Low dimensional sp2 carbon materials: graphene and carbon nanotubes

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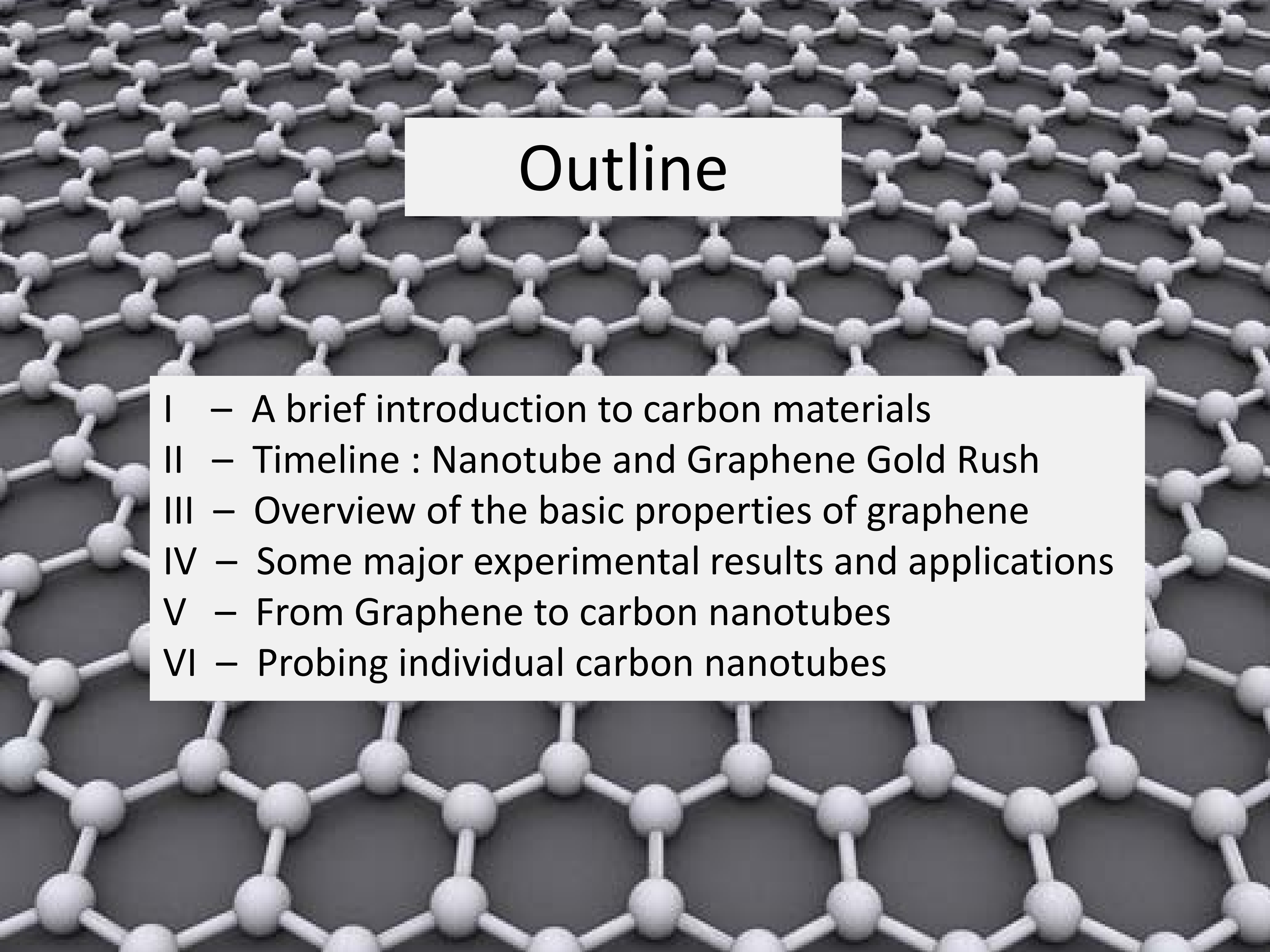


Outline

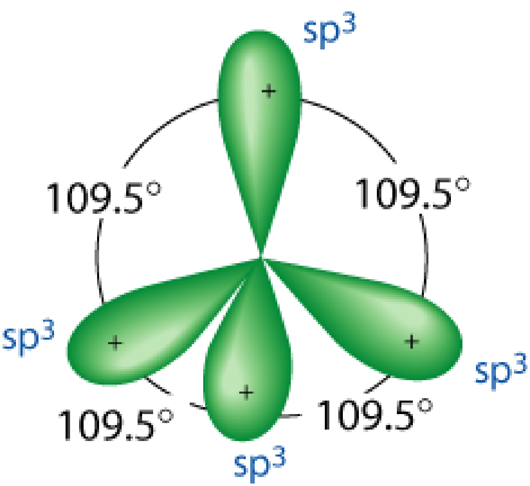
I – A brief introduction to carbon materials
II – Timeline : Nanotube and Graphene Gold Rush
III – Overview of the basic properties of graphene
IV – Some major experimental results and applications
V – From Graphene to carbon nanotubes
VI – Probing individual carbon nanotubes

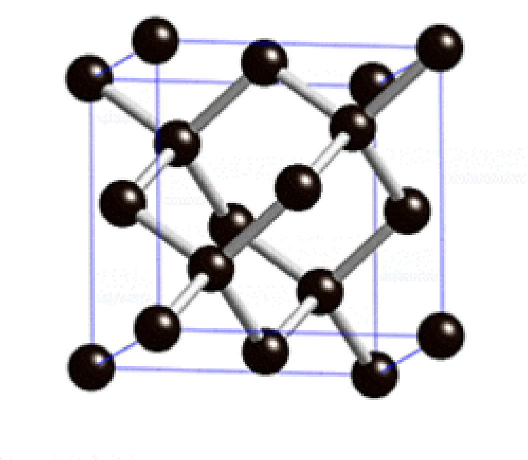
Two popular carbon allotropes

- Carbon ($1s^2\,2s^2\,2p^2$)

sp^3 hybridized carbon: Diamond

- one s orbital and 3 p orbitals
- 3-dimensional structure
- Covalent bonds
- Metastable
- Electrically insulating
- Extremely robust



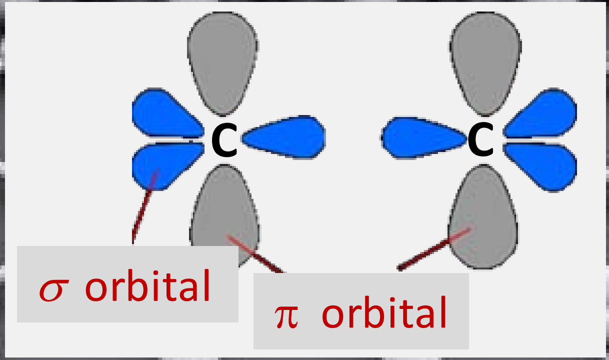


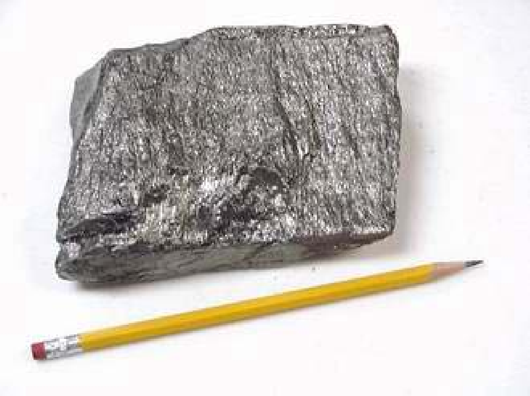
Two popular carbon allotropes

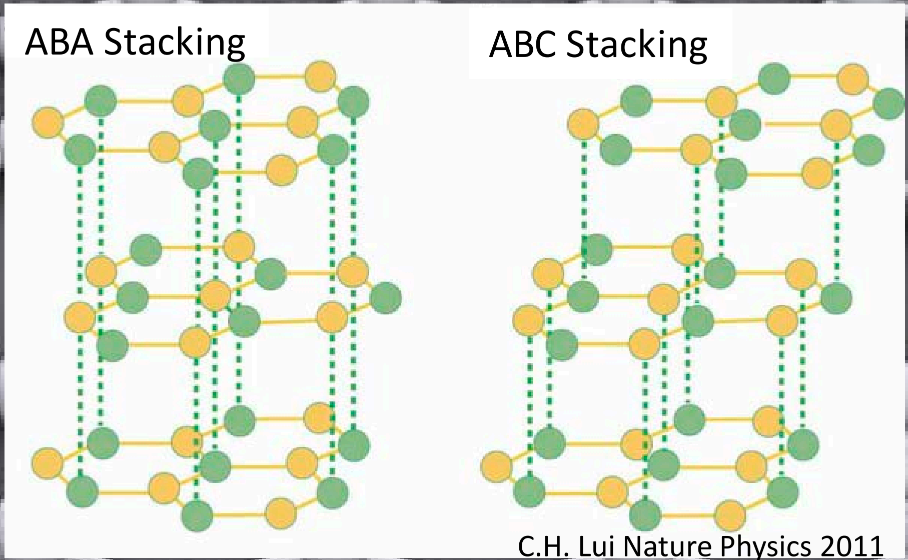
- Carbon ($1s^2\,2s^2\,2p^2$)

sp^2 hybridized carbon: Graphite

- one s orbital and two p orbitals (in plane)
- pz is not hybridized and contains one electron
- 2-dimensional covalent structure + stacking
- Van der Waals interactions (out of plane)
- Cleavable but stiff and robust
- Excellent conductor (semi metal)

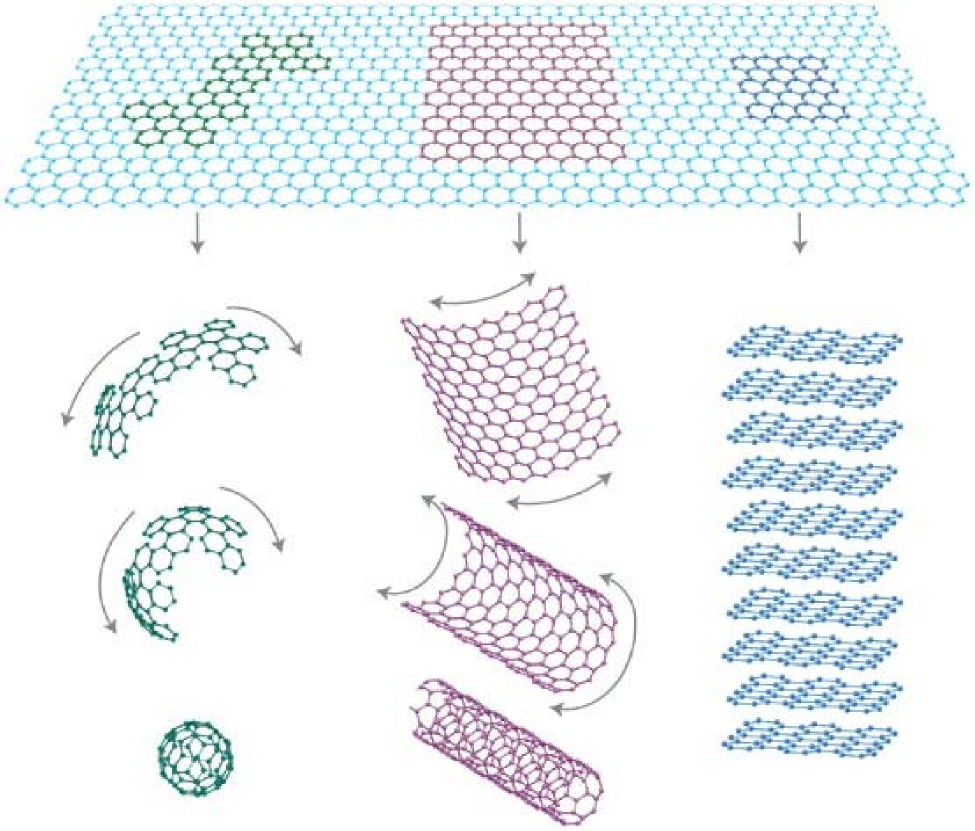






C.H. Lui Nature Physics 2011

Graphitic Materials



Graphene (2D)
- 2005 (Novoselov & Geim)

→ Nobel Prize 2010

Graphite (3D)
γράφειν: “to draw/ to write”
Used since 4000 BC!

- Fullerenes (0D)

→ 1985 (Kroto, Curl ,Smalley)
→ Nobel Prize 1996

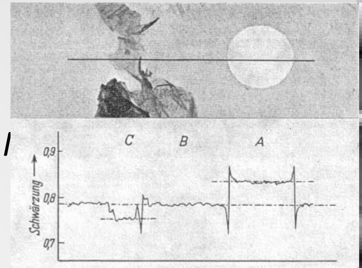
- Single walled nanotubes (1D)

→ 1993 (NEC, IBM)
→ Kavli Prize 2008 (Iijima)

Adapted from Novoselov & Geim « the rise of graphene » Nat. Mater **6** 184 (2007)

The graphene gold rush

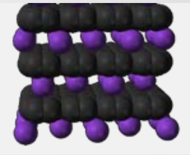
- *1564 : First graphite pencils*
- *1859 : Liquid suspension of graphene oxide (B. Brodie)*
- *1947-1959 : Electronic structure of graphite (Wallace, Slonczevski, Weiss,*
- *1948-1962 : Electron Microscopy: monlayers?*



Boehm *et al.* (1962)

- *1970's : graphite intercalation compounds*
- *1960's-1990's : Epitaxial graphene on SiC*

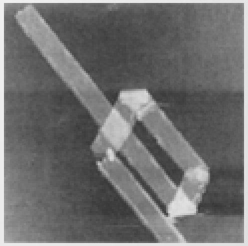
Millie Dresselhaus



K-graphite

- *1980's-now : Fullerenes*
- *1990's-now : Carbon Nanotubes*
  - *→ Fascinating one dimensional systems*
  - *→ Many applications (bottleneck : contacts)*
- *Graphene : easier to pattern and contact*
- *Quasi 1D graphene ribbons ~ nanotubes*

→ New experimental efforts



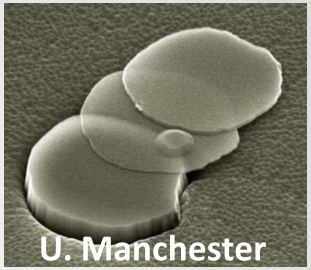
Ebbesen & Hiura (1995)

The graphene gold rush

Late 90's-early 2000's :

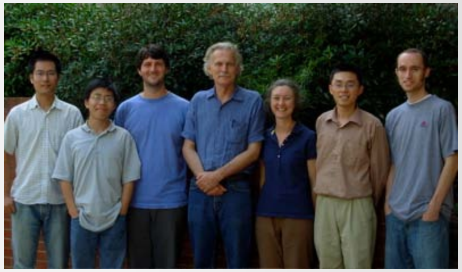
- *Mesoscopic Graphite*

T. Ebbesen *et al.*, R. Ruoff *et al.*, P. Kim *et al.*, W. de Heer *et al.*, etc…
Nano-scrolls, nanocones, nanodisks, origami,…)

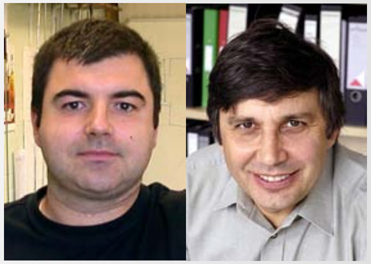


- Several research proposals submitted for a *"graphene-based electronics"*

(Georgia Tech., Manchester, Columbia, Cornell, MIT, etc…)



2004 : First measurements on epitaxial multilayer graphene
C. Berger, W. de Heer *et al.* J Phys. Chem. B. (2004), Science (2006)



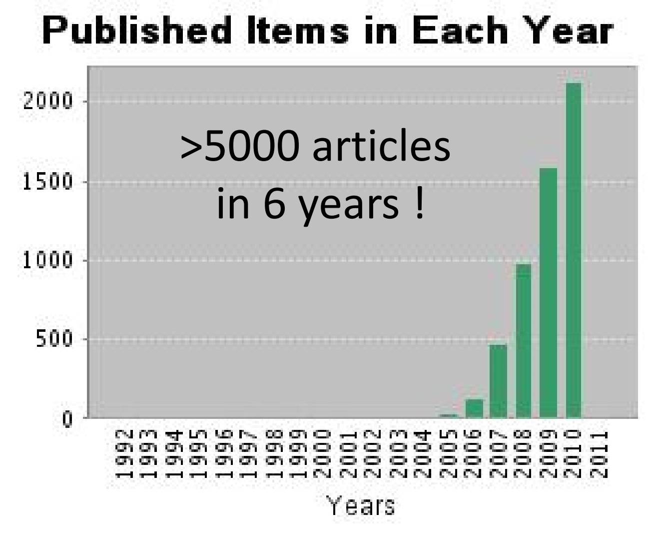
2004 : Electric field effect on 1 to 3 graphene layers
Novoselov, Geim et al. Science (2004)

2005 : Observation of the "half integer" quantum hall effect on a graphene monolayer
*K. S. Novoselov, A. Geim et al. Nature **438**, 197 (2005)*
*Y. Zhang, P. Kim et al. Nature **438**, 201 (2005)*

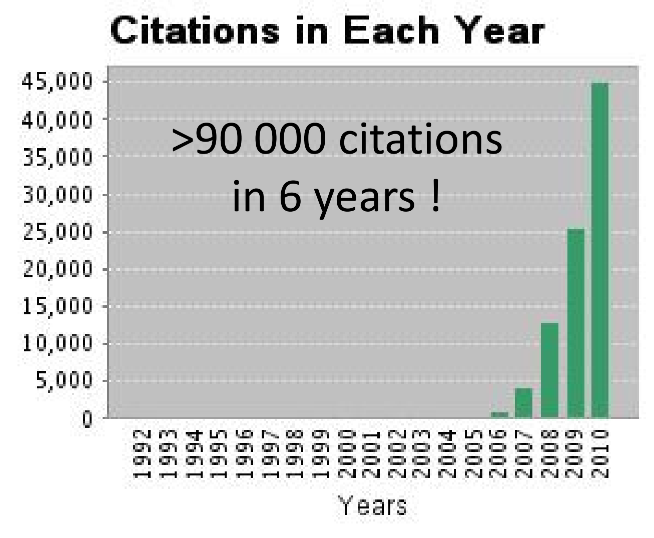

Philip Kim

2008-2010 : Macroscopic growth of graphene
(B-H Hong et al., J. Kong et al., Ruoff et al., J.M Tour et al.)

The graphene gold rush



>5000 articles
in 6 years !



>90 000 citations
in 6 years !

Towards "industrial" production: several start-ups created

GW

GRAPHENE INDUSTRIES

GRAPHENE
SUPERMARKET

Source ISI Web of Knowledge (2010)

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov

"for groundbreaking experiments regarding the two-dimensional material graphene"

Entering "Flatland"

"O day and night, but this is wondrous strange"

FLATLAND

A ROMANCE
OF MANY DIMENSIONS

By A Square

(Edwin A. Abbott)

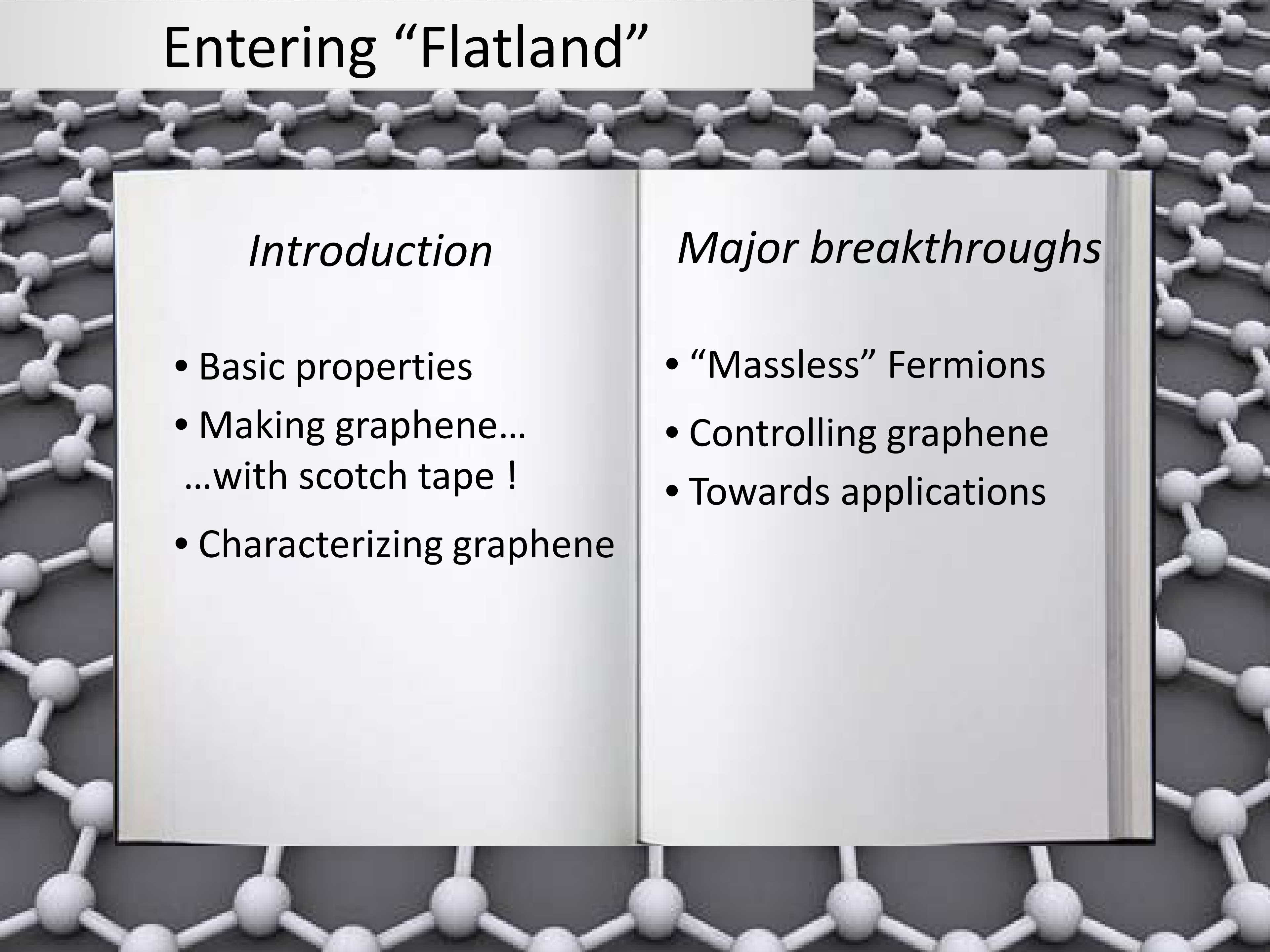
"And therefore as a stranger give it welcome."

