

Carbon Nanotubes / Self-Assembled Monolayers Hybrid Devices

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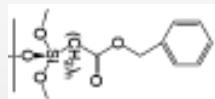
- Molecules electrical functionalities :

Insulators

Long-chain alkanes

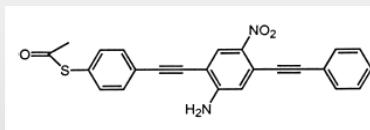
Boulas & al. *Phys. Rev. Lett.* **76**, 4797 (1996)

Diodes



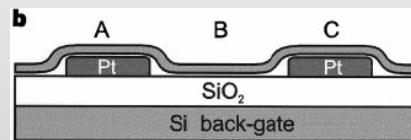
Lenfant & al. *Nano Lett.* **3**, 741 (2003)

Negative Differential Resistance



Chen & al. *Science* **286**, 1550 (1999)

Transistors



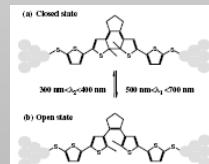
Tans & al. *Nature* **393**, 49 (1998)

Supramolecular switches



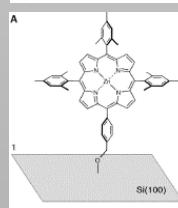
Bissell & al. *Nature* **369**, 133 (1994)

Optical switches



Owrutsky & al. *Chem. Phys. Lett.* **293**, 555 (1998)

Multi-valued memories



Liu & al. *Science* **120**, 3717 (2003)

- Connecting Molecules on a nano-scale : examples

N° of molecules

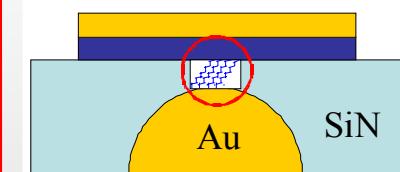
10^4

10^3

10^2

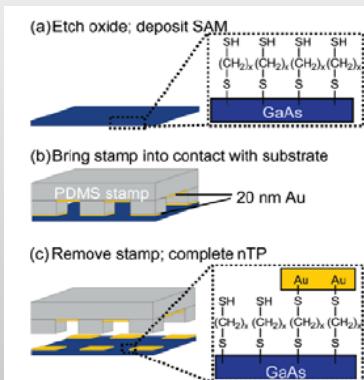
10^1

1



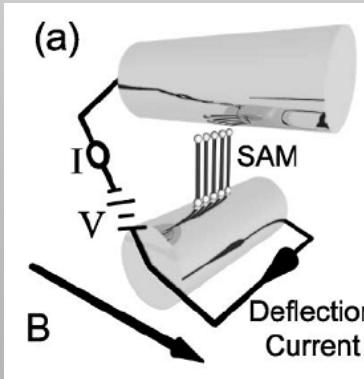
Nanopores

Zhou & al. *Appl. Phys. Lett.* **71**, 611 (1997)



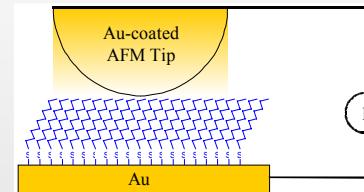
Nano-transfer printing

Loo & al. *JACS* **124**, 7654 (2002)

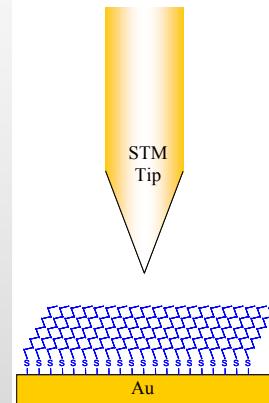


Crossed wires

Kushmerick & al. *Phys. Rev. Lett.* **89**, 086802 (2002)

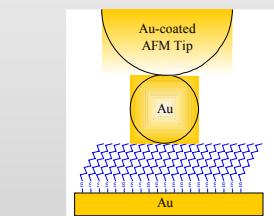


Conducting-probe AFM
Wold & al. *JACS* **123**, 5549 (2001)



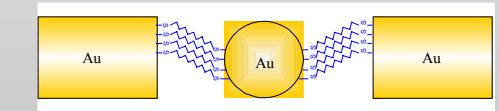
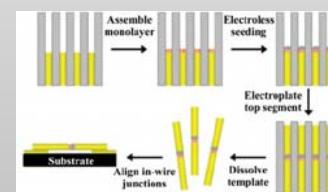
STM

Qian & al. *Langmuir* **19**, 6056 (2003)



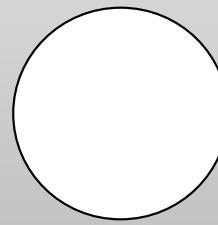
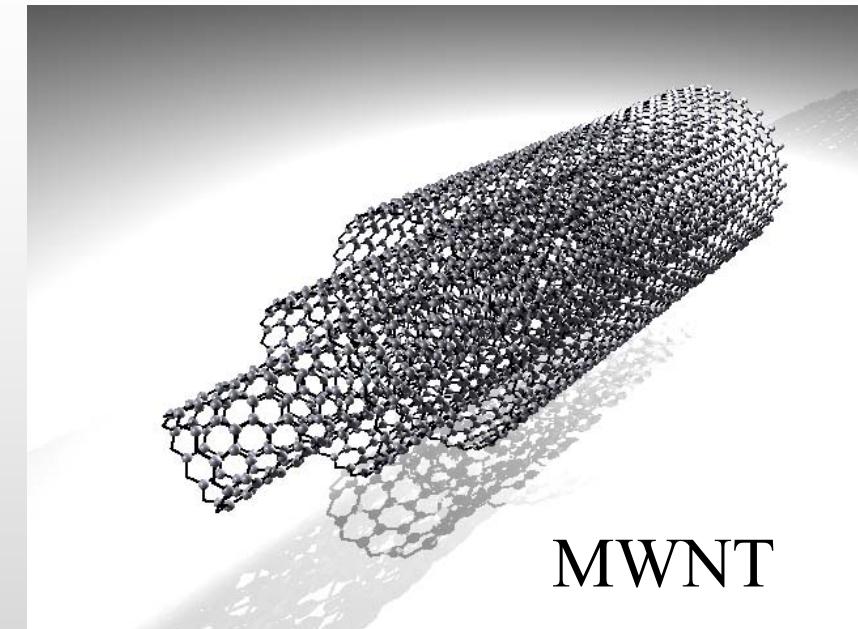
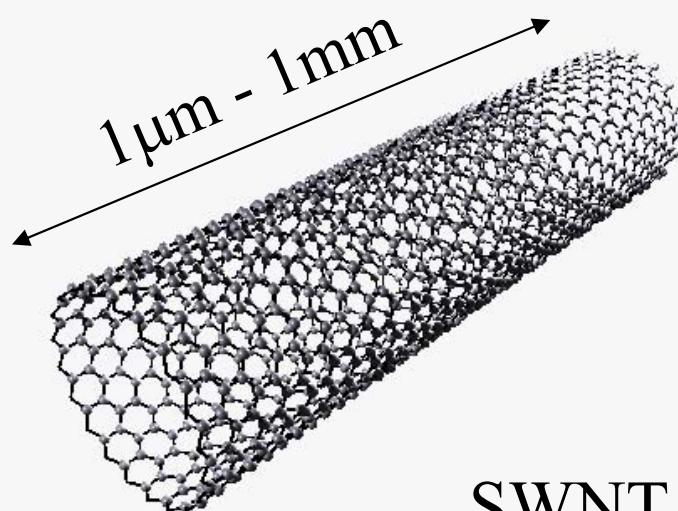
Nanowire

Cai & al. *J. Phys. Chem. B* **108**, 2827 (2004)

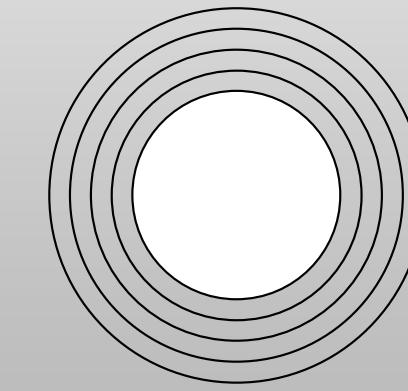


Nanoparticle bridge

Amlani & al. *Appl. Phys. Lett.* **80**, 2061 (2002)



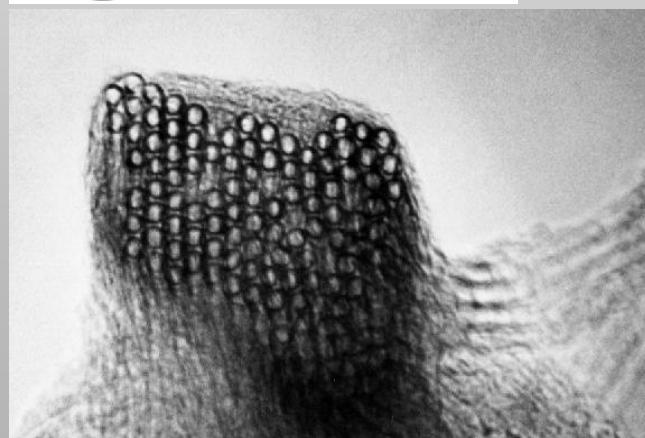
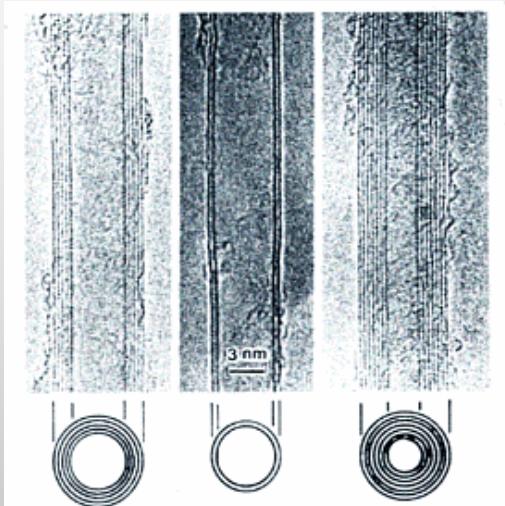
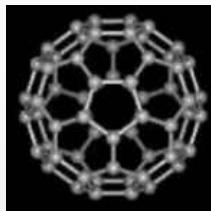
1-2 nm



2 - 50 nm
many concentric shells

- I – Introduction to Carbon Nanotubes
- II – Individual SWNTs as Electrodes for probing transport through SAMs
- III – An insulating SAM as ultra-thin gate dielectric for CNFET

