Carbon-based Nanosciences & Nanotechnology Nanotubes & Graphene at the Heart

Stephan Roche
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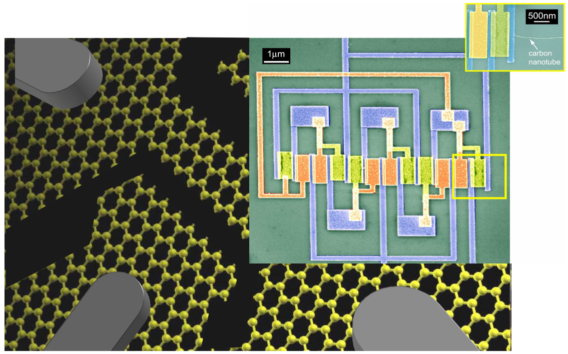
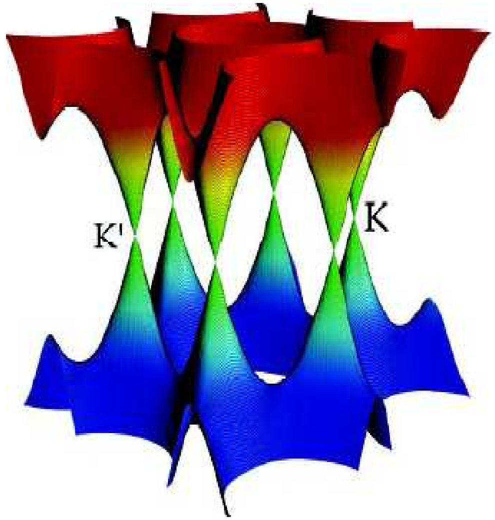


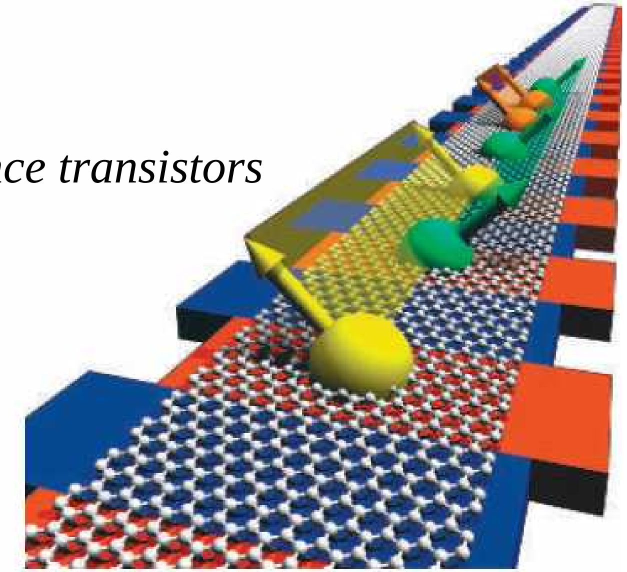
NanoSeminar, Tuesday 21, July 2009

Outline of the talk

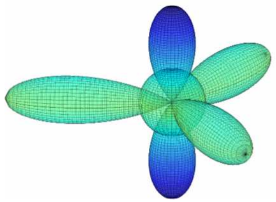
- **Introductory comments**
  - *Some salient facts and features*



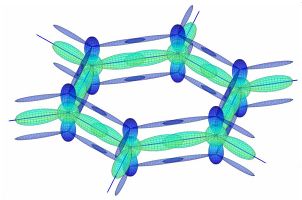
- **Why Nanotubes and Graphene are so special ?**
  - *A story of sp^2, Symmetries and Pseudospin*
- **NANOTUBES inside**
  - *Device & Quantum Mechanics*
  - *Challenges for **I**nnovation*
- **GRAPHENE inside**
  - *From « infinite mobility » to **H**igh **P**erformance transistors*
- **Carbon-based SPINTRONICS**
  - *The new **E**ldorado ?*



The sp^2 Carbon Family



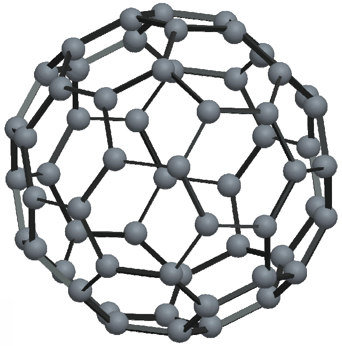
s, p_x, p_y, p_z



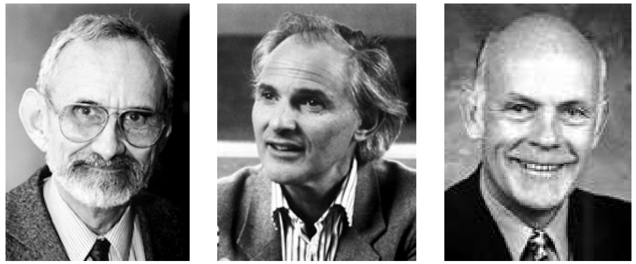
sp2 hybridization (trigonal bonding)

$\Psi_{tr1} = 1/\sqrt{3}\ s + \sqrt{2}/\sqrt{3}\ p_x$
$\Psi_{tr2} = 1/\sqrt{3}\ s - 1/\sqrt{6}\ p_x + 1/\sqrt{2}\ p_y$
$\Psi_{te2} = 1/\sqrt{3}\ s - 1/\sqrt{6}\ p_x - 1/\sqrt{2}\ p_y$
$\Psi_{te2} = p_z$

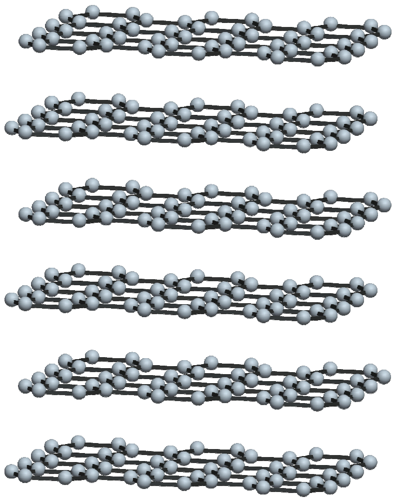
"Buckyball"
fullerenes 0d



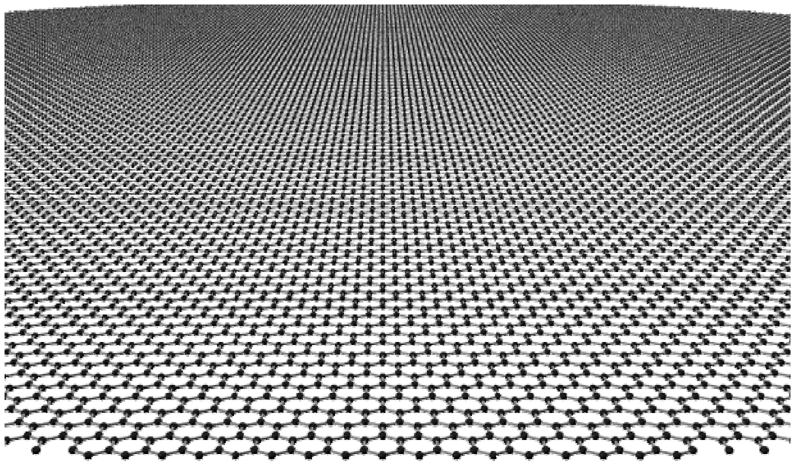
Robert F. Curl, Harold W. Kroto
Richard E Smalley
Discovery : 1985
Nobel prize in Chemistry 1996



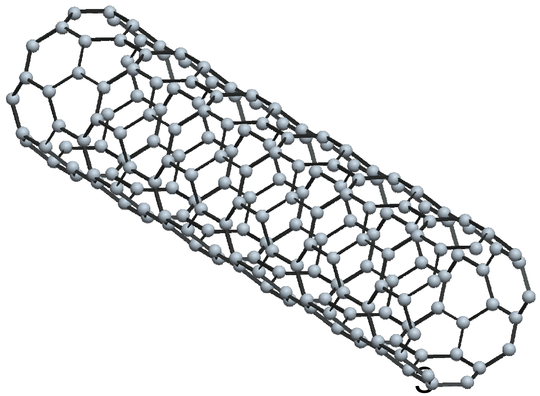
Graphite 3d



Graphene 2d



Carbon Nanotube 1d



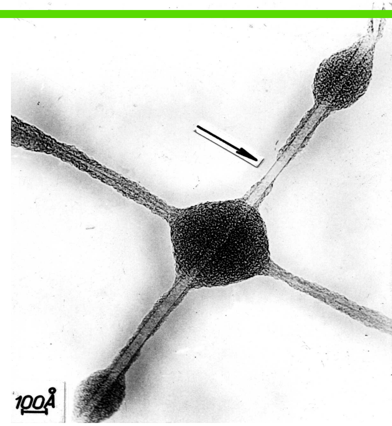
Carbon Nanotubes

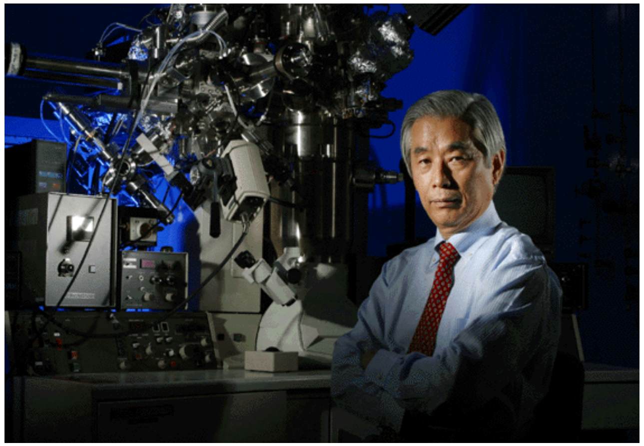
Discovery: 1976 / 1991 ?

Norinobu Endo

(Shinshu Univ., Nagano)

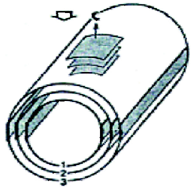
Journal of Crystal Growth 32 (1976) 335–349
© North-Holland Publishing Company





Sumio Iijima

(NEC)



"Helical microtubules of graphitic carbon",
Sumio Iijima,
Nature, 354, 56-58 (1991).

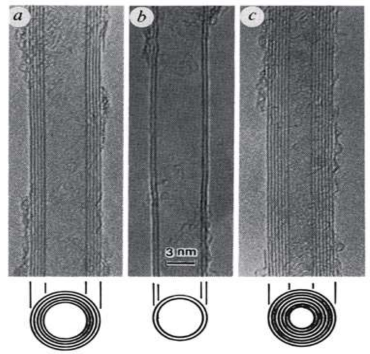


FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

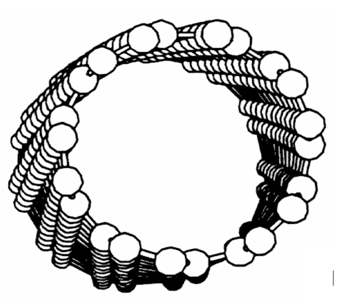
A playground for Low-dimension Quantum Physics

Quantum Confinement Effects

--

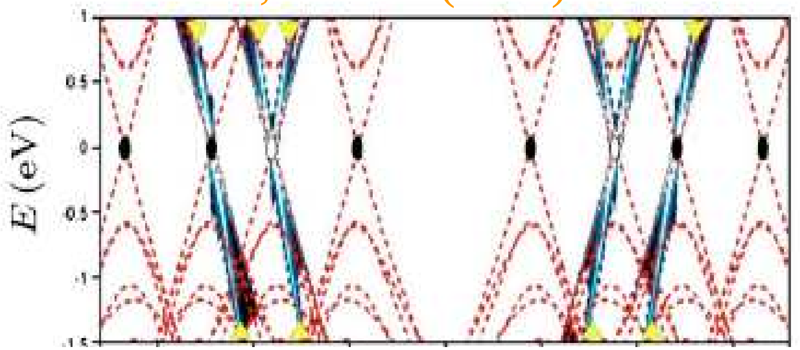
Fundamental Transport Mechanisms in Low-dimension:

Ballistic transport, diffusive weak and strong localization,
Coulomb Blockade, (orbital) **Kondo effect, Luttinger Liquid**,…

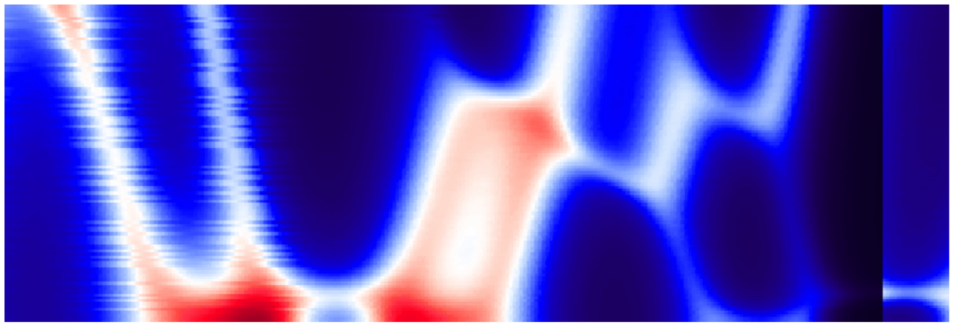


Spin-Charge separation…

Lee, Eggert, Shinohara et al.,
PRL 93, 166403 (2004)

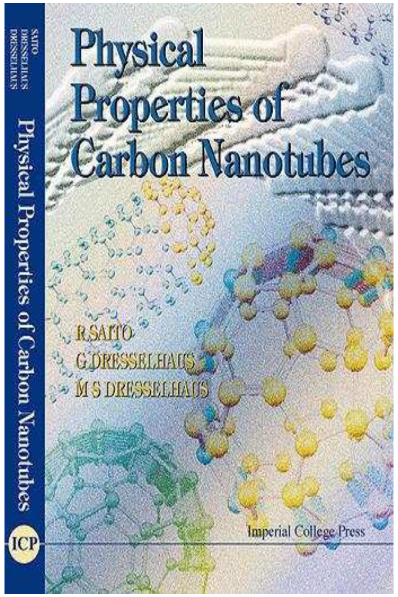


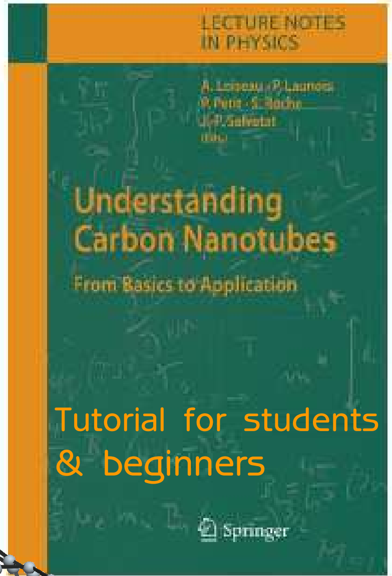
De Franceschi and coworkers
PRL 94, 156802 (2005), Nature **434**, 484 (2005)

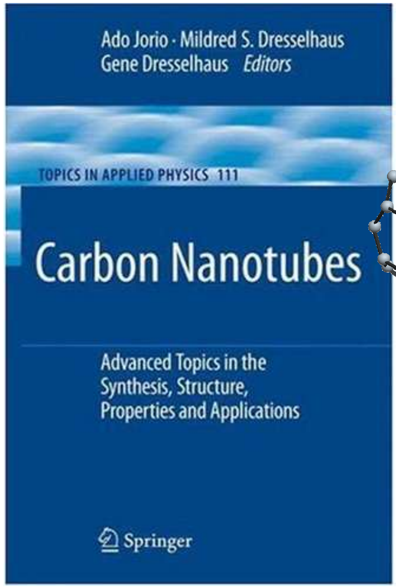


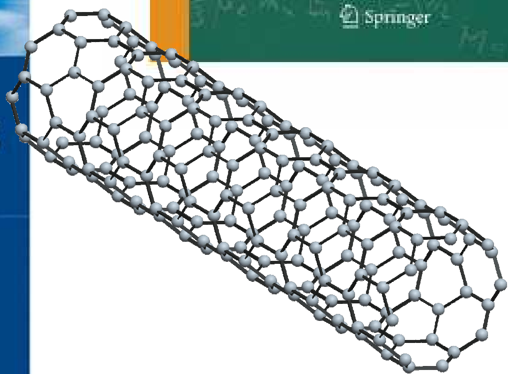
A suited case for teaching Nanosciences….

Basics of CNTs properties to the students….









REVIEWS OF MODERN PHYSICS, VOLUME 79, APRIL–JUNE 2007

Electronic and transport properties of nanotubes

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Xavier Blase†

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(Published 16 May 2007)

This article reviews the electronic and transport properties of carbon nanotubes. The focus is mainly theoretical, but when appropriate the relation with experimental results is mentioned. While simple band-folding arguments will be invoked to rationalize how the metallic or semiconducting character of nanotubes is inferred from their topological structure, more sophisticated tight-binding and *ab initio* treatments will be introduced to discuss more subtle physical effects, such as those induced by curvature, tube-tube interactions, or topological defects. The same approach will be followed for transport properties. The fundamental aspects of conduction regimes and transport length scales will be presented using simple models of disorder, with the derivation of a few analytic results concerning specific situations of short- and long-range static perturbations. Further, the latest developments in semiempirical or *ab initio* simulations aimed at exploring the effect of realistic static scatterers (chemical impurities, adsorbed molecules, etc.) or inelastic electron-phonon interactions will be emphasized. Finally, specific issues, going beyond the noninteracting electron model, will be addressed, including excitonic effects in optical experiments, the Coulomb-blockade regime, and the Luttinger liquid, charge density waves, or superconducting transition.

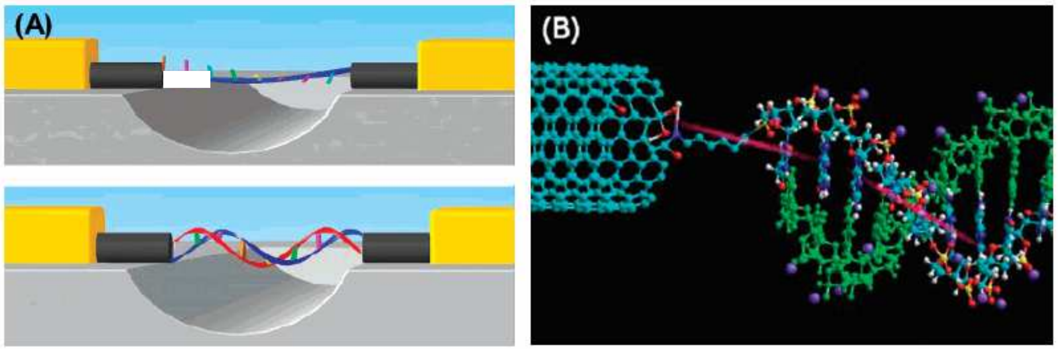
A tool for Nanotechnology

Towards (bio)molecular electronics Lego...

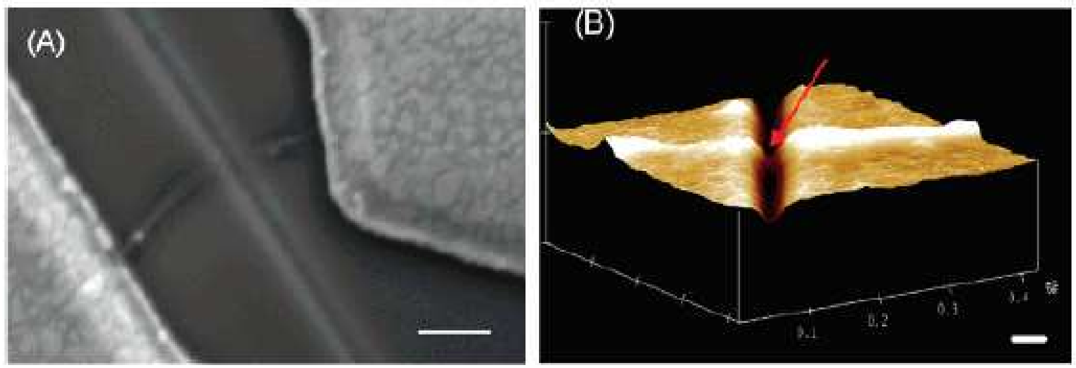
S. Roy et al.,

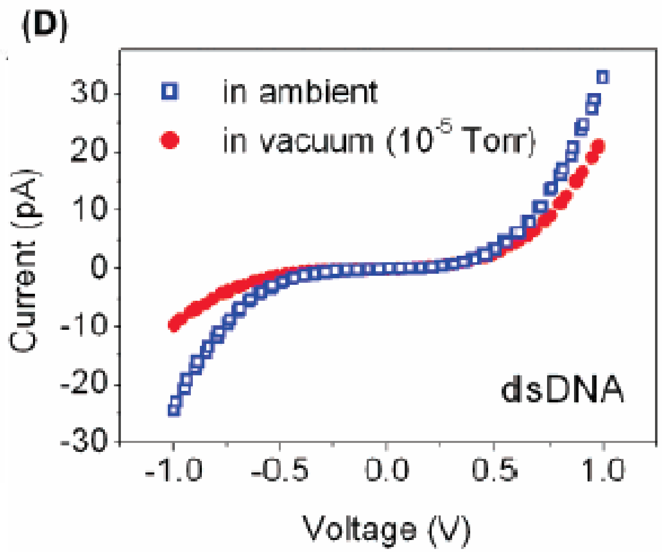
Direct Electrical Measurements on Single-Molecule genomic DNA using Single-Walled Carbon Nanotubes,

Nano Letters vol 8, n°1, 26-30 (2008)



Maximally non-invasive
Conductance measurement
of some influenza virus sequence
(L_{DNA}~30nm)



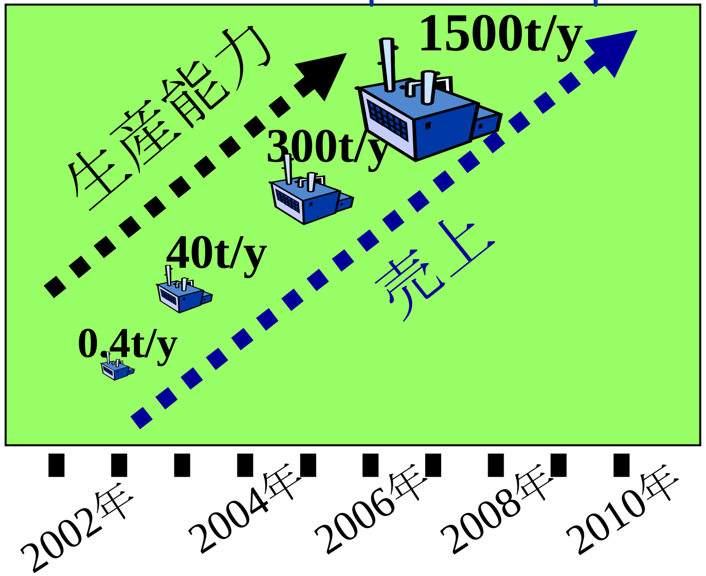


-) *Semiconducting character*

-) *Small polarons mediated charge transfer mechanisms*

Applications of Nanotubes ?

Mitsui 's CNT-production plant



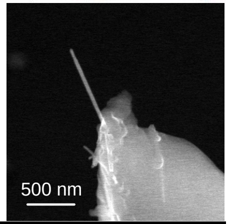
Worldwide production
-2006 ~ few 100 tons
-2008 ~ few 1000 tons

Genesis project

Coordinated by Arkema

6 application domains

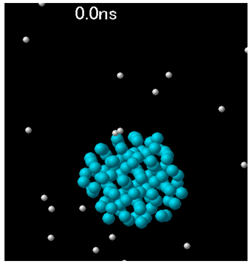
Total budget :: 106 Meuros



Prototype 15" diagonals

Also Clio (Renault)..

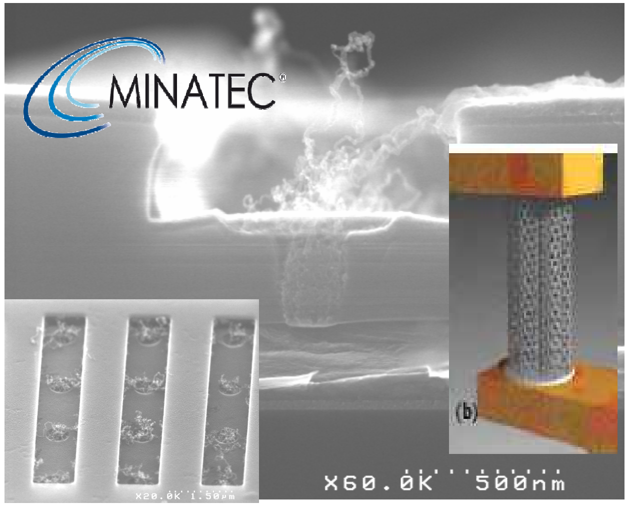
Carbon nanotubes devices ?

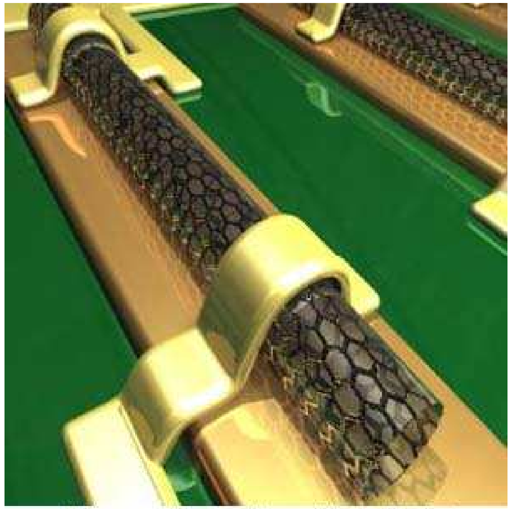


Perspective in the frame of core microelectronics

-Mainstrean CMOS-technologies (MOSFETs)

Interconnects

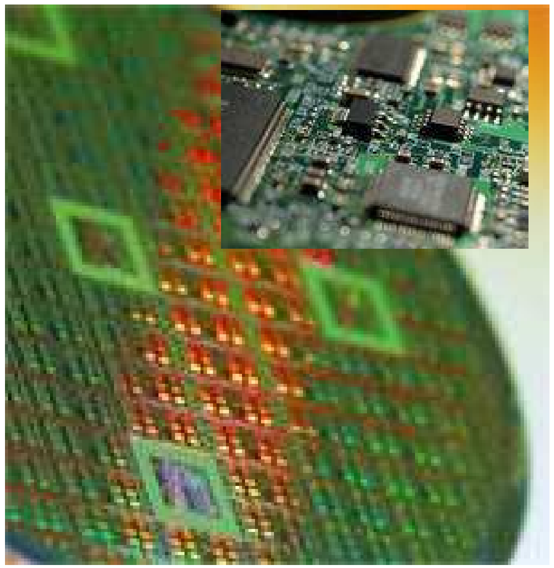




Artist's conception of a gated nanotube transistor logic circuit. Bachtold et al., *Science* **294** (2001) 1317.

