 cm$^2$/V sec (few degrees Kevin)
  ~ 10,000 cm$^2$/V sec (room temperature)

• Can carry high current density

• Robust Material
Graphene Band Structure

A. \( \pi \)-orbital formation from two \( p \)-orbitals

B. Formation of \( \sigma \)- and \( \pi \)-molecular orbitals from two \( sp^2 \) hybridized carbon atoms

\( \pi \) state at \( K \)

\( \pi \) bond and \( \pi^* \) anti-orbitals

www.cem.msu.edu/~reusch/VirtualText/intro3.htm
Graphene Electrical Properties

• Semiconductors
  – Parabolic Dispersion of Energy vs momentum
  
  \[ E = \frac{\hbar^2 k^2}{2m} \]
  
  \[ m^* = \frac{\hbar^2}{(d^2 E/d^2 k)} \]
  
  – Effective Mass defined by change of E vs k

• Graphene
  – Linear Dispersion of energy levels vs momentum (wave vector k)

  \[ E^{\pm}(\delta k) \approx \pm (\sqrt{3} a/2) \gamma_0 || \delta k || \]

  \[ v_F = \sqrt{3} a \gamma_0 / 2\hbar = \frac{3}{2} a_{cc} \gamma_0 / \hbar \]

  \[ E = h c \]

  – light-like linear electronic band dispersion implies massless particles

  – Particles called Dirac Fermions

See p 684 Charlier et al
Graphene

Sources of Graphene

Exfoliation – Scotch tape & graphite

Reaction of SiC(0001)

Other

Bernal Stacking vs Misorientation

Single Layer Properties for misoriented (AA’)
No-Dirac Fermions for 2 to 4 layer Bernal

Inter-layer spacin 3.33 Å for B and
3.42 Å for turbostratic stacked bi-layer

Other mis-orientations possible

Latil, Meunier, and Henrard, PRB 76, 201402_R (2007)
Optical Microscopy
The magic 300 nm SiO₂ substrate

Graphene is modeled as a 0.34 nm thick graphite layer.

Graphite refractive index constant
Between 400 nm to 750 nm

\[ n = 2.6 - i \times 1.3 \]

Contrast dependence is a result of wavelength dependence of SiO₂ reflectivity

SiO₂ reflectivity function of SiO₂ thickness

Nano Scale Optical Properties

Optical Properties of Graphene defined solely by the Fine Structure Constant

- Dynamic Conductivity, $G = \frac{e^2}{4h}$, of Dirac Fermions

- Fine Structure Constant $\alpha = \frac{e^2}{hc} \approx 1/137$

- $T \equiv \left(1 + 2\pi G/c\right)^{-2} = \left(1 + \frac{1}{2} \pi \alpha\right)^{-2}$

- $R \equiv \frac{1}{4} \pi^2 \alpha^2 T$

Nair et al, Manchester group in Science 320, (2008), 1308
Remember Surface Analysis Methods - LEEM

Monolayer Sensitivity

Figure 1: Schematic illustration of LEEM optics.

Figures from J. Thorp /UVa, R. Hull (INDEX)/RPI, R. Tromp /IBM
LEEM analysis of Multilayer Graphene

Electron reflectivity from graphene on SiC(0001) shows quantized oscillations due to quantum well (QW) resonances.

Figure courtesy H. Hibino: Phys. Rev. B. 77, (2008), 075413.
Remember Surface Analysis Methods - LEED

Low Energy Electron Diffraction

Si (111) 7 x7 reconstruction

NIST Surface Science Database & www.cem.msu.edu/~cem924sg/

cnse.albany.edu
LEED Analysis of Graphene

2 (a-d) Graphite, trilayer, bilayer, and monolayer graphene LEED patterns at 42 eV, respectively.
### LEED Analysis of Corrugation of Graphene

| Thickness (ML) | $\Delta k_{||}$ (Å$^{-1}$) | $\Delta \theta_{norm}$ (deg) |
|---------------|----------------|--------------------------|
| 1             | 0.70           | 6.1                      |
| 2             | 0.28           | 2.4                      |
| 3             | 0.20           | 1.7                      |
Remember Surface Analysis Methods – (AR)XPS

- ARXPS maps VB structure
- Bands not described by simple tight binding model
- Quasiparticles observed – e.g., electrons surrounded by phonons
- Potassium Doping opens band gap
- May explain impact of substrate on graphene electrical properties

cnse.albany.edu
Raman of Graphene

See for example: Ni Raman spectroscopy and imaging of graphene
Raman of Graphene
The molecular picture

D band attributed to the breathing modes of sp2-bonded atoms in rings

Benzene
Breathing Mode
Graphene’s Phonon Dispersion

2D band is at ~2700 cm\(^{-1}\) due to a 2 phonon double resonant process involving \(\pi\) band

Wave vector \(K = 0\) Zone Center
Raman 2D Band Sensitive to # graphene layers

Figure Courtesy Robert Geer CNSE (INDEX)
Raman:: Defects & Stacking Configuration

Electron irradiation induced defect density

$L^{-1}$ proportional to Ratio of the intensities of G band to D band

Geer Group unpublished

NanoCharacterization of Nanotubes

Aberration Corrected HR-TEM Imaging

Not Corrected

Heavy atom (Iodine) atomic columns are imaged

Focal Series Corrected

Both K and I atomic columns are imaged

Multi-Slice Simulations of Graphene Stacking

*\( C_5 = 5 \text{mm}, 0.15 \text{ Convergence angle} \)

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Carbon Nanofilm

Horiuchi, et al.

