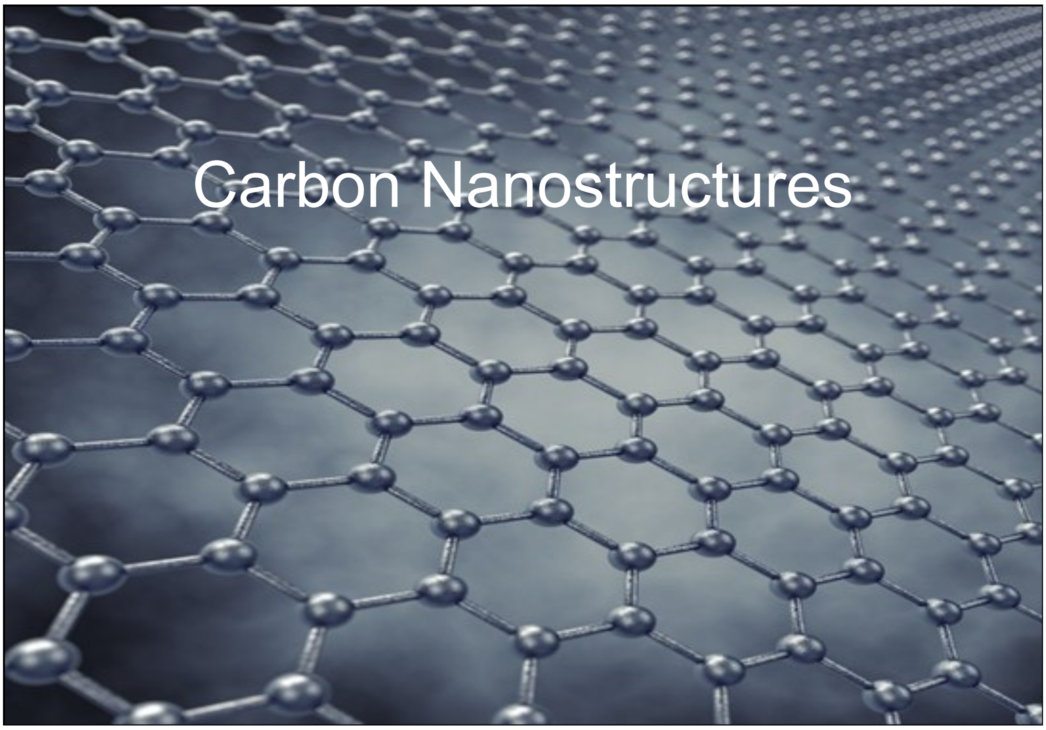
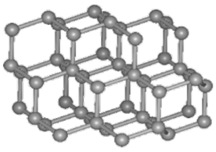
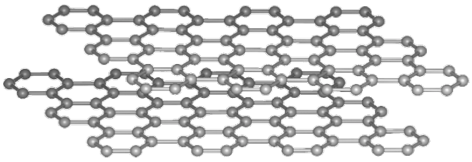


Carbon Nanostructures

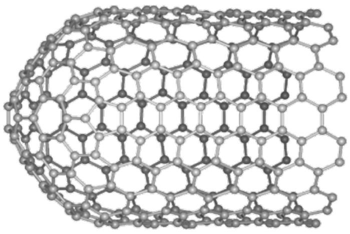
Carbon Structures



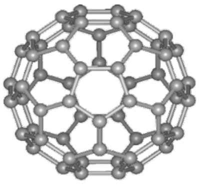
diamond (3D)



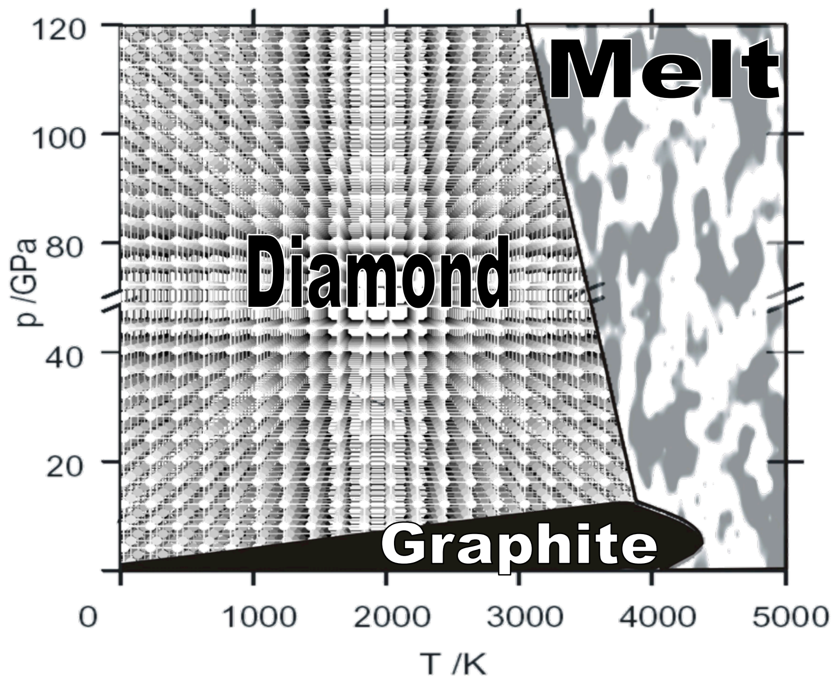
planar graphite (2D)



single-walled carbon nanotube (1D)

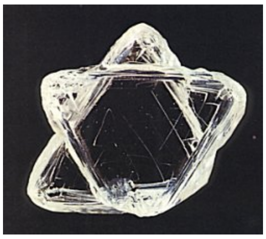


C_{60} (0D)

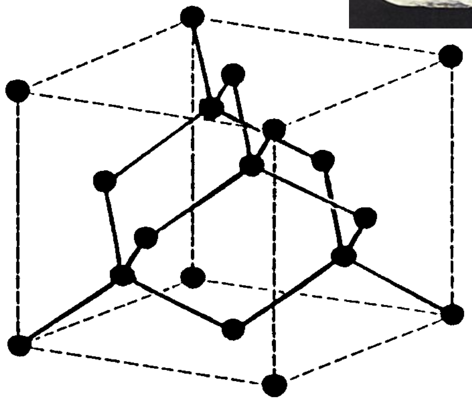


Carbon Modifications

Diamond

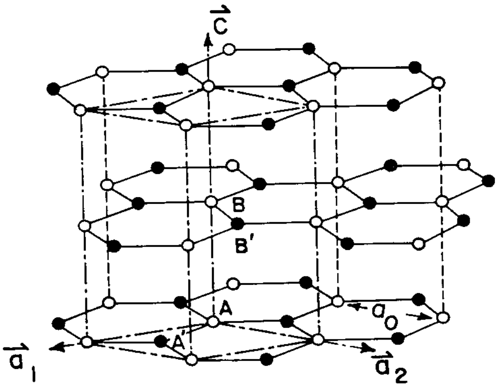


- carbon atoms on tetrahedral sites
- sp^3-hybridisation
- very rigid carbon frame, (bond length 1.54 Å)
- transparent
- insolator (5.5 eV band gap)

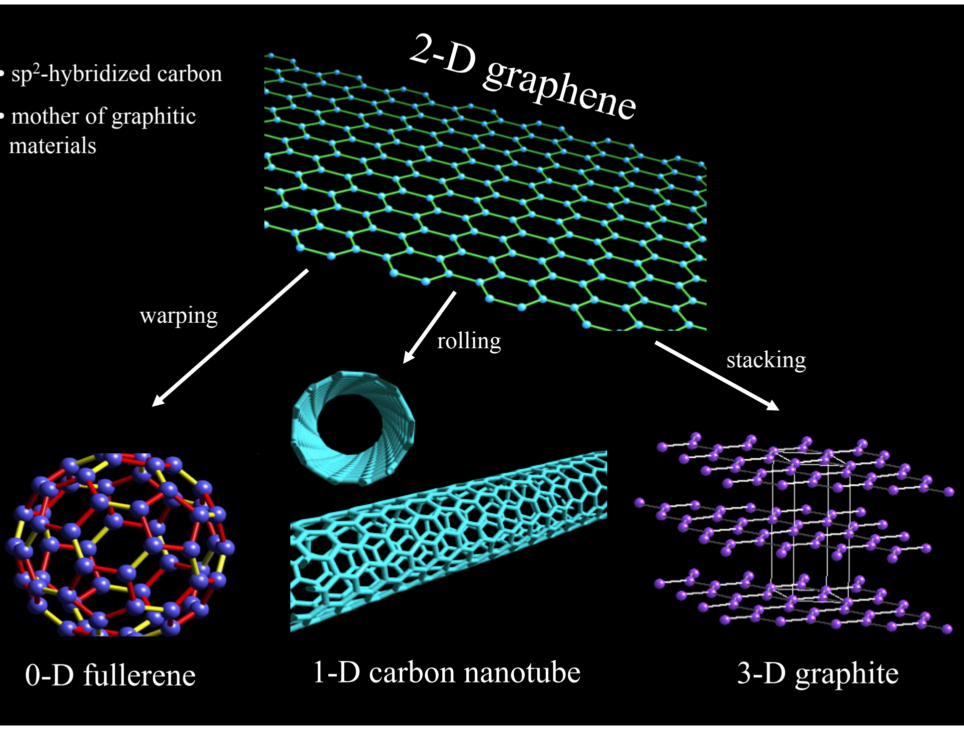


Graphite

- ☐ hexagonal layers
- ☐ sp^2 - hybridisation
- ☐ strong C-C bond in plane (1.42 Å)
- ☐ weak coupling of neighboring layers (distance 3.35 Å)
- ☐ lubricant
- ☐ half-metal, electron transport in plane



- sp^2-hybridized carbon
- mother of graphitic materials



2-D graphene

warping

rolling

stacking

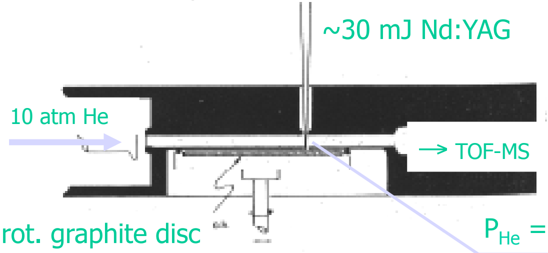
0-D fullerene

1-D carbon nanotube

3-D graphite

New Carbon Materials

- ❑ 1985: Kroto, Heath, O’Brien, Curl & Smalley
- ❑ laser ablation of graphite

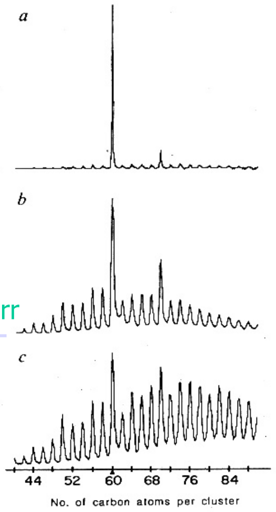


~30 mJ Nd:YAG

10 atm He

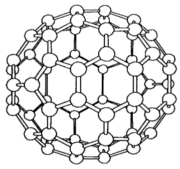
→ TOF-MS

rot. graphite disc



P_{He} = 760 Torr

P_{He} = 10 Torr



❑ carbon frame → soccer ball

- masspectrometry

→ aggregates of 60 C

Kroto et al., Nature 318 (1985) 162

Fullerenes

- ❑ C_{60} and related structures resemble the architecture of Buckminster Fuller
- ❑ → Buckminsterfullerenes, ‘Buckyballs’, gen.: Fullerenes

