Introduction to Nanotechnology
Chapter 5 Carbon Nanostructures
Lecture 2

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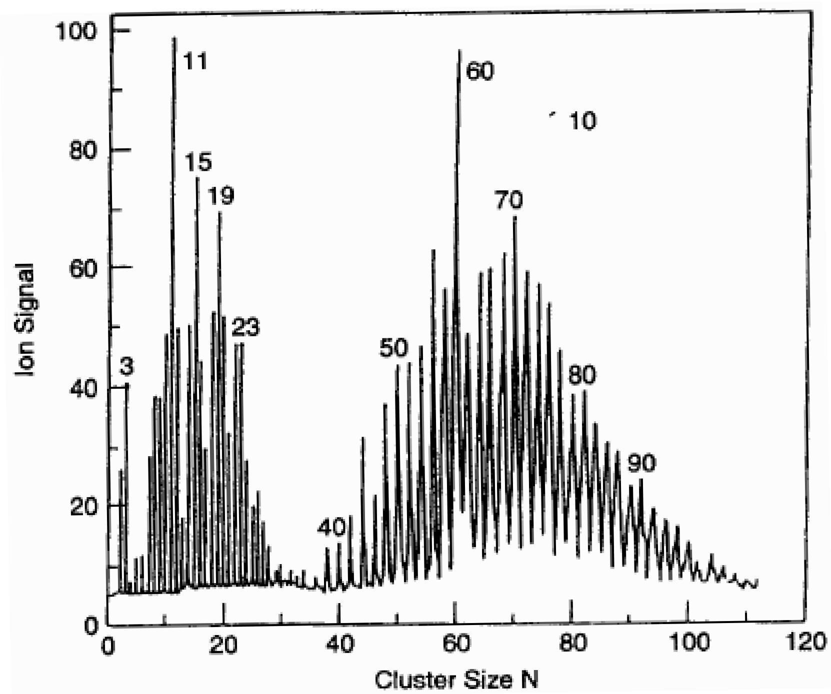


Fig. 5.3 Mass spectrum of Laser evaporated Carbon clusters. The C_{60} and C_{70} peaks are evident.

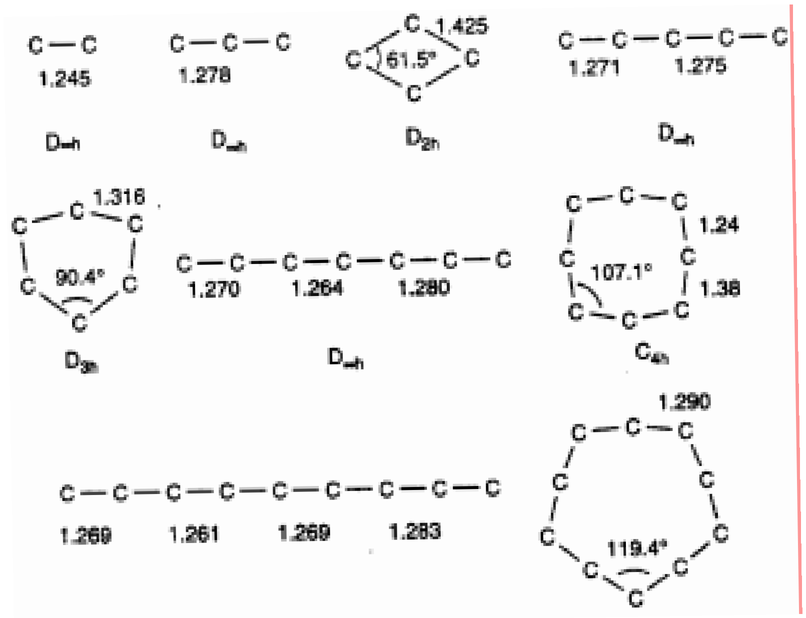
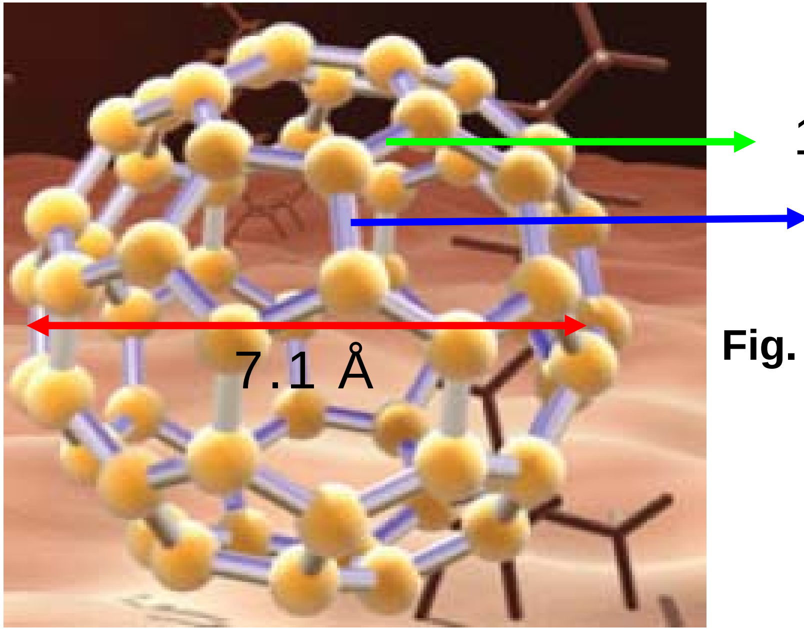


Fig. 5.4 Result of molecular orbital theory for the structure of small clusters

Odd N: linear structure, sp hybridization

Even N: closed structure



1.388 Å (C=C:1.34 Å)

1.432Å (C-C:1.53 Å)

Fig. 5.6 structure of C_{60} fullerene molecule

- **contains 12 pentagonal and 20 hexagonal**
- **The pentagons are needed to produce closed (convex) surfaces, and hexagons lead to a planar surface.**

Electric properties:

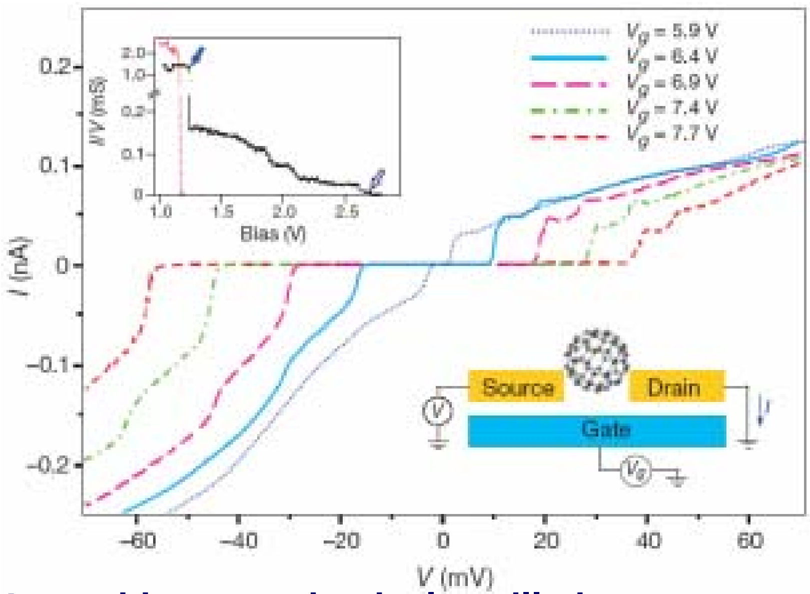
- **Pure C_{60} is an electrical insulator**
- **C_{60} doped with alkali metals shows a range of electrical conductivity:**
  - **Insulator (K_6 C_{60}) to superconductor (K_3 C_{60}) < 30 K!**

C_{60}^{3-} with 3 ionized K^+ , a highly disordered material

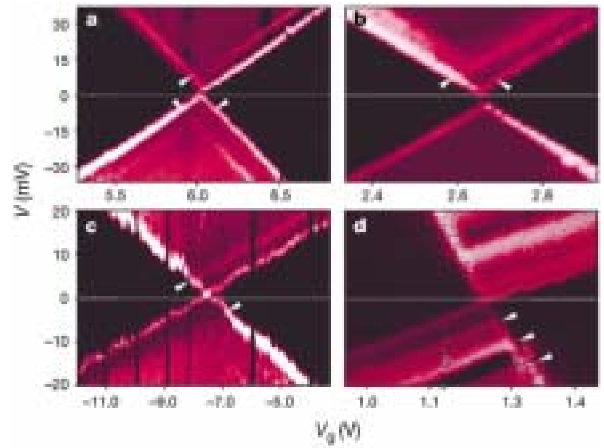
Other superconducting compounds:
Rb_3C_{60}, Cs_3C_{60}, Na_3C_{60}

Nanomechanical oscillations in a single-C_{60} transistor

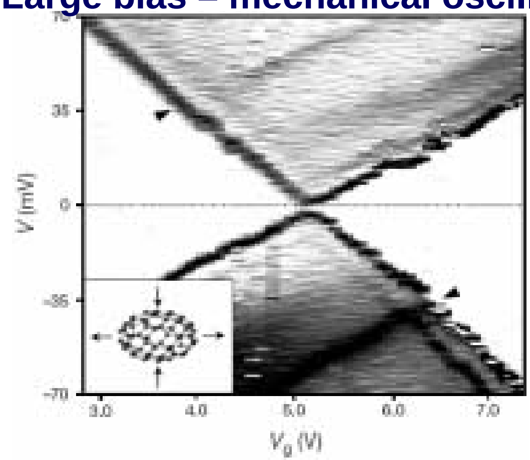
Hingkun Park et al. Nature 407, 58 (2000)

