Carbon Nanomaterials Research at UVa

I. Core Capabilities

II. Nanotubes

III. Endohedral magnetofullerenes

IV. Future Directions
Electron Beam Lithography (~80 nm)

UV-vis-IR Micro-Raman Spectroscopy

Atomic Force Microscopy

Optical Cryostat

…plus CVD nanotube growth, general wafer processing (UVML), and numerous light sources…
Core experimental collaborations…

• Oak Ridge CNMS (high-res Raman etc.)

• VT Chemistry (magnetofullerenes)

• Luna Corp. (193 nm superlenses; trimetaspheres)

• NIST & Argonne (growth of epitaxial graphene; IETS)
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Quick Review of Single-walled Carbon Nanotubes…

- Electronic structure closely related to that of graphene.

- Tight-binding: consider only nearest-neighbor wavefunction overlap.

- Let $\gamma_0$ be the overlap integral between the neighboring atoms
  
  $\rightarrow$ 2D dispersion of graphene$^\dagger$:

$$E(k_x,k_y) = \pm \gamma_0 \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

References

$^\dagger$ P.R. Wallace, Phys. Rev. Lett. 71(9) 622-634, 1947
SWNT as molecular interconnects:

- Cylindrical boundary conditions define a tube:
  \[ C = n a_1 + m a_2 \]

- Chiral indices \((n,m)\) determine the band structure\(^\dagger\):

  \[ |n-m| = 0, 3, 6, \ldots, \text{ metallic}; \]
  
  otherwise \(\text{ semiconducting}.\)

(valid for all but the smallest diameter nanotubes)

Nanotube Resonant Raman

Raman intensity (arbitrary units)

Frequency (cm\(^{-1}\))

Energy (eV)

Science 275 (1997)
Nanotube-based FETs...

- Channel = semiconducting nanotube
- FETs can also be gated by a local wire or by a liquid
- Smallest tubeFET ~100 nm (gap between source and drain)
- Top-down FET logic gates have been made

Tube-FET Logic (Bachtold, Delft)
Room-temp. SETs also possible...

(Postma, Delft)
Chemical Vapour Deposition Growth of Nanotubes

Si/SiO\textsubscript{x} substrate with catalyst

Furnace ~1000°C

Ar, H\textsubscript{2}, CH\textsubscript{4}

Catalyst deposition

Nanotube growth

SEM

E-beam lithography

Transport, Raman etc.

N.b. one of the ‘hands on’ labs for my PHYS 582 nano class...
Catalyst deposition
Nanotube growth
SEM
E-beam lithography
Transport, Raman etc.
Reversal of current blockade in nanotube-based FETs through multiple trap correlations ... at room temperature

- Chan et al. PRB (2009)
Reversal of current blockade in nanotube-based FETs through multiple trap correlations

Stochastic switching between two levels....

... RTS amplitude reaches 80% of current, at room temperature!
Reversal of current blockade in nanotube-based FETs through multiple trap correlations

“trap juggling”
Reversal of current blockade in nanotube-based FETs through multiple trap correlations

Key points:

• Observed in long-channel nanotube FETs

• unprecedentedly high amplitude, at room temperature

• multiple traps with correlated electrostatics

• 1D channel \( \rightarrow \) very sensitive to gate, thus can resolve closely adjacent traps

...and noisy current through nanotubes isn't so unusual; why?
Nanotube transport:

- 1D, ballistic conductance observed
- 2 transport channels
- Contacts are important!

**Metallic SWNT**†: Ti contacts

\[ G \approx 2G_0 \]

**Semiconductors**‡: Pd contacts

\[ G \approx 0.5G_0 \]

\[ G = \frac{2e^2}{h} \sum_{i} T_i = \frac{4e^2}{h} \]

Nanotube transport:

- 1D Tomonaga/Luttinger\(^\dagger\) liquid behavior is anticipated:

\[
G \propto T^\alpha \\
\rho(E) \propto |E|^\alpha
\]

- Observations of LL behavior in SWNT:

  Bockrath, transport studies:
  \[\alpha \sim 0.3\]

  Yao & Postma, intramolecular junction:
  \[g \sim 0.22\]

  Ishii, photoemission studies, on Au:
  \[g \sim 0.18\]

\[\begin{align*}
\alpha_{\text{end}} &= (g^{-1} - 1) / 4 \\
\alpha_{\text{bulk}} &= (g^{-1} + g - 2) / 8 \\
0 &\leq g \leq 1
\end{align*}\]

\[g = 1\] for zero long-range Coulomb interaction (non-correlated electrons)

\[g < 1\] for long-range, repulsive Coulomb interactions

References

EBL with in situ transport measurement...