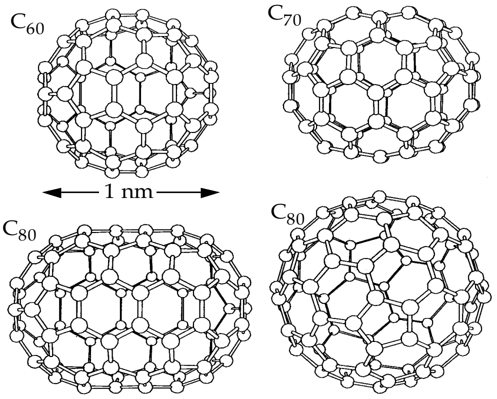
Buckminster Fuller in front of the geodetic Dome

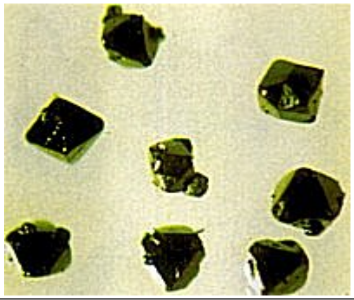
(US Pavillon, Montreal 1967)

June 1954 : U.S. Patent No. 2,682,235

C_{60} and related Species

- ❑ Family of Fullerenes
  C_{60}, C_{70}, C_{260}, C_{960}…
- ❑ 1990 : Krätschmer und Huffmann
  mass production of C_{60} in arc discharge



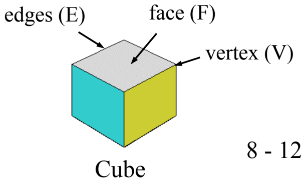


Van der Waals crystals of C_{60} (fcc structure)

Euler characteristic:

$\boxed{C = V – E + F}$

V - number of vertices
E - number of edges
F - number of faces



V = 8
E = 12
F = 6

8 - 12 + 6 = 2

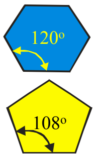
For all simple polyhedra, C = 2

If a structure is made only from pentagons and hexagons, the number of faces is

$F = P + H$, **P** - number of pentagons, **H** - number of hexagons

Each edge is shared by two polygons: **$E= (5P + 6H)/2$**

At least three polygons share a vertex and that for a convex polyhedron the sum of the internal angles of the polygons < 360 degrees. There must not be more than three polygons sharing a vertex. Thus, there are exactly three polygons meeting at each vertex, so **$V = (5P + 6H)/3$**

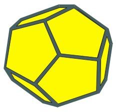


Using **$C = 2$**, we end up with **$12 = P + 0 \cdot H$**

A simple polyhedron made from pentagons and hexagons must contain exactly 12 pentagons! The number of hexagons can be arbitrarily given!

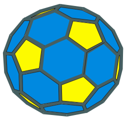
$\boxed{V = 20 + 2H}$

Thus, fullerenes must contain an even number of carbon atoms and must contain at least 20 Carbons, making C_{20} the smallest fullerene!



C_{20}

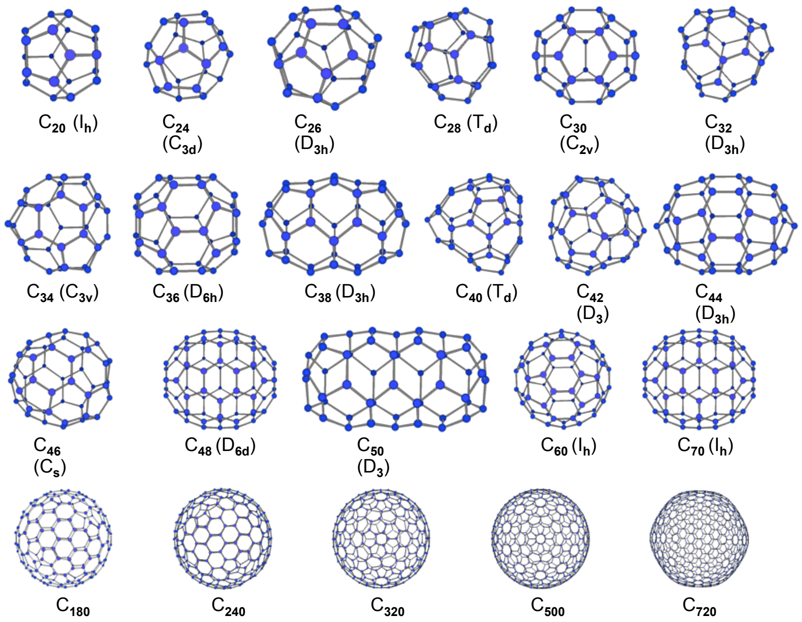
V = 20
E = 30
F = 12 (12 pentagons)
20 - 30 + 12 = 2



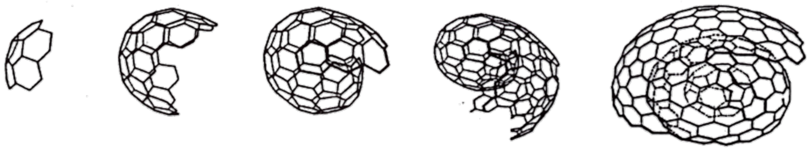
C_{60}

V = 60
E = 90
F = 32 (12 pentagons + 20 hexagons)
60 - 90 + 32 = 2

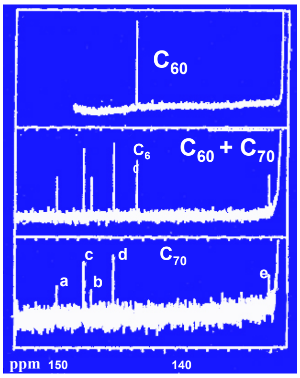
The Fullerene Family

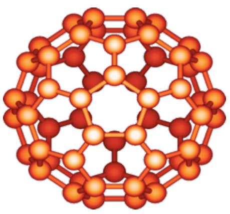


Formation of the Fullerenes

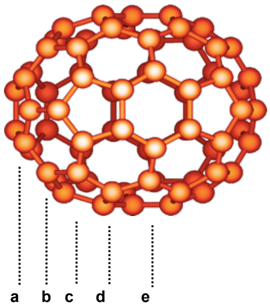


NMR spectra



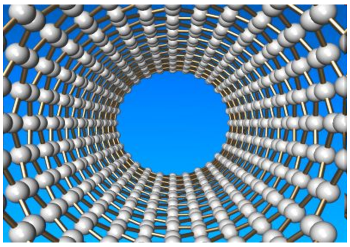


C_{60}
one single line

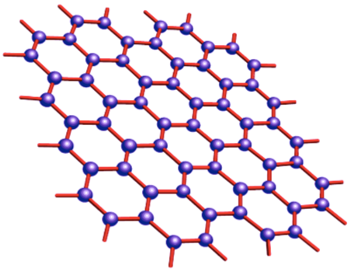


C_{70}
five lines

resistivity
carrier concentration
carrier mobility
band gap
charging energy



1D
(0D)

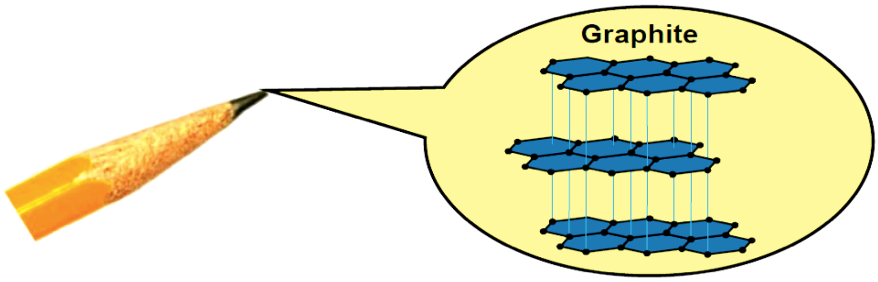


2D

Graphene

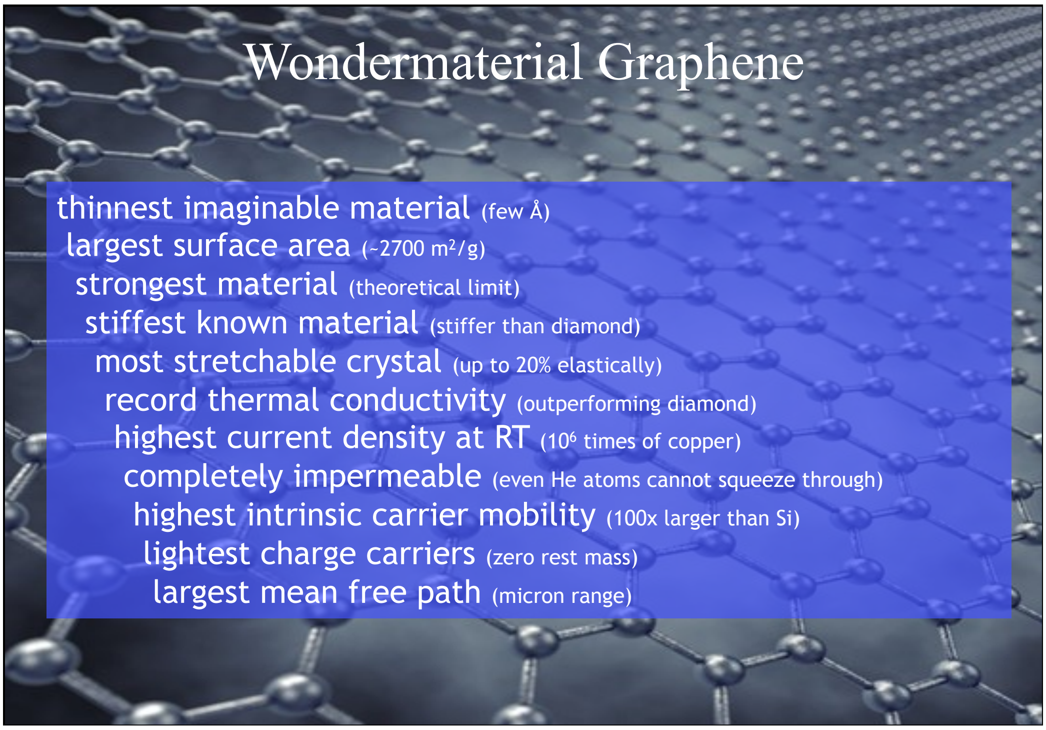
- introduction
- synthesis
- electronic structure
- possible applications