- Some key dates



1985 : Kroto, Smalley, Curl (Rice Univ.),
Laser vaporization of graphite -> C₆₀

1991 : Iijima (NEC), Multiwalled Nanotubes

1993 : Iijima (NEC) / Bethune (IBM),
Singlewalled Nanotubes

1996 : Ebessen (NEC), conductivity measurement
of MWNTs

1996 : Smalley et al. (Rice Univ.), Well ordered
SWNTs ropes by laser ablation

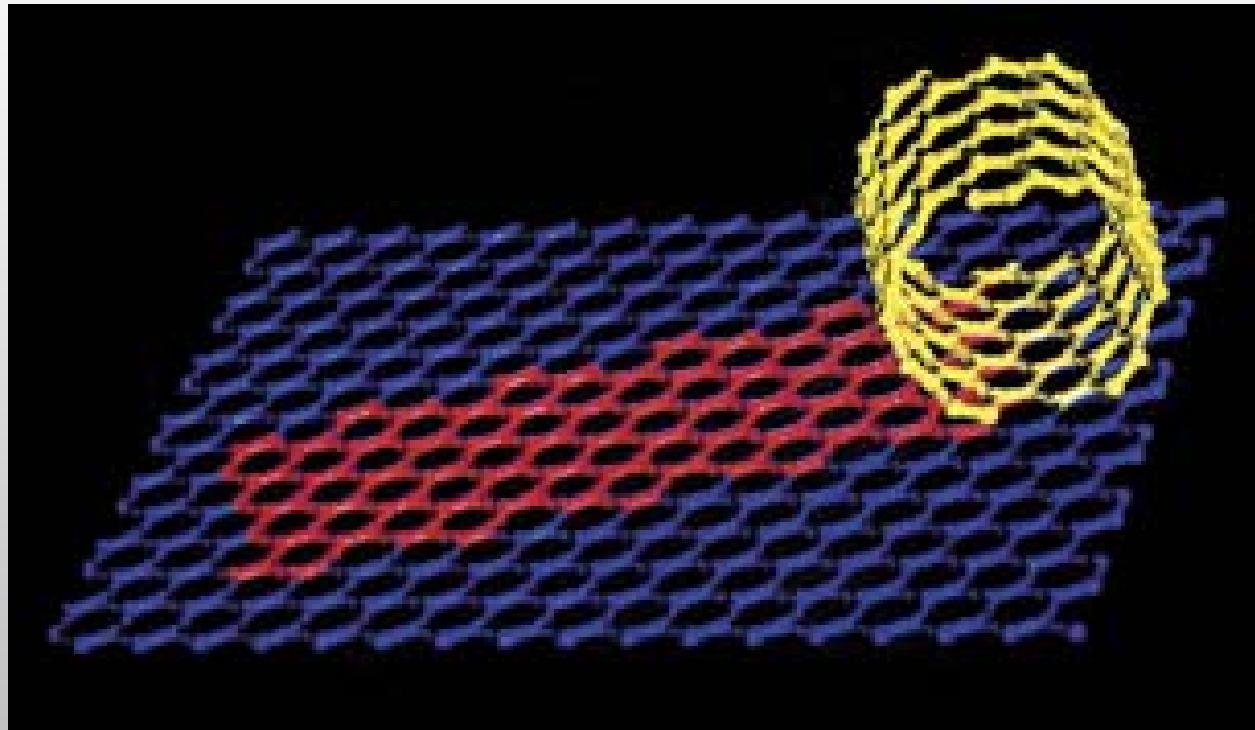
1996 : Dekker, SWNTs as quantum wires

1998 : Dekker (Delft Univ.) / Lieber (Harvard)
structure and elect. prop. by STM

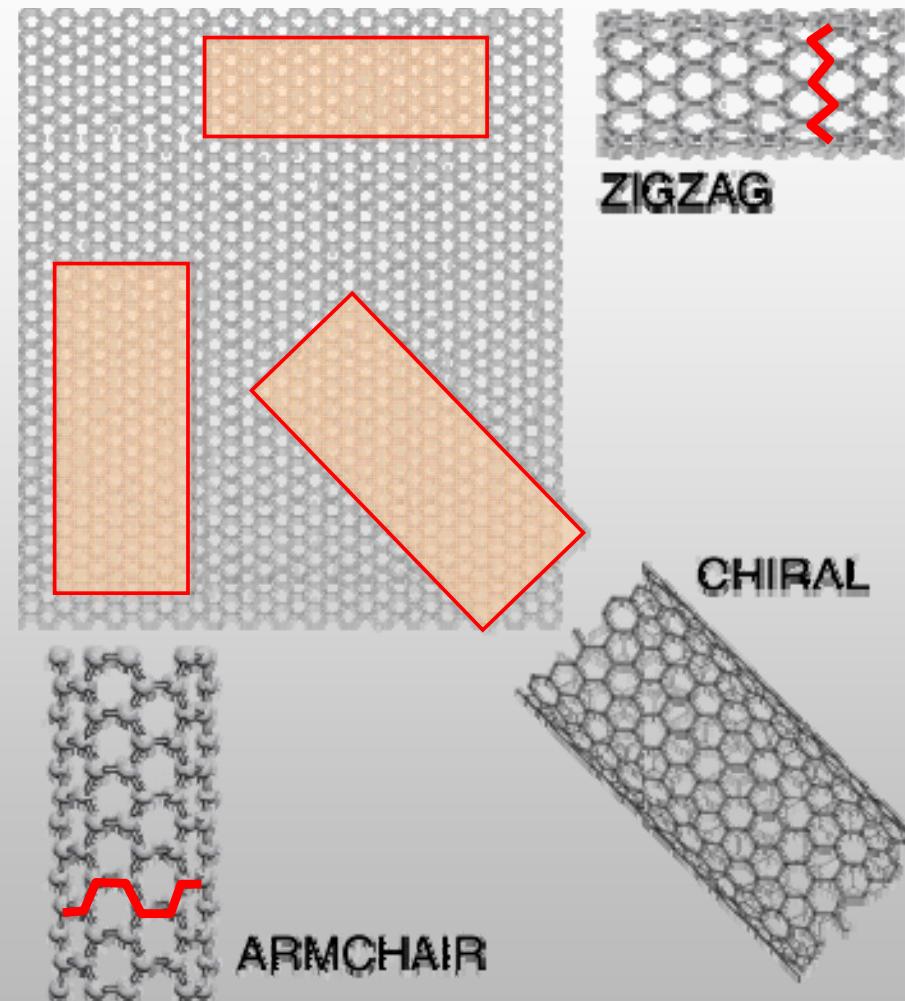
1998 : Dekker (Delft Univ.), Martel (IBM),
Nanotube FETs

- Structure

Rolling up a single sheet of graphene

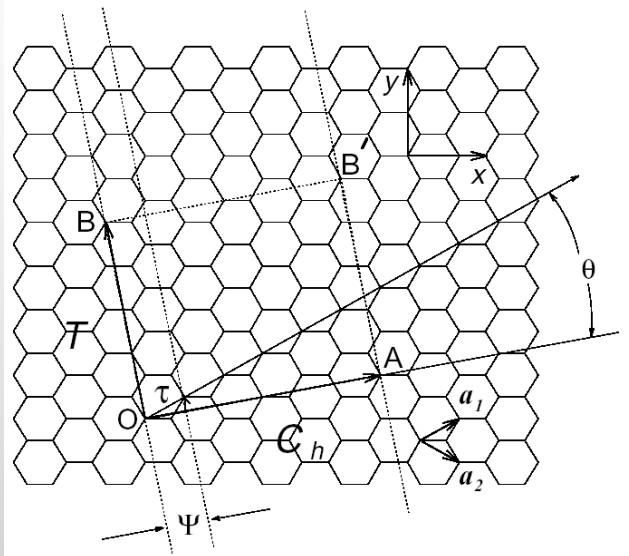


- Structure

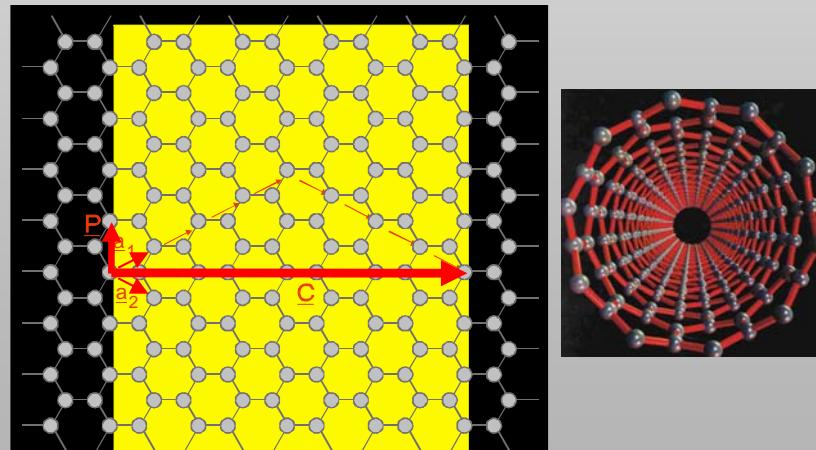


- Structure

How to differentiate the possible geometries : \vec{C}

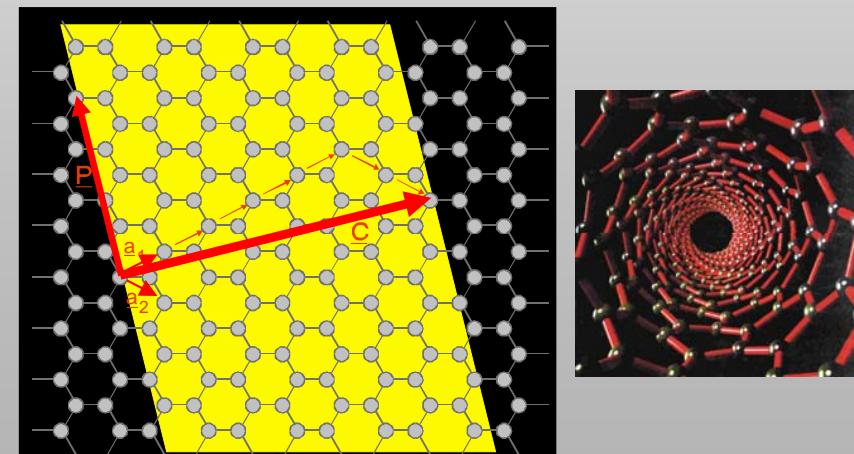


(4,4) Tube



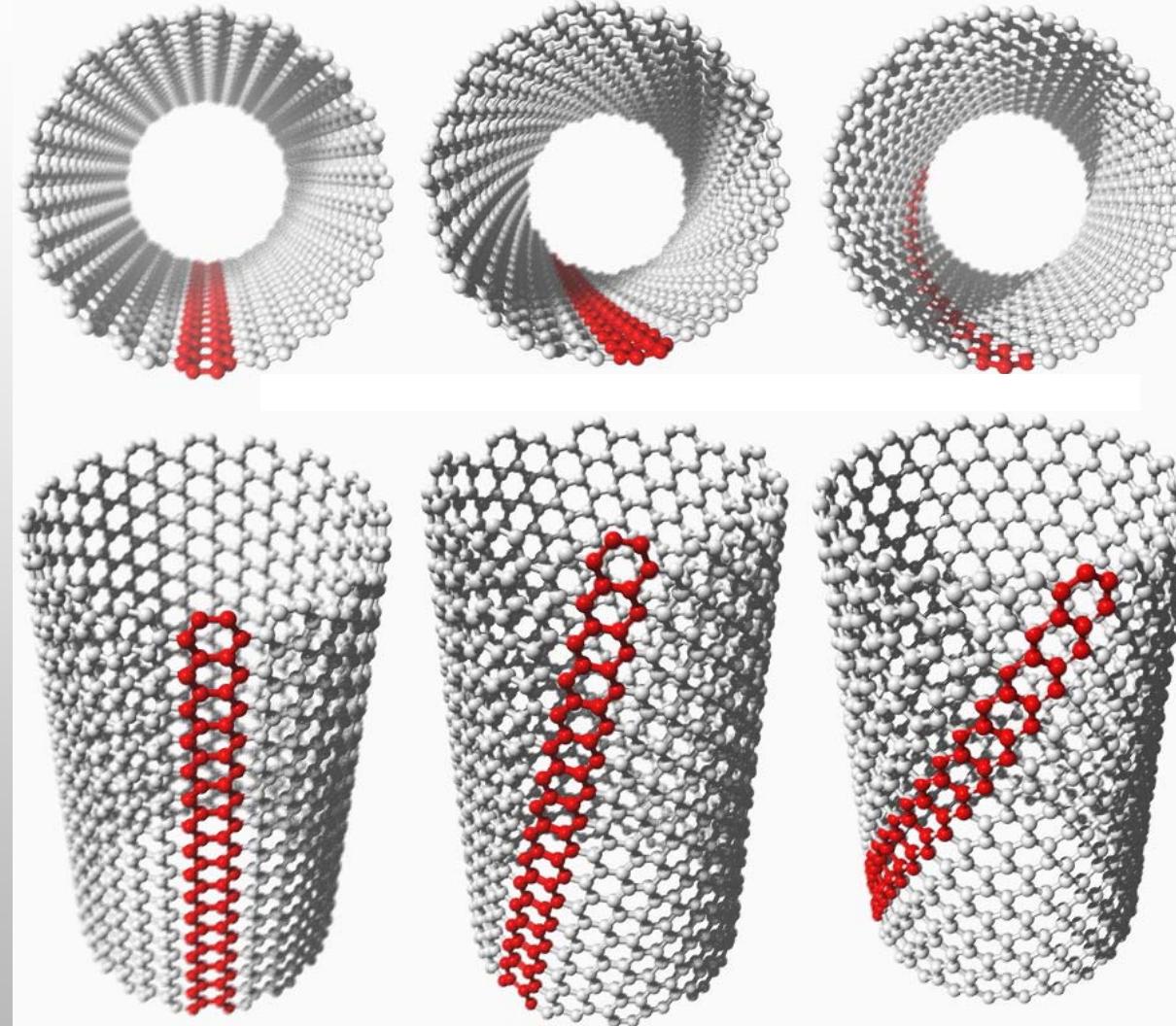
$$\mathbf{C} = n \mathbf{a}_1 + m \mathbf{a}_2$$

(5,2) Tube



- Structure

(n,m) - Examples



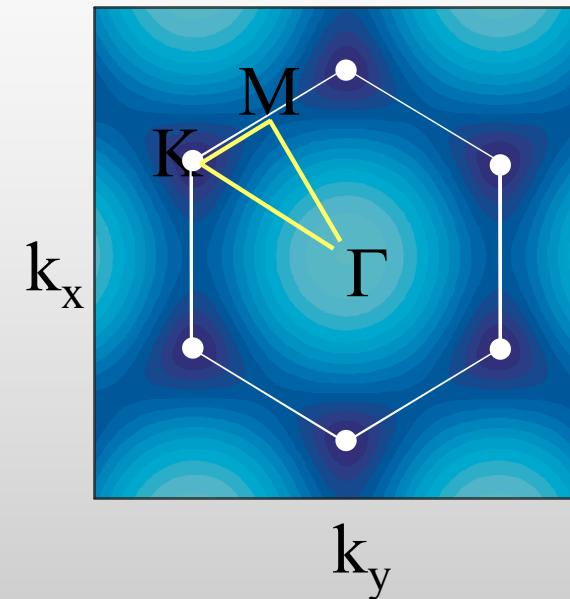
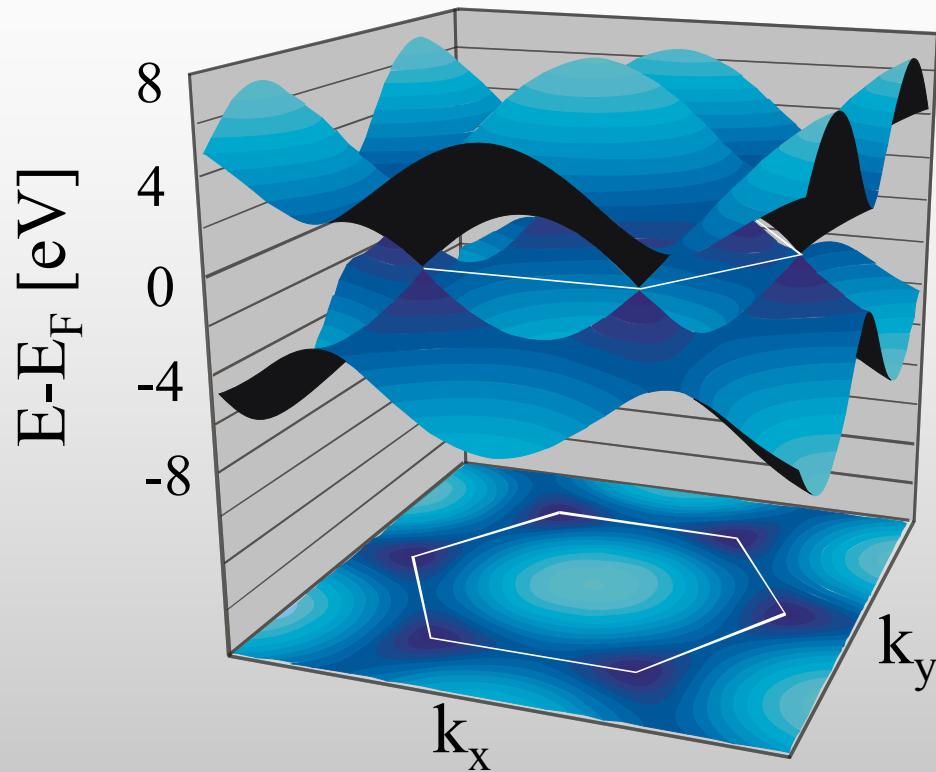
ARMCHAIR
(13,13)

ZIG-ZAG
(25,0)

CHIRAL
(20,10)



- Graphene Band structure



Two bands crossing E_F at 6 individual K points:

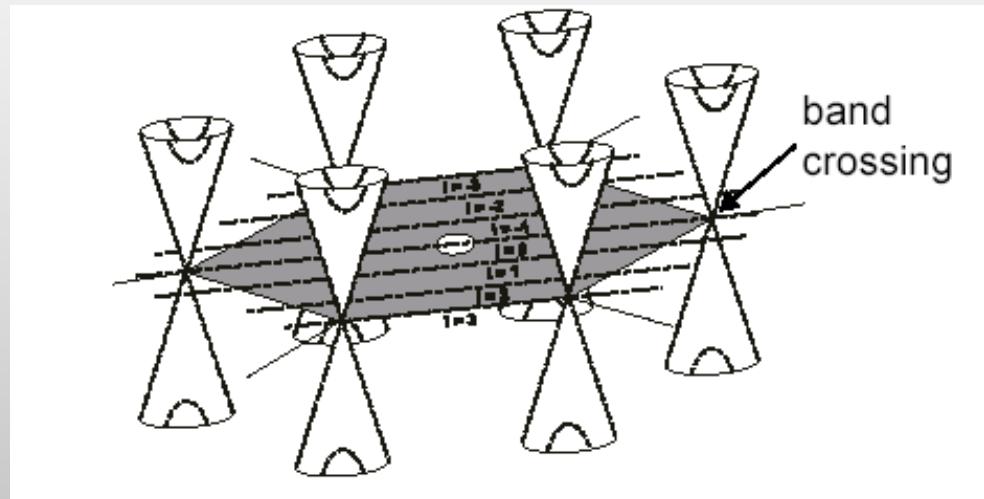
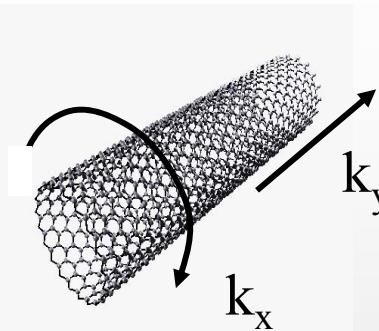
- No band gap \rightarrow not a semiconductor
- DOS at $EF = 0 \rightarrow$ not a metal

Semi-metal

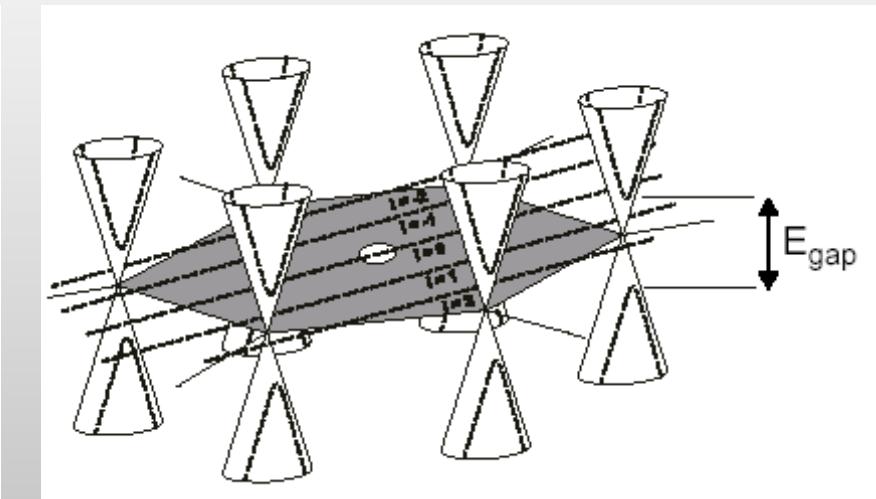
- Nanotube Band structure

Periodicity of the wave function
→ quantization of k_x

$$\mathbf{k} = 2\pi i / C_{(n,m)}$$



Metallic Nanotube



Semiconducting Nanotube

$n-m = 3i$ **Metallic** 1/3

$n - m \neq 3i$ **Semiconductor** 2/3

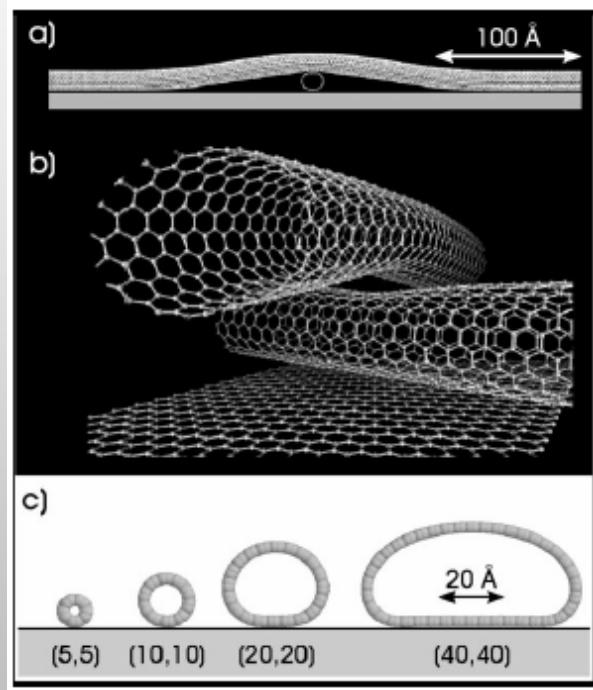
- SC gap inversely proportional to nanotube diameter
- SC gap of 1.4 nm tube = 600 meV
($k_B T = 26$ meV)

- Electrical Conduction

- Current density up to 4.10^9 A.cm^{-2}
 $\approx 10^3$ times higher than metal wires current capacity
- Scattering mechanisms :
 - defects : $l_{\text{def}} \approx 1\text{-}4 \mu\text{m}$
 - acoustic phonons : $l_{\text{ac phon}} \approx 0.1\text{-}1 \mu\text{m}$
 - optical phonons : $l_{\text{opt phon}} \approx 10 \text{ nm}$
- Short Carbon Nanotubes are ballistic conductors at room temperature : $G = 2 G_0$
- Long Nanotubes : diffusive conductors – mobility $\mu > 70\,000 \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$

- Mechanical Properties

- Young modulus $E \approx 1 \text{ TPa}$ (steel $E = 200 \text{ GPa}$)
- Flexibility

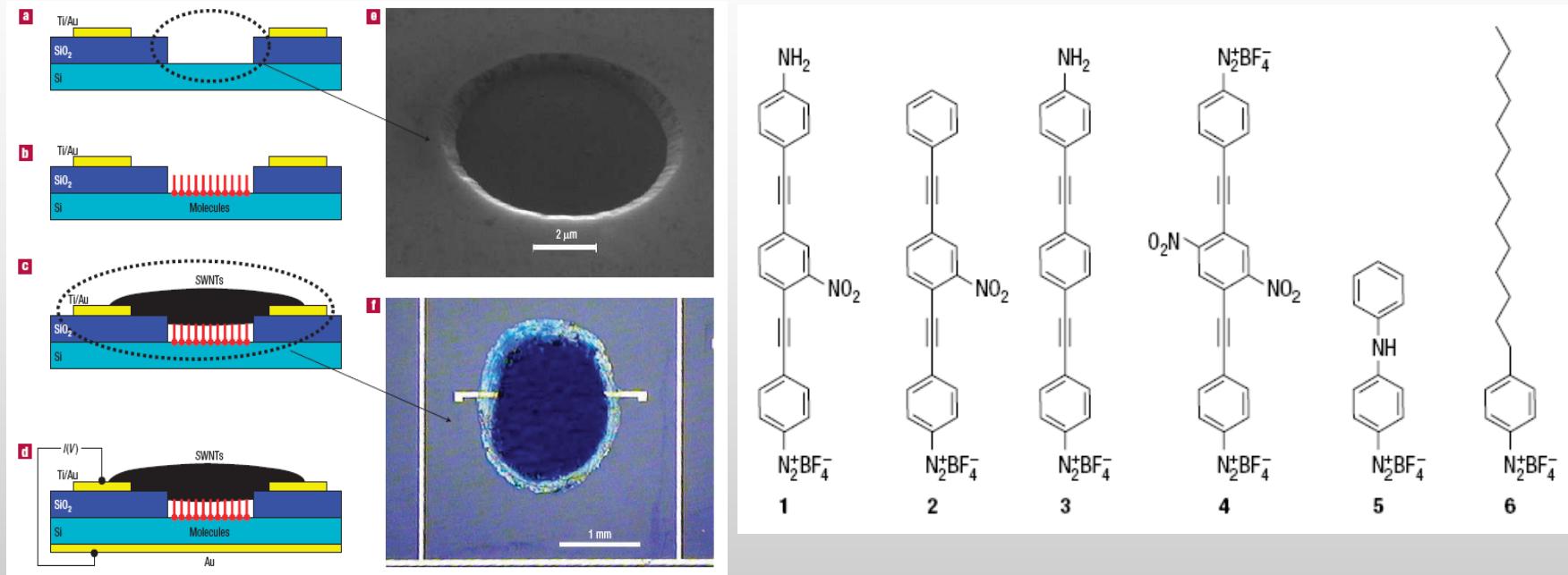


Hertel & al. *Phys. Rev. B* **58**, 13810 (1998)

- Compatible with any kind of substrate

- Nanotubes mat based testbed Memory

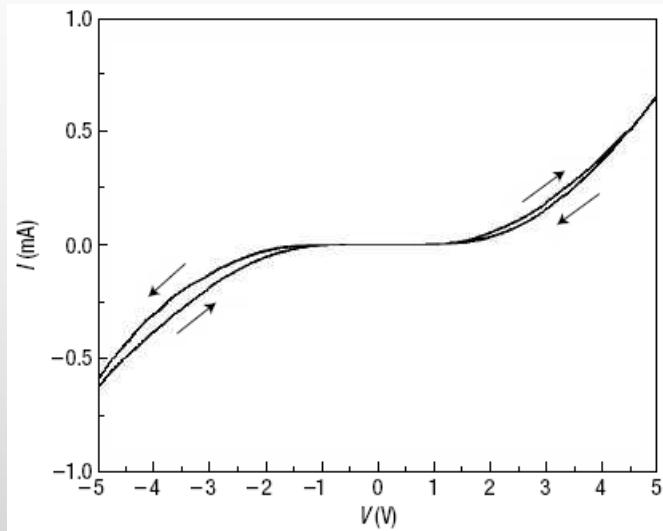
He & al. *Nature Mater.* 5, 63 (2006)



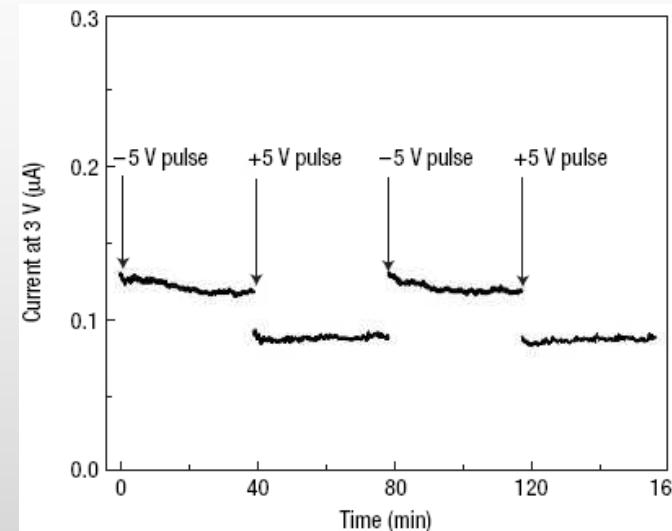
- SAMs : OligoPhenylEthynylenes (OPEs) grafted onto Si
- Well size : a few μm diameter
- Nanotubes Mat resistance $< 100 \Omega$

- Nanotubes mat based testbed Memory

He & al. *Nature Mater.* 5, 63 (2006)