Proof of concept

Ballistic transistor



However massive (**wafer scale**) integration of billions of CNT-FETs in complex architectures **at moderate temperatures** has been facing *overwhelming challenges…*

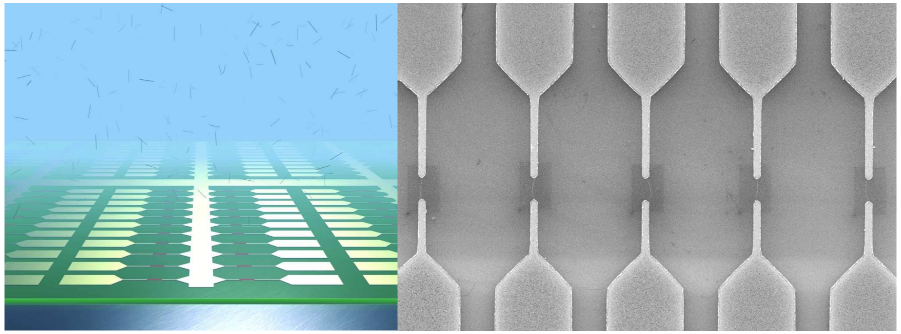
Self-assembling & other fields of applications

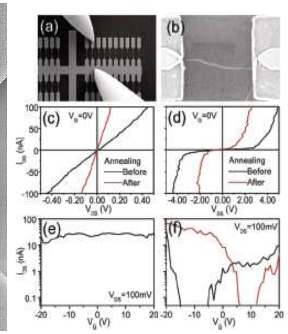
Ultra-Large-Scale Directed Assembly of Single-Walled Carbon Nanotube Devices

Aravind Vijayaraghavan,† Sabine Blatt,† Daniel Weissenberger,‡ Matti Oron-Carl,† Frank Hennrich,† Dagmar Gerthsen,‡ Horst Hahn,† and Ralph Krupke*,†

Institut für Nanotechnologie, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany, and Laboratorium für Elektronenmikroskopie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

NANO LETTERS
2007
Vol. 7, No. 6
1556–1560





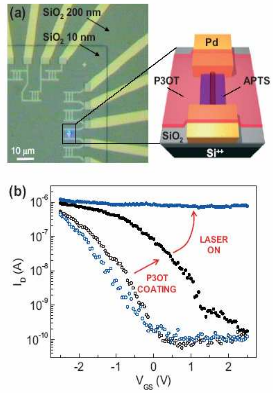
ADVANCED MATERIALS

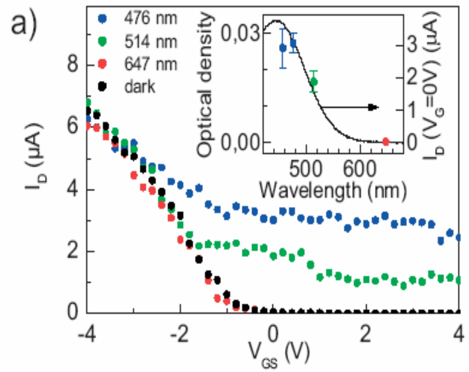
DOI: 10.1002/adma.200601138

Optoelectronic Switch and Memory Devices Based on Polymer-Functionalized Carbon Nanotube Transistors**

By *Julien Borghetti, Vincent Derycke,* Stéphane Lenfant, Pascale Chenevier, Arianna Filoramo, Marcelo Goffman, Dominique Vuillaume,* and *Jean-Philippe Bourgoin*

COMMUNICATIONS

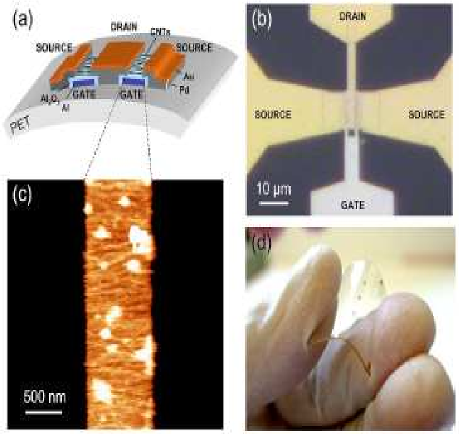


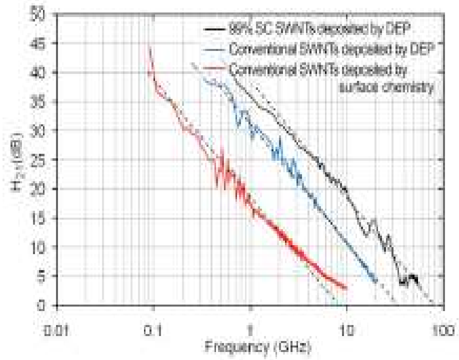


APPLIED PHYSICS LETTERS 94, 243505 (2009)

80 GHz field-effect transistors produced using high purity semiconducting single-walled carbon nanotubes

L. Nougaret,[1] H. Happy,[1,a)] G. Dambrine,[1] V. Derycke,[2] J.-P. Bourgoin,[2] A. A. Green,[3] and M. C. Hersam[3]
[1]*Institut d'Electronique, de Microélectronique et de Nanotechnologie, UMR-CNRS 8520, BP 60069, Avenue Poincaré, 59652 Villeneuve d'Ascq Cedex, France*
[2]*Laboratoire d'Electronique Moléculaire, Service de Physique de l'Etat Condensé (CNRS URA 2464), CEA, IRAMIS, 91191 Gif sur Yvette, France*
[3]*Department of Materials Science and Engineering and Department of Chemistry, Northwestern University, Evanston 60208-3108, Illinois, USA*





Growth of « Nanotube conference… »

NT08

Ninth International Conference on the Science and Application of Nanotubes
Le Corum, Montpellier, France, June 29 - July 4, 2008

~ 780 participants

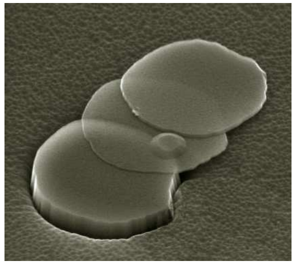
NT09 (June 21-26, Beijing, China)

> 800 participants

NT10 (Montreal), NT11 (Cambridge), NT12 (Nagoya),…

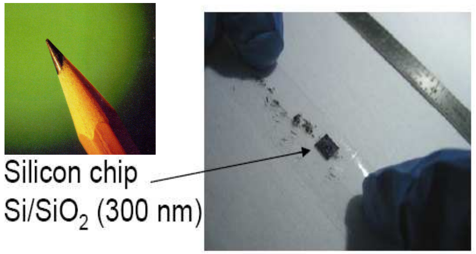
2D Graphene

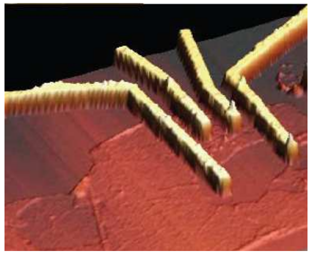
Singling out the 2D graphite layer...: 2004

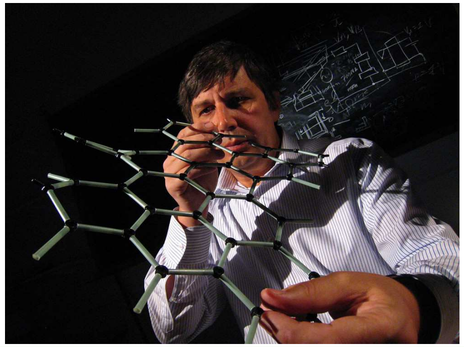


Kostya Novoselov & Andre Geim

(Manchester University, UK)

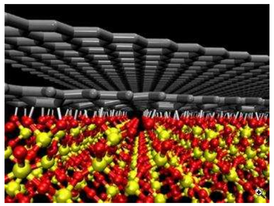


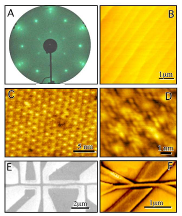


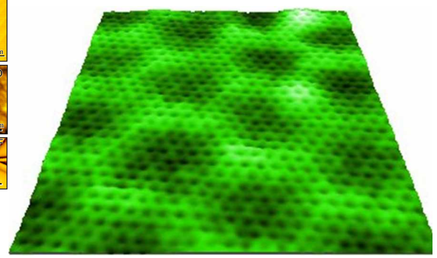


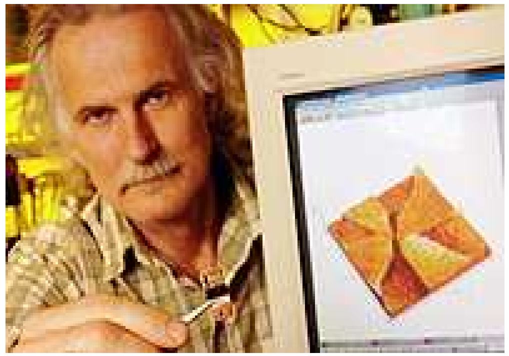
C. Berger & Walt De Heer

(Atlanta University, USA)

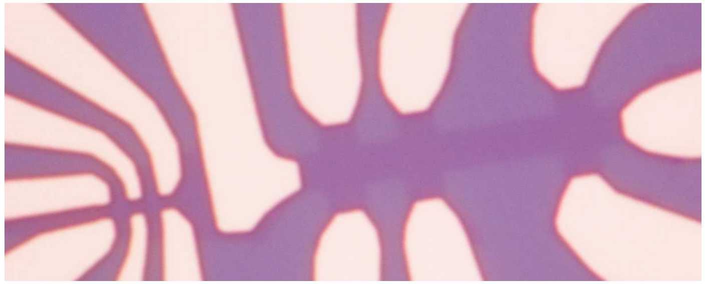


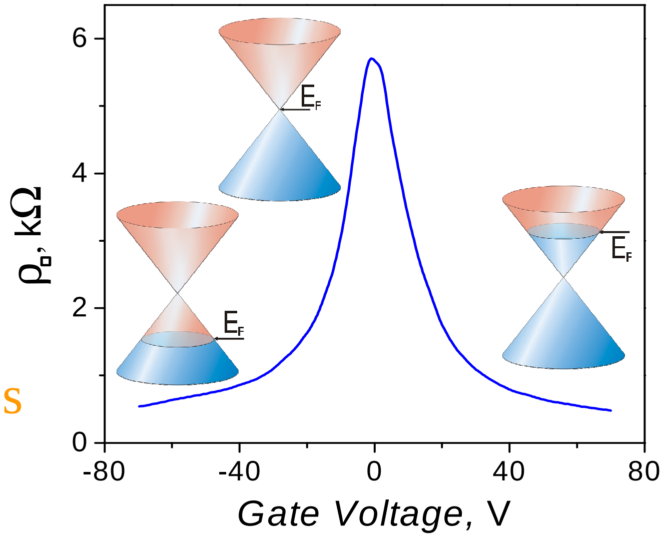






First “metallic” field effect transistor !

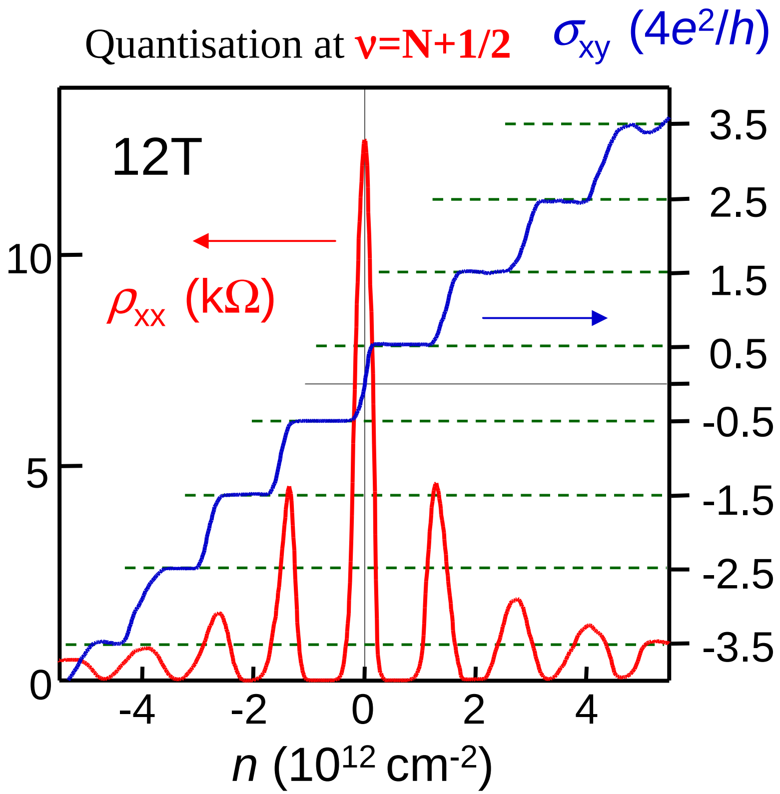




Huge Mobility: 20.000-100.000 cm^2/V·s

(order of magnitude better than silicon)

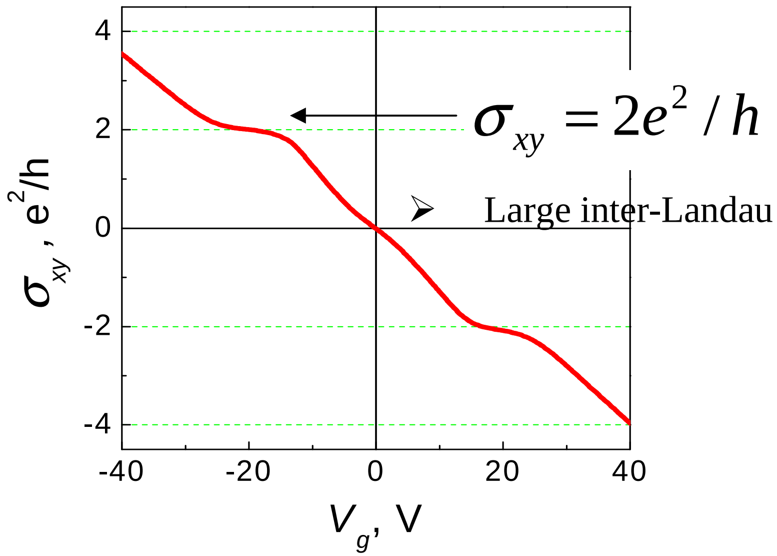
Quantisation at **ν=N+1/2**



Room Temperature and **low magnetic field**

Integer Quantum Hall effect !

Quantization at room temperature



➢ Large inter-Landau level distance

“Is graphene the new silicon?”

2D Graphene :: Zero-gap semiconductor
Graphene Nanoribbons: Semiconductor with adjustable gap

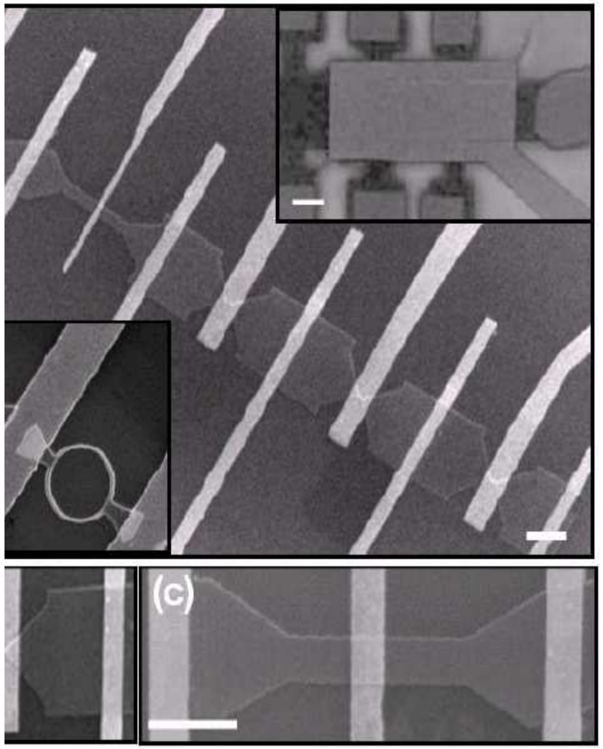
Carbon-based Nanoelectronics

Interconnects (huge current densities)
Active devices (Field effect transistors)

CMOS Hybridation
Innovative architectures

RT- Ballistic & Coherent transport 2D
(massless Dirac Fermions,..)

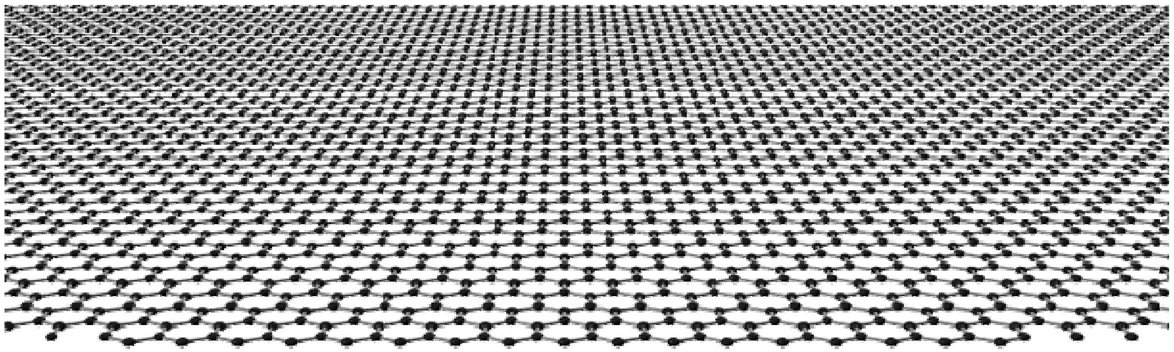
→ **New device principle**

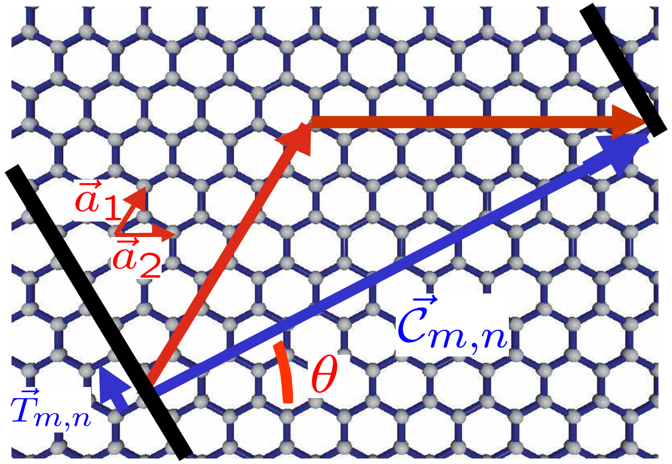


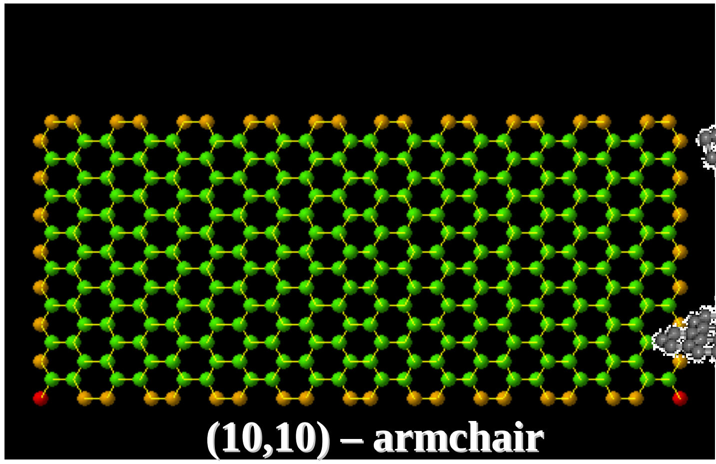
Why Nanotubes and Graphene are so special ?

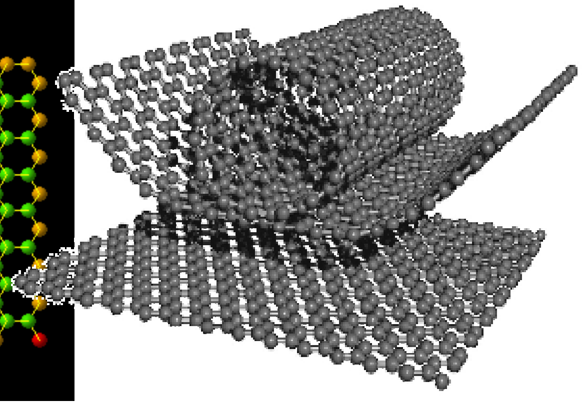
A story of sp^2-symmetries & pseudospin

Graphene (ribbons) & Carbon Nanotubes









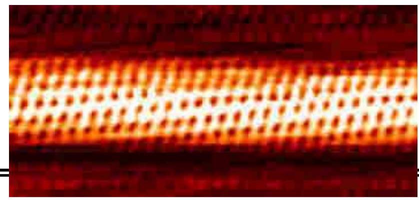
Chirality

$$\vec{C}_{m,n} = m\vec{a}_1 + n\vec{a}_2$$

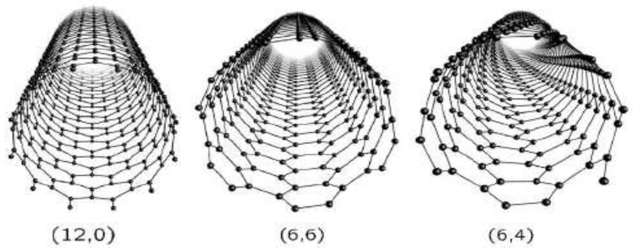
$\Longrightarrow$

Diameter

$$d_t = \frac{|\vec{C}_{m,n}|}{\pi}$$

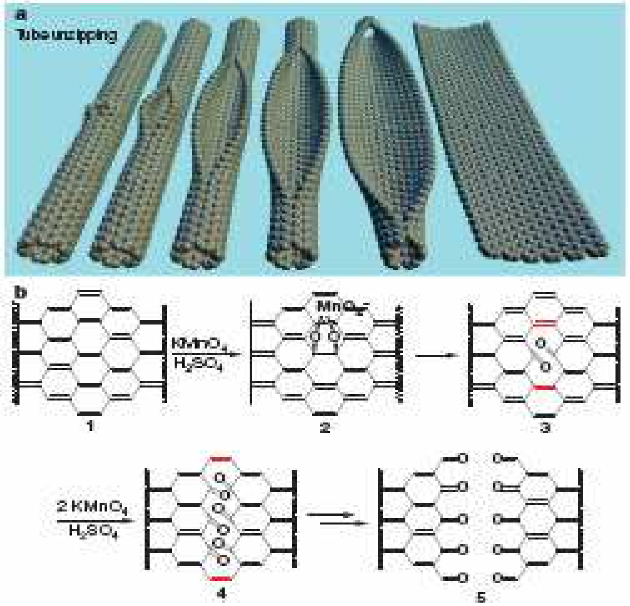


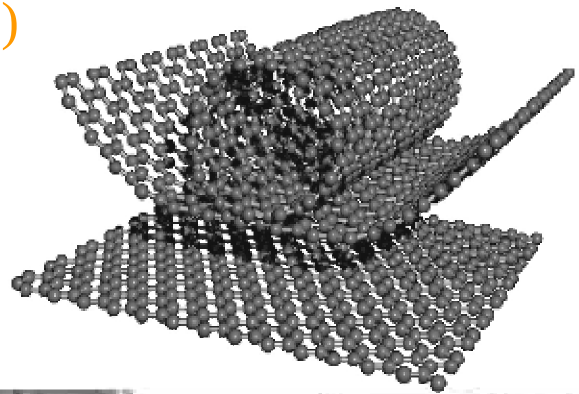
Symmetries

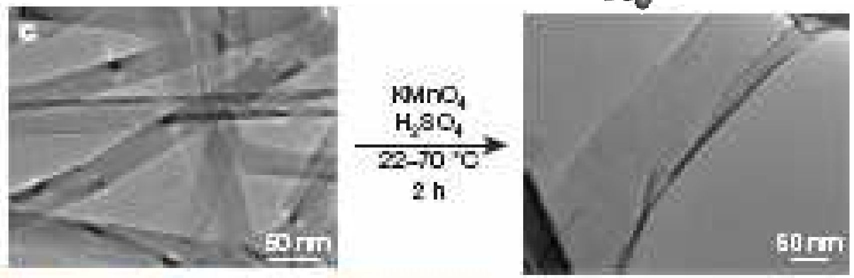


Unzipping Nanotubes to form Graphene Ribbons

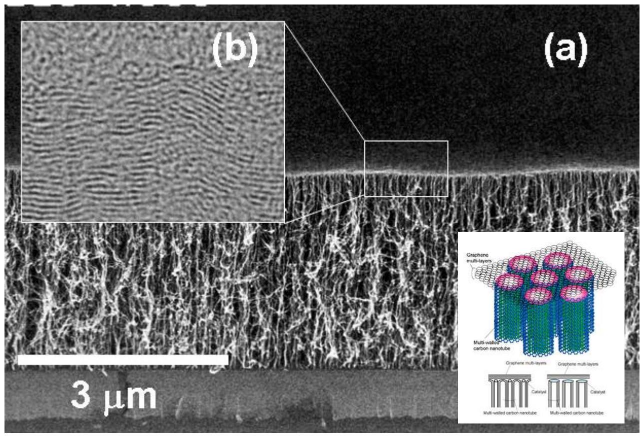
J. Tour et al., Nature 458, 872 (16 April 2009)







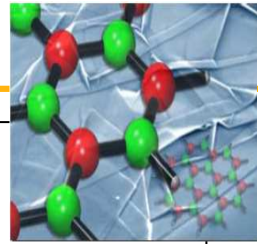
The all-carbon Architectures ….



FUJITSU THE POSSIBILITIES ARE INFINITE

Atsugi, Japan, March 3, 2008 — The newly-discovered composite structure is synthesized at a temperature of **510 °C,** cooler than for conventional graphene formed at temperatures too high for electronic device applications, thereby paving the way for the feasible use of graphene as a material suitable for future practical use in electronic devices which are vulnerable to heat.