...and attach gas cylinders to vent chamber to O$_2$, H$_2$, etc.

...this allows us to write *across* contacted nanotubes and look for current noise generated by surface charging and/or beam damage...
...a portion of the tube channel is exposed to e-beam after the FET device is completed...
Recall scatter / backscatter / proximity issues with e-beam lithography:

Recall scatter / backscatter / proximity issues with e-beam lithography:
(responsible for ‘undercut’ seen in resist)

Recall scatter / backscatter / proximity issues with e-beam lithography:

From Casino, 30kV
exposure with positive back gate

exposure without gate

vacuum / pristine

exposure with negative backgate

-Chan, JCP (2009)
Transport after exposure with ...+ gate  ...- gate  ...+ gate  ...- gate  ...+ gate  ...- gate  ...+ gate...
Raman disorder band reveals beam damage to the nanotube...

- Raman spectra of CNTs irradiated by e-beam with different doses
- D-band is induced by e-beam
- Electron energy =15 kV; beam current = 200 pA

(N.b. data vertically offset)
...persistent noise induced by e-beam exposure....
Key points:

- possible to sever tubes with fairly low energy e-beam

- charge trapping observed → two-state current flicker

- substrate charging may contribute overall shift in ambipolar curve; this effect is related to backgate bias during exposure

- fine-scale writing of traps and tunnel barriers may be possible; multiply-segmented tubes currently being explored
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UVa, 22 October 2009
Magneto-Raman Apparatus (completed Fall 2009)

Sample in cryo
Previous work: Modified Optical Cryostat (10.2 – 300 K)
Susceptibility data shows inflection in Gd$_3$N@C$_{80}$

-Measured in Despina Louca’s lab at UVa
Optical cryostat delivered Fall ’09…

… permits micro-Raman + transport in a B-field at ~2K
… DARPA subcontract via Luna Corp.
C\textsubscript{80} Cage Modes

Squashing $H_g(1) 227 \text{ cm}^{-1}$

Twist $H_g(2) 355 \text{ cm}^{-1}$

Breathing $A_g(1) 430 \text{ cm}^{-1}$

Pentagon Breathing $A_g(2) 1471 \text{ cm}^{-1}$

Pentagon Distortion $H_g(8) 1517 \text{ cm}^{-1}$
Gd$_3$N Modes

Scissor 94.8 cm$^{-1}$

Wagging 511.5 cm$^{-1}$

Breathing 112.1 cm$^{-1}$

Asymmetric Stretch 747.8 cm$^{-1}$
Gd$_3$N@C$_{80}$ Modes

Gd–cage 141.7 cm$^{-1}$ (Exp 165.2 cm$^{-1}$)

H$_g$(1) 217.9 cm$^{-1}$ (Exp 234.5 cm$^{-1}$)

H$_g$(2) 370.7 cm$^{-1}$ (Exp 361.3 cm$^{-1}$)

A$_g$(1) 428.5 cm$^{-1}$ (Exp 430.4 cm$^{-1}$)
Raman Spectra of Gd$_3$N@C$_{80}$ (CNMS)

- **90 K**
  - Wavenumber (cm$^{-1}$): 165.2, 155, 148.4, 141.4, 100, 91.5, 83.6, 81.2, 76, 57, 52.6, 44.6
  - Intensity (a.u.)

- **300 K**
  - Wavenumber (cm$^{-1}$): 165, 77, 54, 34
  - Intensity (a.u.)

