Electron Transport in Molecules, Nanotubes and Graphene

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Rolling Up Graphene: Periodic Boundary Condition

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<th>Allowed states</th>
<th>Metallic nanotube</th>
<th>Semiconducting nanotube</th>
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Periodic Boundary Condition

\[ C_h \cdot \vec{k}_{\perp} = 2\pi q \]

E(k_{2D})

\[ + \text{ band} \]
\[ - \text{ band} \]
Tuning Carrier Density by Electric Field Effect

Atomic force microscope image of nanotube device

Metallic nanotube

Semiconducting nanotube

Induced charge: \( C_g V_g = e n = e (\text{D.O.S}) \Delta E_F \)
Electrical Transport in Nanotube Devices

Metallic nanotube

- $V_{sd} = 10$ mV

- $I$ (nA) vs. $V_g$ (V)

Semiconducting nanotube

- $V_{sd} = 10$ mV

- $I$ (nA) vs. $V_g$ (V) with ON and OFF states

- $E_F$, $k_{1D}$, $E_F^*$,
Controlled Growth of Ultralong Nanotubes

**Figure 3.** SEM and TEM images of ultralong MWNTs. (a) Schematic representation for the diameter-dependent stabilization of reaction gas flows. By inserting the smaller tube inside the outer chamber, microscopic turbulent flows can be stabilized into laminar flows with lower Reynolds numbers. (b) SEM image of MWNTs, which are several centimeters long. Scale bar, 2mm. (c) A SEM image of MWNTs grown across a 100 μm slit. Scale bar, 20μm. D, HRTEM images showing single, double, triple, and multi-walled CNTs. Scale bars, 5 nm.

Extraction of Inner Shells from MWNTs

AFM manipulation of long MWNTs

Hong, et al, PNAS (2005)
Intershell and Intrashell Nanotube Devices

Hong, et al, PNAS (2005)
Extremely Long SWNT Field Effect Transistor

FET characteristics

\[ V_{sd} = 20 \text{ V} \]

\[ I_{sd} (\text{nA}) \]

\[ V_g (\text{V}) \]

\[ \rho \sim 10^{-7} \, \Omega \cdot \text{m} \]
Electron Transport in Long Single Walled Nanotubes

Multi-terminal Device with Pd contact

* Scaling behavior of resistance: 
  \[ R(L) \]

Ballistic Transport and Mean Free Path

Electron Transport in 1D Channel

Diffusive transport: \( l_e \ll L \)

\[ R(L) = \rho L \]

Ballistic transport: \( L < l_e \)

\[ R(L) = \frac{h}{Ne^2} = R_Q \]

Resistance of \( N \)-1D Channel:

\[ R(L) = \frac{h}{Ne^2} + \frac{h}{Ne^2} \frac{L}{l_e} \]

For a nanotube, \( N = 4 \) (2 from spin and 2 from \( K \) and \( K' \))
Electron Mean Free Path of Nanotube

\[ R(L) = R_c + \frac{h}{4e^2} + \frac{h}{4e^2 l_e} \]

\[ \frac{h}{4e^2} = 6.45 \text{ k}\Omega \]

Non-ideal contact resistance \( R_c < 2 \text{ k}\Omega \)

\( l_e \sim 0.5 \mu\text{m} @ \text{RT} !! \)
Extremely Long Mean Free Path: Hidden Symmetry?

Carbon nanotube:
\[ l_e \sim 10 \, \mu m \text{ @ } 1.6 \, K \]
\[ l_e \sim 0.5 \, \mu m \text{ @ } 300 \, K \]

Ga[Al]As HEMT:
\[ l_e \sim 100 \, \mu m \text{ @ } 1.6 \, K \]
\[ l_e \sim 0.06 \, \mu m \text{ @ } 300 \, K \]

• Small momentum transfer backward scattering must be inefficient.

Selection rules by hidden symmetry in graphene?

T. Ando, JPSJ (1998); McEuen at al, PRL (1999)
Electric Field Effect in Mesoscopic Graphite

Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices

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(Received 31 August 2004; accepted 11 December 2004; published online 7 February 2005)

FIG. 1. (a) Scanning electron microscopic image of an HOPG crystallite mounted on a microcantilever. Inset: bulk HOPG surface patterned by masked anisotropic oxygen plasma etching. (b) Schematic drawing of the nanodrilling process. (c) Thin graphite samples cleared onto the SiO$_2$/Si substrate. (d) A typical mesoscopic device fabricated from a cleared graphite sample.

PRL 94, 176803 (2005)

Electric Field Modulation of Galvanomagnetic Properties of Mesoscopic Graphite

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(Received 31 August 2004; published 3 May 2005)
Electric Field Effect in Atomically Thin Carbon Films


We describe monocrystalline graphitic films, which are atomically thin but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conduction bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to $10^{13}$ per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nonconventional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (1) and carbon nanotubes (2). It has long been tempting to extend the use of the field effect to metals [e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies than traditional semiconducting devices (3)]. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances (<1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable (>%1) field effect (4).

We report the observation of the electric field effect in a naturally dimensional (2D) material: few-layer graphene (FLG), name given to a single layer densely packed into a beaker, and is widely used to test the limits of many carbon-based materials, for example, carbon nanotubes, amorphous graphene sheets rolled up into cylinders (5-7). Planar graphene has been shown to exist in its unstable state with respect to curved structures such as so-called nanotubes (5-7).