Graphene – The point of a pencil



4 valence electrons in carbon

- 3 bonds to neighbors (sp^2 σ-bonds)
  structural rigidity within planes
  weak van-der-Waals attraction between planes
- 1 delocalized π electron
  electrical conductivity



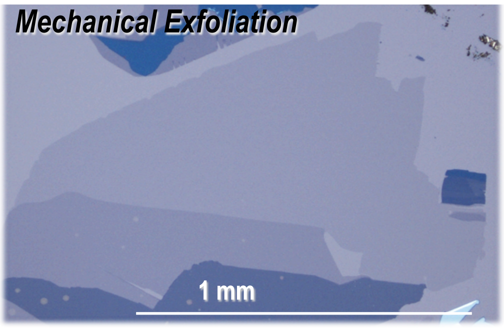
Wondermaterial Graphene

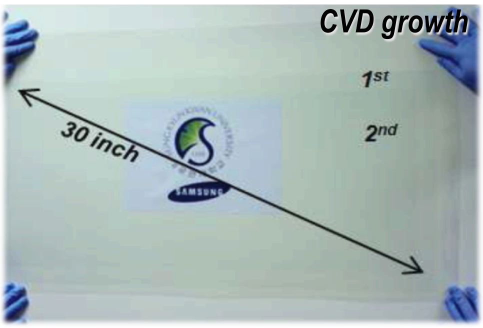
thinnest imaginable material (few Å)
largest surface area (~2700 m^2/g)
strongest material (theoretical limit)
stiffest known material (stiffer than diamond)
most stretchable crystal (up to 20% elastically)
record thermal conductivity (outperforming diamond)
highest current density at RT (10^6 times of copper)
completely impermeable (even He atoms cannot squeeze through)
highest intrinsic carrier mobility (100x larger than Si)
lightest charge carriers (zero rest mass)
largest mean free path (micron range)

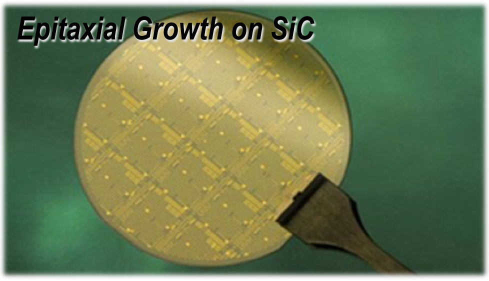
Graphene

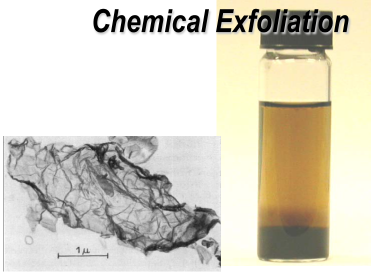
- introduction
- synthesis
- electronic structure
- possible applications

Overview of synthesis methods

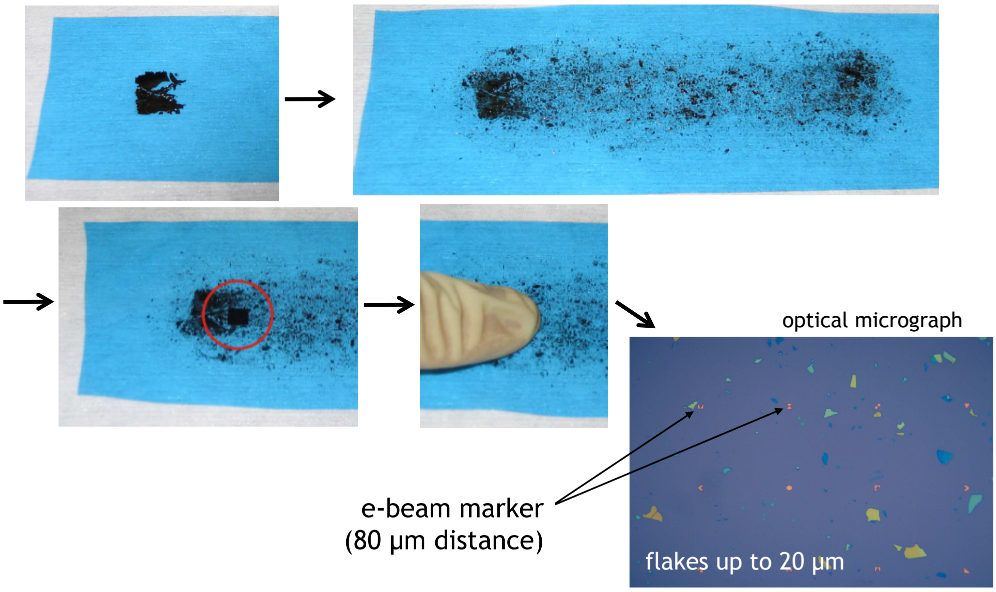








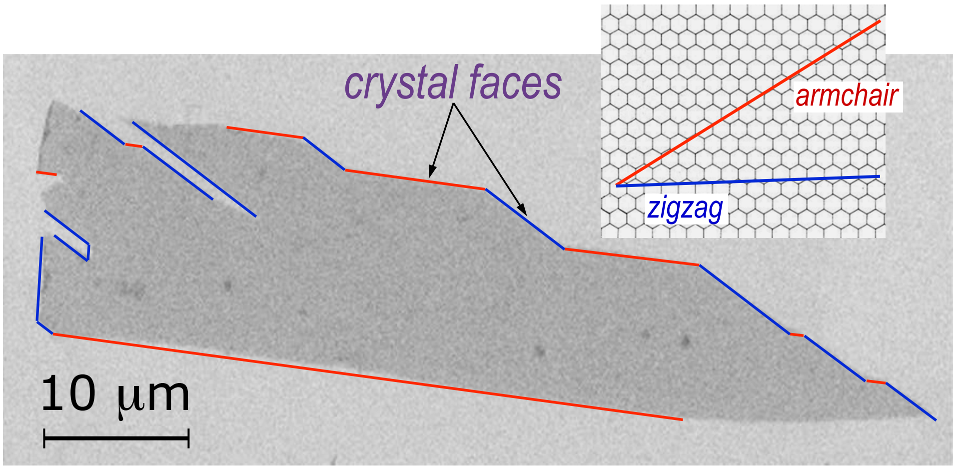
Mechanical exfoliation of HOPG


optical micrograph

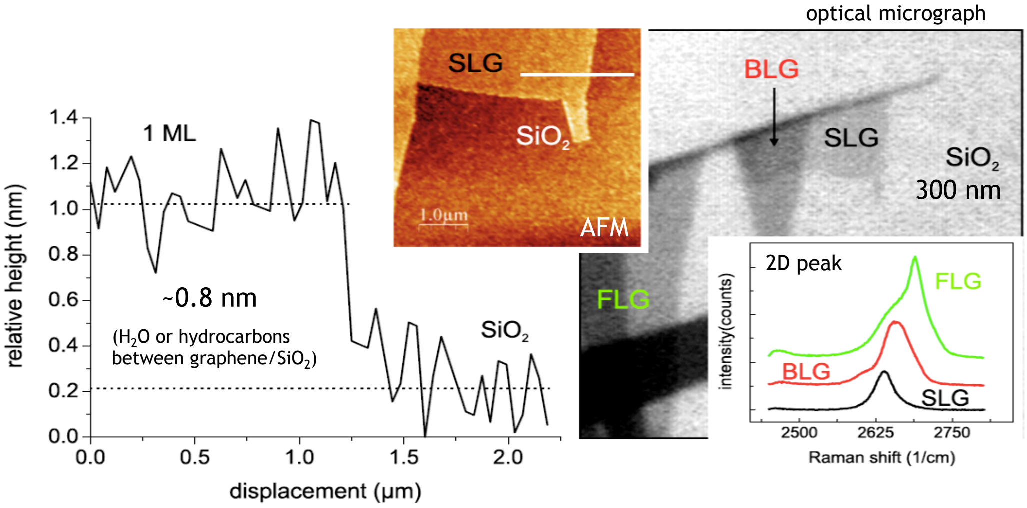
e-beam marker
(80 µm distance)

flakes up to 20 µm

Mechanically exfoliated graphene



Identifying graphene monolayers

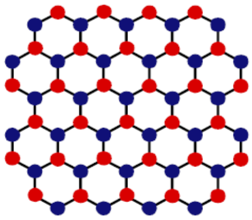


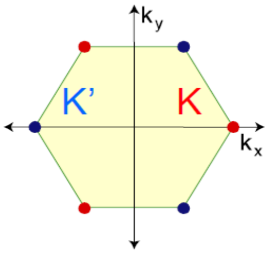
S. Akcöltekin et al.; Nanotechnology 20 (2009), 155601.

Graphene

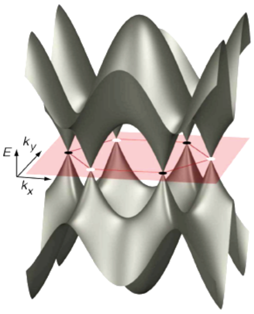
- introduction
- synthesis
- electronic structure
- possible applications

Electronic band structure of graphene


Honeycomb Lattice



Brillouin Zone

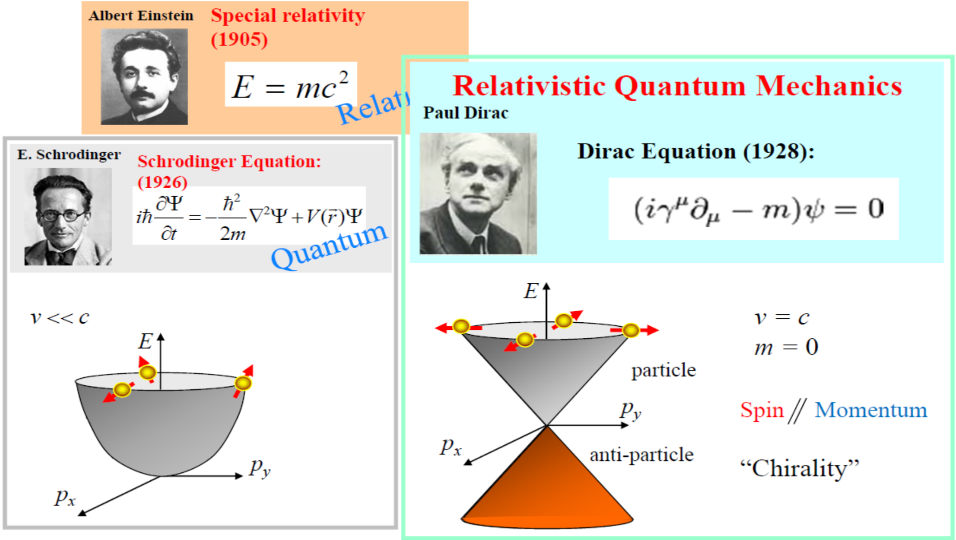


- The conduction band and valence band touch at two “Fermi points” K and K’
- Near K and K’ the dispersion is “relativistic” (i.e., linear)