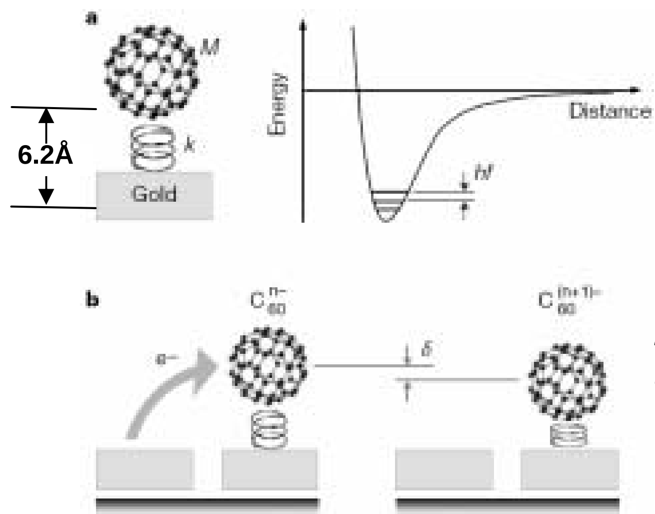


Small bias – Quantized levels



Large bias – mechanical oscillation





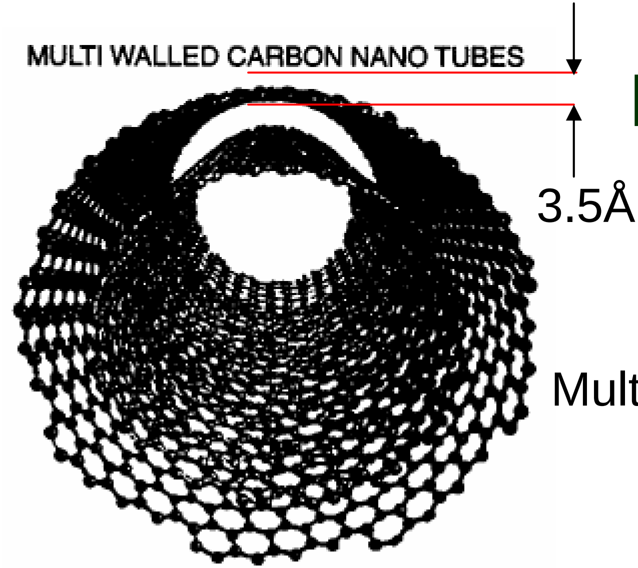
K ≈ 70N/m

f **≈ 1.2THz**

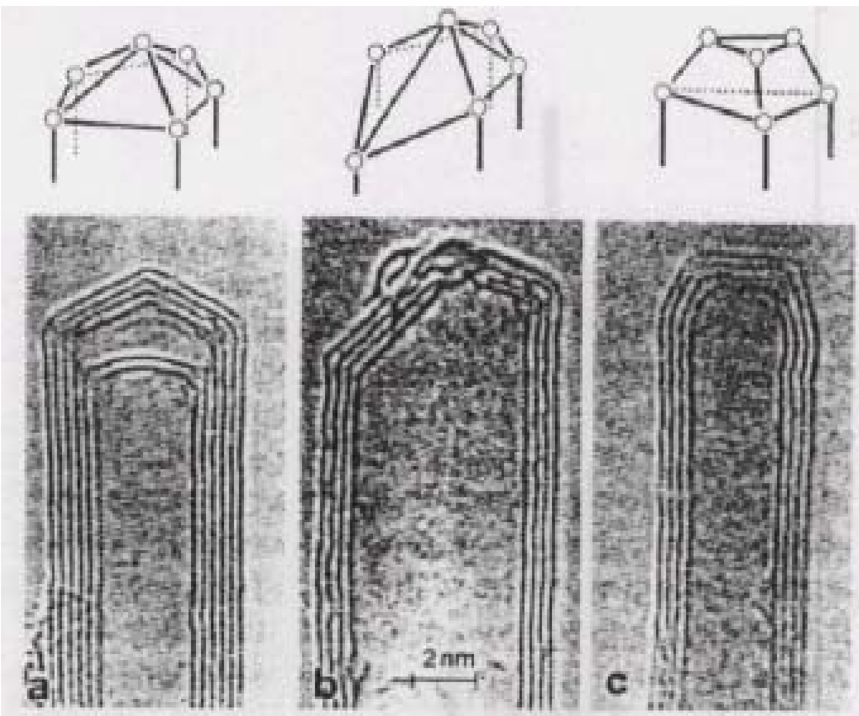
hf **≈ 5meV**

δ ≈ 4pm

Multiwalled carbon nanotubes

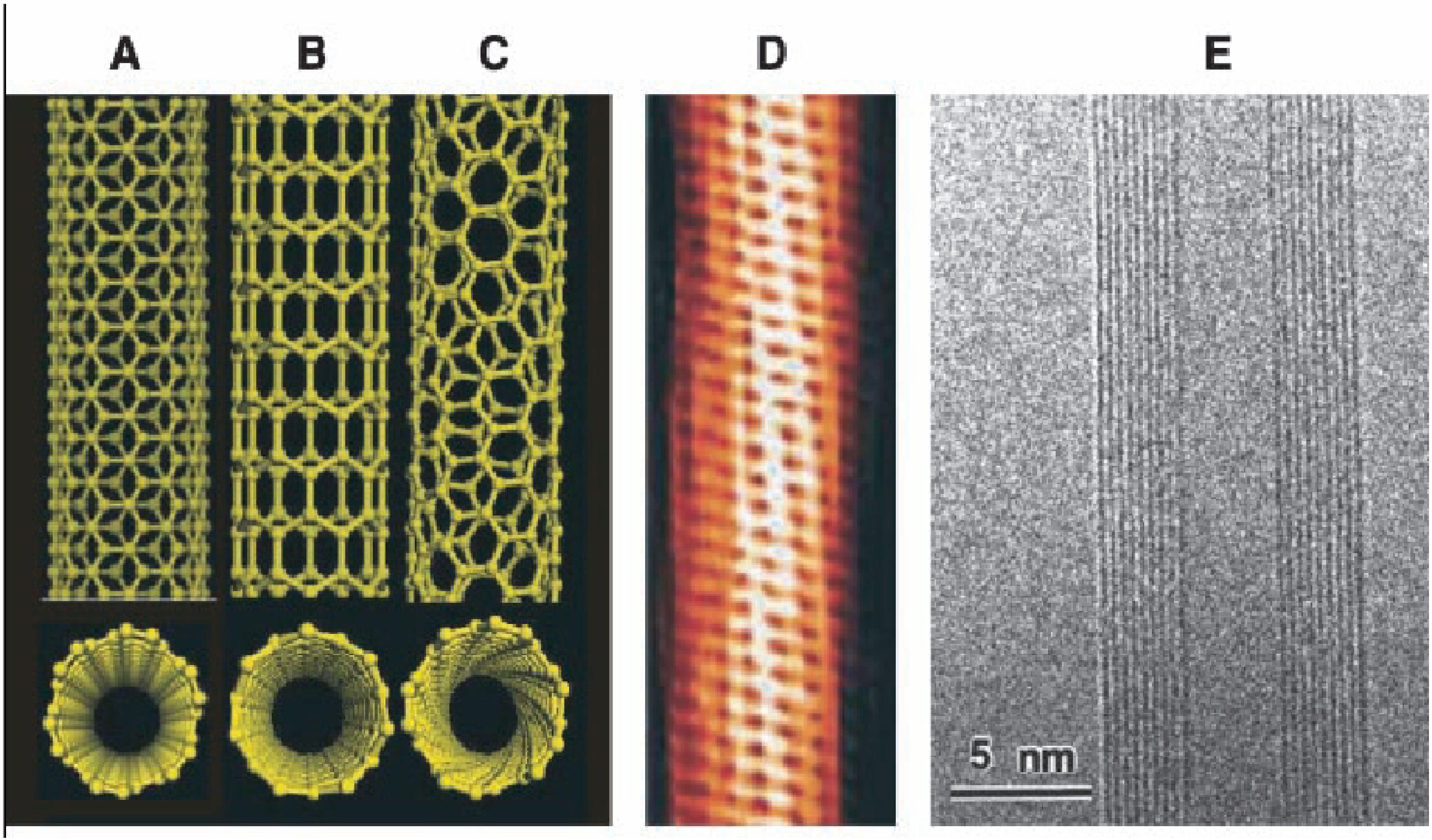


Multiwalled nanotube consists of capped concentric cylinders separated by ~ 3.5 Å.



Three common cap terminations

a) **A symmetric polyhedral cap**
b) **An asymmetric polyhedral cap**
c) **A symmetrical flat cap**



(a) Armchair (b) zigzag (c) chiral (d) by STM (e) by TEM, multiwalled

Three major categories of nanotube structures can be identified based on the values of *m* and *n*

