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**Fourth Stig Lundqvist Conference on
Advancing Frontiers of Condensed Matter Physics**

3 - 7 July 2006

**Electron transport in molecules,
nanotubes and graphene**

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These are preliminary lecture notes, intended only for distribution to participants

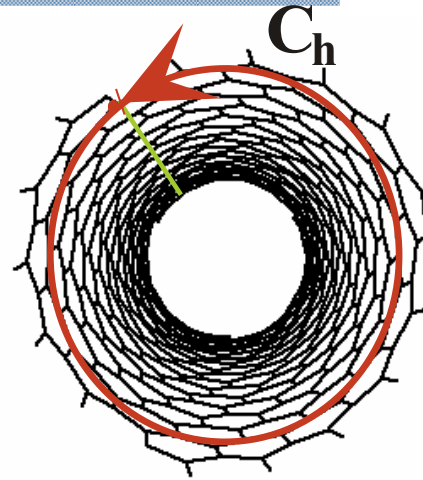
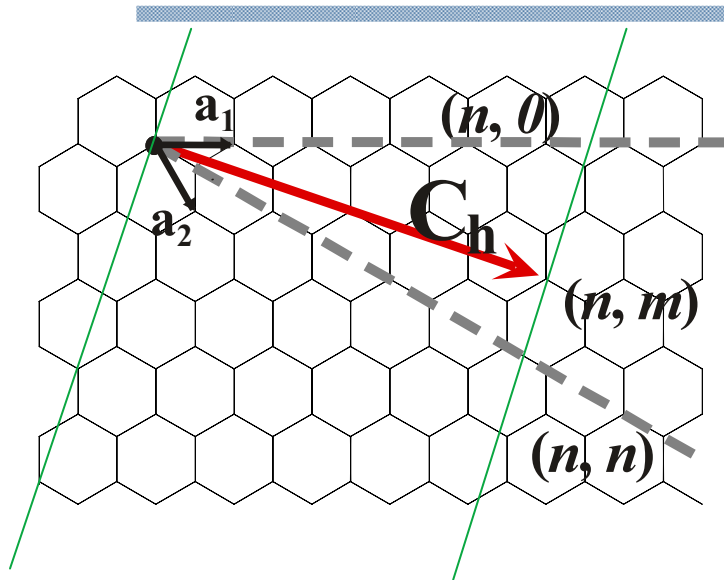
Electron Transport in Molecules, Nanotubes and Graphene

Philip Kim

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Columbia University**

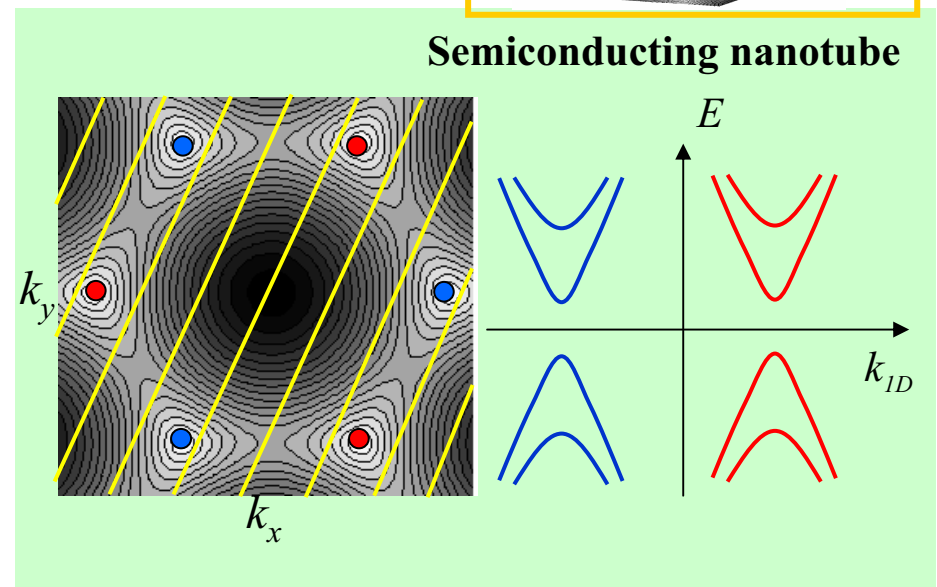
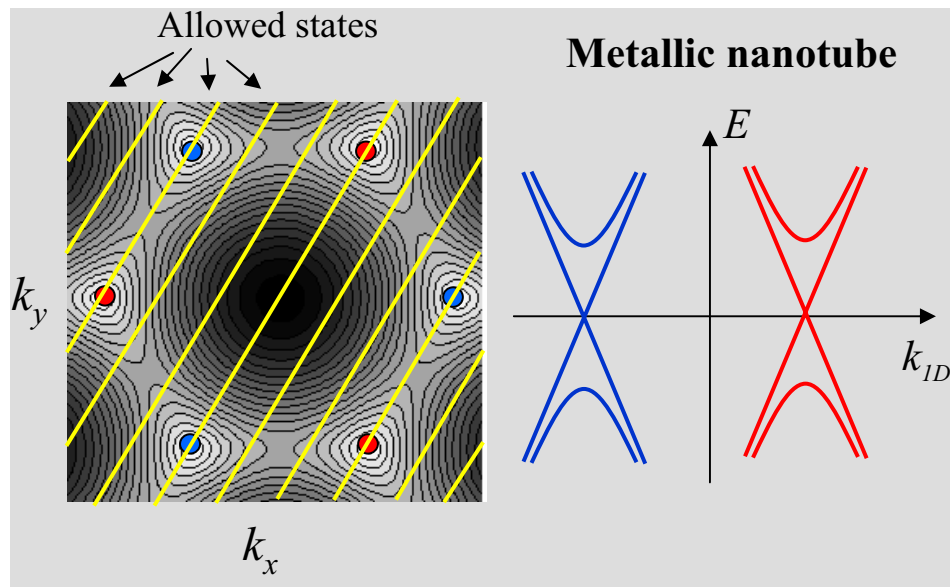
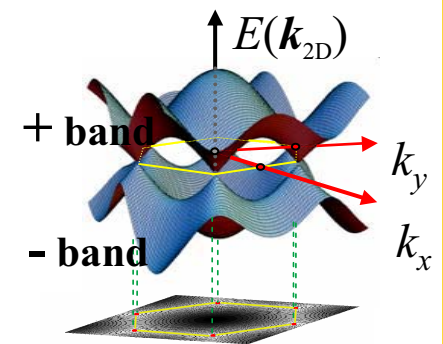


Rolling Up Graphene: Periodic Boundary Condition



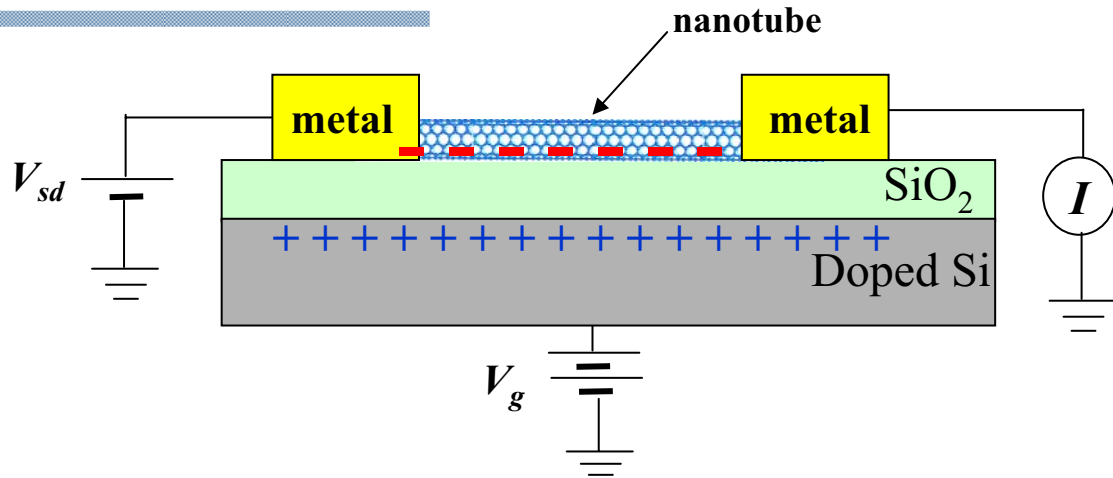
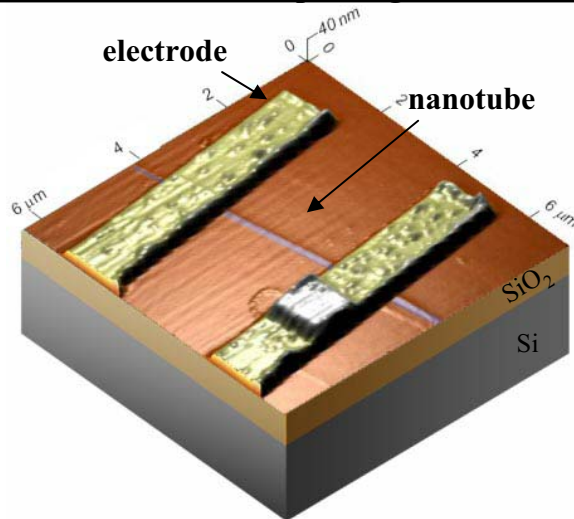
Periodic Boundary Condition

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



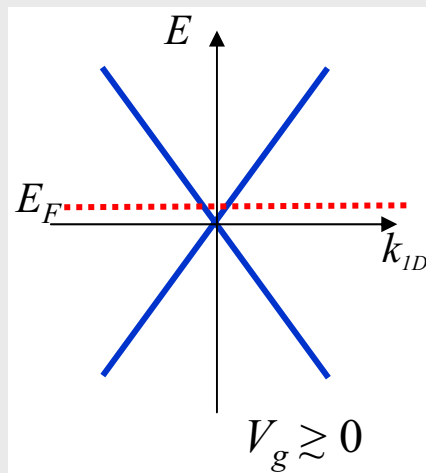
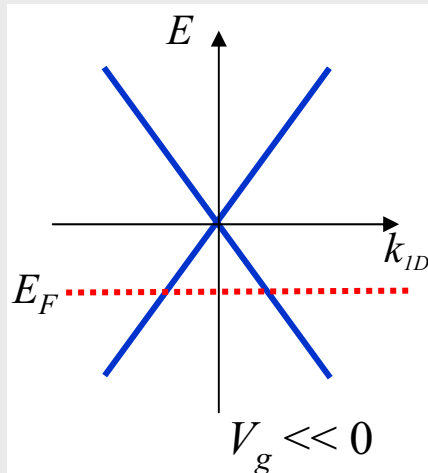
Tuning Carrier Density by Electric Field Effect

Atomic force microscope image of nanotube device

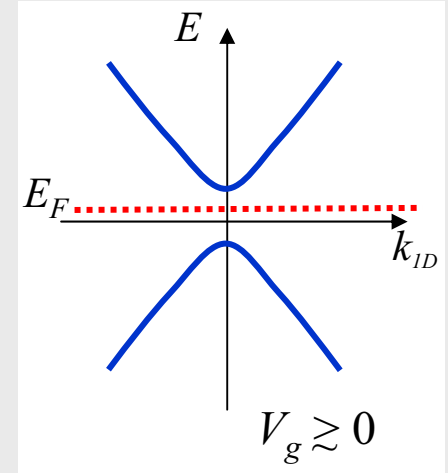
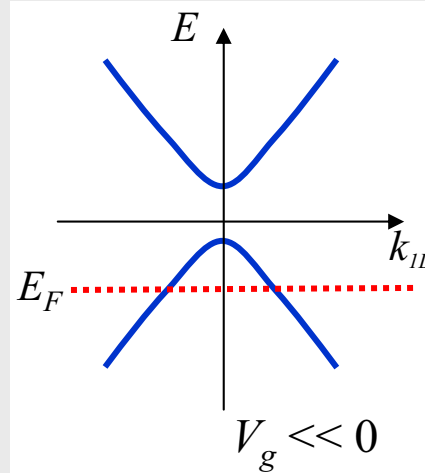


$$\text{Induced charge: } C_g V_g = e n = e (\text{D.O.S}) \Delta E_F$$

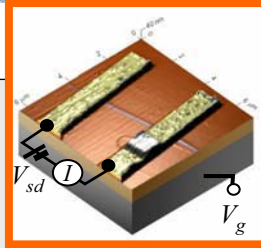
Metallic nanotube



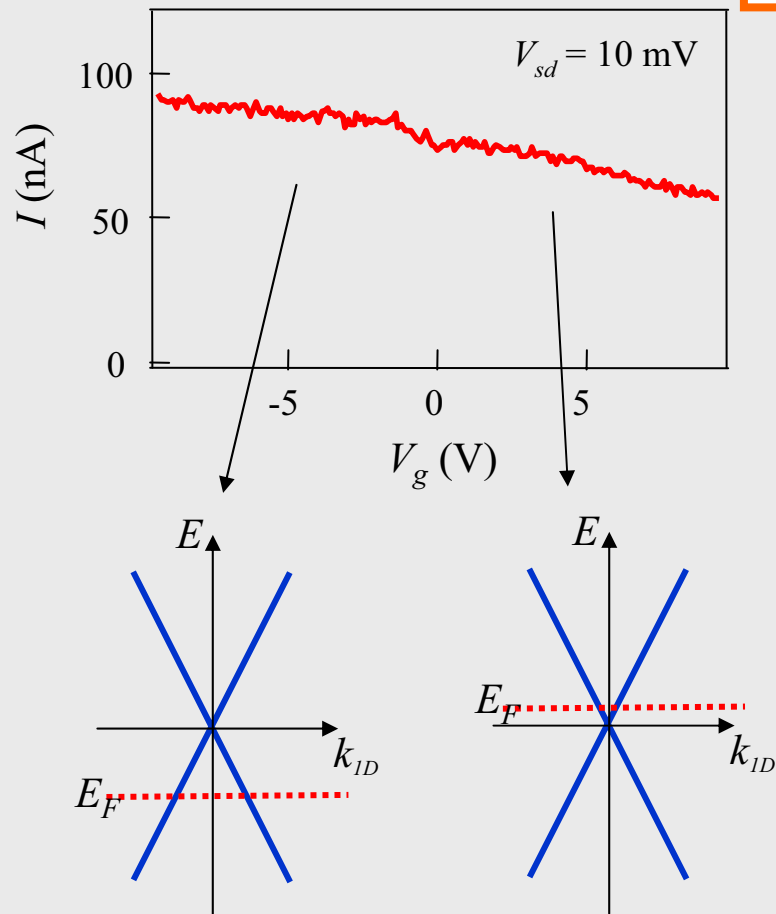
Semiconducting nanotube



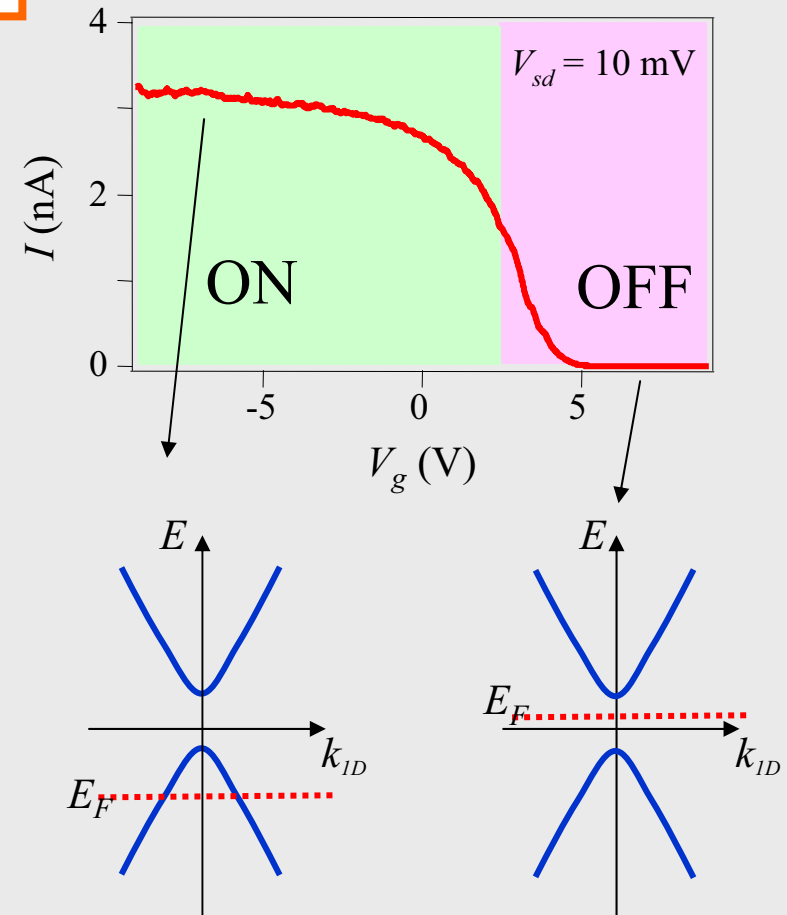
Electrical Transport in Nanotube Devices