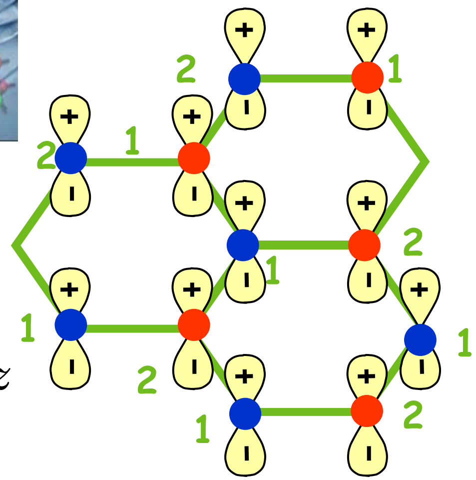
π Effective Model



Hybrid Molecular Orbitales

Cohesion $s, p_x, p_y \equiv \sigma$

Electronic Properties in the vicinity of E_F $p_z \equiv \pi$



2 atoms/ cell γ_0 nearest neighbor orbital overlap

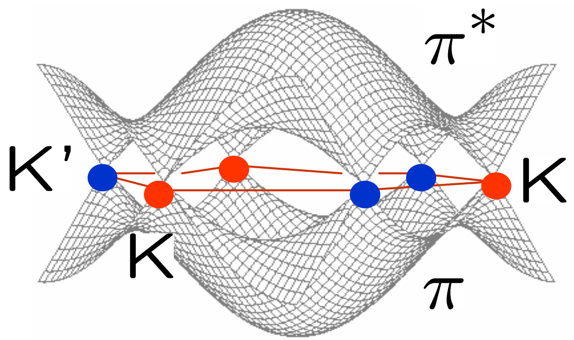
$$H(\vec{k}) = \begin{bmatrix} 0 & f(\vec{k}) \\ f^*(\vec{k}) & 0 \end{bmatrix} \qquad f(\vec{k}) = \gamma_0 \sum_\alpha e^{i\vec{k}.\vec{\tau}_\alpha}$$

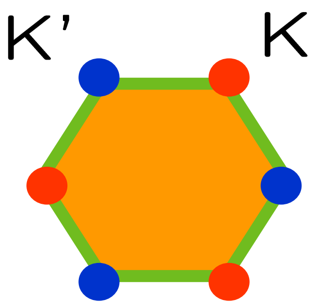
$$E_\pm(k_x, k_y) = \pm\gamma_0\left(3+4\cos(\frac{\sqrt{3}k_x a}{2})\cos(\frac{k_y a}{2})+2\cos(k_y a)\right)^{1/2}$$

$E_+(k_x, k_y)$

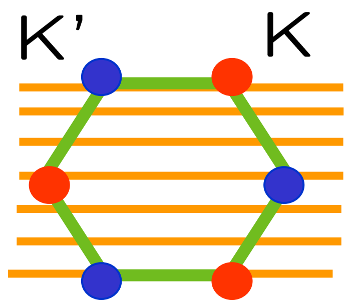
$E_F = 0$

$E_-(k_x, k_y)$





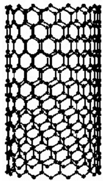
2D



Quasi-1D

1 Brillouin Zone

Nanotubes: Electronic Properties

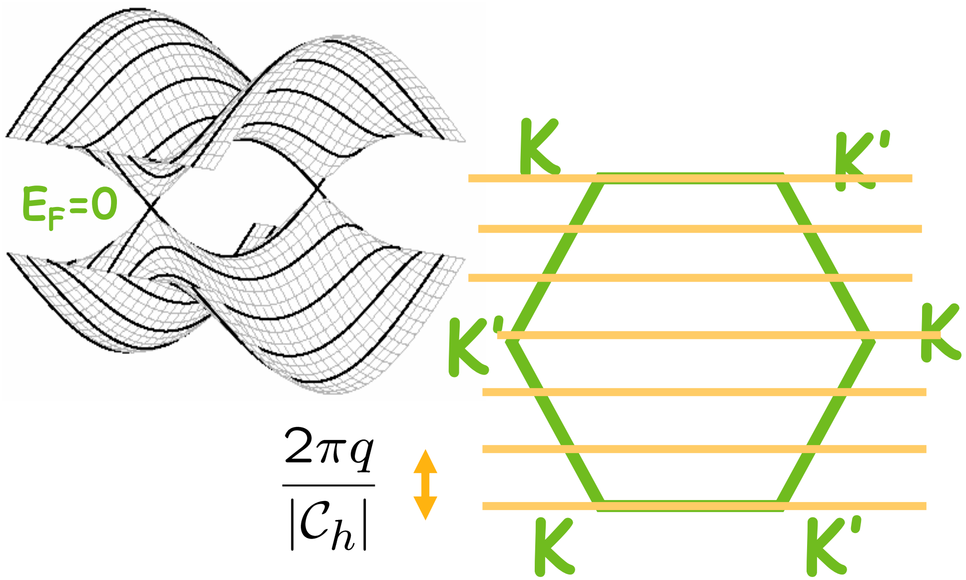


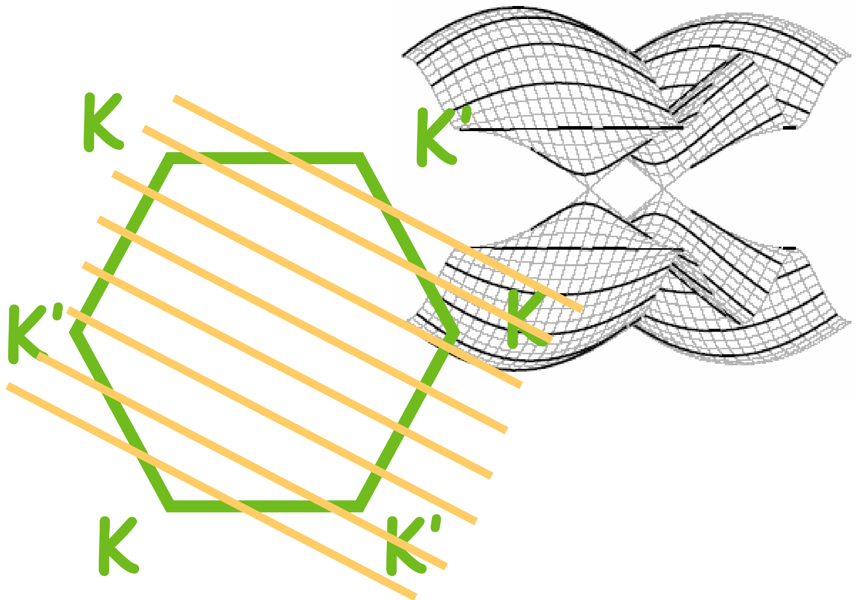
Periodic Boundary conditions

$$-\frac{\pi}{|\vec{T}_{(n,m)}|} \leq k_y(=k) \leq +\frac{\pi}{|\vec{T}_{(n,m)}|} \qquad k_x = \frac{2\pi q}{|\vec{C}_{(n,m)}|}(q = 1, N)$$

Symmetry choice

$$\vec{C}_{n,n} = n(\vec{a}_1 + \vec{a}_2) \qquad \vec{C}_{n,m} = (3p \pm 1)\vec{a}_1$$





Metallic versus Semiconducting Nanotubes

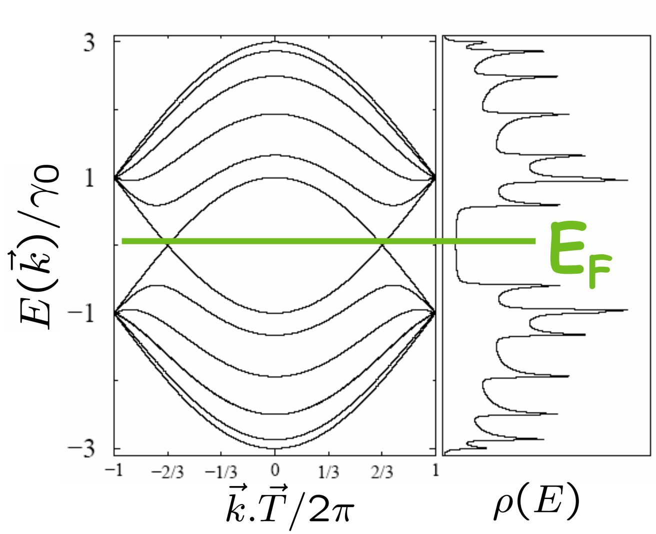
Theoretical prediction 1992

R. Saito, M. Dresselhaus, G. Dresselhaus APL 92

J. Mintmire & C.T. White, PRL 92

Metallic

$$E_q^{\pm}(k) = \pm\gamma_0\sqrt{1 \pm 4\cos\frac{ka}{2}\cos\frac{q\pi}{n} + 4\cos^2\frac{ka}{2}}$$

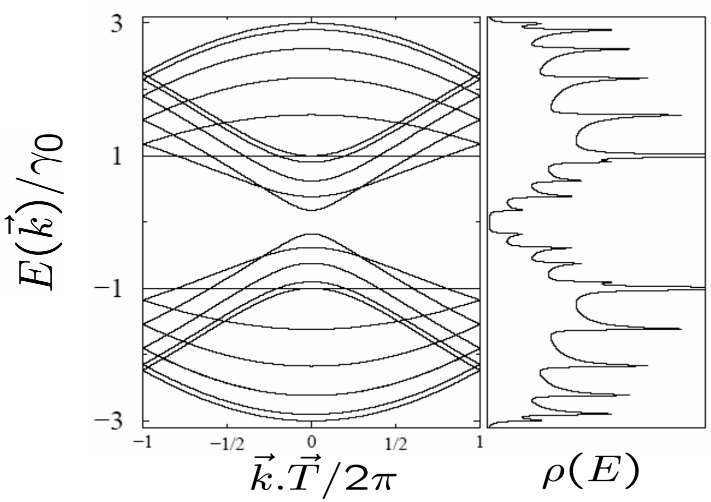


Unique case of 1D METAL !!

Robust against Peierls transition

Semiconducting

$$E_q^{\pm}(\delta\vec{k}) \simeq \pm\frac{\sqrt{3}a}{2}\gamma_0\sqrt{\left(\frac{2\pi}{|\vec{\mathcal{C}}_h|}\right)^2\left(q \pm \frac{1}{3}\right)^2 + k^2}$$



$$\Delta_g = 0.59eV \qquad d_{tube} = 1.4nm$$

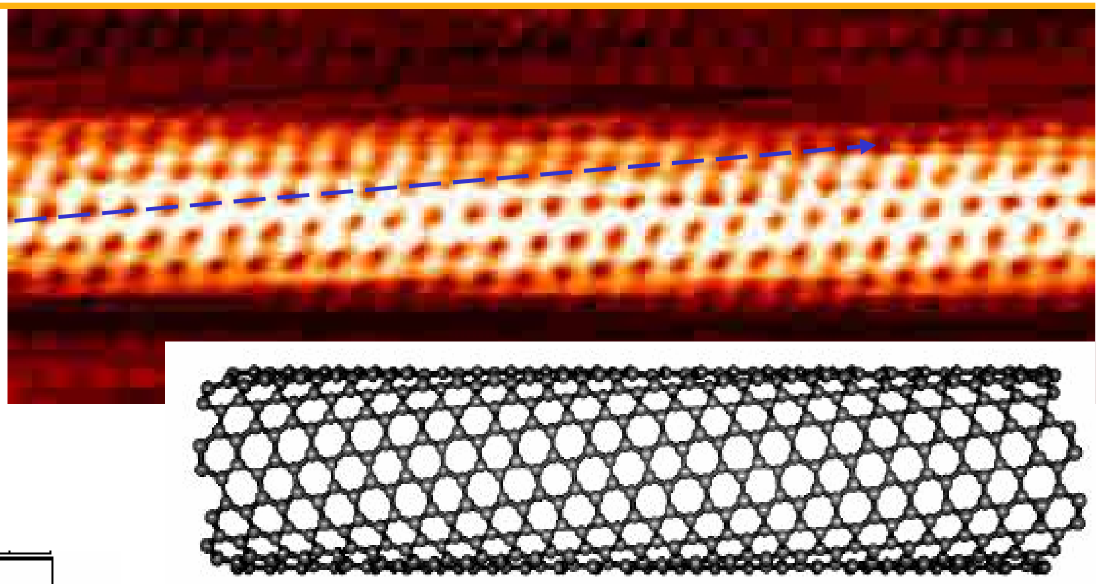
$$\frac{2\pi a\gamma_0}{\sqrt{3}\,|\vec{\mathcal{C}}_h|} = \Delta_g \;;$$

Gap engineering possible if growth is controlled !

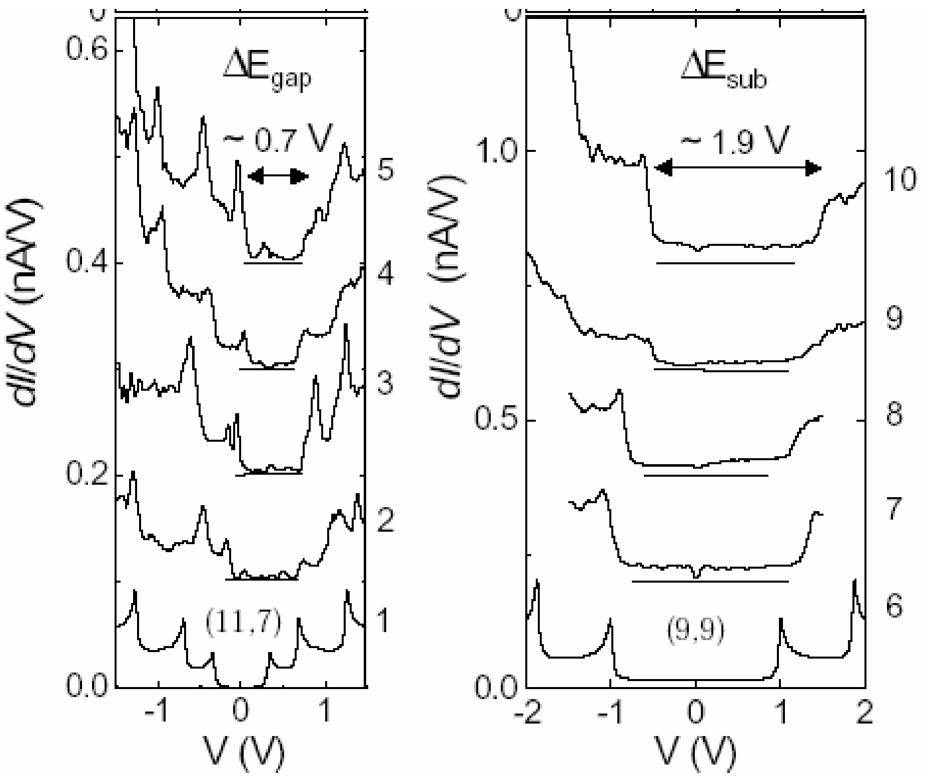
Electronic structure & STS experiments

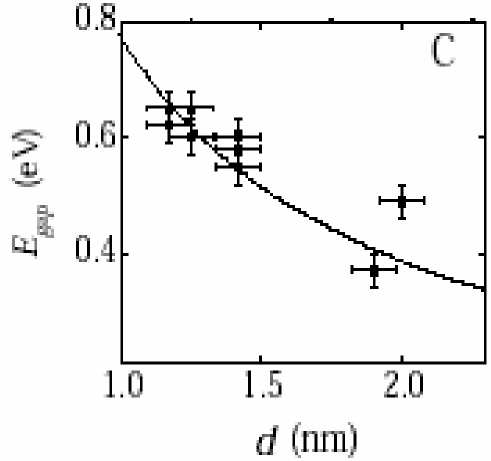
S. Tans et al.
Nature **386**, 474 (1997)

Helicity



Metallic vs semiconducting

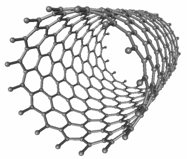


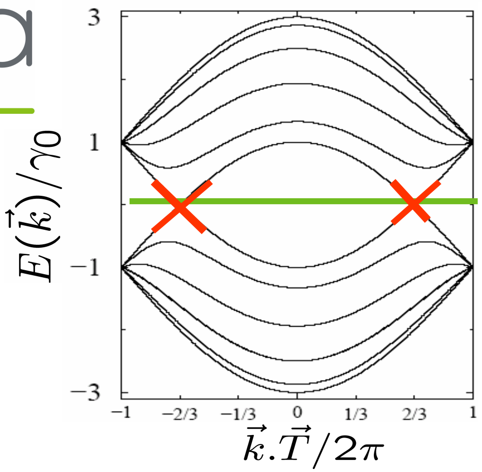


$$\Delta_g \sim \frac{1}{d_{nt}}$$

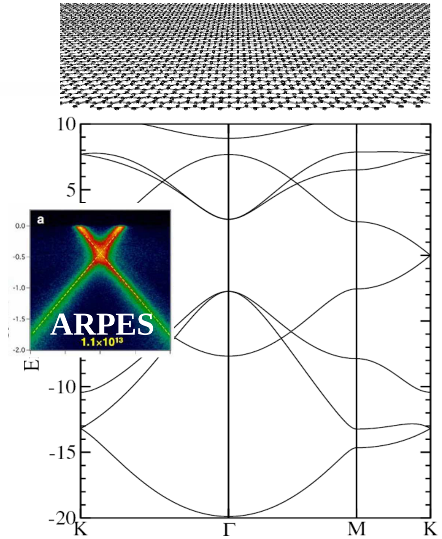
Remark :Massless Dirac Fermions in 2D vs 1D

Nanotubes
(n,n) armchairs

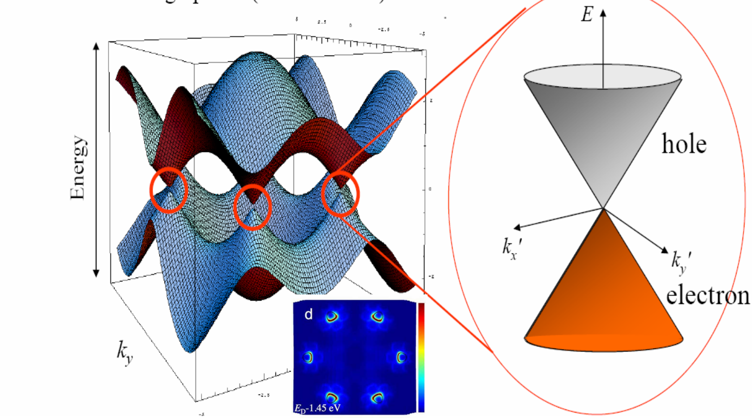




2D Graphene



Band structure of graphene (Wallace 1947)



$$\vec{Q} = \vec{K}_\pm + \vec{p}/\hbar$$

$$\mathcal{H}_{K_+}(\vec{p}) = v_F(p_x\sigma_x + p_y\sigma_y)$$

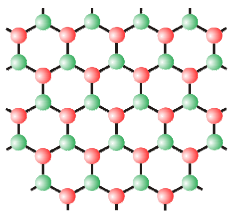
(in the sublattice basis)

Dispersion relation $s = \pm 1$

$$E(\vec{p}) = s v_F |\vec{p}|$$

Massless particles

$$E(\vec{p}) = s\sqrt{v_F^2 p^2 + m^{*2}c^4}$$

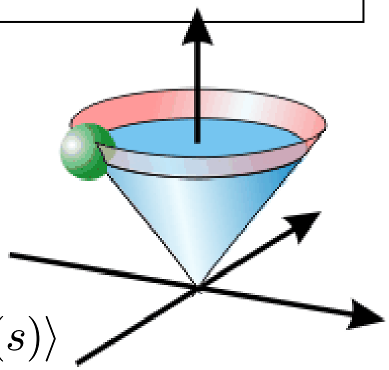


Eigenstates (pseudospin symmetry)

$$|\Psi^+_{\vec{p}}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} \psi^+_p(A) \\ \psi^+_p(B) \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} s e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix}$$

$$\hat{h} = \frac{1}{2}\hat{\vec{\sigma}}.\frac{\vec{p}}{|\vec{p}|}$$

$$\hat{h}|\Psi^+_{\vec{p}}(s=\pm 1)\rangle = \pm\frac{1}{2}|\Psi^+_{\vec{p}}(s)\rangle$$



Helicity (good qut. Nb) is the projection of the spin on the quantum momentum

Pseudospin symmetry & backscattering effects

- 1D metallic nanotubes : *Absence of backscattering,*
- 2D graphene : *Anti-localization phenomenon,*
suppression of quantum correction

Long range potential

(charges trapped in surrounding oxide, ripples,..)

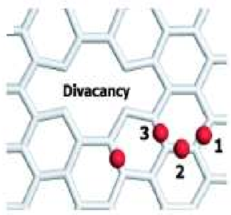
Short range potential

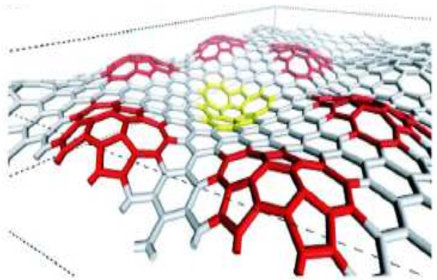
(vacancies, etc..)

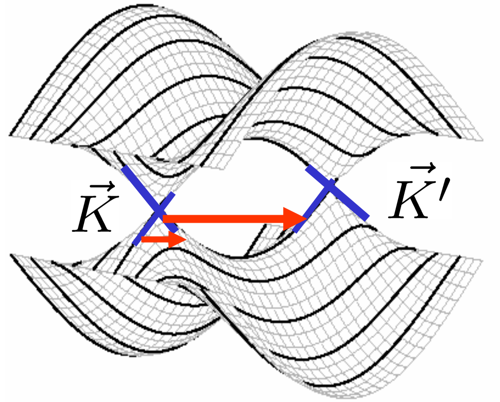
Potential fluct. with respect to lattice spacing

Intravalley *(pseudospin conservation)*

Intervalley *(pseudospin symmetry broken)*

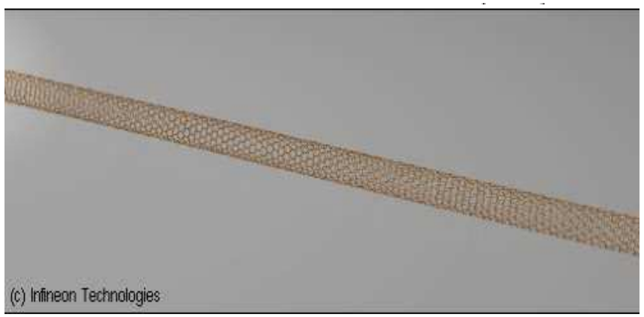






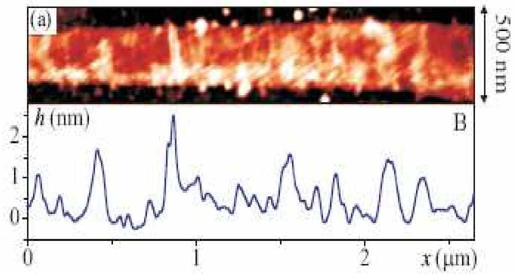
1d $|\langle\psi_{\mathbf{k},s}|\mathcal{T}|\psi_{\mathbf{k}',s'}\rangle|^2 = 0$

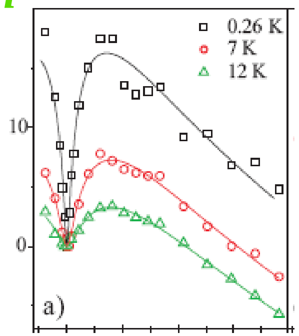
$\langle s|\mathcal{R}[\theta_k]R^{-1}[\theta_{-k}]|s\rangle = \cos(\theta_k + \theta_{-k})/2, \qquad \theta_k + \theta_{-k} = \pm\pi$



T. Ando, T. Nakanishi and R. Saito, J. Phys. Soc. Jpn 67, 2857 (1998)

2d ***Transition Weak localization / Anti-weak localization***



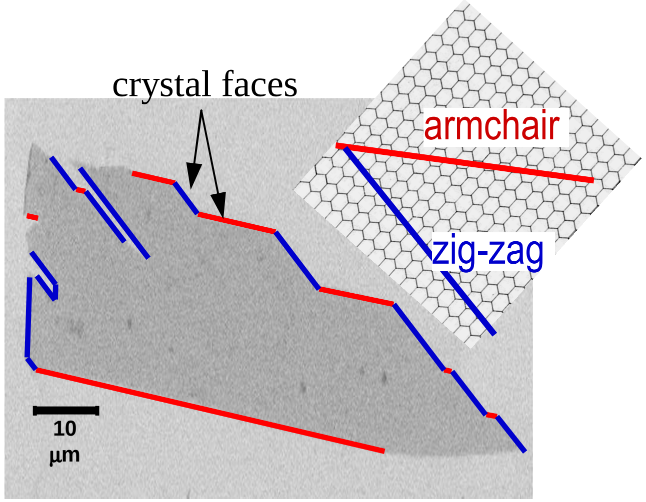


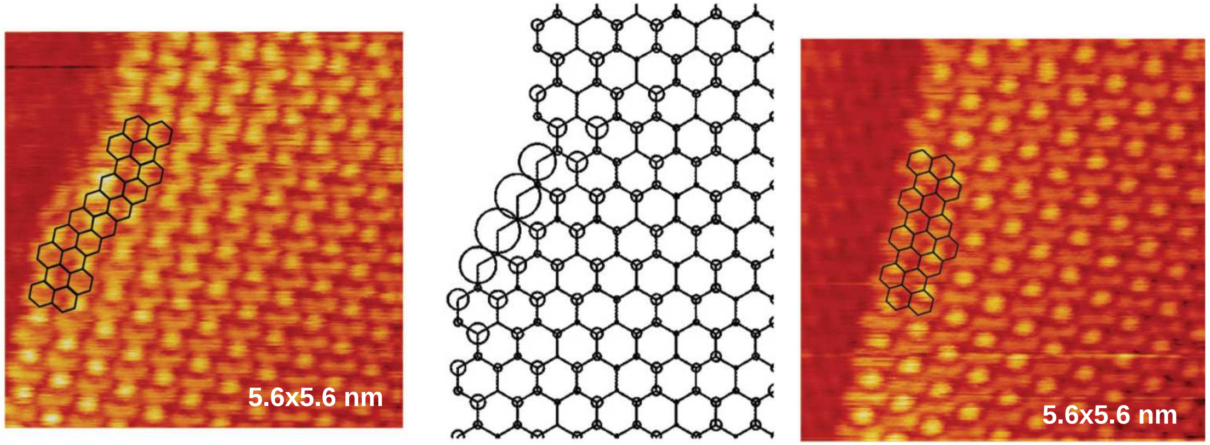
E. McCann *et al.*, Phys. Rev. Lett. 97, 146805 (2006)

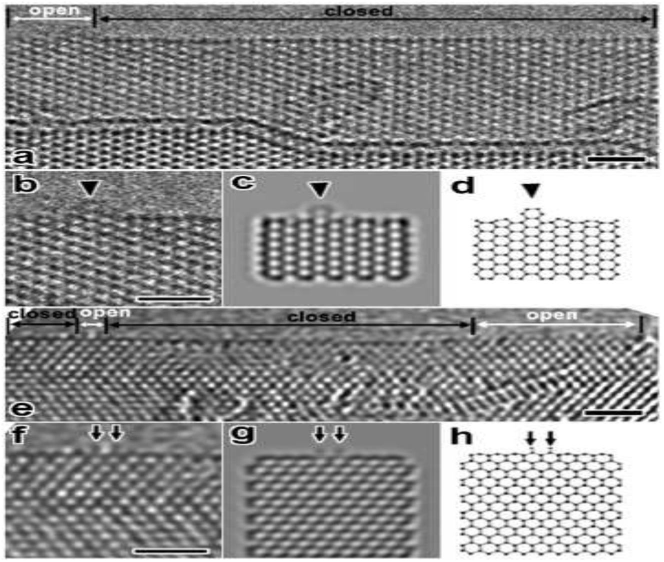
F.V. Tikhonenko et al., Phys. Rev. Lett. 100, 056802 (2008)

Edge symmetries & edge defects

T. Enoki et al., *Int. Rev. Phys. Chem.*, **2007**, 126, 609



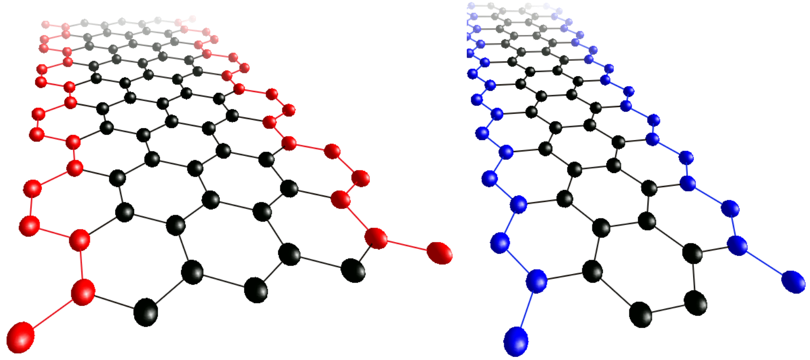




Z. Liu, K. Suenaga, P.J.F Harris, S. Iijima,
Phys. Rev. Lett. 102, 015501 (2009)

✓ **Zig-zag and armchair edges stable in ambient**

Armchair ribbon **Zigzag ribbon**

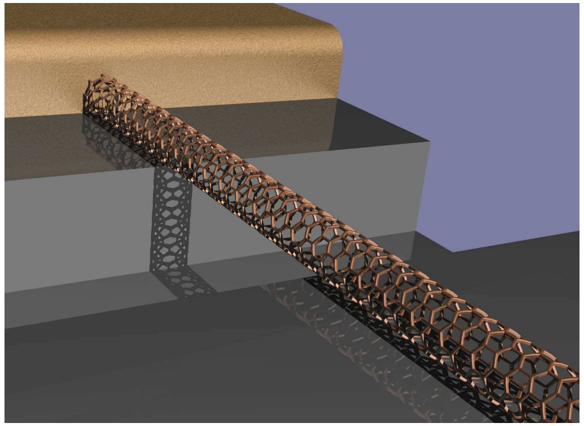


High edge chemical reactivity!!