BASIL BLACKWELL · OXFORD

Price Seven Shillings and Sixpence net

Flatland, a romance of many dimensions, E.A. Abbott (1884)

Entering "Flatland"



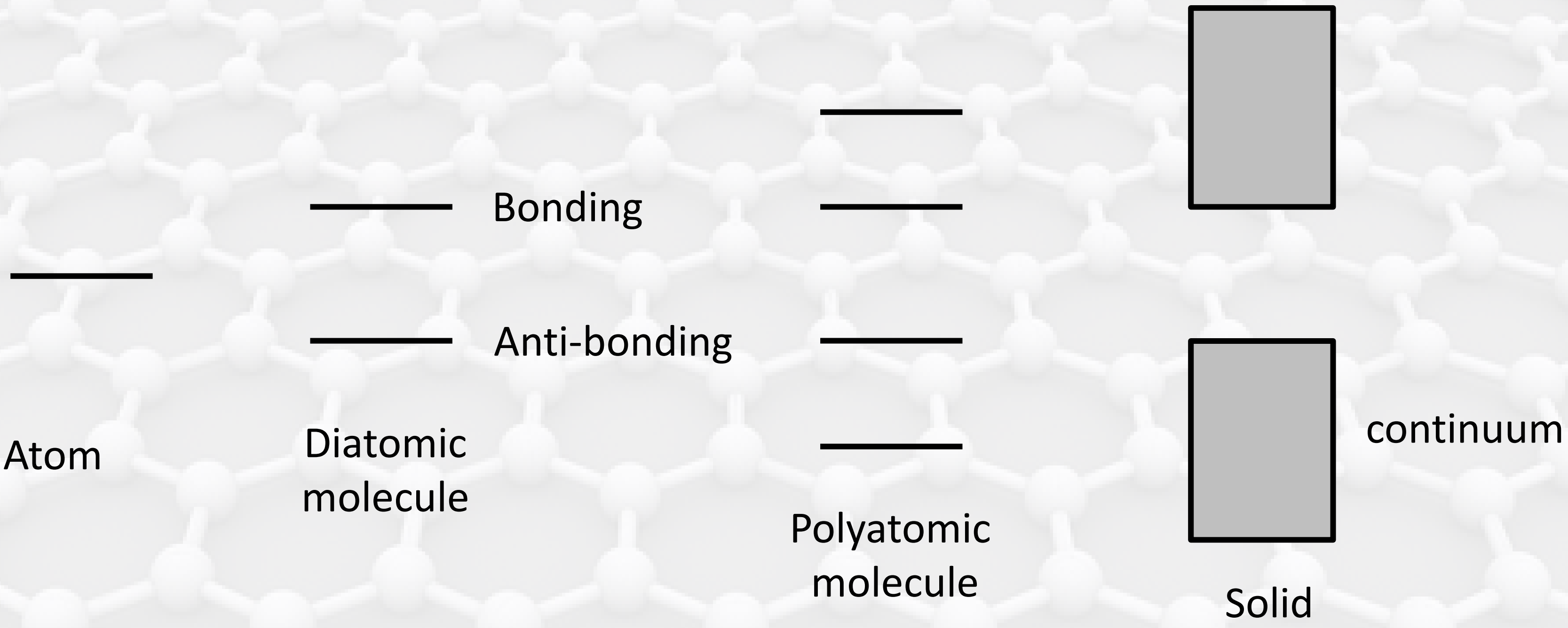
Introduction

- Basic properties
- Making graphene…
  …with scotch tape !
- Characterizing graphene

Major breakthroughs

- "Massless" Fermions
- Controlling graphene
- Towards applications

Atoms, molecules and solids



Bonding

Anti-bonding

Atom

Diatomic
molecule

Polyatomic
molecule

continuum

Solid

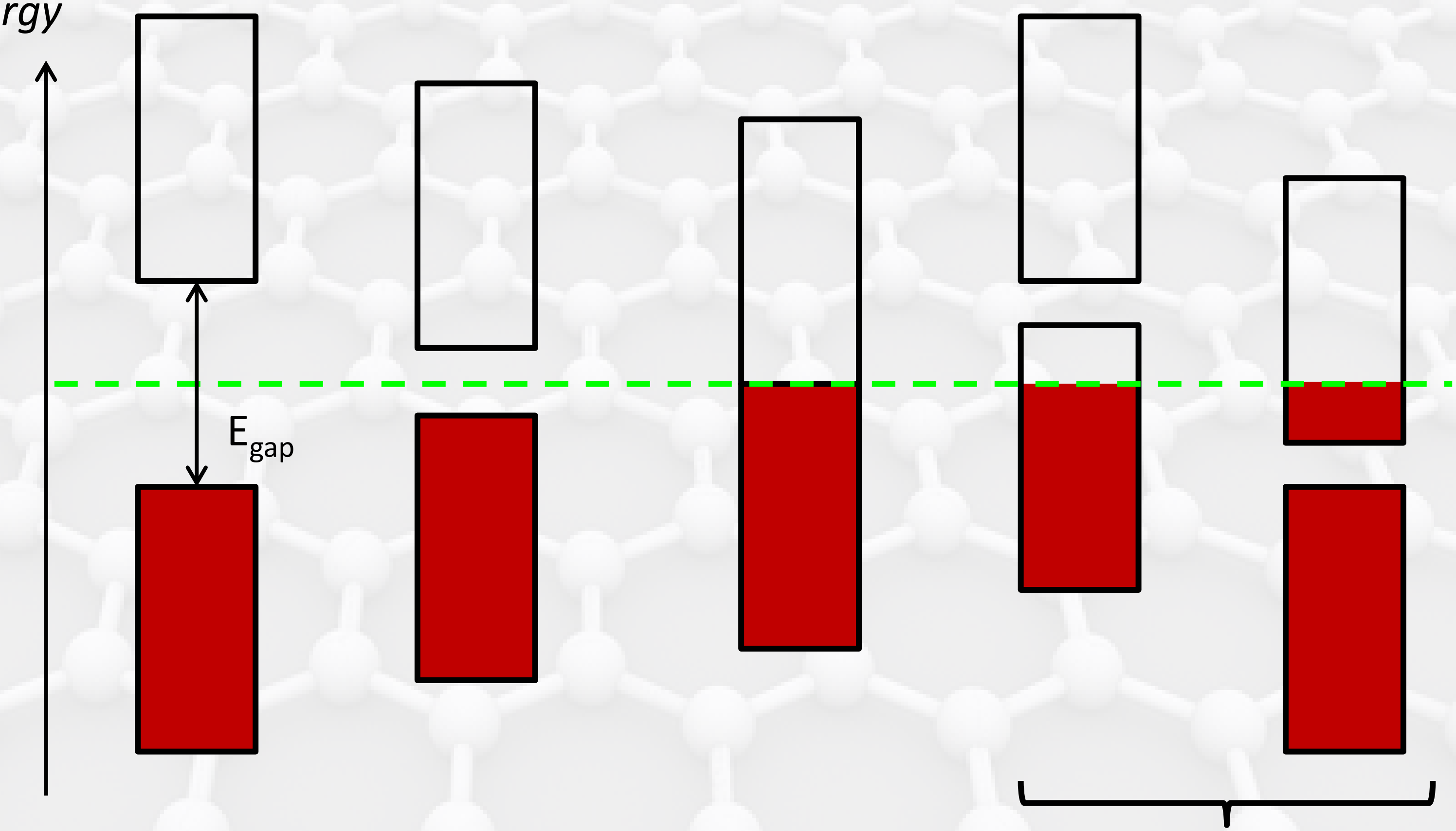
- In free space, all states are allowed for electrons
- In a crystal : the periodic boundary conditions give rise to a band structure with allowed and forbidden bands (bandgaps)
- Dispersion relation between electron momentum (**k**) and energy (E)

➢ Let us fill the bands…

Electrons in solids: band filling

Pauli principle (1925) : at most one electron per quantum state

Energy



Conduction Band
Empty states

Fermi energy
highest occupied
electronic states

E_{gap}

Valence Band
occupied States

Insulator
(wide gap > 5eV)

Semiconductor
(small gap ~1eV)

Semi-metal
Gapless

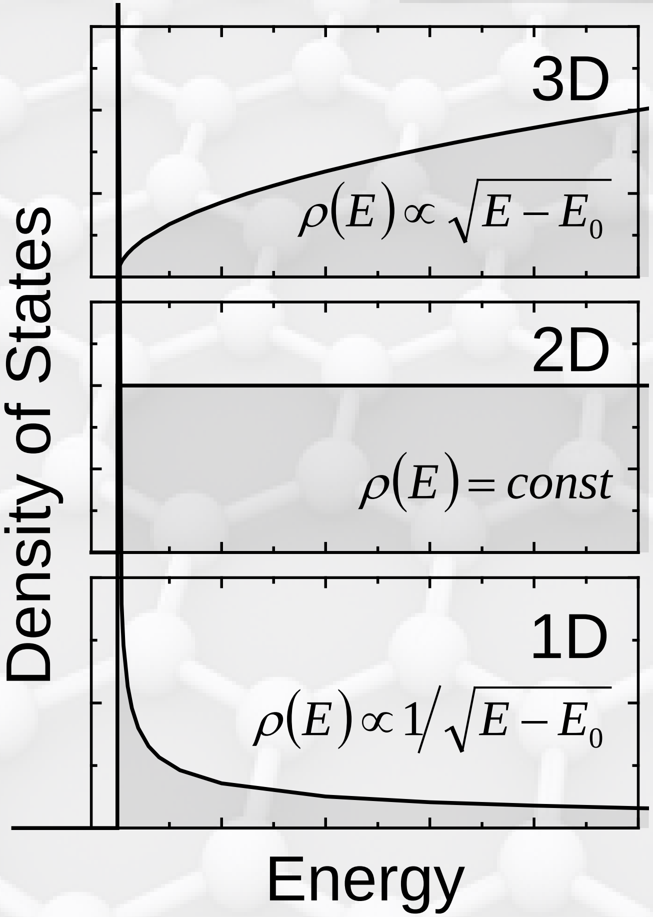
Metal

Electrons in solids: dimensionality matters!

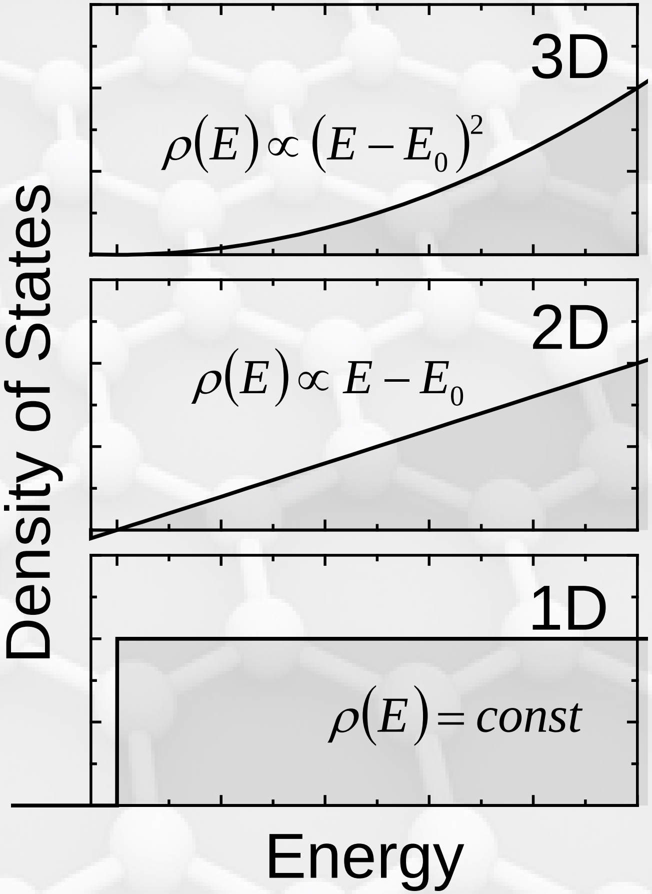
Electron density of states (DOS) $\rho(E)=\frac{dN(E)}{dE}$ ← Number of states with energy $\in[E,E+dE]$

Parabolic bands :
(effective mass approximation)

$$E-E_0=\frac{p^2}{2m_{eff}}=\frac{(\hbar k)^2}{2m_{eff}}$$



Linear bands : $E-E_0=\hbar k\, v_{Fermi}$

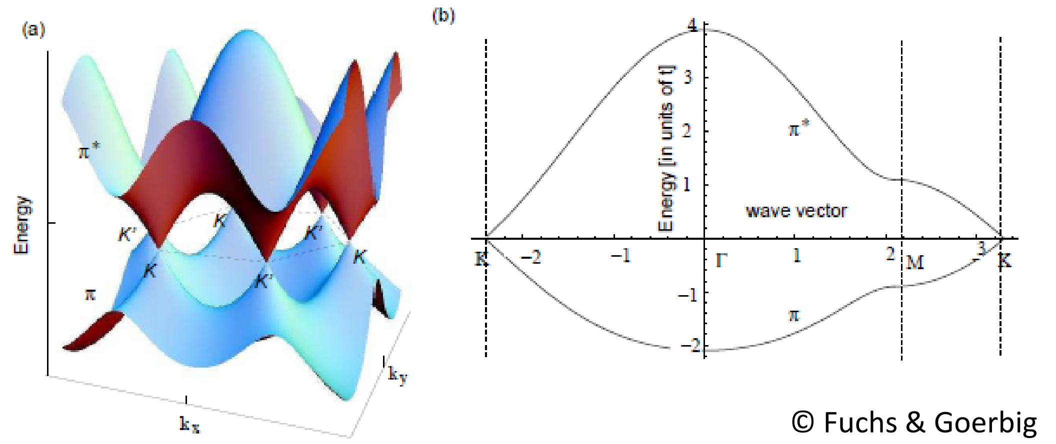


The electronic structure of graphene

*Electronic Structure known since 1947**

Tight binding approach (up to 2nd nearest neighbor)
- π and π^* bands (valence and conduction bands)
- Two atoms per unit cell (two sublattices)
- Nearest neighbor hopping : $t \sim 2.8$ eV
- 2nd nearest neighbor hopping : $t' \sim 0.1$ eV

→ Electron-hole asymmetry

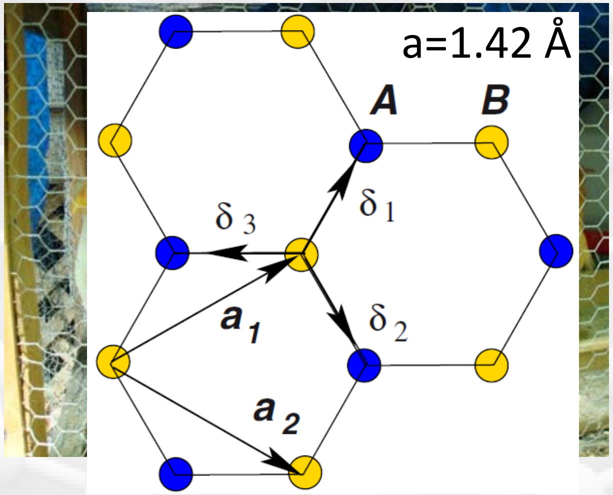


© Fuchs & Goerbig

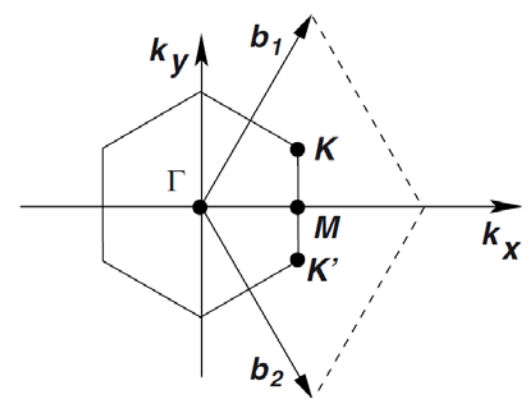
$$E_\pm(\mathbf{k}) = \pm t\sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k})$$

$$f(\mathbf{k}) = 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\cos\left(\frac{3}{2}k_x a\right)$$

Real space



Reciprocal (k) space



$$\boldsymbol{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \quad \boldsymbol{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right)$$

Castro Neto *et al.* RMP 2009

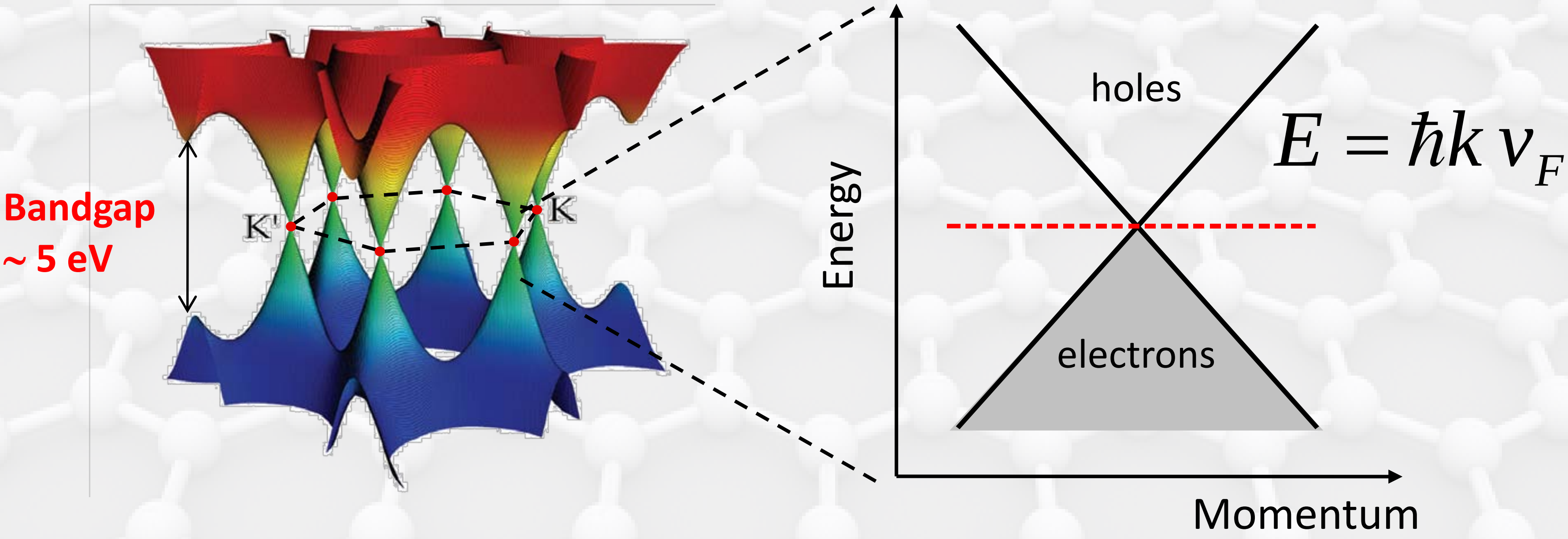
*P. R. Wallace, Phys. Rev. **71**, 622 (1947),
McClure, J. W., 1957, Phys. Rev. **108,** 612 (1957), Slonczewski, J. C., and P. R. Weiss, Phys. Rev. **109,** 272 (1958)

Massless Fermions in graphene

1 electron per p_z orbital

$\Rightarrow$ Half-filled bands : Fermi level at the K and K’ points (in undoped graphene)

$\Rightarrow$ Graphene is a Semi-metal



- *Linear low energy dispersion “Dirac Cones”*

$\rightarrow$ Formally identical to that of photons : $m_{eff} = 0$!

$\rightarrow$ “Relativistic” electrons with $v_{Fermi} = 10^6 \, m \, s^{-1} \approx 3.3 \, 10^{-3} c$

Cf. Lecture by Klaus Richter Friday morning

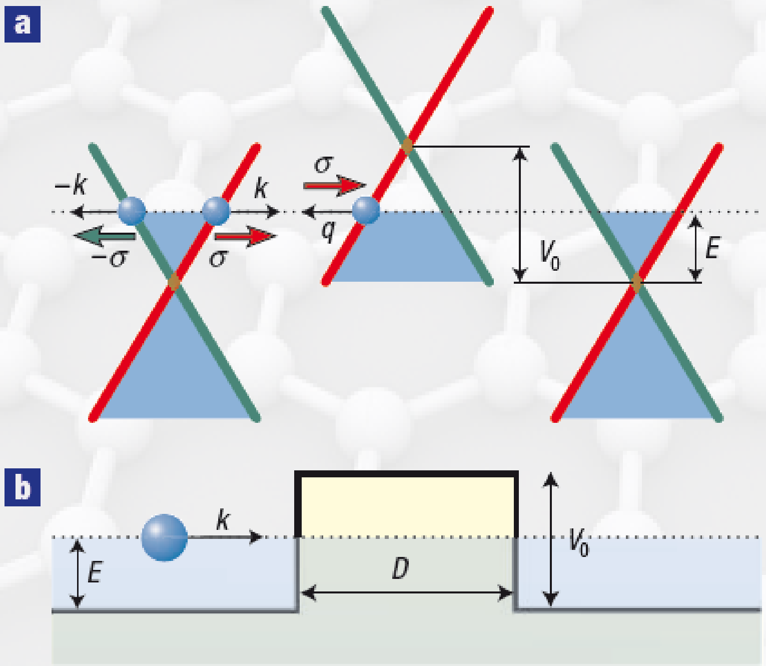
“Unstoppable” fermions

For massless relativistic particles

- Absence of back-scattering in a defect-free sample
- Klein tunnelling:

→ Crossing a potential barrier with a 100% probability

→ Different from tunelling by a massive particle (exponential probability)

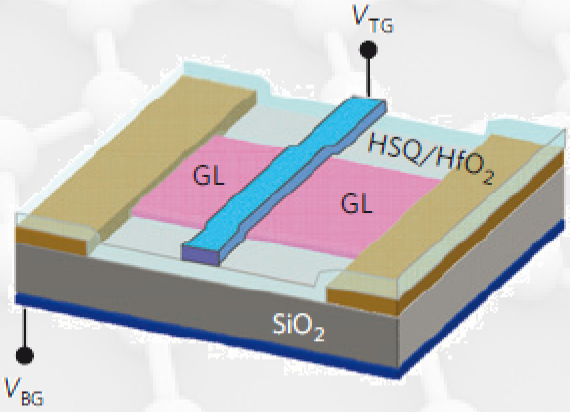


T. Ando et al. J. Phys Soc. Japan (1998)

M. Katsnelson, Novoselov & Geim, Nature Phys. (2006)

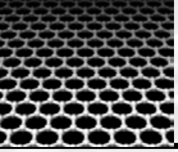
Experimental realization :

Héterojunctions



B. Huard *et al.* PRL (2008)

A.F. Young *et al.* Nature Phys (2009)



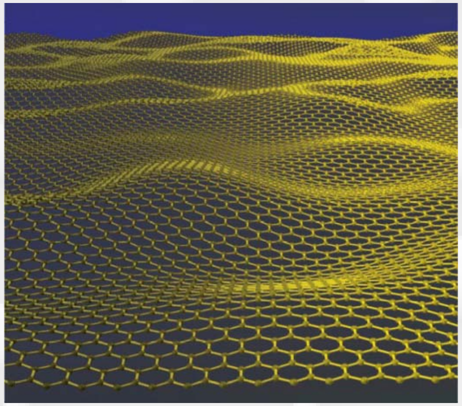
Are 2D crystals stable?

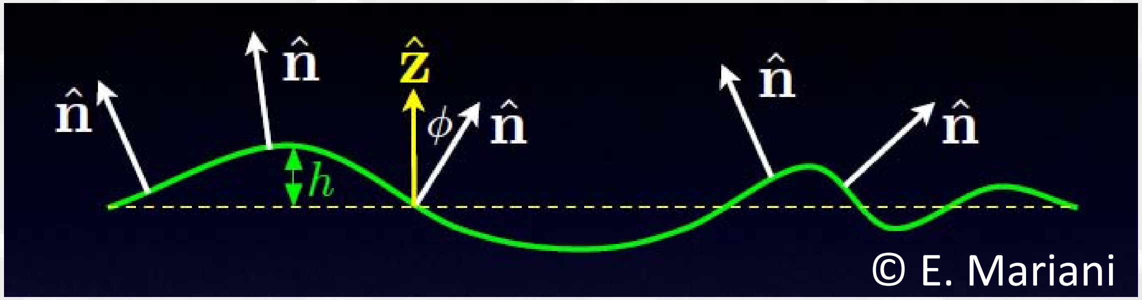
Long range fluctuations make 2D systems unstable

- Coupling between bending and stretchind modes stabilizes 2D membranes
- Microscopic ripples on the graphene surface?

Stability in a 3D world

- *Bottom-up approach:* growth on a substrate (CVD or epitaxy)
- *Top-down approach:* mechanical exfolation
- Graphene is ultraflat on an ultraflat substrate (Lui et al. Nature 2009)
- Effect on rippling on the electronic properties of graphene ?





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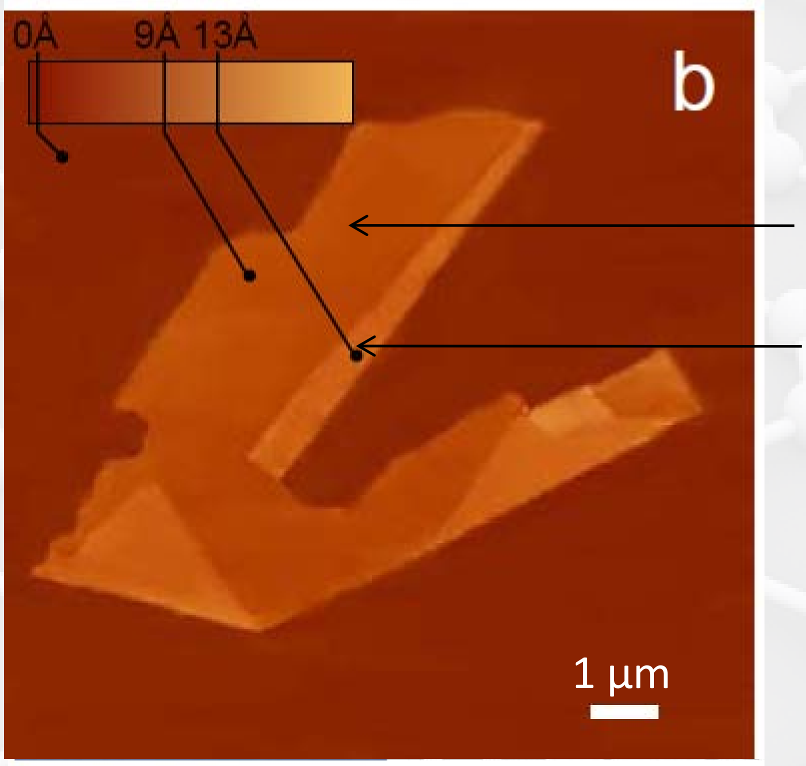
Observation of 2D crystals

" Top-Down" approach : mechanical exfoliation of mesoscopic graphite (MIT, Cornell, Columbia, Manchester)

In 2005, the Manchester team introduces the "scotch tape method" !



Monolayer h=0.9 nm

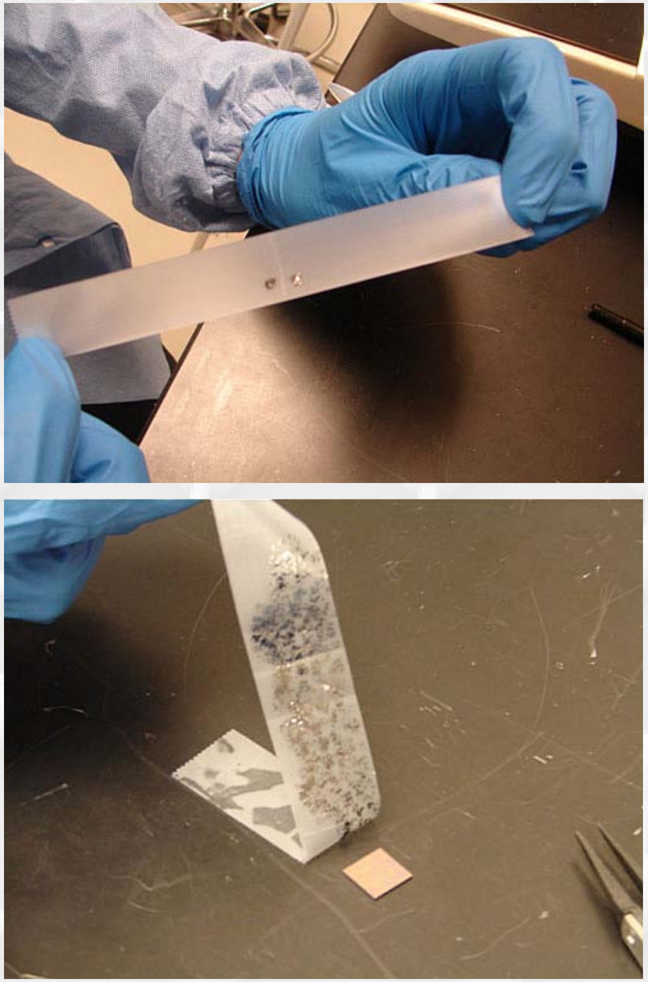
Folder monolayer
h'=h+0.35 nm

Observation 2D atomic crystals
(a) NbSe2, (b) graphite, (c) Bi2Sr2CaCu2Ox , (d) MoS$_2$

Unambiguous fingerprint of graphene?