M. Krause et al, Angew. Chem. 44, 1557 (2005)
Analysis of low-energy Raman lines of Gd₃N@C₂ⁿ (40 ≤ n ≤ 44) taken at 90 K indicating a hindered rotation due to the coupling of the core complex to the cage.
Mode Comparison: $Y_3/Gd_3N@C_{80}$ (90 K)

Comparison of $Y_3N@C_{88}$ and $Gd_3N@C_{88}$ Raman data taken at 90 K. Analysis of the data identifies $C_{88}$ cage modes, hindered rotation modes and center of mass modes. Prominent peak correlations are denoted by dashed lines.
IETS of Gd$_3$N@C$_{80}$ (90 K)

IETS: no symmetry selection rules

Experimental IETS spectrum obtained for Gd$_3$N@C$_{80}$ with modulation amplitude $V_\omega = 4$ mV, scan rate = 1.5 mV/s and time constant = 1 s. The anti-symmetric Gd–N stretch mode is identified at 81.6 mV (658 cm$^{-1}$) as well as Raman C$_{80}$ cage modes at 155.1 mV (1251 cm$^{-1}$) and 187.5 mV (1512 cm$^{-1}$).
Kondo Scattering in Gd$_3$N@C$_{80}$?

$\Gamma \sim 12$ meV

$T_K \sim 70$ K

Experimental conductance data of Kondo effect and zero-bias anomaly in Gd$_3$N@C$_{80}$ taken at 4.2 K. Inset shows the experimental setup: Au crossed-wire apparatus forms a junction with the Gd$_3$N@C$_{80}$ thin film.
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Graphite edge decoration with cationic nanoparticles…
Graphite edge decoration with nanoparticles...
Nanoparticle enhanced Raman Spectrum...

Normal Raman spectrum of HOPG

Raman spectrum of HOPG with Ag
(514.5 nm excitation)
Same samples- different points…
E-beam writing on epi-graphene + transport…

… I/V and Hall measurements in preparation; collab with Lloyd Harriott’s group.
E-beam writing on epi-graphene + transport…

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N.b. Seminar next Thursday by Brian Leroy…
ABSTRACT:

Combining scanning probe microscopy with electrical transport measurements is a powerful approach to probe low-dimensional systems. The local information provided by scanning probe microscopy is invaluable for studying effects such as electron-electron interactions and scattering. Using this approach, we have probed the local electronic properties of mono- and bilayer graphene with atomic resolution. We studied the effect of ripples, charged impurities and defects on the local density of states. We find that long-range scattering from ripples and impurities shifts the Dirac point leading to electron and hole puddles. Short-range scattering from lattice defects mixes the two sublattices of graphene and tends to be strongly suppressed away from the Fermi energy. In addition, in bilayer graphene we observe an opening of a band gap due to the application of a transverse electric field.
Artificial Cilia for the Investigation of Cell Cooperativity in Wound Healing*

Keith Williams  Physics
Brian Helmke  Biomedical Engineering
Mool Gupta  Electrical & Computer Engineering
Kurt Kolasinski  Chemistry, West Chester University

Undergrad currently working on this project: Aagya Mathur

*Work seeded in Fall 2008 by NanoSTAR
Nanopillars fabricated in the group of co-PI Gupta (UVa).
Current group:

Drs. Brian Burke (graduating Fall ‘09)
Drs. Jack Chan (graduating Spring ‘10)
Drs. Caixia Bu
Drs. Nattawut (a.k.a. Tom) Anuniwat
Kridsanaphong (a.k.a. Tor) Limtragool
Aagya Mathur

Collaborations:

Avik Ghosh (UVa, ECE, theory)
Lloyd Harriott (UVa, ECE, graphene device fab)
Giovanni Zangari (UVa, graphene electrochem)
Harry Dorn (VT, endofullerenes)
Kurt Gaskill (NRL, epi graphene)
Nathan Guisinger (Argonne, epi-graphene)
James Kushmerick (NIST, IETS on fullerenes)
David Geoghegan (Oak Ridge CNMS, high-res, low freq. Raman)
Luna Corp. Blacksburg and Danville (193nm superlens; magneto-Raman)

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