Metallic nanotube



Semiconducting nanotube



Controlled Growth of Ultralong Nanotubes

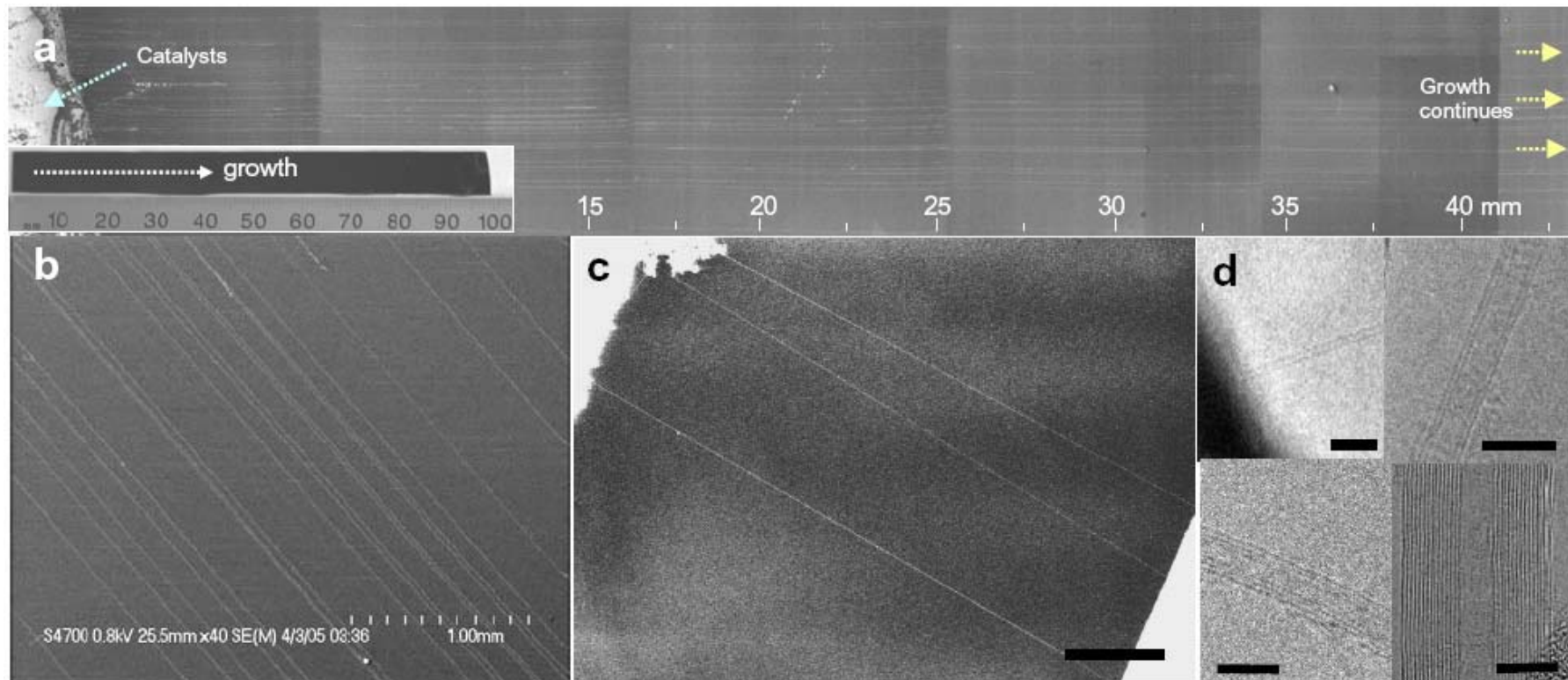
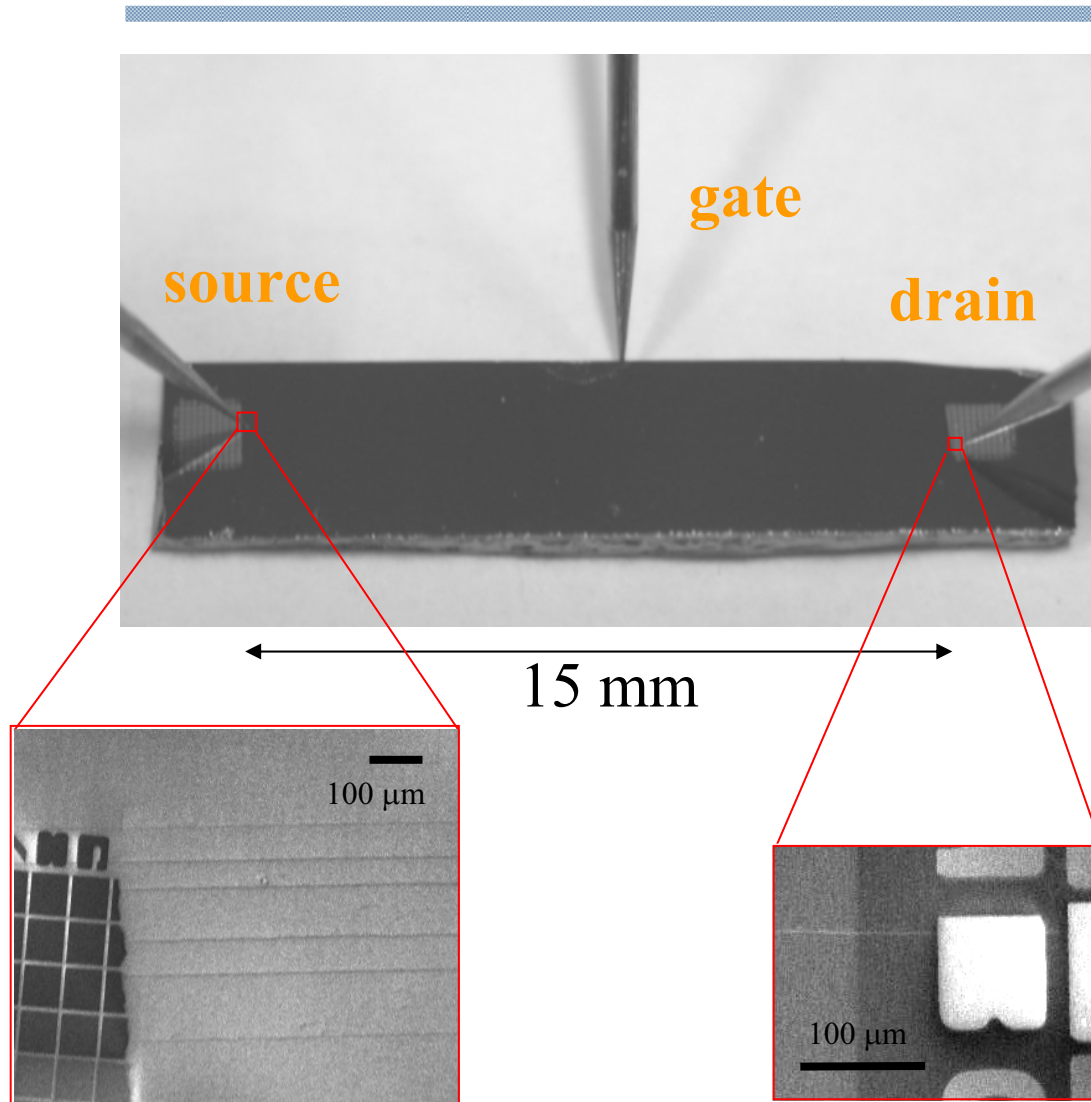
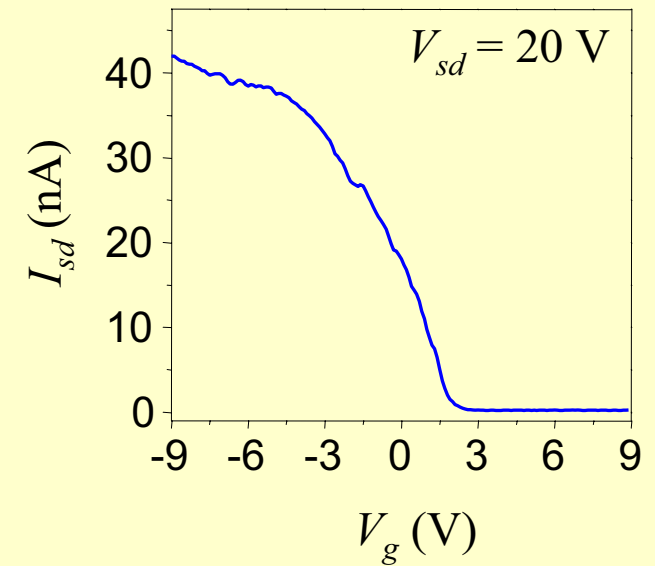


Figure 3. SEM and TEM images of ultralong MWNTs. (a) Schematic representation for the diameter-dependent stabilization of reaction gas flows. By inserting the smaller tube inside the outer chamber, microscopic turbulent flows can be stabilized into laminar flows with lower Reynolds numbers. (b) SEM image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