K. Novoselov *et al.* Two-dimensional atomic crystals PNAS (2005)

Graphite, adhesive tape,…



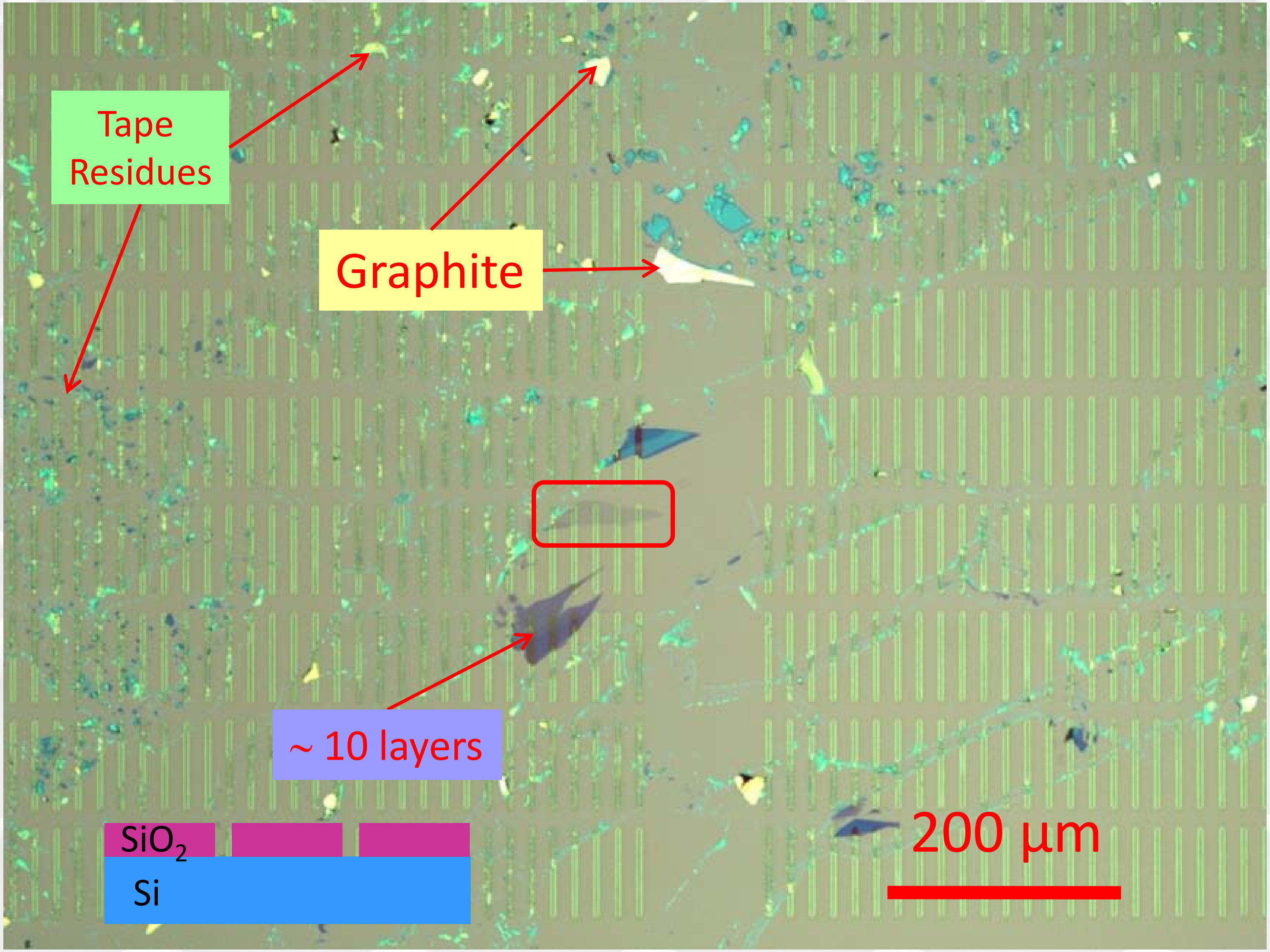
-Scientific American
@ Columbia University

Micro-mechanical exfoliation using adhesive tape !

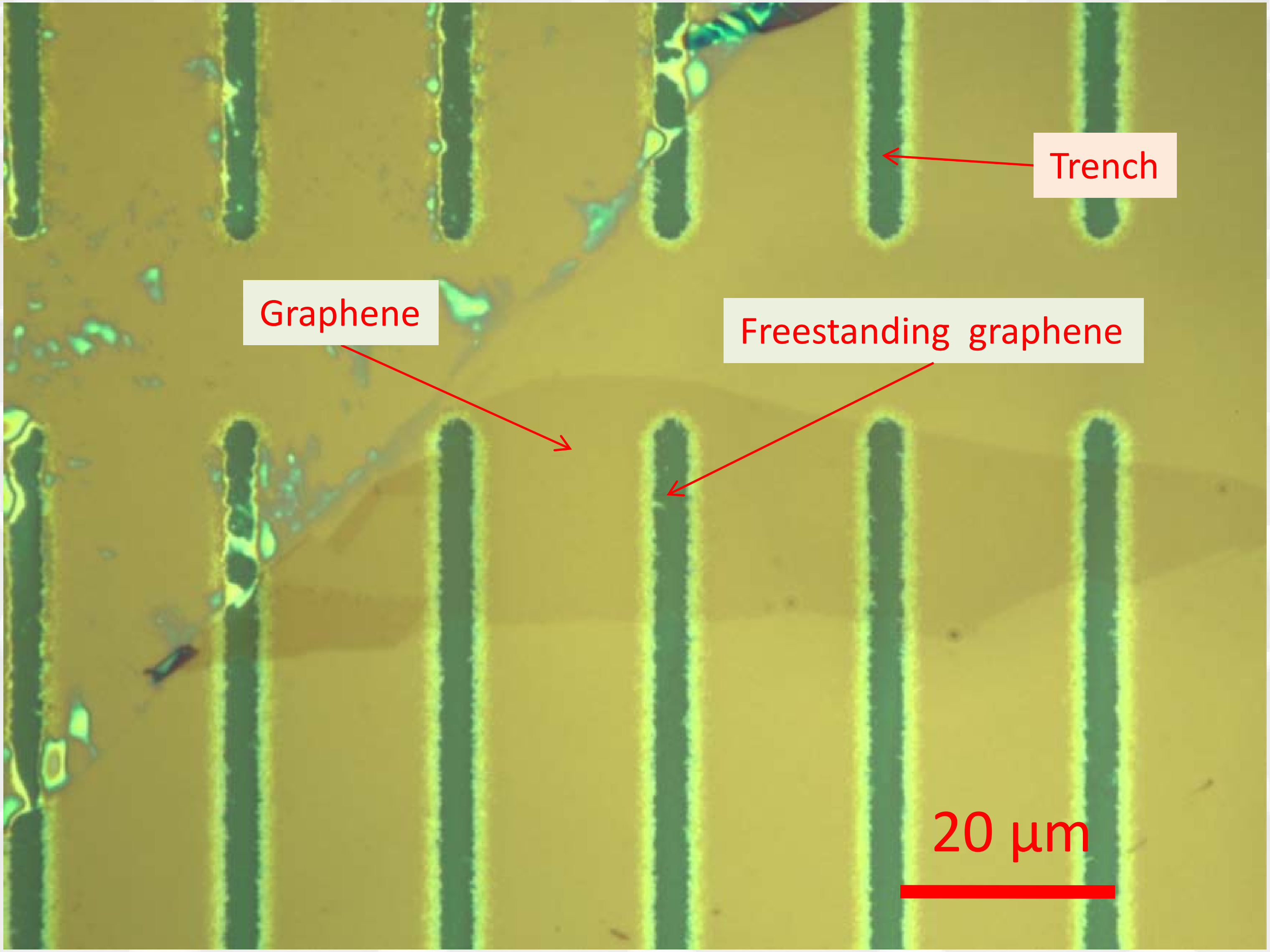
Low yield, *but*
Very high quality samples

K. S. Novoselov *et al.* PNAS (2005)

… and a good bit of patience

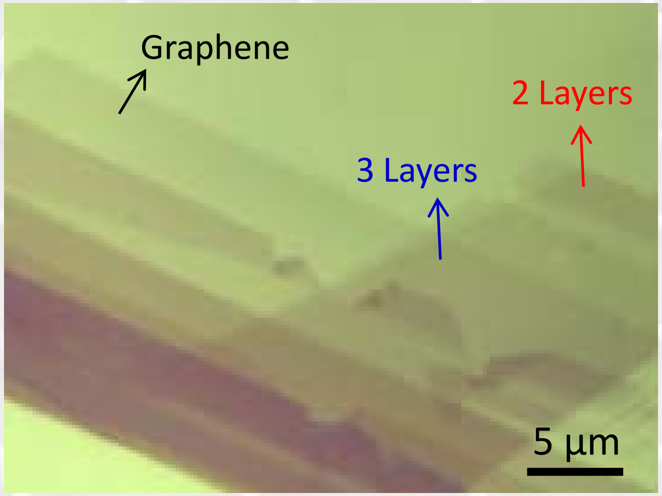


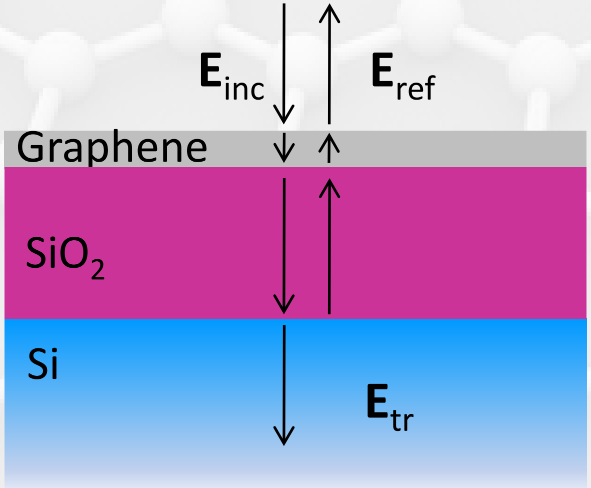
… and a good bit of patience



Seeing atomically thin materials

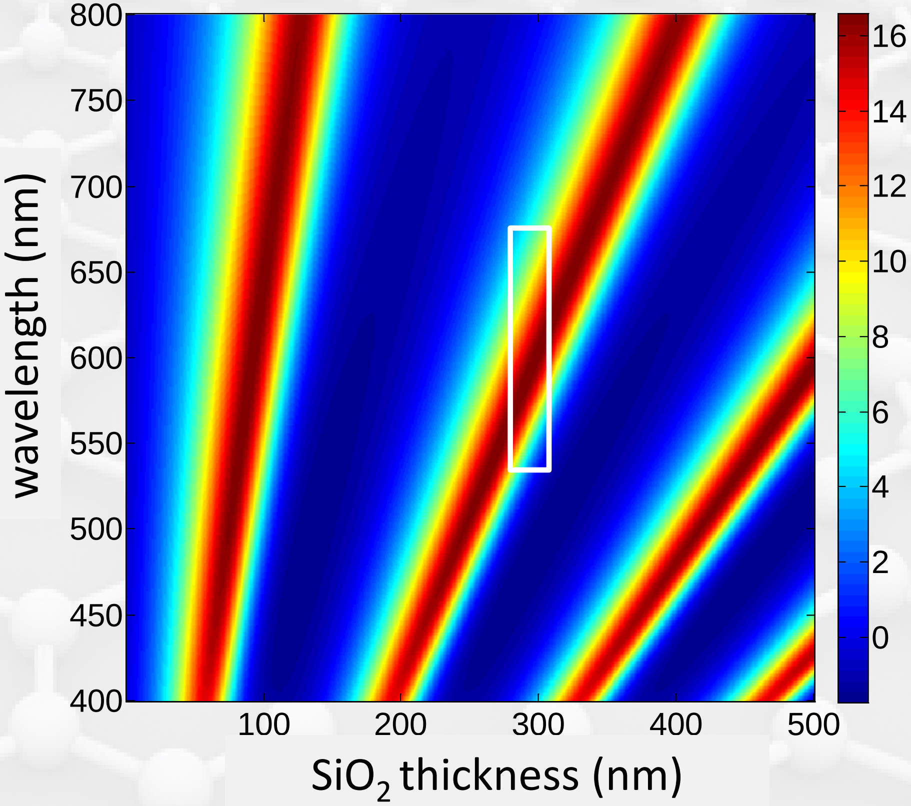
Optical microscope image





Multiple wave interference

Optical Contrast (%) of graphene on $Si0_2/Si$

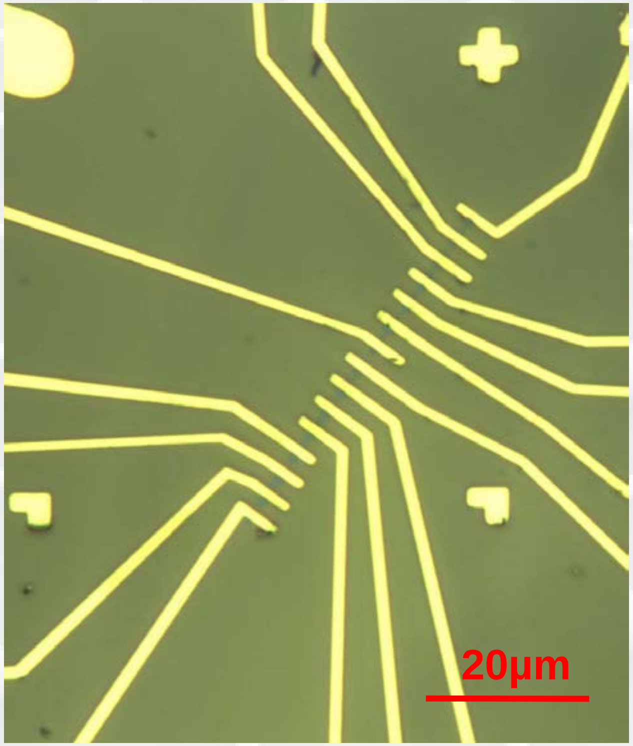


A graphene monolayer (0.34nm thin) induces an appreciable contrast

Device fabrication in the clean room

- electron beam lithography
- pattering by plasma etching
- metal deposition (contacts)
- wirebonding
- mesurements …!

StNano Clean Room (Strasbourg)



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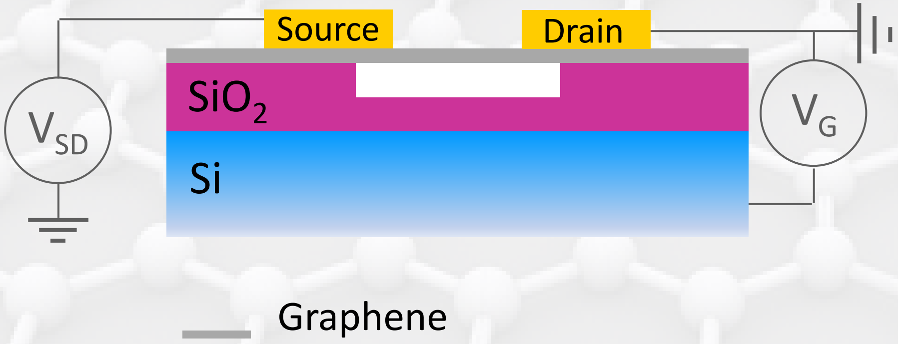
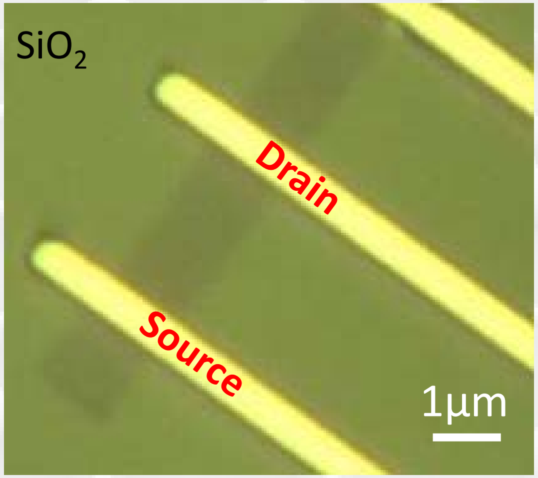
Graphene Devices

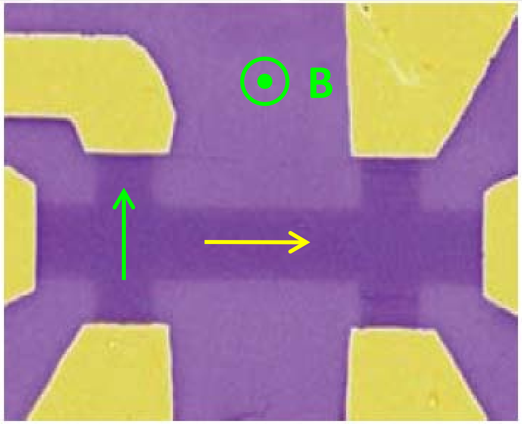
Field effect transistors





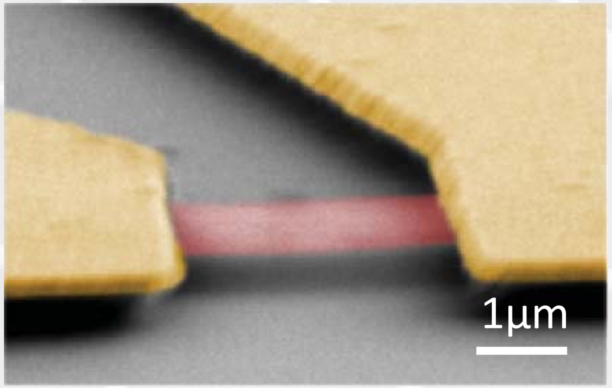
© M . Han (Columbia U.)

Hall cross



F. Schedin *et al.* Nature Mater. (2007)

Freestanding device



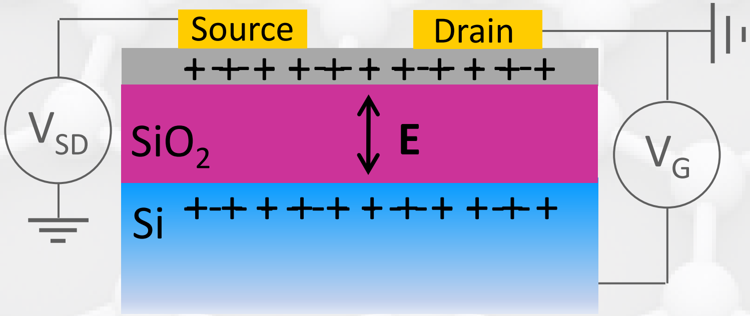
K. Bolotin *et al.* Nature (2009)

The field effect

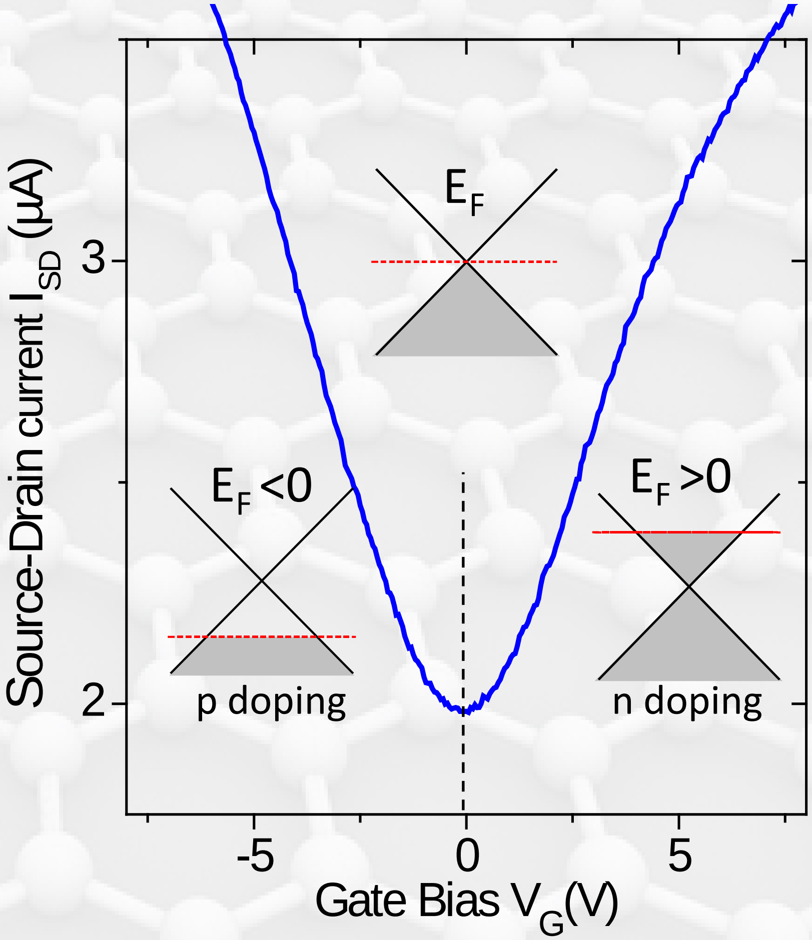
- $V_{SD} \neq 0 \rightarrow$ source-drain current
- Si/SiO_2/graphene: parallel plate capacitor

$\rightarrow$ Gate-controlled I_{SD}

- $V_G = 0 \rightarrow$ "universal" minimal conductivity
- $V_G > 0 \rightarrow$ hole current
- $V_G < 0 \rightarrow$ electron current



Ambipolar behavior



First observed on a ~3 layer sample by Novoselov, Geim et al. (Science 2004)

Much of graphene's potential arises from its great CONTROLLABILITY

Graphene in a magnetic field

- Quantized motion of electrons in a ⊥ magnetic field

$\rightarrow$ Formation of Landau levels

- In a 2D “parabolic” electron gas

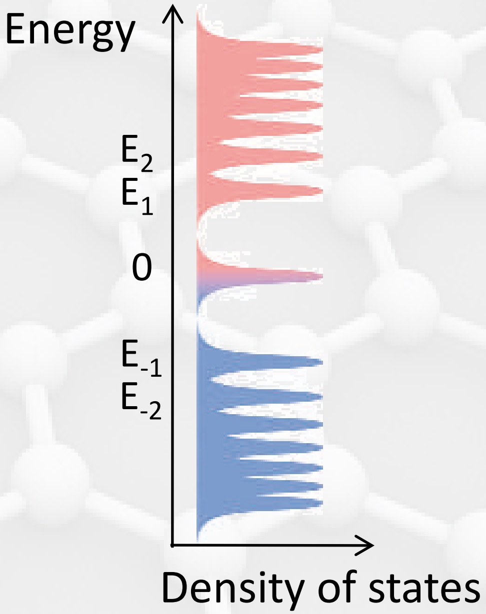
$\rightarrow$ Equidistant levels separated by: $E_n = \hbar\omega_C\left(n + \frac{1}{2}\right)$ $\omega_C = eB/m^*$

Graphene : ***linear*** dispersion ($E = \hbar k\, v_F$):

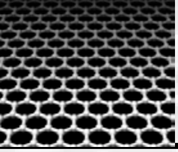
$$E_n = \mathrm{sgn}(n)\sqrt{2e\hbar v_F^2 B|n|}$$

$$\omega_C \propto \sqrt{B}$$

- NON-équidistant levels
- Scaling as $\sqrt{|n|}$
- Half filled level at E=0



McClure Phys Rev. (1959)



Quantum hall effect in graphene

“Classical” Hall effect

Transverse current in the presence of **B** ⊥

Quantum Regime *(K. von Klitzing, Nobel 1985)*

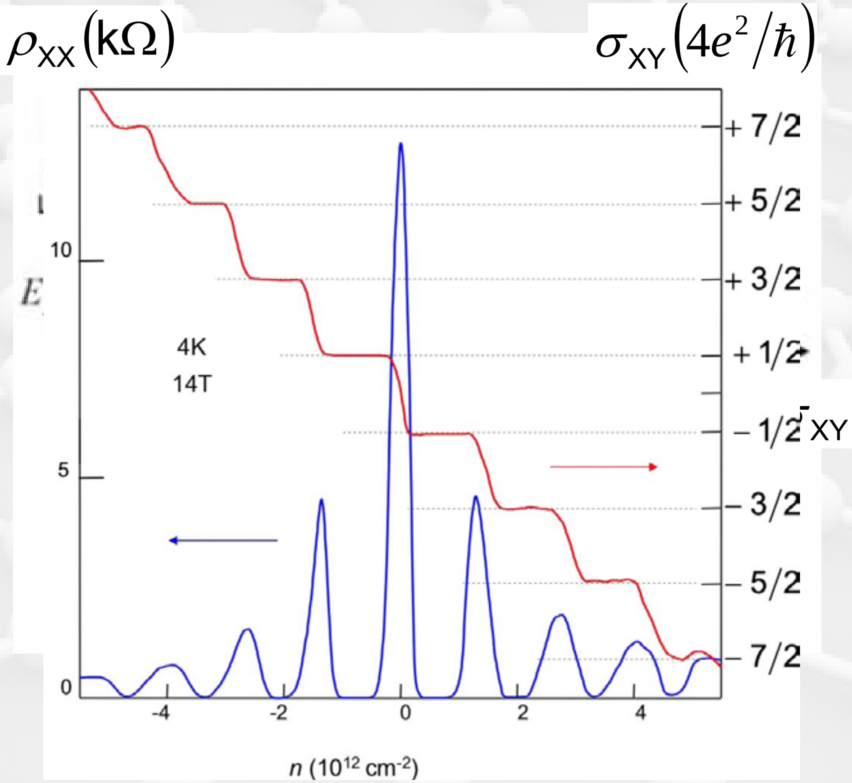
- When crossing a Landau Level

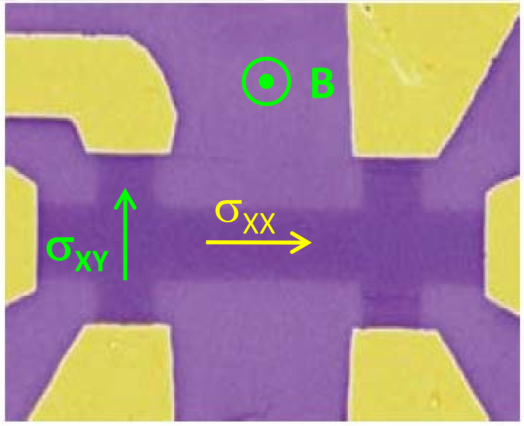
✓ Zero longitudinal resistivity ρ_{xx}

✓ Quantized plateau of Hall conductivity σ_{xy}

In practice :

Filling by electric field effect at constant **B**





Half integer quantum hall effect
→ hallmark of graphene

K. S. Novoselov, A. Geim et al. Nature ***438****, 197 (2005)*
Y. Zhang, P. Kim et al. Nature ***438****, 201 (2005)*

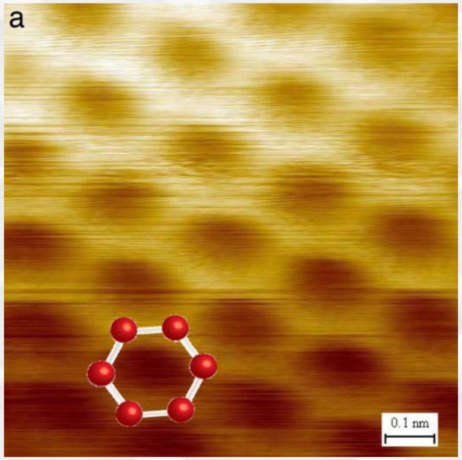
High resolution structural chracterization