***m* = *n* "Armchair"**
***m* = 0 or *n* = 0 "Zigzag"**
***m* ≠ *n* "Chiral"**

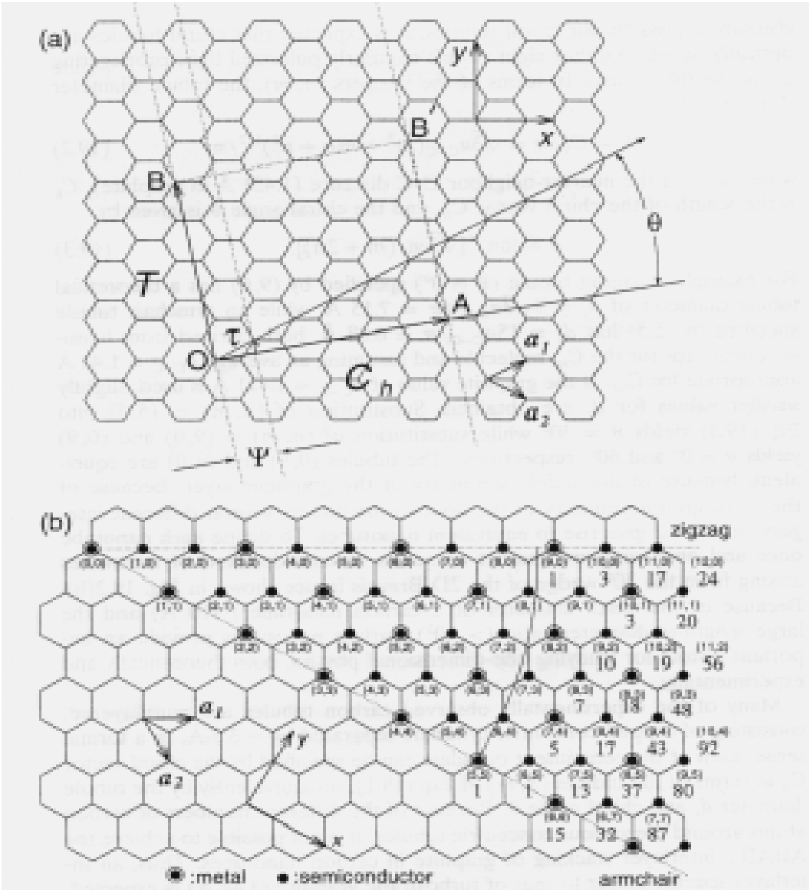
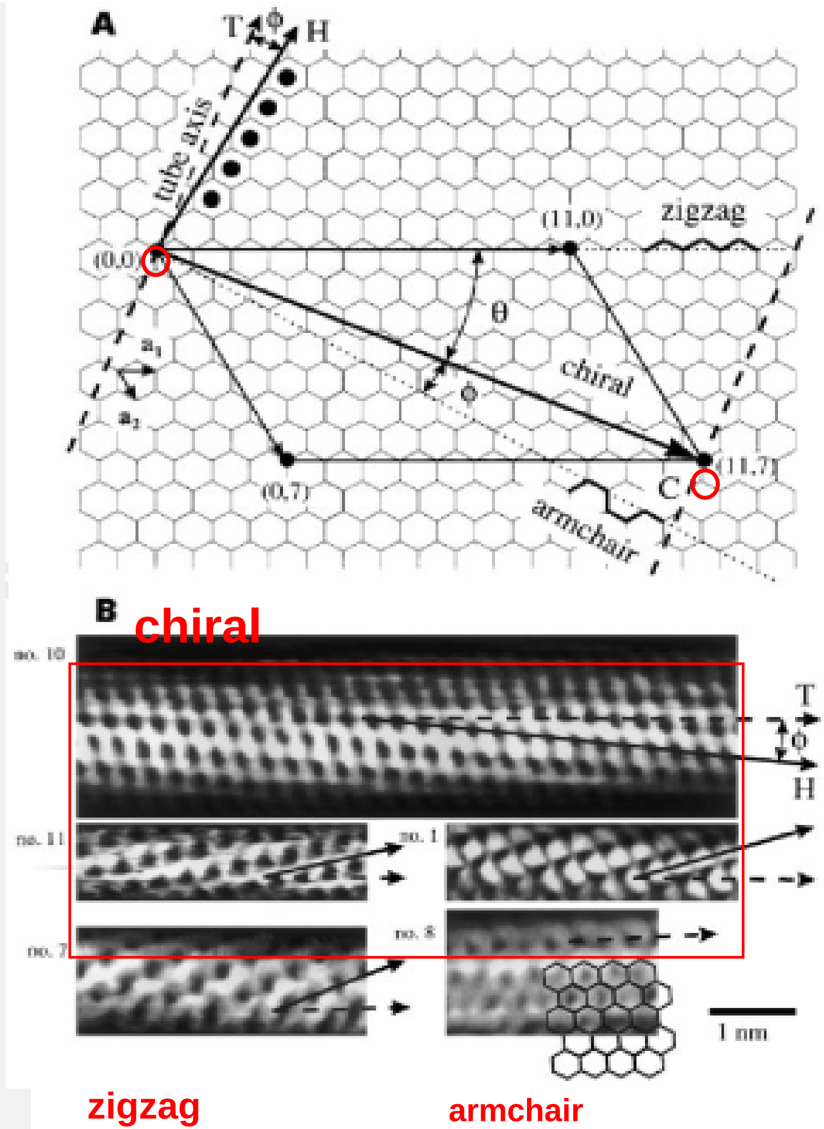


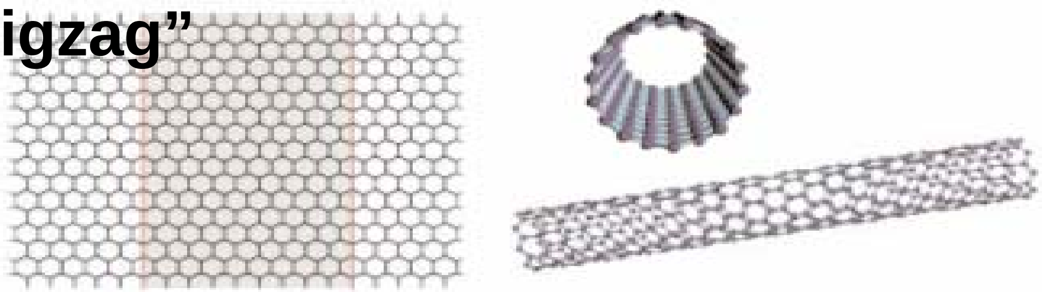
Fig. 19.2. (a) The chiral vector $\vec{OA}$ or $C_h = na_1 + ma_2$ is defined on the honeycomb lattice of carbon atoms by unit vectors a_1 and a_2 and the chiral angle θ with respect to the zigzag axis. Along the zigzag axis, $\theta = 0°$. Also shown are the lattice vector $\vec{OB} = T$ of the 1D tubule unit cell and the rotation angle ψ and the translation τ which constitute the basic symmetry operation $R = (\psi|\tau)$ for the carbon nanotube. The diagram is constructed for $(n, m) = (4, 2)$. (b) Possible vectors specified by the pairs of integers (n, m) for general carbon tubules, including zigzag, armchair, and chiral tubules. Below each pair of integers (n, m) is listed the number of distinct caps that can be joined continuously to the carbon tubule denoted by (n, m) [19.4], as discussed in §19.2.3. The encircled dots denote metallic tubules while the small dots are for semiconducting tubules.

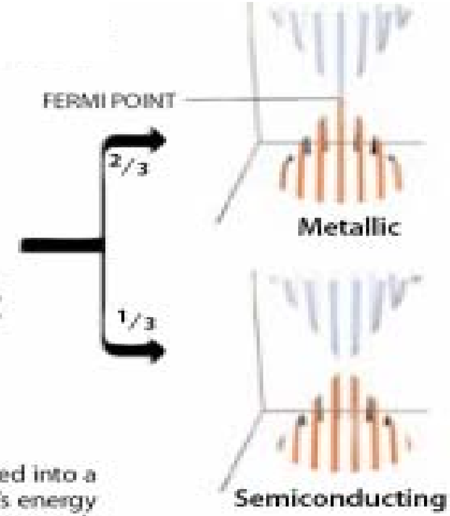
Nature 391, 59, (1998)



ternal boosts, only a few electrons can access the narrow path to a conduction state.

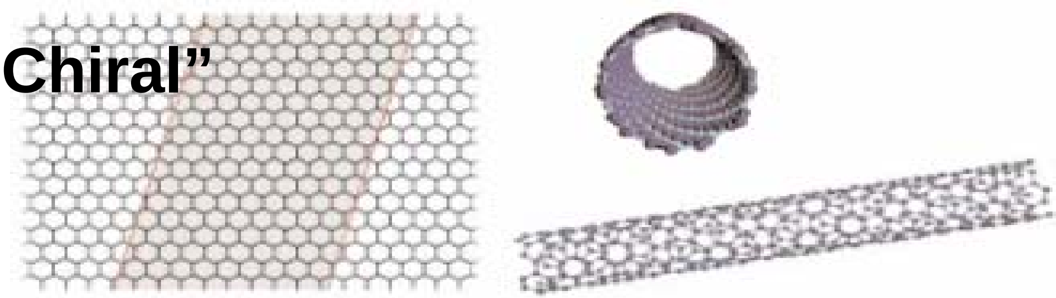
“Zigzag”

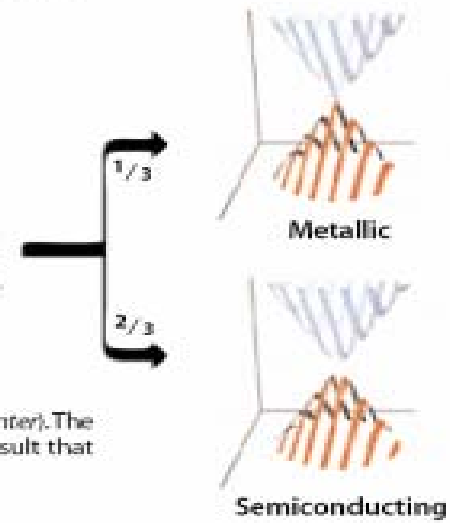




STRAIGHT NANOTUBES look like a straight swath cut from a sheet of graphite (*left*) and rolled into a tube (*center*). The geometry of nanotubes limits electrons to a select few slices of graphite's energy states (*right*). Depending on the diameter of the tube, one of these slices can include the narrow path that joins electrons with conduction states. This special point, called the Fermi point, makes two thirds of the nanotubes metallic. Otherwise, if the slices miss the Fermi point, the nanotubes semiconduct.

“Chiral”



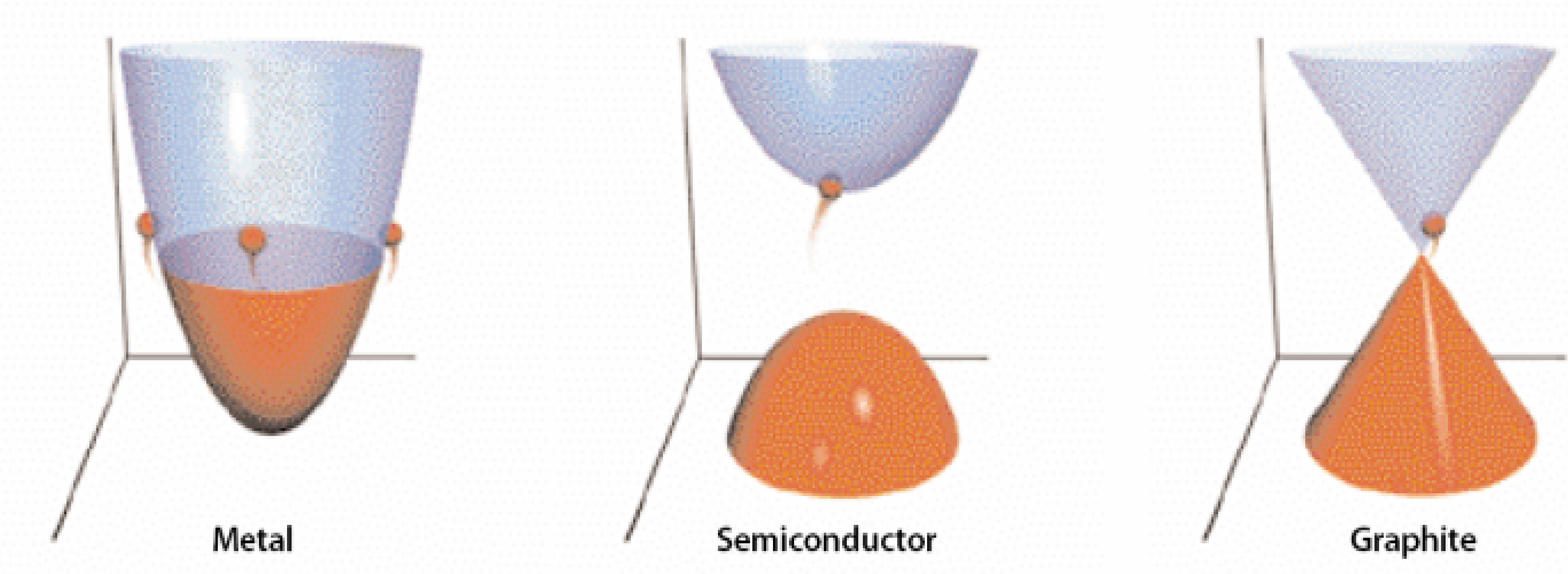


TWISTED NANOTUBES, cut at an angle from graphite (*left*), look a bit like barbershop poles (*center*). The slices of allowed energy states for electrons (*right*) are similarly cut at an angle, with the result that about two thirds of twisted tubes miss the Fermi point and are semiconductors.