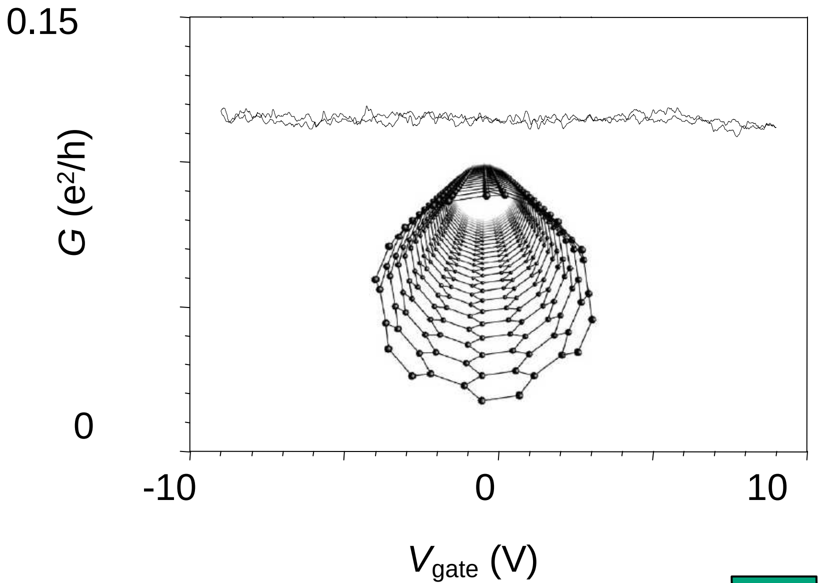
NANOTUBES inside

Device and Quantum Mechanics

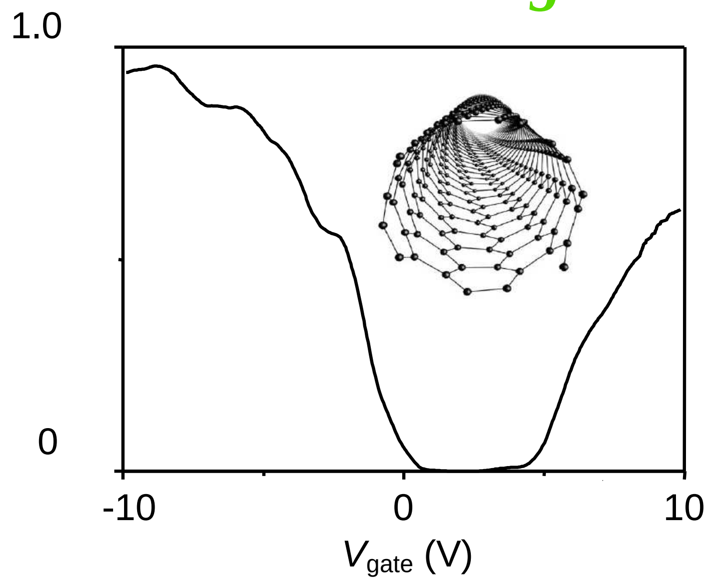
Monitoring Field effect capability



Metallic nanotube



Semiconducting nanotube

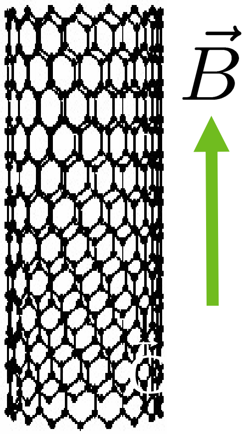


Conducting nanoscale interconnects

?

Field Effect Transistors

Aharonov-Bohm effects on the Electronic Spectrum



$\vec{B}$

$\{\vec{\mathcal{C}}_h/|\vec{\mathcal{C}}_h|, \vec{T}/|\vec{T}|\}$

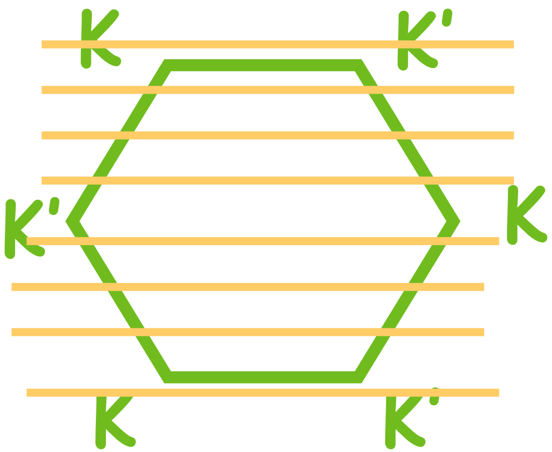
Landau gauge

$$\vec{\mathcal{A}} = (\phi/|\mathcal{C}_h|, 0)$$

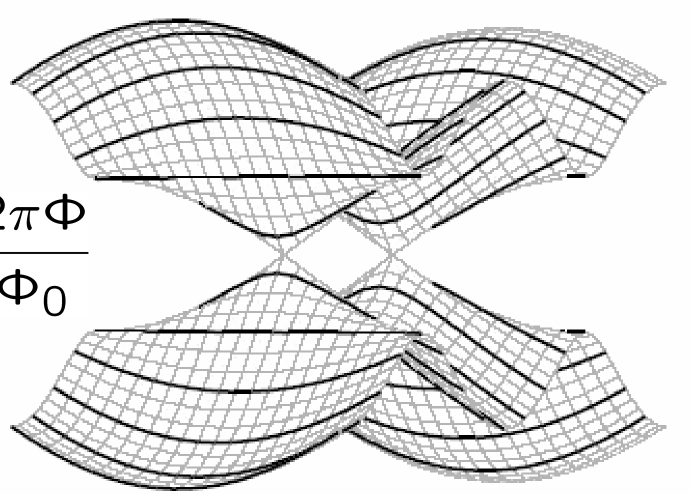
Wavefunction

$$\Psi \sim e^{ik_y y} e^{i(k_x x + \frac{e}{h}\int \vec{\mathcal{A}}.d\vec{r})}$$

$$\delta\vec{k}(\phi)\cdot\vec{\kappa}_x = \delta\vec{k}(0)\cdot\vec{\kappa}_x + 2\pi\phi/(\phi_0|\vec{\mathcal{C}}_h|)$$

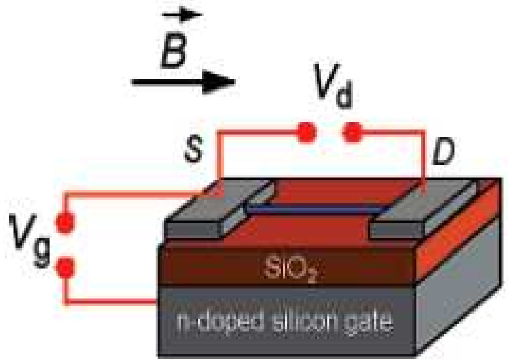


$$k_x = \frac{2\pi q}{|\mathcal{C}_h|} + \frac{2\pi\Phi}{\Phi_0}$$

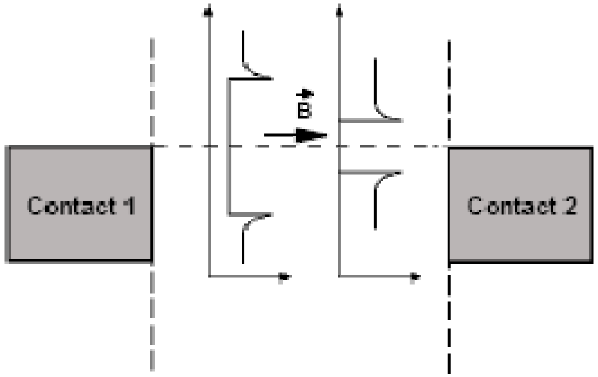


H. Akiji and T. Ando, J. Phys. Soc. Jpn 62, 2470 (1993)
H. Akiji and T. Ando, J. Phys. Soc. Jpn 65, 505 (1996)

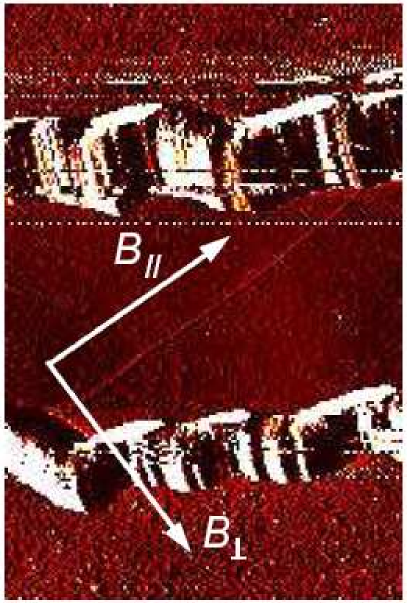
Basic Principle to engineer a B-modulated FET ?

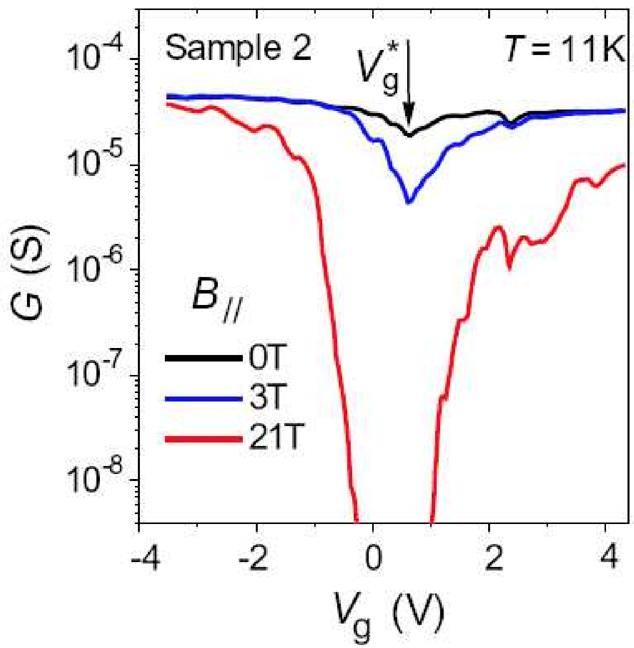


?

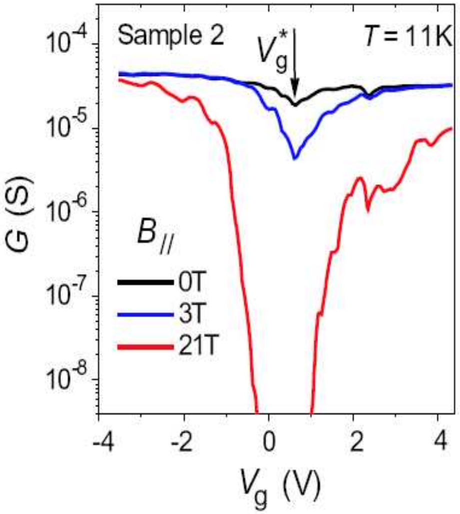


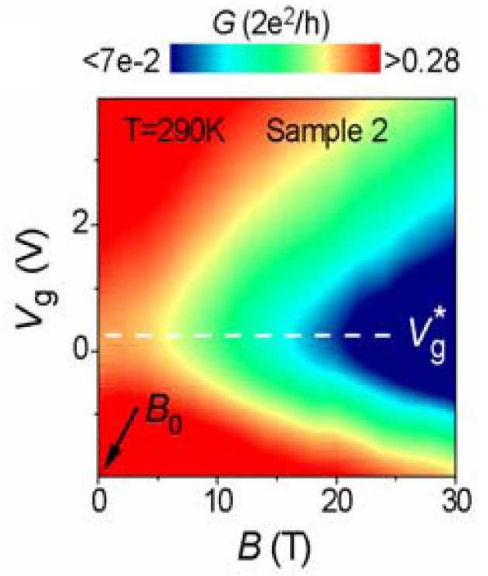
G Fedorov, A Tselev, D Jiménez, S Latil, N Kalugin, P Barbara, D Smirnov, SR,
Nano Lett. 7, 960 (2007)

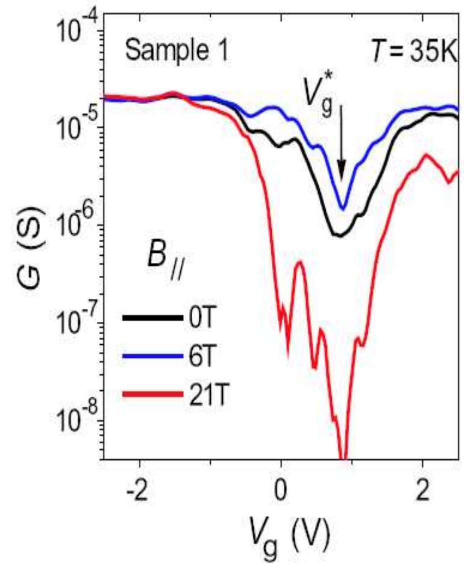


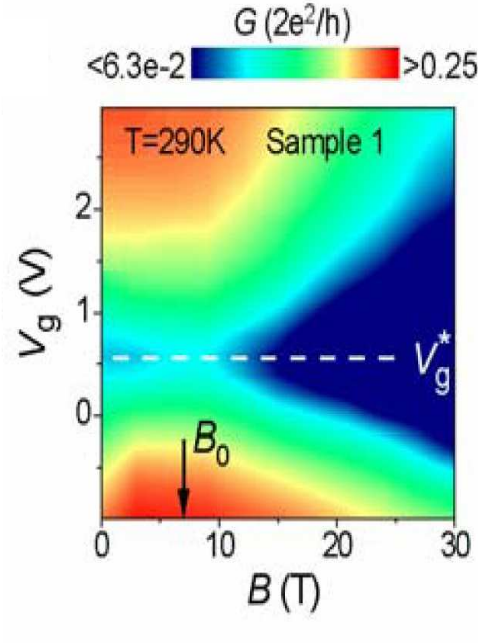


Chirality identification !





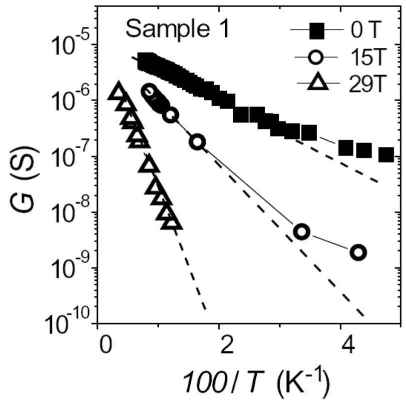




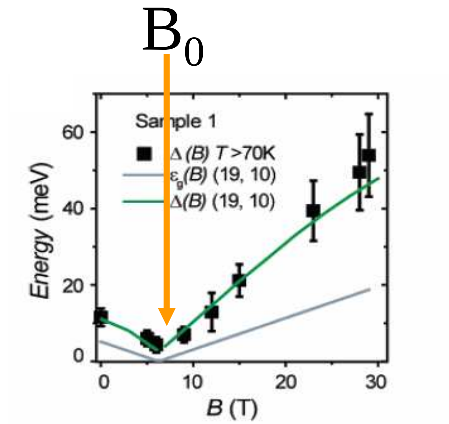
Charge transport mechanism

Temperature-dependent conductance

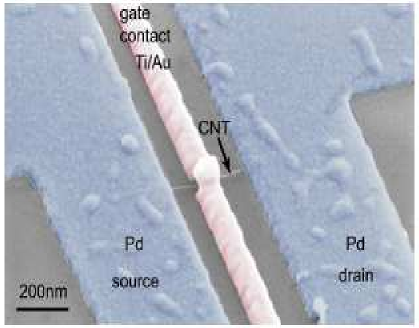
Tunneling regime through a Schottky barrier
(B-dependent features)



Arrhenius plots



Ohmic vers Schottky FET ?



Nanotechnology

A barrier falls

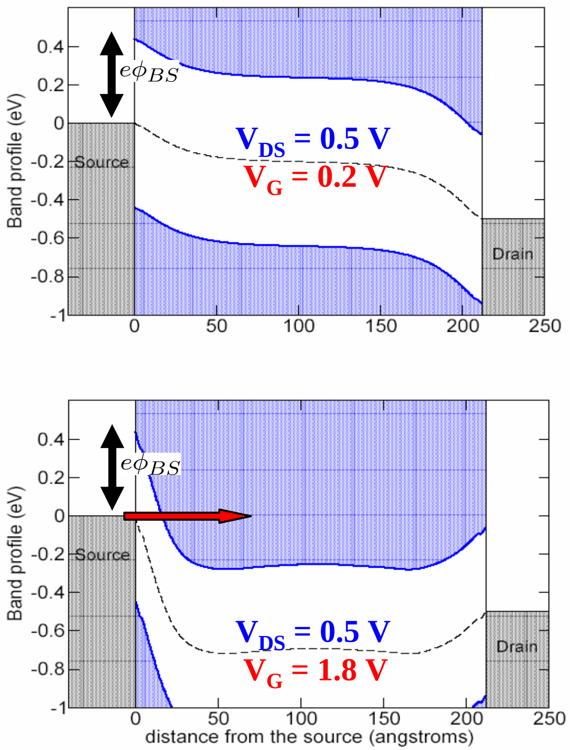
J. Tersoff

Electronic devices based on carbon nanotubes have a bright future — even more so now that a way has been found to eliminate the 'Schottky barrier' that hinders the injection of electrons into them.

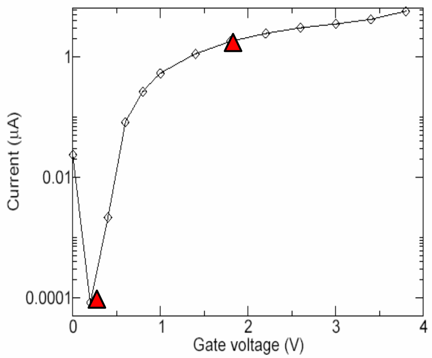
Nature 424, 623 (2003)

Semiconducting Nanotubes / PALLADIUM

Diameter = 1 nm



Schottky Transistors

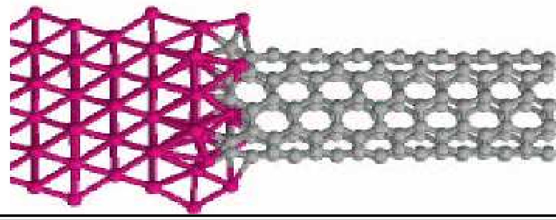


OhmicTransistors

$e\phi_{BS} = 0$

Semiconducting Nanotubes / PALLADIUM

Diameter = 2~3nm



→ **Ab initio simulation**
The golden way…

Puzzling dissipative regime…

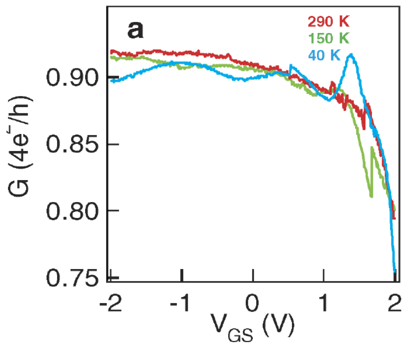
Javey et al PRL **92**, 106804 (2004); Nature 424, 654 (2003)

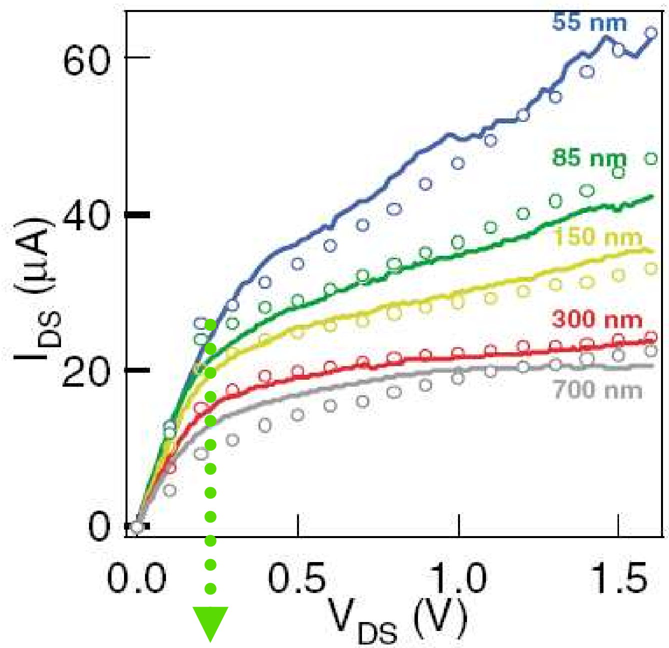
LOW-BIAS

$$dI/dV = \frac{4e^2}{h}$$

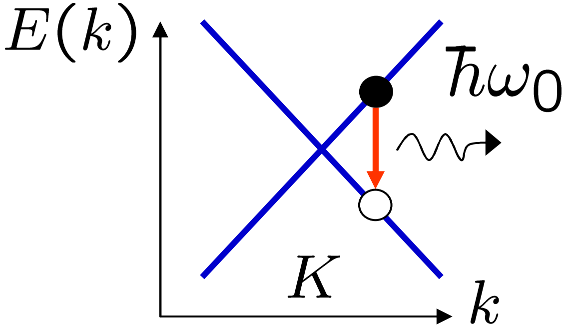
Ballistic regime

$$L_{tube} < \ell_{ie}$$





$$V_{DS} = \hbar\omega_0$$

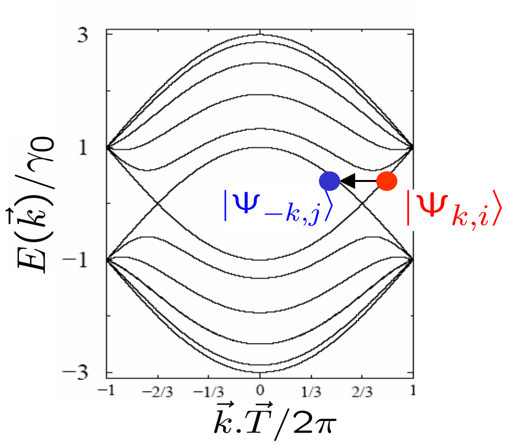


Bias provides energy supplyfor
optical phonon emission

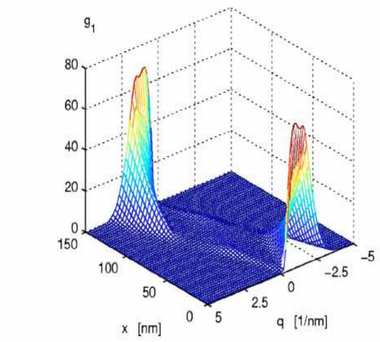
HIGH-BIAS

Dissipation takes place

Born-Oppenheimer apprx + FGR



$$\tau_{ie}^{-1} \sim \left|\langle\Psi_{k+q,j}|\Gamma_{k+q,j;k,i}|\Psi_{k,i}\rangle\right|^2 \qquad \ell_{ie} = v_F.\tau_{ie}$$



$$n(x,t) = 1/(e^{\hbar\omega/k_b T_{\mathrm{eff}}(x,t)} - 1)$$

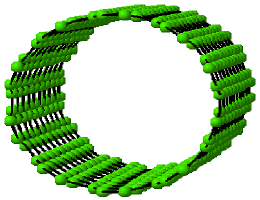
$$\sim 3 - 80!!$$

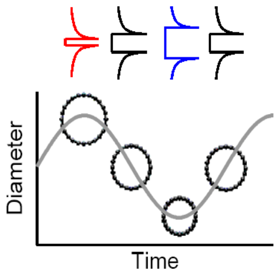
$$T_{eff} \sim 1000 - 100.000K$$

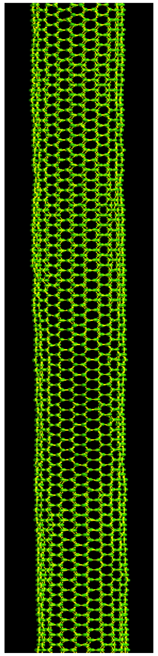
Breakdown of The Born-Oppenheimer approx.