Scanning tunneling microscopy (STM)

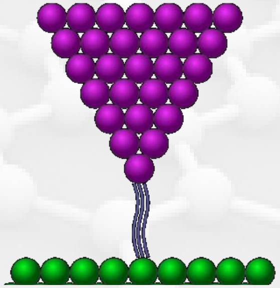
Electron microscopy (TEM)

⊕ Atomic resolution

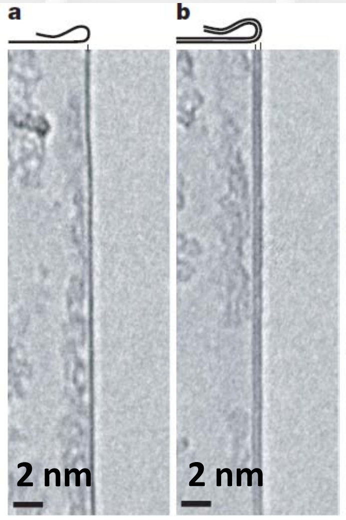
⊖ “Invasive methods”



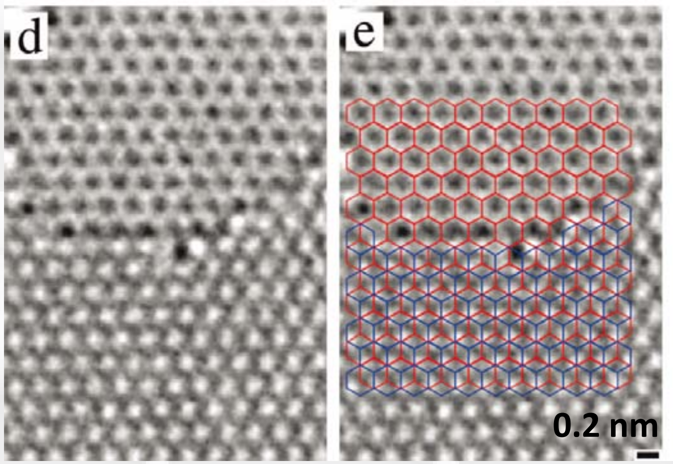
E. Stolyarova *et al.* PNAS (2007)



Measurement of a tunnel current



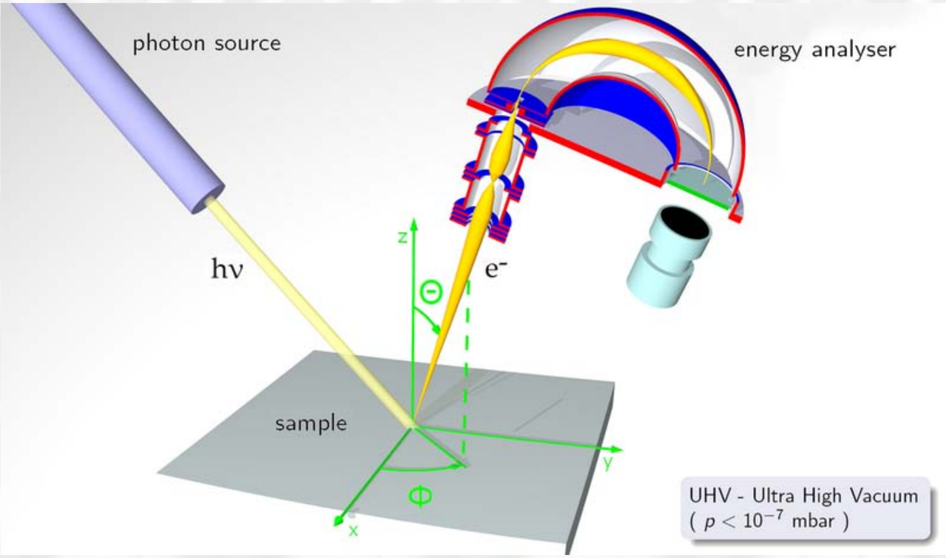
J. Meyer *et al.* Nature (2007)



J. Meyer *et al.* Nano Lett. (2008)

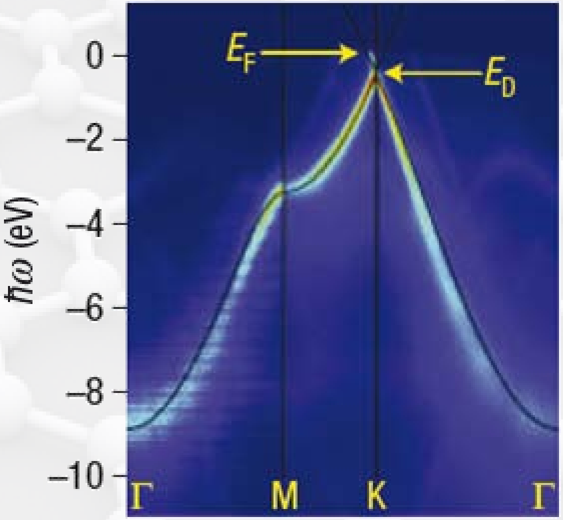
Visualizing graphene's band structure

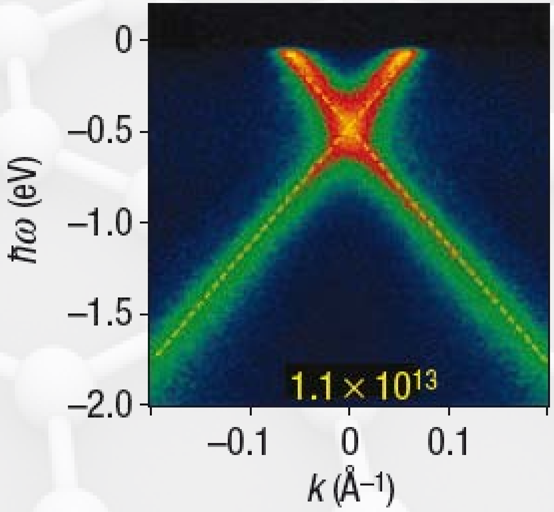
Angle resolved photoemission spectrscopy (ARPES)



$$\hbar\omega_{phot} = E(\mathbf{k}) + W_{ion} + \delta E_C$$

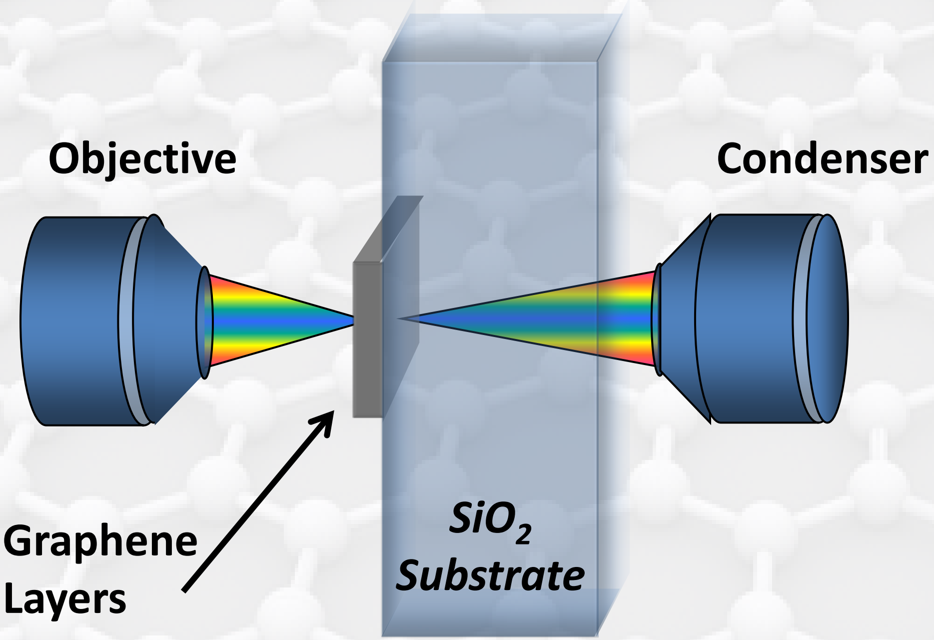
$$\hbar\mathbf{k}^{//}_{phot} = \hbar\mathbf{k}^{//}_{i} - \hbar\mathbf{k}^{//}_{f}$$

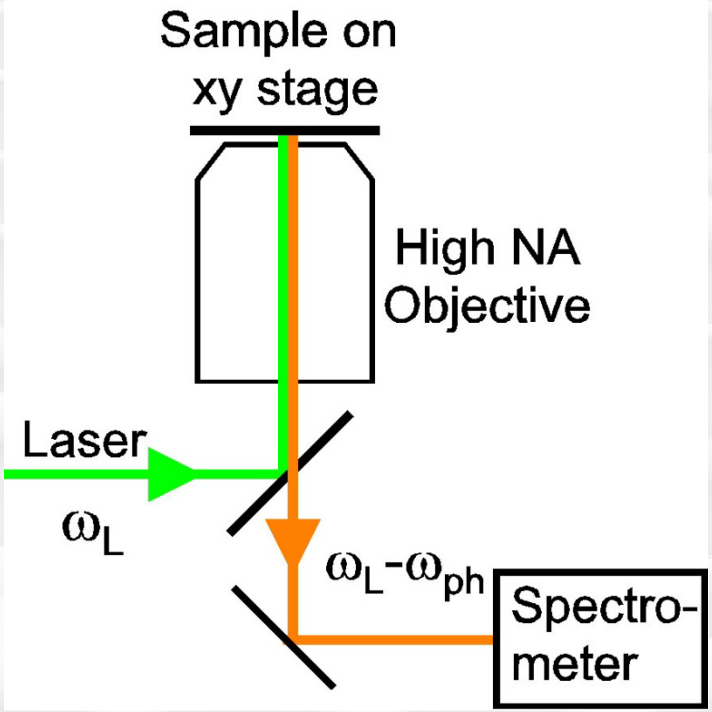




Bostwick *et al.,* Nature Physics (2007)

Optical absorption and Raman spectroscopy





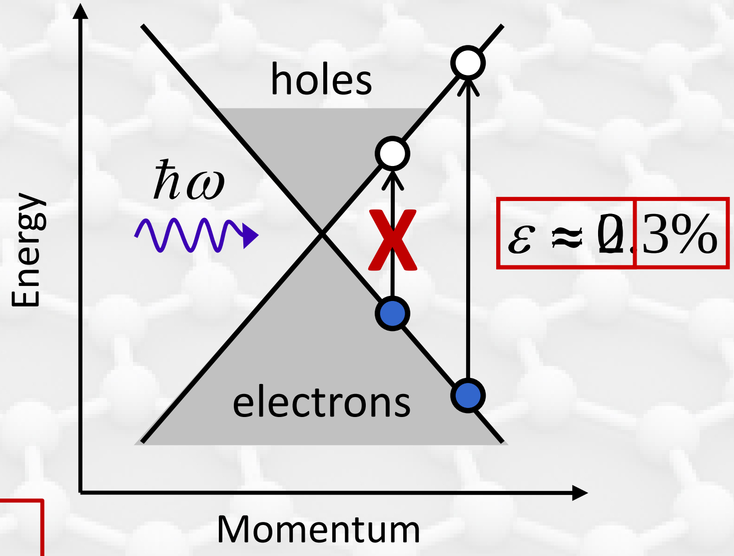
- Diffraction limited spatial resolution : micro-spectroscopy
- Mapping capabilities
- Easily combined with other measurements (electron transport)
- « Macro » versions also available for samples with large enough areas
- Electrical access, Magnetic Field, Low Temperature,…

A. Ferrari (Cambridge), A. Geim and k. Novoselov (Manchester), D. Basov (UCSD) T. Heinz & L. Brus Groups (Columbia),
F. Wang Group (Berkeley), J. Kong & M. Dresselhaus (MIT), M. Pimenta & A. Jorio (UFMG, Brazil),
Berlin groups (Reich, Thomsen, Maultzsch), H. Cheong (Korea), + French groups

Optical Spectroscopy of Graphene

Absorbance : $\varepsilon = \pi \underbrace{\frac{e^2}{\hbar c}}_{} \approx 2.3\%$

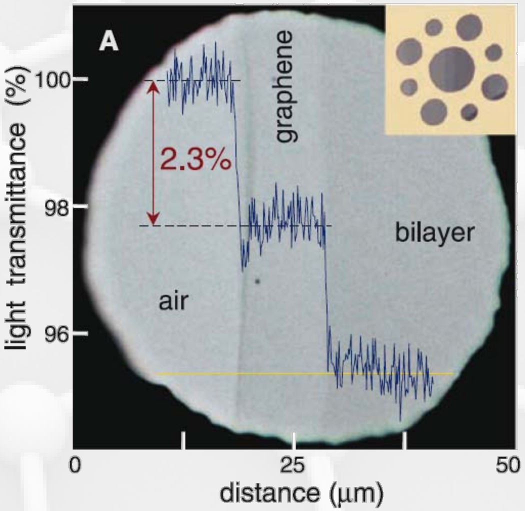
Fine structure Constant



Linear Bands in 2 dimensions:

→ ε(ω) is constant

- *Visible* : **Measurement of the Number of layers**
- *UV : trigonal warping & many body effects*
- *Infra-Red* : *Gate tunable absorption edge*



R. Nair *et al.*, Science (2008), K-F. Mak *et al.,* PRL (2008) PRL (2011), F. Wang *et al.* Science (2008), Z-Q. Li et al. Nat. Phys (2008)

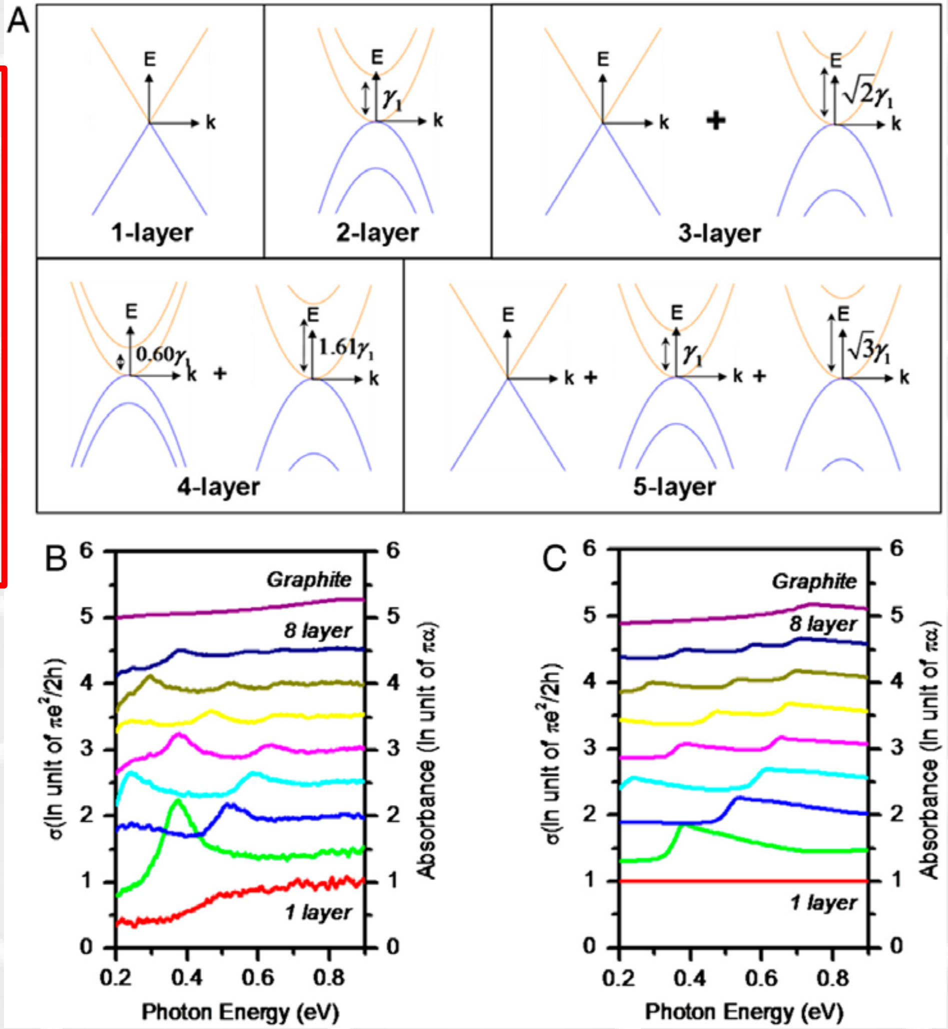
From Graphene to Graphite

Zone folding approach

- *Electronic Structure of graphene multilayers from cuts in the 3D electron dispersion of graphite along the* $\boldsymbol{k_z}$ *direction at quantized values of* $\boldsymbol{k_z}$*.*
- Single and Bi-Layer band structures can be seen as building blocks for the band structure of multi-layer graphene.
- Analoguous method for nanotubes

Finer effects

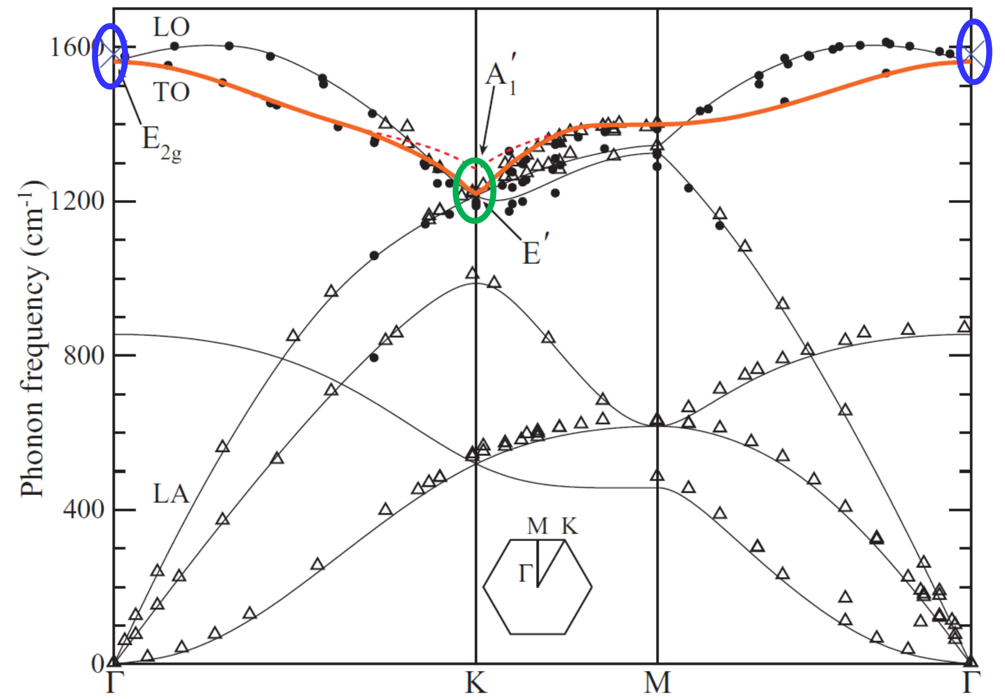
- Influence of stacking ABA $\neq$ ABC
- Many Body effects (saddle point excitons)
- Electron-phonon coupling : Fano Physics
- Gate tunable absorption



K.F. Mak *et al.* PNAS (2010), PRL (2010), PRL (2011)

Vibrational properties

Phonon dispersion (3 acoustic and 3 optical modes)



Venezuela *et al.* PRB (2011)

Energy and momentum conservation

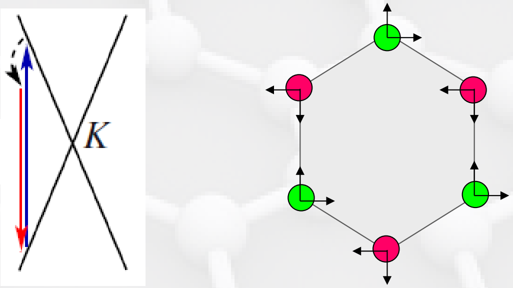
✓ ***for a one phonon process***

$$\hbar\omega_{in} = \hbar\omega_{out} + \hbar\omega_{phonon}$$

$$\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{q}_{phonon}$$

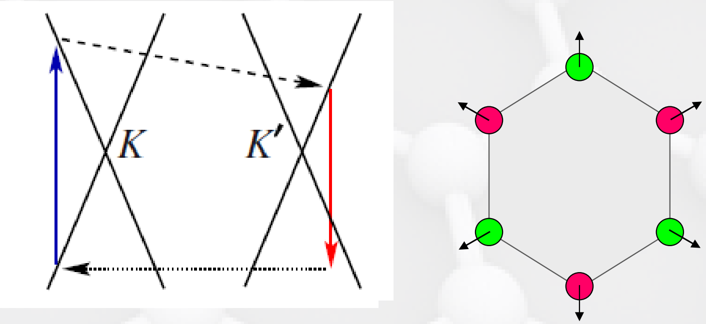
$$k_{in} \approx k_{out} \approx 0 \Rightarrow q_{phonon} = 0$$

G mode: Γ point LO and TO phonons



D and 2D modes

TO phonons near K and K'



✓ *Processes with $q_{phonon} \neq 0$?*

- Two phonons with opposite momenta

→ Symmetry allowed

- One phonon and one elastic collision on a defect

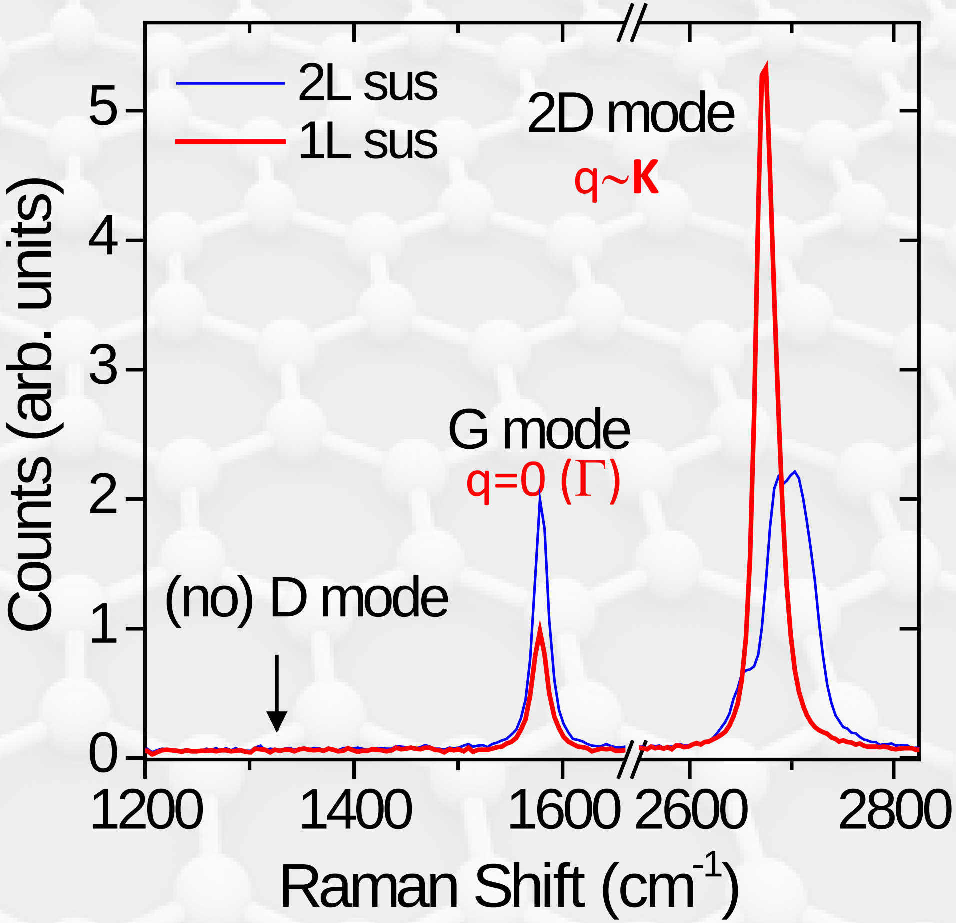
→ Symmetry forbidden

Raman spectroscopy of graphene layers

Strong coupling to zone center **(Γ)** and zone edge **(K)** phonons

Highly sensitive probe of:

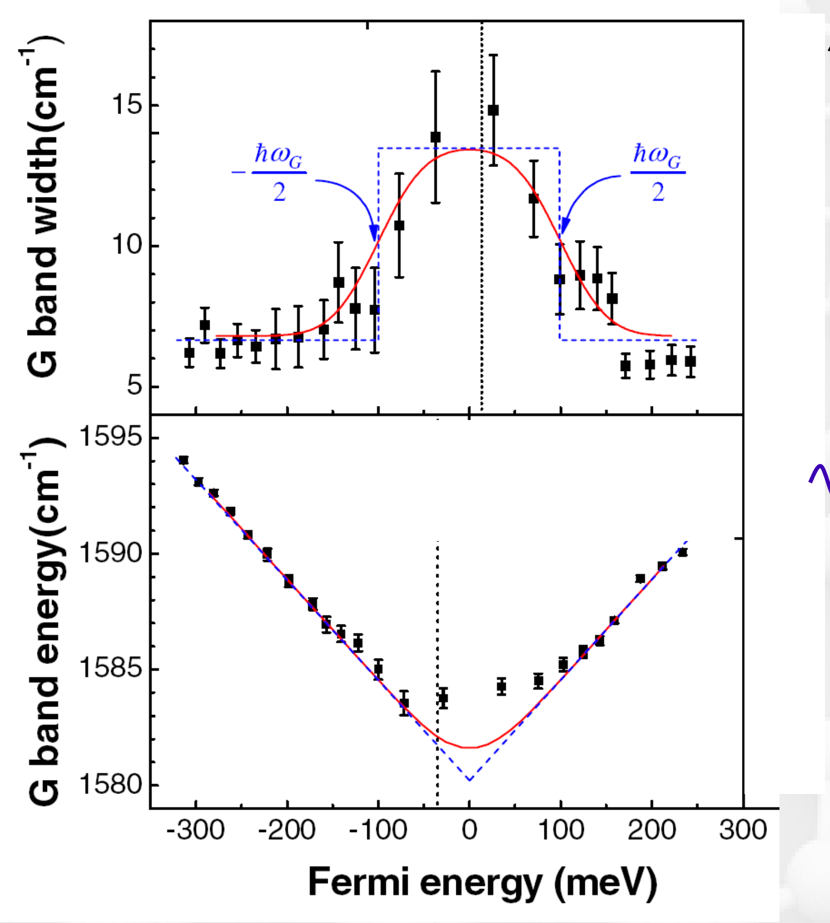
- → Number of Layers
- → Doping level, Disorder, Strain
- → **Temperature**



S. Berciaud *et al.*

Ferrai *et al.* PRL (2006) Graf *et al.* Nano Lett (2007), Gupta *et al.* Nano Lett (2006)
Reviews: A. C. Ferrari, Solid State Commun. (2007) L. M. Malard *et al.*, Physics Reports (2009)

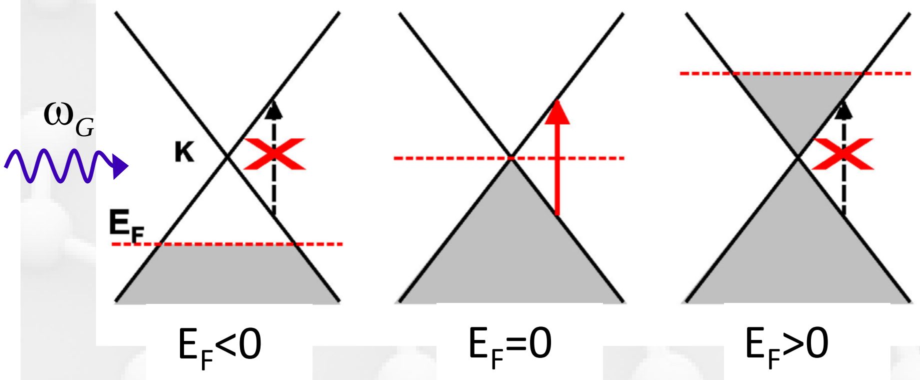
Gate tunable electron-phonon coupling



A Shift of the Fermi Energy induces:

i) G Phonon renormalization: $\omega_G \uparrow$ when $|E_F| \uparrow$

ii) Narrowing of the G mode linewidth



- Strong coupling to resonant e-h pair generation

$\rightarrow$ Reduced Landau Damping when $|E_F| \neq 0$

J. Yan *et al.*, PRL **98,** 166802 (2007)
Similar results by: Pisana *et al.,* Nature Mater. (2007), Das *et al.,* Nature Nano. (2008)

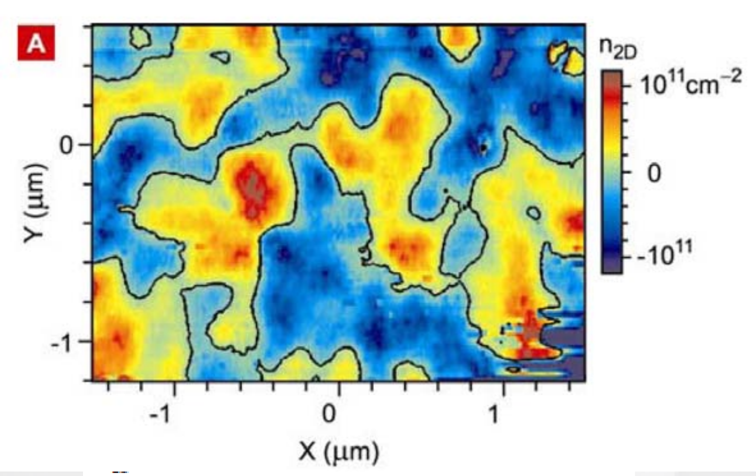
Even better with freestanding graphene!