Scientific American December 62 2000

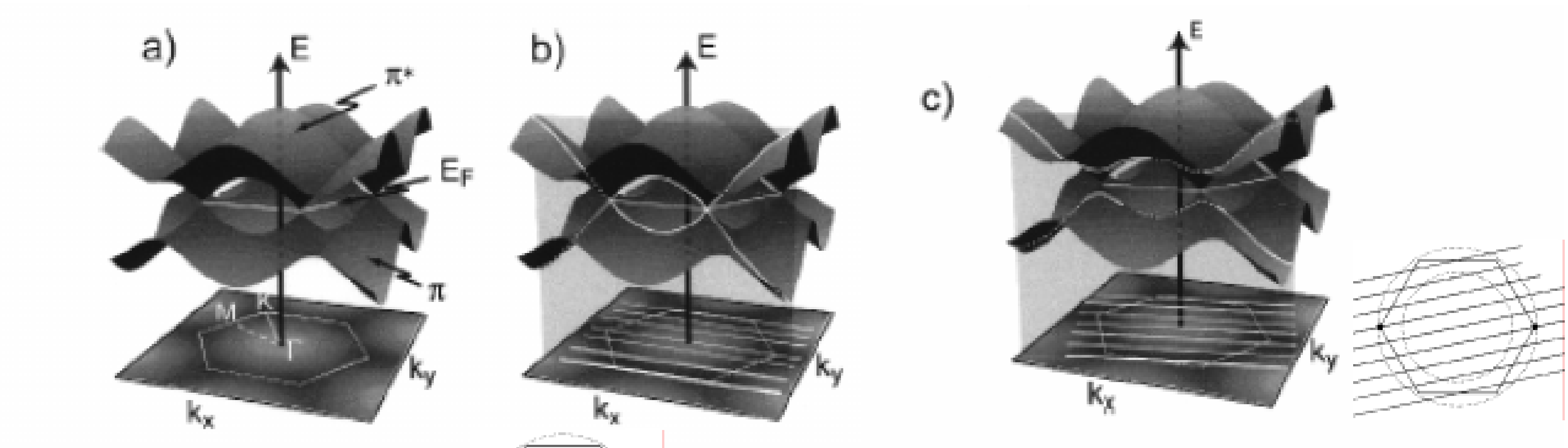
“Armchair” always metallic

A Split Personality



ELECTRICAL PROPERTIES of a material depend on the separation between the collection of energy states that are filled by electrons (*red*) and the additional "conduction" states that are empty and available for electrons to hop into (*light blue*). Metals conduct electricity easily because there are so many electrons with easy access to adjacent conduction states. In semiconductors, electrons need an energy boost from light or an electrical field to jump the gap to the first available conduction state. The form of carbon known as graphite is a semimetal that just barely conducts, because without these external boosts, only a few electrons can access the narrow path to a conduction state.

Scientific American December 62 2000



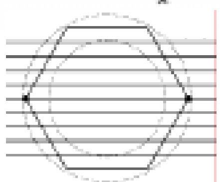


Fig. 2. (a). Band structure of a graphene sheet (top) and the first Brillouin zone (bottom). (b) Band structure of a metallic (3,3) CNT. (c) Band structure of a (4,2) semiconducting CNT. The allowed states in the nanotubes are cuts of the graphene bands indicated by the white lines. If the cut passes through a K point, the CNT is metallic; otherwise, the CNT is semiconducting.

J. Tersoff, APL, 74, 2122, (99)

http://www.ece.eng.wayne.edu/~jchoi/06012004.pdf

a) Graphite

Valence(π) and Conduction (π*) states touch at 6 Fermi points

Carbon nanotube:

Quantization from the confinement of electrons in the circumferential direction

circumference = $n\lambda_F$

b) (3,3) CNT; allowed energy states of CNT cuts pass through Fermi point → metallic

c) (4,2) CNT; no cut pass through a K point ⟶ semiconducting

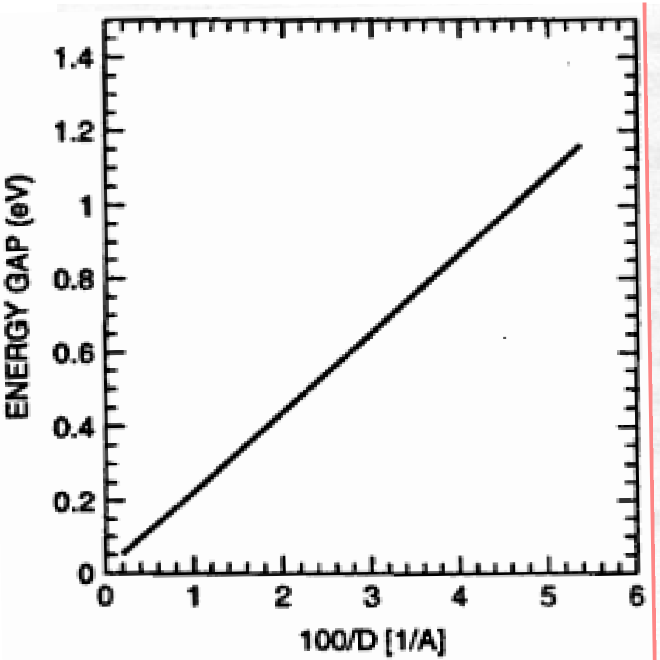
$$E_{gap} = \frac{4\hbar v_F}{3d_{CNT}}$$

In general, for a chiral tubule, we have the following results:

n - m = 3q metallic, no gap

n - m ≠ 3q semiconductor with gap

$$d_{CNT} = \frac{2.46\sqrt{n^2 + nm + m^2}}{2\pi}\ \text{nm}$$



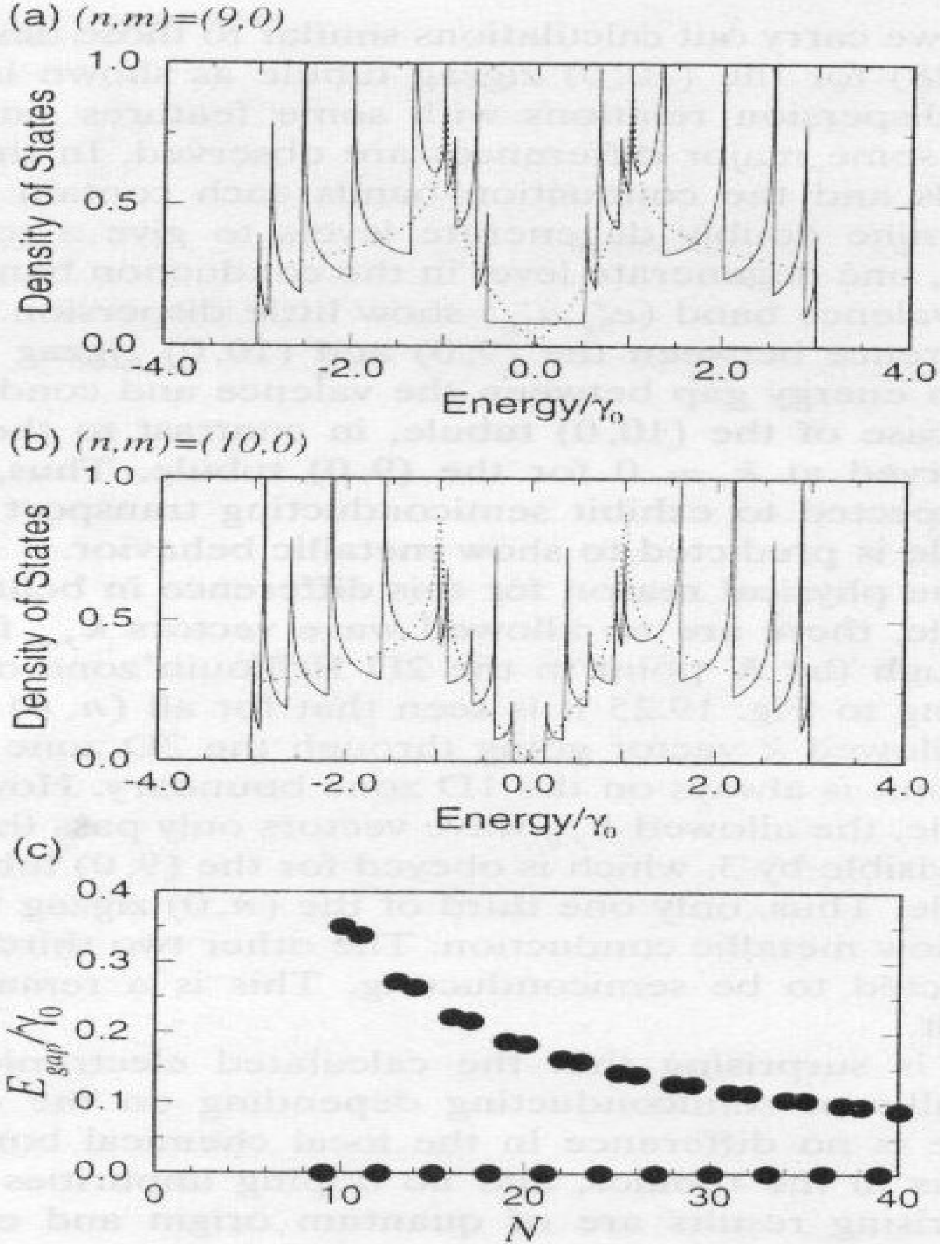


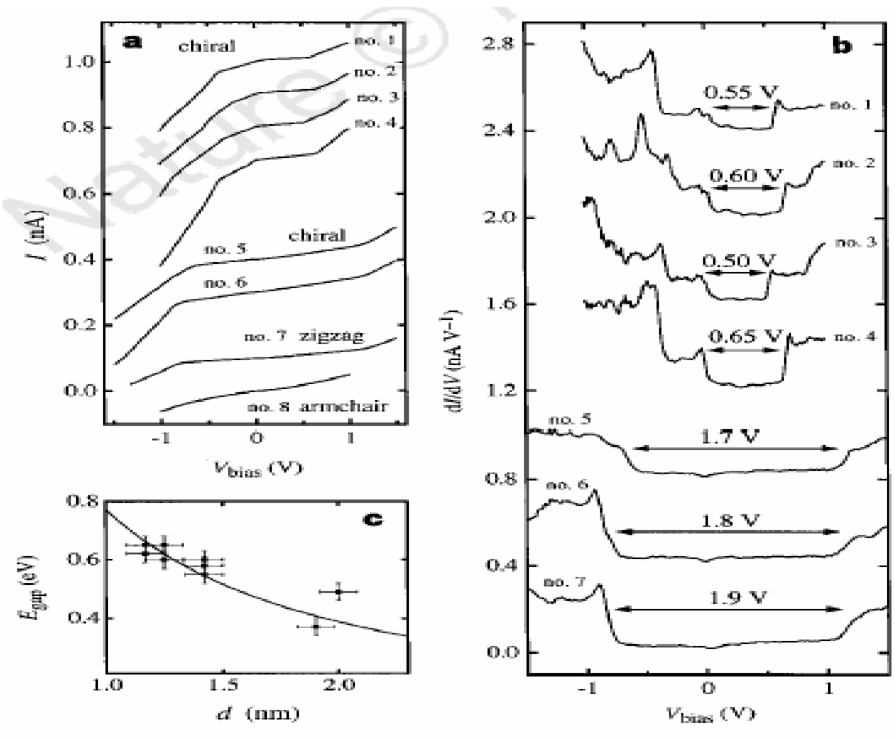
Fig. 19.27. Electronic 1D density of states per unit cell for two (n, m) zigzag tubules based on zone folding of a 2D graphene sheet: (a) the (9,0) tubule which has metallic behavior, (b) the (10,0) tubule which has semiconducting behavior. Also shown in the figure is the density of states for the 2D graphene sheet (dashed curves) [19.98]. (c) Plot of the energy gap for $(n, 0)$ zigzag nanotubes plotted in units of γ_0 as a function of n, where γ_0 is the energy of the nearest-neighbor overlap integral for graphite [19.100].

≈2.5eV

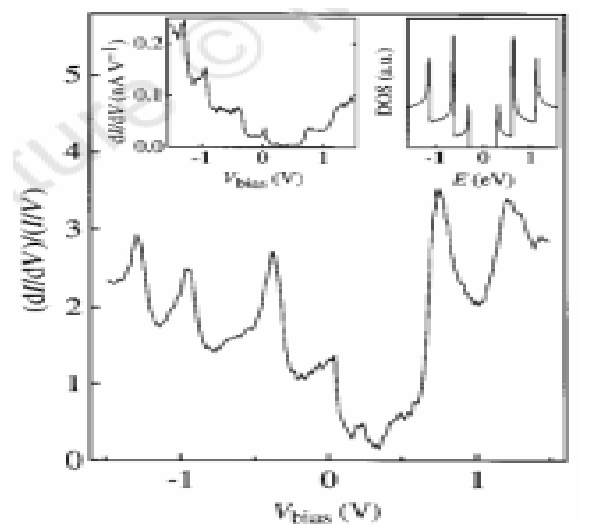
Curves Nos 1-7 show a low conductance at low bias, followed by several kinks at larger bias voltages, however, the armchair tube does not show clear kinks in the range -1 to +1 V.

Gaps are indicated by arrows. Two categories of gaps: one with gap values around 0.5 - 0.6eV(semiconducting); the other with significantly larger gap values,1.7 - 1.9eV (metallic).

Gap *Egap* versus diameter *d* for semiconducting tubes: solid line denotes a fit of $E_{gap} = 2\,\gamma_0\, a_{C\text{-}C}/d$ with $\gamma_0 = 2.7$eV.



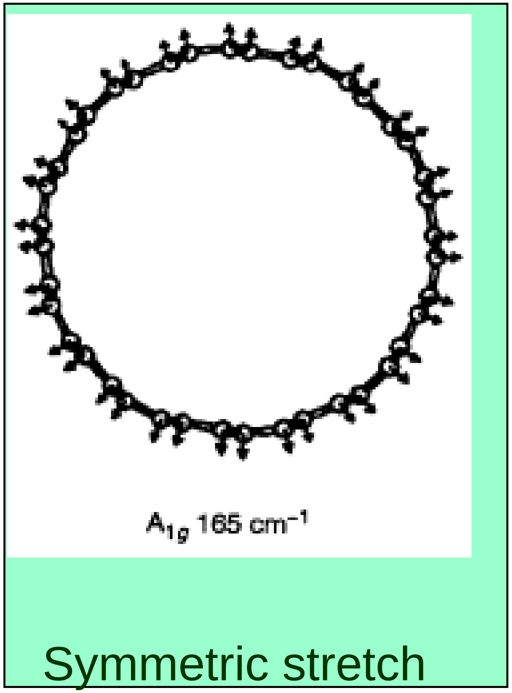
Van Hove singularities in the DOS, reflecting the one-dimensional character of carbon nanotubes.



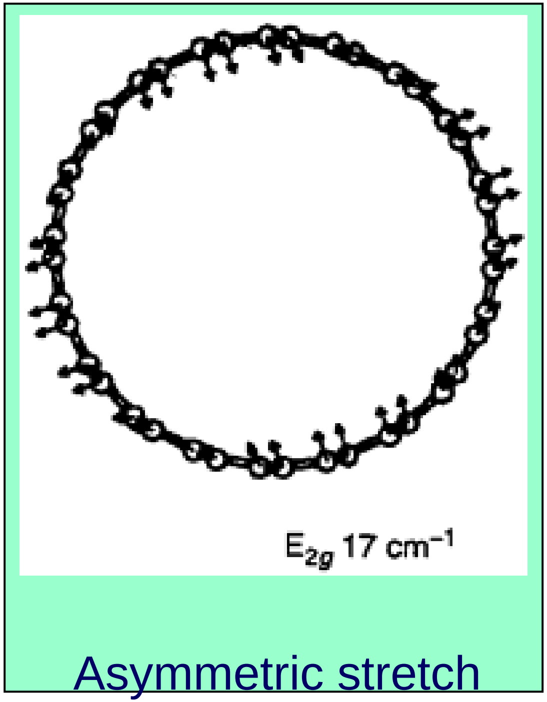
Nature 391, 59, (1998)

Tube no.9, (16,0)

Cross-section view of the vibration modes

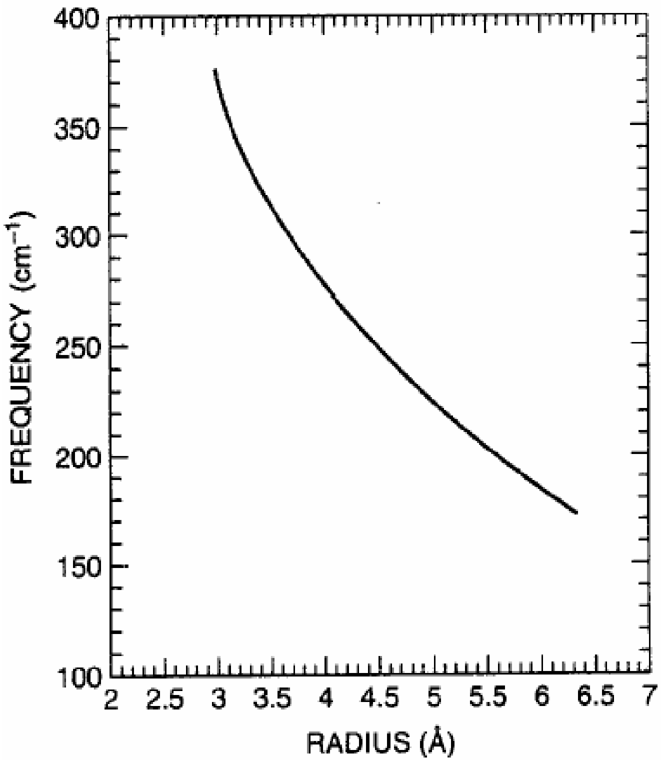


Symmetric stretch



Asymmetric stretch

Determination of the tube diameter from A_{1g} Raman vibration frequency



One can then "guess" a set of (m,n) from

$$d_{CNT} = \frac{2.46\sqrt{n^2 + nm + m^2}}{2\pi}\ \text{nm}$$

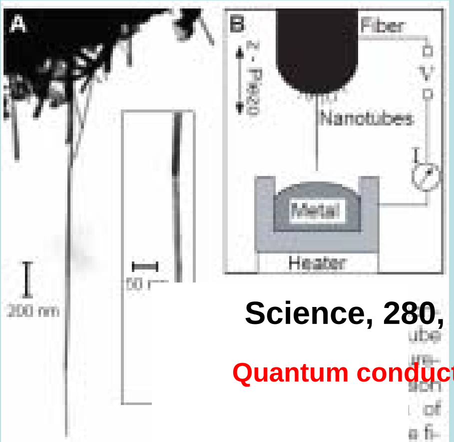
Figs. 5-19 and 5-20

Properties of Carbon Nanotubes:

- High carrier mobility – ballistic transport($<$1-10µm);~$>$10,000 cm^2/V-sec($>$10µm) (Si$<$500 cm^2/V-sec).
- High current carrying capabilities: $J=10^9 A/cm^2$ (Most metal fails at $<10^6 A/cm^2$, Si ~ $10^3 A/cm^2$).
- No Interface states - any dielectric is in principle possible (Si devices need SiO_2).
- Potential for optical devices – direct bandgap material, bandgap determined by diameter (Si is indirect).
- Potential for sensor applications – all the atoms are on the surface.
- Diameter determines semiconducting (2/3) vs metallic tubes (1/3), and placement.