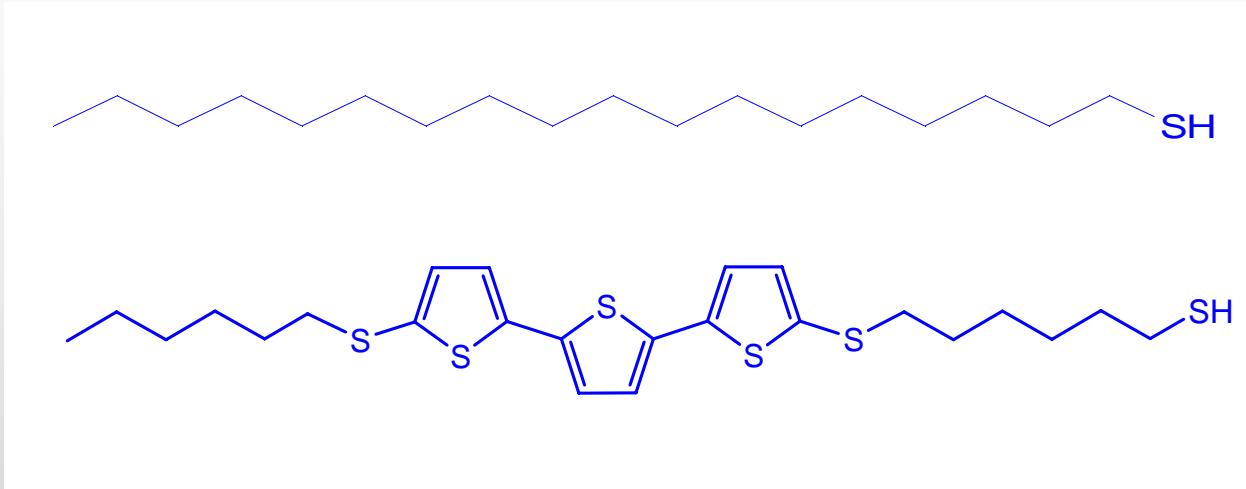
- Hysteresis



- No relationship to the molecule structure

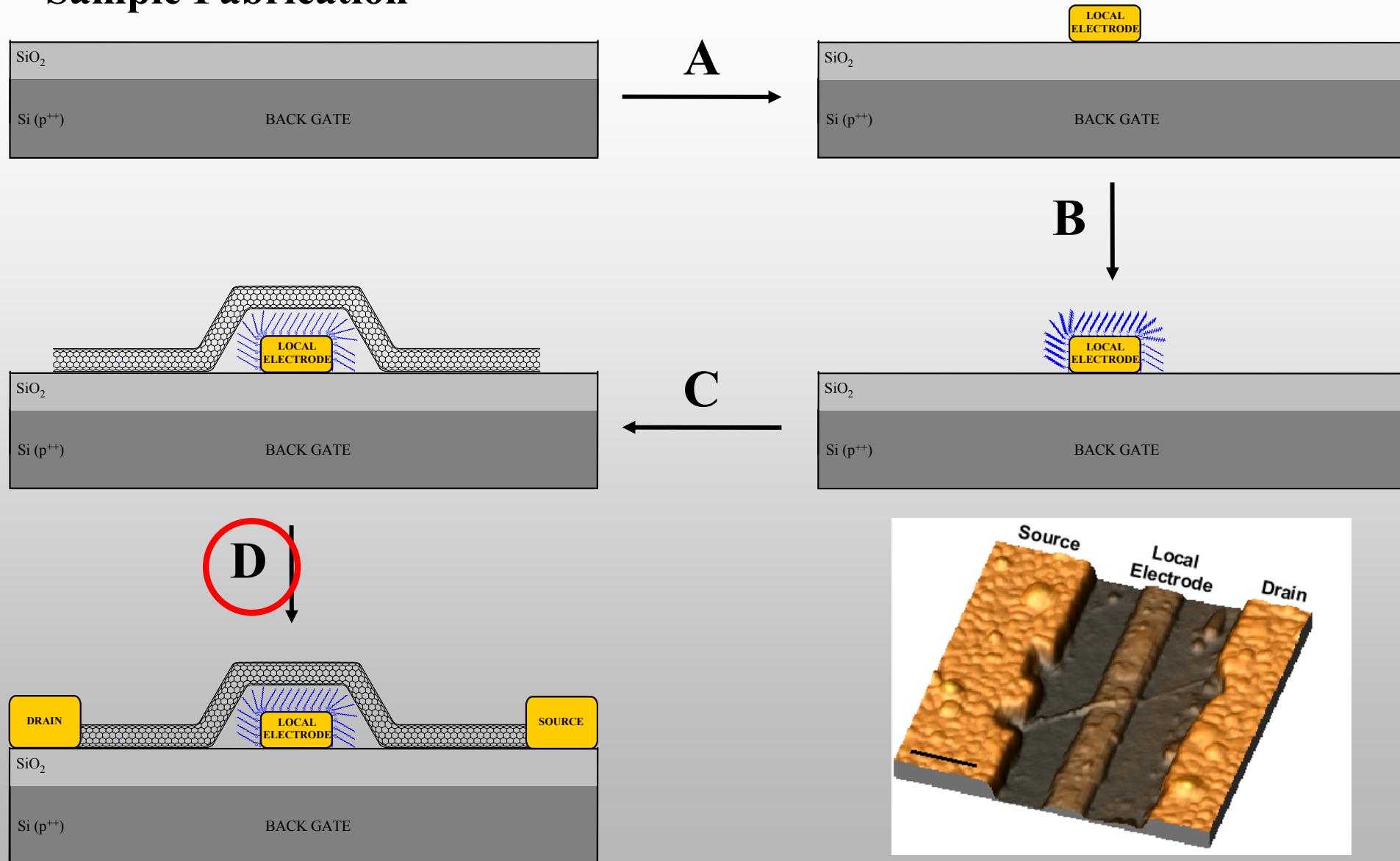
- I – Introduction to Carbon Nanotubes
- II – Individual SWNTs as Electrodes for probing transport through SAMs
- III – Application : an insulating SAM as ultra-thin gate dielectric for CNFET

- Studied molecules

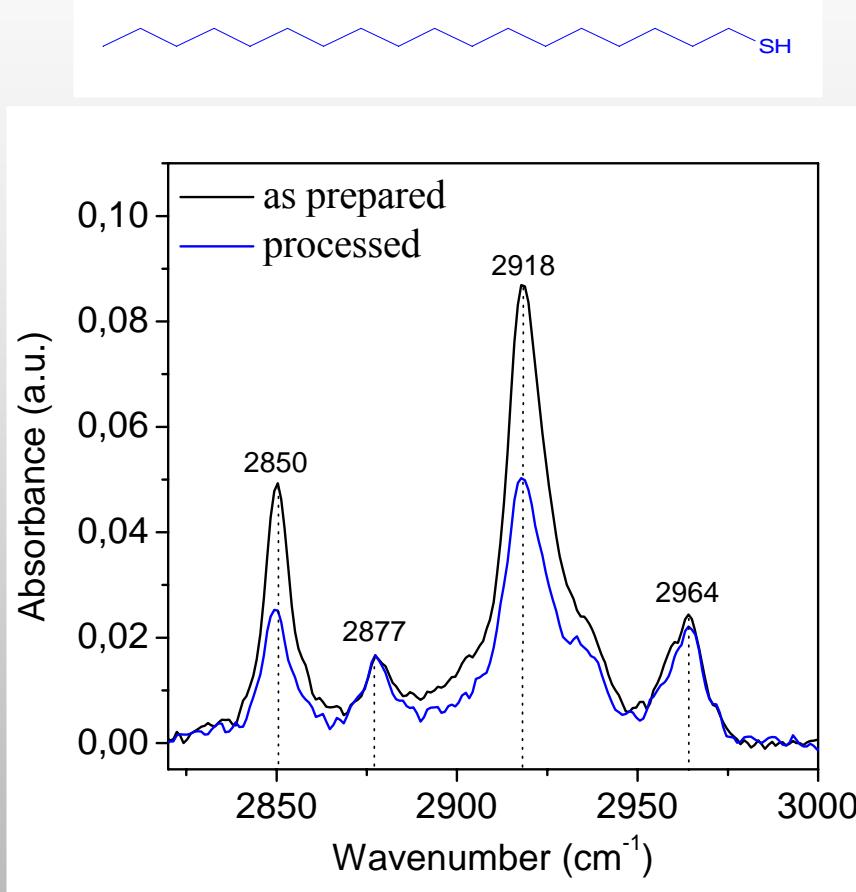


- Octadecanethiol (ODT) : insulator
- Terthiophene-derivative (DHT3) : σ - π - σ system (synthesized at SPCSI, CEA Saclay : see B. Jousselme talk on Thursday)
- Thiol end : SAMs on Au
- Immersion of a clean gold surface in a 10^{-3} M solution of the molecule for 15h

- Sample Fabrication



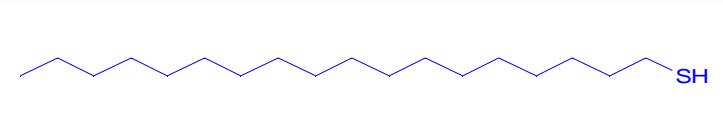
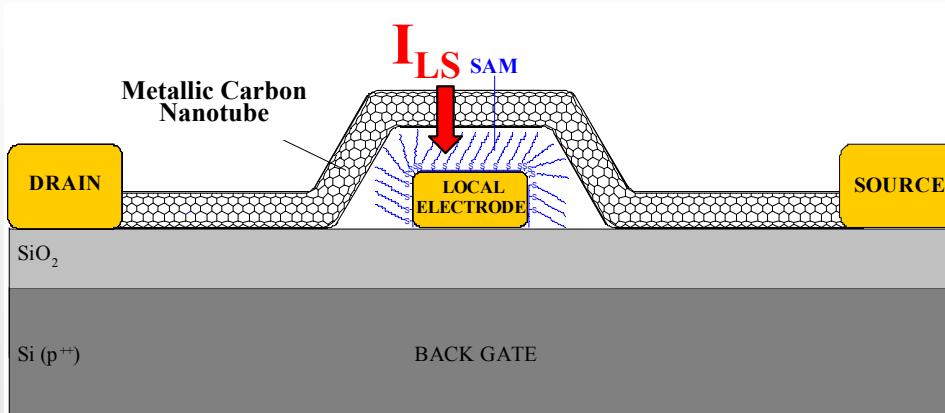
- SAM stability over process
→ Surface Infra-Red Spectroscopy (PMIRRAS)



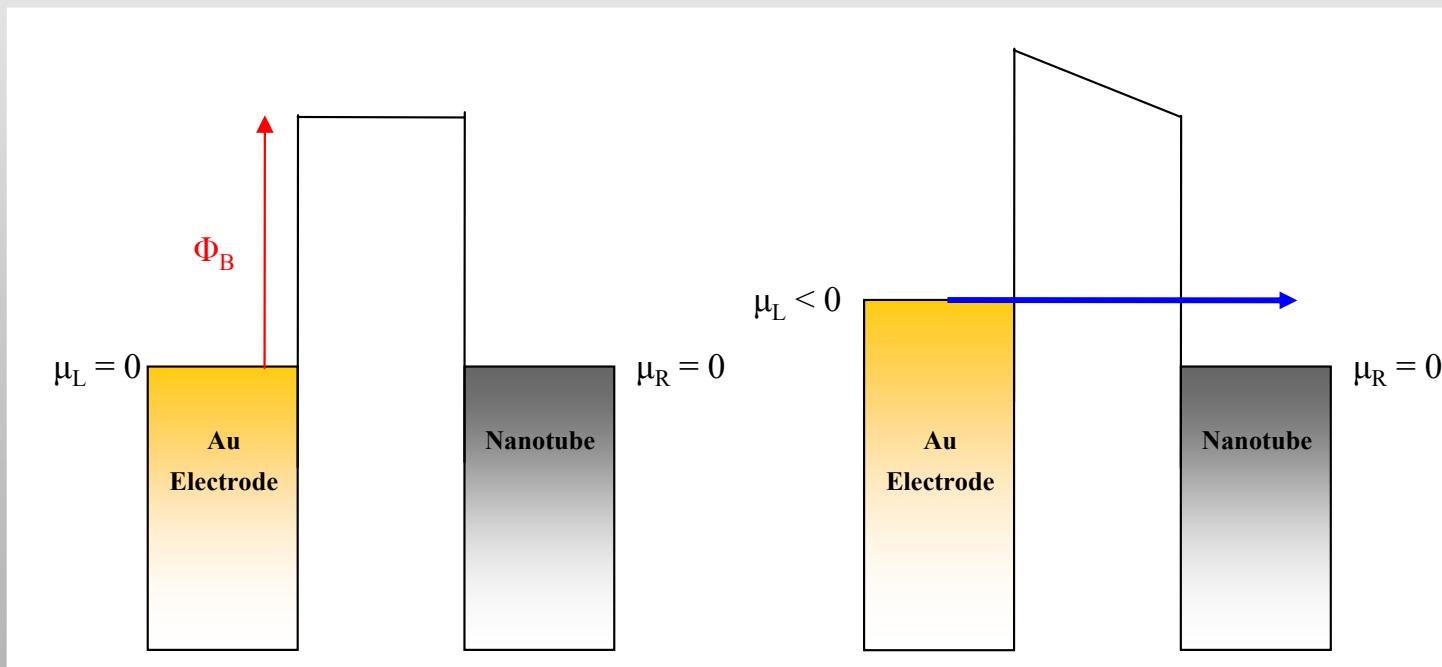
- No frequency shift
- Lowering of methylene stretching peaks intensities

- Reconstruction of the SAM
- ODT Chains oriented more toward the normal to the Au surface

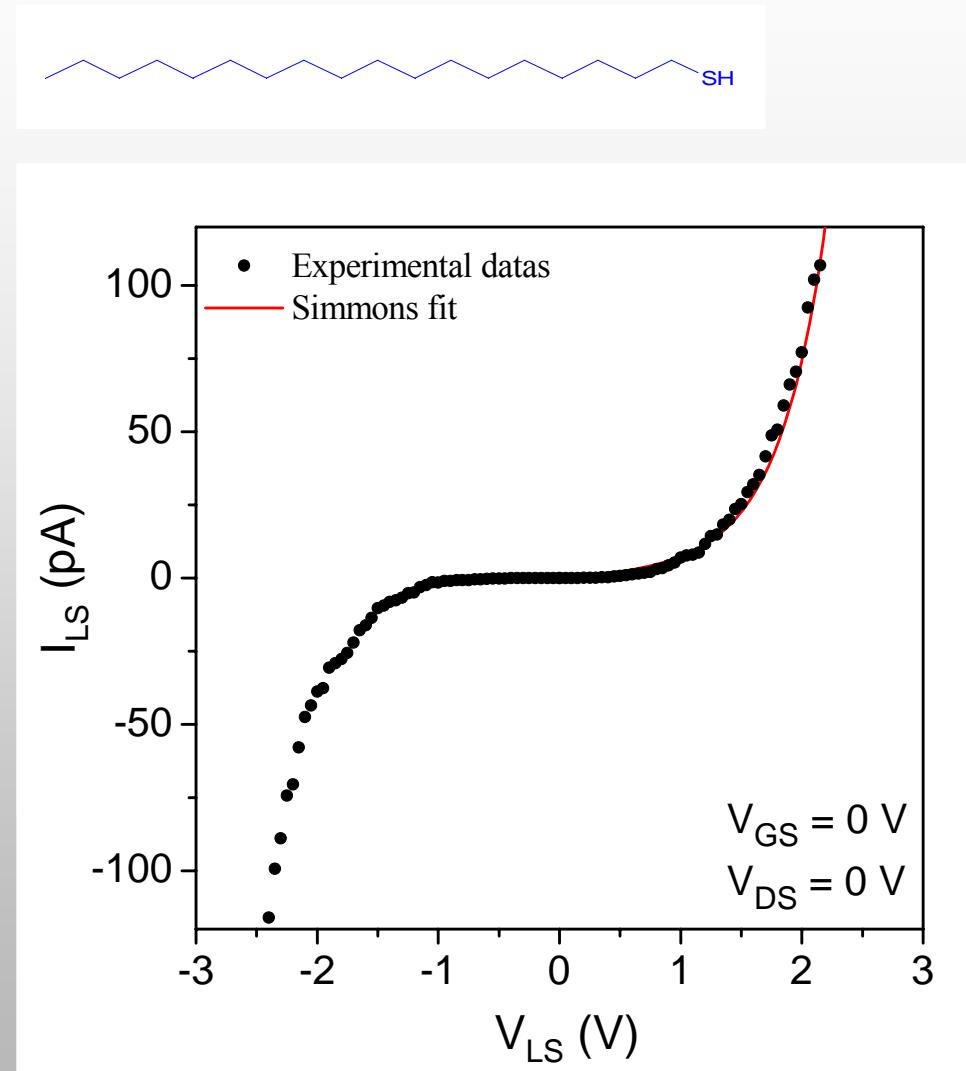
- [Metallic NT - Insulating SAM –Au] Junctions Transport properties



- Metal – Insulator – Metal (MIM) configuration
- $G(\text{NT}) \gg G(\text{MIM})$



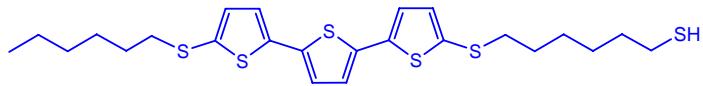
- [Metallic NT - Insulating SAM –Au] Junctions Transport properties