The underlying SiO_2 has a negative impact on electron transport

- Unintentional doping
- Residual charge inhomogenity (puddles)
- Coupling to substrate polar phonons

“Ultra clean” freestanding samples

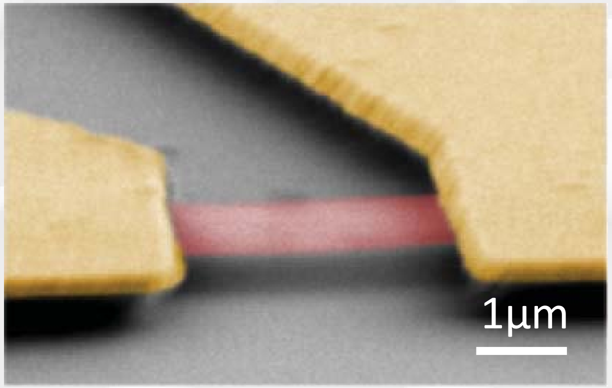
- Quasi ballistic transport
- Approaching the Dirac point

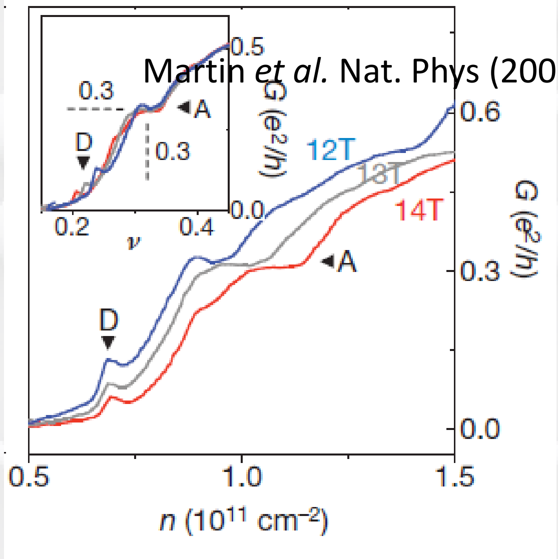


Martin *et al.* Nat. Phys (2008)

Mobility $\mu = \frac{\sigma}{n e}$ improved by a factor ~ 10

$\mu \sim 200{,}000\ cm^2\ V^{-1}\ S^{-1}$ at T= 300K



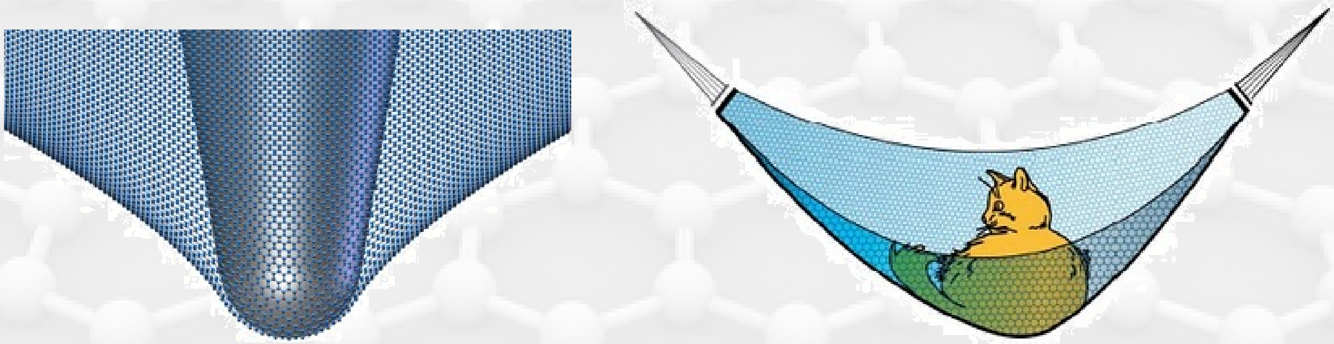


K. Bolotin *et al., Sol Sta. Commun. (2008),* Nature (2009)
X. Du *et al.* Nature Phys. (2008), Nature (2009)

Mechanical properties of freestanding graphene

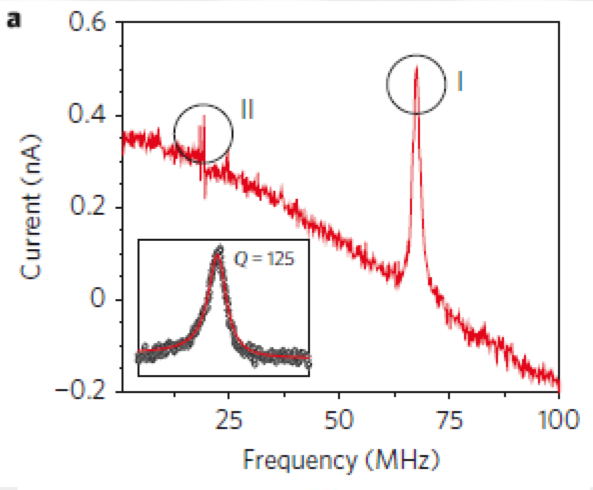
- *Intrinsic strength of 43 N/m for a monolayer!*

→ A 1m^2 graphene hamac would support…a 4.4 kg cat!!!



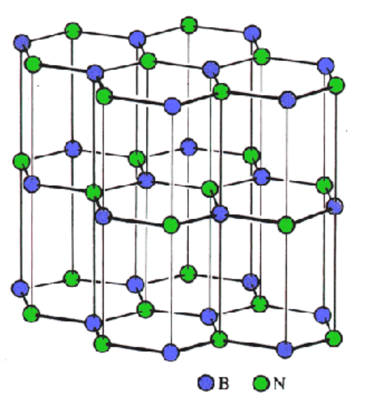
C. Lee *et al.*, Science (2008)

- *Electromechanical micro resonators:*
- RF modulation of the gate bias
  - → Vibration → variation of the capacitance
    - → Resonant current modulation
    - → Mass sensor (2. 10^{-21} g)

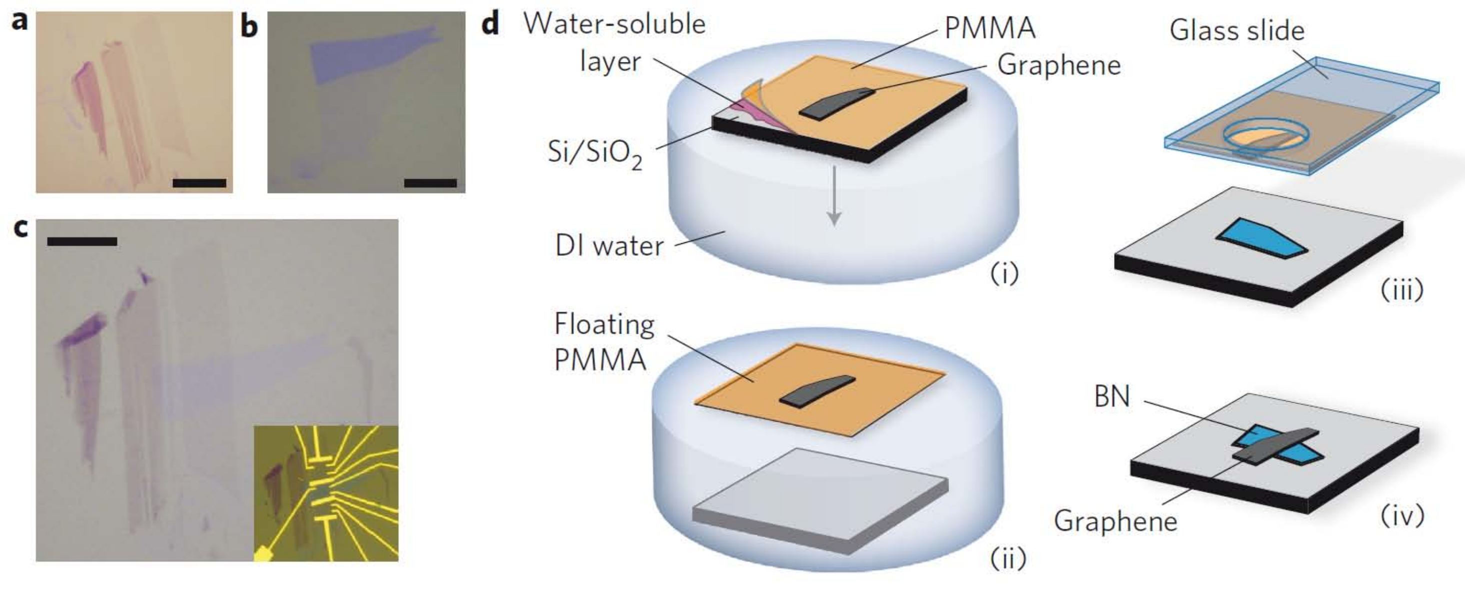


C. Chen *et al.*, Nature Nano. (2009)
J.S. Bunch *et al.*, Science (2007)

Boron Nitride: best substrate so far



Hexagonal BN : small (1.7%) lattice mismatch wrt graphene
Large band gap ~ 6 eV : good gating material



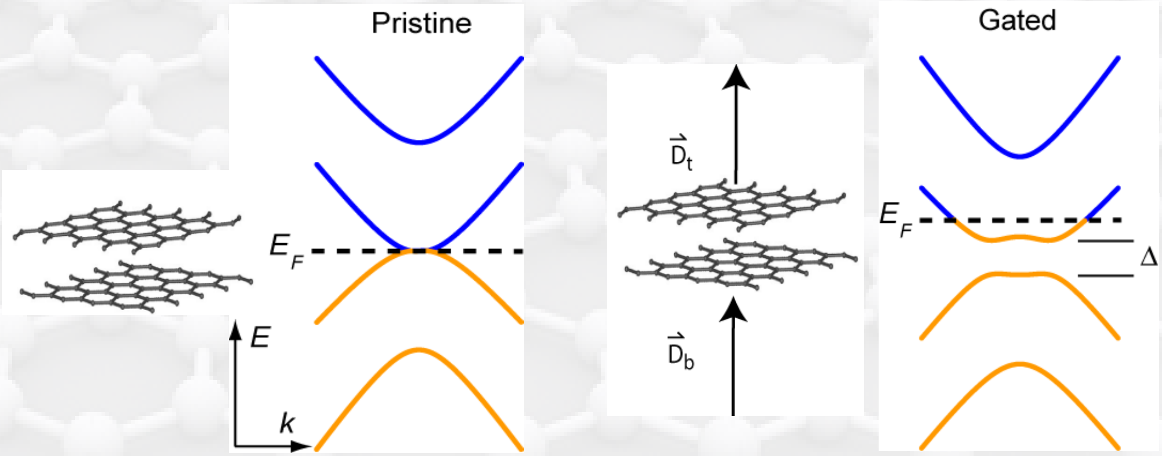
C. Dean Nature Nanotechnology (2010)

- Excellent transport properties (fractional quantum hall effect)
- Large doping levels attainable without collapsing
- State of the art for high performance devices

Bandgap Engineering in Graphene

➢ *Bilayer Graphene*

→ Gate tunable Bandgap (up to 250meV)



Feng Wang et al. (Berkeley), Nature **459**, 820 (2009)

➢ *Graphene Nanoribbons*

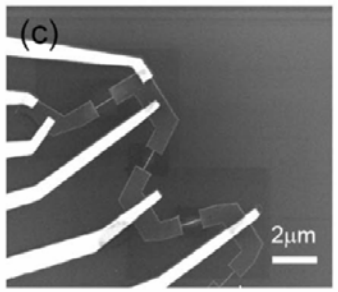
→ Size tunable Bandgap

- e-beam lithography (Columbia, IBM,…)
- Chemical derivation (Stanford, Rice, Mainz,…)

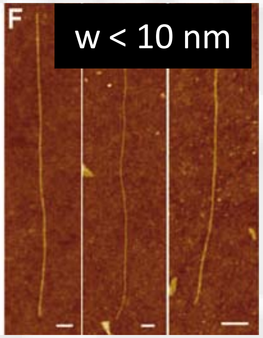
→ from expandable graphite + sonication

→ “Unzipping” carbon nanotubes

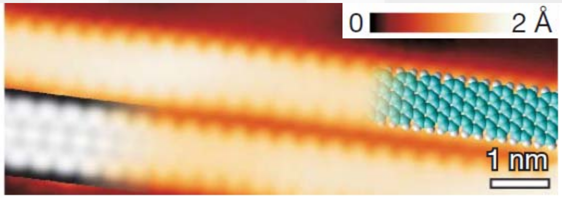
→ Bottom-up fabrication (polycyclic aromatic hydrocarbons)



Han *et al.* PRL **97**, 206805 (2007)



Li *et al.* Science **319**, 1229 (2008)

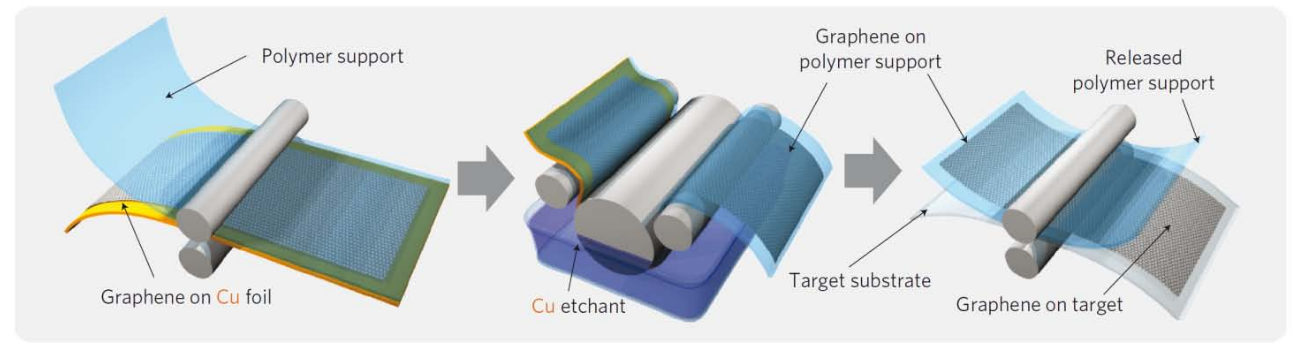


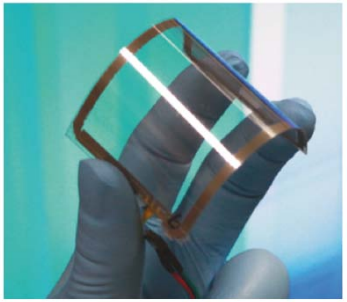
Cai *et al.* Nature **466**, 470 (2010)

Graphene: Towards "Real" Applications

Bae et al. Nature Nano. **5**, 574 (2010)
A. Reina Nano Lett. **9**, 30 (2008)
K-S Kim et al Nature **457**, 706 (2009)
X. Li et al. Science **324**, 1312 (2009)

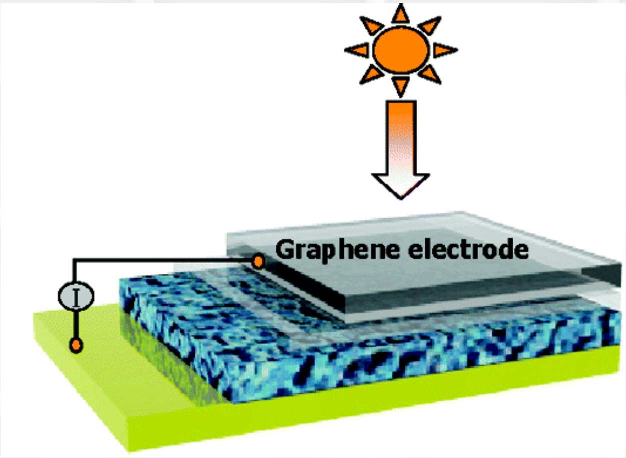
➢ *Large Scale Production (CVD growth on Cu foils)*





➢ *Graphene electrodes*

- → Transparent & flexible
- → Graphene could replace ITO
- → Application to solar cell technology



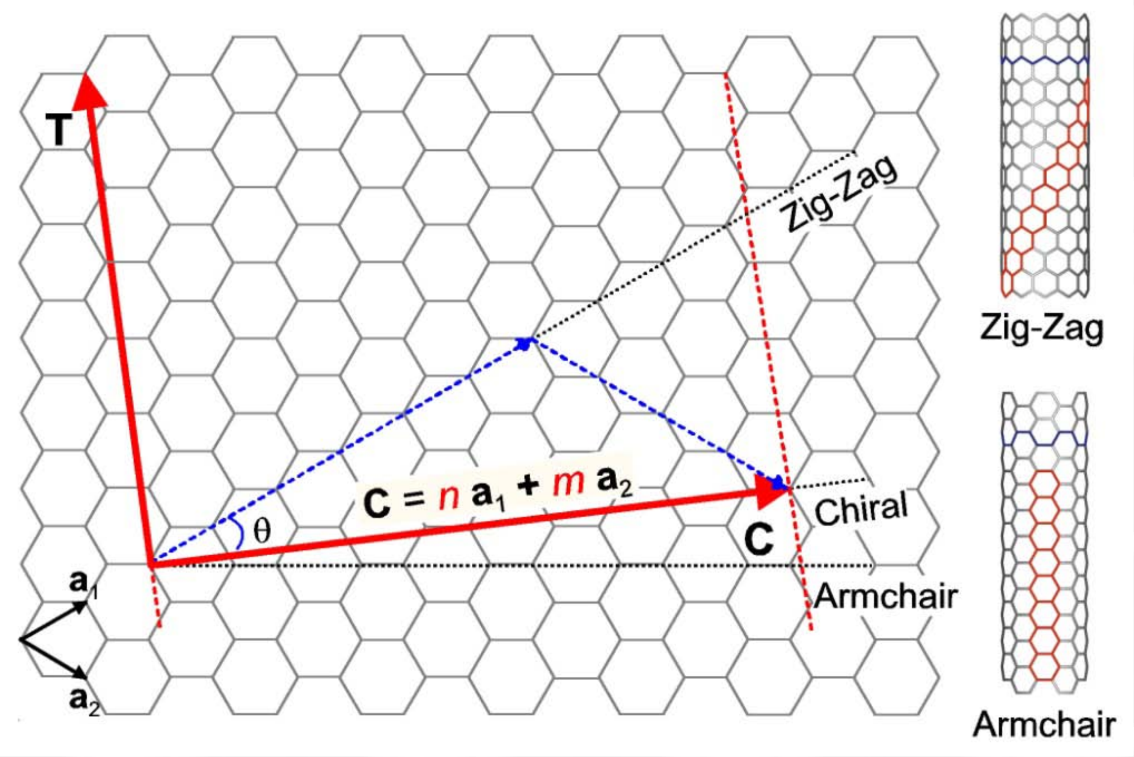
Wang *et al.* Nano Lett. **8**, 323 (2008)

Single Walled Carbon Nanotubes (SWNTs)

➢ *Quasi-1D Systems: rolled-up graphene sheets*

- Diameter, chirality & electronic structure given by two integers (n,m) :
  - → 1/3 Metallic tubes (non-luminescent) if ν = mod(n-m,3)=0
  - → 2/3 Semiconducting tubes (luminescent, $\eta \sim 1\%$) if ν = mod(n-m,3)=1,2
- Strong Coulomb interactions between electrons and holes in 1D systems

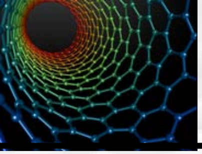
→ Enhanced excitonic effects



Here:

(6,4) ***S***-SWNT

d = 0.7nm, θ =23 deg



Carbon nanotube timeline

1991: *First observation of a multiwalled nanotube by Iijima*

1992: *Zone folding approach (Saito and Dresselhaus)*

1993: *First Single walled nanotubes observed (Iijima, Bethune)*

1993-1996: Large Scale Synthesis (Ebbesen, Iijima, Rice…)

Mechanical and thermal properties

1997: Raman Radial Breathing mode (RBM)

1998: *STM images, first nanotubes Transitors (IBM, Delft)*

1999-2005: Breakthroughs in1D transport in nanotubes

Nanotube devices, NEMS, etc…

2002: *Observation of luminescence from individualized tubes*

Optical structure assignment (Bachillo, Weisman, Smalley)

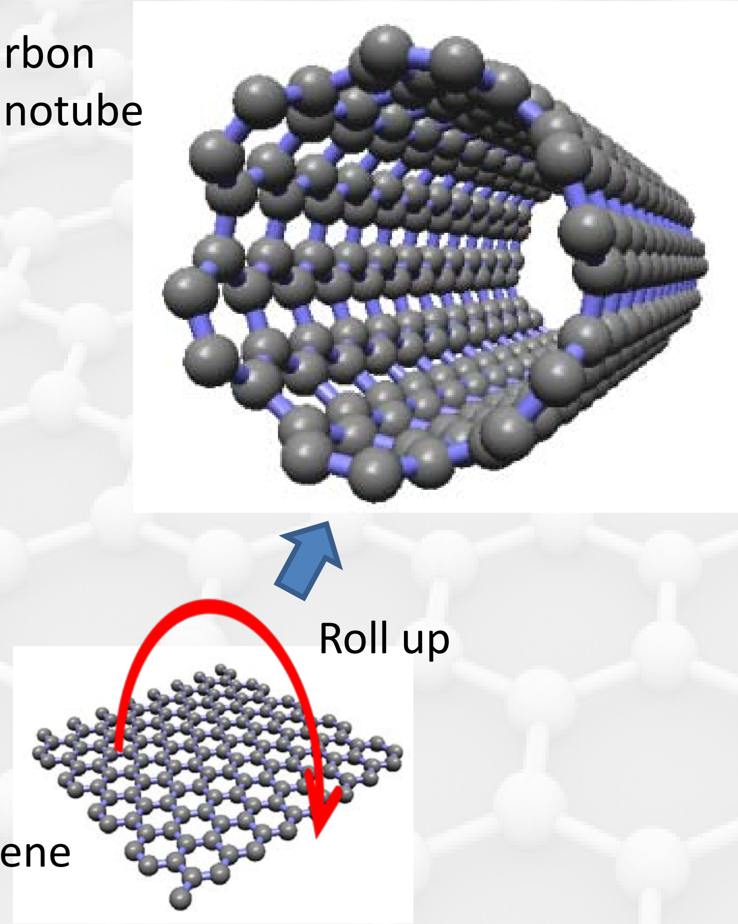
2003: Observation of individual tubes (Rochester)l

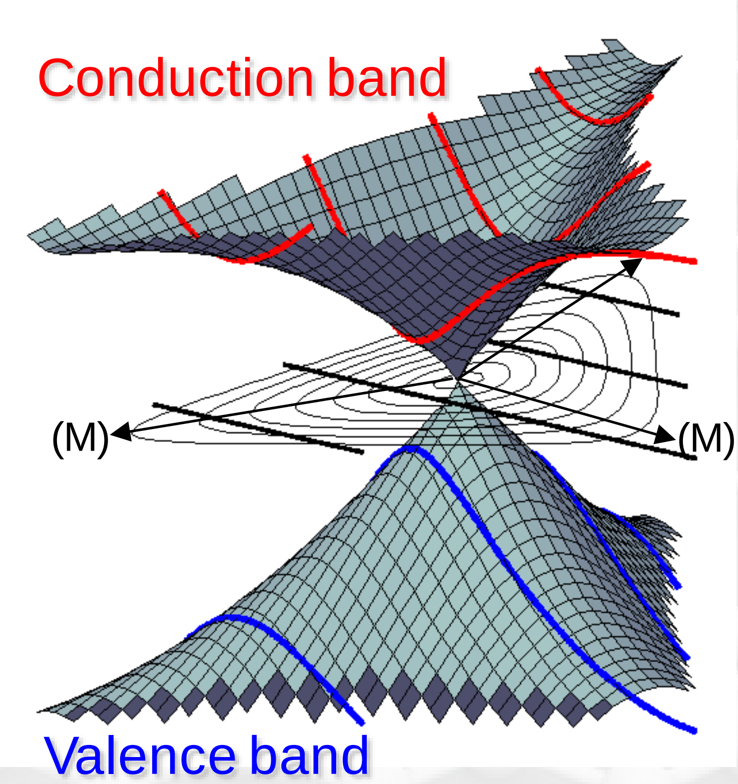
2005: *Observation of excitons (Columbia, Berlin) predicted in 1996 by Ando*