$$E(\mathrm{K}+\vec{q}) = \pm\hbar v_F\,|\vec{q}\,|$$

Fermi velocity
$v_F \approx 7 \times 10^5$ m/s ≈ c/300

Relativistic quantum physics



Albert Einstein Special relativity (1905)

$$E = mc^2$$

E. Schrodinger Schrodinger Equation: (1926)

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V(\vec{r})\Psi$$

$v << c$

Relativistic Quantum Mechanics

Paul Dirac

Dirac Equation (1928):

$$(i\gamma^\mu\partial_\mu - m)\psi = 0$$

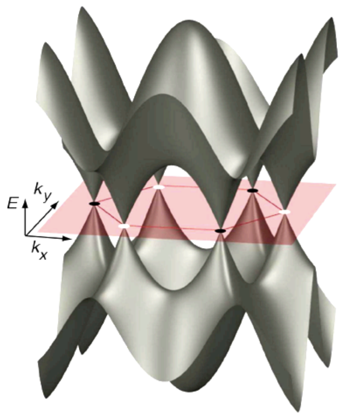
$v = c$
$m = 0$

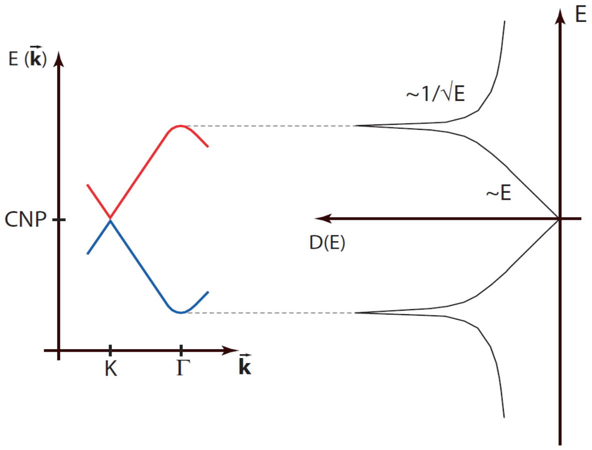
Spin // Momentum

“Chirality”

P. Kim, Colombia University.

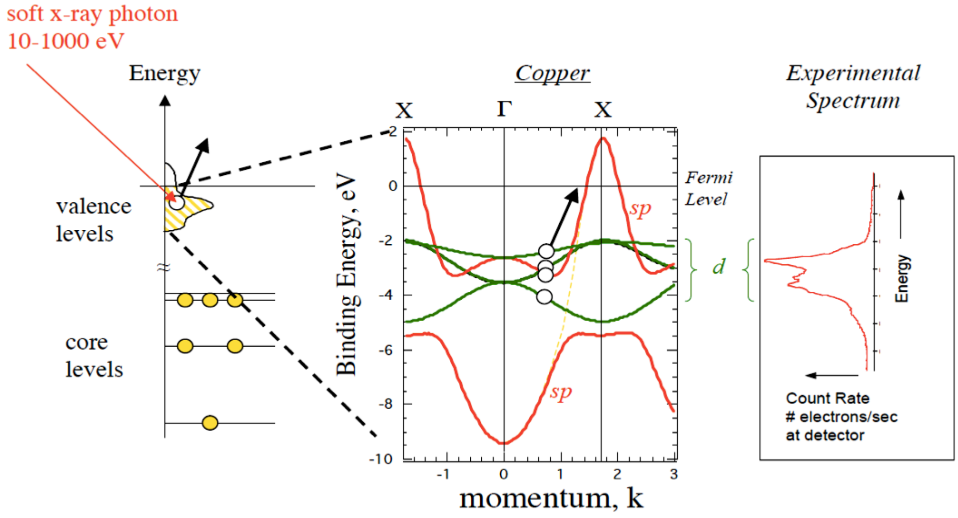
Density of states



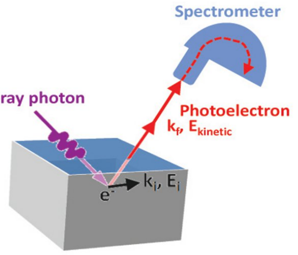


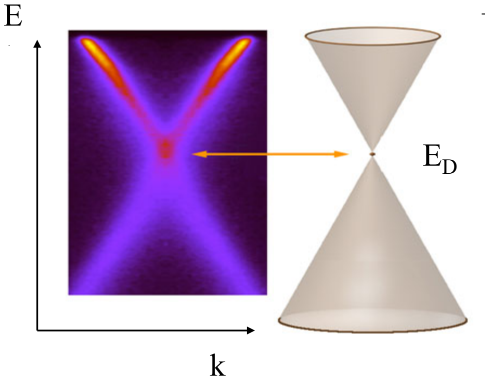
$$D(E) \propto \frac{|E|}{v_F^2}$$

Experimental band structure – ARPES



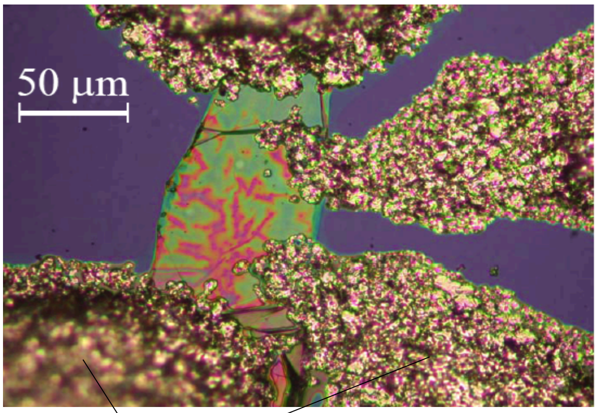
Graphene -ARPES





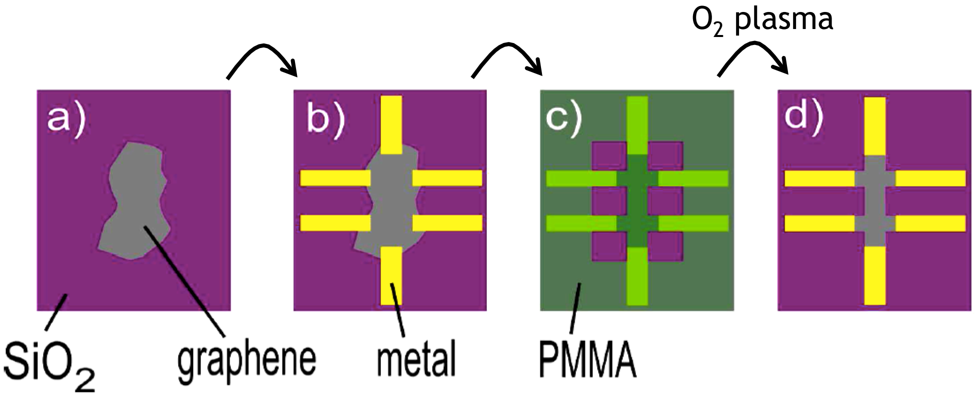
Electrical contacting of graphene sheets

First devices by Manchester group

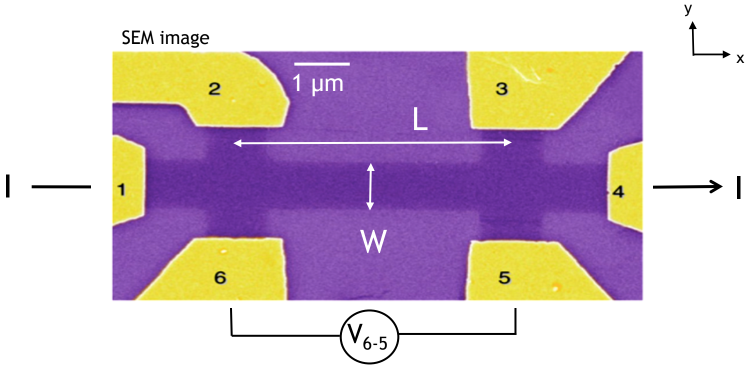


K. Novoselov et al.; unpublished.

Sheet resistivity – Hall bar measurements

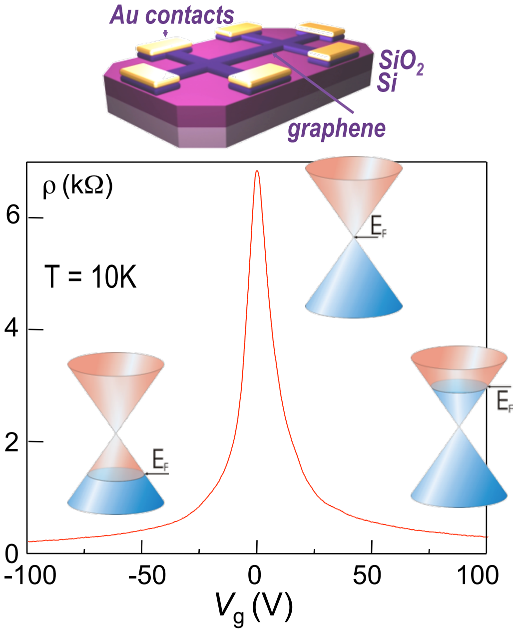


Sheet resistivity – Hall bar measurements

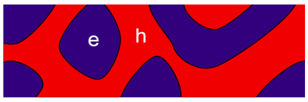


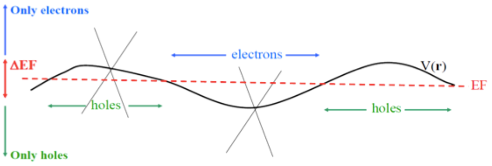
sheet resistivity $$\rho_{xx} = R_{1-4,6-5}\frac{W}{L} = \frac{V_{6-5}}{I_{1-4}}\frac{W}{L}$$

Resistivity vs. gate voltage



- ambipolar field effect
- finite minimum sheet conductivity $\sigma_s \approx 4\ e^2/h$ (ionized impurities near the graphene plane → electron-hole puddles)

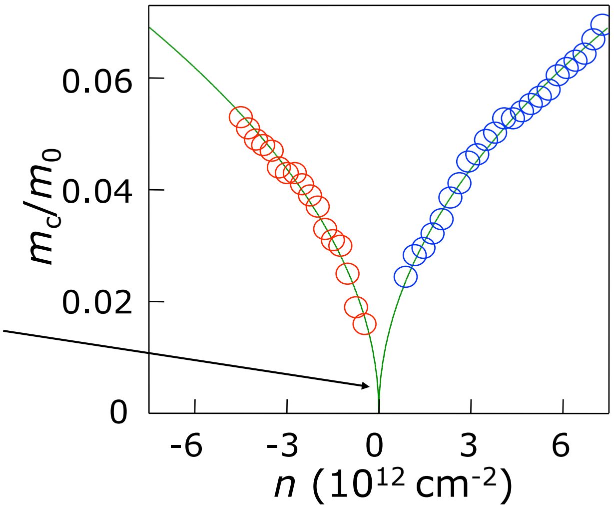




Effective carrier mass

'fictious' relativistic mass:

$$\boxed{m_c = \frac{E_F}{v_F^2} = \sqrt{\frac{\pi \hbar^2 n_{2D}}{v_F^2}}}$$



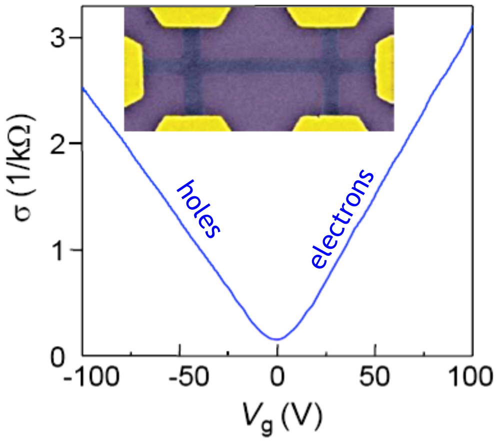
vanishing (rest) mass at Dirac point

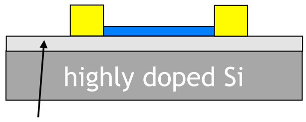
K. Novoselov et al.; Nature (2005).