Extremely Long SWNT Field Effect Transistor



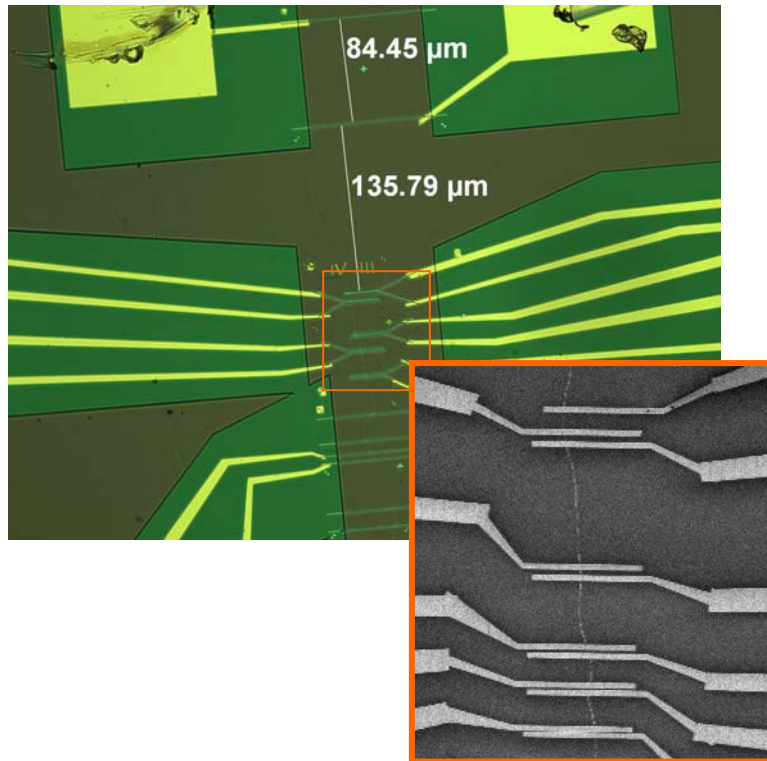
FET characteristics



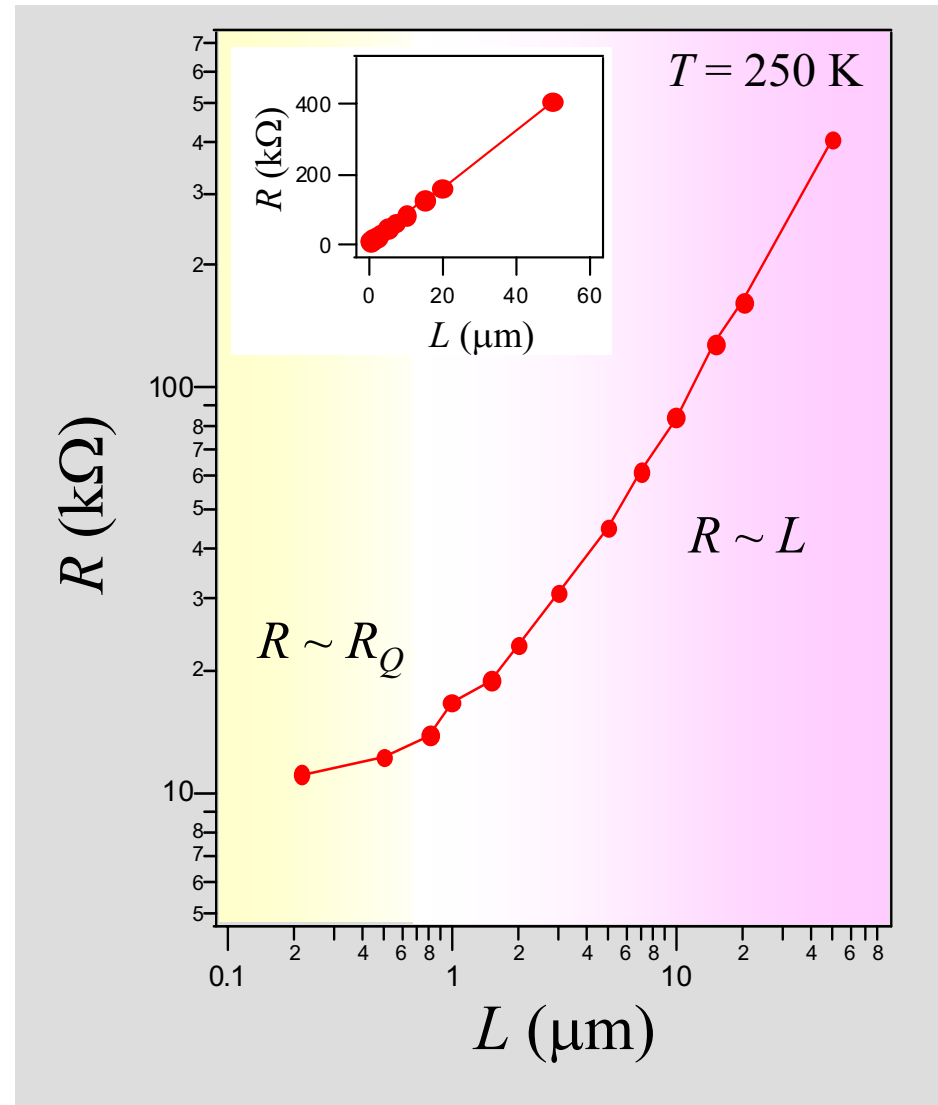
$$\rho \sim 10^{-7} \Omega \text{ m}$$

Electron Transport in Long Single Walled Nanotubes

Multi-terminal Device with Pd contact

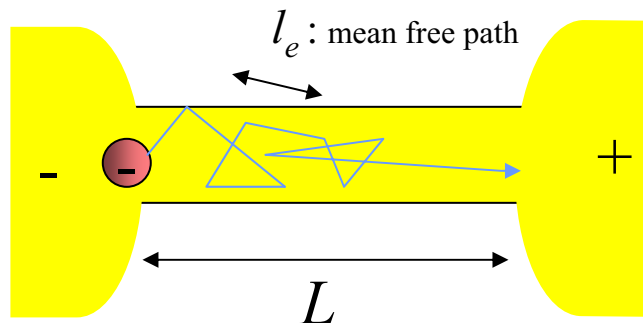


* Scaling behavior of resistance:
 $R(L)$



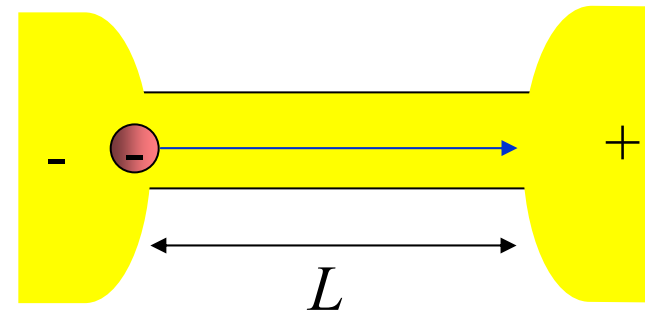
Ballistic Transport and Mean Free Path

Electron Transport in 1D Channel



Diffusive transport: $l_e \ll L$

$$R(L) = \rho L$$



Ballistic transport: $L < l_e$

$$R(L) = \frac{h}{N e^2} = R_Q$$

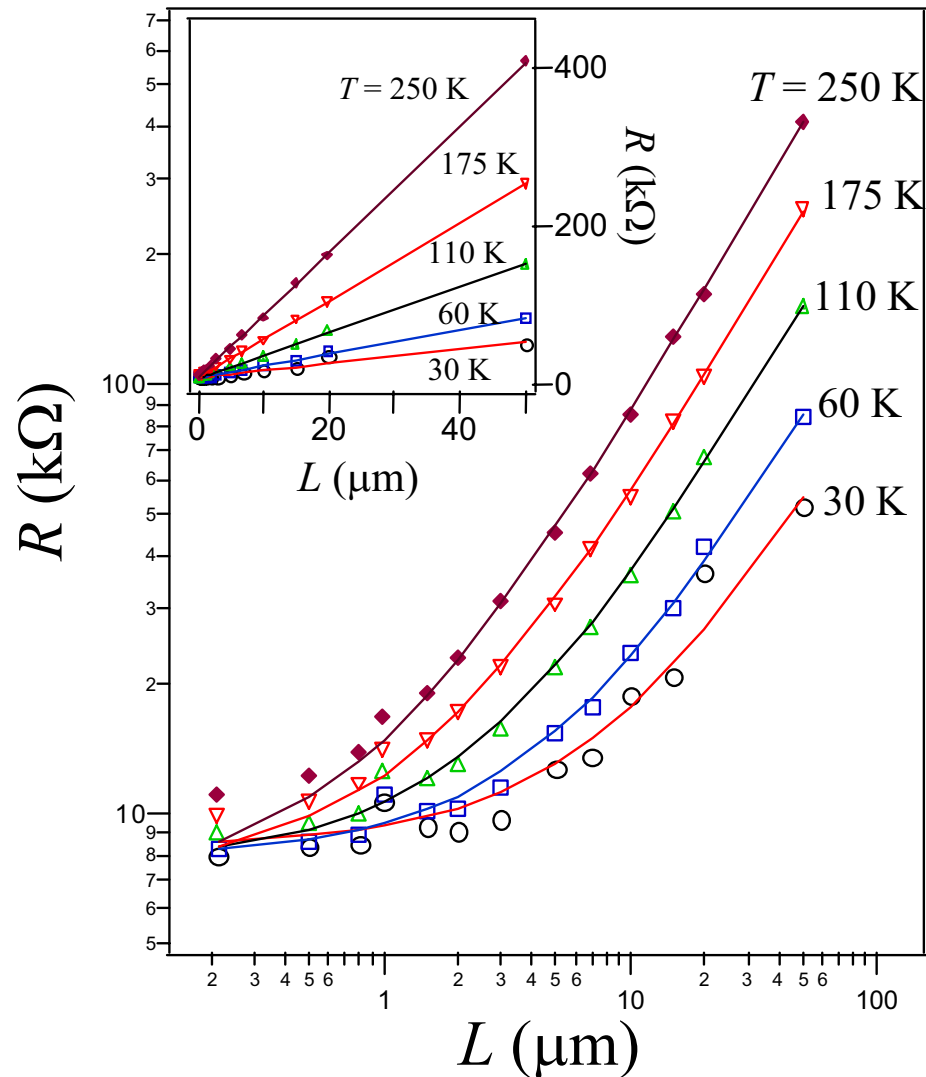
of channel

Resistance of N - 1D Channel:

$$R(L) = \frac{h}{N e^2} + \frac{h}{N e^2} \frac{L}{l_e}$$

For a nanotube, $N = 4$ (2 from spin and 2 from $\mathbf{K}$ and $\mathbf{K}'$)

Electron Mean Free Path of Nanotube

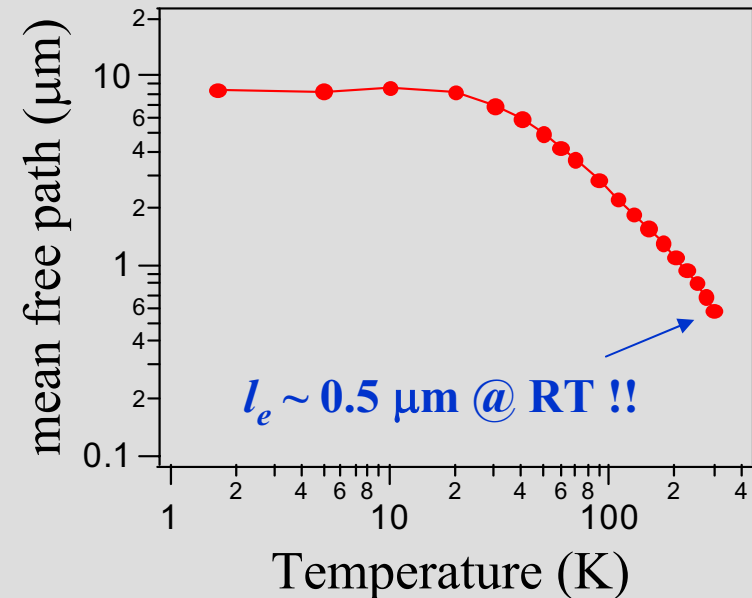


Lines are fit to

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

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

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



Extremely Long Mean Free Path: Hidden Symmetry ?

Carbon nanotube:

$$l_e \sim 10 \mu\text{m} @ 1.6 \text{ K}$$

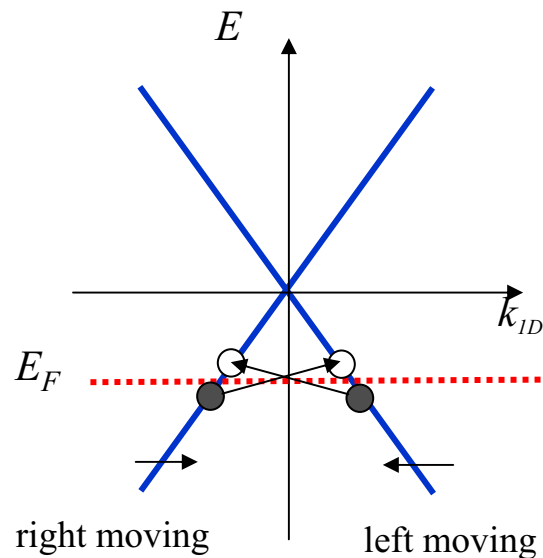
$$\underline{l_e \sim 0.5 \mu\text{m} @ 300 \text{ K}}$$

Ga[Al]As HEMT:

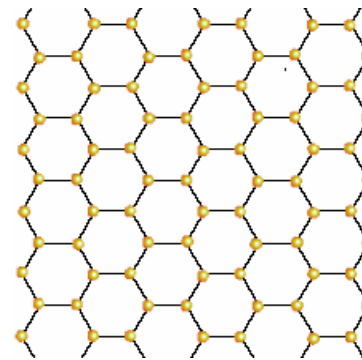
$$l_e \sim 100 \mu\text{m} @ 1.6 \text{ K}$$

$$l_e \sim 0.06 \mu\text{m} @ 300 \text{ K}$$

- Small momentum transfer backward scattering must be inefficient.



Selection rules by hidden symmetry in graphene?



Electric Field Effect in Mesoscopic Graphite

APPLIED PHYSICS LETTERS 86, 073104 (2005)

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)

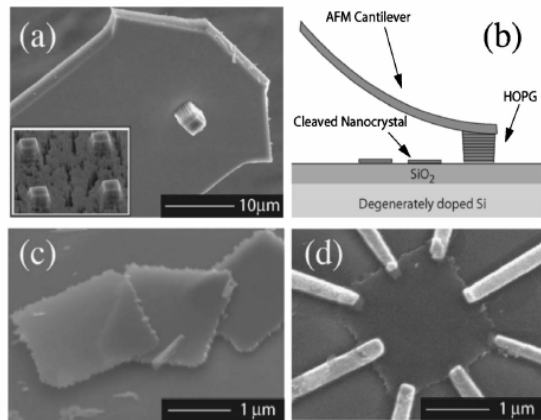
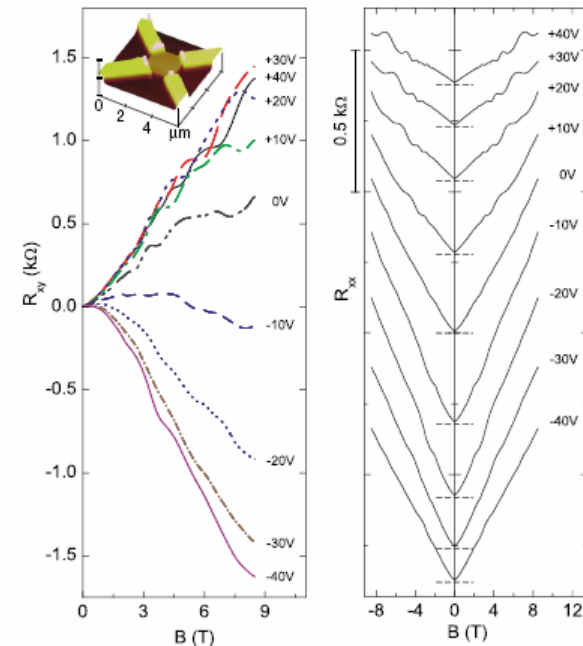
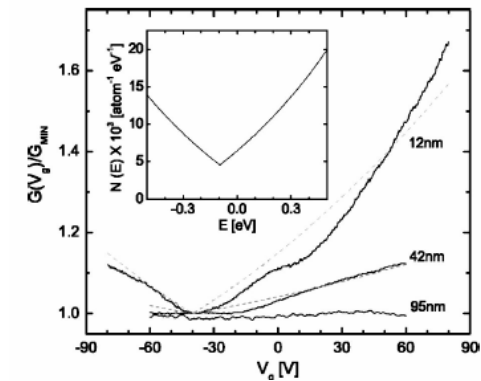


FIG. 1. (a) Scanning electron microscope image of an HOPG crystallite mounted on a microcantilever. Inset: bulk HOPG surface patterned by masked anisotropic oxygen plasma etching; (b) schematic drawing of the microcleaving process; (c) thin graphite samples cleaved onto the SiO₂/Si substrate; (d) a typical mesoscopic device fabricated from a cleaved graphite sample.



PRL 94, 176803 (2005)

PHYSICAL REVIEW LETTERS

week end:
6 MAY 2005

Electric Field Modulation of Galvanomagnetic Properties of Mesoscopic Graphite

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(Received 31 August 2004; published 3 May 2005)

Simple Yet Efficient Mechanical Extraction

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,¹ A. K. Geim,^{1*} S. V. Morozov,² D. Jiang,¹ Y. Zhang,¹ S. V. Dubonos,² I. V. Grigorieva,¹ A. A. Firsov²

We describe monocrystalline graphitic films, which are a few atoms thick 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 $\sim 10,000$ 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

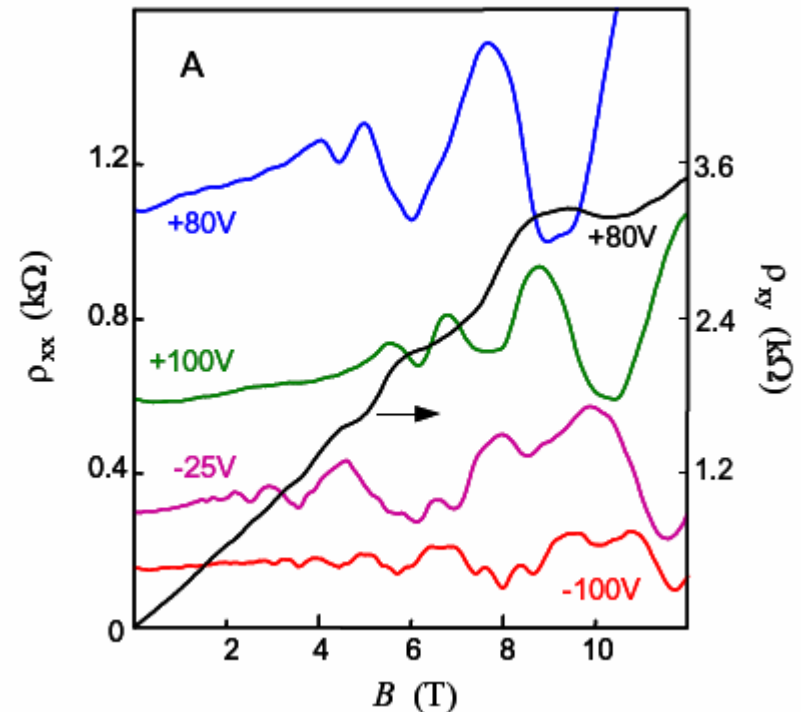
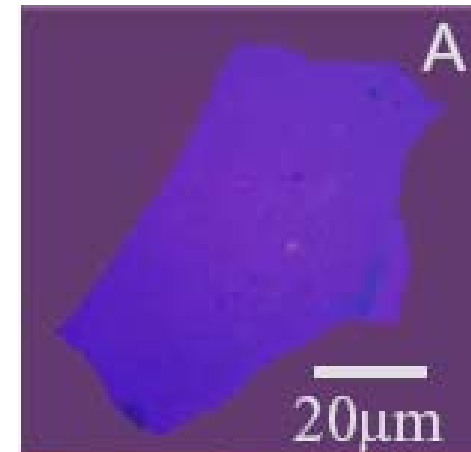
¹Department of Physics, University of Manchester, Manchester M13 9PL, UK. ²Institute for Microelectronics Technology, 142432 Chernogolovka, Russia.

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semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional 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

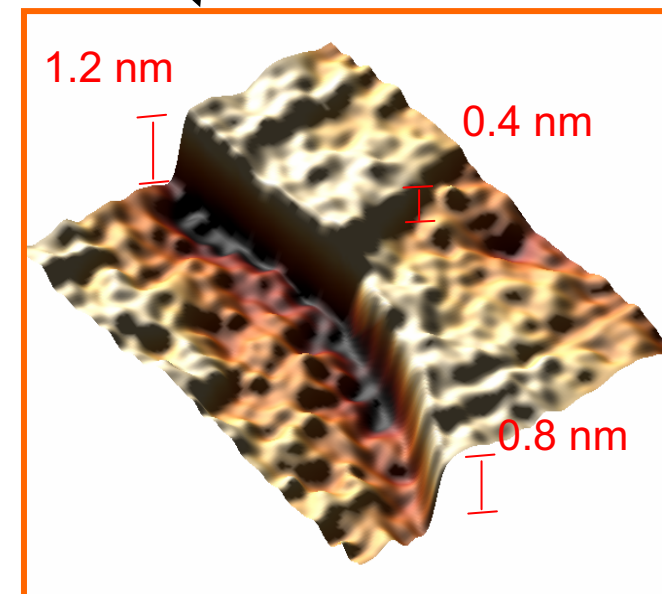
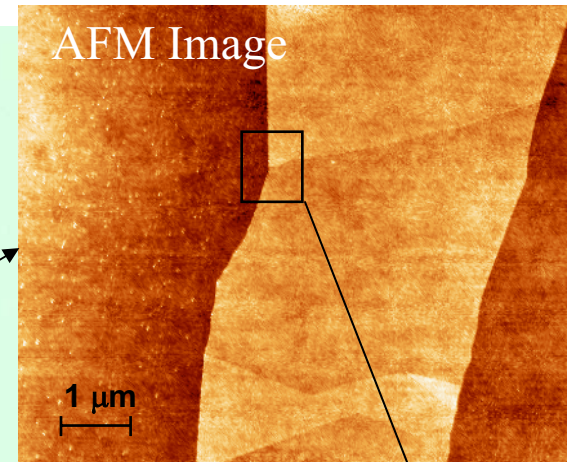
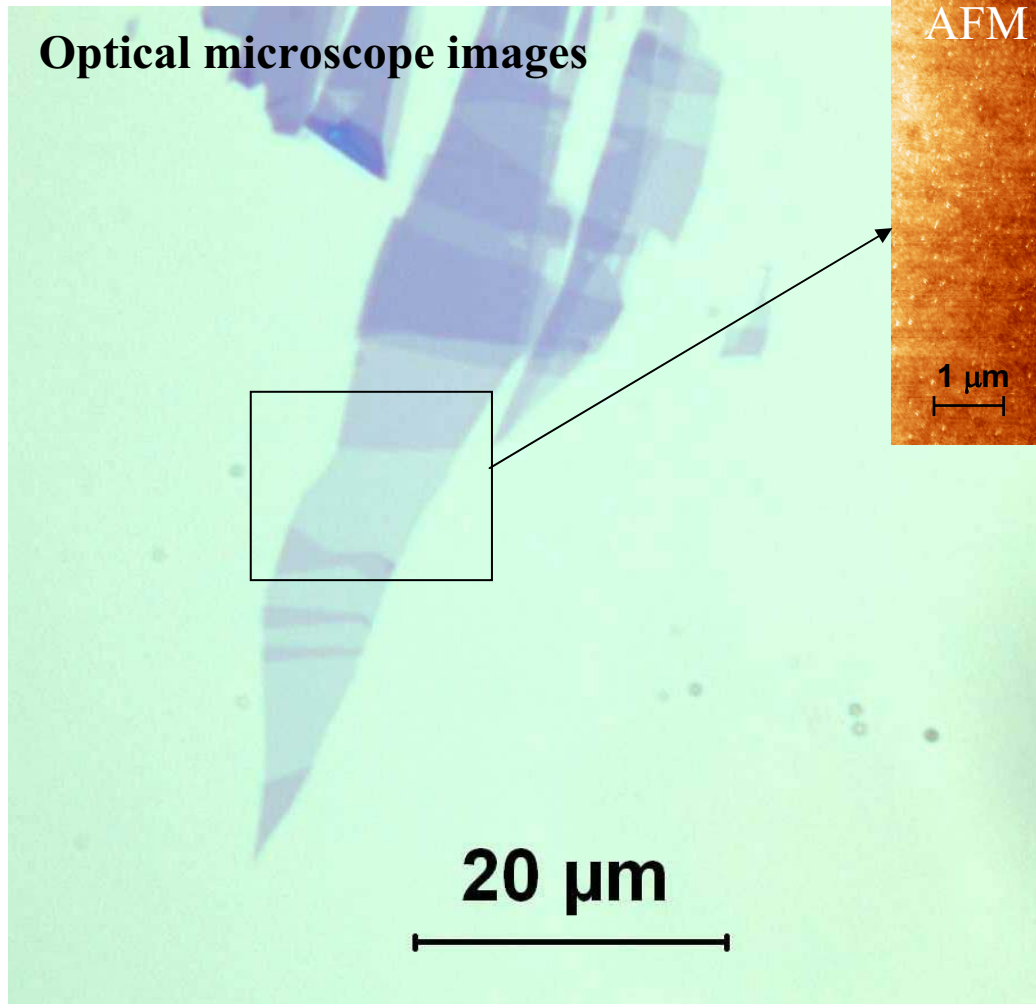
than traditional semiconducting devices (3)]. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances (<1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. 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 two-dimensional (2D) material: few-layer graphene (FLG), a name given to a single layer densely packed into a hexature, and is widely used to tubes of many carbon-based in graphite, large fullerenes, nan carbon nanotubes are usual graphene sheets rolled up into cylinders (5–7). Planar graphene has been presumed not to exist being unstable with respect to curved structures such as nanotubes (5–14).