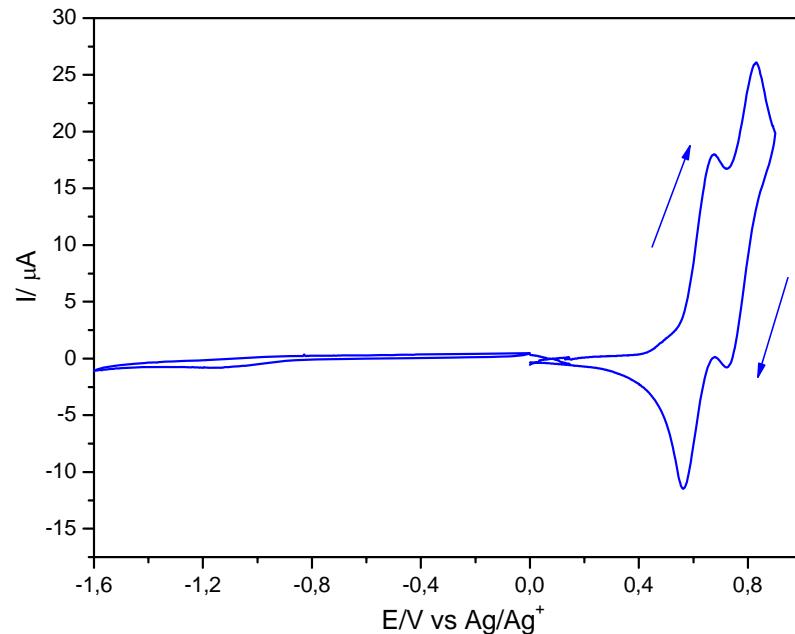
- $G(\text{NT}) \gg G(\text{NT/SAM/Au})$

- Clear insulating characteristic
- $\Phi_B = 2.4 \text{ eV}$ (Simmons fit)

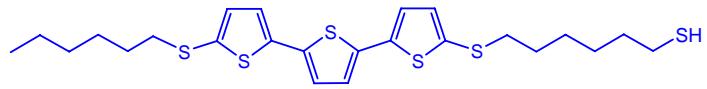
- σ - π - σ System Electrochemical Properties



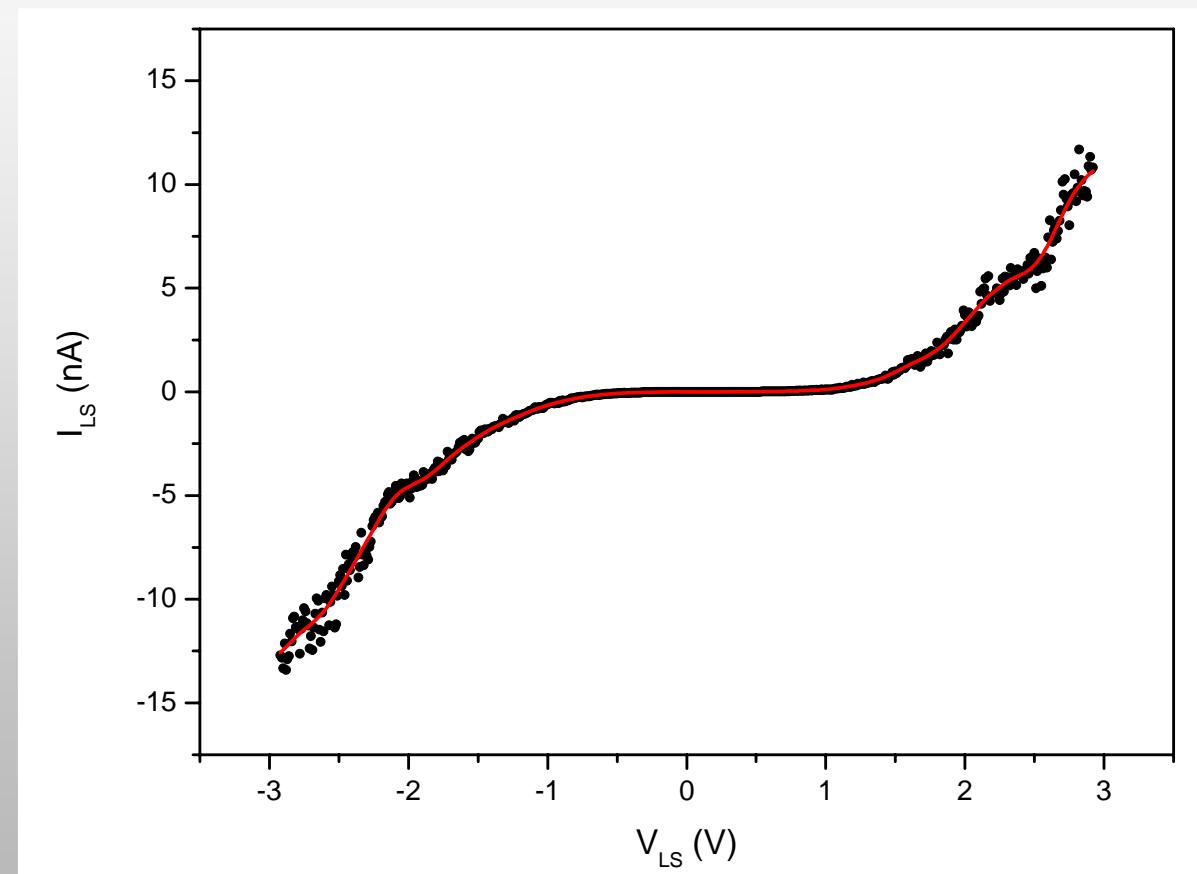
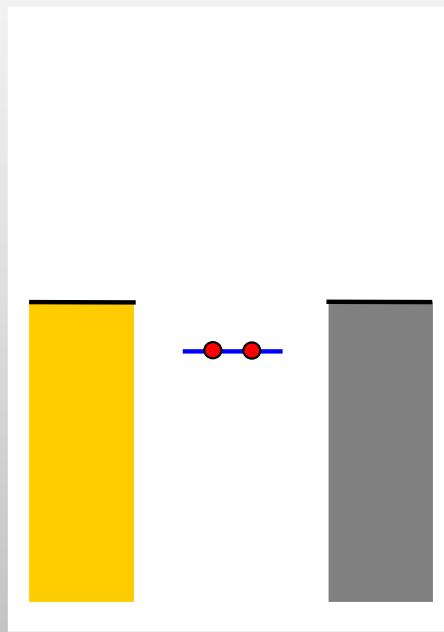
- Cyclci Voltammetry in solution :



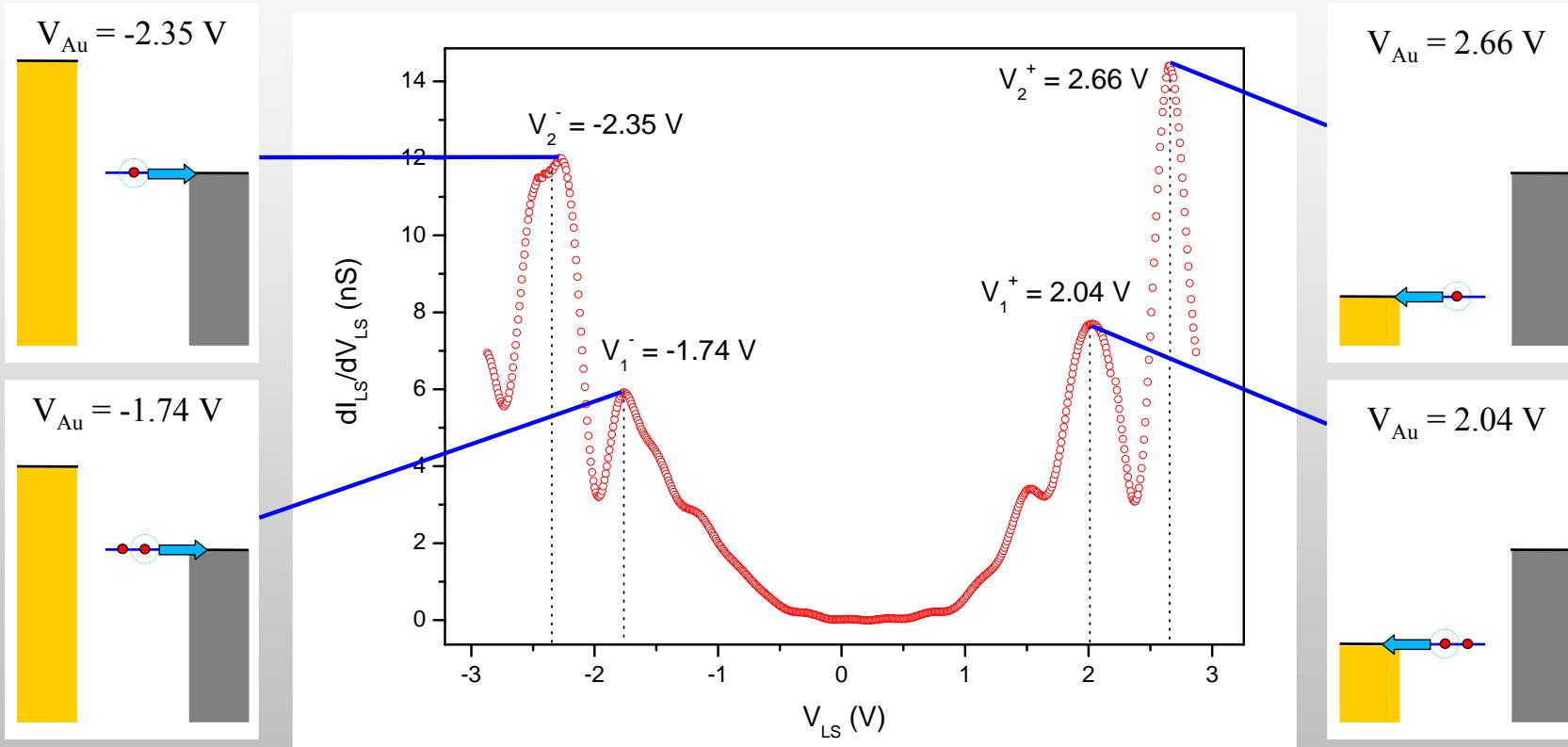
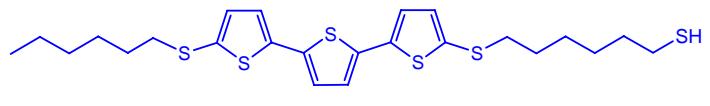
- [Metallic NT – σ - π - σ SAM – Au] Junctions Transport properties



- Possible resonance through molecular levels ?

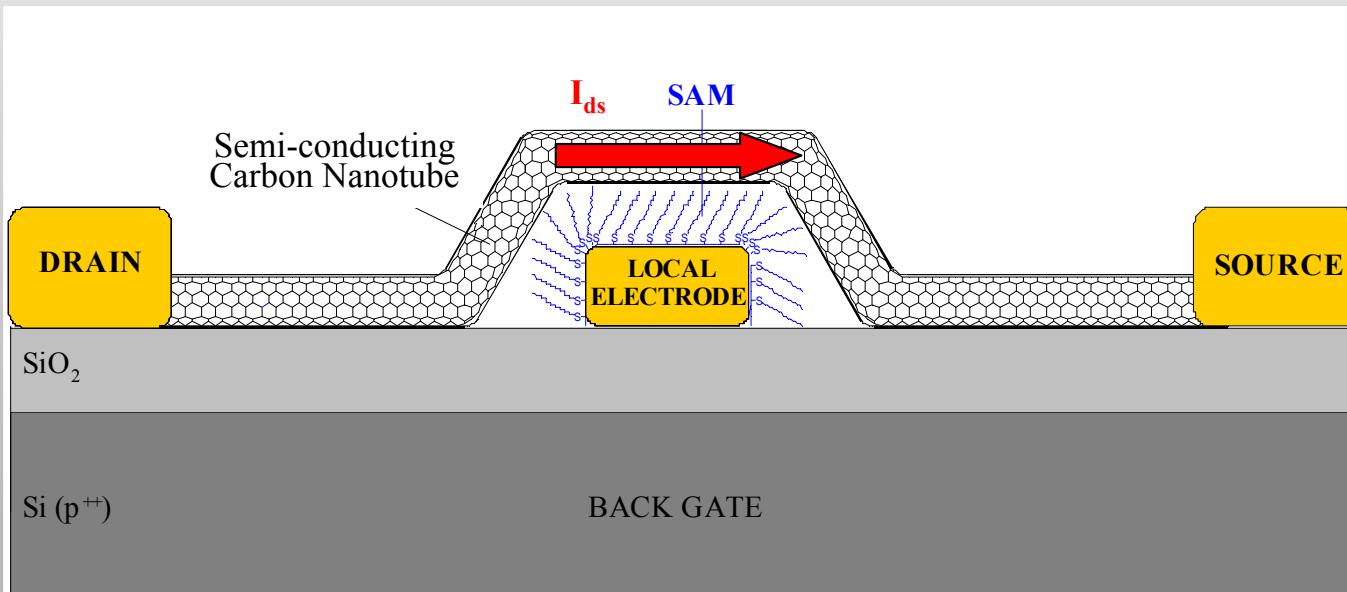


- [Metallic NT – σ - π - σ SAM – Au] Junctions Transport properties

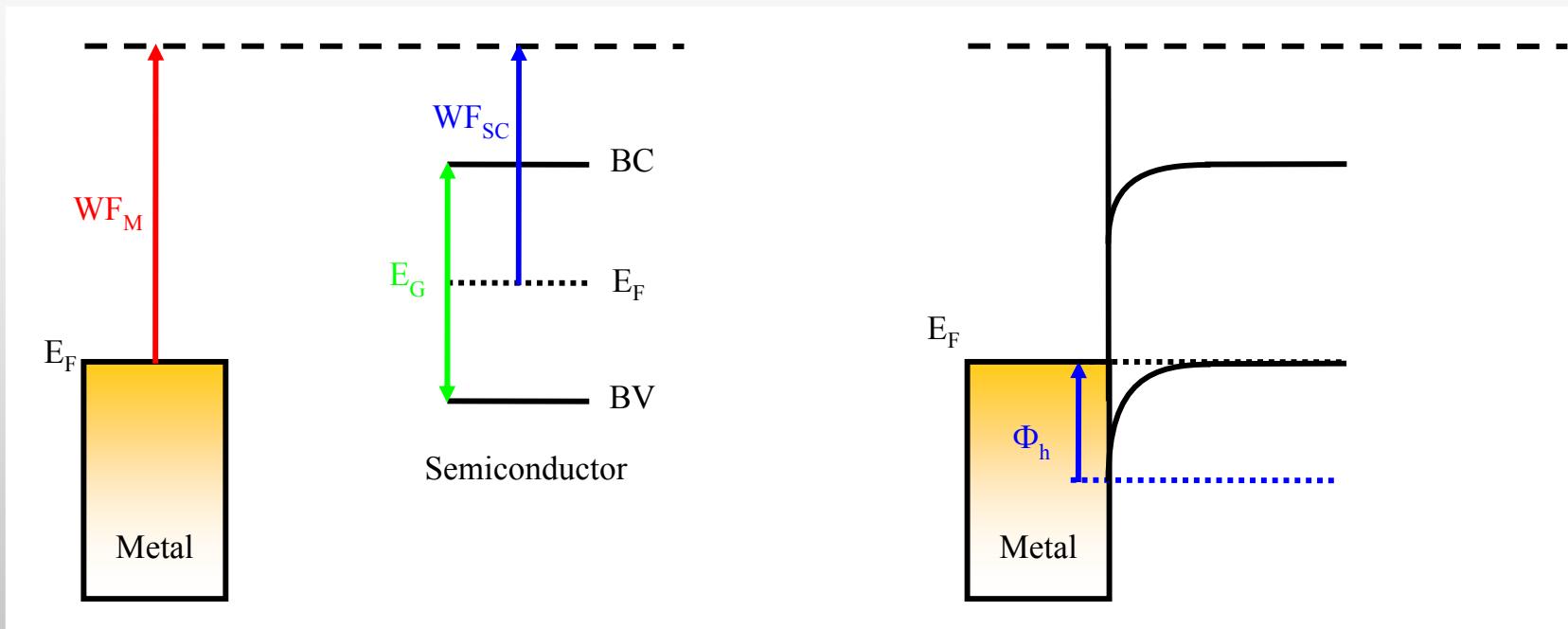


- $V_1^+ / V_1^- = V_2^+ / V_2^- \rightarrow$ tunneling through the 2 same orbitals at opposite biases
- Deduced level position $E_{H0} = 5.8 \text{ eV}$
- Charging energy : $E_c = 300 \text{ mV}$