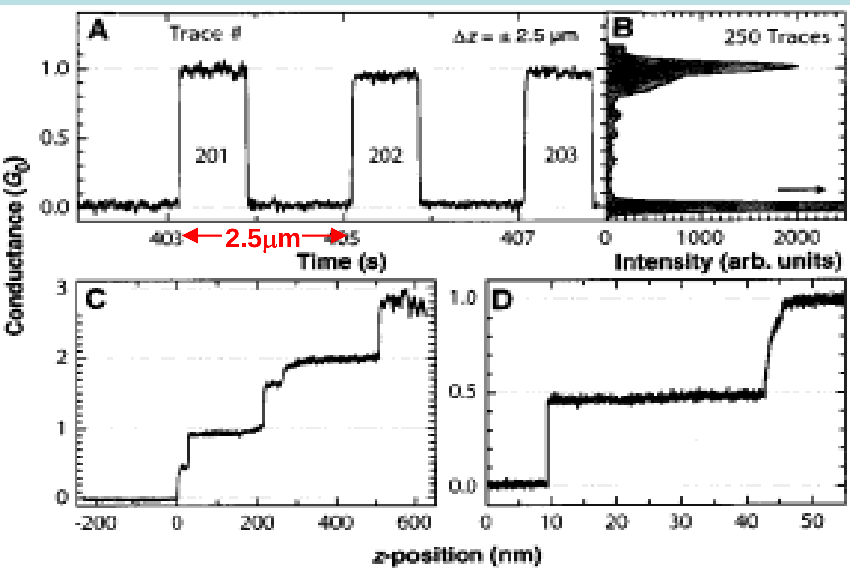
http://www.cns.cornell.edu/documents/CornellUniversity_PN_Diode_2005_Final_1of3_000.pdf

Conductance quantization for metallic carbon nanotubes



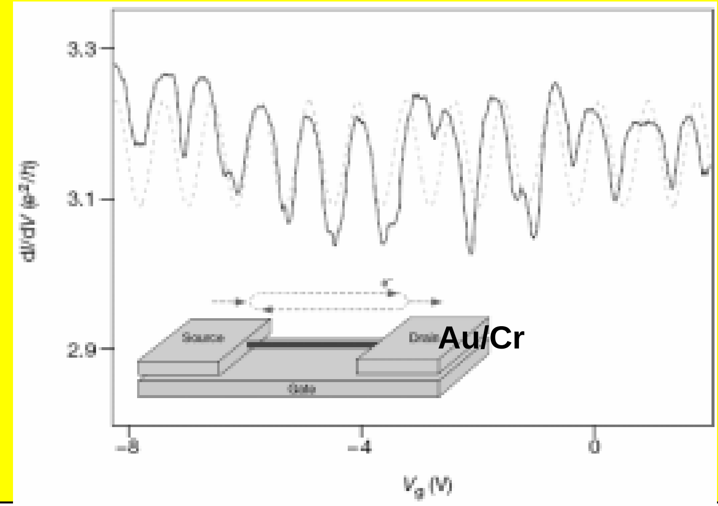
Science, 280, 1774 (98)

Quantum conductance in Multiwalled CNTs



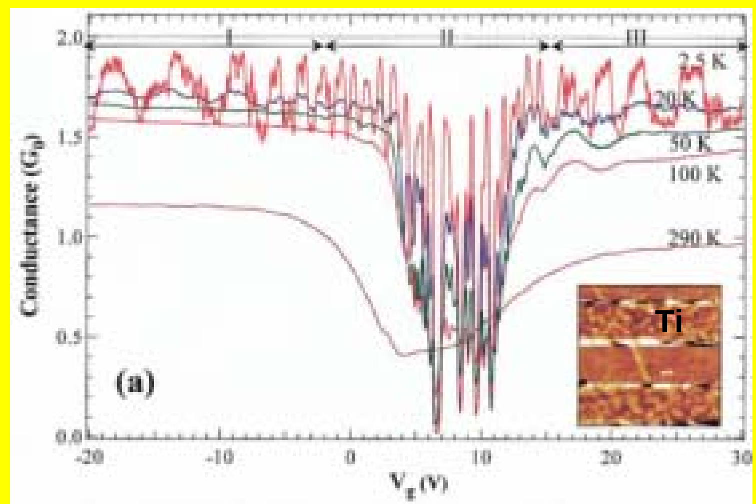
Fabry-Perot interference in a nanotube electron waveguide

Nature, 411,665 (01)

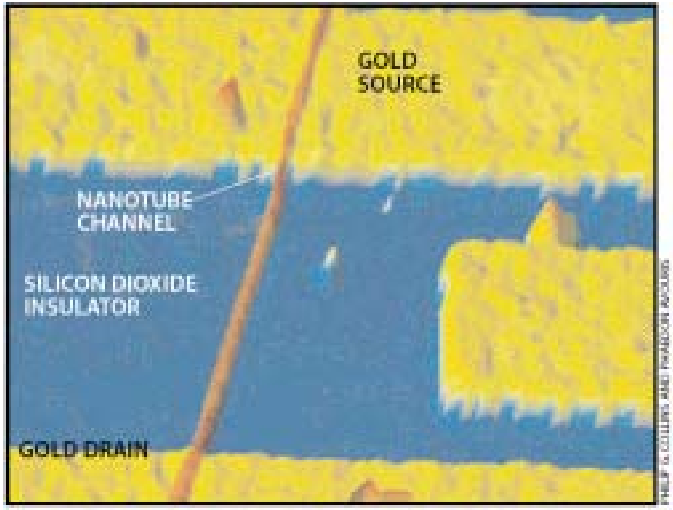


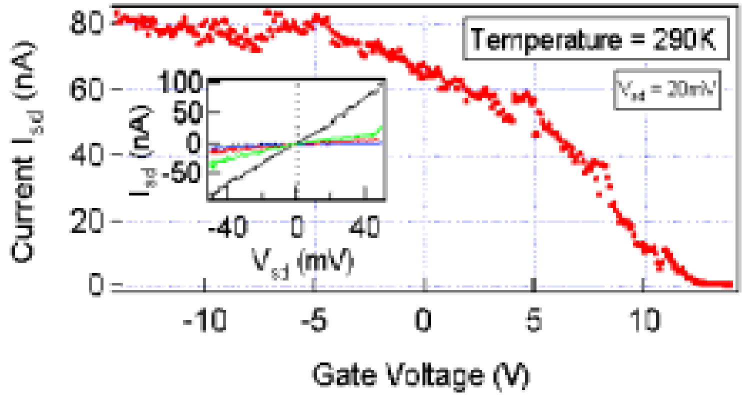
Quantum Interference and Ballistic Transmission in Nanotube Electron Waveguides

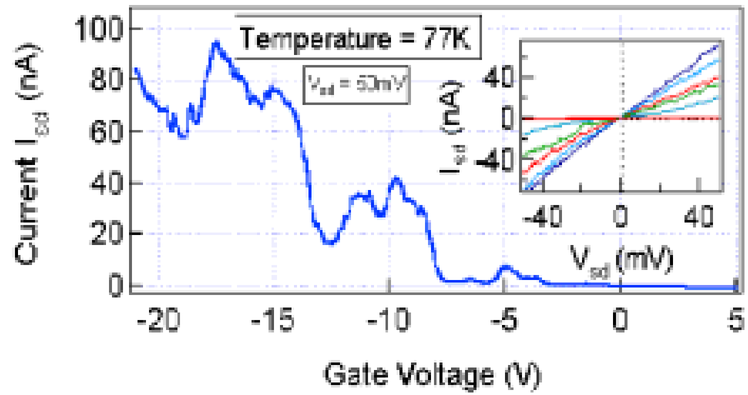
PRL, 87, 106801 (01)

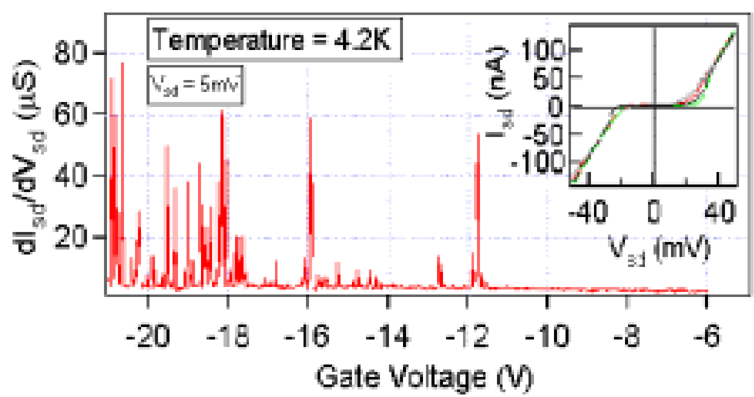


Transition from FET to SET





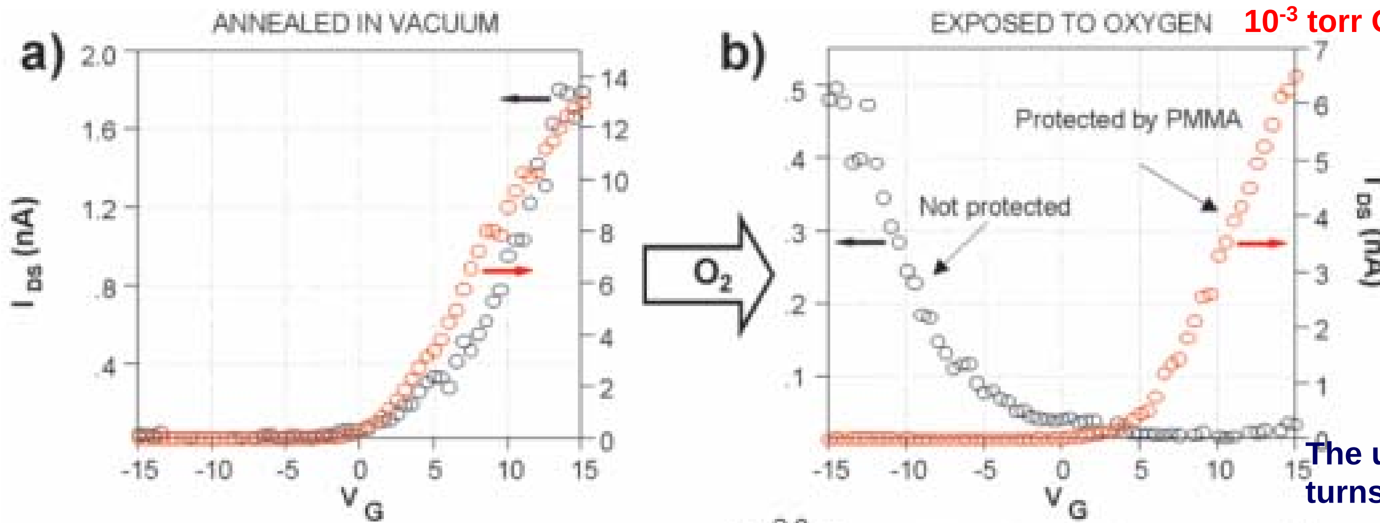




As we cool the FET down from room temperature to 4 degree Kelvin (minus 460 degree Fahrenheit) we see the device behavior change dramatically. While the device acts like a field-effect transistor at room temperature, at 4K it behaves like a single-electron transistor (SET).