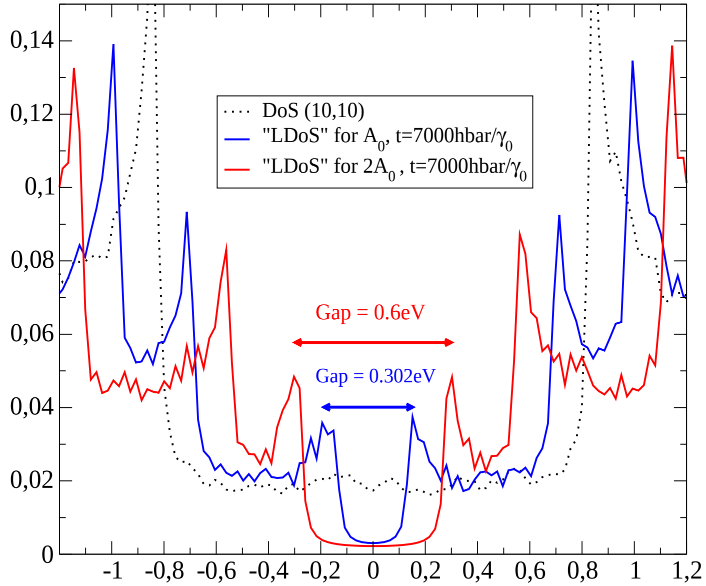
J. Kono et al. (Rice University) NL 2006

generation and detection of RBM of coherent lattice vibrations in single-walled carbon nanotubes using ultrashort laser pulses.

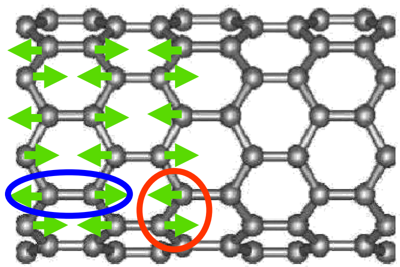




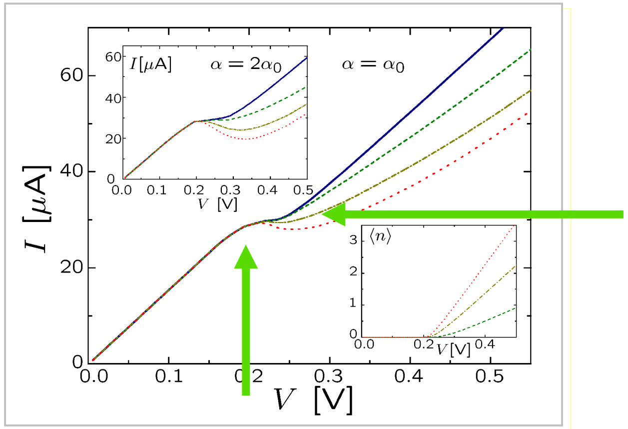




$$H_{e-ph} = \sum_{\langle i,j\rangle_{vib}} \left[\gamma_{i,j}^{e-ph}\, c_i^{+} c_j (b^{+} + b) + h.c.\right],$$



Transport + Raman experiments ?



Onset of current saturation at

$$I_{sat} = \frac{4e}{h}\hbar\omega_0$$

$$\simeq 30\mu\text{A}$$

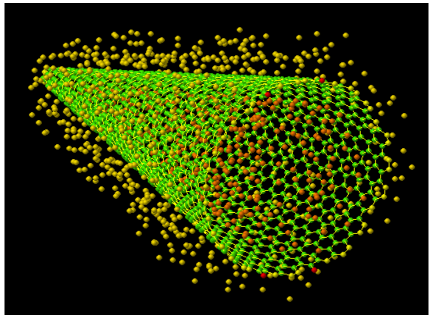
Activation mode LO $\quad V_{DS} = \hbar\omega_0 \simeq 196\text{meV}$

L.E.F. Foa-Torres, SR, **Phys. Rev. Lett. 97, 076804 (2006)**
L.E.F. Foa-Torres, R. Avriller, SR, **Phys. Rev. B 78, 035412 (2008)**

NANOTUBE inside

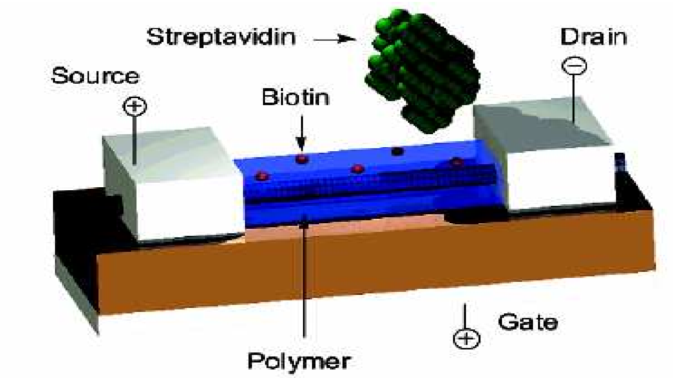
Challenges for ***I****nnovation*

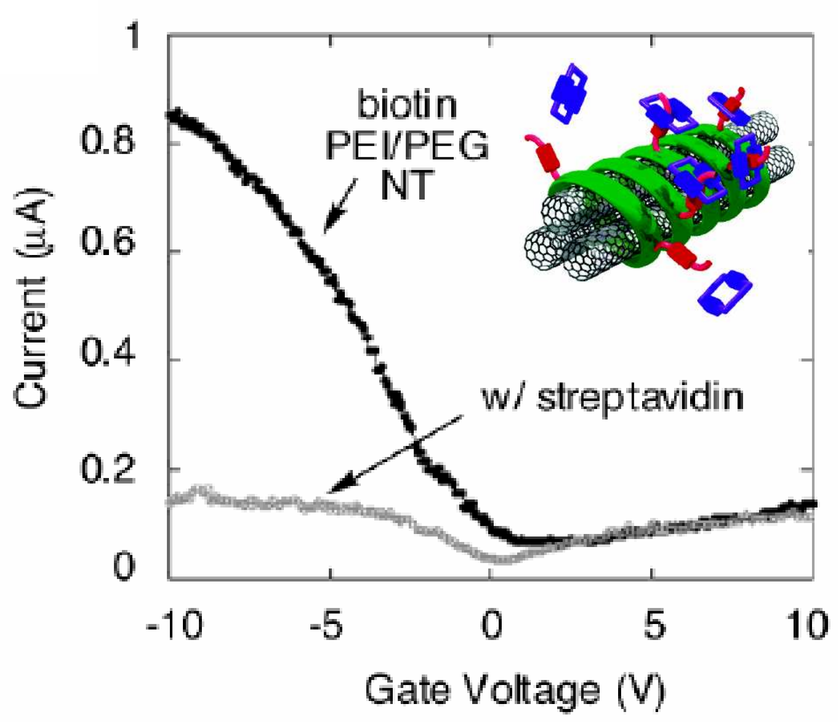
(bio)chemical sensors



Sensitivity and selective electrical signals of molecular Adsorption events ?

Protein interaction , pH, enzymatic activity



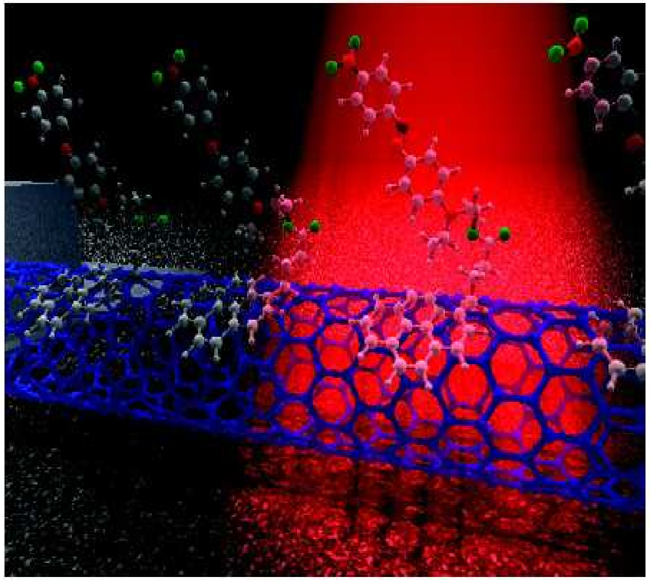


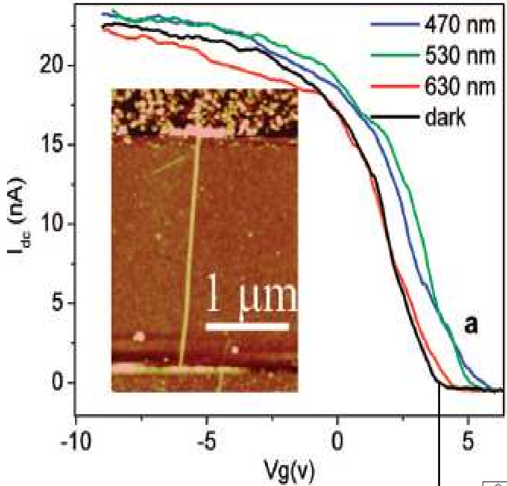
A.Star, Jean-Christophe P. Gabriel, K. Bradley, G. Grüner
Nanoletters 3, 459 (2003)

Optical detectors based on Hybrid CNTs

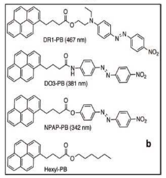
Transfer characteristics of (azobenzene) chromophore-Nanotube Hybrid Devices

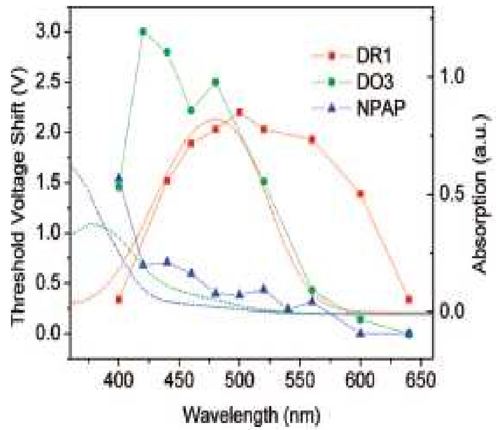
Zhou et al.,
Nano Letters 9, 1028 (2009)

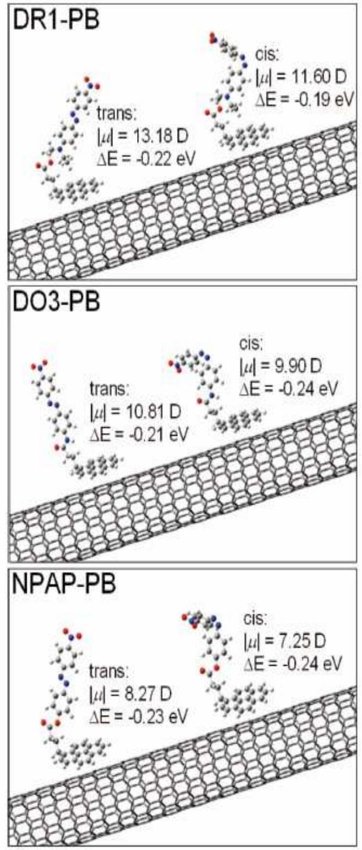




Threshold voltage shift of devices functionalized with different chromophores





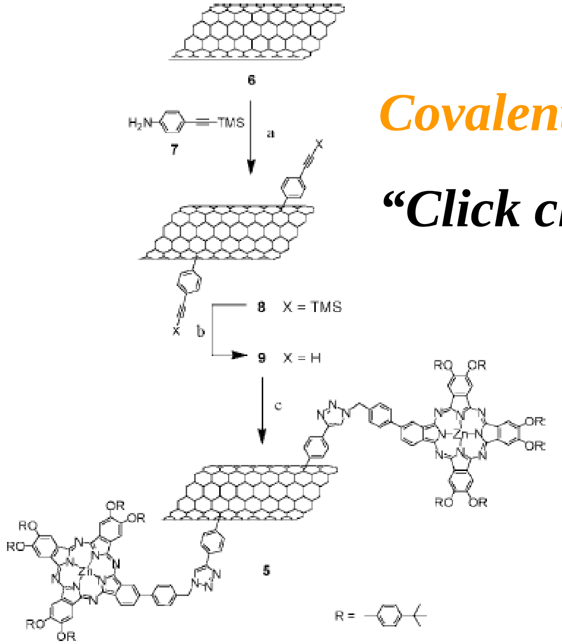


Simulation : strong binding but Low tube disturbance
Large dipole modulations upon isomerization from gs-trans to excited state cis

By synthesizing chromophores with specific absorption windows in the visible spectrum and anchoring them to the nanotube surface, controlled detection of visible light of low intensity in narrow ranges of wavelengths is demonstrated

Challenges for Innovation

Optical switches & Photovoltaic applications



Covalent functional

"Click chemistry"

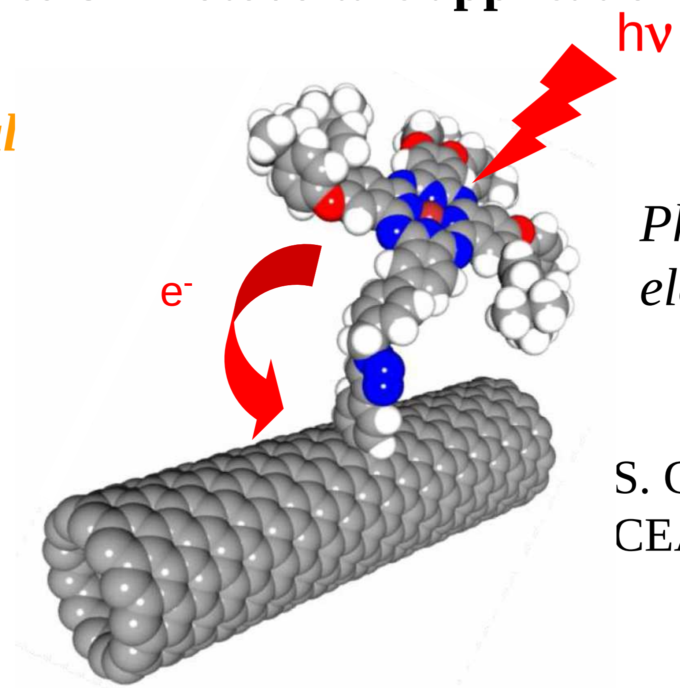
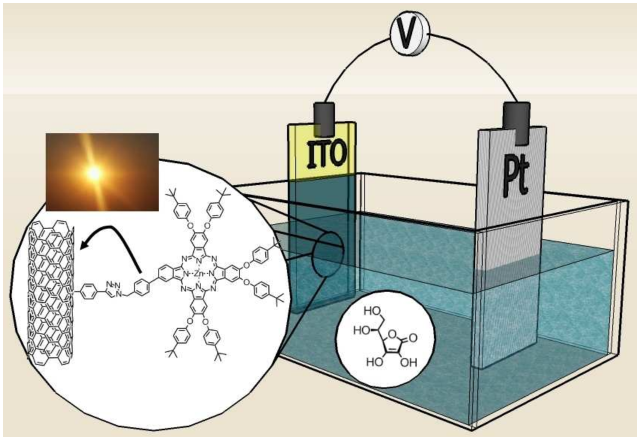
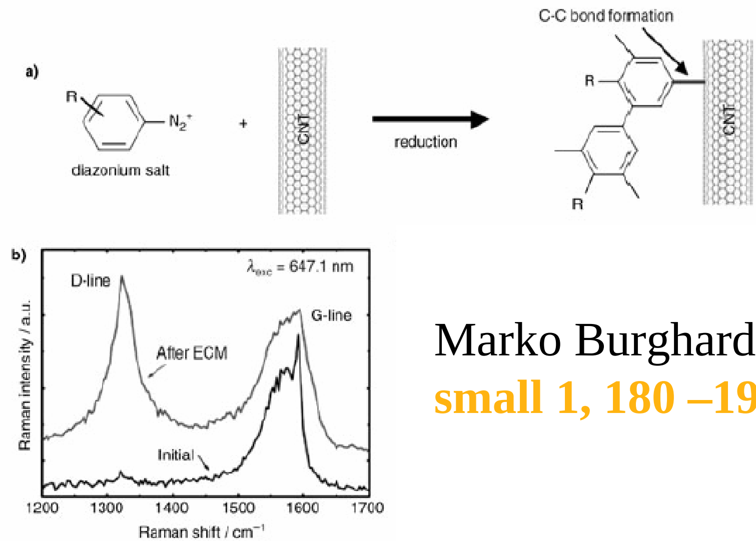


Photo-induced electron transfer

S. Campidelli,
CEA (IRAMIS/Saclay)



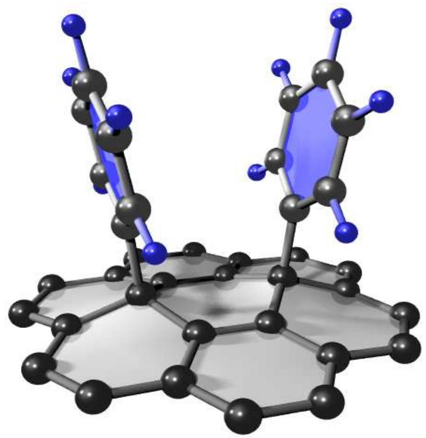
JP. Simonato (LITEN)



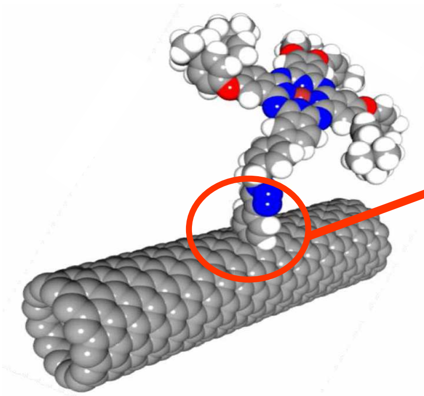
Marko Burghard,
small 1, 180 –192 (2005)

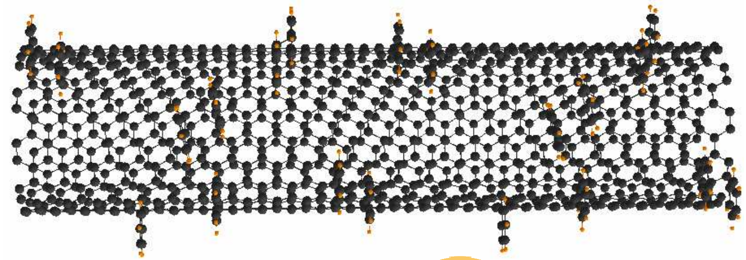
Hybrid Carbon Based Materials

Is sp^2 bonding
is broken/preserved ?



sp^3 versus sp^2 functionalization : conductance ?

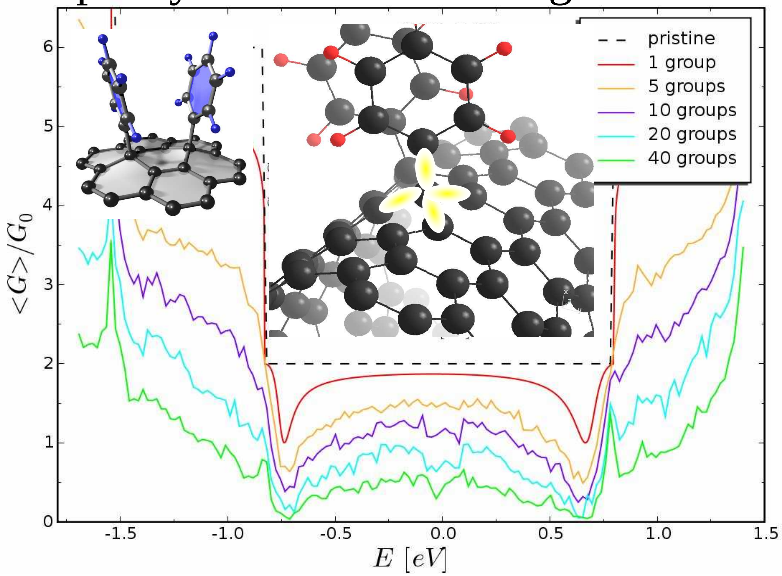




sp^3

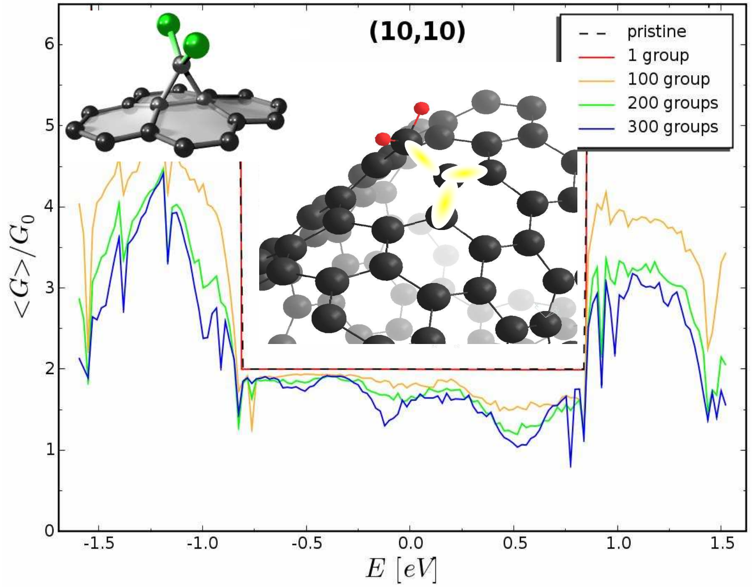
sp^2

Biphenyls - CNTs with length : 300 nm



Diffusive transport

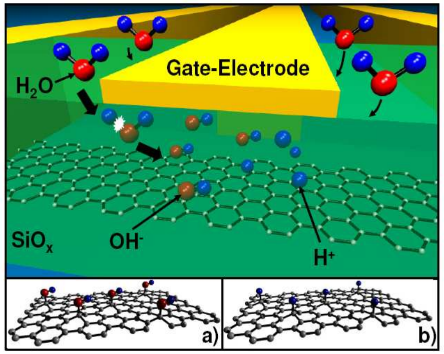
Carbene- CNT : 1000 nm



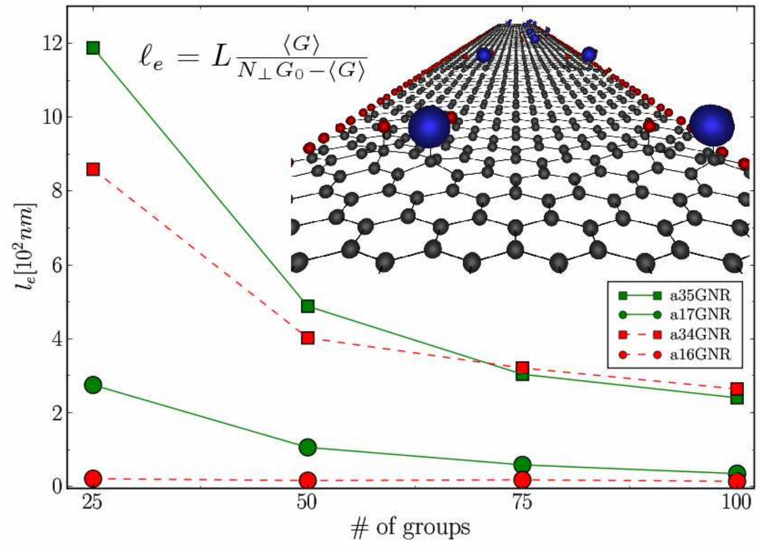
Quasiballistic transport

A. Lopez-Bezanilla, F. Triozon, S. Latil, X. Blase, S.R. **Nano Letters 9, 940 (2009)**

Functionalized Graphene Nano-Ribbons –

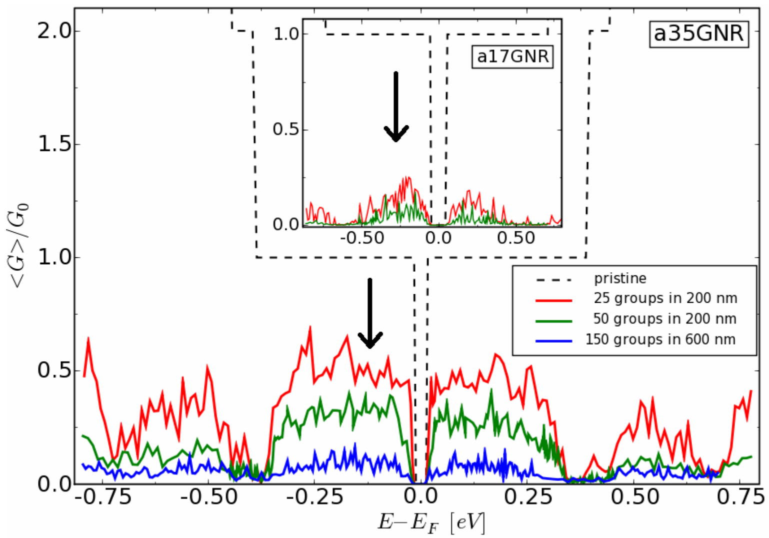


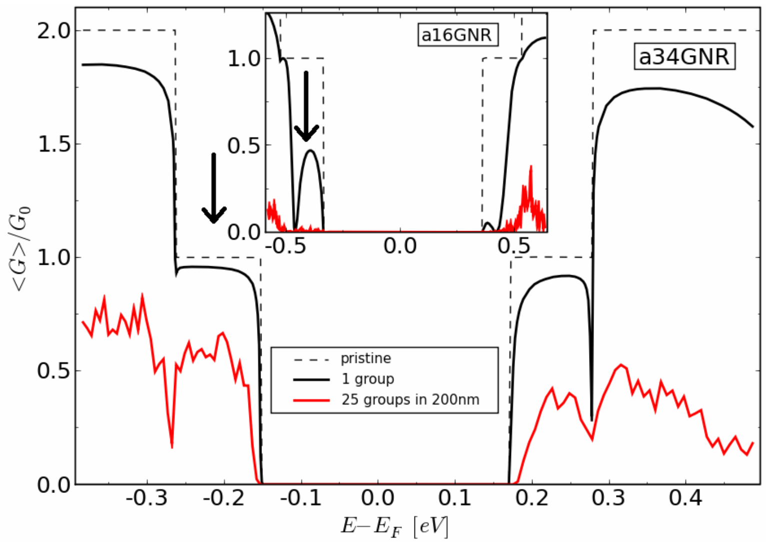
$OH^- + H^+$
(Grafted pairs)
↓
sp^3 defect
(covalent bond)



Low functionalization limit
Transport regimes and mobility gaps are strongly dependent on GNR width

A. Lopez-Bezanilla, F. Triozon, S.R
Nano Letters 9, 2737 (2009)





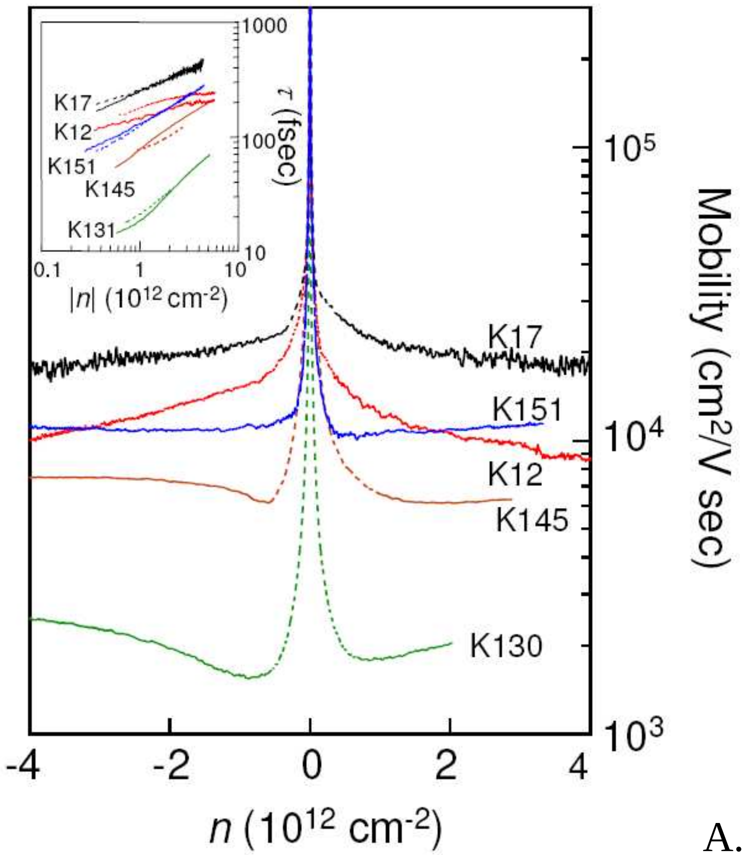
GRAPHENE inside

From infinite mobility to Graphene nanoribbon transistor

Graphene an exceptionally good conductor...