Determination of carrier mobility

Conductivity vs. gate voltage

$$\sigma = 1/\rho = n(V_g)\, e\mu$$





SiO_2
thickness t,
dielectric constant ε

parallel plate capacitor:

capacitance per area

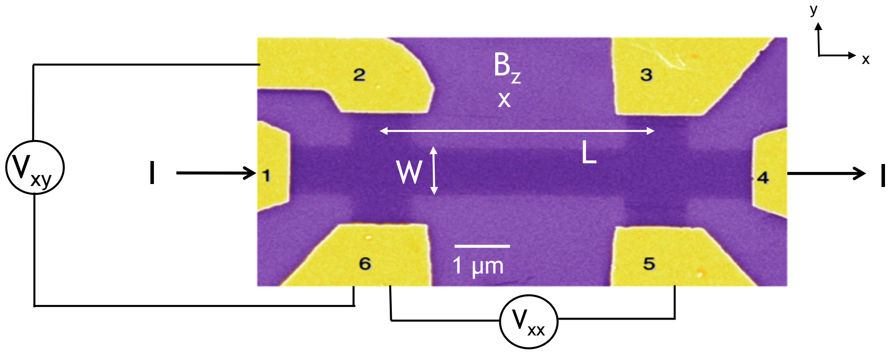
$$n(V_g) = \boxed{\frac{\varepsilon_0 \varepsilon}{t}} \frac{V_g}{e} = \alpha V_g$$

$$\alpha \approx 7.2 \cdot 10^{10}\ \mathrm{cm}^{-2}\ \mathrm{V}^{-1}$$

(for 300 nm SiO_2 dielectric)

$$\Rightarrow \boxed{\mu = \frac{slope}{\alpha e}}$$

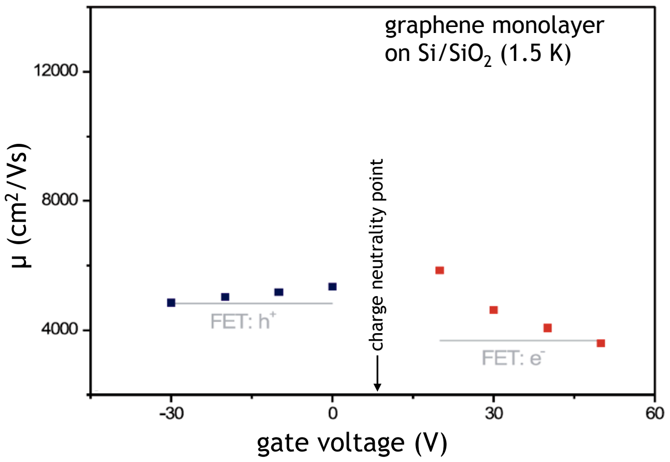
Mobility from Hall measurements



⇒ Hall mobility $\boxed{\mu = \frac{\sigma_{xx}}{q n_{2D}} = \frac{R_{xy}}{\rho_{xx} B} = \frac{L}{WB} \frac{V_{xy}}{V_{xx}}}$

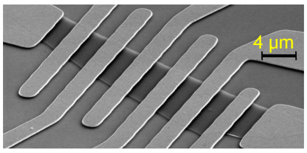
Mobility from Hall measurements

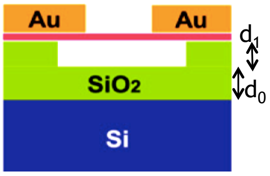
Comparison with field-effect mobility



G. Ulbricht et al.; unpublished.

Mobility enhancement – Suspended sheets





dip of entire device into
buffered HF for 90 sec
(→ removal of ~150 nm SiO$_2$)

↓

before current annealing:
μ = 20,000 cm^2 V^{-1}s^{-1} (4 K)

after current annealing:
μ = 200,000 cm^2 V^{-1}s^{-1} (4 K)

force between sheet and gate:

$$F = \frac{\varepsilon_0 \varepsilon^2 L W V_{gate}^2}{2(d_0 + d_1 \varepsilon)^2} \approx 3 \cdot 10^{-8}\,\mathrm{N}$$

(at V_{gate} = ±5V)

→ sheet collapse for V_{gate} > 20 V

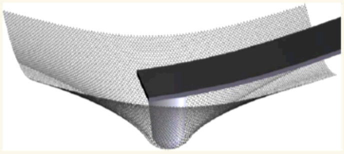
K.I. Bolotin et al.; Sol. State Commun. 146 (2008), 351.

Graphene

- introduction
- synthesis
- electronic structure
- possible applications

Applications of graphene

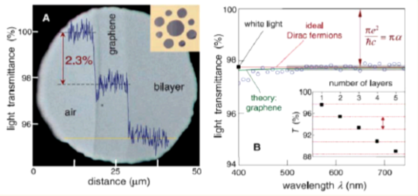
Thin, light, strong and tough



C. Lee, X. Wei, J. W. Kysar, & J. Hone, *Science* 321, 385 (2008)

Young's modulus: 1 TPa (Steel ~ 0.2 TPa)
Critical Strain: ~ 25%

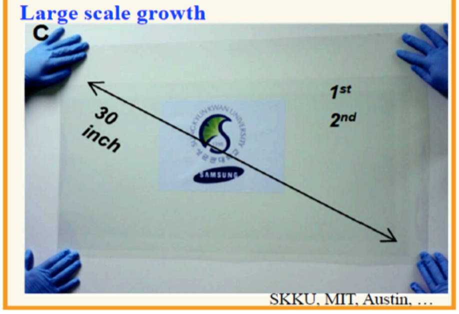
Optically transparent (Nair et al, Sience 2008)



Flexible and conducting

K. S. Kim et al., *Nature*, **457**, 706 (2009)

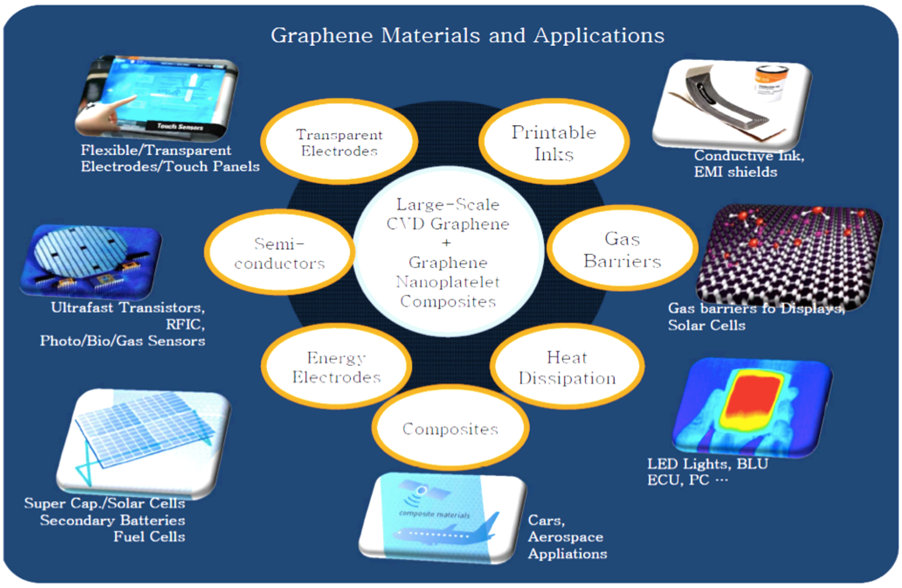
Large scale growth



SKKU, MIT, Austin, …

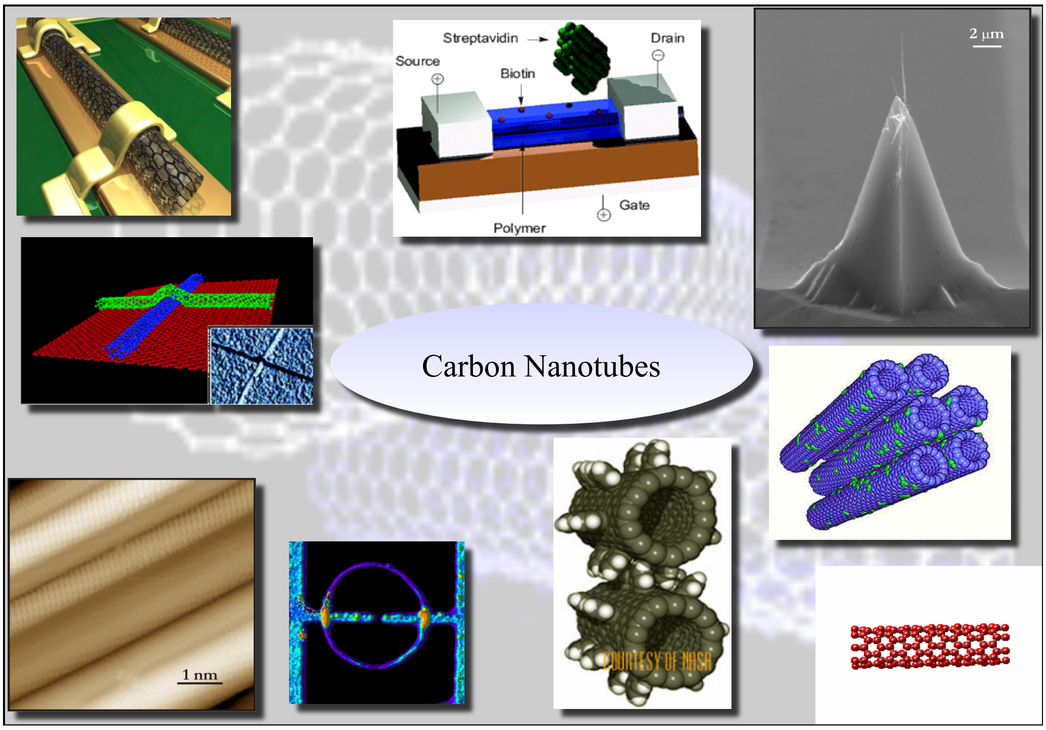
P. Kim, Colombia University.