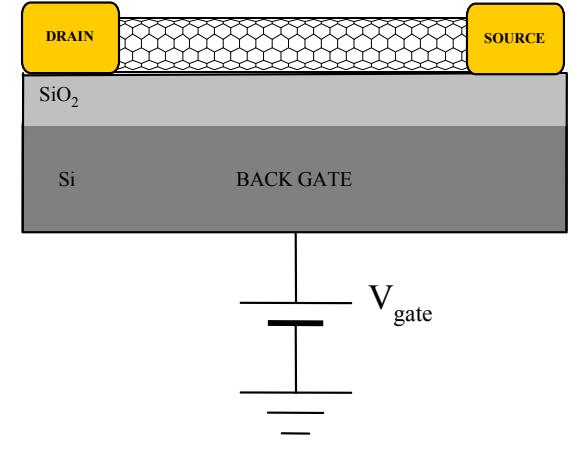
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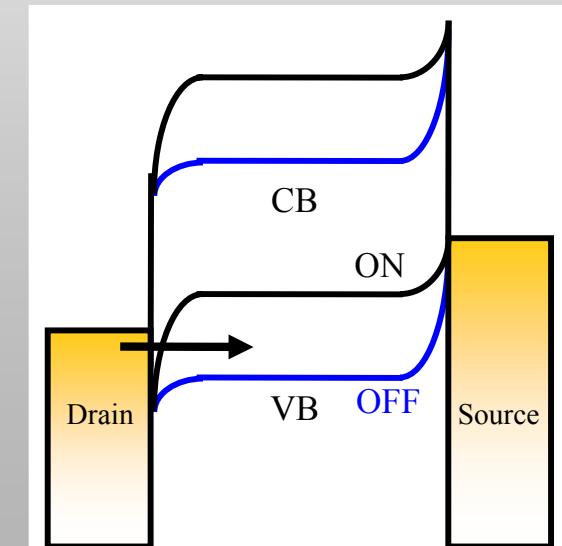
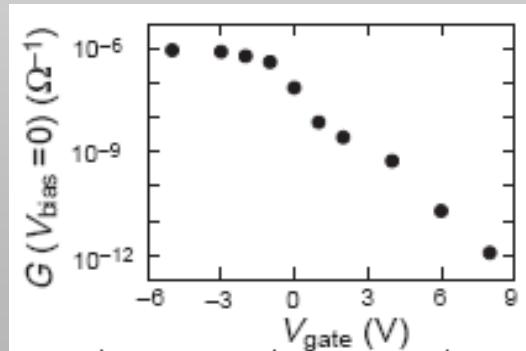
- Carbon Nanotube Field-Effect Transistors (CNTFETs)
 - Schottky (metal / Semiconductor) barriers at source / SC NT and drain / SC NT interfaces



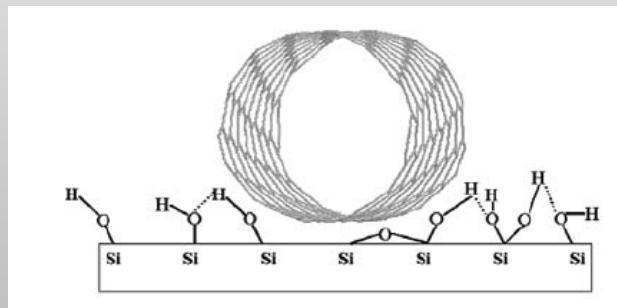
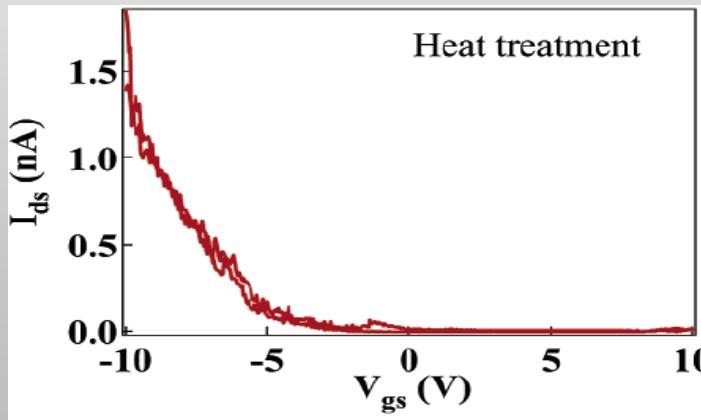
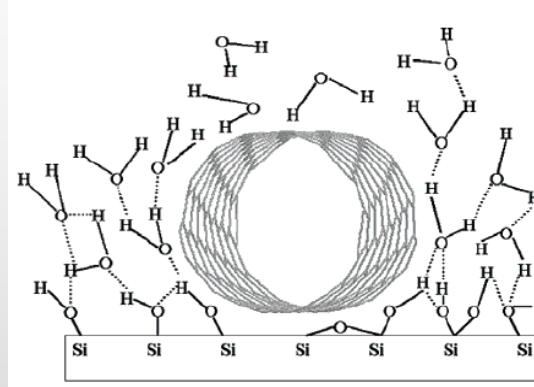
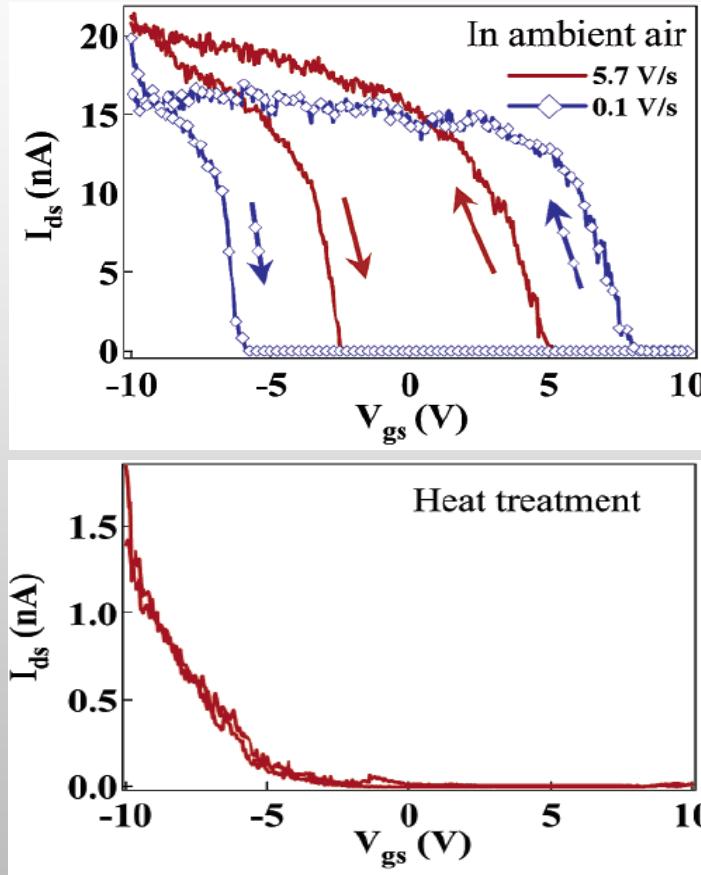
- Carbon Nanotube Field-Effect Transistors (CNTFETs)
 - CNTFETs are Schottky barrier transistors (Heinze & al. *Phys. Rev. Lett.* **89**, 106801 (2002))



- In ambient conditions, CNTFETs are p-type transistors :

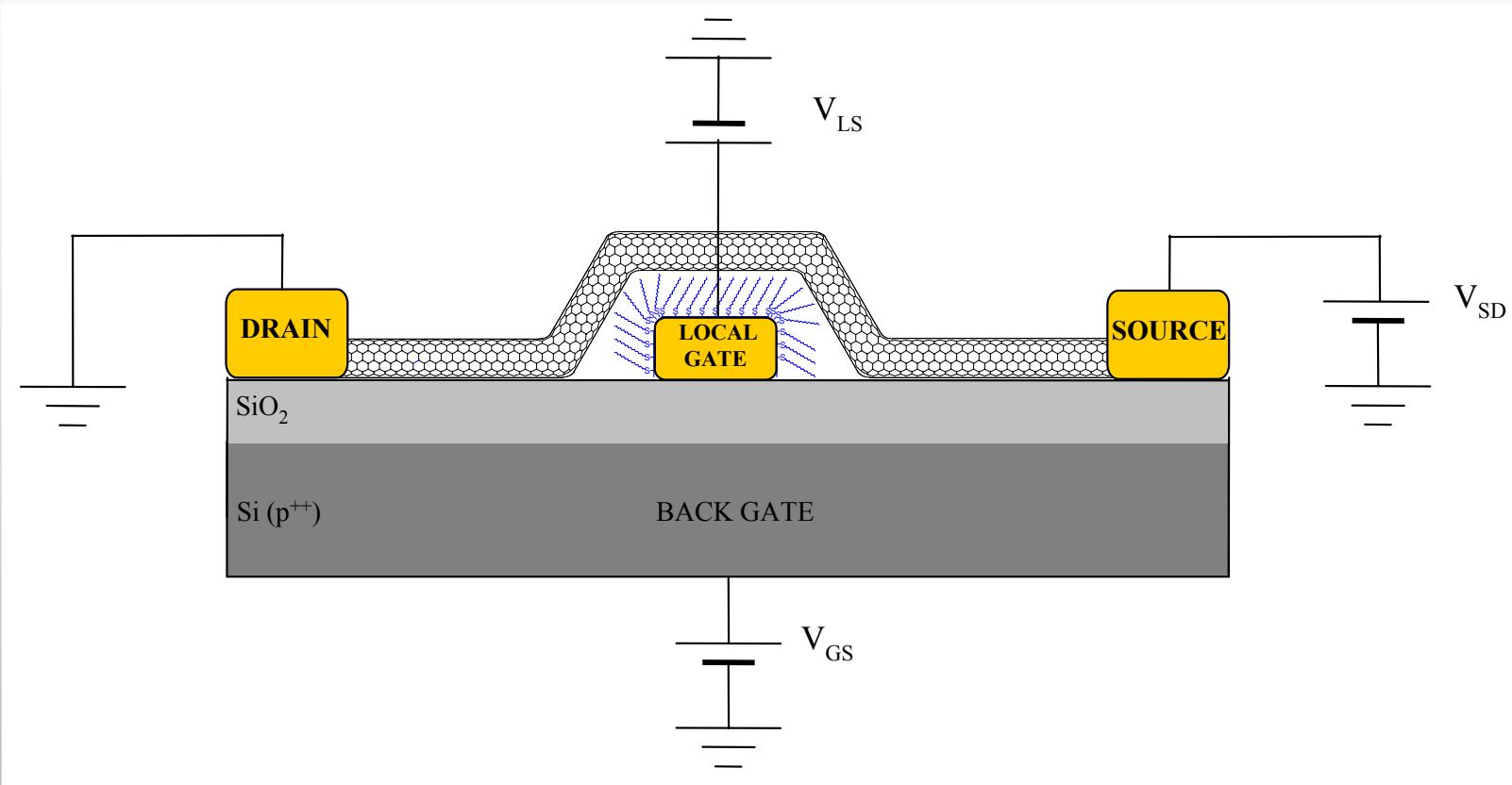


- Carbon Nanotube Field-Effect Transistors (CNTFETs)
- Hysteresis in CNTFETs is due to charge traps



Kim & al. *Nano Lett.* 3, 193 (2003)