Charge mobilities going to infinity!...?

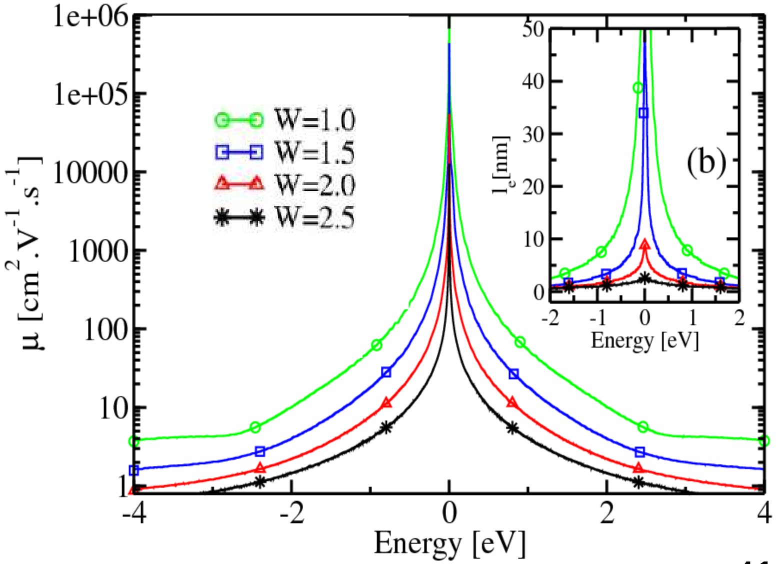
Ph. Kim et al., Phys. Rev. Lett. 99, 246803 (2007)



$$\mu(E) = \sigma_{sc}(E)/en(E)$$

$$\sigma_{SC} = e^2\rho(E)v(E)\ell_e$$

Diverges if charge density tends to zero

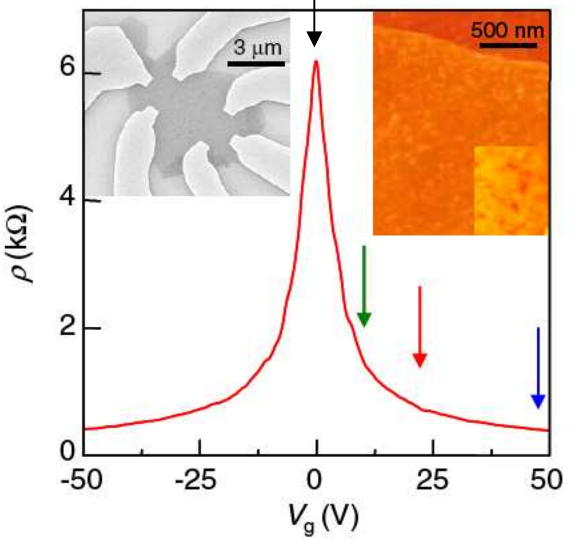


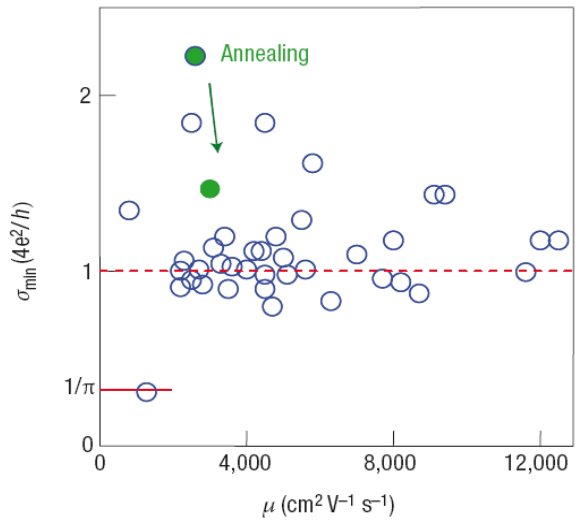
A. Lherbier, B. Biel, YM. Niquet, SR, **PRL 100, 036803 (2008)**

Minimum conductivity in 2D graphene ?

Novoselov, Geim and Zhang, Stormer, Kim, Nature 2005

Minimum conductivity





$$\sigma(E = CNP) = \sigma_{min} \sim \frac{4e^2}{h}$$

$$\rho(E = CNP) \sim \frac{h}{4e^2}$$

Mobility can fluctuates by one order of magnitude from sample to sample

$$R \sim \frac{\rho L}{W}$$

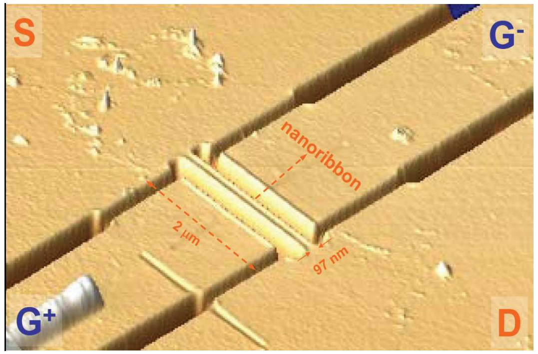
Not ballistic transport & conductance quantization

Field effect is poor due to semi-metallic character of graphene bandstructure
Resistivity saturation (down to low temperature) : absence of localization effects ??

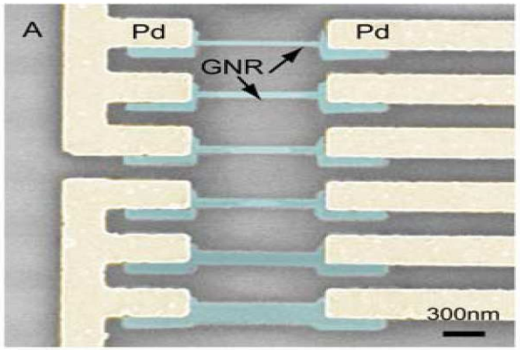
Graphene Nano-ribbon Transistors ?

Using top-down lithography to fabricate GNRs…

• Ribbons down to ~ **10 nm width**

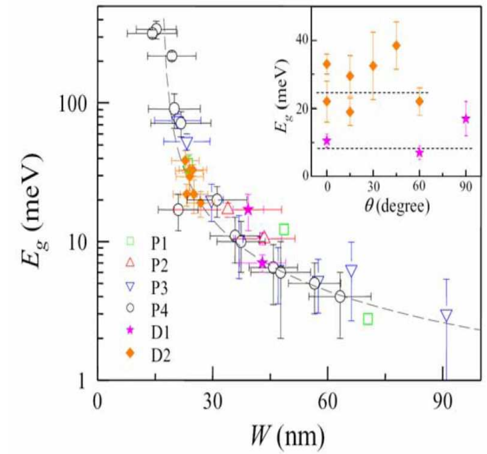


E. Dujardin (CEMES, France)

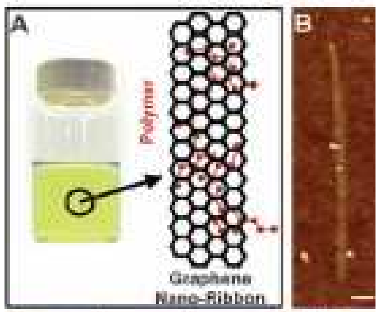


Ph. Avouris *et al*. (IBM, USA)

P. Kim *et al* (Columbia Univ. USA)



To compete with ultimate MOSFETs, clean GNR-FET with ~ 3nm are necessary !!!



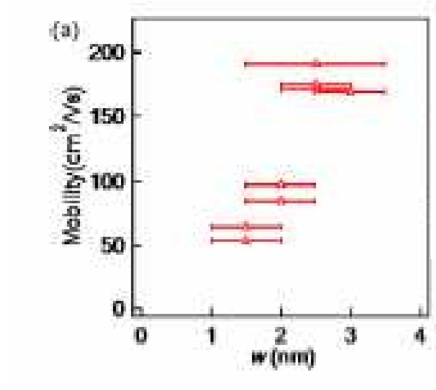
W ≈ 2 nm !

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

X. Wang et al., Phys. Rev. Lett. 100, 206803 (2008)

Strong Mobility decay !!!

same problem for massive integration as for nanotubes…

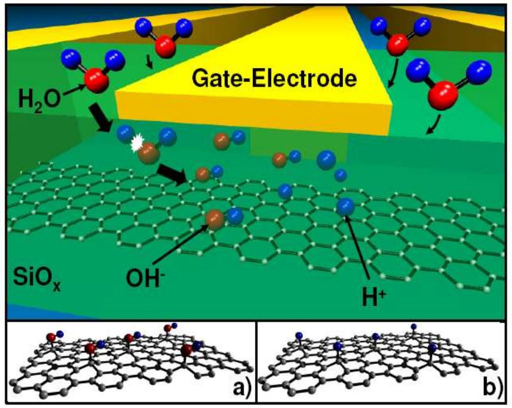


« Holy Grail »

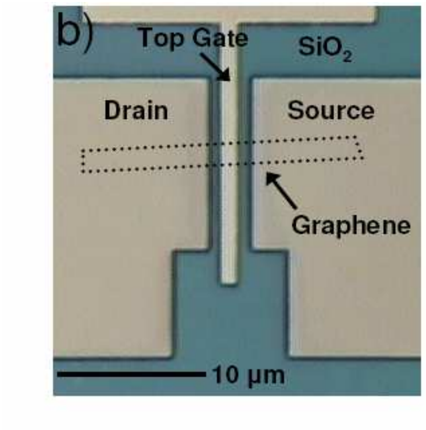
2D Graphene and Graphene ribbons $W \geq 10$ nm

Create or enlarge energy/conduction band gaps

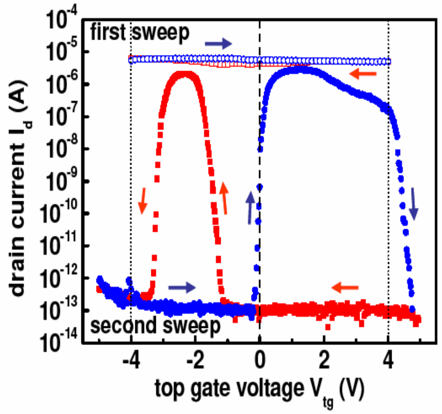
Chemically-induced device functionalities?

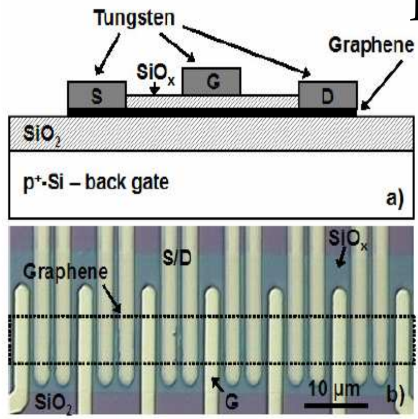


T. Echtermeyer, M.C. Lemme, M. Baus, B.N. Szafranek, A.K. Geim, H. Kurz,
Electron Device Letters, IEEE 29, 952 (2008)

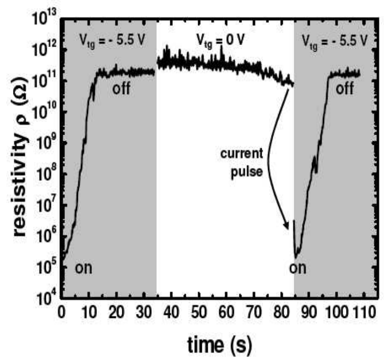


A graphene-based electrochemical switch





Non-volatile switching in graphene FED



Chemical Doping of 2D graphene

J.H. Chen et al, **Nature Physics 4, 377 (2008)**

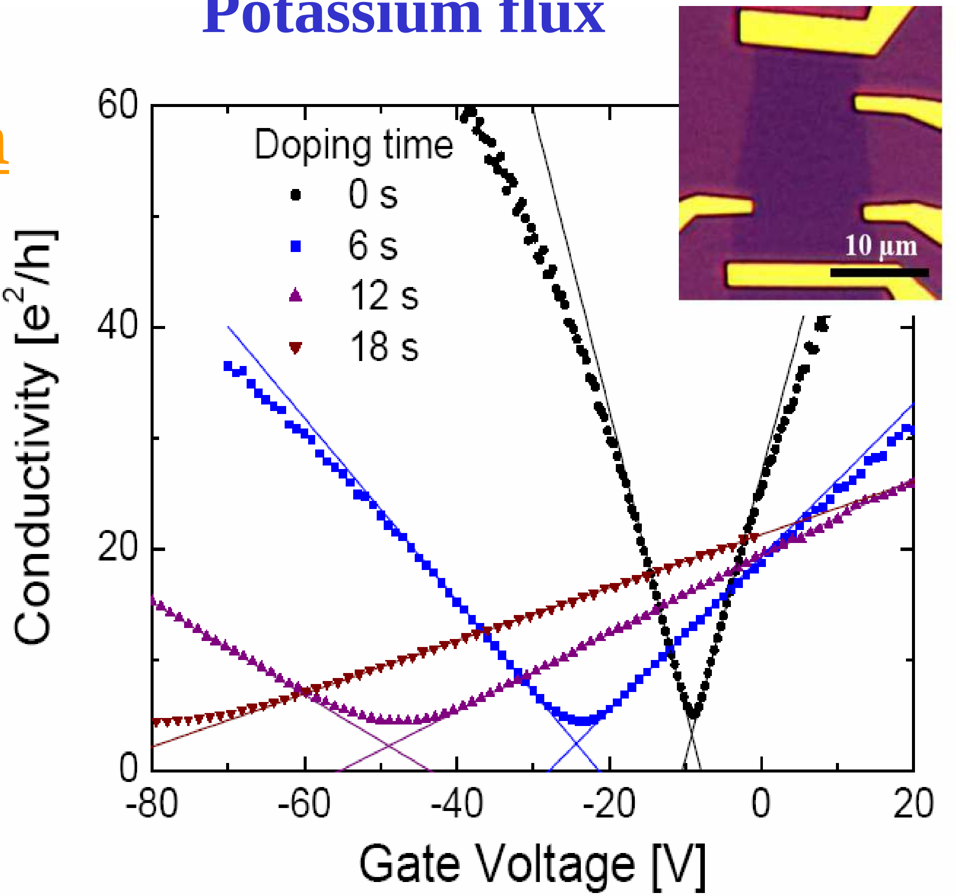
Physisorption of Potassium

*) *Shift of Dirac point with doping density*

**) *Conductivity decay resulting from impurity-induced backscattering*

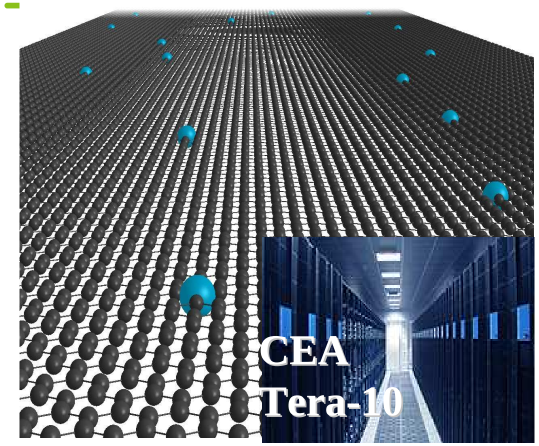
$$\sigma \sim 4 - 7e^2/h$$

Potassium flux

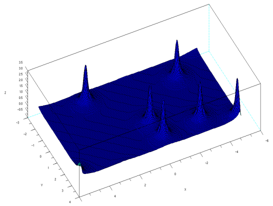


Boron & Nitrogen doped 2D graphene

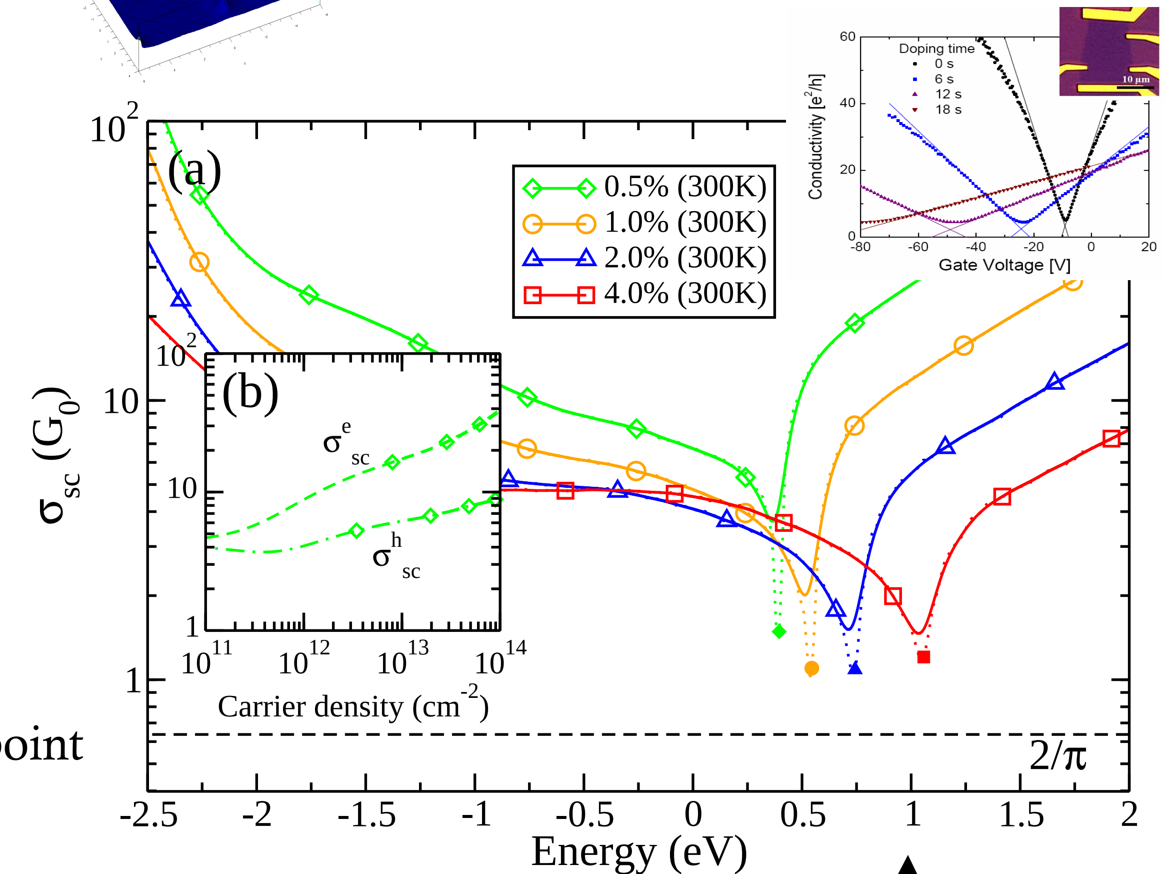
siesta A linear-scaling density-functional method



$0.5\mu m^2$



Ab initio calculation of the impurity scattering potential



Mobility very large close to Dirac point

$$\sim 10.000 - 10^6 \mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$$

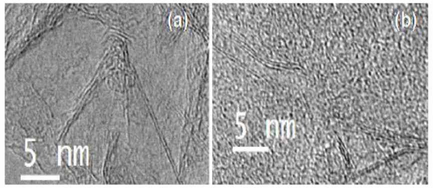
Electron-hole assymetry remains weak (factor 2-3)

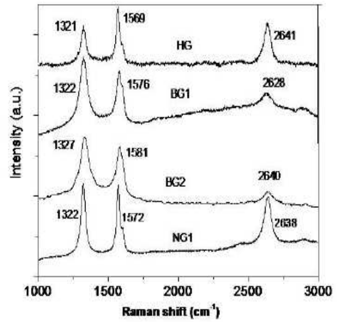
Shift of the « Dirac point » upon doping
(electrostatic effects)

A. Lherbier, X. Blase, F. Triozon, YM. Niquet, SR, Phys. Rev. Lett. 101, 036808 (2008)

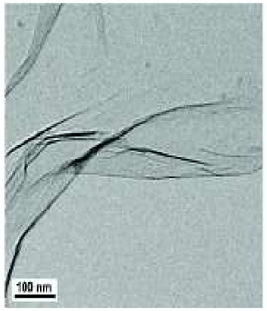
B&N-doped graphene just fabricated !

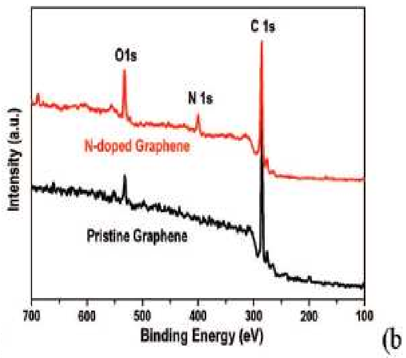
By Arc-discharge technique
(graphitic electrodes, H_2+B_2H_6, H_2+NH_3,..)
LS. Panchakarla et al. ***arXiv***



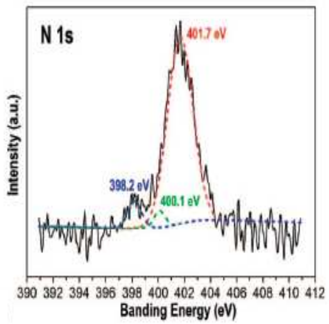


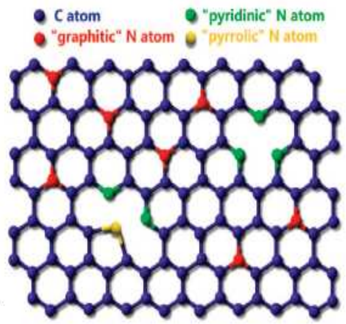
By CVD technique
(25nm thick Cu film-800°C, CH_4, NH_3)
D. Wei et al. ***Nano Letters*** *(in press)*



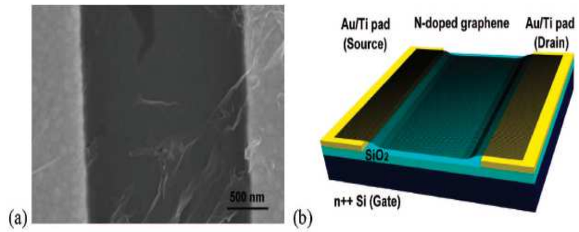


XPS spectra





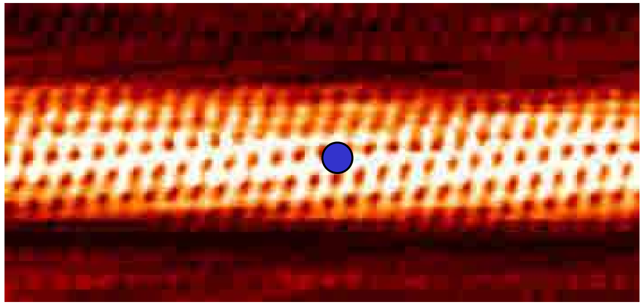
N-doped graphene-FET



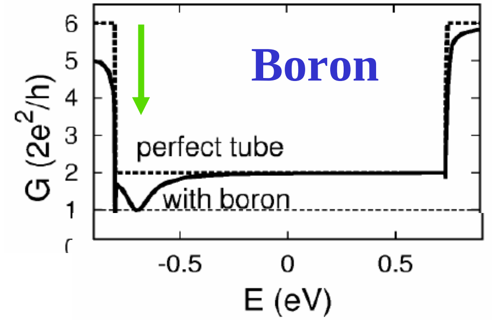
→ 4 order of magnitude gained on Ion/Ioff
(nature of N-type defects-~ 10% N!…)

Transport in Chemically-doped CNTS and GNRS

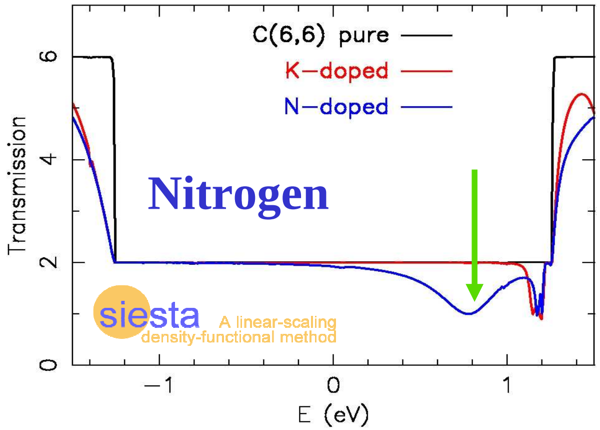
Single-impurity case

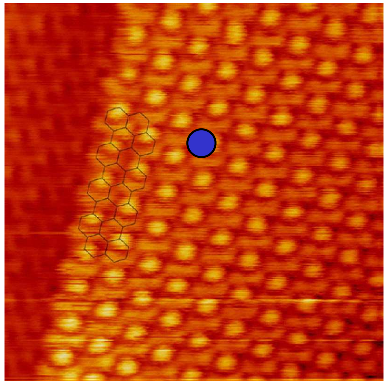


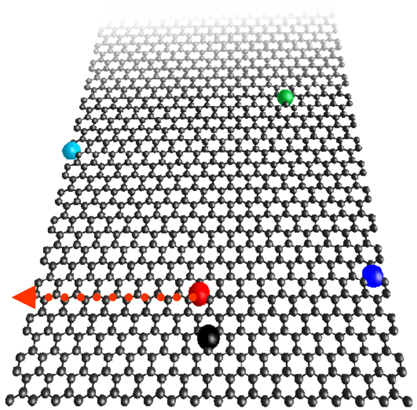
Choi *et al.* PRL **84**, 2917 (2001)

