Departament de
Física Aplicada

Nanotubs de carboni: física, materials i dispositius

Núria Ferrer Anglada

Departament de Física Aplicada
Universitat Politècnica de Catalunya

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Índex

- 1- Perquè nano?
  - Llei de Moore
  - Feynman: "There is plenty of room …"
- 2- Nanotubs i nanofibres. Grafè.
  - els Nanotubs de Carboni, CNT. Què són?
  - Obtenció, propietats
- 3- Fenòmens associats a "nano"
  - Fenòmens quàntics observables
  - transport de càrrega: I(V) no òhmica, bloqueig de Coulomb
  - el color depèn de la mida!
- 4-Tècniques
  - de fabricació
  - d'observació y caracterització
  - de càlcul
- 5- Aplicacions
  - Compòsits: CNT-polímer, CNT-metall
  - Dispositius d'un sol nanotub: transistors. Sensors
  - Dispositius amb molts nanotubs: electrodes transparents, flexibles. Sensors.

1- Perquè Nanos?

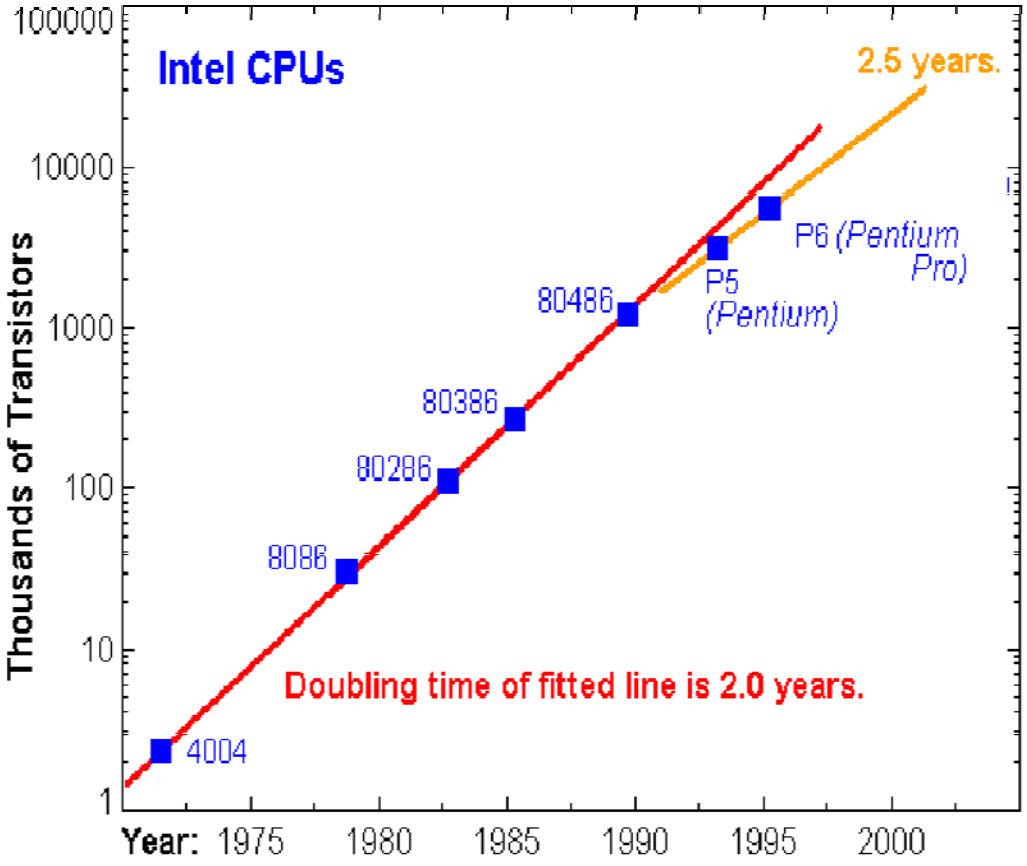
- 1965 - Llei de Moore (Gordon Moore, INTEL)