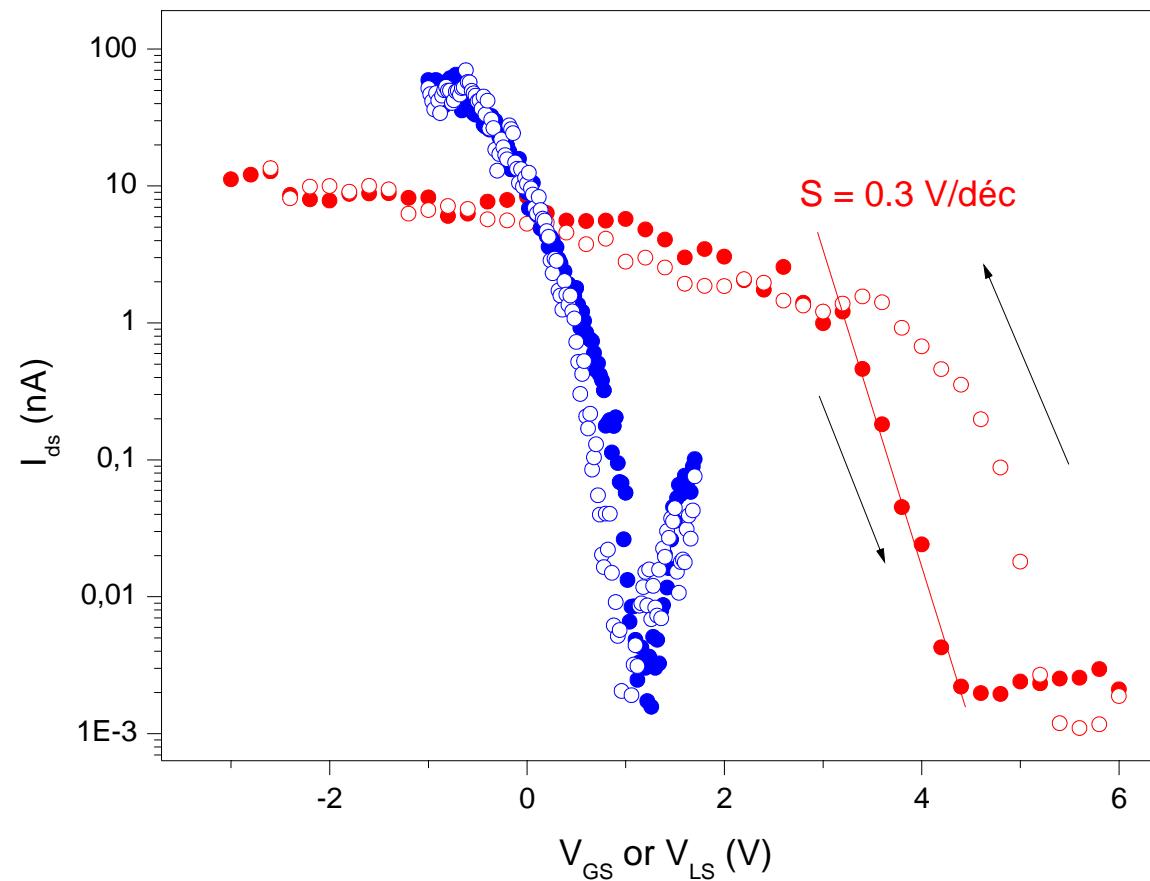
- Double back-gated CNTFET



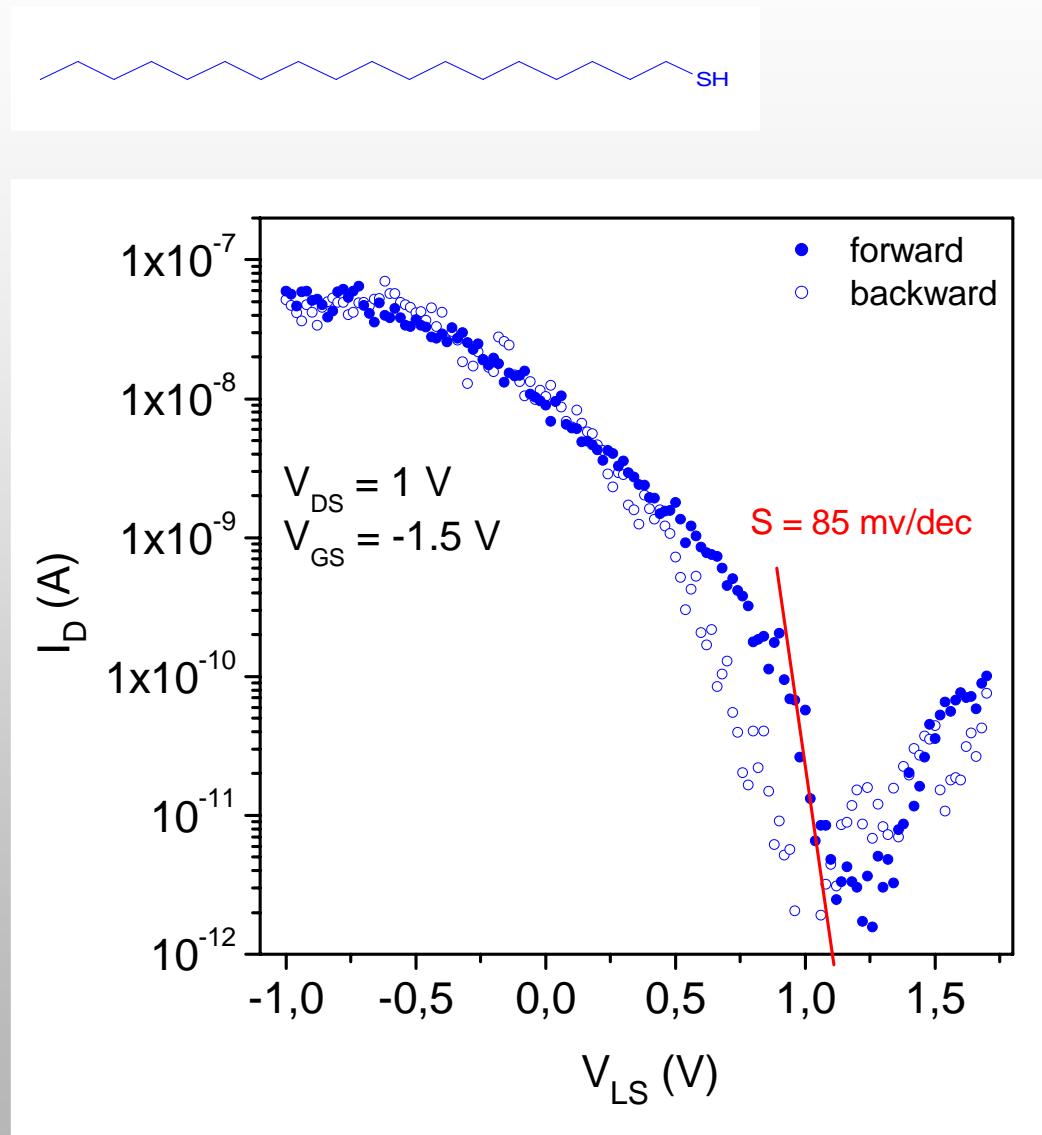
- Transfer characteristics : back-gate vs local gate

SH

- Measurements in air :



- Local gate transfer characteristic

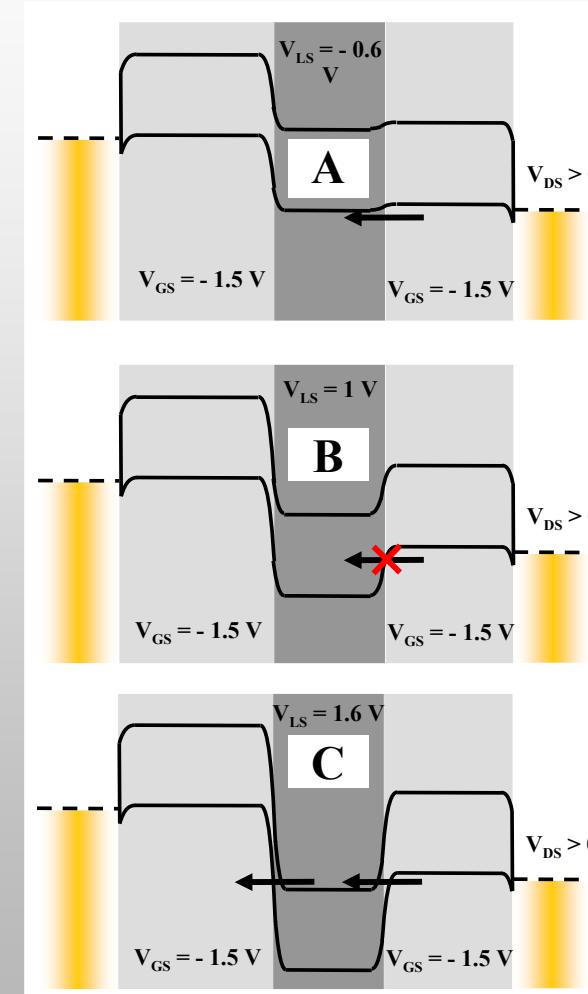
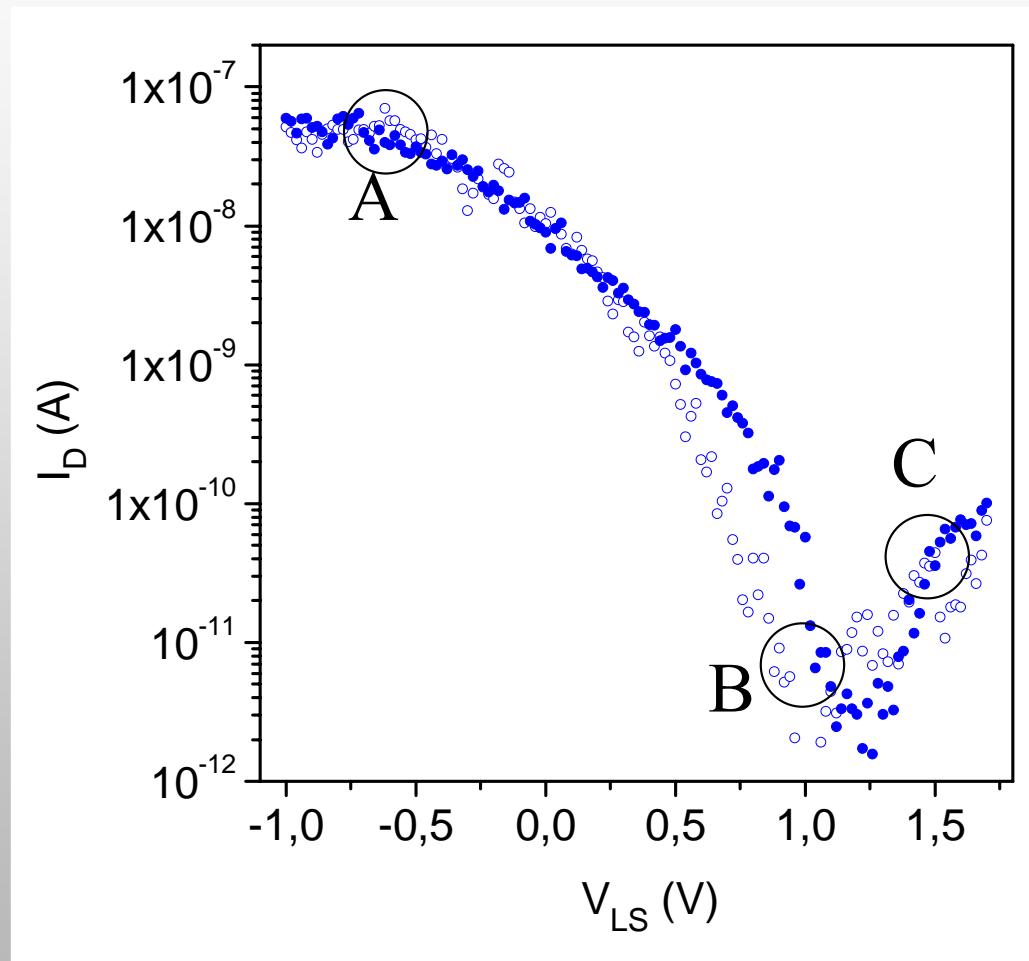


Measurements in air :

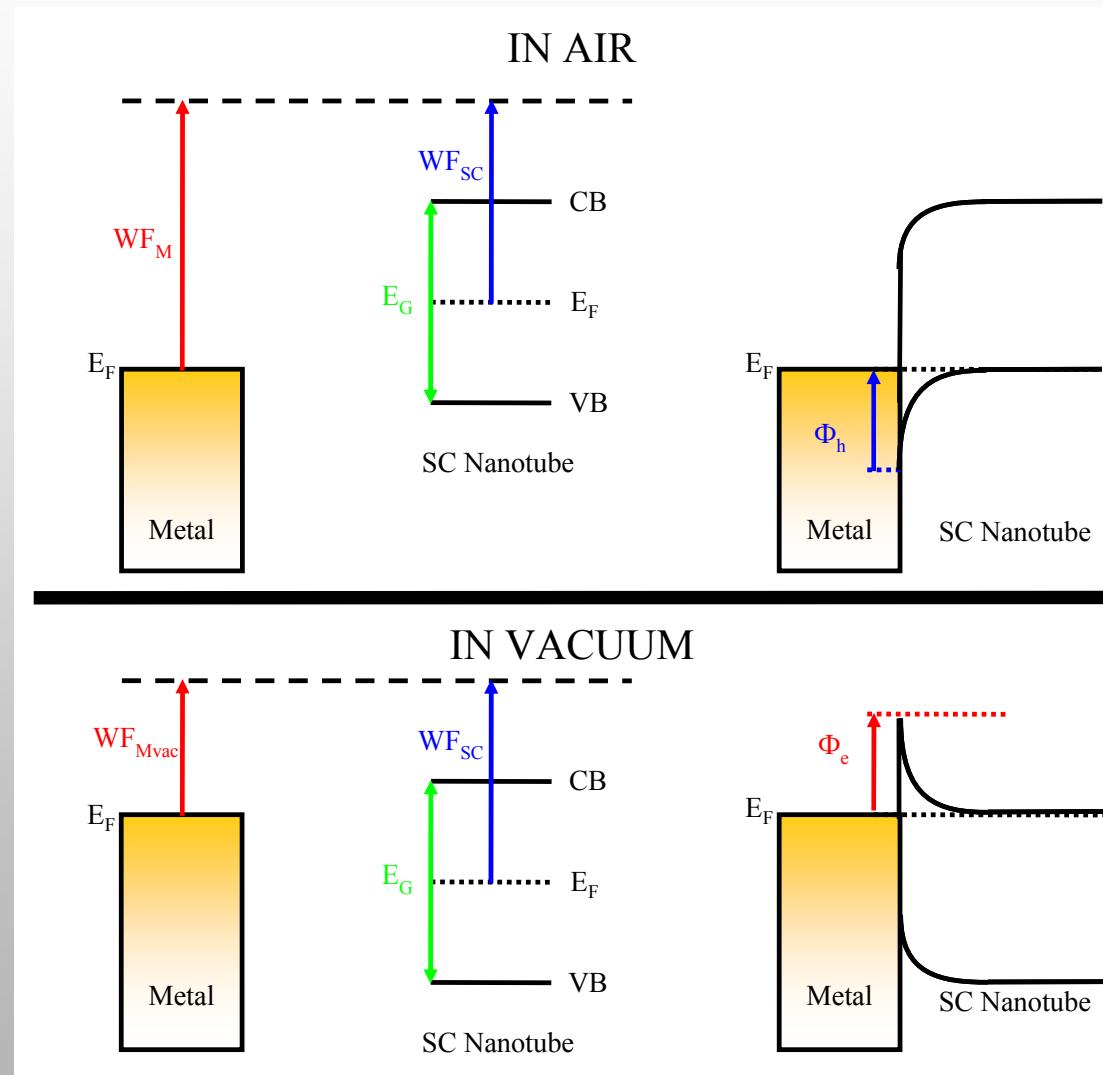
- Steep subthreshold slope
- Reduced hysteresis