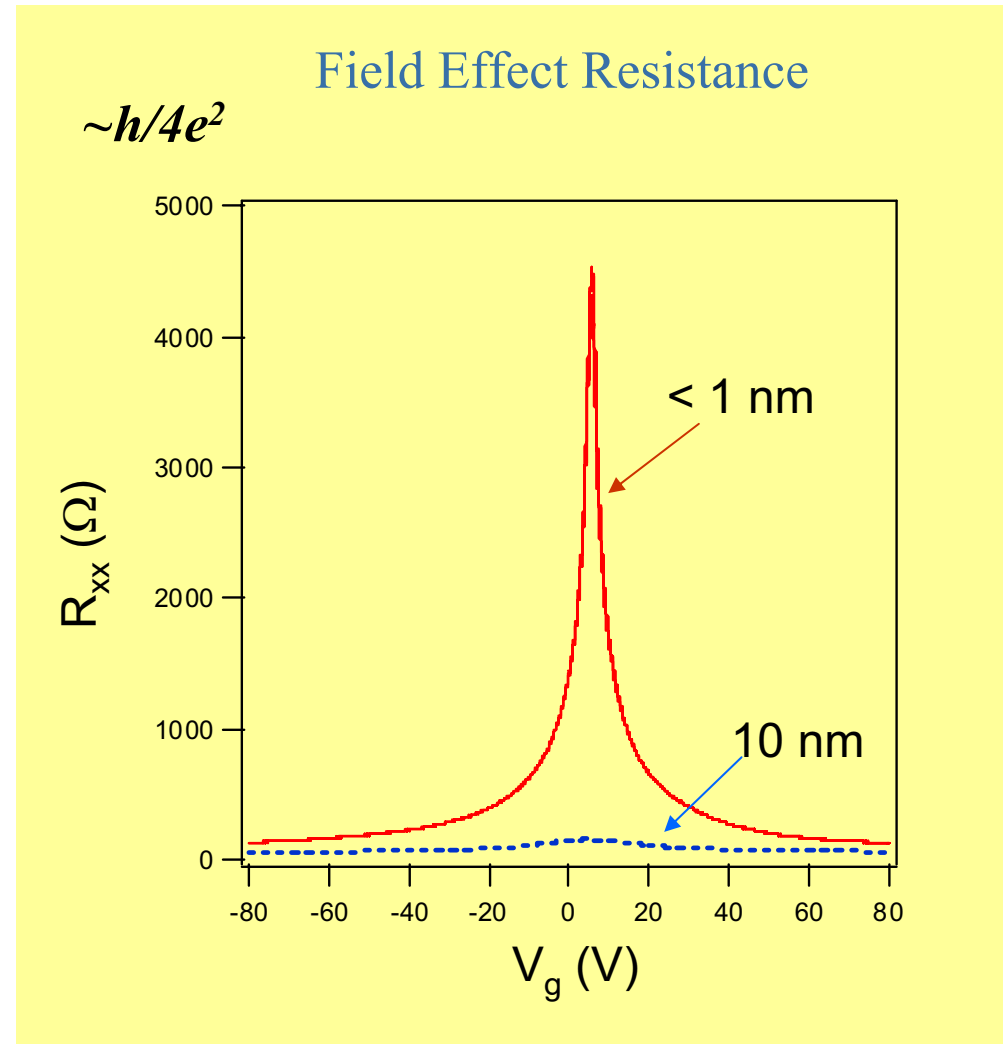
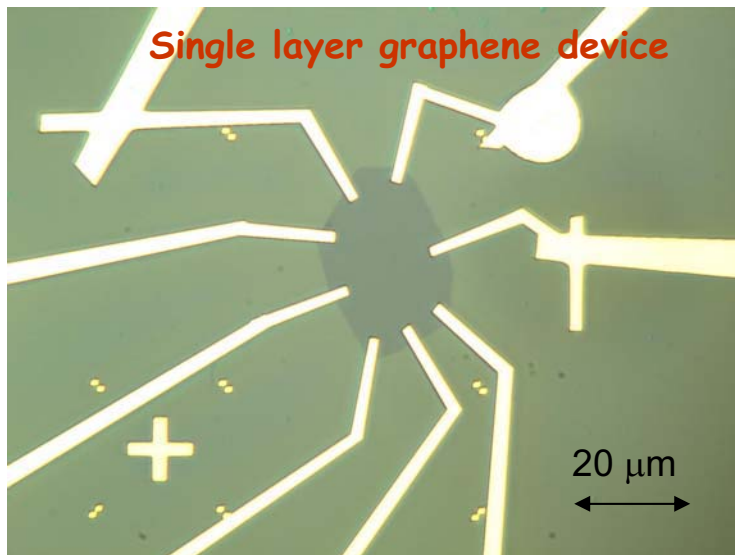


Using Scotch Tape is Essential!!

A Few Layer Graphene on SiO₂/Si Substrate



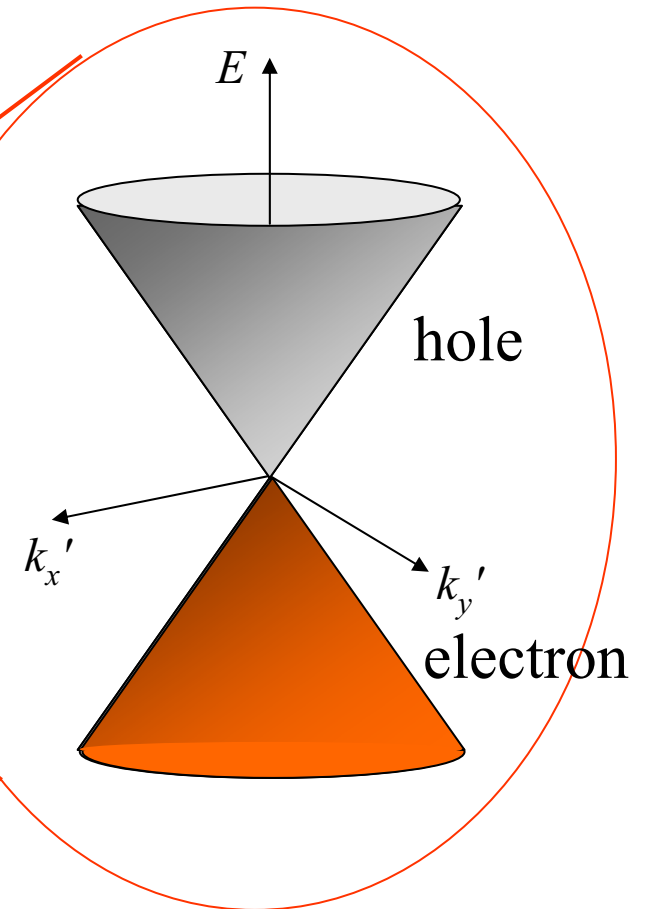
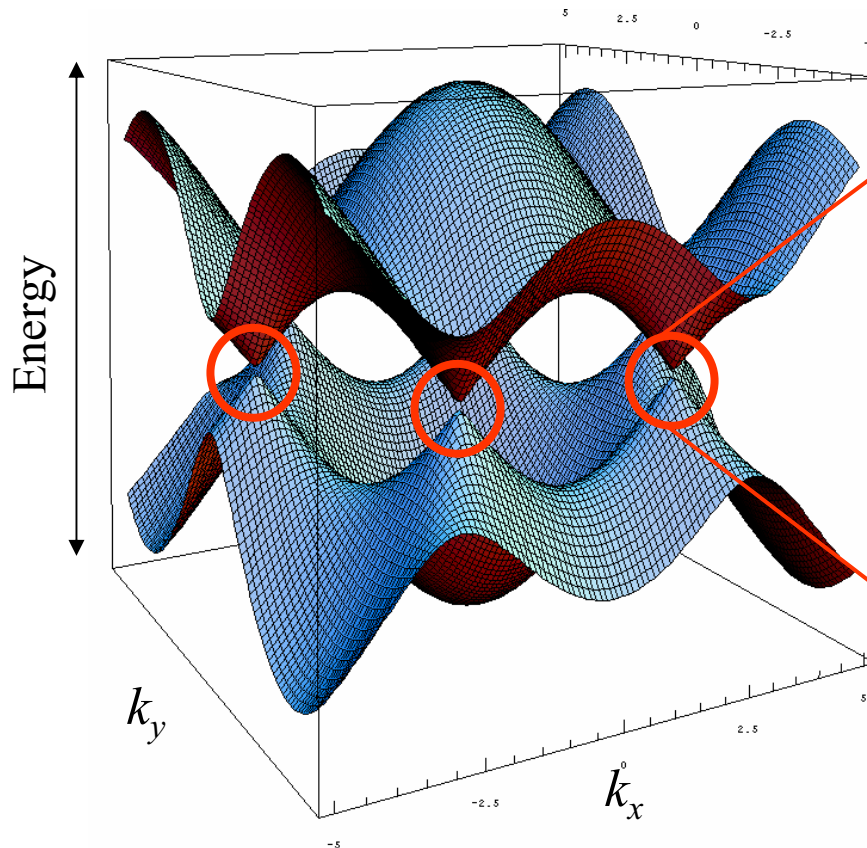
Transport Single Layer Graphene



Zhang, Tan, Stormer & Kim (2005), see also Novoselov et al (2005).

Graphene : Dirac Particles in 2D Box

Band structure of graphene



$$E \approx \hbar v_F \left| \vec{k}'_{\perp} \right|$$

Massless Dirac Particles with effective speed of light v_F .

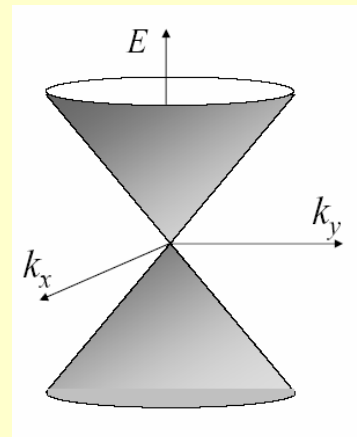
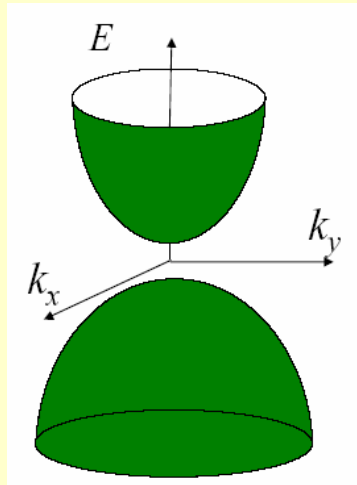
Graphene v.s. Conventional 2D Electron System

Conventional 2D Electron System

Band structures

$$E = \frac{\hbar^2 k^2}{2m_e^*}$$

$$E = -\frac{\hbar^2 k^2}{2|m_h^*|}$$

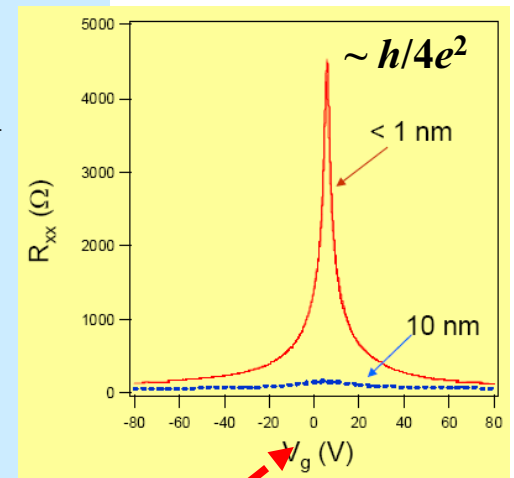
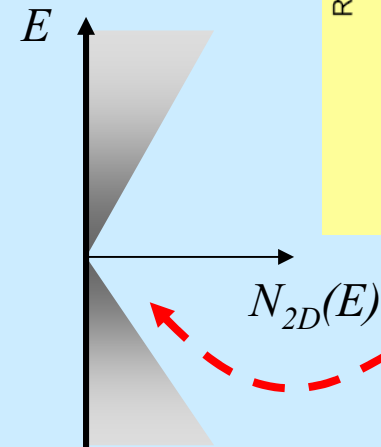
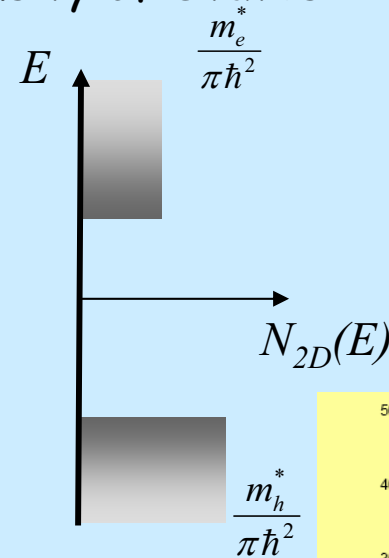


$$E = \hbar v_F |\vec{k}'|$$

Graphene

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

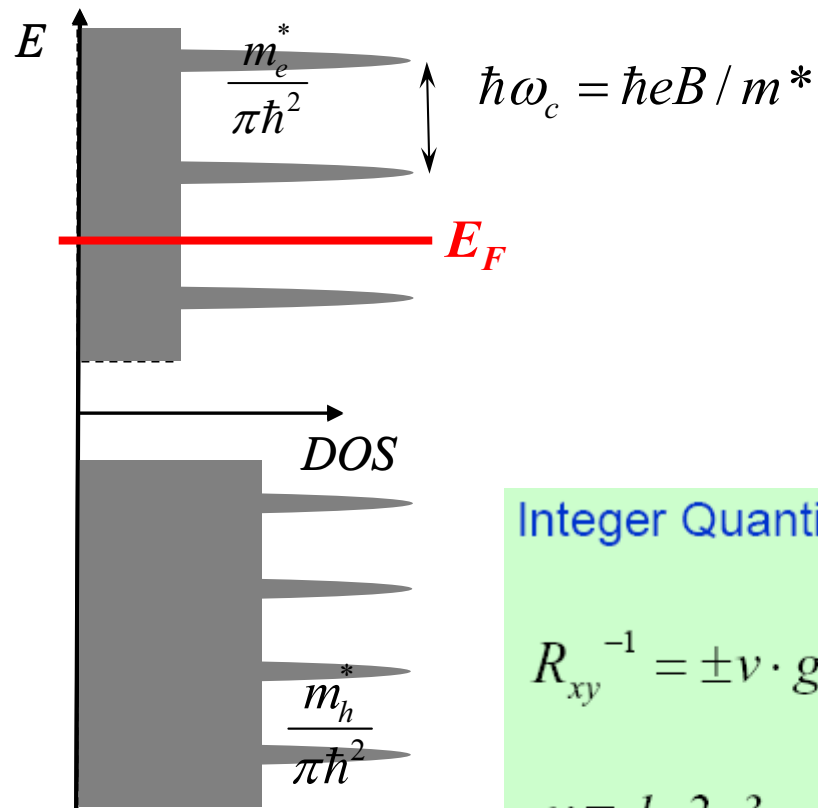
Density of States



2D Gas in Quantum Limit : Conventional Case

Density of States

Landau Levels in Magnetic Field



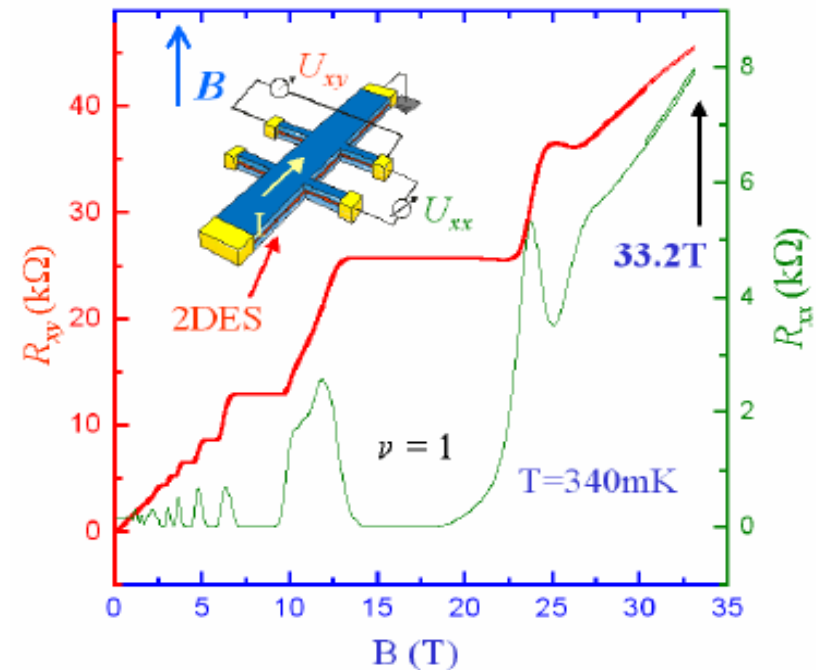
Integer Quantization:

$$R_{xy}^{-1} = \pm \nu \cdot g_s \cdot \frac{e^2}{h}$$

$$\nu = 1, 2, 3 \dots$$

$$g_s = 2 \text{ (spin)}$$

Quantum Hall Effect in GaAs 2DEG



Graphene

- Vanishing carrier mass near Dirac point
- Strict electron hole symmetry
- Electron hole degeneracy $\omega_c = \frac{eB}{m^*}$