Applications of graphene



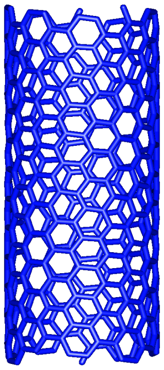
Carbon Nanotubes

- introduction
- synthesis
- electronic structure
- electrical transport
- mechanical properties

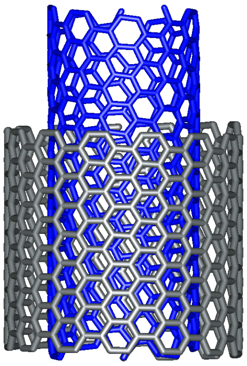


Carbon Nanotubes

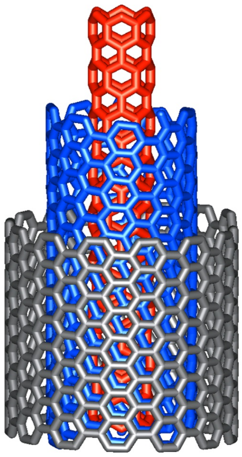
CNTs – Types



single wall nanotubes
(SWCNTs)



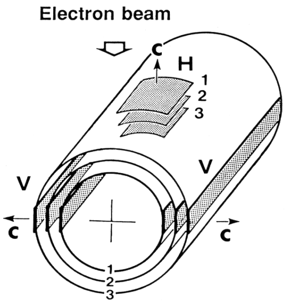
double wall nanotubes
(DWCNTs)



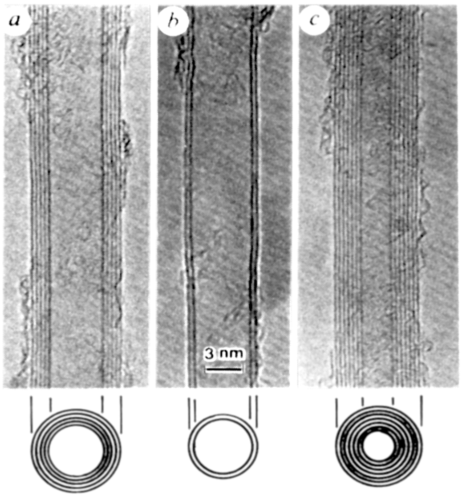
multi wall nanotubes
(MWCNTs)

CNTs – Discovery

- ☐ In 1991 by Iijima (NEC, Japan)



- ☐ Multiwall nanotubes (MWNTs)



Transmission Electron Mmicroscope (TEM) images

Iijima, Nature 354, 56, (1991)

CNTs – Physical Structure

rollup vector

$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$

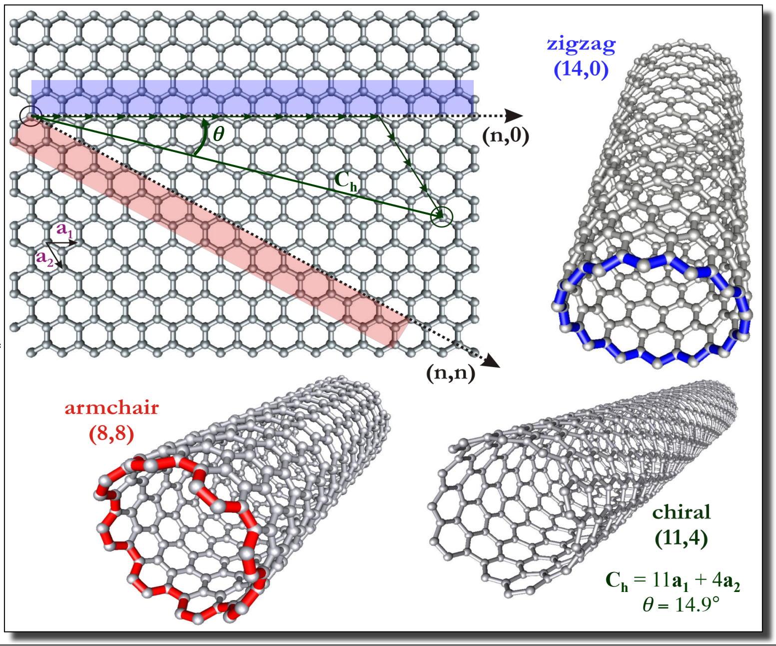
↓

SWNTs specified as

(n, m)

chiral angle

$\theta = \tan^{-1}[\sqrt{3}m/(2m+n)]$



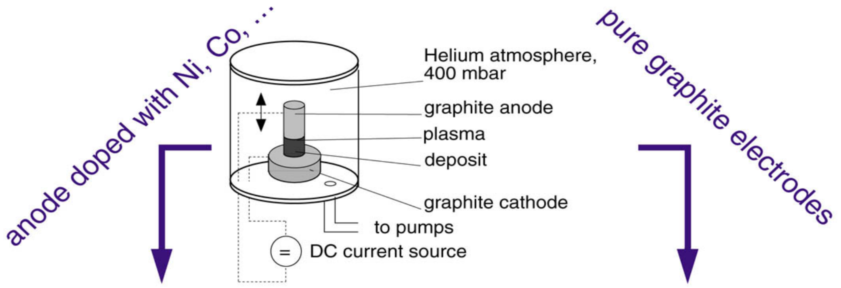
Outstanding properties of CNTs

Attribute	Comment
Thermal conductivity: 10^4 Wm^{-1}K^{-1}	**> that of diamond**
Young´s modulus: 1TPa	**stiffer than any other known material**
Tensile strength: 150GPa	**~600 times the strength/ weight of steel**
Supports current density of 10^9A/cm^2	**~100 times greater than for copper wires**
Carrier mobility: 10^4-10^5cm^2/Vs (at RT)	**> that of GaAs**
Thermally stable up to 2800°C (vacuum)	

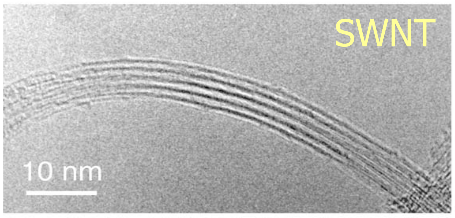
Carbon Nanotubes

- introduction
- synthesis
- electronic structure
- electrical transport
- mechanical properties

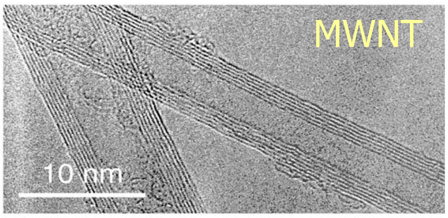
Arc discharge process



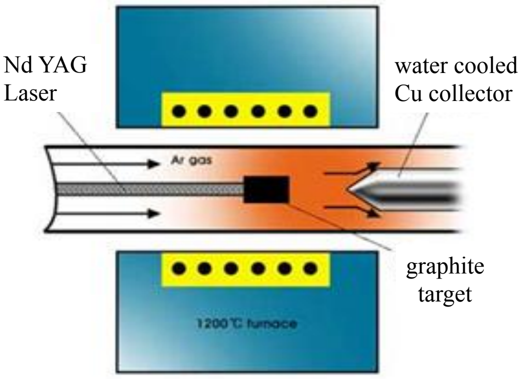
Single wall nanotubes



Multiwall nanotubes



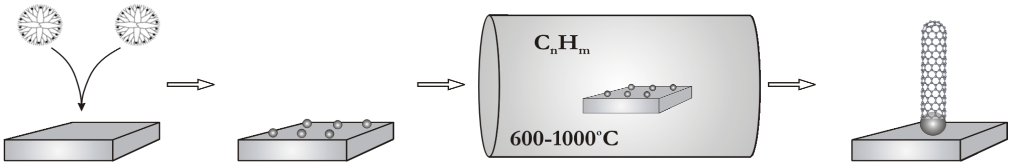
Laser ablation method



- ~1.4nm average tube diameter
- NTs are formed as bundles

Ajayan et al., Carbon Nanotubes 80, 391, (2001)

Chemical Vapor Deposition (CVD)



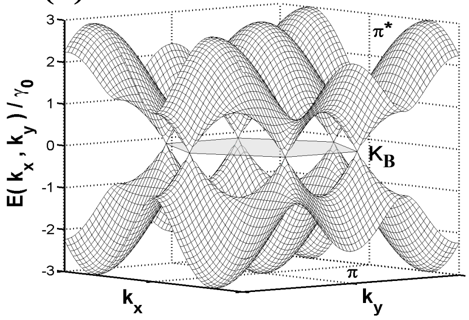
- relatively low temperature (600°-1000°C)
- Fe, Ni, or Co nanoparticles as catalyst
- mostly isolated SWCNTs are obtained
- SWCNT diameter control through particle size

Carbon Nanotubes

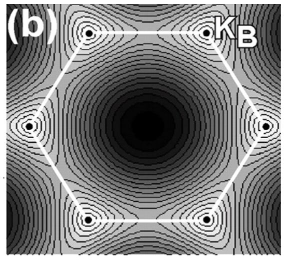
- introduction
- synthesis
- electronic structure
- electrical transport
- mechanical properties