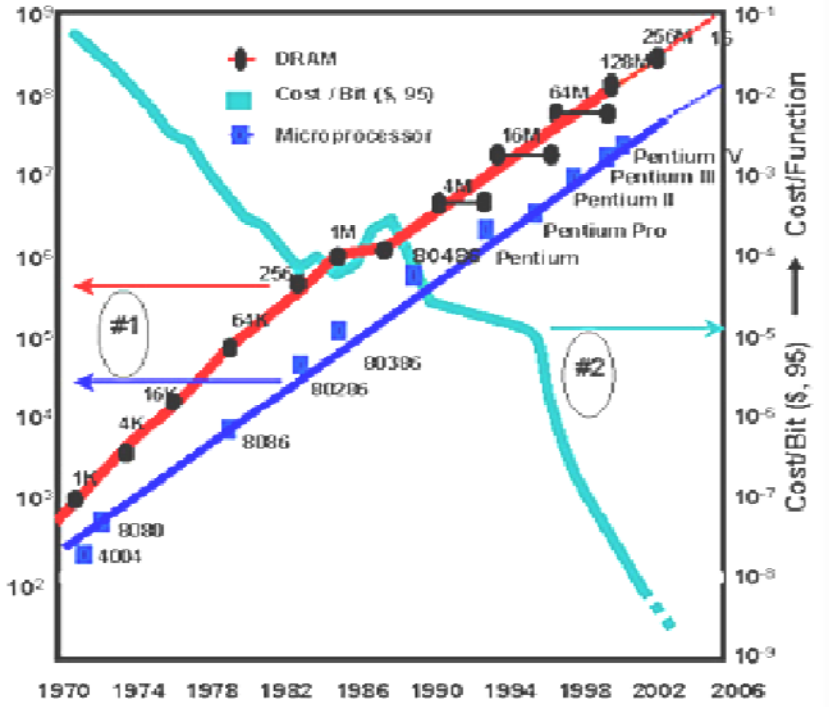
  Els transistors són més i més petits :
  - El número de transistors en un “xip” es x2 cada 18 - 24 mesos!
  - a un preu més baix
    - 1965: en un xip, 60 transistors
    - 2004: en un chip, 1,7 bilions de transistors!

- 1960’s- R. Feynman

  “There’s Plenty of room at the Bottom”

Llei de Moore





R. Feynman

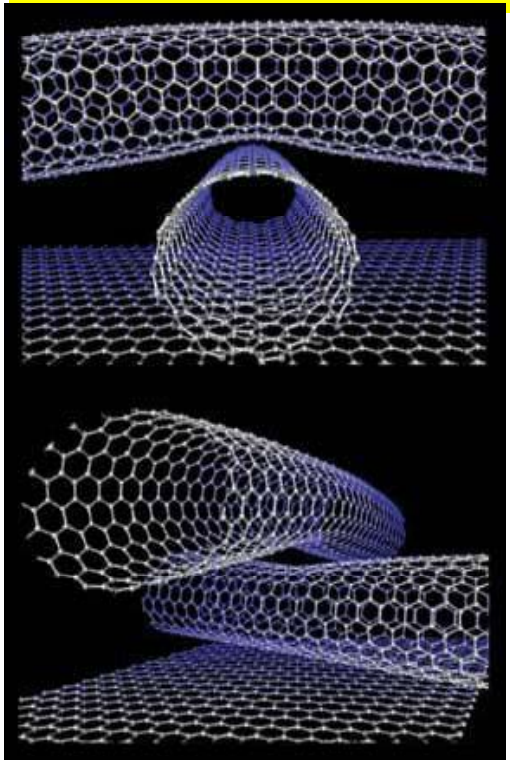
"There's Plenty of room at the Bottom"

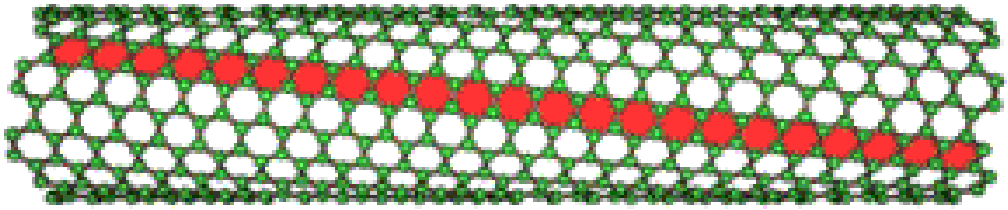
…hi ha molt lloc, allà baix!