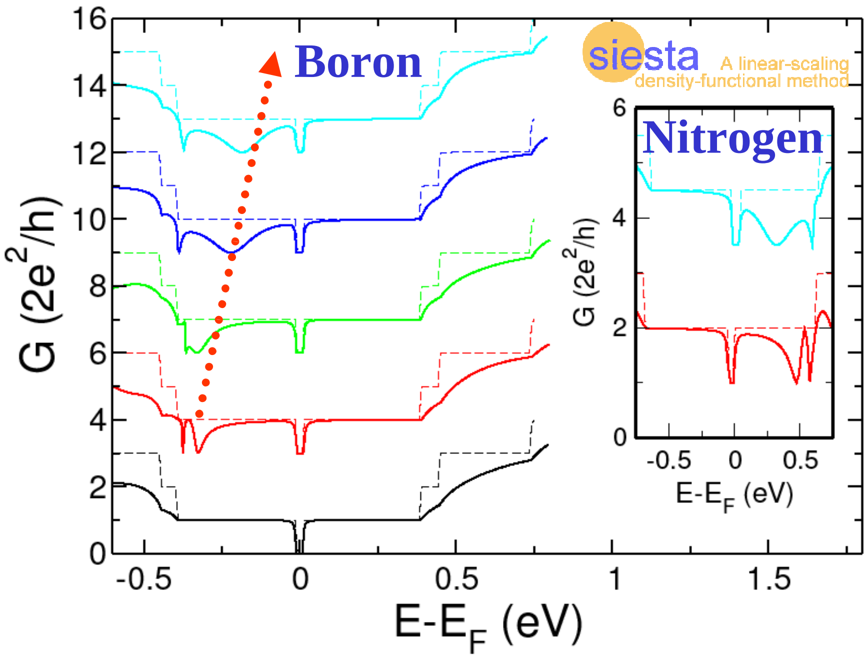


Enhanced backscattering





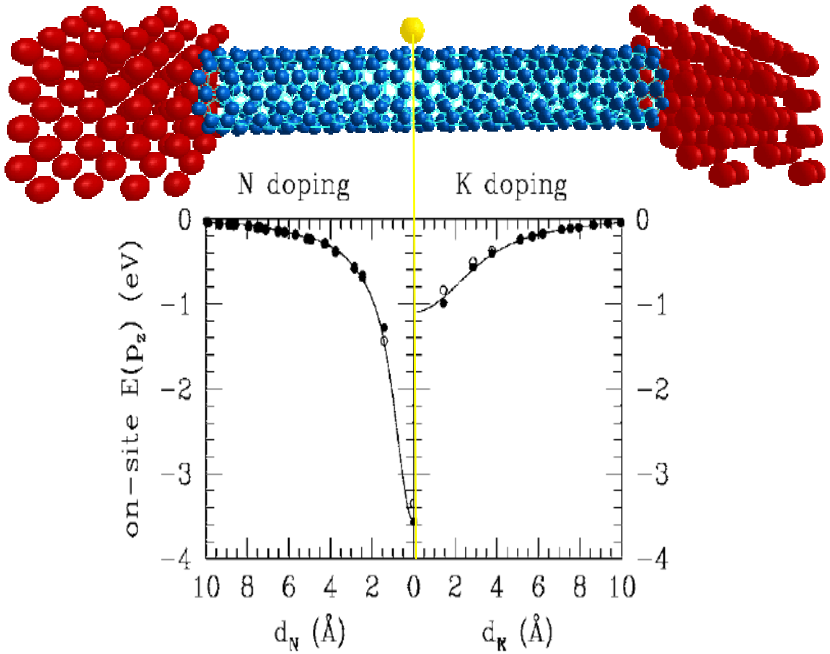




Floating up of quasibound states energy

Scaling study of quantum conductance

siesta A linear-scaling density-functional method



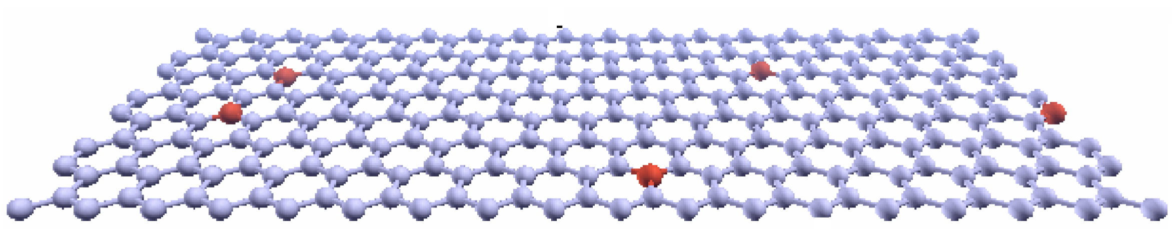
Effective Tight-Binding model

$$-\tilde{\gamma}_0 \sum_{\langle i,j \rangle} \hat{c}_i^\dagger \hat{c}_j + \text{hc} + \sum_i \tilde{V}_{\alpha i} \hat{c}_i^\dagger \hat{c}_i$$

Landauer-Büttiker formalism
(Green's functions & decimation techniques)

$$\mathcal{G}(\epsilon) = \mathcal{G}_0 T(\epsilon)$$

$$T(\epsilon) = \text{Tr}\{\hat{t}_{LR}(\epsilon)\hat{t}^\dagger_{LR}(\epsilon)\}$$

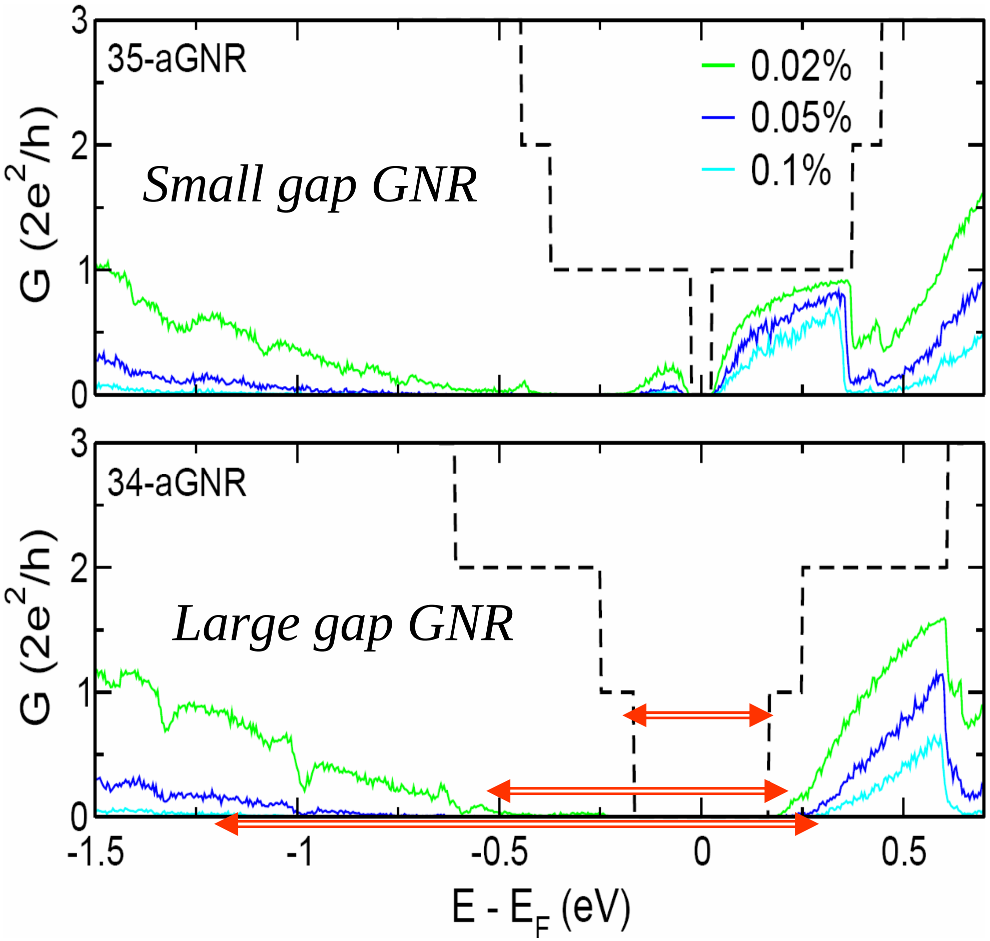


Chemically disordered graphene Nanoribbons

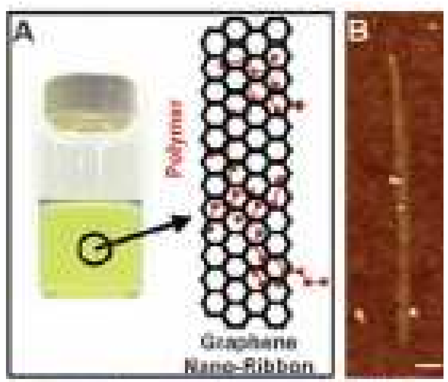
Random distribution of impurities (varying density),
- **Length up to micronmeter,**
- **Width several tens of nanometers**

Quantum Transport in Chemically doped GNRs

Boron-doped GNRs



5nm width



Huge Electron-Hole Transport asymmetry

Mobility Gaps !

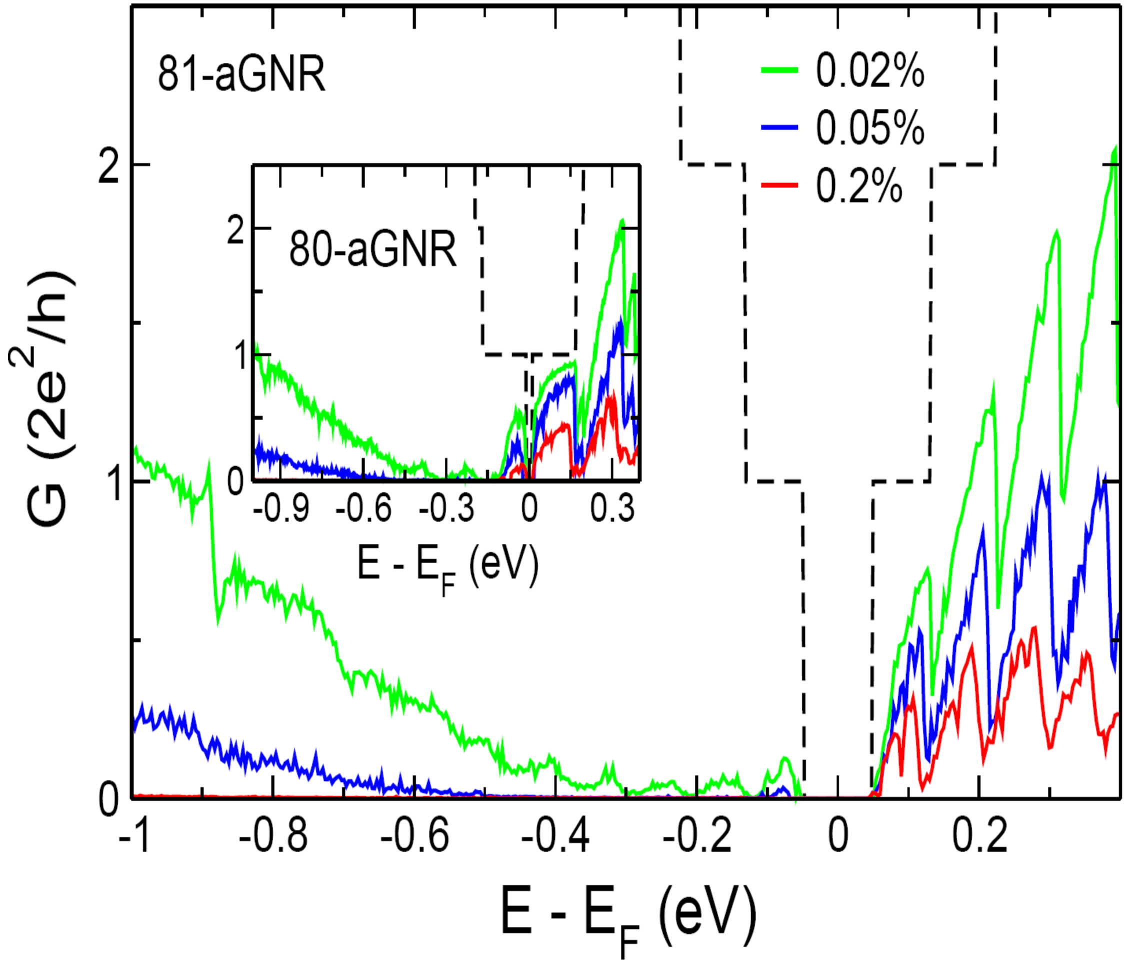
$\sim$1eV

Doping should allow upscaling GNRs-FET (Ion/Ioff) performances

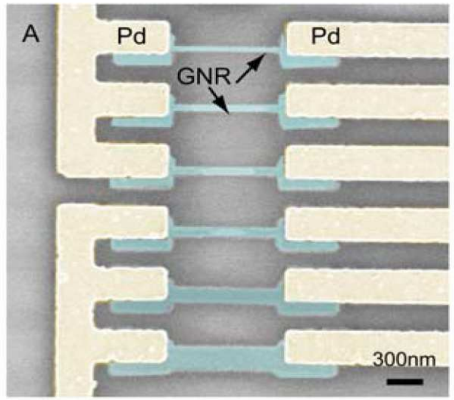
However are those properties robust for large ribbon width ?

Engineering high-performances GNR-FET

Robustness upon width upscaling



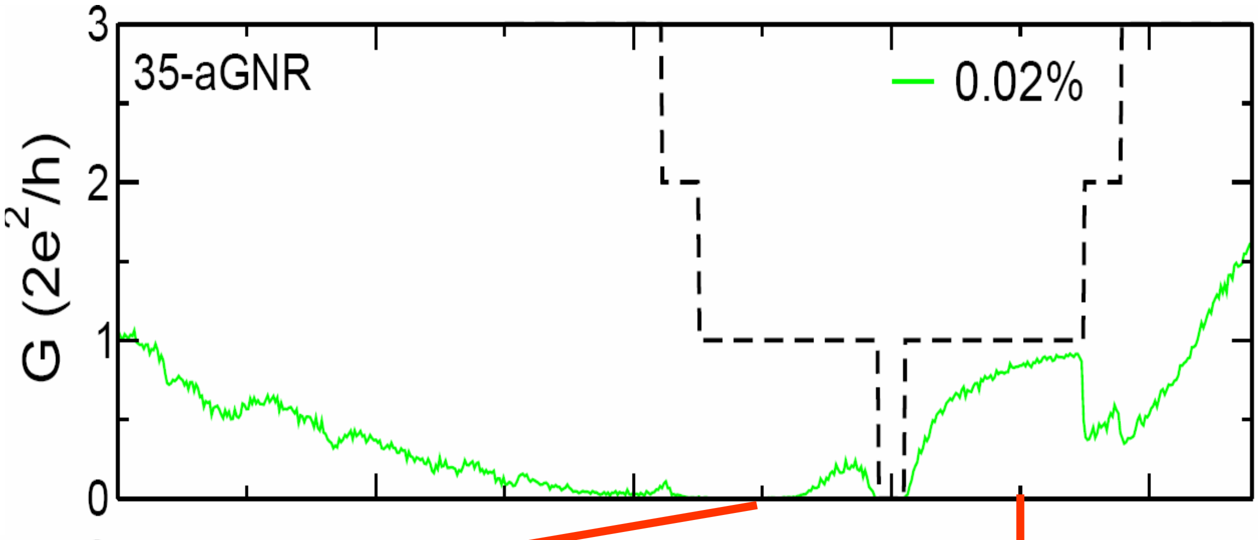
10 nm width

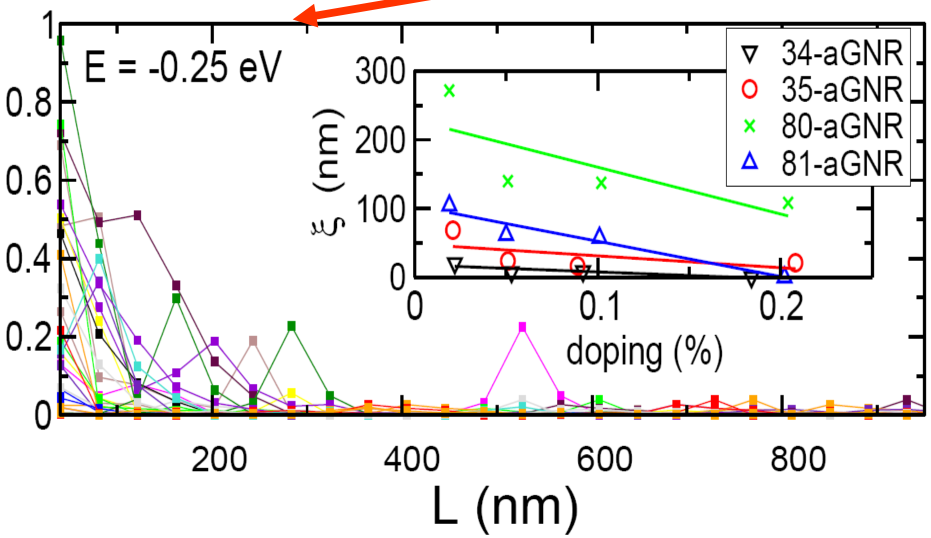


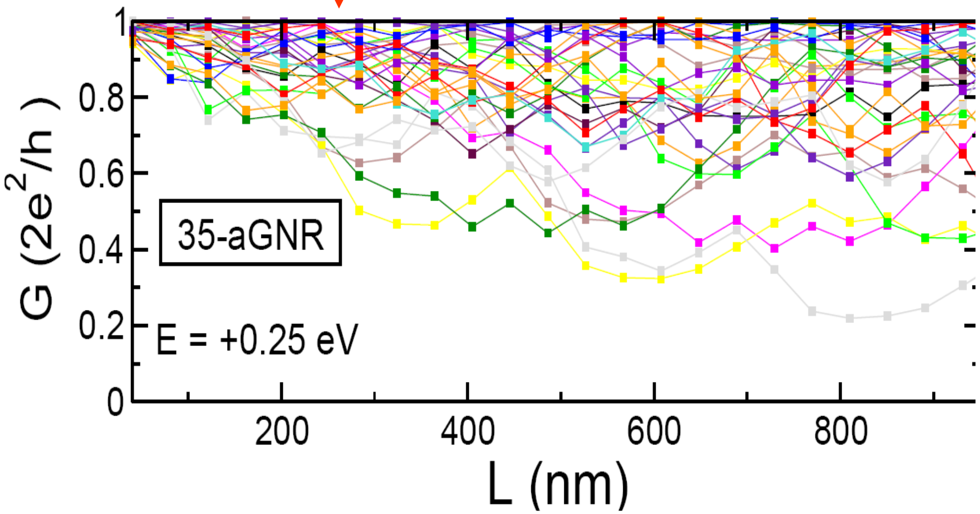
Within the reach of Lithography!

B. Biel, F. Triozon, X. Blase, SR, **Nano Letters 9, 2725 (2009)**

Origin of Mobility gaps







Strong localization regime

Quasiballistic regime

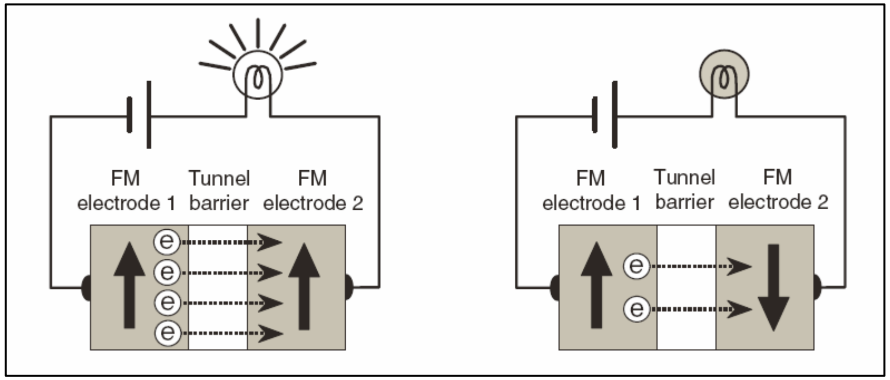
Carbon based Spintronics

*The new **E**ldorado ?*

Carbon-based coherent spintronics

- Spintronics is a branch of electronics based only on spin-related properties
- Information is stored, transmitted and read via electrical carrier's spin orientation

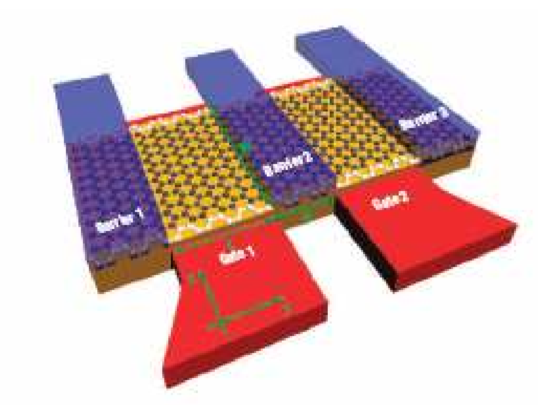
  (hence spin injection, coherent spin transport and spin collection)
- It requires an artificial manipulation of the spins orientation



$$MR = \frac{R_{AP} - R_P}{R_P}$$

M. Julliere, Phys. Lett. A 54, 225 (1975)

Why Carbon ?



Spin relaxation in carbon nanotubes :: $\tau_{sf} \approx$ 1-50 ns

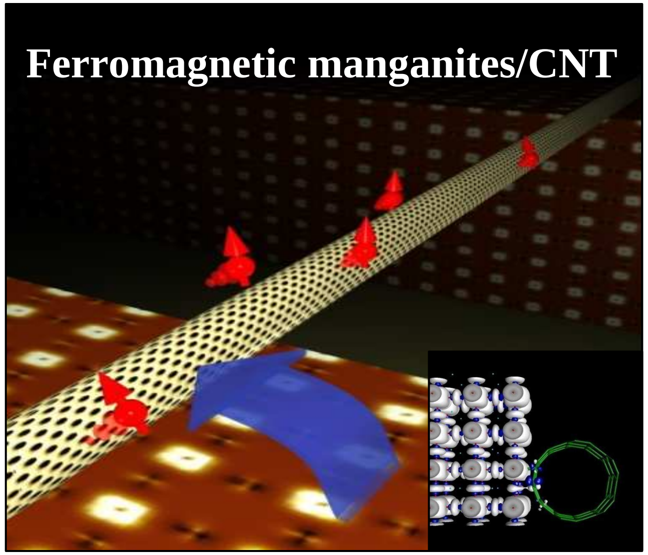
- Small spin-orbit coupling
- Small hyperfine interaction

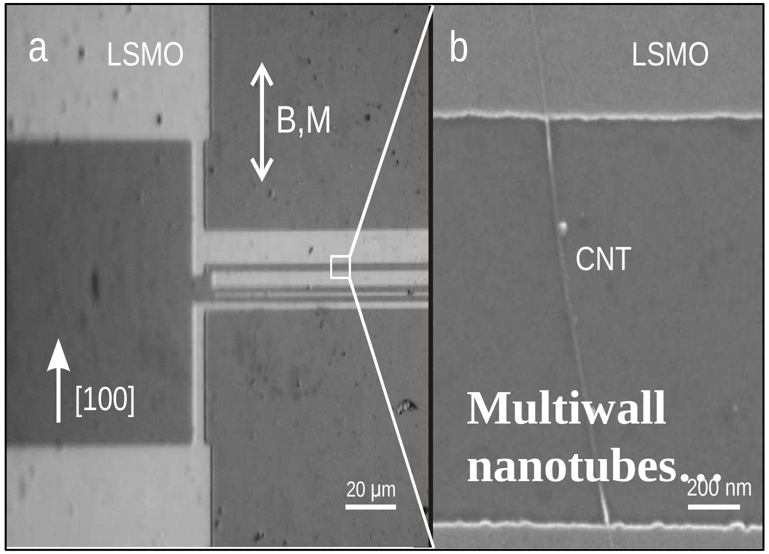
High Fermi velocity $v_f \approx 1\times10^7$ ms^{-1}

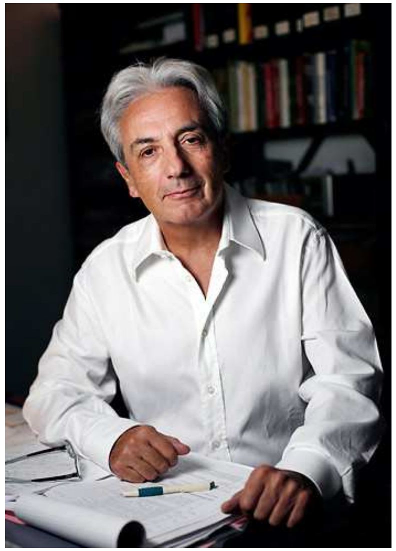
Magnetoresistance controlled by the relation between dwell and spin lifetime

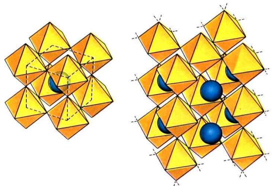
A. Fert et al., IEEE Electron Devices 54, 921 (2007)

Transformation of spin information into electrical signals







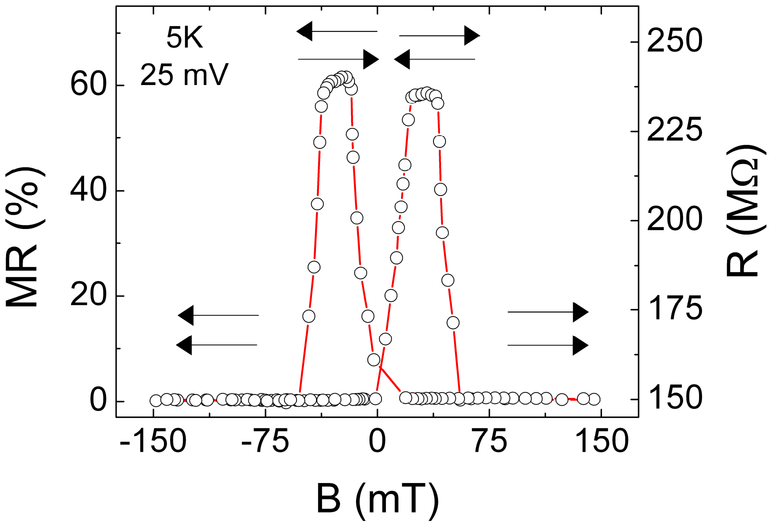


$La_{2/3}Sr_{1/3}MnO_3$

(spin polarization ~ 90 %)

Hueso, Mathur, Fert et al.