2005-2006: Combined TEM and optical studies(Montpellier, Columbia)

2006-2010: Major advances in nanotube sorting

Band structure of carbon nanotubes

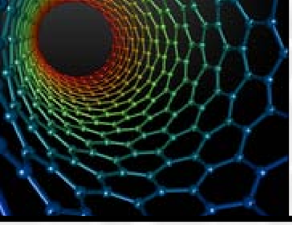




- Quantification of the transverse momentum
- SWNT sub-bands defined by equidistant cutting lines in the 2D graphene dispersion
- *Metallic nanotube if the cutting line crosses K*

$$\delta k_t = \frac{2}{d} \qquad d = a\sqrt{n^2 + m^2 + nm}$$

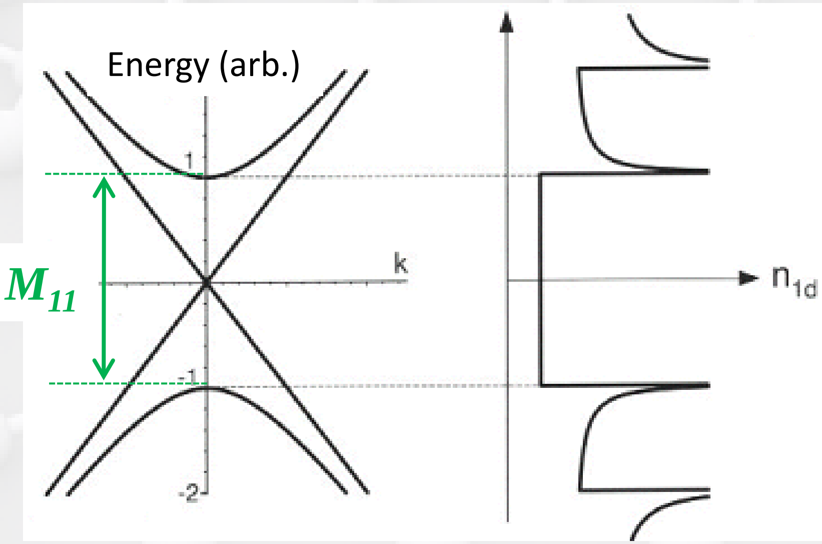
a = 0.249 nm



Metallic and Semiconducting SWNTs: (simplest) one electron picture

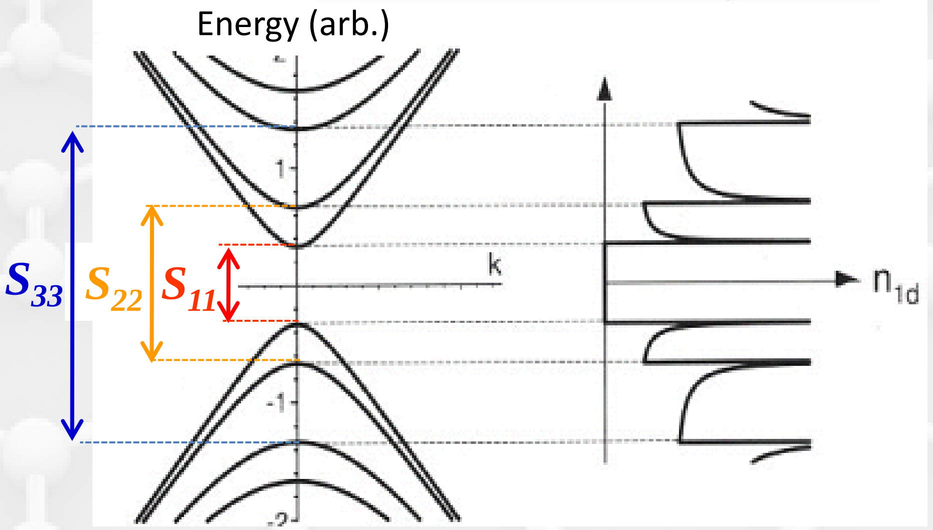
$$E_0 = 2\frac{\gamma_0\, a}{\sqrt{3}\, d_t}$$

M-SWNTs: $\nu=0$



$M_{11} = 3\,E_0$ $M_{22} = 6\,E_0$

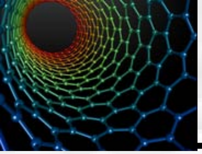
S-SWNTs: $\nu = \pm 1$



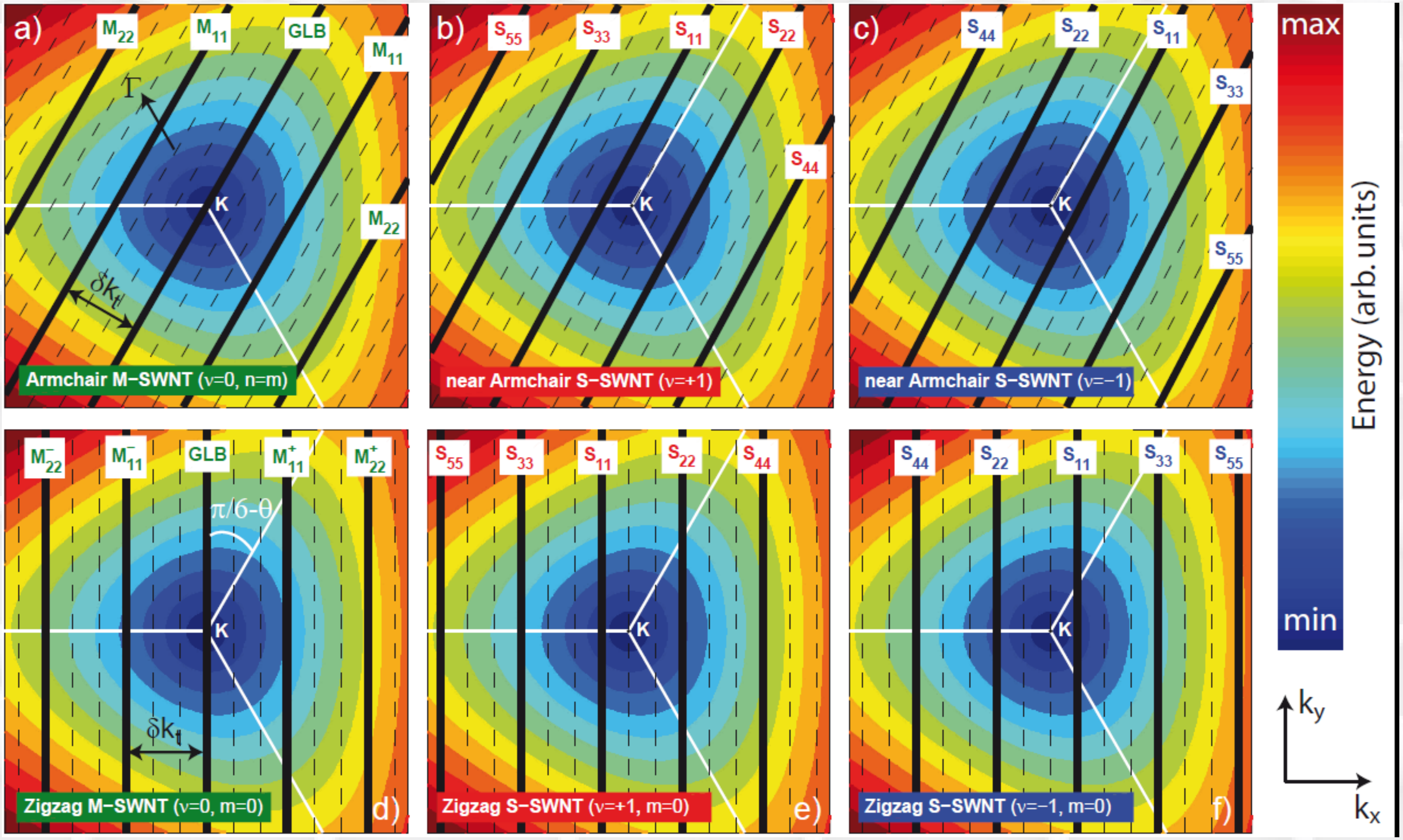
$S_{11} = E_0$ $S_{22} = 2\,E_0$ $S_{33} = 4\,E_0$ $S_{44} = 5\,E_0$

M- and S- SWNTs with similar diameters have very different transition energies:
→ Combined measurements (d_t M_{ii}, S_{ii})

ν= mod (n-m,3)



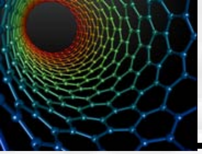
Consequences of trigonal warping



For a given chiral angle θ, “cutting lines” equidistant from K cut different energy contours.

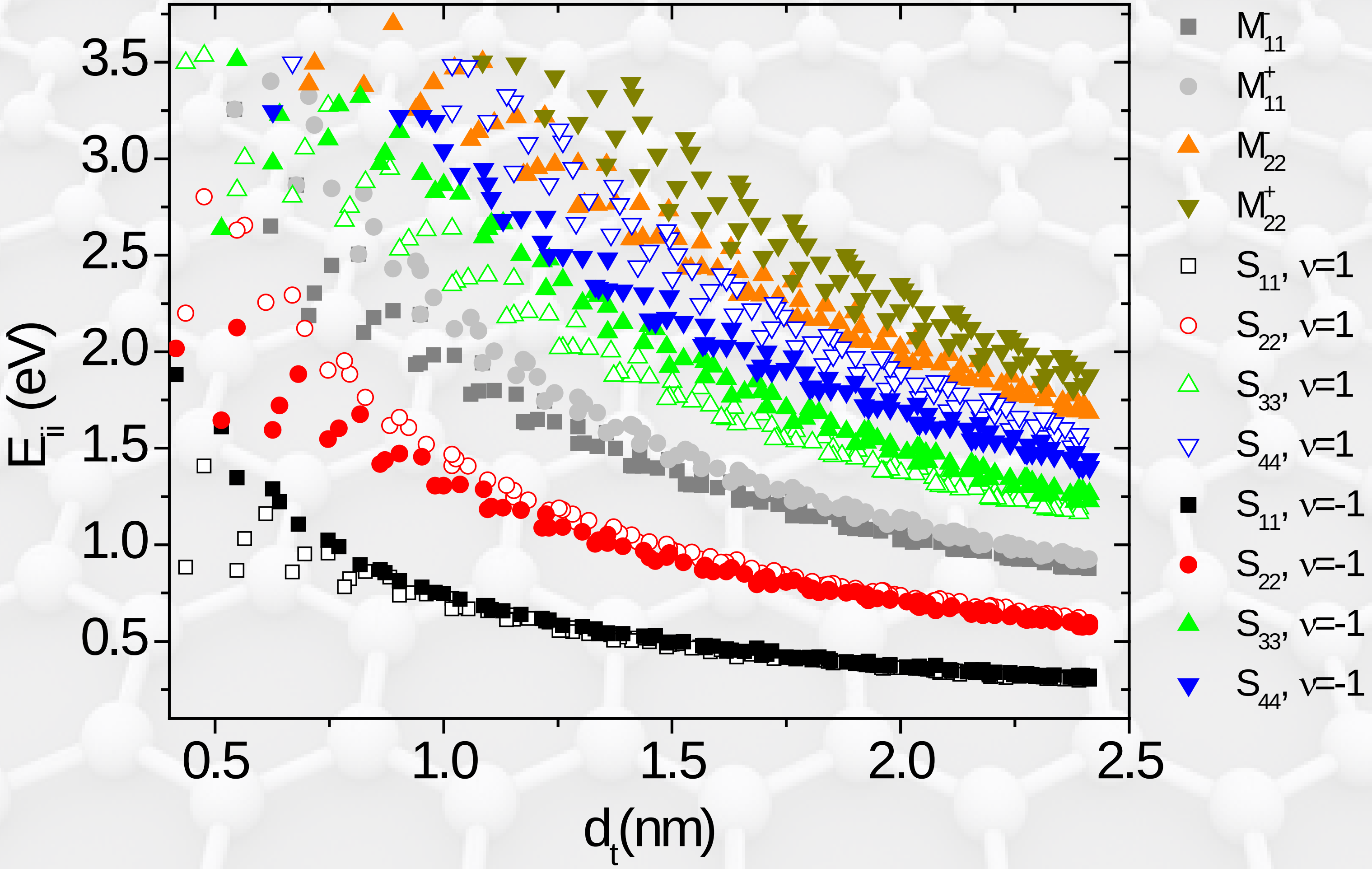
→ Splitting of M_{ii} transitions into M_{ii}^{+} and M_{ii}^{-}

→ “Family behavior” (ν=1 and ν=-1 have different $S_{i+1,i+1}/S_{ii}$ ratios)

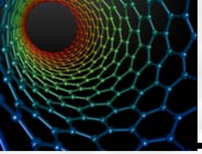


Kataura Plot (E_{ii} *vs.* d_t)

First introduced by Kataura et al., Sythetic Metals **103**, 2555 (1999)



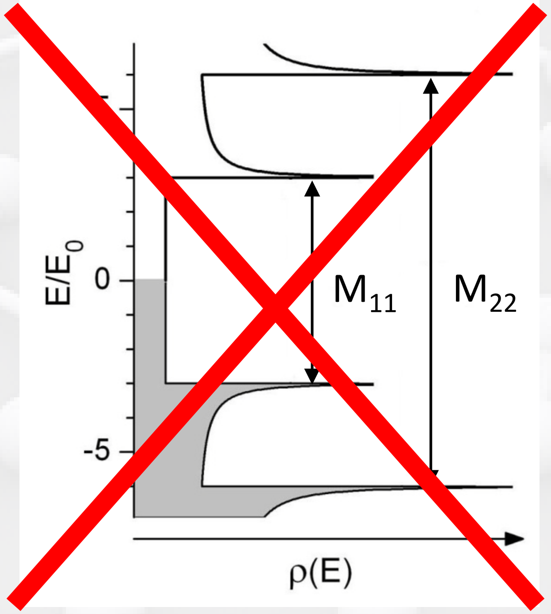
Kataura Plot adapted from V. N. Popov, N. J. Phys (2004)



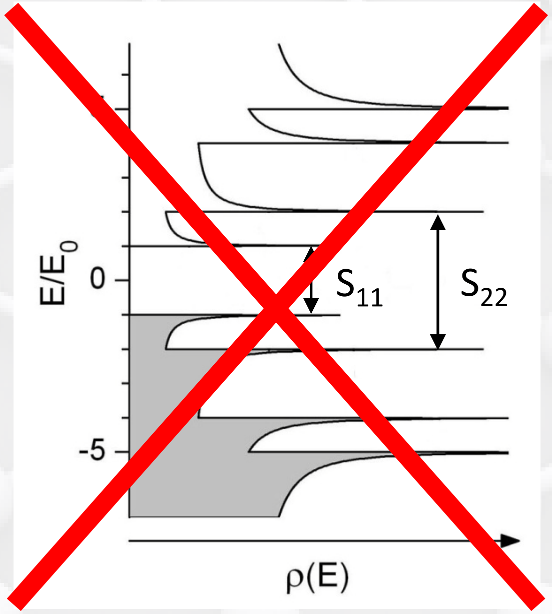
Optical Properties of Carbon Nanotubes

1D Density of states dominated by sharp van Hove singularities ($\propto (E-E_{ii})^{-1/2}$)

- *Metallic* SWNTs

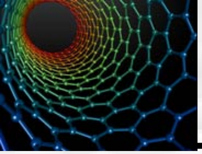


- *Semiconducting* SWNTs:

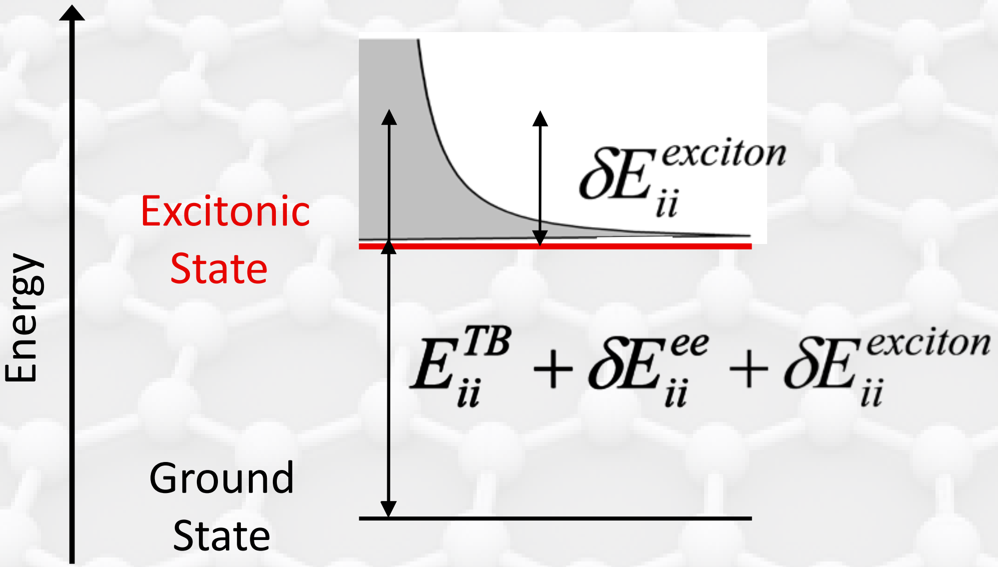


- One electron picture

→ Band to band optical transitions



Excitonic effects in Carbon Nanotubes



Energy

Excitonic State

Ground State

$$\delta E_{ii}^{exciton}$$

$$E_{ii}^{TB} + \delta E_{ii}^{ee} + \delta E_{ii}^{exciton}$$

$$\delta E_{ii}^{ee} \approx -\delta E_{ii}^{exciton}$$

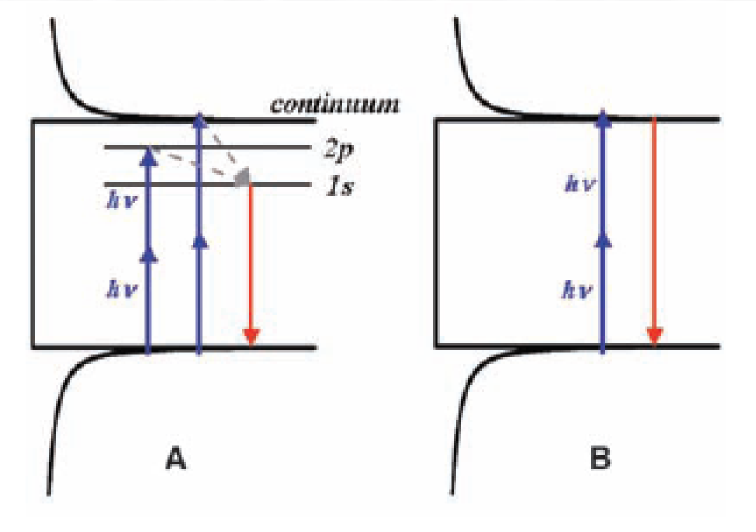
$$E_{ii}^{measured} \approx E_{ii}^{TB}$$

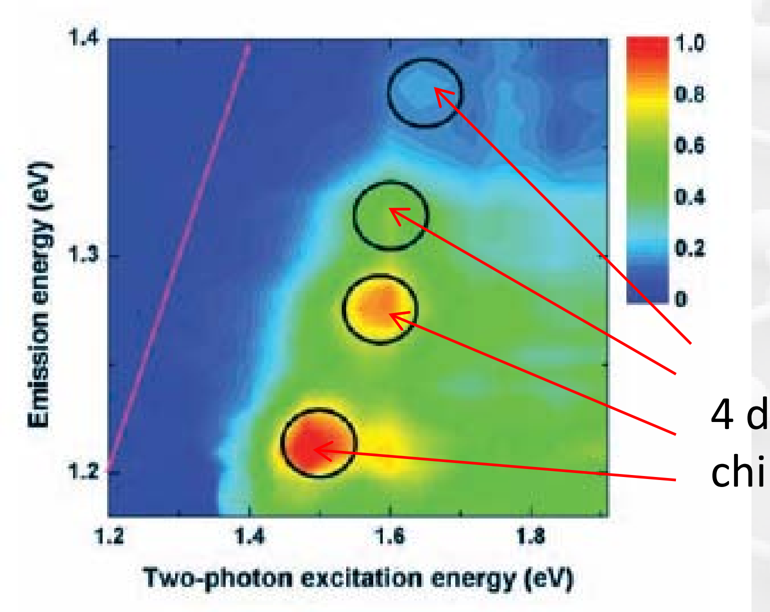
- *Complex excitonic manifold*
  - K-K’ degeneracy lifting: 4 singlet + 12 triplet states
  - Transverse excitons (E_{ij})
  - “Rydberg” States

In practice the lowest optically active exciton carries most of the oscillator strength

Th: IBM, S. Louie Group (Berkeley), Kane & Mele (U. Penn), E. Molinari group (U. Modena), Zhao & Mazumdar (Az. State U.), T. Ando (Tokyo), etc…
Exp: F. Wang *et al.*, Science **308**, 838 (2005), J. Maultzsch *et al.*, PRB **72**, 241402 (2005), Lefebvre and Finnie, PRL **98**, 167406 (2007) (*Sc SWNTs*)
F. Wang *et al.*, PRL **99** 227401 (2007) (*M-SWNTs*)

1D Excitons in Semiconducting SWNTs





4 different chiralities

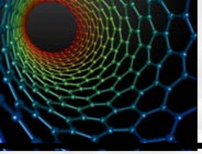
Binding energy ~ 400 meV

- ➢ Two photon absorption couples to an excited excitonic state above the bright exciton.
- ➢ *Exciton photophysics in SWNTs: a very active reserach field .*

Exciton manifold? Exciton lifetime ? exciton mobility ? Multiple excitons vs multiexcitons ? Role of the local environment ? How to improve the luminescence quantum yield?

F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, Science 308, 838 (2005)

J. Maultzsch, et al., Phys. Rev. B 72, 241402 (2005).

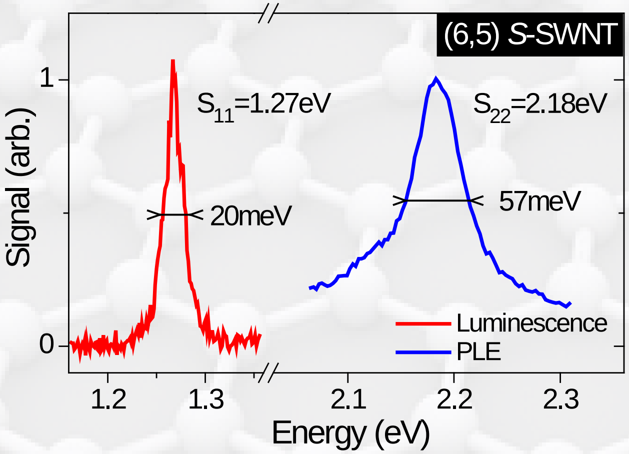


Optical characterization of individual SWNTs

• Luminescence Spectroscopy

(Rice, Rochester, Ottawa, Los Alamos, Munich, Bordeaux, Kyoto,…)

→ Limited to individual Semiconducting SWNTs



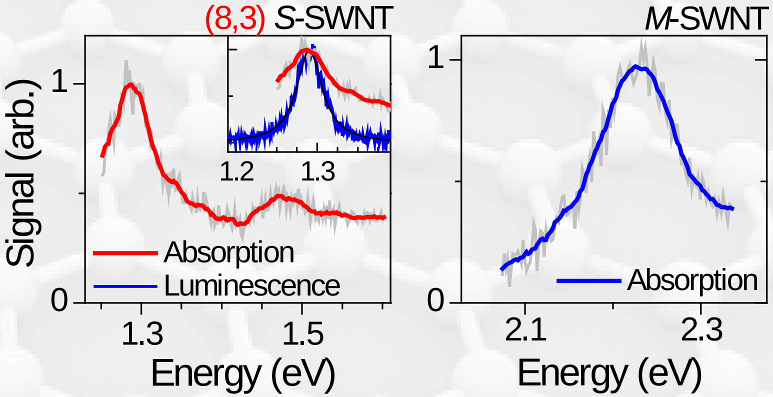
S. Berciaud *et al.* , PRL **101**, 077402 (2008)

• Absorption Spectroscopy

(Bordeaux, Berkeley)

→ Semiconducting & Metallic SWNTs

→ Limited spectral Range



S.Berciaud *et al.* Nano Lett. **7**, 1203 (2007)

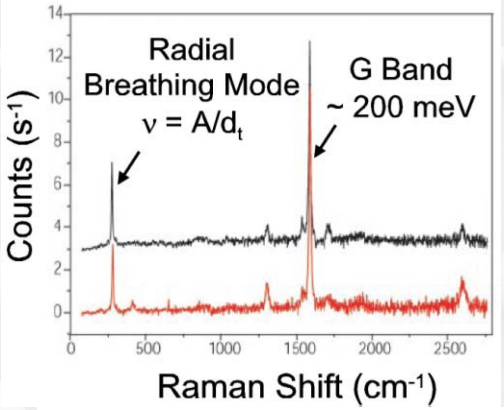
• Raman Scattering Spectroscopy

(MIT+Belo Horizonte, Columbia, TU Berlin, Rochester,,…)

→ Semiconducting & Metallic SWNTs

→ Weak signal

→ Indirect method (fitting procedure)