Using Scotch Tape is Essential!!
A Few Layer Graphene on SiO$_2$/Si Substrate

Optical microscope images

AFM Image

1.2 nm
0.4 nm
0.8 nm

20 \mu m

1 \mu m
Transport Single Layer Graphene

Field Effect Resistance

\[ R_{xx}(\Omega) \approx \frac{h}{4e^2} \]

Zhang, Tan, Stormer & Kim (2005), see also Novoselov et al (2005).
Graphene: Dirac Particles in 2D Box

Band structure of graphene

Massless Dirac Particles with effective speed of light $v_F$. 

$E \approx \hbar v_F |\vec{k}'_\perp|$
Graphene v.s. Conventional 2D Electron System

**Band structures**

**Conventional 2D Electron System**

\[ E = \frac{\hbar^2 k_x^2}{2m_e} \]

\[ E = -\frac{\hbar^2 k_y^2}{2|m_h^*|} \]

**Graphene**

- Zero band mass
- Strict electron hole symmetry
- Electron hole degeneracy

\[ E = \hbar v_F |k'_\perp| \]

\[ N_{2D}(E) \]

\[ m_e^* \]

\[ m_h^* \]

\[ \sim \frac{\hbar}{4e^2} \]

\[ < 1 \text{ nm} \]

\[ 10 \text{ nm} \]

\[ R_x (\Omega) \]

\[ V_g (V) \]
2D Gas in Quantum Limit: Conventional Case

Density of States

Landau Levels in Magnetic Field

\[ \hbar \omega_c = \hbar eB / m^* \]

Graphene

- Vanishing carrier mass near Dirac point
- Strict electron hole symmetry
- Electron hole degeneracy

\[ \omega_c = \frac{eB}{m^*} \]
Quantum Hall Effect in Graphene

Quantization:

\[ R_{xy}^{-1} = 4 \left( n + \frac{1}{2} \right) \frac{e^2}{h} \]

\[ T = 1.5K, B = 9T \]
Relativistic Landau Level and Half Integer QHE

Haldane, PRL (1988)

\[ E_n = \pm \sqrt{2e\hbar v_F^2 |n| B} \]

Landau Level Degeneracy
\[ g_s = 4 \]
2 for spin and 2 for sublattice

Quantized Condition
\[ R_{xy}^{-1} = \pm g_s \left( n + \frac{1}{2} \right) \frac{e^2}{h} \]
\[ \nu = \pm g_s \left( n + 1/2 \right) \]

Quantum Hall Effect in Graphene

\[ T = 1.7 \, \text{K} \]
\[ B = 9 \, \text{T} \]

Mobility
\[ \sim 60,000 \, \text{cm}^2/\text{V} \, \text{s} \]
Nanotube Electrodes for Molecular Electronics

- Nanotubes are inherently small, yet compatible to microfabrication processes
- Covalent chemistry between electrode and molecules
- Potentially good conduction via $\pi$-bonding network
Nanotube Nanogaps

Narrow (<10nm) trench via e-beam lithography
Thin PMMA coating

Oxygen Plasma etching creates gaps (0-10 nm) in tubes.
Cut ends likely to be carboxyl-terminated

Hone, Wind, Nuckolls, and Kim Collaboration
Nanotube Nanogaps

Process are optimized to Yield of cut tubes: 25% of ~2600 devices

Columbia NSEC (Hone, Wind, Nuckolls, and Kim) Collaboration
Molecular Bridges

- Self-assembled
- Covalently bonded
- Conduction through $\pi$-back bone

Bis-oxazole

Does It Work?

~ 10-15% of reconnection out of ~ 100 fully cut tubes

Semiconducting Nanotube + Molecular Bridge

Metallic Nanotube + Molecular Bridge

Vsd = 50 mV
Control Experiments

* Pyridine + EDCI without molecules  No connection

* Bis-oxazole without amines  No connection

* Bis-oxazole with Monoamine  No connection

* 1,12 dodecane diamine (insulator)  No connection
Oligoaniline: PH sensing

[Diagram showing chemical structures and pH sensing mechanism]

B.

- High conductance
- Low conductance

C.

- Graph showing switching cycles between pH 3 and 11
Transport Measurement

Bis-oxazole + metallic SWNT

\[
\begin{align*}
I \text{ (nA)} & \quad V_{sd} \text{ (mV)} \\
-100 & \quad -50 \\
0 & \quad 250 \text{ K} \\
50 & \quad 180 \text{ K} \\
100 & \quad 120 \text{ K} \\
-100 & \quad 50 \text{ K} \\
0 & \quad 10 \text{ K} \\
50 & \quad 1.6 \text{ K}
\end{align*}
\]
Temperature Dependence Transport Spectroscopy

$\frac{dI}{dV} (10^{-8} S)$

$V_{sd} \text{ (mV)}$

$S_{01} (10^{-8} S)$

$V_{sd} \text{ (mV)}$
Gate Voltage Dependence

\[ \frac{dI}{dV} (\mu \text{S}) \]

\[ V_g (\text{V}) \]

\[ V_{sd} (\text{mV}) \]

\[ \frac{dI}{dV_{sd}} (\mu \text{S}) \]
Summary

• Transport in long nanotubes:
  Subshell extraction in MWNTs
  Extremely long mean-free path in SWNTs

• Transport in graphene:
  Unusual quantum Hall effect
  Graphene nano ribbon devices
  Gate dependent Raman spectroscopy

• Nanotube electrode for
  single molecular electronics
Acknowledgement

Special Thanks to:
Yuanbo Zhang
Meninder Purewal
Byung Hee Hong
Josh Small
Melinda Han
Barbaros Oezyilmaz

Collaboration:
Stormer, Pinczuk, Heinz,
Nuckolls, Brus, Flynne, Hone,

Funding: NSF, NYSTAR, DARPA, Office of Naval Research, Samsung