Relativistic Landau Level and Half Integer QHE

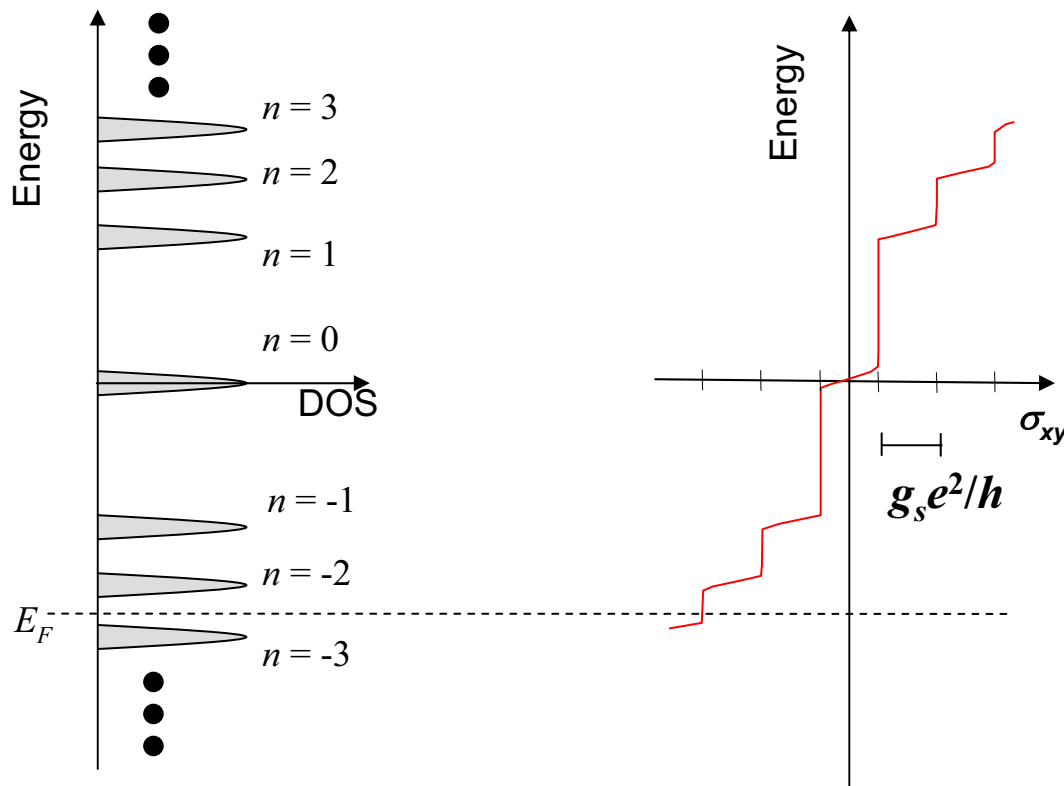
Haldane, PRL (1988)

Landau Level $E_n = \pm \sqrt{2e\hbar v_F^2 |n| B}$

Landau Level Degeneracy

$$g_s = 4$$

2 for spin and 2 for sublattice



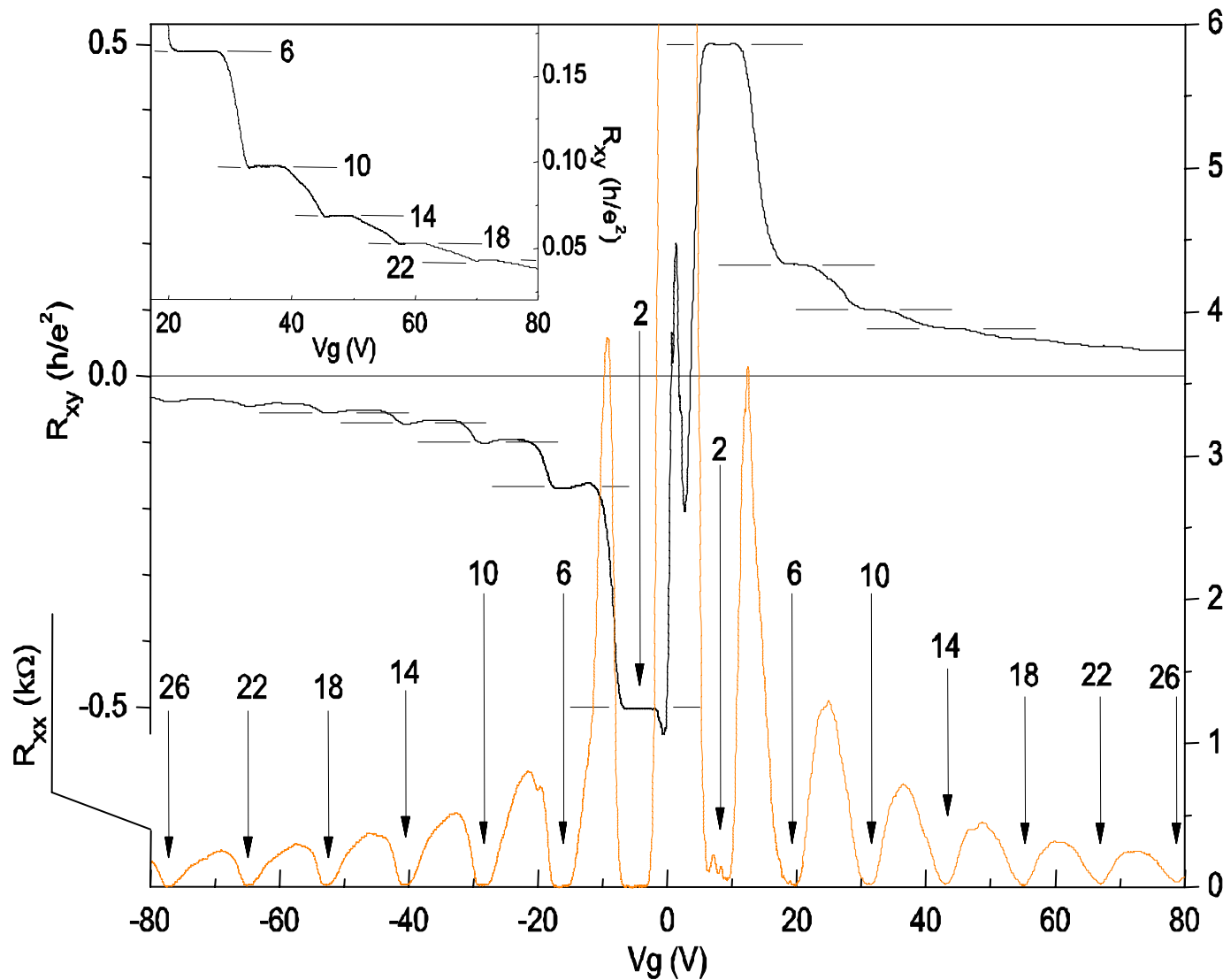
Quantized Condition

$$R_{xy}^{-1} = \pm g_s \left(n + \frac{1}{2}\right) \frac{e^2}{h}$$

$$\nu = \pm g_s \left(n + \frac{1}{2}\right)$$

T. Ando et al (2002)

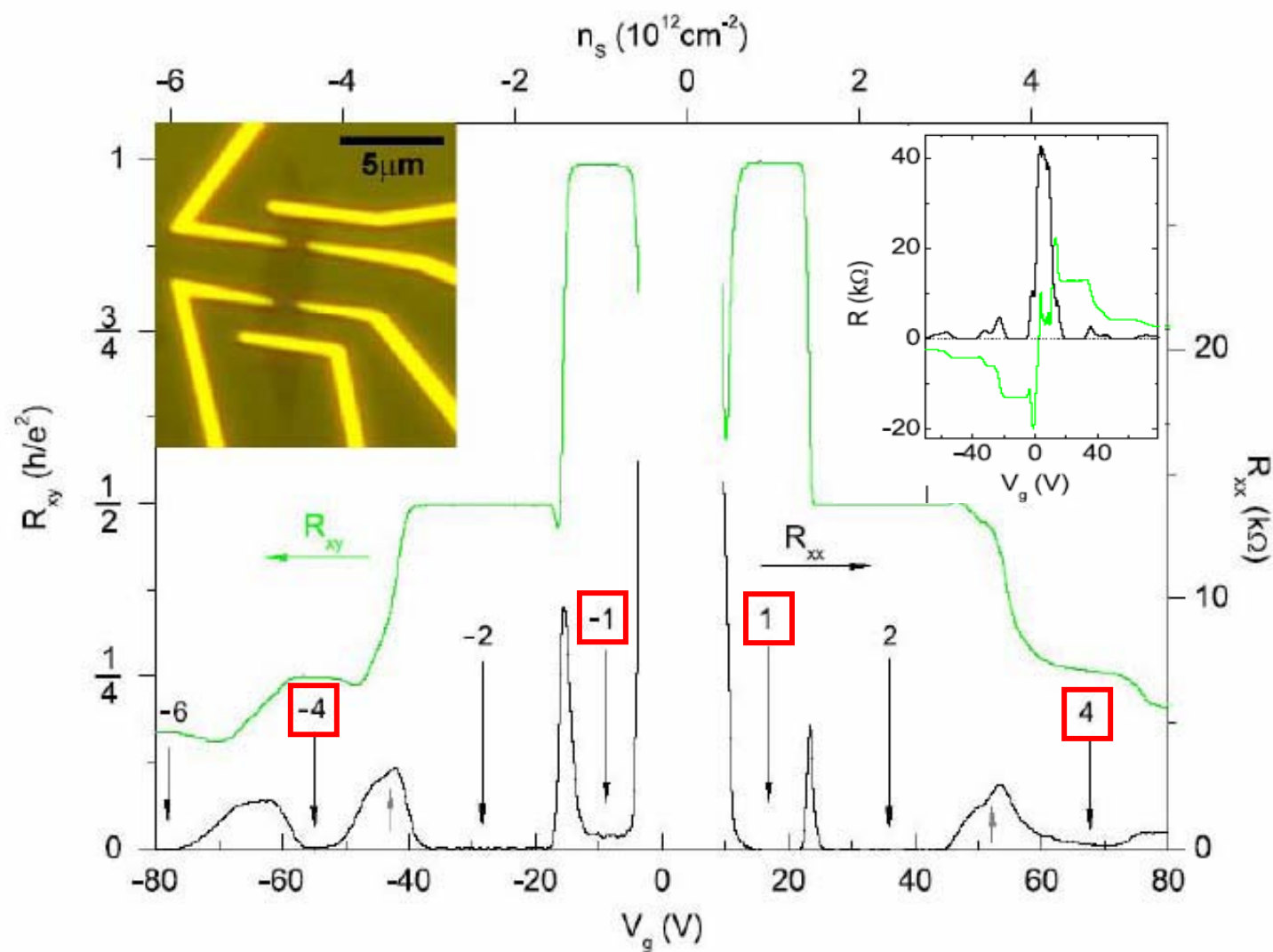
Quantum Hall Effect in Graphene



Mobility
 $\sim 60,000 \text{ cm}^2/\text{V s}$

T = 1.7 K
B = 9 T

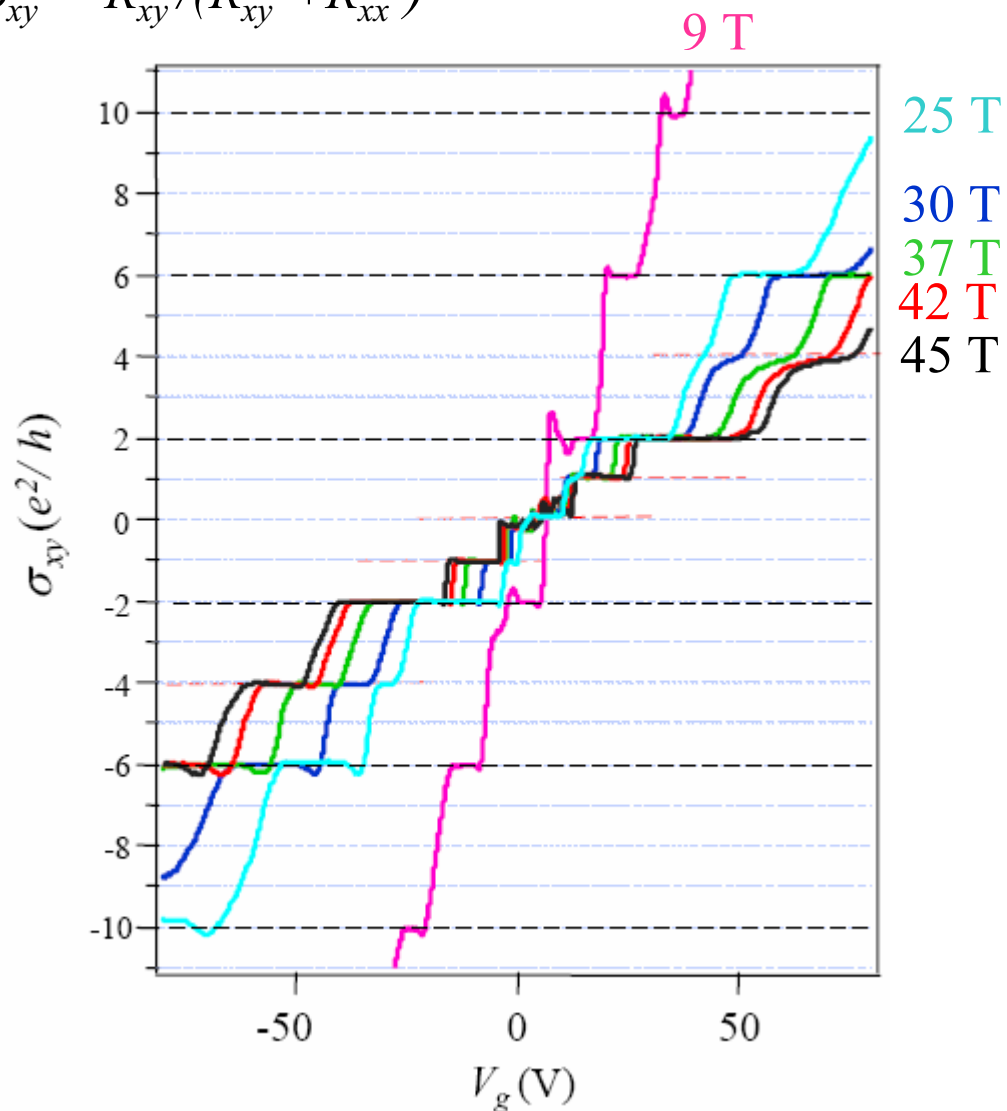
Quantum Hall Effect in Graphene at High Magnetic Field



Zhang *et al*, Phys. Rev. Lett. (2006)