http://www.research.ibm.com/nanoscience/fet.html

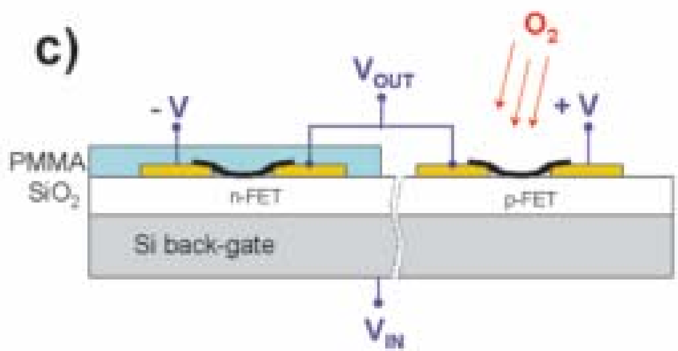
A SWCNT “NOT” GATE

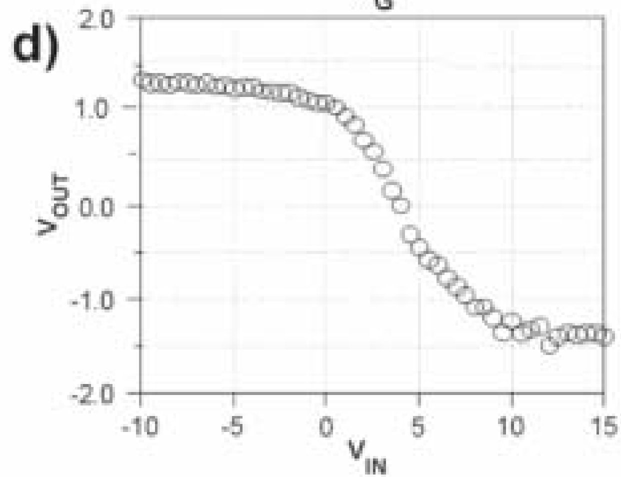


10^{-3} torr O_2 for 3min

The unprotected one turns back to p-type

Two originally p-type CNTs are converted into n-type



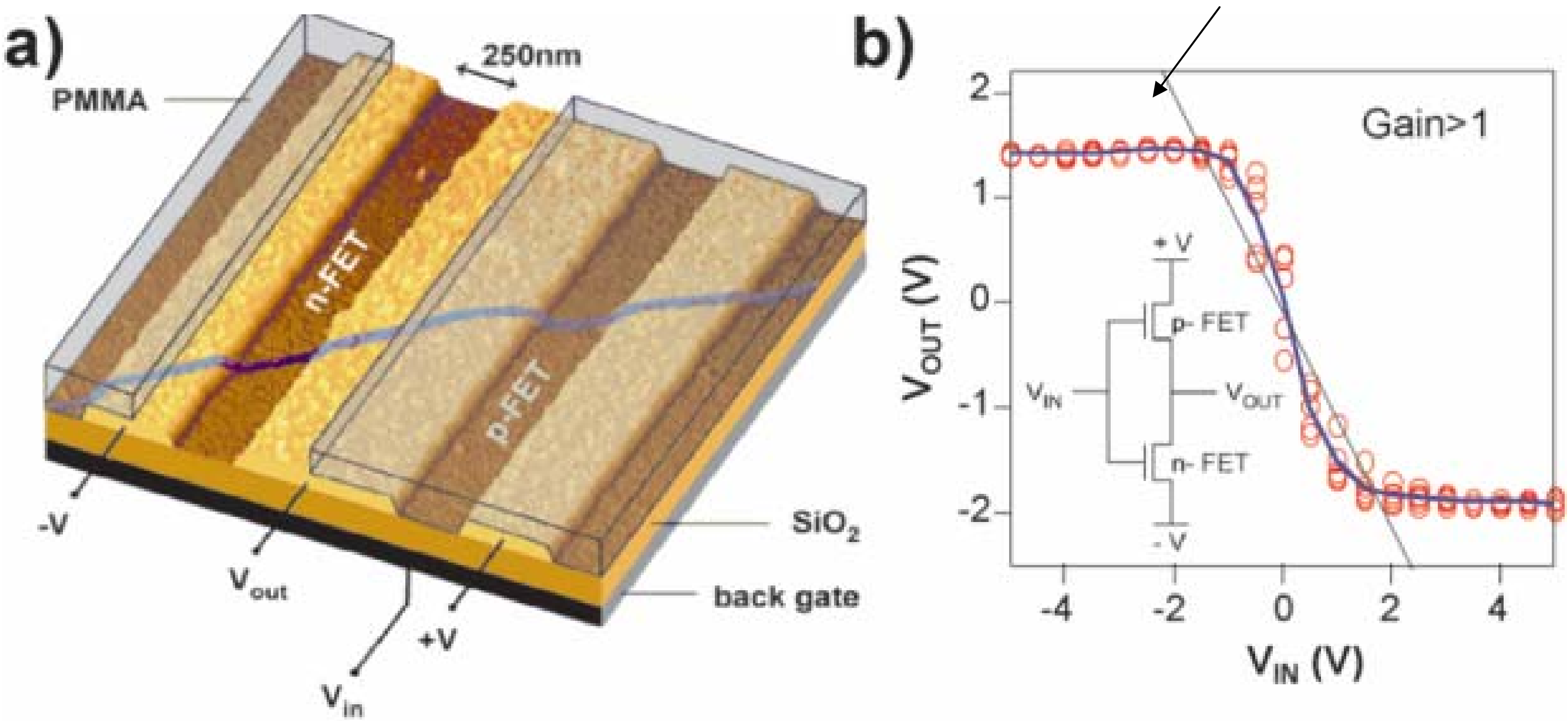


form an inverter

Wiring two CNT in a CMOS circuit

V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris
Nano Letters, 1, 453 (2001)

A SWCNT CMOS device



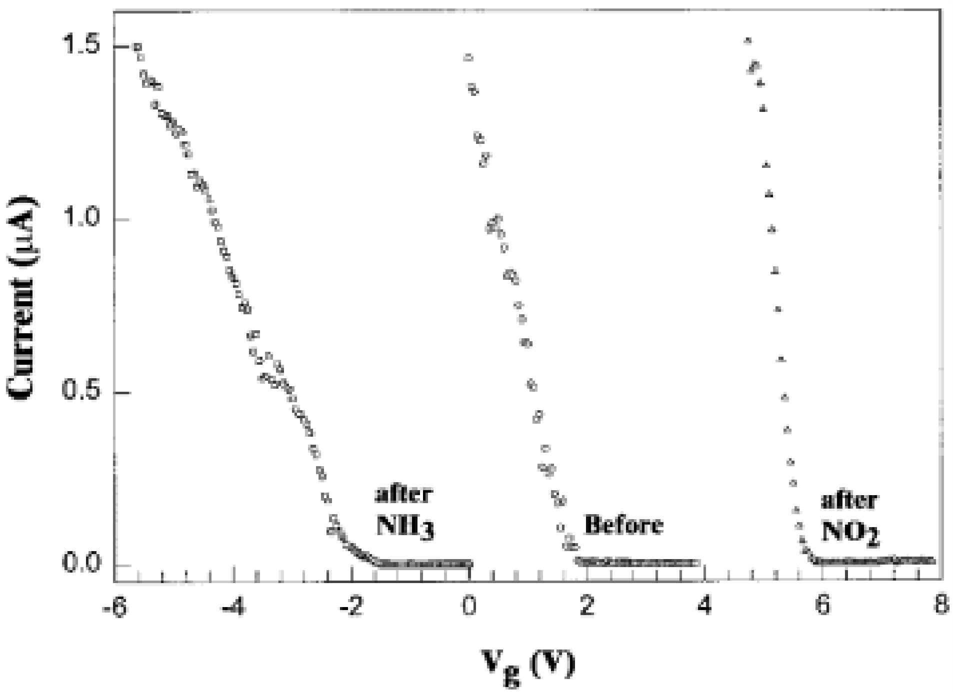
1. Two p-type CNT FETs in series
2. Potassium bombardment on the unprotected one results in a p→n conversion
3. CMOS CNT FET with gain ≡ $(V_{out}/V_{in}) > 1$

Nanotube Molecular Wires as Chemical Sensors

Science, 287, 622 (2000) J. Kong et al

NH_3 : suppresses conduction
NO_2 : increases conduction

NO_2 binding causes transferring of charge
From CNT to NO_2, resulting increased hole
Concentration in CNT.