Electronic structure of CNTs derived from graphene

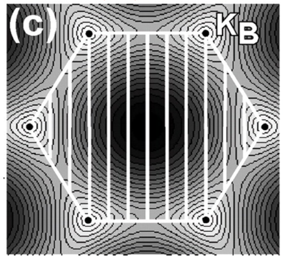
(a) energy bands of graphene sheet



energy contour (2D) plot



allowed 1D wavevectors for **(9,0)** tube

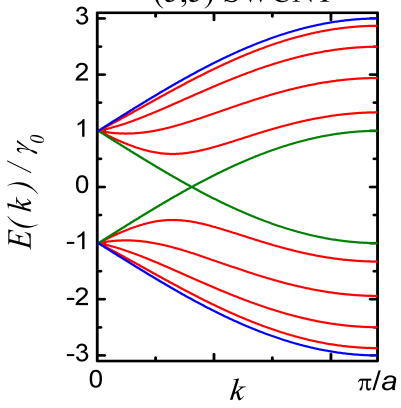


periodic boundary conditions:

$$\underline{C}_h \cdot \underline{k} = 2\pi q$$

CNTs – Electronic Structure

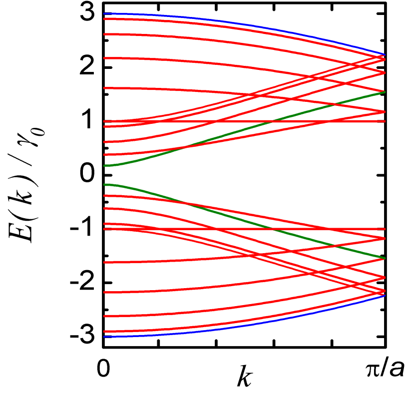
Bad structure of a (5,5) SWCNT



armchair (n=m)

metallic

Band structure of a (10,0) SWCNT



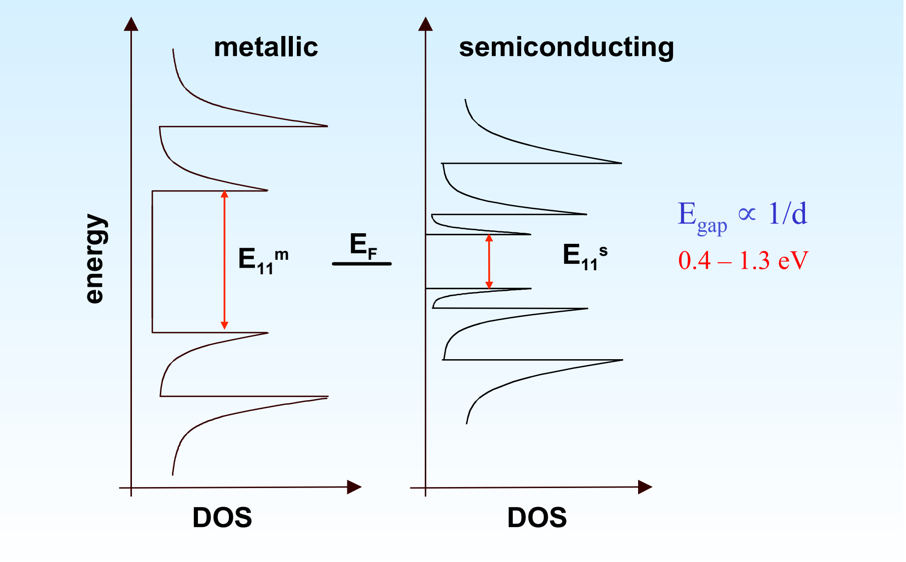
zigzag (n,0) & chiral (n,m)

metallic if (n-m)=3i

semiconducting if (n-m)≠3i

$\gamma_0 = 2.5$eV
a = 1.44 A°

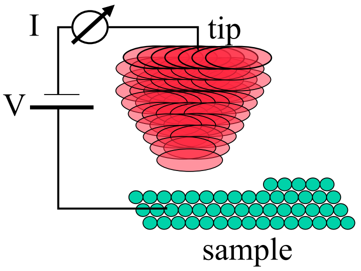
CNTs – Electronic Structure



$E_{gap} \propto 1/d$

0.4 – 1.3 eV

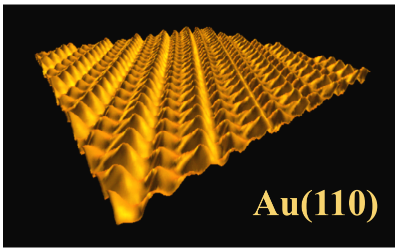
Scanning Tunneling Microscopy (STM)



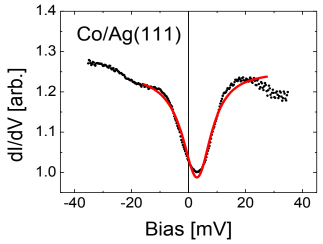
$$I(V,x,z) \propto e^{-A\cdot z}\int_0^{eV}\rho_s(E,x)dE$$

$$\frac{dI}{dV}(V,x,y) = \rho_S(eV,x,y)$$

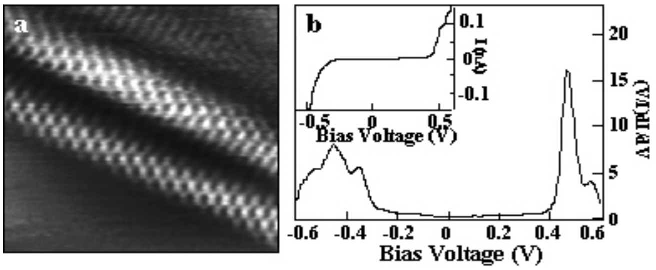
Topography „z (x, y, I=const)“



Spectroscopy „dI/dV“ (STS)

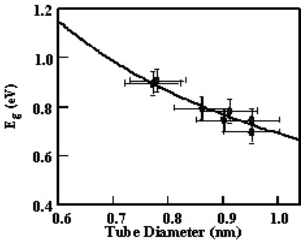


Scanning Tunneling Spectroscopy on SWCNTs



(14,-3) SWNT
⇒ **semiconducting**

Band gap as a function
of tube diameter

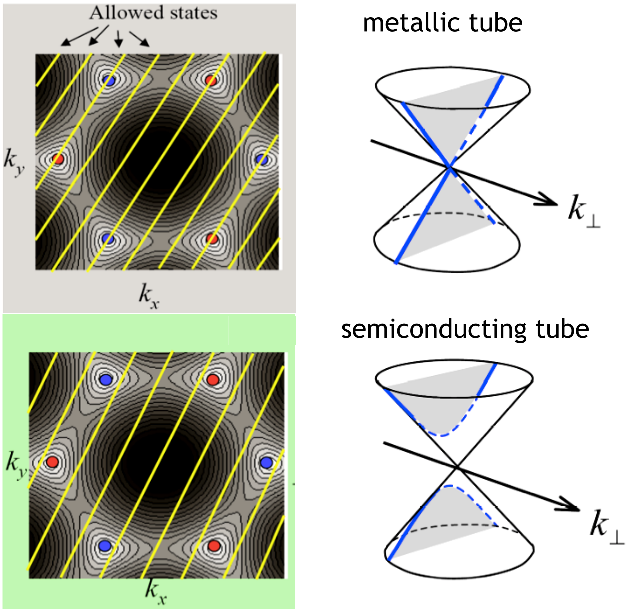


Carbon Nanotubes

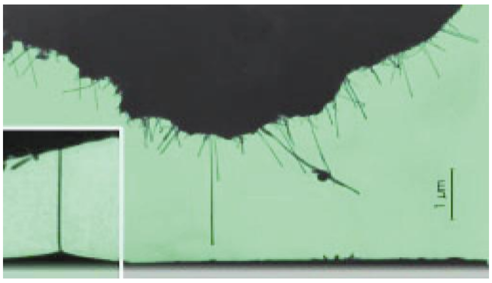
- introduction
- synthesis
- electronic structure
- electrical transport
- mechanical properties

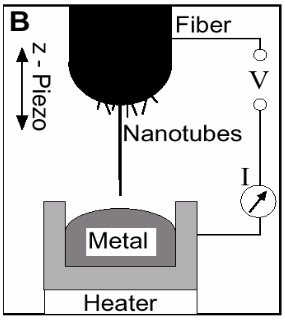
Ballistic transport in a 1D conductor

Carbon nanotubes (CNTs)

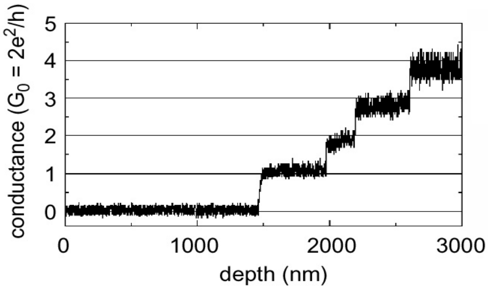


CNT – Quantum conductance





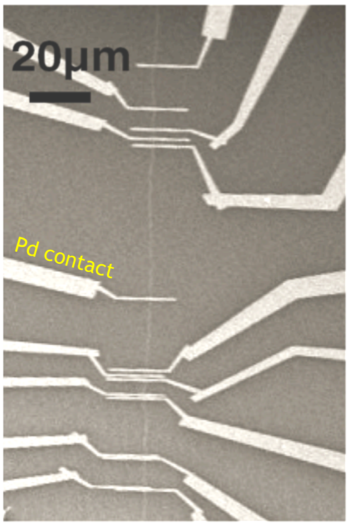
- ❑ MWCNT on a piezo-controlled tip
  - → quantised conductance
  - $nG_0 = n\,(2e^2/h) = n\,([12.9k\Omega]^{-1})$
- ❑ Ballistic electron transport
  - resistance independent of tube length
  - upto 25mA per nanotube

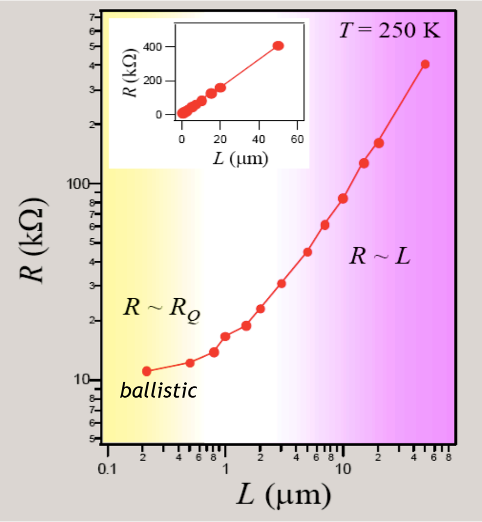


Frank et al., Science 280, 1744, (1998)

Evaluation of mean free path in SWCNTs

Many contacts on long metallic tube:

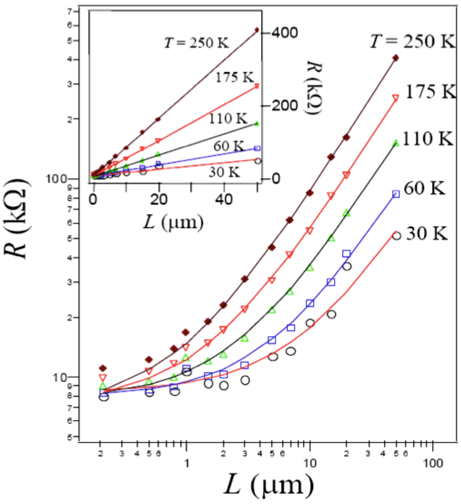




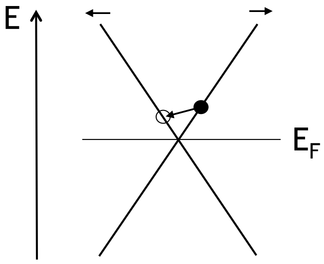
M.S. Purewal et al.; PRL 98 (2007), 186808.