Trilayer Graphene at 80kV, 0 \( C_s \)

F. Nelson (INDEX) this conference
Aberration Corrected TEM
First Images of Single Layer Graphene showing atomic structure

Simulated HR TEM Image at 300 keV with Cs = 0

TEAM TEM  80 keV Cs = -17 um

Figure Courtesy C. Kisielowski - Nano Lett.8, (2008), 3582–3586
Observation of Corrugation: TEM Nano-Diffraction

Length ~ 25 nm

Height ~ 1 nm

2009 – Aberration Corrected TEM of Stacking 2 – Layers with 30° Misorientation

Warner, et. al. (Briggs), Nano Letters (2009), 102
Hall Measurements

Carrier Sheet Density

\[ N_S = \frac{IB}{q|V_H|} \]

Determine the sheet resistance \( R_S \) using a van der Paw test structure

Mobility

\[ \mu = \frac{|V_H|}{R_S IB} = \frac{1}{qN_SR_S} \]

Quantum Hall Effect

\[ \sigma = v \frac{e^2}{h} \quad \text{conductivity} \]

where \( v \) is either an integer or rational fraction
Graphene Mobility Data

Suspended graphene sheet
Red is after annealing


Quantum Hall Effect

- In a Magnetic Field the Electrons have circular cyclotron orbits
  \[ \omega_C = \frac{eB}{mc} \]

- When orbits are treated QM they have discrete energy levels
  - Landau Levels \[ E_n = \frac{h}{2\pi} \omega_C (n+1/2) \]

- At certain values of field, energy levels are filled up to \( N \) and there is no electron scattering

- Conductivity \( \sigma \) will have discrete steps \( g_s e^2/h \) where \( g_s \) is the degeneracy factor (spin & sublevels)
  \[ \sigma \sim N \frac{e^2}{h} \]

\[ J_x \text{ (Hall current)} = \sigma_{xy} E_y \quad J_y \text{ (current)} = \sigma_{yy} E_y \]
Quantum Hall Effect in Graphene $\sigma \sim (n+1/2)e^2/h$

Stormer and Kim - QHE proves Dirac nature of carriers

Berry Phase – angle of vector quantities in closed loop path

http://www.mi.infm.it/manini/berryphase.html
Nanoscale Quantum Phenomena

The Berry Phase (angle) in Graphene confirms Dirac particle

- At low magnetic fields, Shubnikov de Hass oscillations in the resistance $R_{xx}$ perpendicular to current flow.

$$\Delta R_{xx} = A \cos[2\pi(B_F/B + \frac{1}{2} + \beta)]$$

- $\beta$ (Berry Phase) = $\frac{1}{2}$ for Dirac particles

- $B_F$ is frequency SdH oscillations

- $B$ is magnetic field strength

Berry Phase, $\beta$, refers to correction to semiclassical dynamics – not needed when a full QM theory is used.

Single Electron Microscopy
Electron Hole Puddles – Are they due to Graphene Corrugation from SiO$_2$?

The intrinsic disorder length scale in graphene is $\sim$ 30 nm.

“The SET tip is capable of measuring the local electrostatic potential with microvolt sensitivity and a high spatial resolution close to its size.”

Observation of Graphene Corrugation by STM

Corrugation has a height variation of 5°Å over an area of 30 × 30 nm².

Lateral extent of these corrugations ~ few nanometers

Corrugation mimics the SiO₂ surface

Deshpande, Bao, Miao, Lau, and LeRoy, Spatially resolved spectroscopy of monolayer graphene on SiO₂
STM Observation of Stacking Misorientation

Latil, Meunier, and Henrard, PRB 76, 201402_R (2007)
3 layer graphene on SiC
Graphene Ribbons
Can We Measure properties of Ribbons?

Fig. 6. GNR edges. (a) Zigzag edge, (b) armchair edge

Han, et al (Kim’s Group), PRL 98, 206805 (2007)
What we can Measure

• Where graphene is (for some samples)

• Number of graphene layers & orientation

• Corrugation

• Electrical – mobility, carrier density, conductance
Conclusions

• Graphene displays novel properties due to nanoscale dimensions and unique electronic structure

• Metrology must continue to advance to meet needs of new materials such as graphene

• Despite these advances- metrology and device fabrication are amazingly difficult
Acknowledgements

• Florence Nelson and Tianhao Zhang

• Christian Kisielowski

• Theme VI team
  – Ray Ashouri, Karl Berggren, Robert Geer, Julia Greer, Tony Heinz, Robert Hull, Philip Kim, Charlie Marcus

• NRI – NERC – INDEX Funding