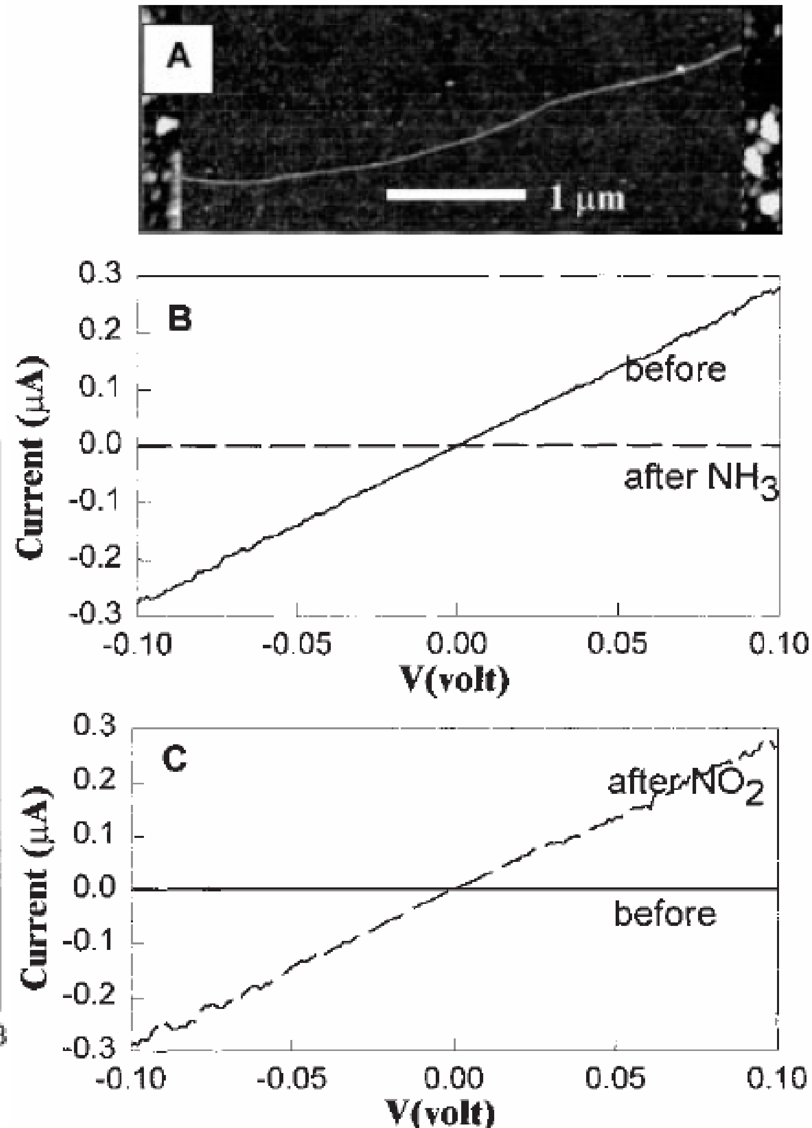


Fig. 5.25 of the text book

Application in Field Emission Display

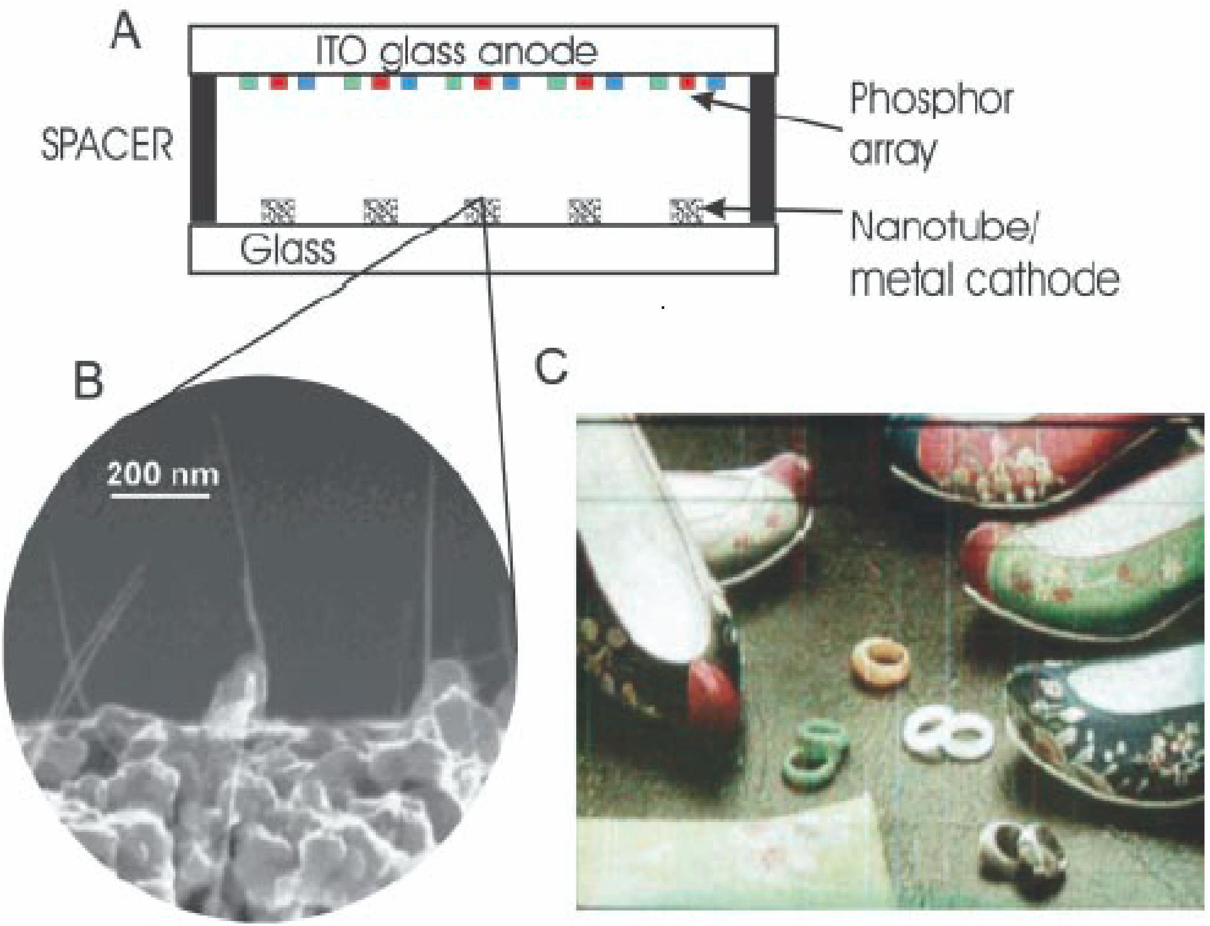


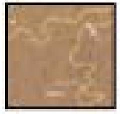
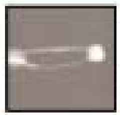
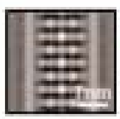
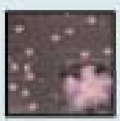
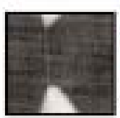
Fig. 2. (**A**) Schematic illustration of a flat panel display based on carbon nanotubes. ITO, indium tin oxide. (**B**) SEM image (49) of an electron emitter for a display, showing well-separated SWNT bundles protruding from the supporting metal base. (**C**) Photograph of a 5-inch (13-cm) nanotube field emission display made by Samsung.

prospective

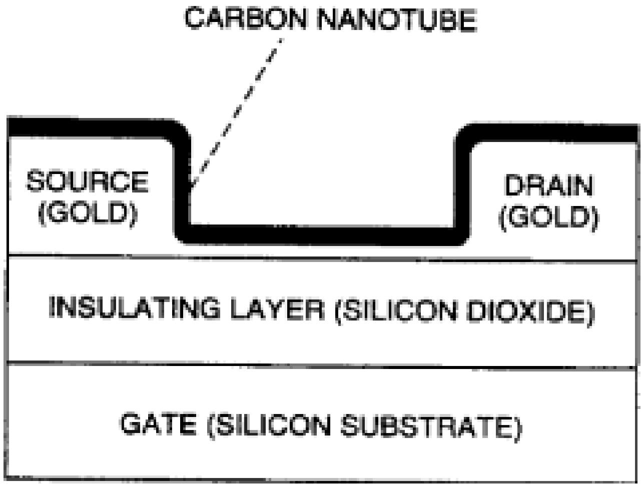
Other Uses for Nanotubes

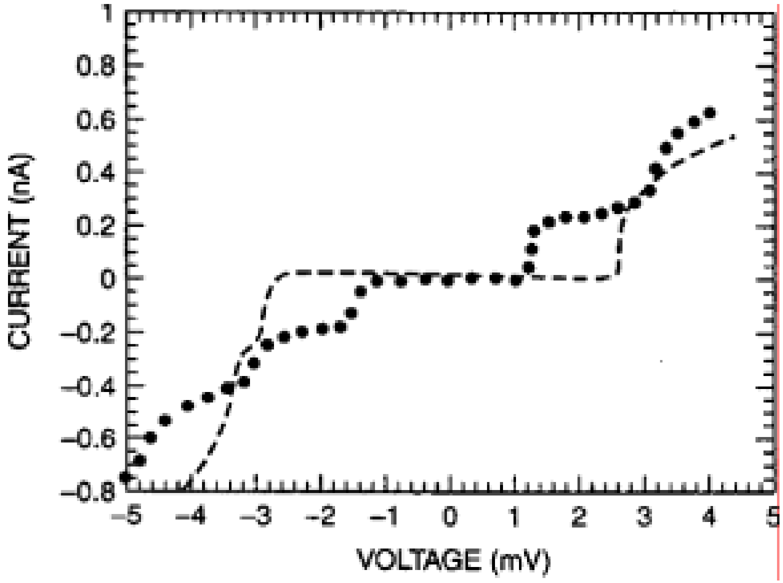
Beyond Electronics

Feasibility Ratings
0 = Science Fiction
2 = Demonstrated
4 = Ready for Market

	THE IDEA	OBSTACLES	FEASIBILITY
 **Chemical and Genetic Probes** Tagged strand of DNA	A nanotube-tipped atomic force microscope can trace a strand of DNA and identify chemical markers that reveal which of several possible variants of a gene is present in the strand.	This is the only method yet invented for imaging the chemistry of a surface, but it is not yet used widely. So far it has been used only on relatively short pieces of DNA.	3
 **Mechanical Memory** Nonvolatile RAM	A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to contact (the "on" state) and others to separate (the "off" state).	The switching speed of the device was not measured, but the speed limit for a mechanical memory is probably around one megahertz, which is much slower than conventional memory chips.	2
 **Nanotweezers** Pincers five microns long	Two nanotubes, attached to electrodes on a glass rod, can be opened and closed by changing voltage. Such tweezers have been used to pick up and move objects that are 500 nanometers in size.	Although the tweezers can pick up objects that are large compared with their width, nanotubes are so sticky that most objects can't be released. And there are simpler ways to move such tiny objects.	2
 **Supersensitive Sensors** Oxygen sticks to tubes	Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens and other gases at room temperature, raising hopes for better chemical sensors.	Nanotubes are exquisitely sensitive to so many things (including oxygen and water) that they may not be able to distinguish one chemical or gas from another.	3
 **Hydrogen and Ion Storage** Atoms in hollow core	Nanotubes might store hydrogen in their hollow centers and release it gradually in efficient and inexpensive fuel cells. They can also hold lithium ions, which could lead to longer-lived batteries.	So far the best reports indicate 6.5 percent hydrogen uptake, which is not quite dense enough to make fuel cells economical. The work with lithium ions is still preliminary.	1
 **Sharper Scanning Microscope** Individual IgM antibodies	Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments' lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules.	Although commercially available, each tip is still made individually. The nanotube tips don't improve vertical resolution, but they do allow imaging deep pits in nanostructures that were previously hidden.	4
 **Superstrong Materials** Nanotube stress test	Embedded into a composite, nanotubes have enormous resilience and tensile strength and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake.	Nanotubes still cost 10 to 1,000 times more than the carbon fibers currently used in composites. And nanotubes are so smooth that they slip out of the matrix, allowing it to fracture easily.	0

Compiled by W. Wayt Gibbs, staff writer





Questions:
Electros are in extended state throughout the entire tube or in the segment between two lead?
Will presence of defects cause electron to localize?