Evaluation of mean free path in SWCNTs

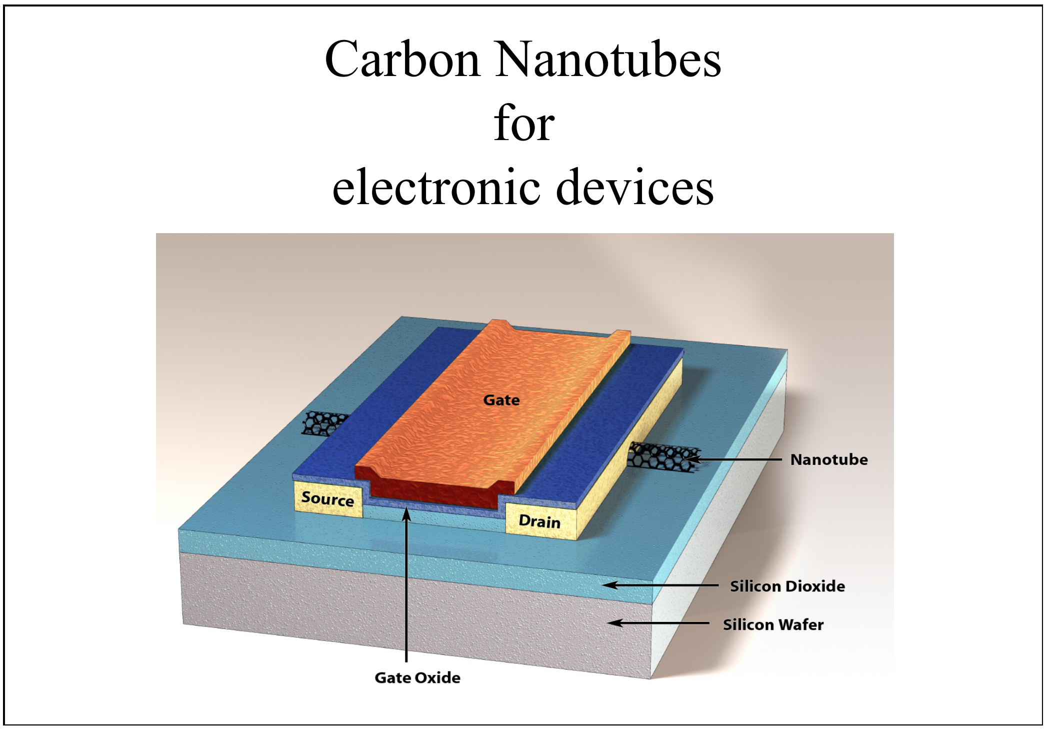
Temperature dependence of resistance:



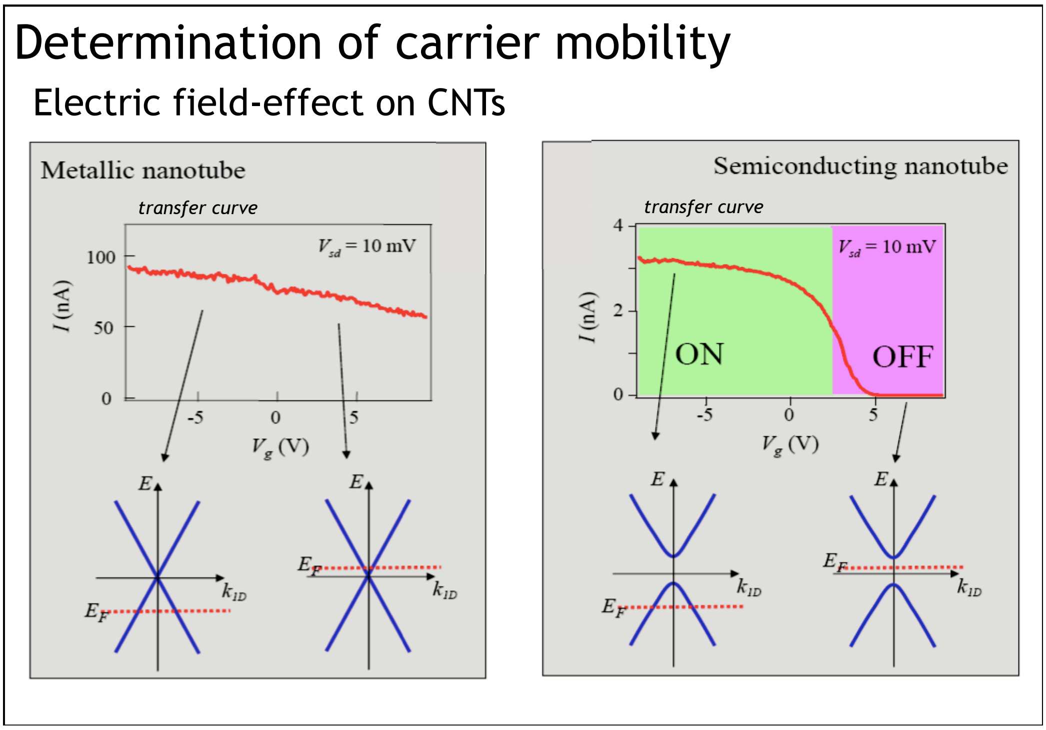
ballistic transport is limited by (acoustic) phonon scattering



M.S. Purewal et al.; PRL 98 (2007), 186808.



Carbon Nanotubes
for
electronic devices



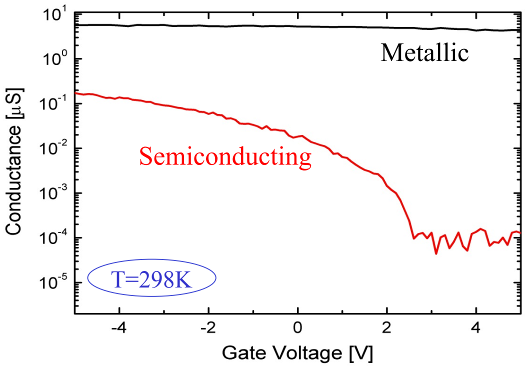
Determination of carrier mobility

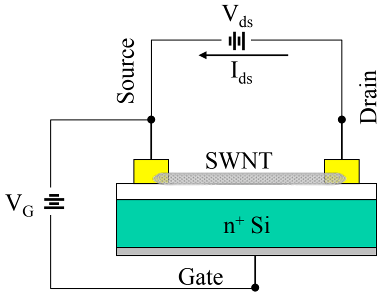
Electric field-effect on CNTs

Electronic Transport in SWCNTs

(**room** temperature)

Gate Dependence
of conductance

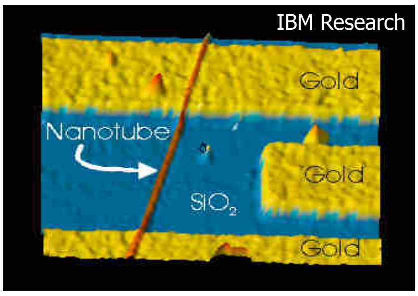


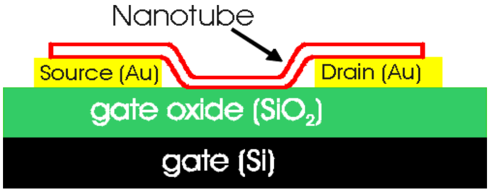


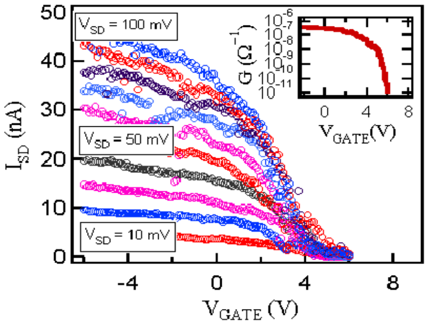
Conductance

I_{ds} / V_{ds}

CNT Field-Effect Transistor







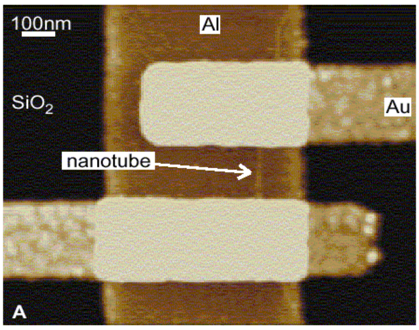
☐ FET with SWCNT or MWCNT

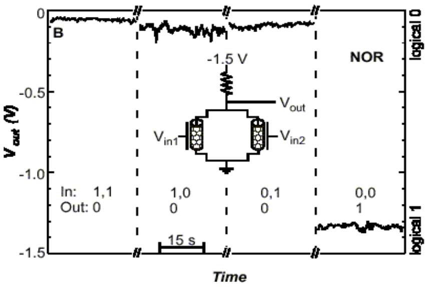
☐ Applying V_{gate}

$\Rightarrow$ Control of current I_{SD} through NT

Martel et al., Appl. Phys. Lett. 73, 2447, (1998)

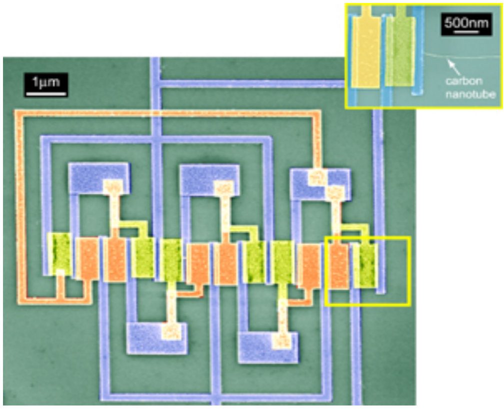
Carbon Nanotube Logic

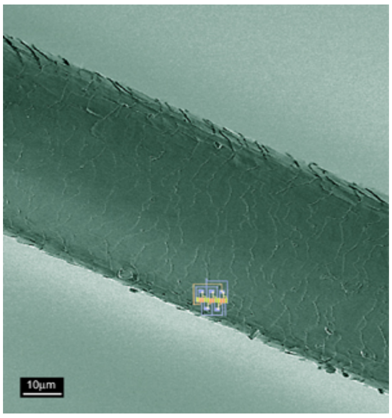




Bachtold et al., Science 294, 1317, (2001)

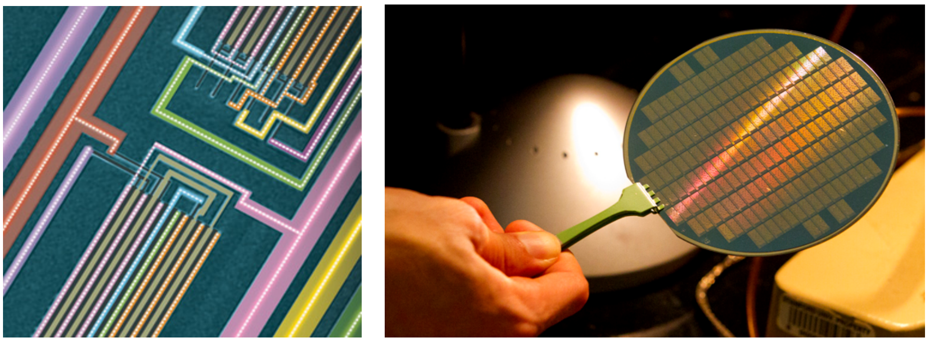
Circuit built on Single Carbon Nanotube





Z. Chen et al., Science 5768, 1735 (2006)

First Carbon Nanotube Computer



M. Shulaker et al., Nature 501, 526 (2013)