Splitting of Landau Levels in High Magnetic Fields

$$\sigma_{xy} = -R_{xy} / (R_{xy}^2 + R_{xx}^2)$$



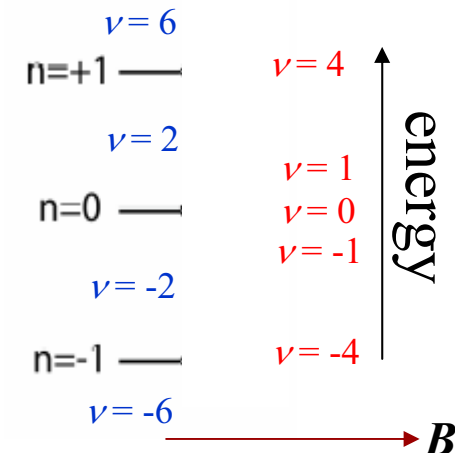
Low fields ($B < 10$ T)

$$\nu = \pm 2, \pm 6, \pm 10, \dots$$

High fields ($B > 20$ T)

$$\nu = 0, \pm 1, \pm 2, \pm 4, \pm 6, \dots$$

Landau Level $E_n = \text{sgn}(n) \sqrt{2e\hbar v_F^2 |n| B}$



Graphene Electronics

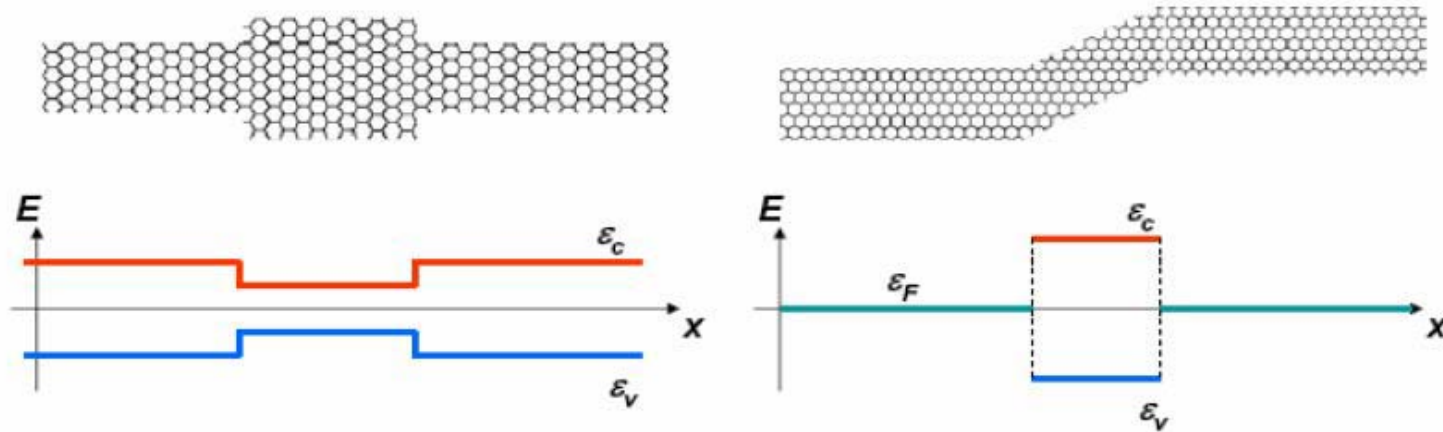
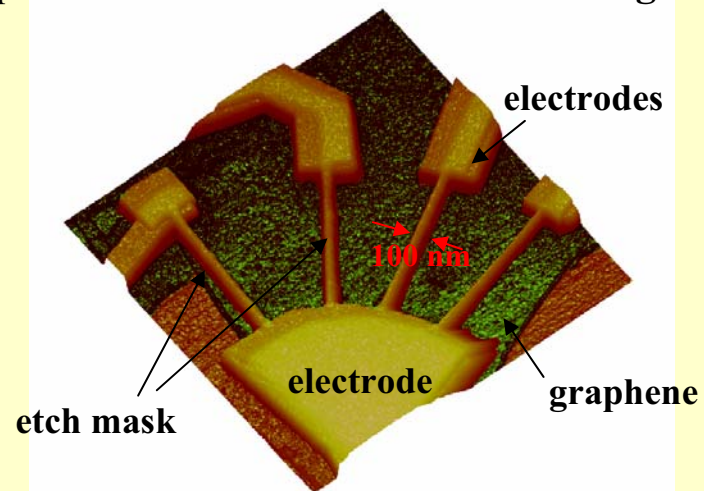
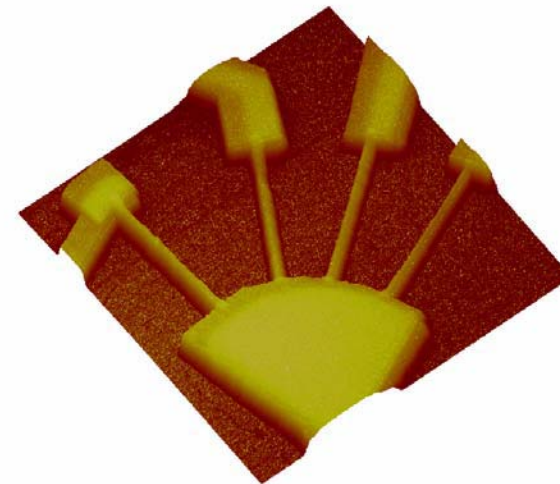


Fig 6. Examples of all graphene device with their band diagram

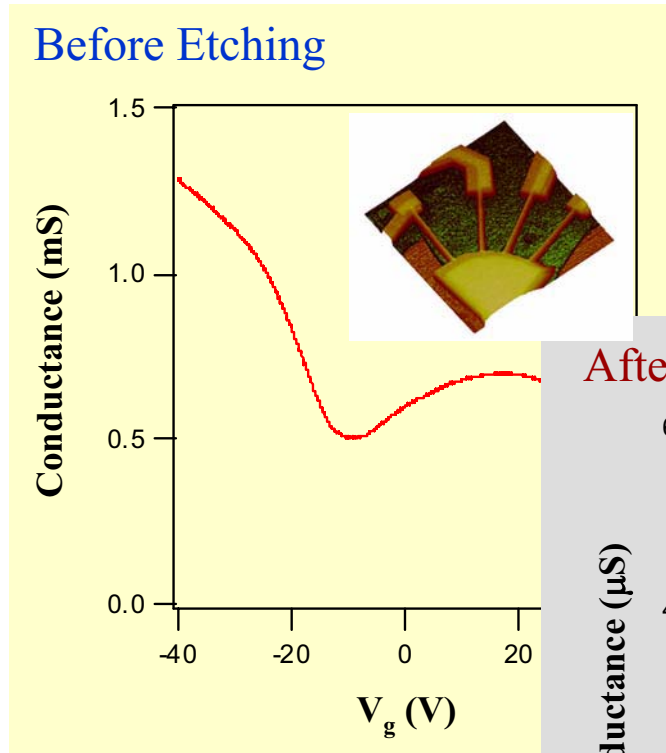
Graphene ribbon device : before etching



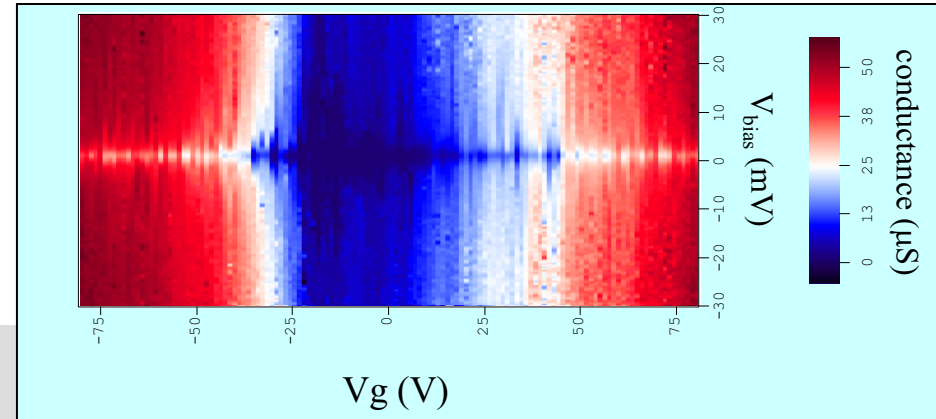
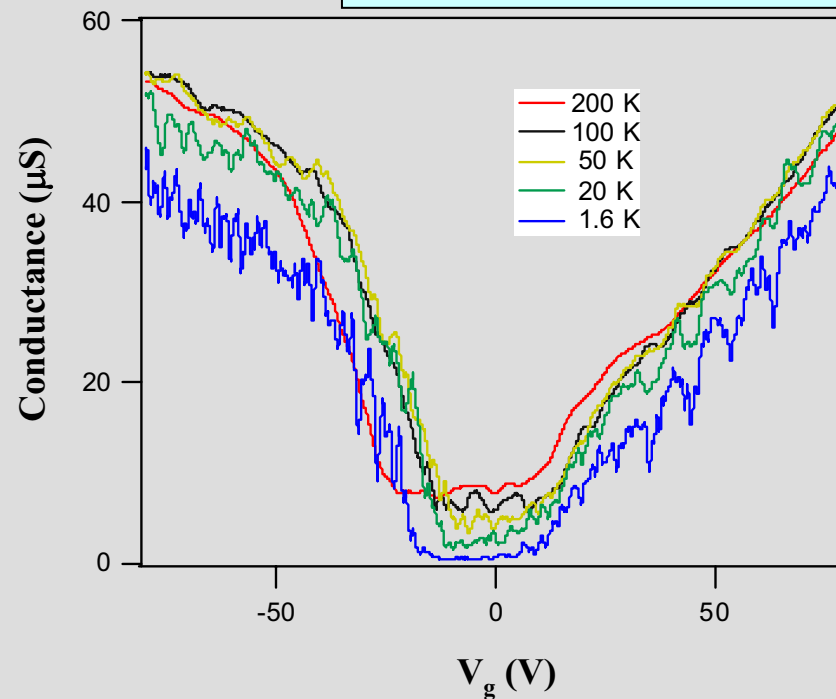
Graphene ribbon device : after etching



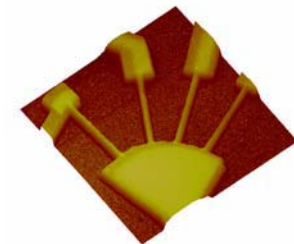
Graphene Ribbon Devices (Preliminary)



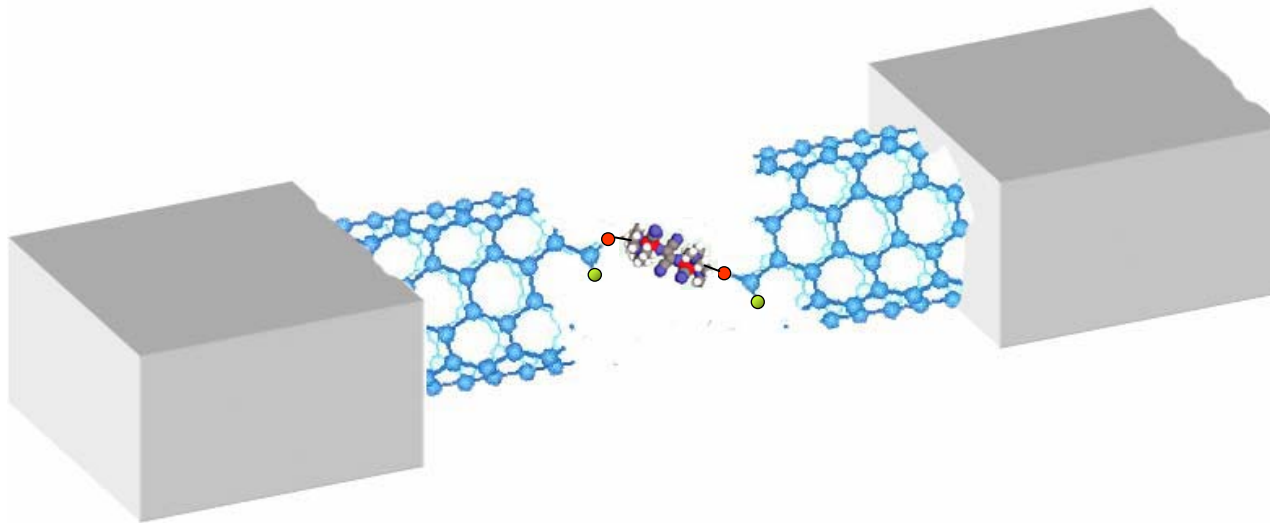
After Etching



Gap Opening
 ~ 10 meV
For ~ 80 nm
Graphene ribbon

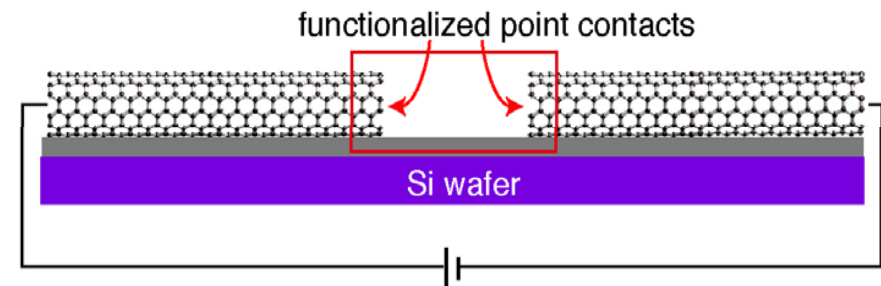
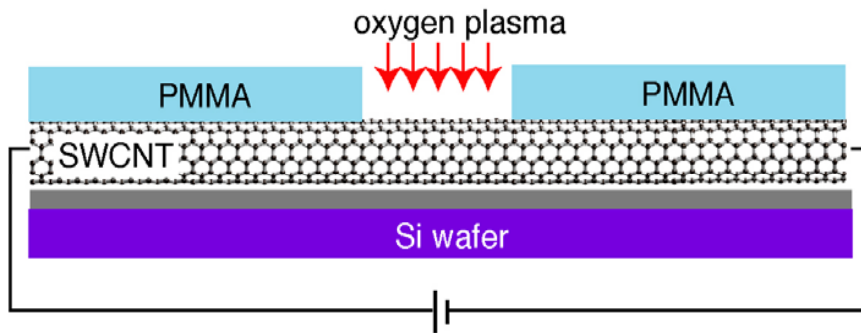
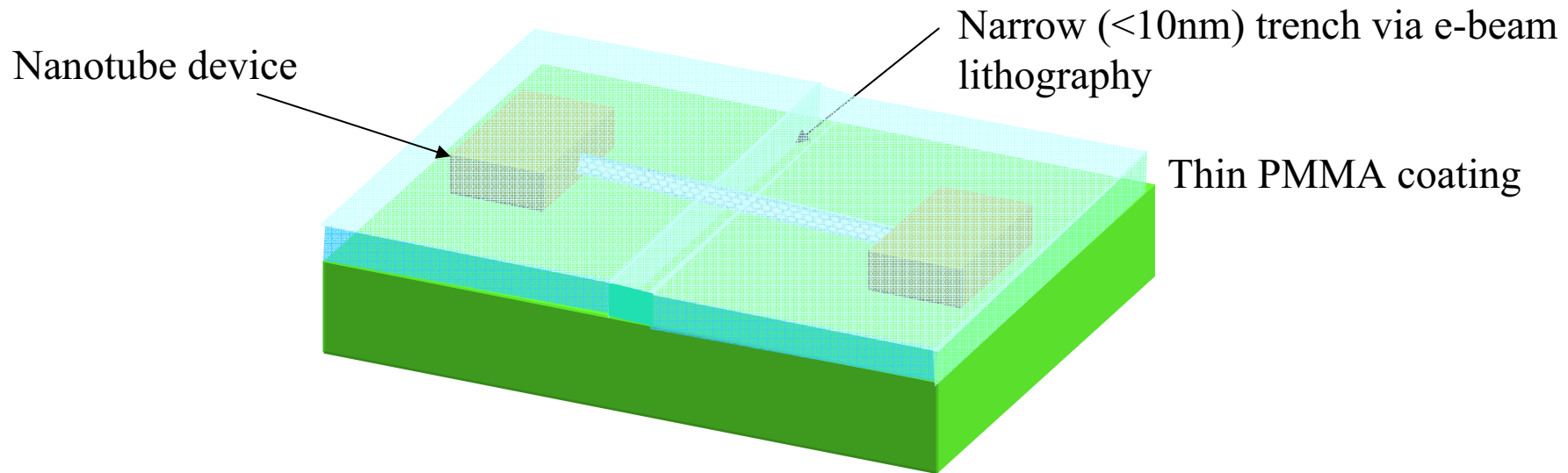


Nanotube Electrodes for Molecular Electronics



- **Nanotubes are inherently small,
yet compatible to microfabrication processes**
- **Covalent chemistry between electrode and molecules**
- **Potentially good conduction via π -bonding network**

Nanotube Nanogaps

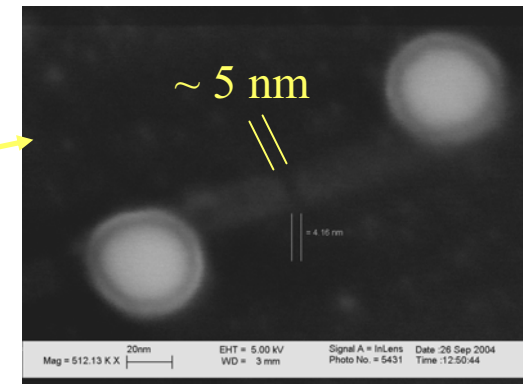
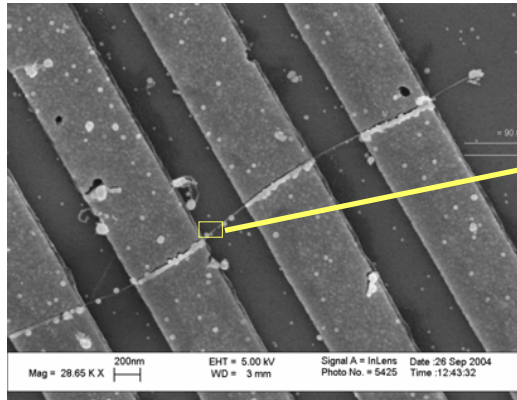


Oxygen Plasma etching creates gaps (0-10 nm) in tubes.