- Band-to-Band Tunneling

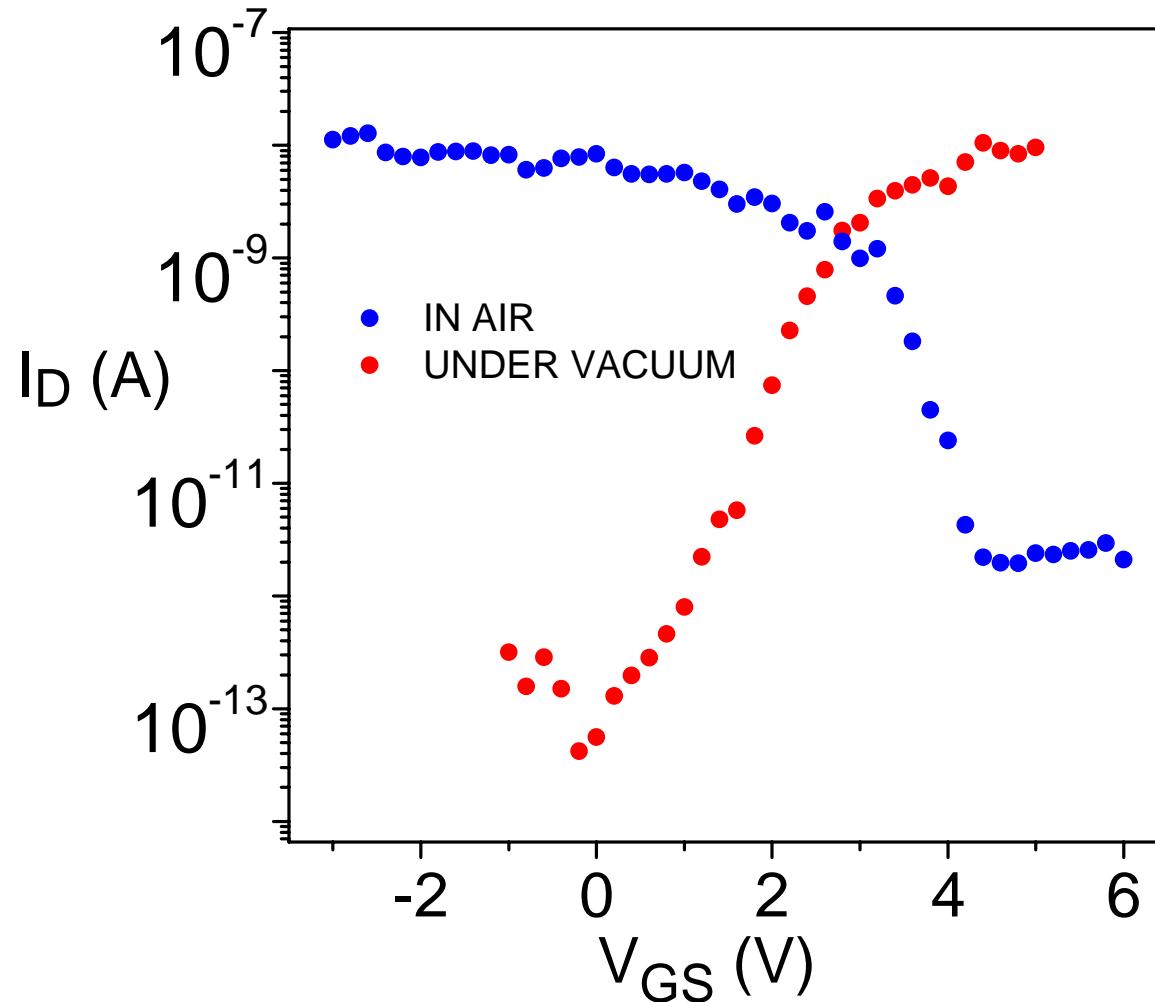
BTB Mechanism :



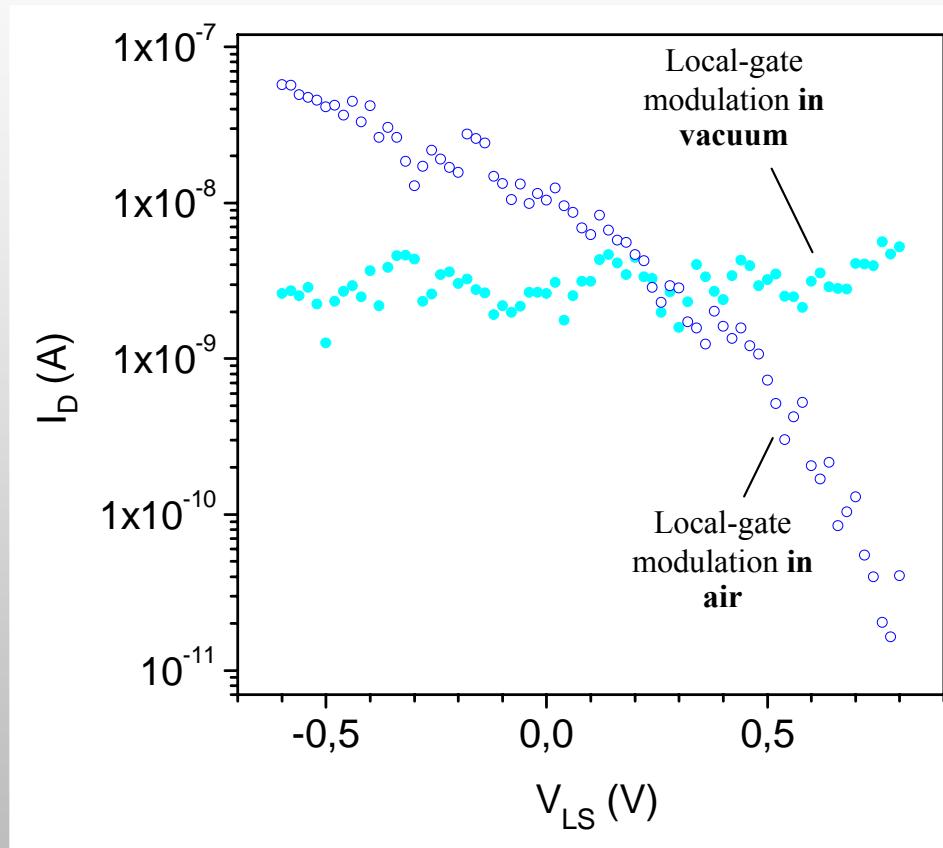
- Schottky barrier modification
- Under vacuum : impurities desorption at drain (source) / nanotube interface



- Back gate transfer characteristic : air vs vacuum



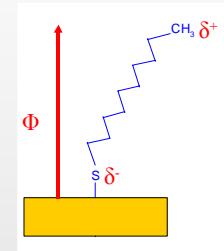
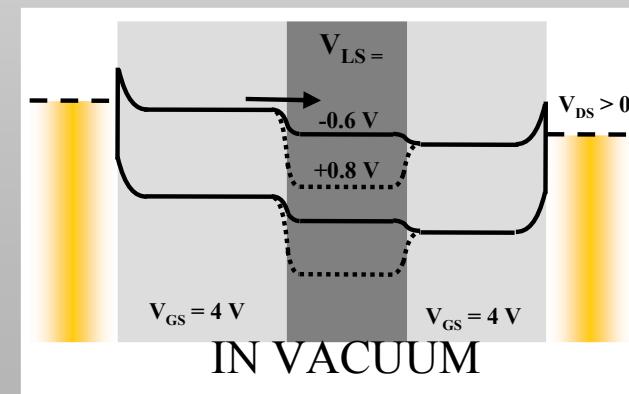
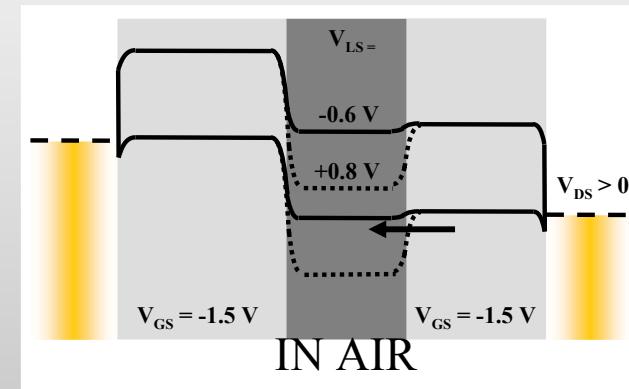
- Transfer characteristic in vacuum



Robert & al., Appl. Phys. Lett., accepted for publication

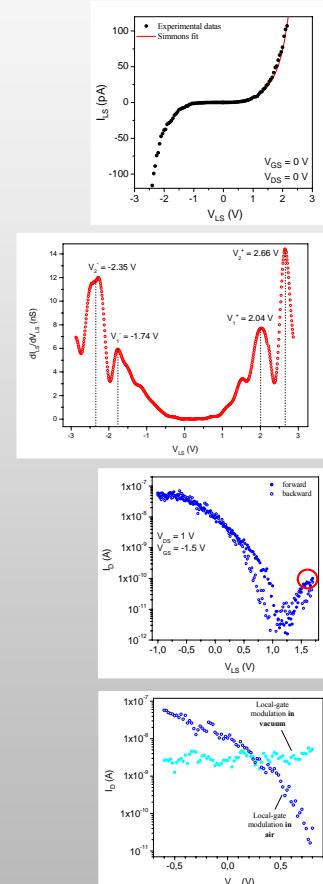
Measures in vacuum :

- No modulation
 - Surface dipole
- downward band bending



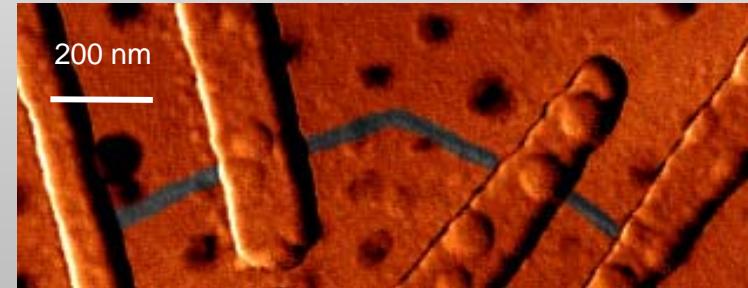
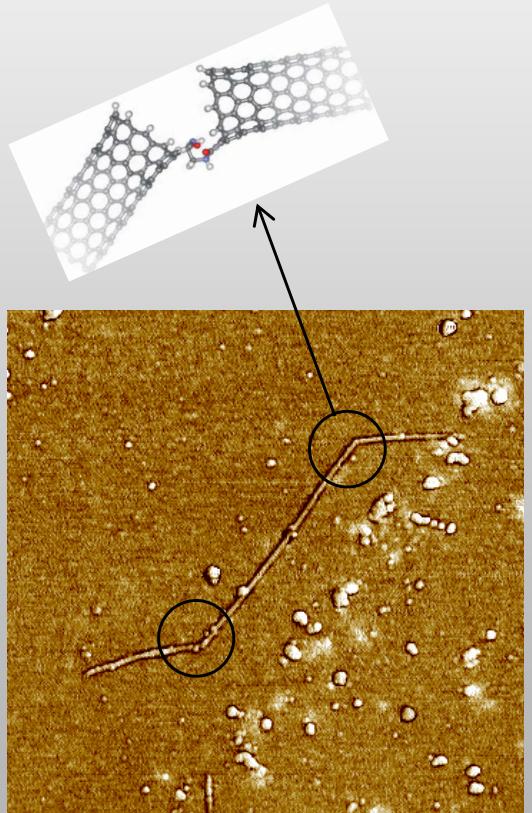
- Metallic NTs as Electrodes for probing transport through SAMs :

- insulating SAM : high tunneling barrier
- σ - π - σ system SAM : tunneling through molecular orbitals



- Insulating SAM as a dielectric for a CNFET : high performances transistor – role of the SAM dipole

- Metallic NTs as Electrodes for probing transport through SAMs :
 - SAMs on Si : towards NDR
 - memories
- SWNTs as electrodes for Single Molecules



- CEA – IRAMIS :

LEM

Vincent Derycke

Jean-Philippe Bourgoin

Nathalie Lidgi-Guigui

Stéphane Streiff

Stéphane Campidelli

Pascale Chenevier

Arianna Filoramo

Marcelo Goffman

Pascal Lavie

- IEMN – Lille :

Stéphane Lenfant

David Guérin

Dominique Vuillaume

LCSI

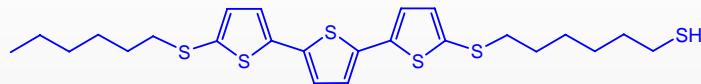
Fabrice Moggia

Bruno Jousselme

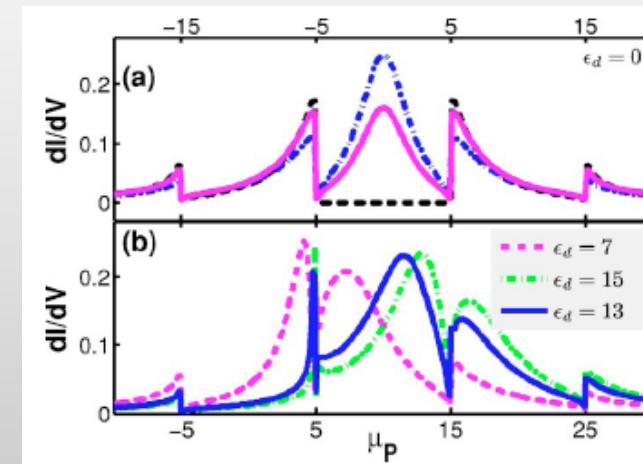
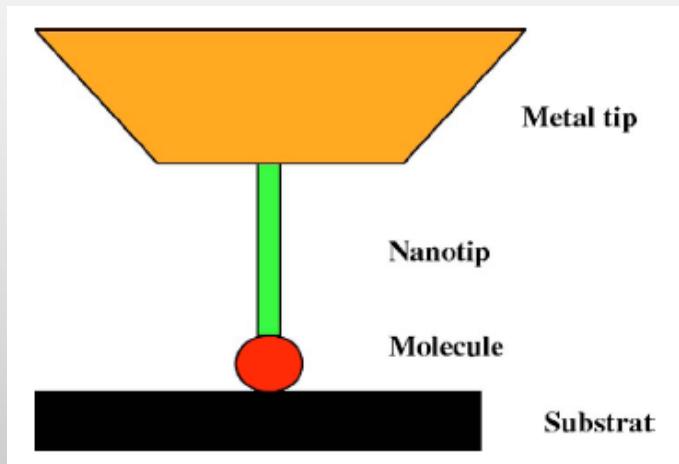
Serge Palacin

धन्यवाद !

- [Metallic NT – σ - π - σ SAM – Au] Junctions Transport properties



- Influence of the 1-D NT DOS :



[Gao & al. *Phys. Rev. B* 73, 235421 (2006)]