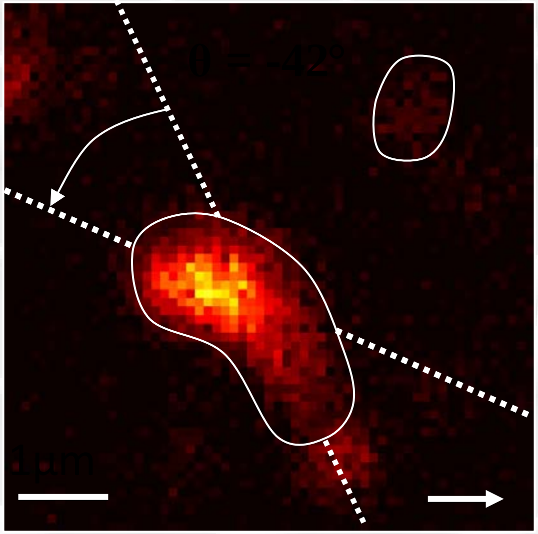


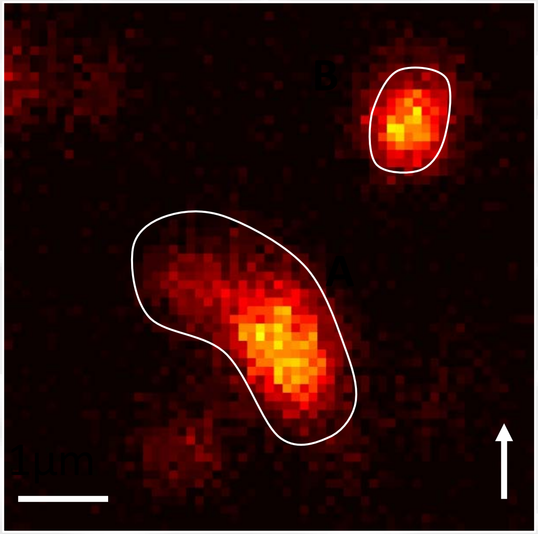
A. Hartschuh *et al.* Science **301**, 1354 (2003)

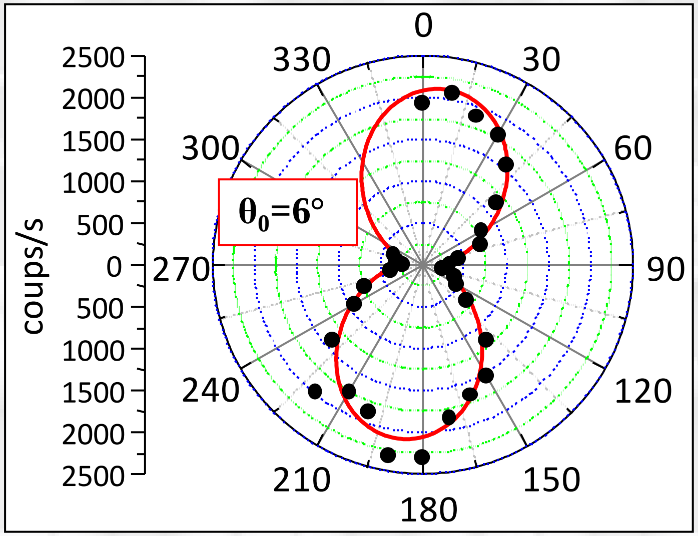
One dimensional effect: polarization dependence

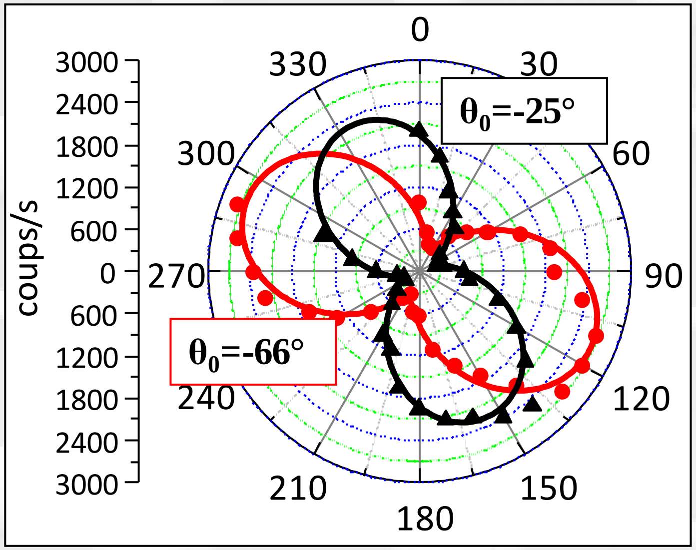
Confocal luminescence images with 2 orthogonal polarizations

Diffraction limited spot (~0.5 µm)



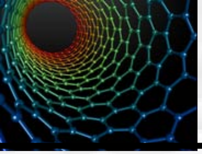






Maximum signal for **E //** tube axis

Strong depolarization effect for **E** ⊥ tube axis



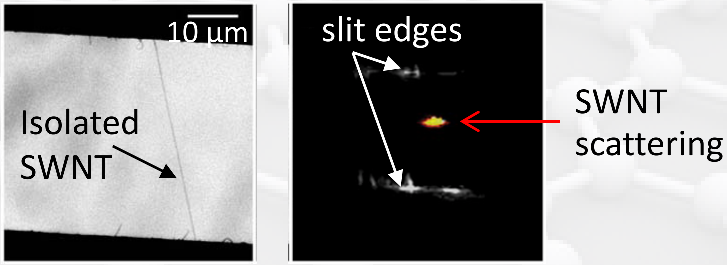
Structure assigned individual nanotubes

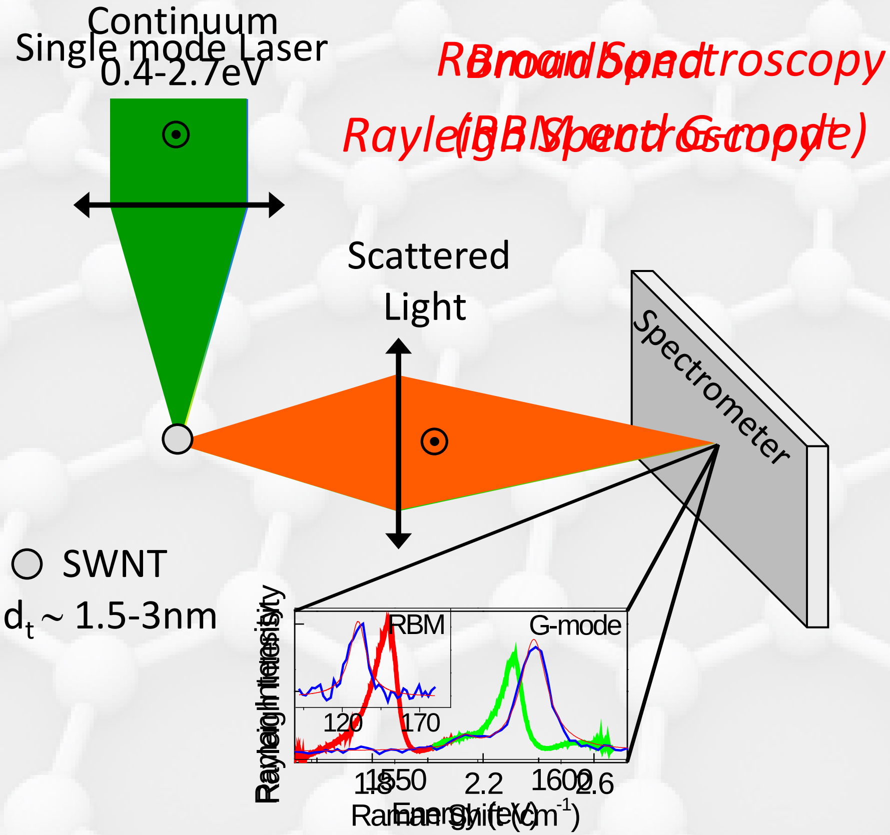
- *Isolated free-standing SWNTS*

→ Minimal environmental perturbations

→ Clear and "simple" spectroscopic features

CVD growth across ~ 100μm wide slits





- Electronic transitions (Rayleigh)+

→ Rapid determination of d_t and θ

→ Metallic or Semiconducting

- Vibrational Properties (Raman)*

→ $\omega_{RBM} \propto 1/d_t$

→ Chirality dependent e-ph coupling (G-mode)

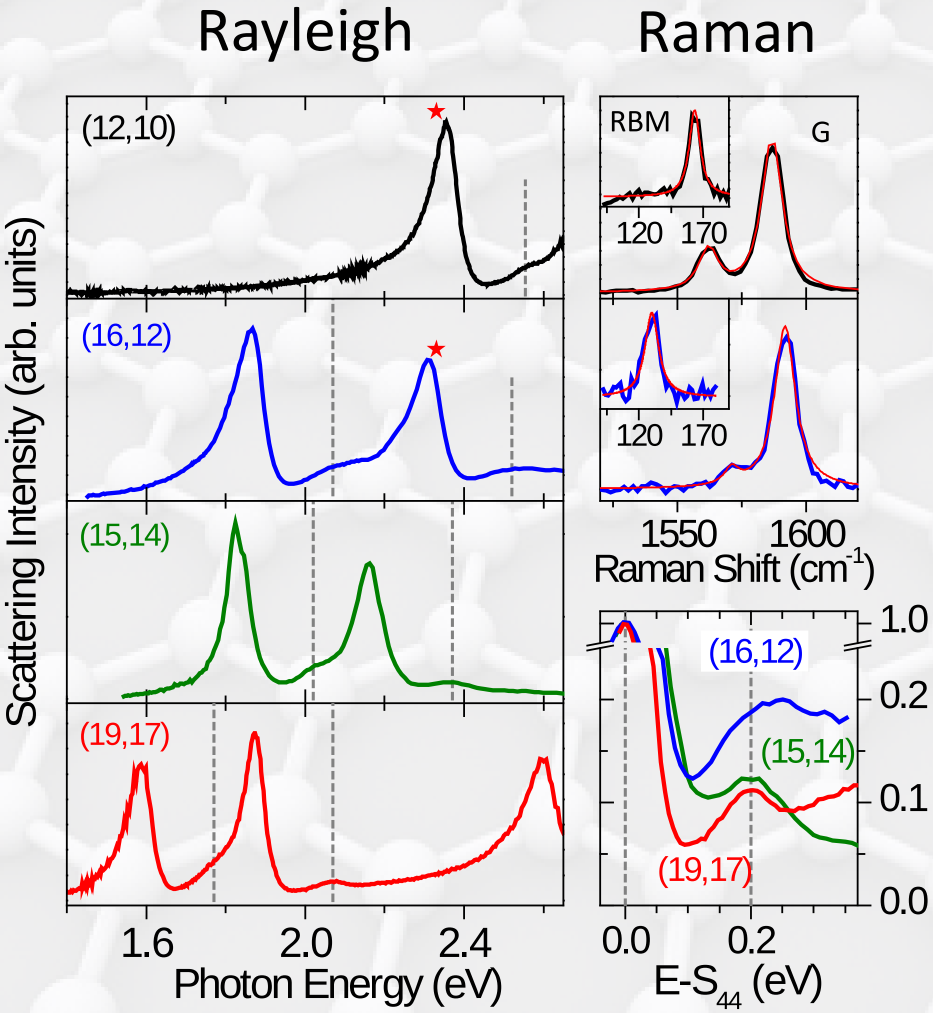
+ Sfeir *et al.*, Science **306**, 1540 (2004) (Rayleigh)

Sfeir *et al.*, Science **312**, 554 (2006) (Rayleigh **+TEM**)

* Wu et al., PRL **98**, 027402 (2007) (Rayleigh+Raman)

Semiconducting nanotubes

S-SWNTs with d_t=1.5-2.0nm: S_{33} *and* S_{44} *transitions*



- Chirality dependent S_{44} /S_{33} ratio
- Sidebands at ~200meV

→ Exciton-optical phonon coupling

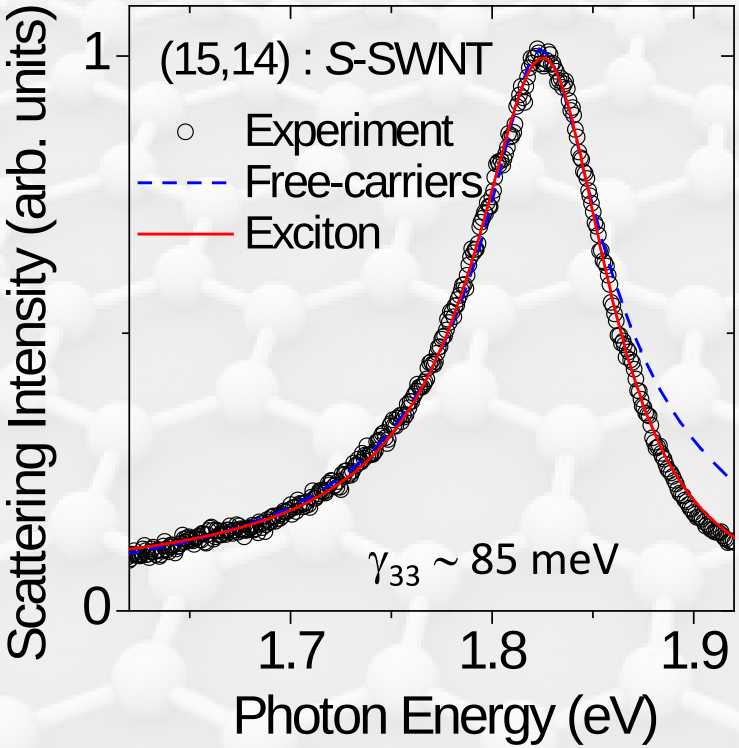
→ High-order transitions = Excitonic

- Bi-Modal (Narrow) G-mode

→ LO-TO phonon splitting

S. Berciaud *et al.* PRB **81**, 041414(R) (2010)

S-SWNTs: exciton vs. free-carriers models



$$\sigma_{Rayleigh} \propto \omega^3 \left|\chi(\omega)\right|^2$$

- Excitonic model (Lorentzian)

$$\chi(\omega) \propto \chi_B + \left[(\omega - \omega_0) - i\gamma/2\right]^{-1}$$

- Free-carriers model
(band to band transitions in 1D)

$$\chi_2(\omega) = \frac{\omega_p^2}{\omega^2} \frac{\sqrt{\eta + \sqrt{1+\eta^2}}}{\sqrt{1+\eta^2}}, \quad \eta = \frac{\omega - \omega_0}{\gamma/2}$$

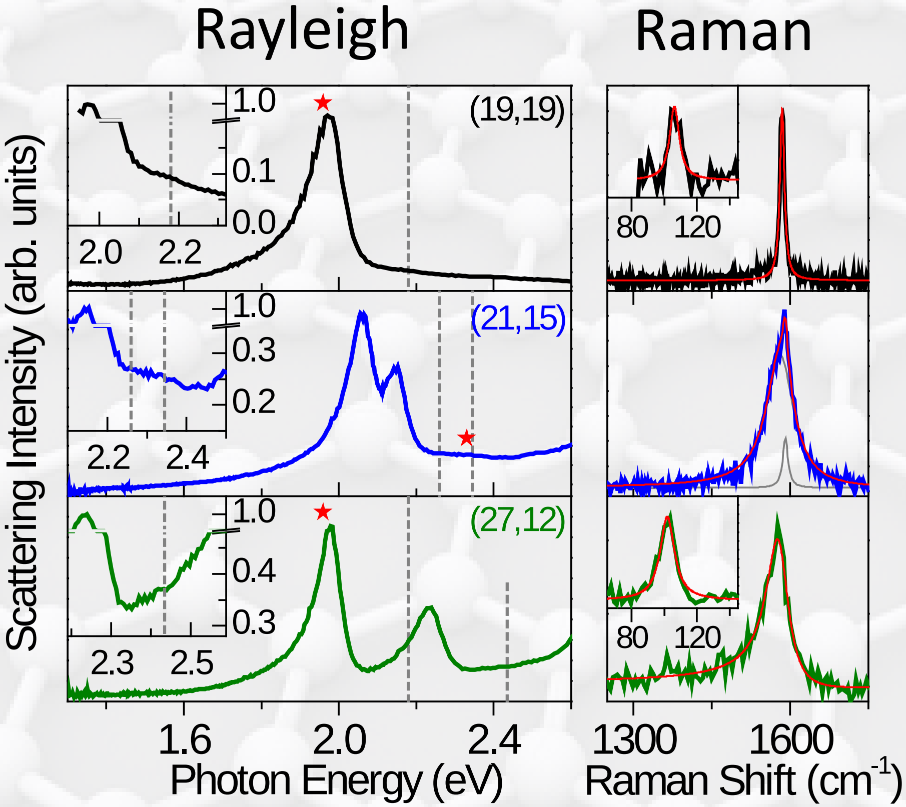
$\chi_1(\omega)$ From Kramers-Krönig transform

- Very fast (~ 20 fs) $S_{33} \rightarrow S_{22}$ decay
- γ_{33} << binding energy
  → Exciton stability

Excitonic model more appropriate

Metallic nanotubes

M-SWNTs with d_t=2.5-2.75 nm : *M_{22} transitions*



- Chirality dependent *TW* splitting ***and*** electron-phonon coupling*
- Broad and asymmetric G^- feature
- No observable Phonon sidebands

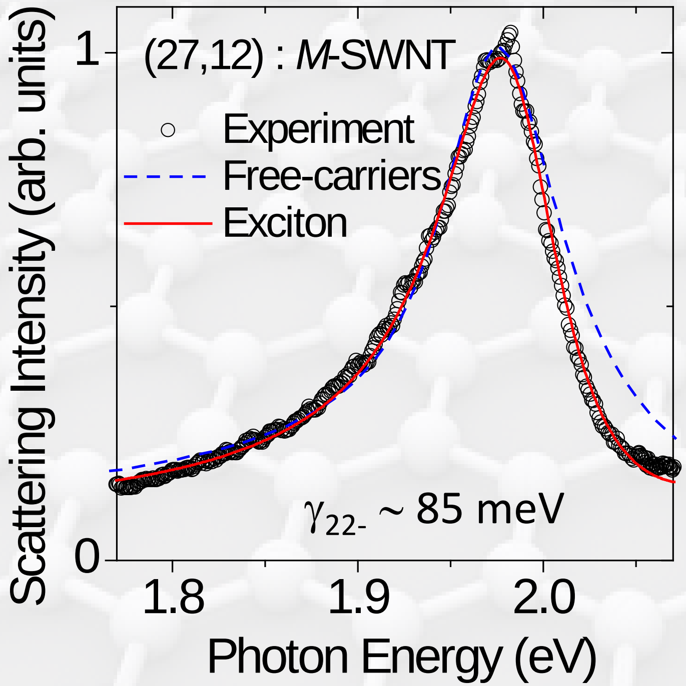
→ Reduced strength of excitonic effects

→ PSBs (if any) overlap with band-to band transitions

* Wu et al., PRL **98** 027402 (2007)

S. Berciaud *et al.* PRB **81**, 041414(R) (2010)

M-SWNTS: exciton *vs.* free-carriers models



→ Very fast (~ 20 fs) $M_{22} \rightarrow M_{11}$ decay

→ Similar intersubband decay times in *M*- and *S*-SWNTS

$$\sigma_{Rayleigh} \propto \omega^3 |\chi(\omega)|^2$$

- Excitonic model (Lorentzian)

$$\chi(\omega) \propto \chi_B + [(\omega - \omega_0) - i\gamma/2]^{-1}$$

- Free-carriers model (band to band transitions in 1D)

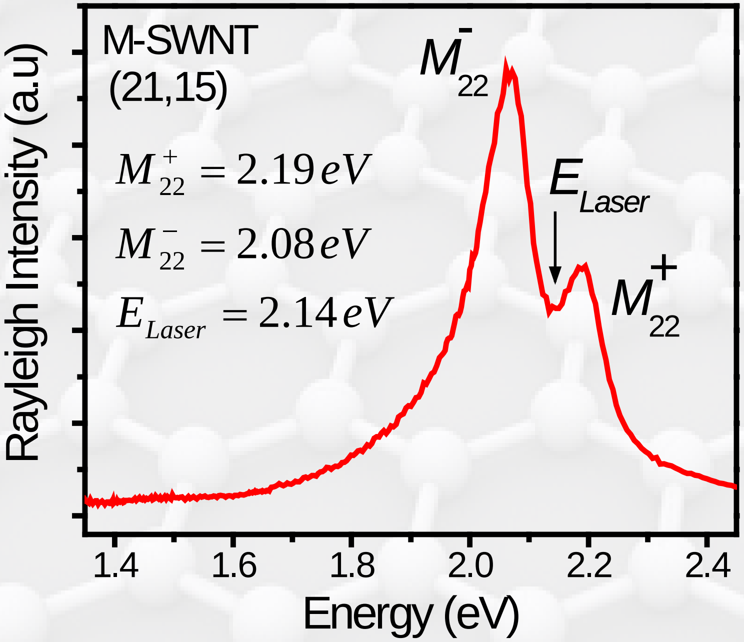
$$\chi_2(\omega) = \frac{\omega_p^2}{\omega^2} \frac{\sqrt{\eta + \sqrt{1+\eta^2}}}{\sqrt{1+\eta^2}}, \quad \eta = \frac{\omega - \omega_0}{\gamma/2}$$

$\chi_1(\omega)$ From Kramers-Krönig transform

- Reduced strength of excitons in 1-D Metals (No PSBs) *BUT* excitonic features remain observable

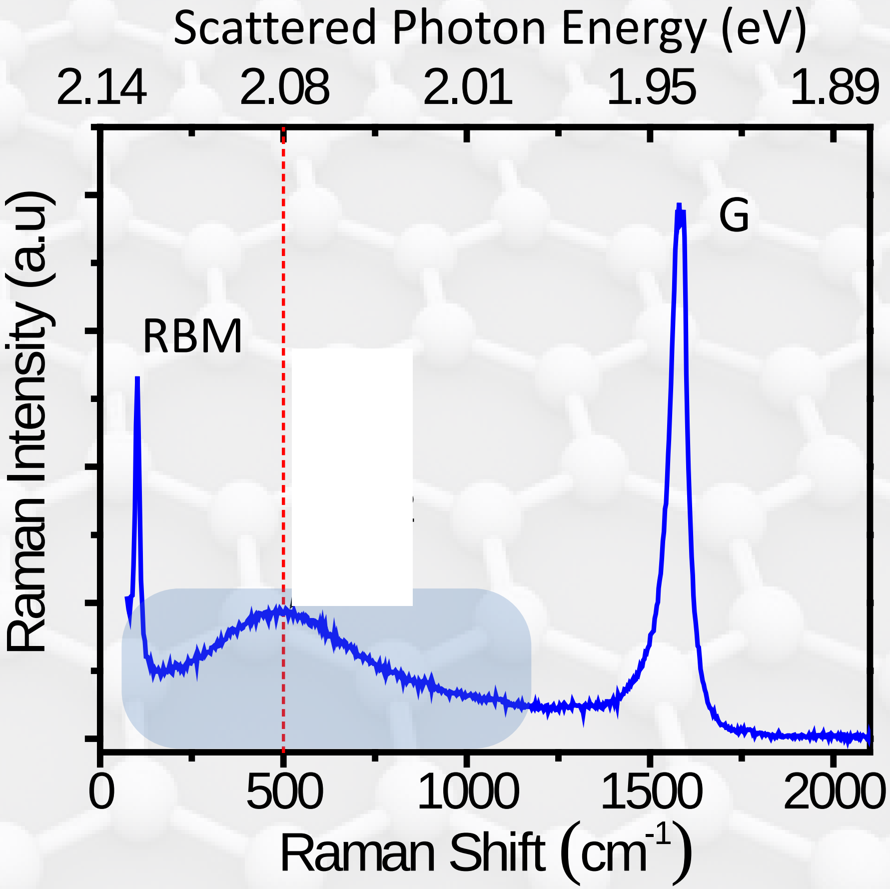
A “new” feature in the Raman Spectra of *M*-SWNTs

Rayleigh Spectrum



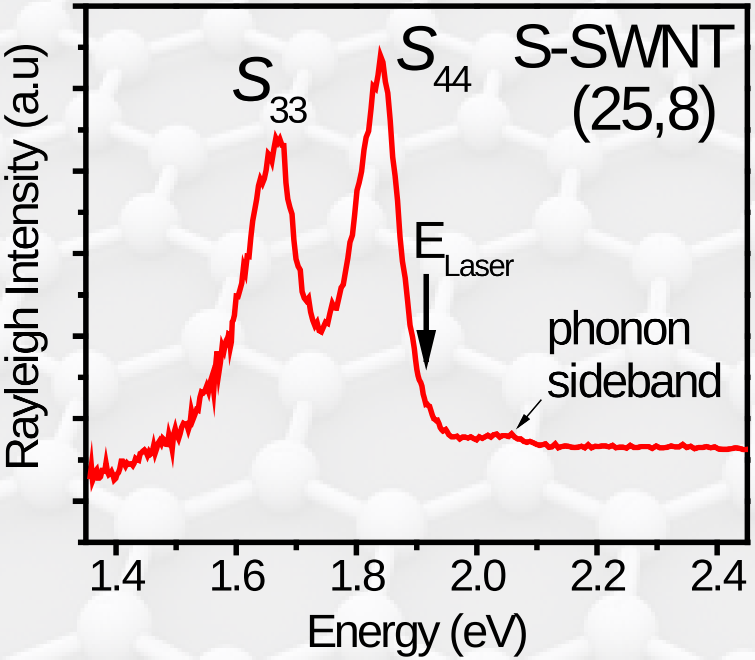
$$E_{Laser} - M_{22}^{-} \approx 60\,meV \approx 500\,cm^{-1}$$