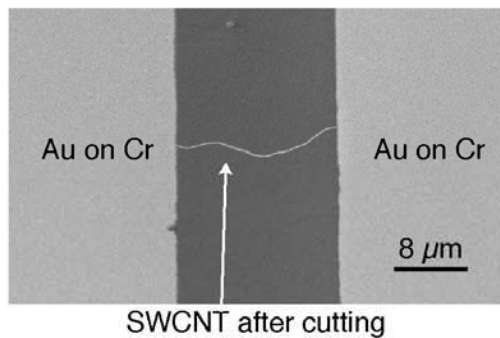
Cut ends likely to be carboxyl-terminated

Nanotube Nanogaps

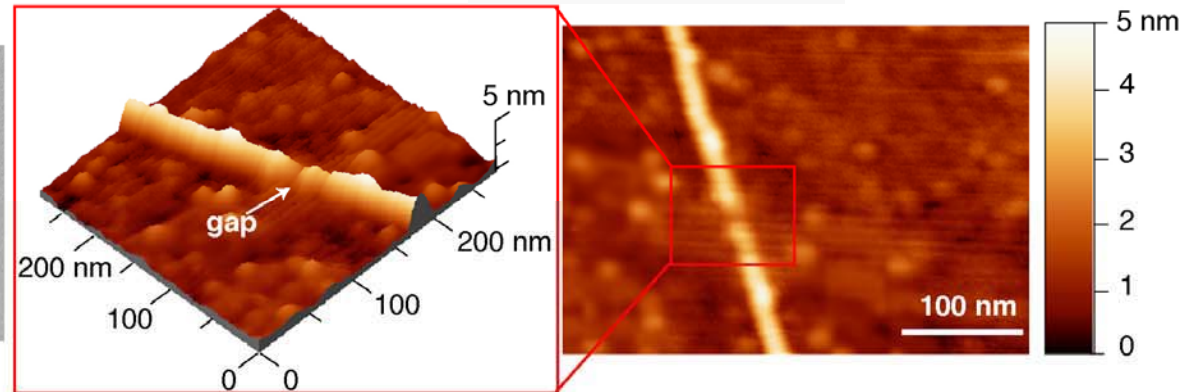
SEM micrograph



SEM micrograph



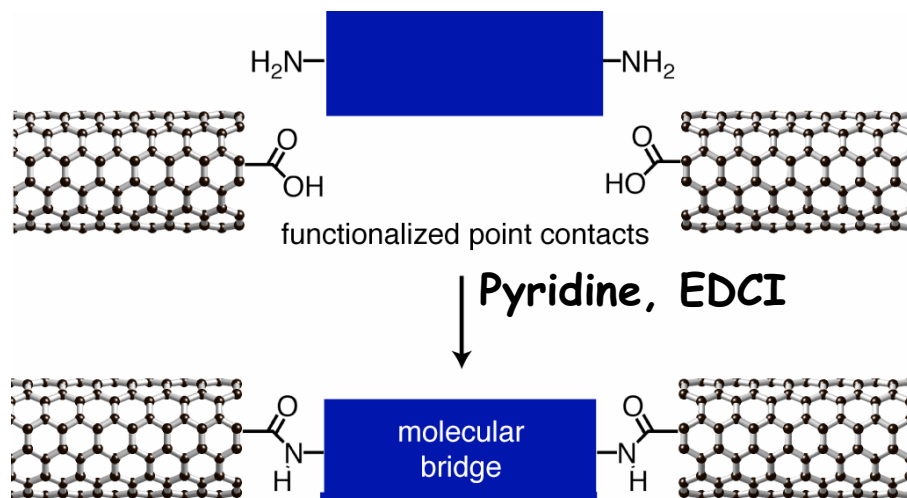
AFM micrograph



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

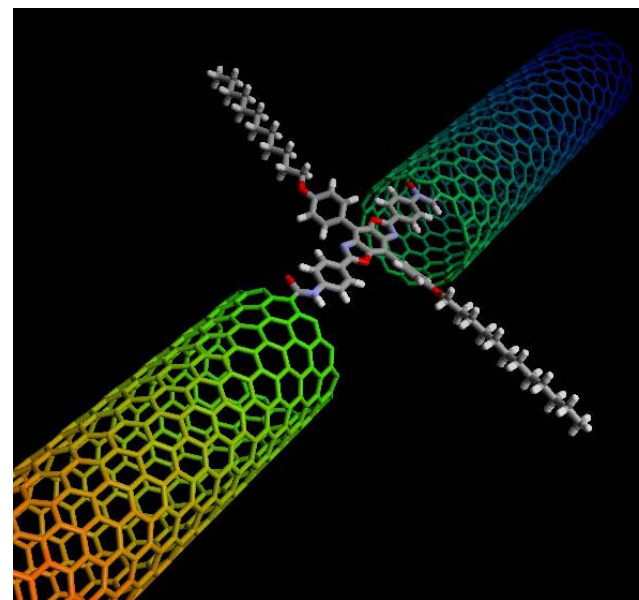
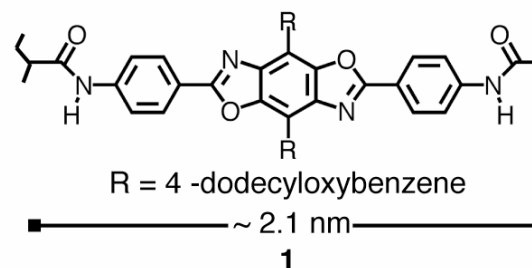
Columbia NSEC (Hone, Wind, Brewslow, Nuckolls, and Kim) Collaboration

Molecular Bridges

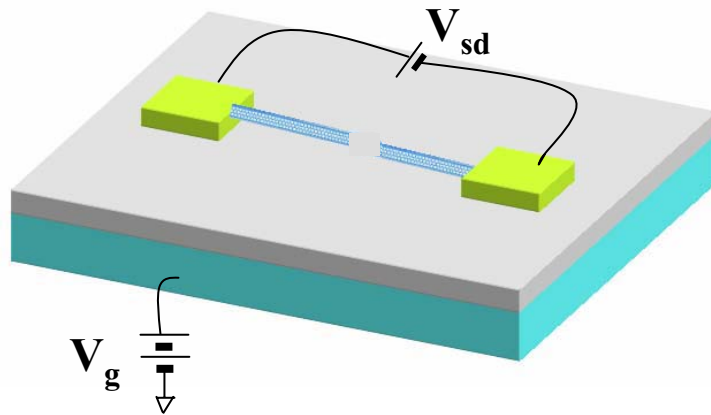


- Self-assembled
- Covalently bonded
- Conduction through π -back bone

Bis-oxazole

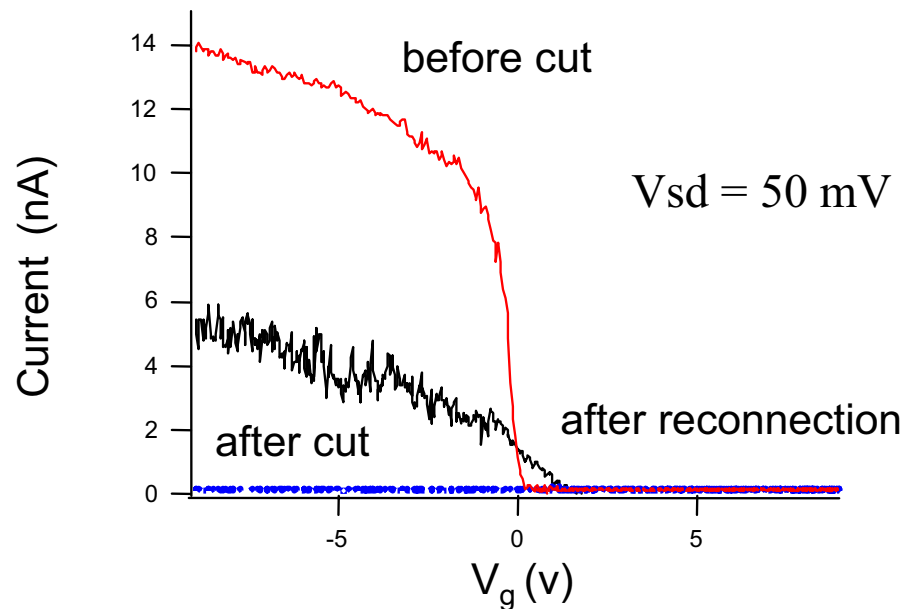


Does It Work?

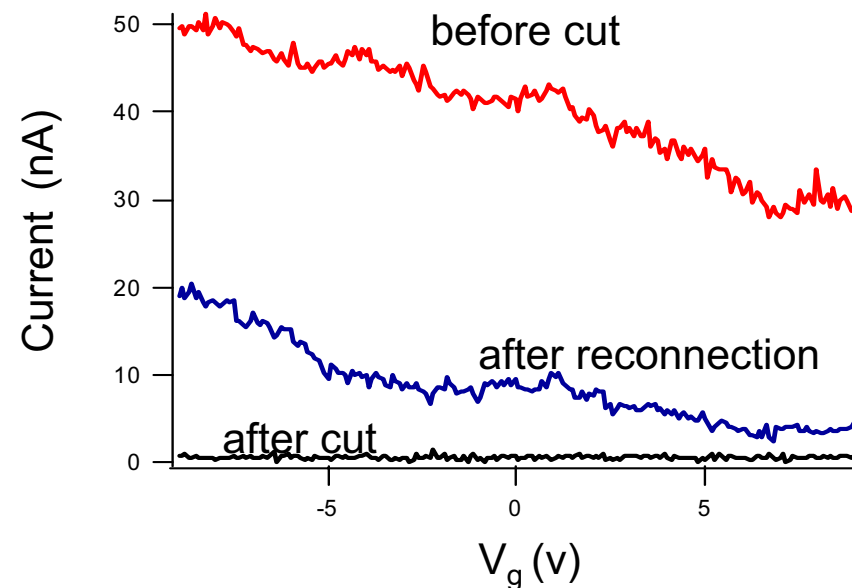


~ 10-15% of reconnection
out of ~ 100 fully cut tubes

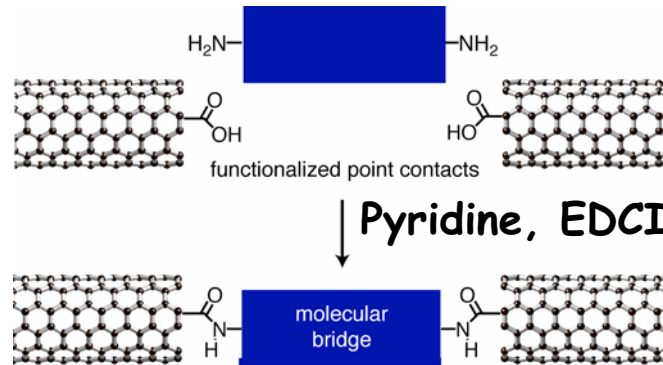
Semiconducting Nanotube + Molecular Bridge



Metallic Nanotube + Molecular Bridge



Control Experiments



Connection
with diamine bisoxazole

* Pyridine +EDCI without molecules

No connection

* Bis-oxazole without amines

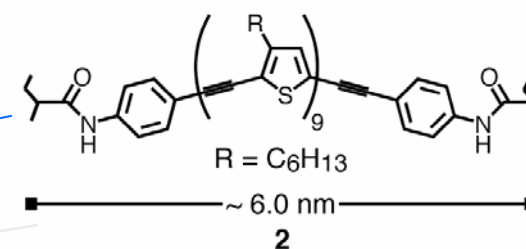
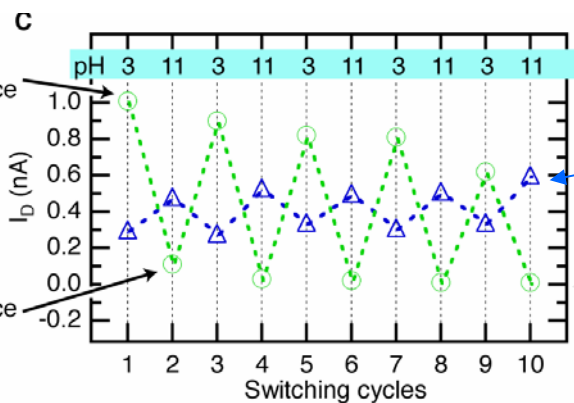
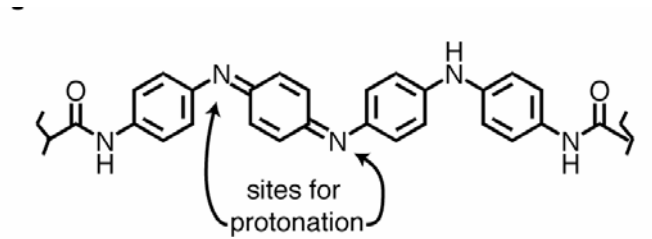
No connection