Nature 445, 410 (2007)

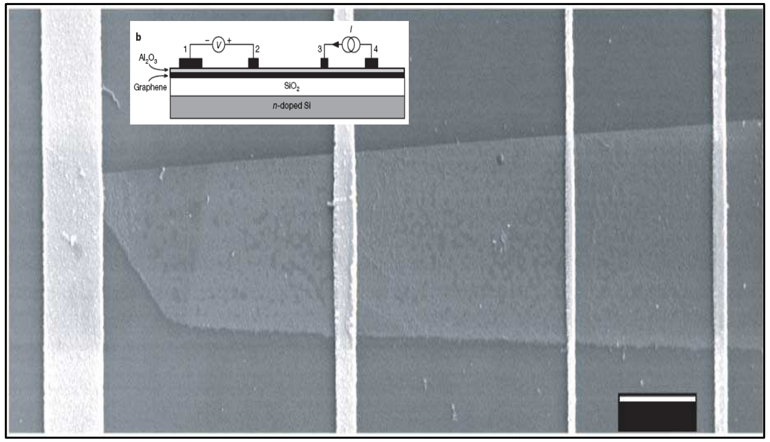


$$\tau_{sf} = 30ns \qquad \ell_{sf} = 50\mu m$$

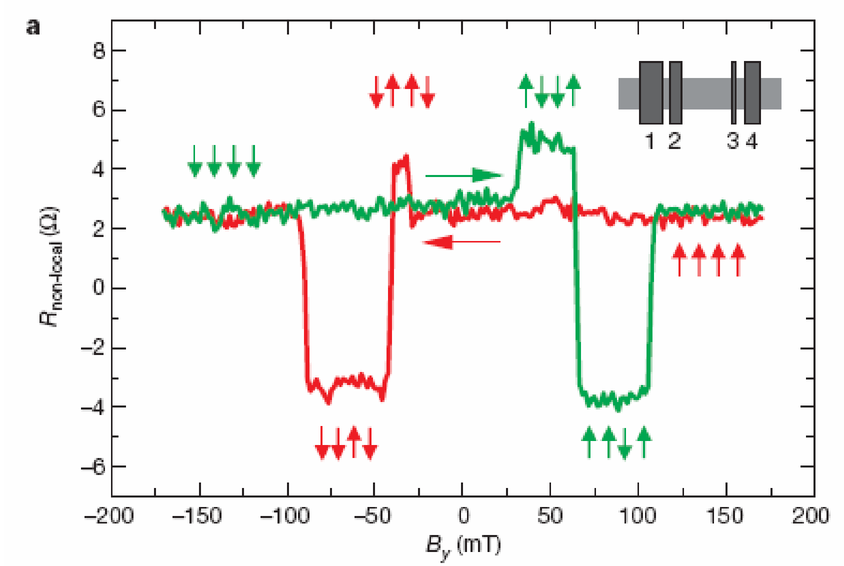
Interface resistance large enough to overcome "conductivity mismatch" but not too large to induce large spin decoherence

Graphene Spintronics : promising first results

(including epitaxial graphene & multilayer graphene)



$$R_{\text{non-local}} = \frac{V_+ - V_-}{I}$$



$$R_{\text{non-local}} \sim \lambda_{sf} e^{-L/\lambda_{sf}}$$

Room Temperature $\lambda_{sf} \sim 2\mu m$

Graphene

N. Tombros *et al.*, Nature 448, 571 (2007)

S. Cho *et al.*, Appl. Phys. Lett. 91, 123105 (2007)

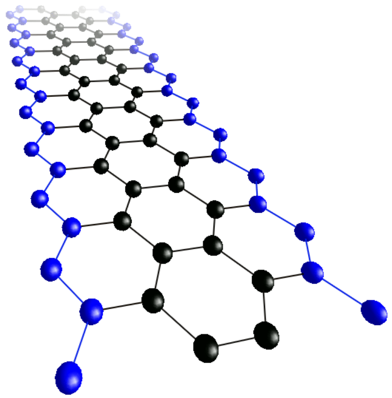
Multilayer graphene

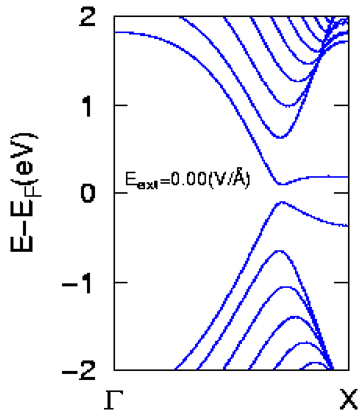
M. Nishioka *et al.*, Appl. Phys. Lett. 90, 252505 (2007)

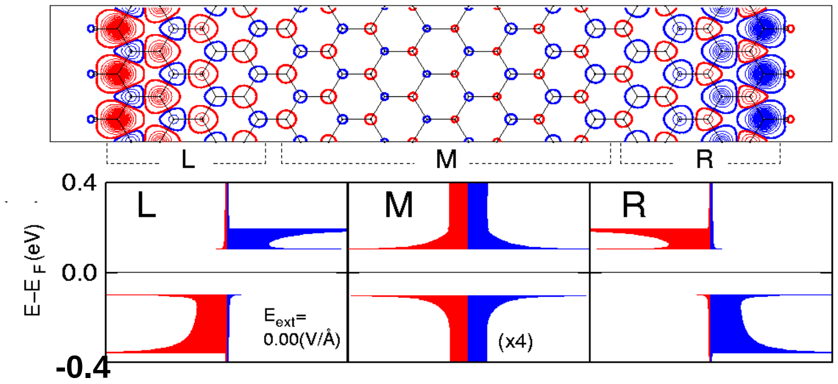
H. Goto *et al.*, Appl. Phys. Lett. 93, 212110 (2008)

A fully spin polarized intrinsic transport

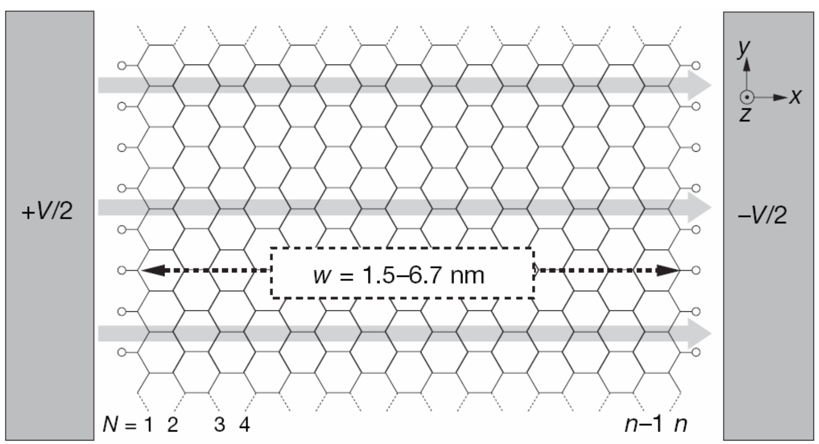
Zigzag GNRs are semiconductors with edge-states near E_F

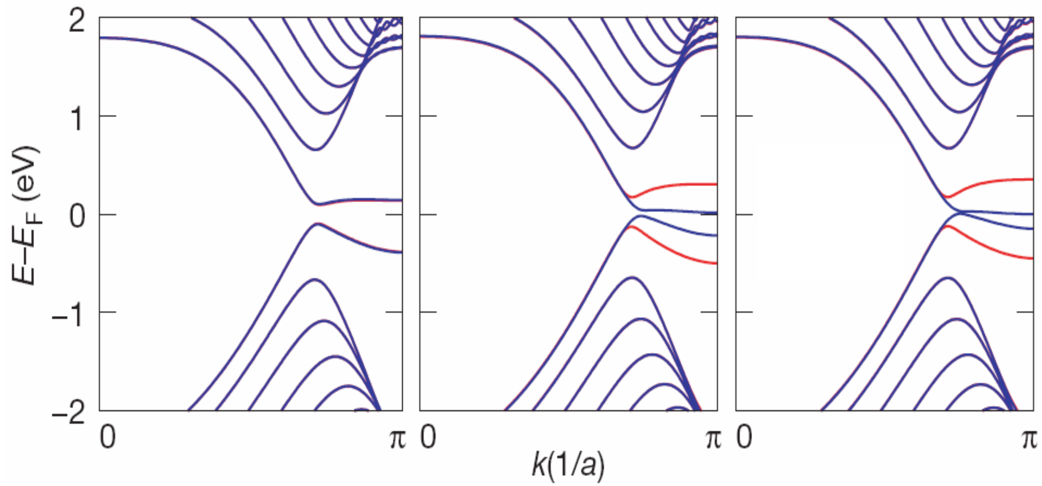






α-spin β-spin





Transverse electric fields in split-gate geometry

Y.-W. Son *et al*, Nature 2008

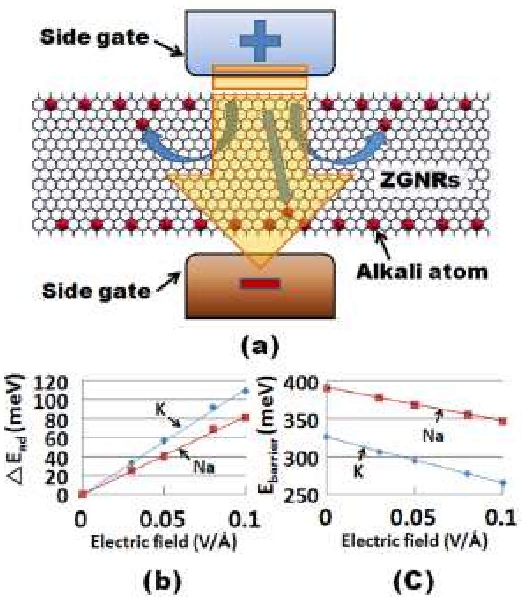
E_{ext}=0.0 V/Å E_{ext}=0.05 V/Å E_{ext}=0.10 V/Å

field induced half-metal

And more… Spin-dependent transport, Spin Qubits,…

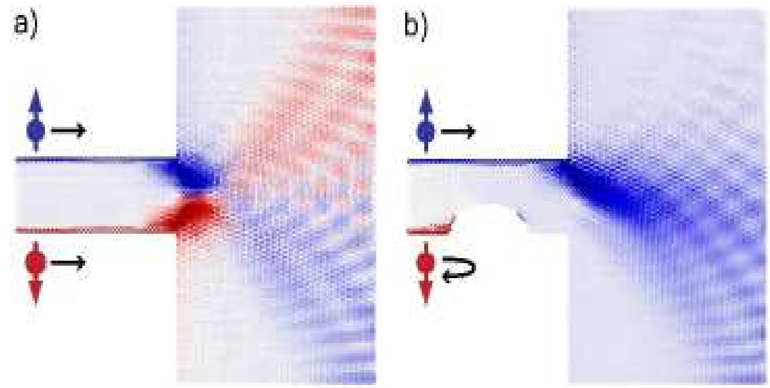
Spin valve based on GNR functionalization

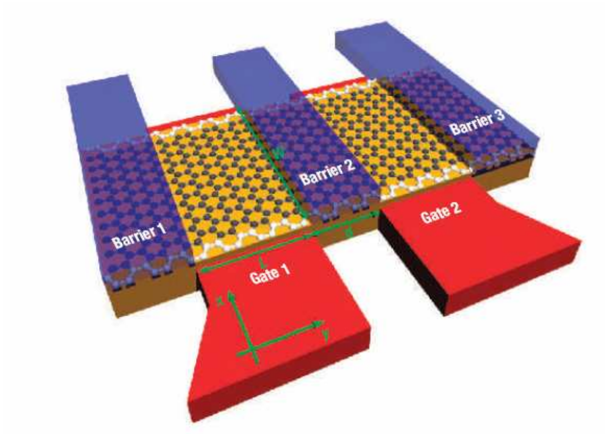
S.-M. Choi and S.-H. Jhi Phys. Rev. Lett. 101, 266105 (2008)



Spin injection in rough Graphene ribbons

M. Wimmer et al., Phys. Rev. Lett. 100, 177207 (2008)





ARTICLES

Spin qubits in graphene quantum dots

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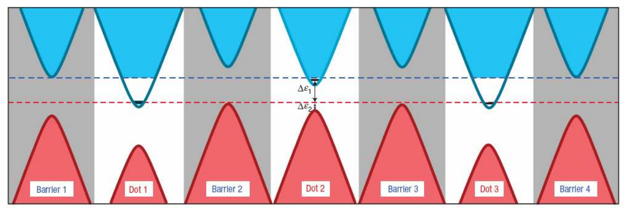
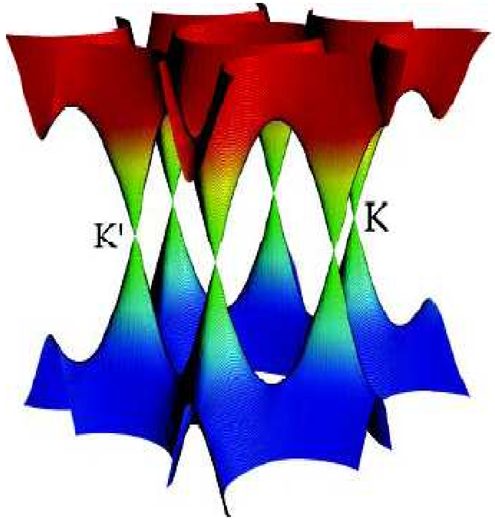
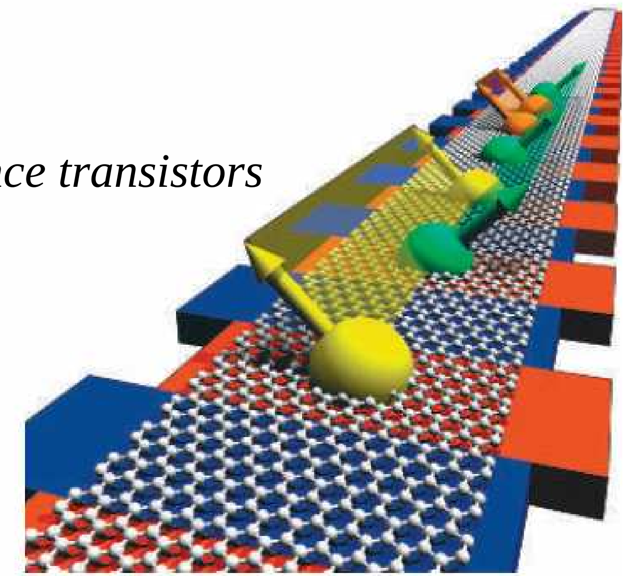


- **Introductory comments**
  - *Some salient facts and features*



- **Why Nanotubes and Graphene are so special ?**
  - *A story of sp*^{2}*, Symmetries and Pseudospin*
- **NANOTUBES inside**
  - *Device & Quantum Mechanics*
  - *Challenges for* ***I****nnovation*
- **GRAPHENE inside**
  - *From « infinite mobility » to* ***H****igh* ***P****erformance transistors*
- **Carbon-based SPINTRONICS**
  - *The new* ***E****ldorado ?*



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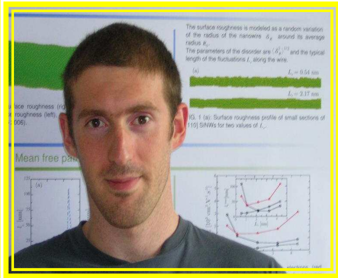
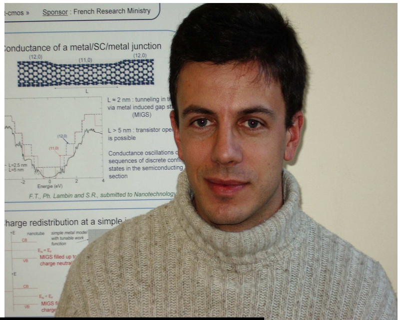




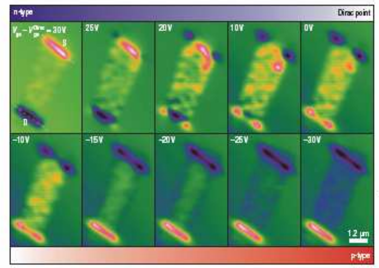


Metal deposition & chemical doping of graphene

E. J.H. Lee, K. Balasubramanian, R. Weitz, M. Burghard, K. Kern, **Nature Nanotechnology** 3, 486 (2008)

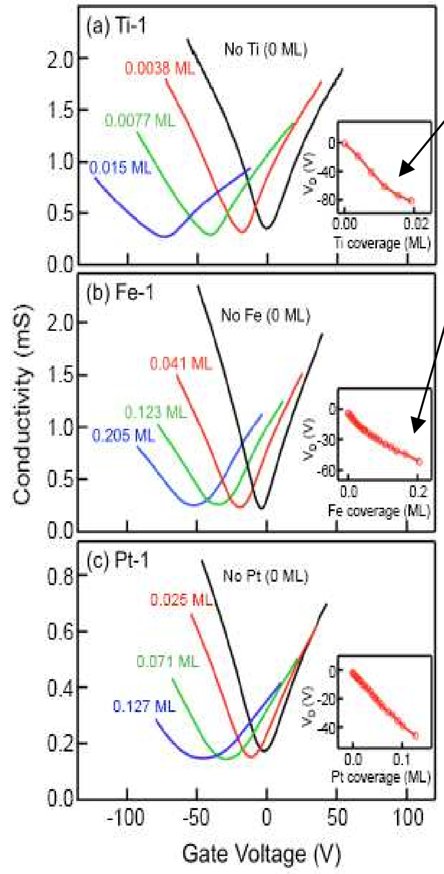
Graphene/Ti n-doping of graphene Graphene/Au p-doping

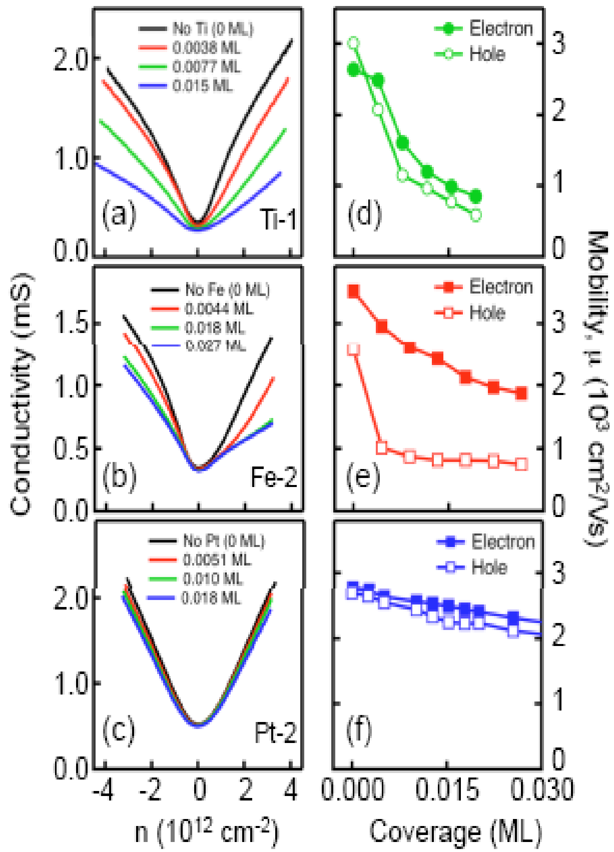
transfered charge density ~ 6.10^{12} charges cm^{-2}.



Electronic doping and scattering by Transition metal on Graphene
(K. Pi et al. unpublished)

Shift of Dirac point





Electron/hole transport asymmetry ~ *factor 2-3*

Reveals different type of metal/graphene interaction (charge transfer)

New types of electro-mechanical memories…

NANO LETTERS

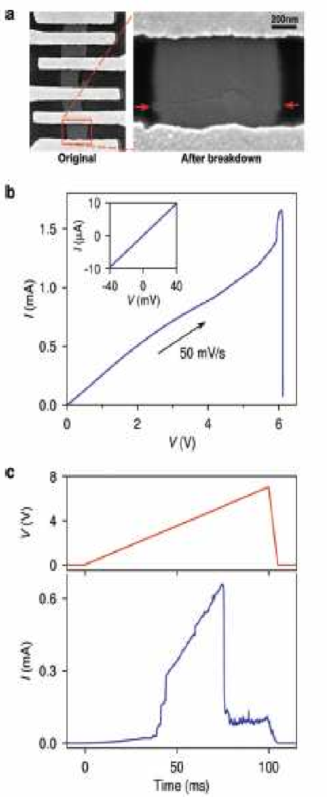
Subscriber access provided by CEA

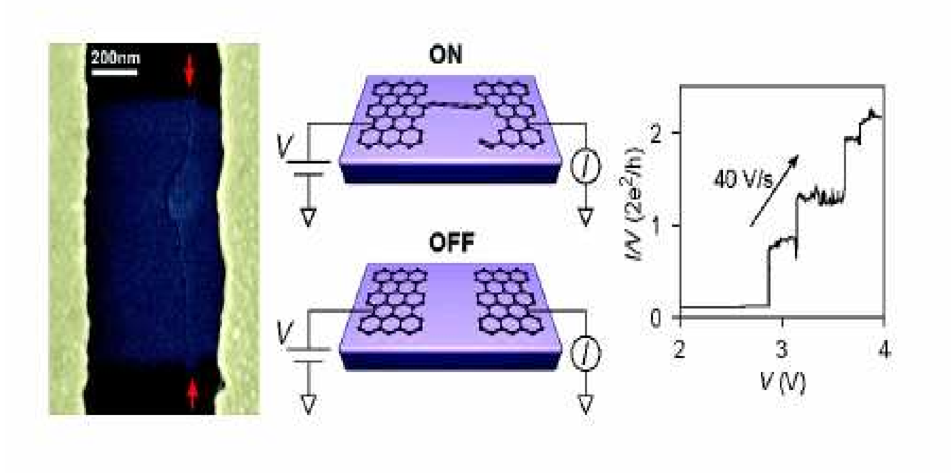
Letter

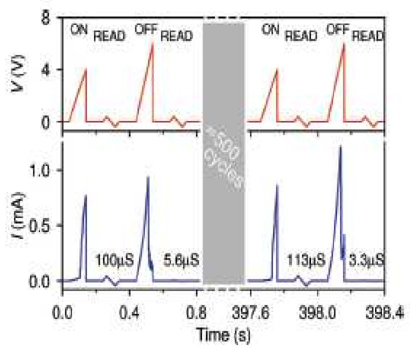
Graphene-Based Atomic-Scale Switches

Brian Standley, Wenzhong Bao, Hang Zhang, Jehoshua Bruck, Chun Ning Lau, and Marc Bockrath

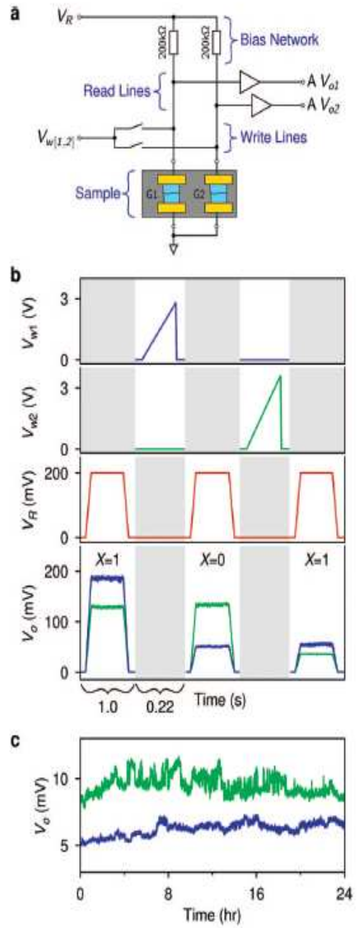
Nano Lett., 2008, 8 (10), 3345-3349 • DOI: 10.1021/nl801774a • Publication Date (Web): 26 August 2008

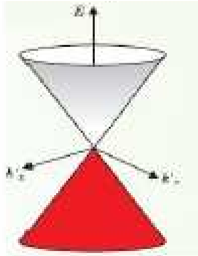


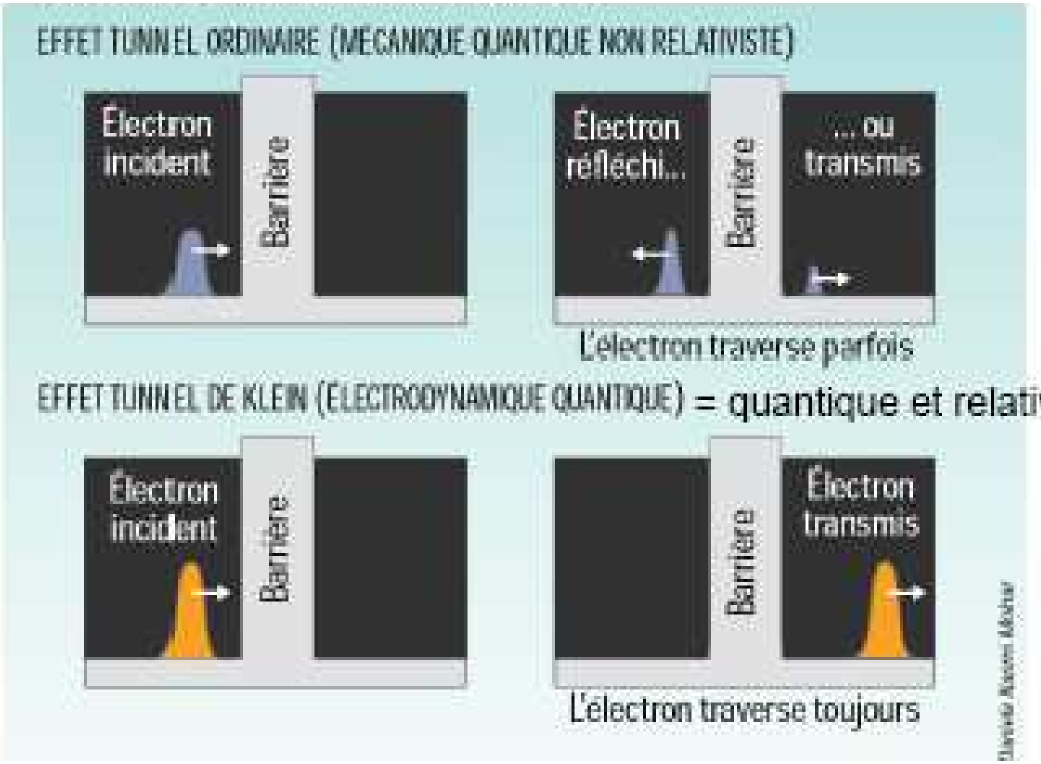




The device properties of these junctions can be exploited to make logic gates and store information. However, one potential obstacle is the relatively modest ON/OFF ratio, ~50−100, while 10^5-10^6 is typically achieved in CMOS devices. Here we demonstrate a novel concept for a memory cell that we call rank coding.[27] A bit is stored not by the absolute value of the device conductance but by the comparison of the conductance of 2 or more devices in a cell. The information capacity for an N device cell is therefore $\log_2 N!$ bits. Note that for large N, the capacity even exceeds that of a conventional memory cell.







= quantique et relativiste

O. Klein

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