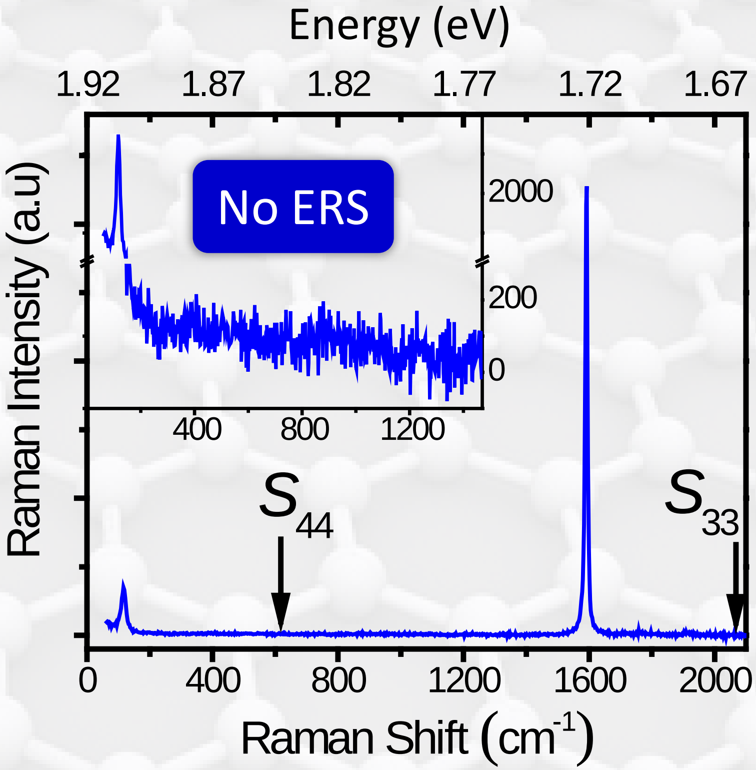
Broad feature at 500 cm^{-1}



H. Farhat, S. Berciaud *et al.* PRL **107** 157401 (2011)

Flat Raman Background in *S*-SWNTs

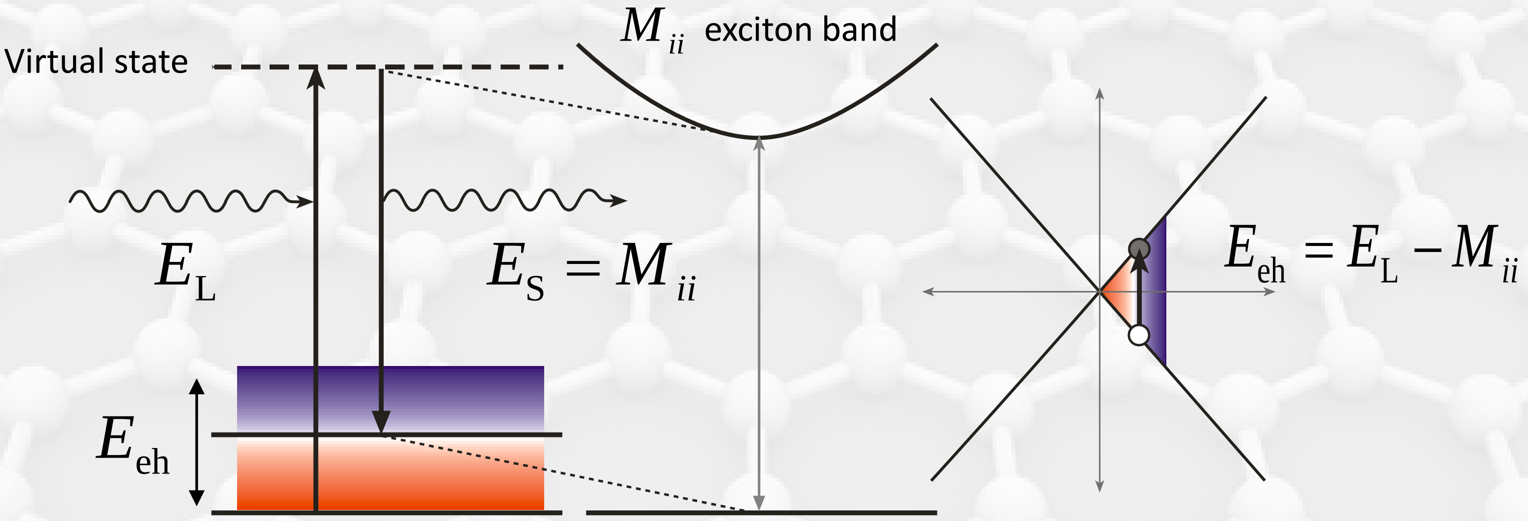




- *No observed broad feature in S-SWNTs*

Interpretation: Electronic Raman Scattering

- Inelastic Scattering involving a broad range of e-h quasi-particles
- **Resonant enhancement** for $E_S = M_{ii}^{-/+}$



In this picture, the low-energy continuum plays an essential role

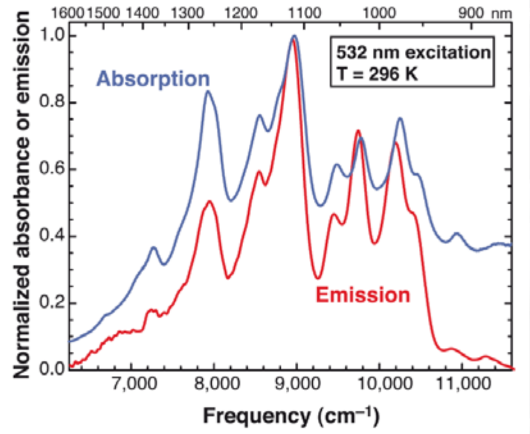
→ No ERS expected in *S*-SWNTs

→ Anti-Stokes ERS can occur in *M*-SWNTs for $E_L < M_{ii}$

H. Farhat, S. Berciaud *et al.* PRL **107** 157401 (2011)

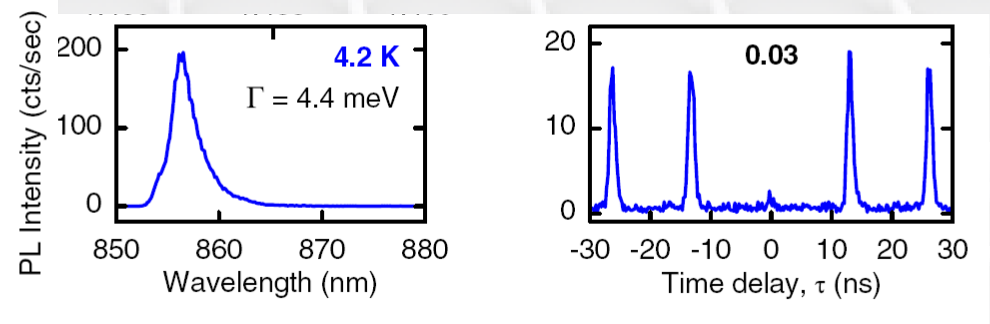
Carbon nanotube opto-electronics

- *Size tunable "bandgap" emission*



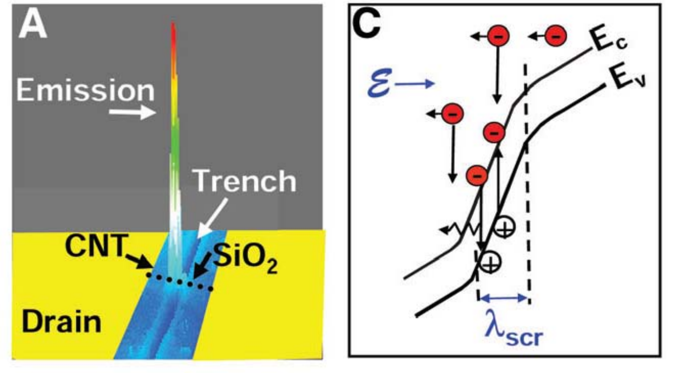
Rice group: Science **297**, 593 (2002)

- *Single photon emission*



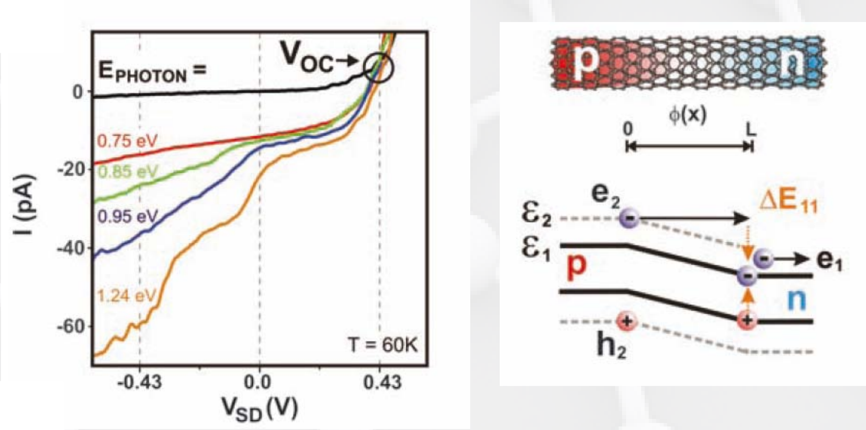
Högele *et al.* PRL **100**, 217401 (2008)

- *Electrically induced emission*



IBM, Science **310**, 1172 (2005)
See also: Science **300**, 783 (2003), Nature Nano. **5**, 27 (2010)

- *Carrier multiplication in p-n junctions*



Gabor et al., Science **325**,1367 (2009)

Outlook

- *Fascinating phenomena occur in reduced dimensions*

➢ *Graphene: a truly 2-dimensional system*

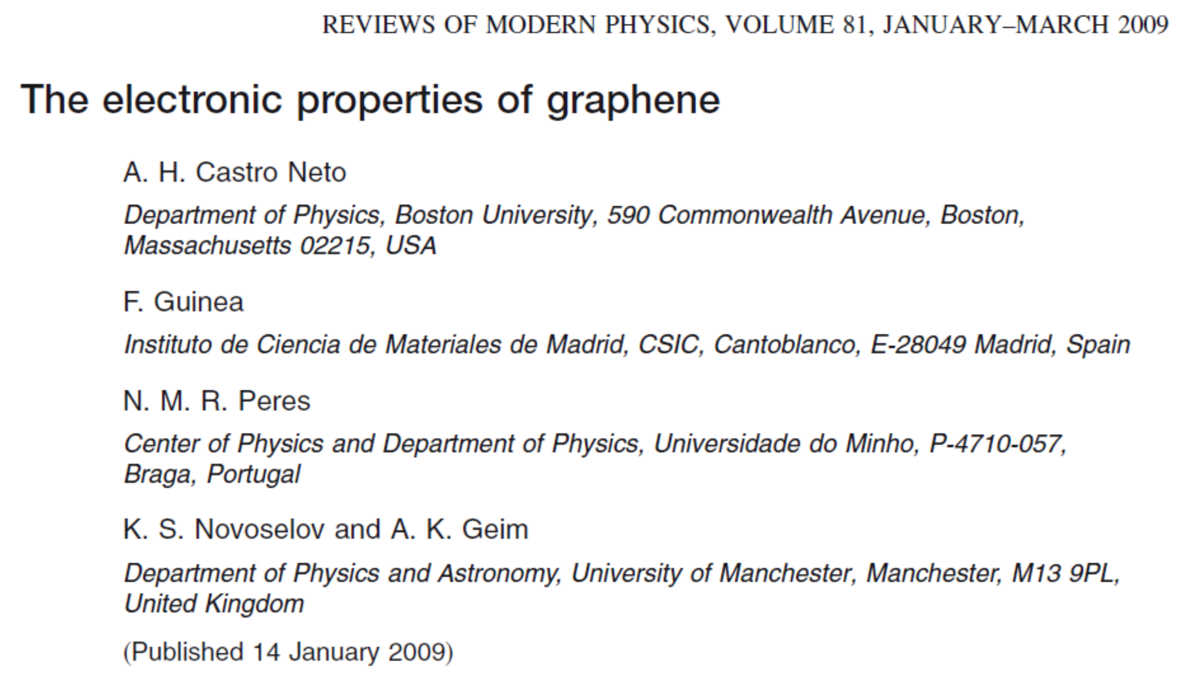
- Massless dispersion
- Easily processable
- Gate tunable properties (high sensitivity)
- Now available in macroscopic quantities for applications

➢ *Carbon Nanotubes: model quasi 1D systems*

- Large variety of carbon nanotube species with distinct properties: all-optical structure assignment
- Strong coulombic effects (excitons, ee interactions)
- "Physics-rich" Raman spectra (especially for *M*-SWNTs)
- Chirality sorted nanotubes are now available (great for applications)

Suggested reading

The Rise of Graphene
A.K Geim and K.S. Novoselov, Nature Materials 6 183 2007



REVIEWS OF MODERN PHYSICS, VOLUME 81, JANUARY–MARCH 2009

The electronic properties of graphene

A. H. Castro Neto

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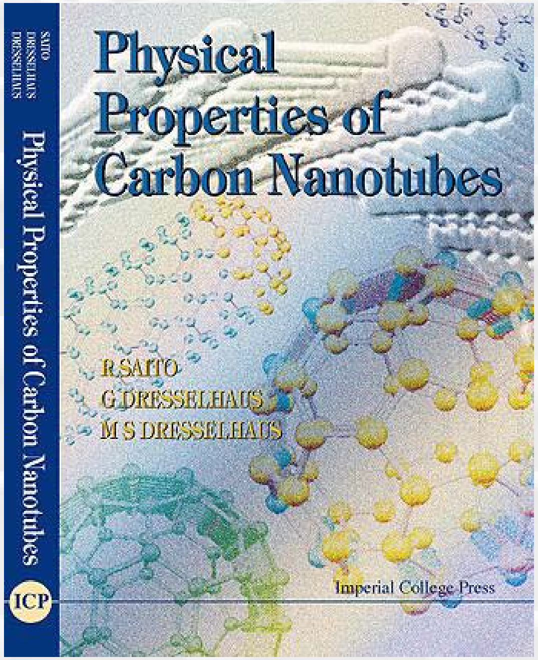
Braga, Portugal*

K. S. Novoselov and A. K. Geim

*Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL,
United Kingdom*

(Published 14 January 2009)

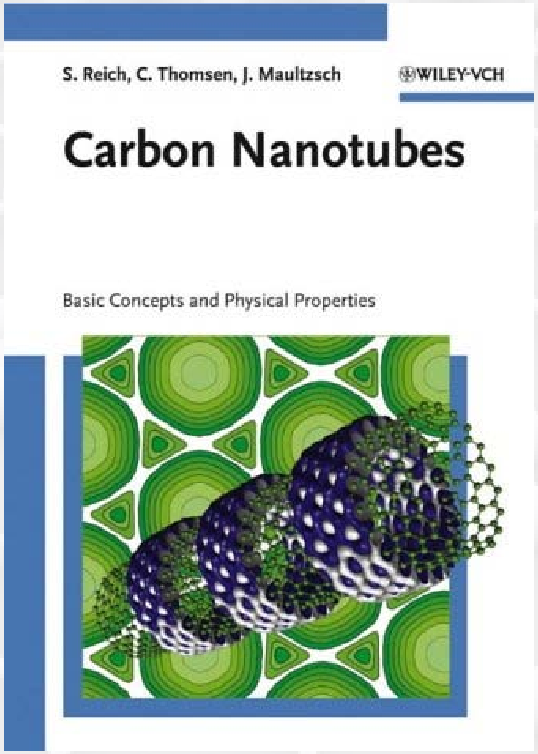
Suggested reading



Physical Properties of Carbon Nanotubes

R SAITO
G DRESSELHAUS
M S DRESSELHAUS

Imperial College Press

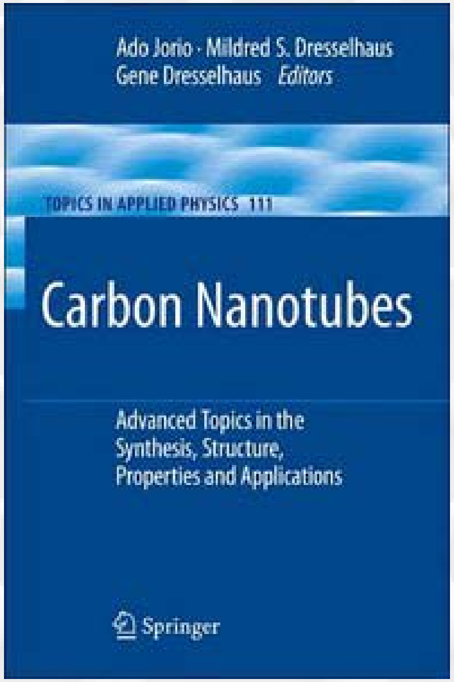


S. Reich, C. Thomsen, J. Maultzsch

WILEY-VCH

Carbon Nanotubes

Basic Concepts and Physical Properties



Ado Jorio · Mildred S. Dresselhaus
Gene Dresselhaus *Editors*

TOPICS IN APPLIED PHYSICS 111

Carbon Nanotubes

Advanced Topics in the
Synthesis, Structure,
Properties and Applications

Springer

P. Avouris, M.Freitag, V. Perebeinos,

Carbon-nanotube photonics and optoelectronics

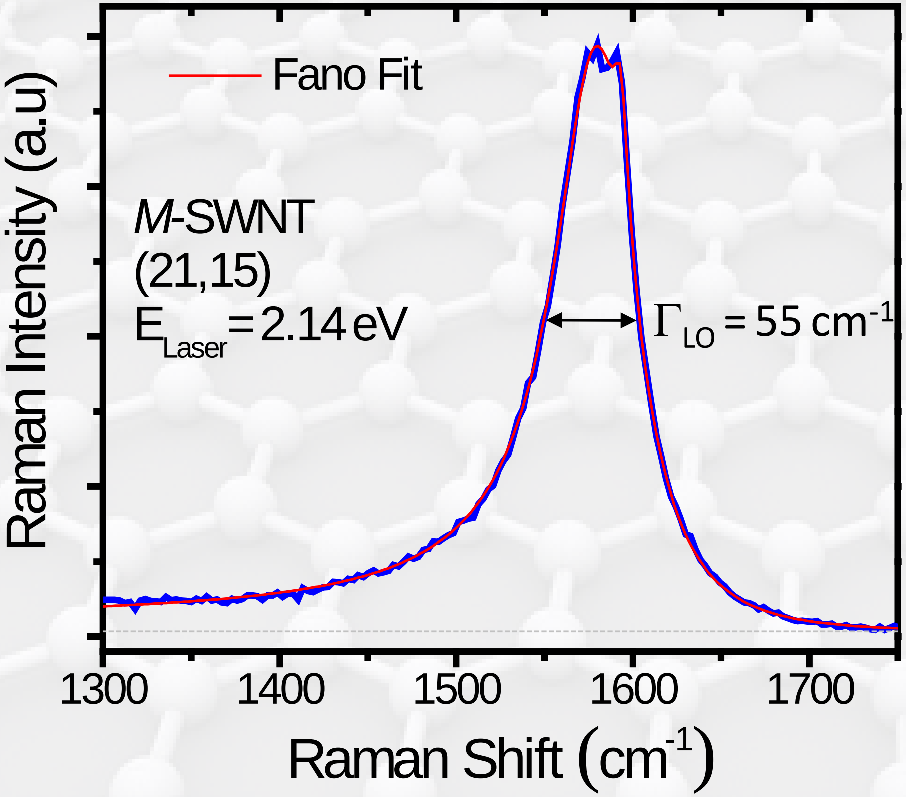
Nature Photonics 2, 341 - 350 (2008) doi:10.1038/nphoton.2008.94

Mildred S. Dresselhaus, Gene Dresselhaus, Riichiro Saito and Ado Jorio
Exciton Photophysics of Carbon Nanotubes
Annual Review of Physical Chemistry Vol. 58: 719-747 (May 2007)
DOI:10.1146/annurev.physchem.58.032806.104628

Andre Geim: Nobel AND…igNobel Laureate!
For levitating a frog in a strong magnetic field

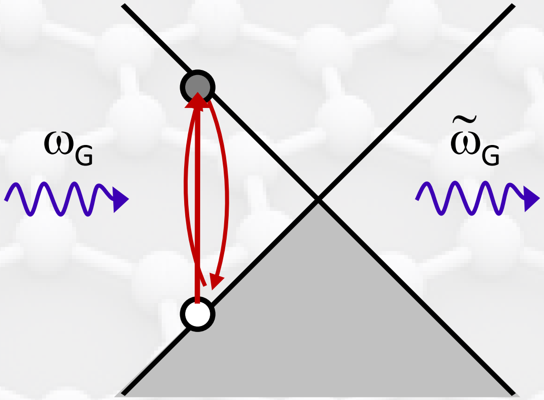
Also works with strawberries…

Broad and Asymmetric G^- Mode in *M*-SWNTs



Phonon Softening and Broadening

- Strong electron-phonon coupling
- Analogous physics in graphene



T. Ando, M. Lazzeri & F. Mauri, K Sasaki & R. Saito, etc…

Origin of the G^- mode Asymmetry (a 10 year old debate…)*

- Tube-tube interactions (only in bundles) ?
- Incoherent superposition to a low-energy background ?
- Fano interference with a continuum (low energy e-h pairs, plasmons)?

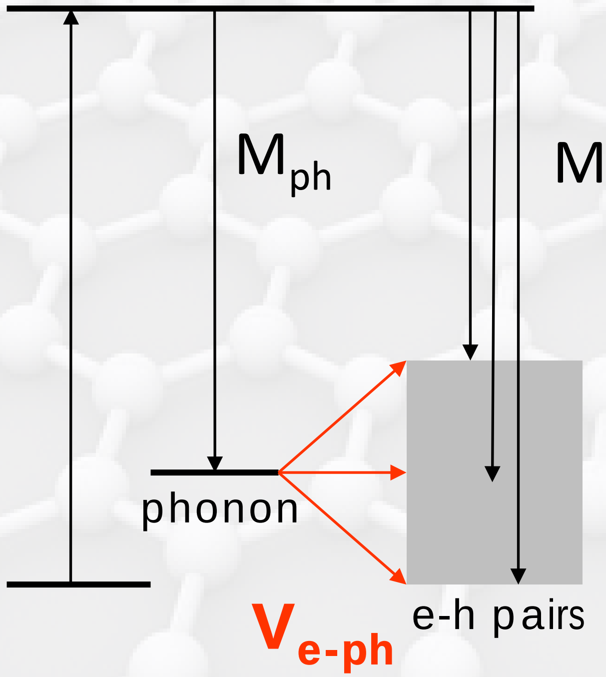
*Brown (PRB 2001), Paillet (PRL 2005), Oron Carl (Nano Lett 2005), Farhat (PRL 2007), Wu PRL (2007), etc…

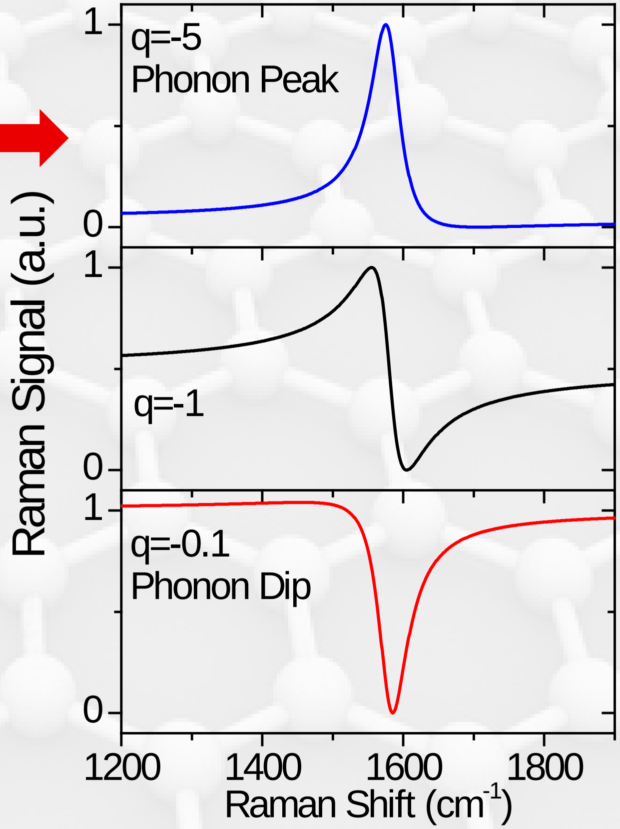
How does ERS affect the G-mode lineshape?

Fano interference between:

- one discrete state (LO phonon)
- and a continuum of states (e-h pairs)

$$I_{LO}(\omega) = I_0 \frac{\left[q\Gamma_{LO} + (\omega - \omega_{LO})\right]^2}{(\omega - \omega_{LO})^2 + \Gamma_{LO}^2}$$



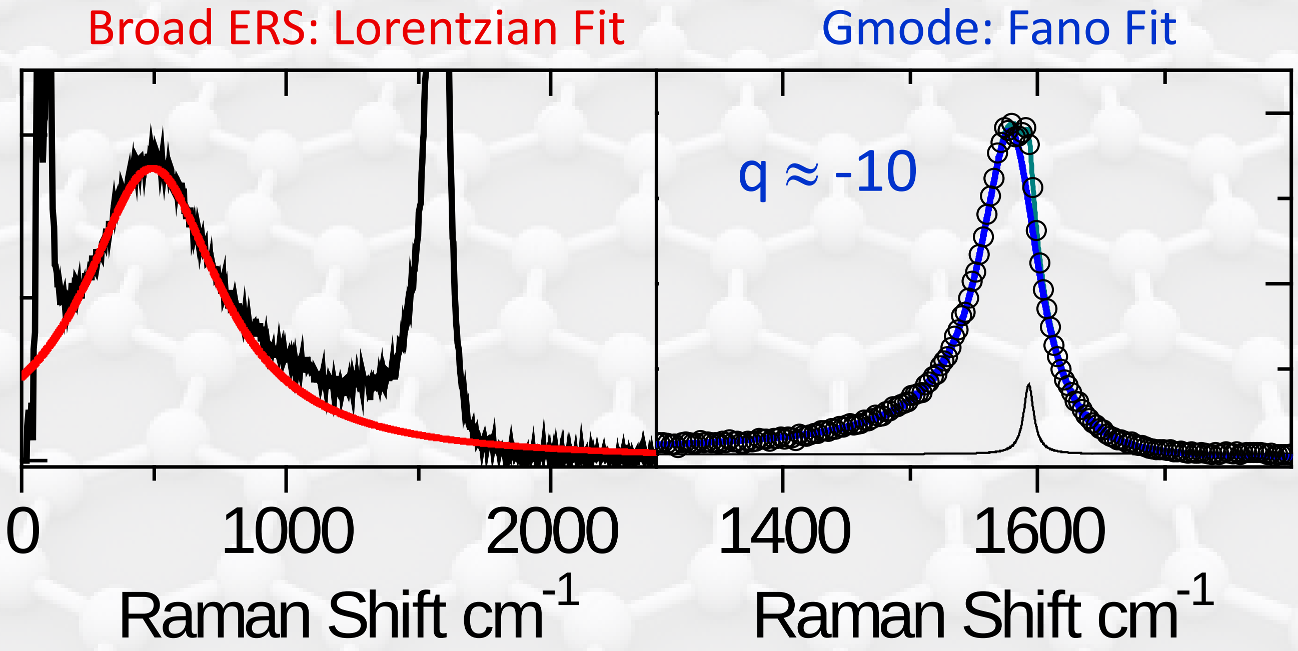


$$\frac{1}{q} = \frac{M_e}{M_{ph}} V_{e-ph}$$

U. Fano Phys Rev. 1961

Related data: IR spectroscopy in gated bilayer graphene
F. Wang group Nature Nano. 2010, A. Kuzmenko *et al.* PRL 2010

How does ERS affect the G-mode lineshape?


Broad ERS: Lorentzian Fit

Gmode: Fano Fit

$$\frac{1}{q} \sim \frac{M_e}{M_{ph}} V_{e-ph}$$

The G-mode remains weakly asymmetric

after subtraction of the ERS backgound

- This asymmetry is an intrinsic feature of *M*-SWNTS
- q ≈ -10 ⇒ The "phonon channel" largely dominates

H. Farhat, S. Berciaud *et al.* unpublished