* Bis-oxazole with Monoamine

No connection

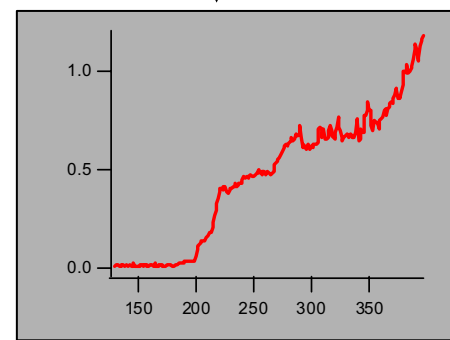
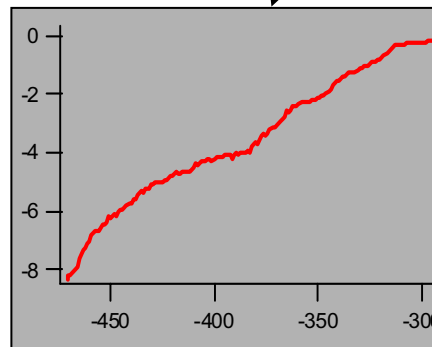
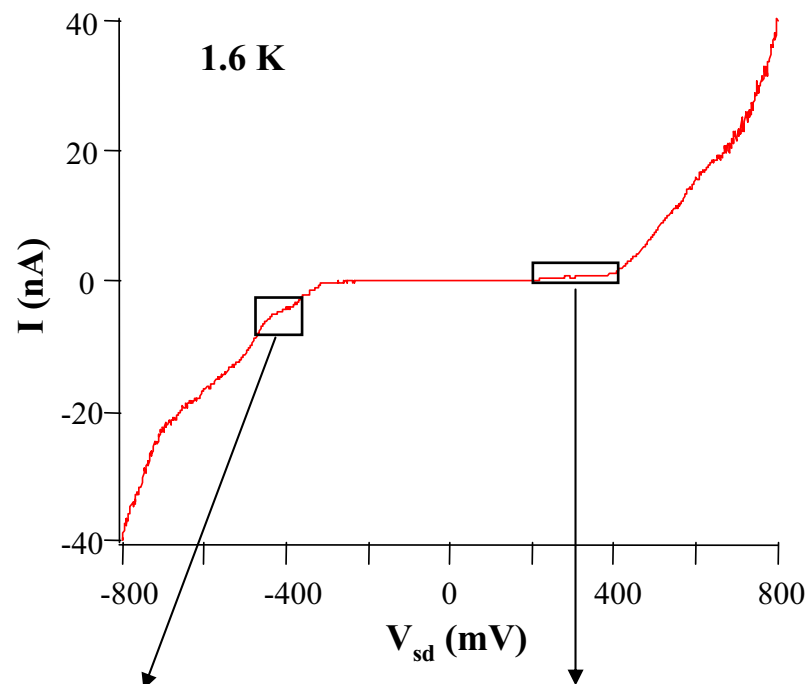
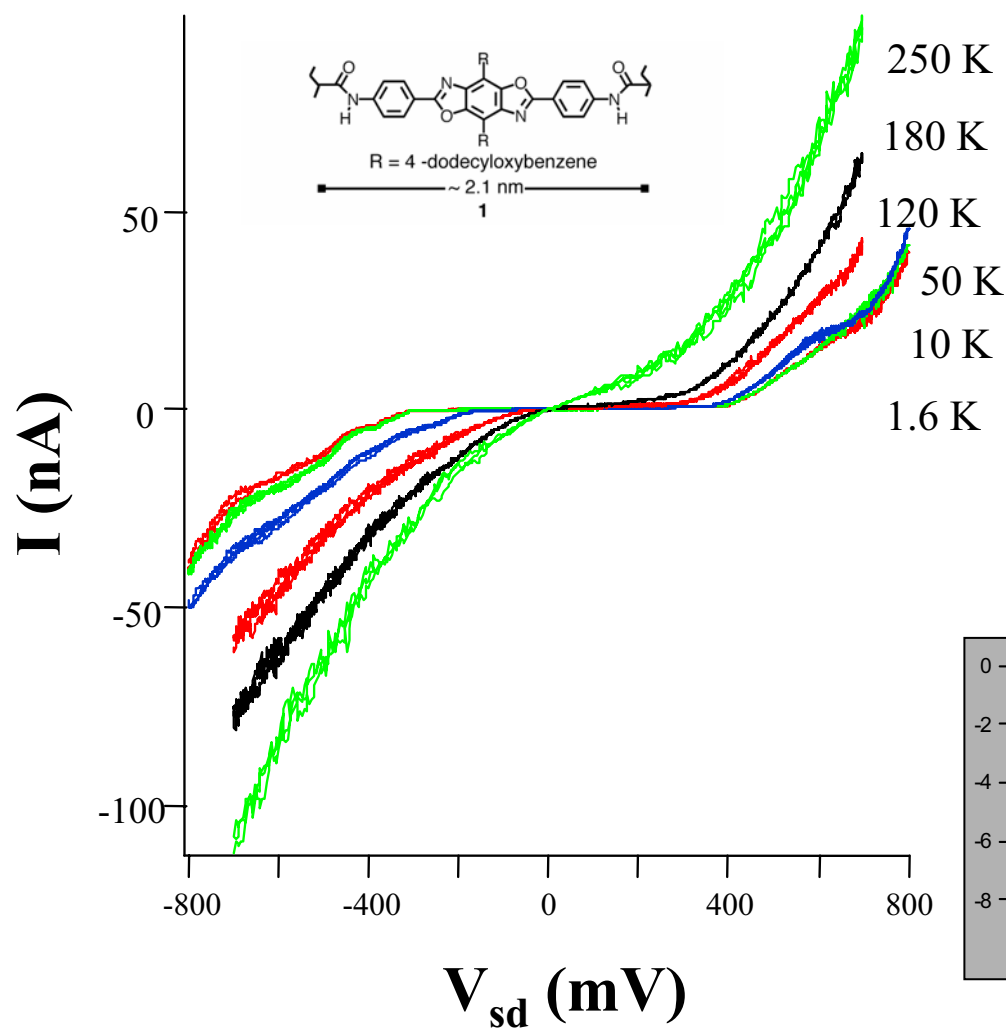
* 1,12 dodecane diamine (insulator)

No connection

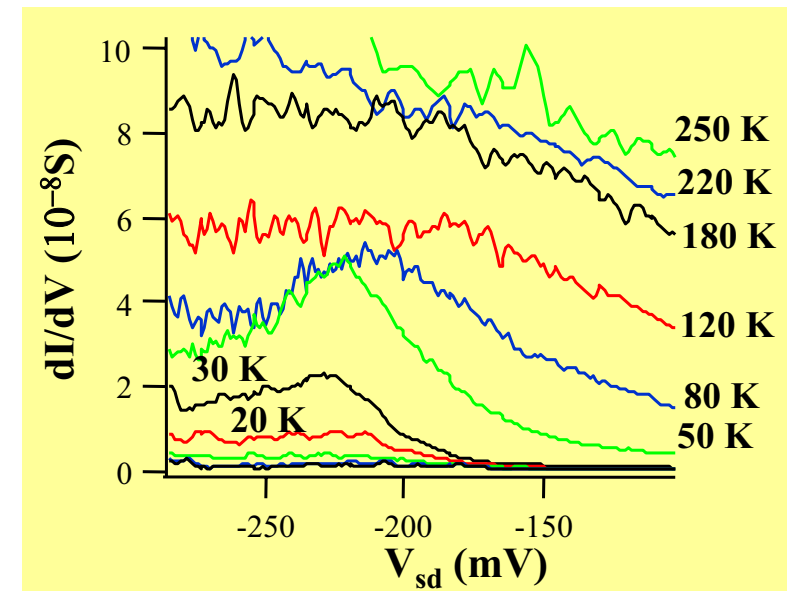
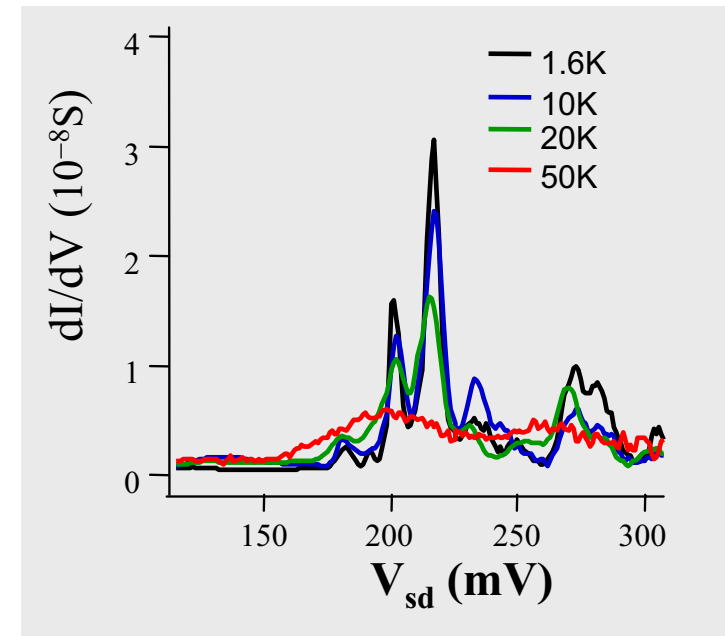
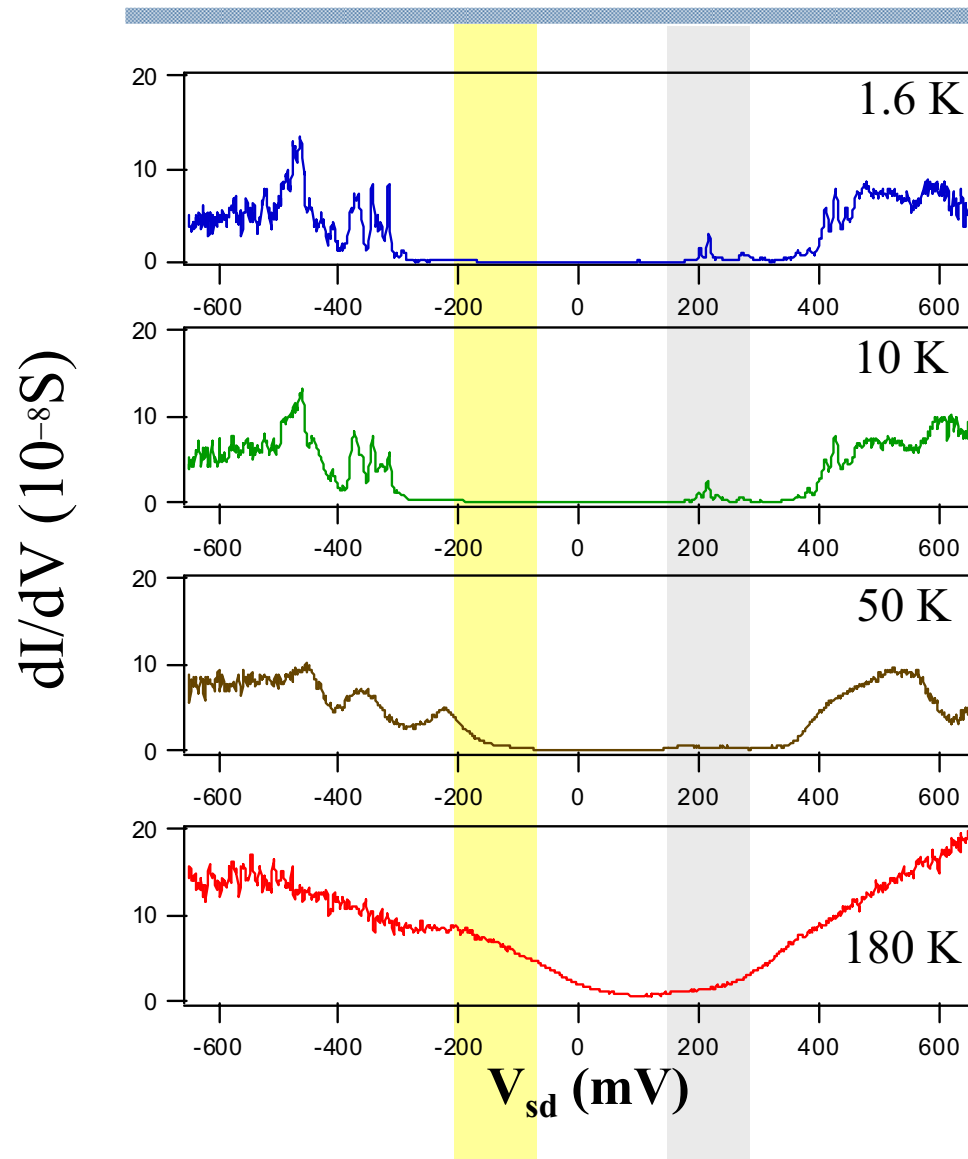


Transport Measurement

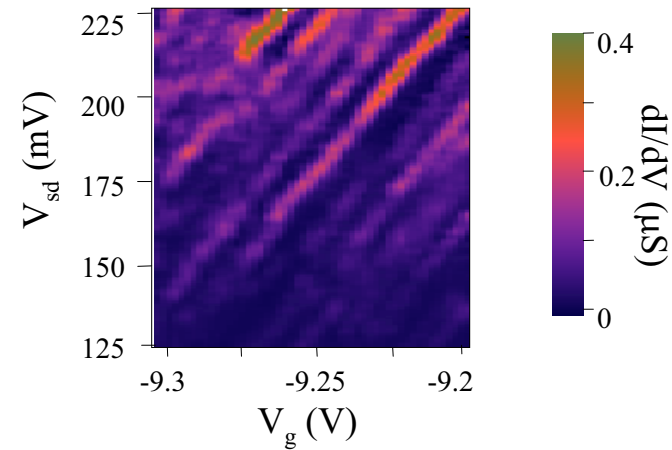
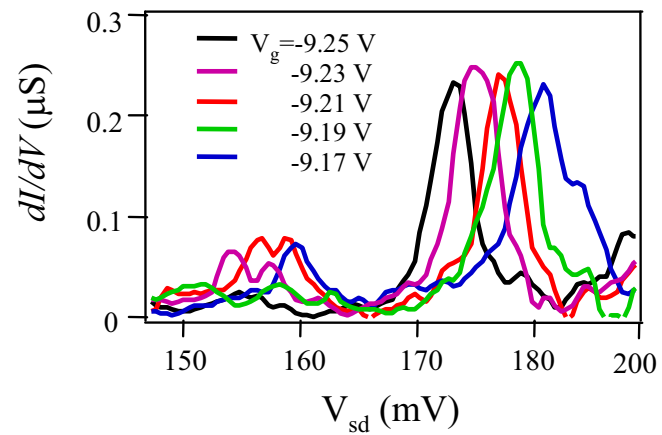
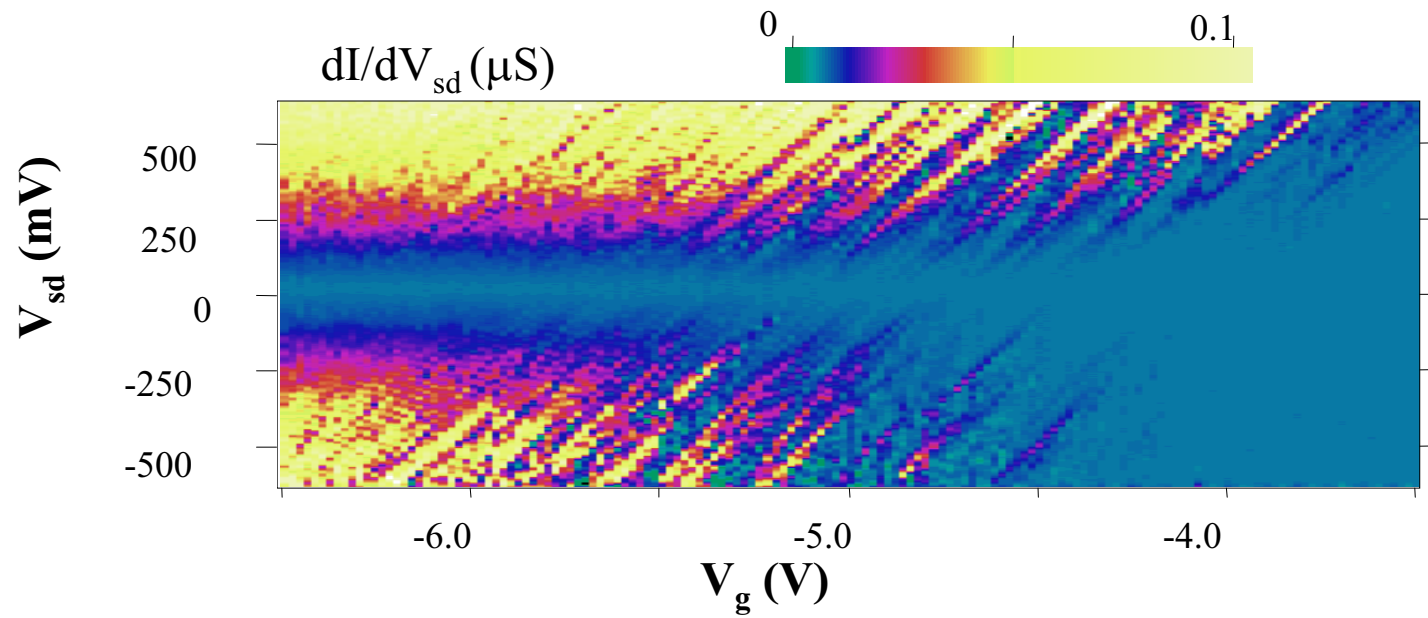
Bis-oxazole + metallic SWNT



Temperature Dependence Transport Spectroscopy

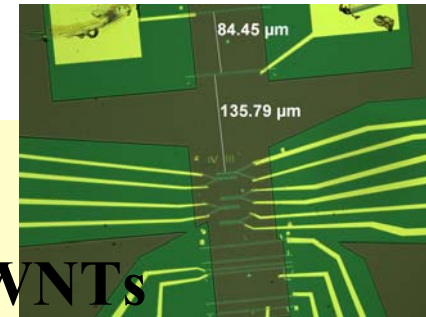


Gate Voltage Dependence

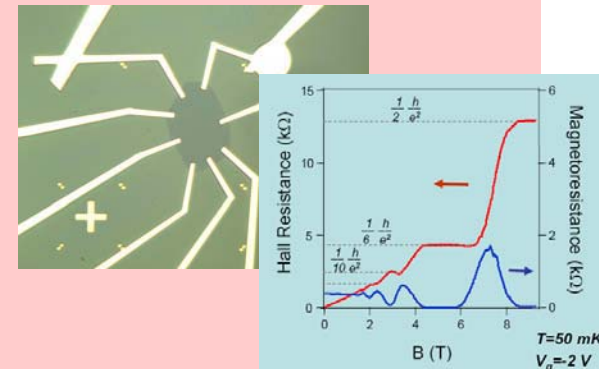


Summary

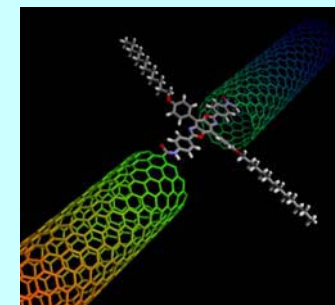
- Transport in long nanotubes:
Extremely long mean-free path in SWNTs



- Transport in graphene:
Unusual quantum Hall effect
Graphene nano ribbon devices



- Nanotube electrode for
single molecular electronics



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