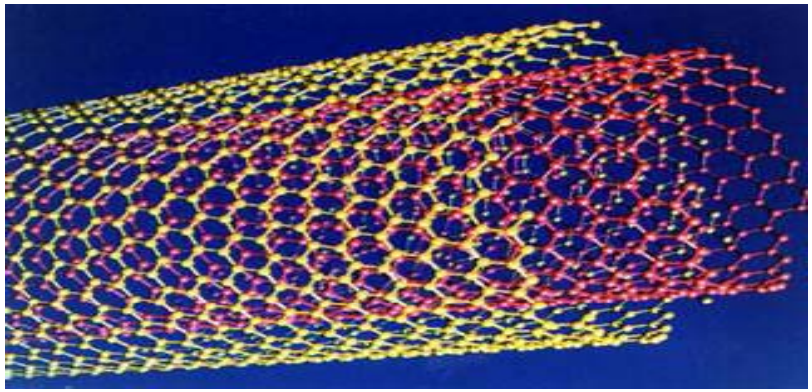
- Podríem escriure els 24 volums de l'enciclopèdia Britannnica en una agulla de cap?
- Sí !! si reduíssim el tamany de cada caràcter en 1/25.000
  - 1 punt = 8 nm de diàmetre = 32 àtoms
- caldria: Millors microscopis electrònics, miniaturització, nanolitografia, …

nanomaterials, nanotecnologies

Nanotubs de Carboni: CNT
Què són?





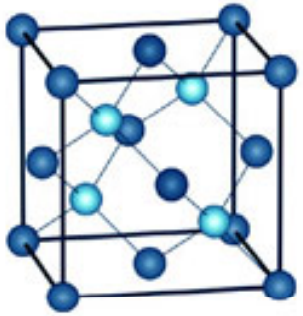


Una forma de Carboni en estat sòlid, nova?

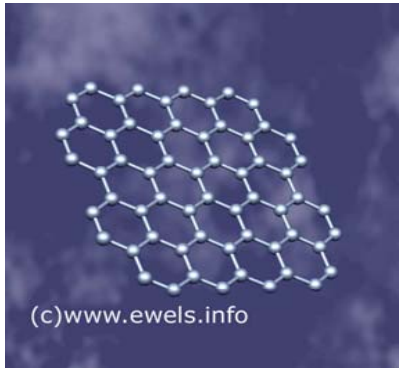
Similar al grafit: conductor elèctric, opac, negre, tou
o al diamant: aïllant, transparent, molt dur

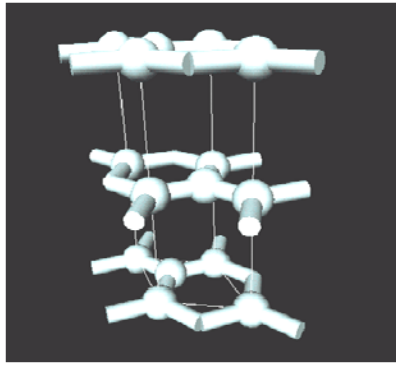
Diferents formes del carboni sòlid

- Diamant
  - Orbitals sp3



- Grafit - grafè
  - Orbitals sp2

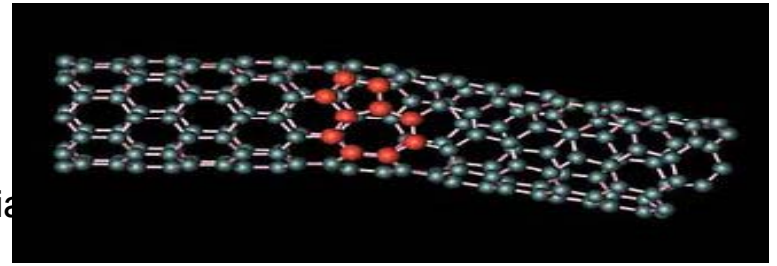




- Ful·lerè carboni

Buckminsterfullerene

Nanotub de



Història dels CNT

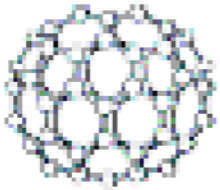
- **1985**, ful.lerens C_{60}
-
- **1991**: Multi-walled
- **1993**: Single-walled carbon nanotubes by S, Iijima, (Nature, 1991) D. S. Bethune et al. (Nature, 1993)
- **2001**: Single crystals of single-walled carbon nanotubes (R. R.Schlittler et. al., Science 292, 1136, 2001).

Ful·lerens (C_{60} , C_{70}) i Nanotubs de Carboni, CNT

- Ful·lerens

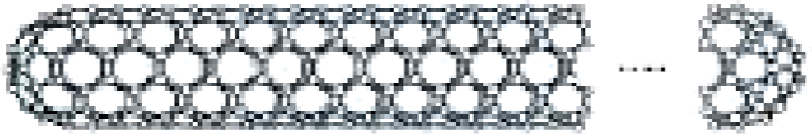
C_{60}

C_{70}

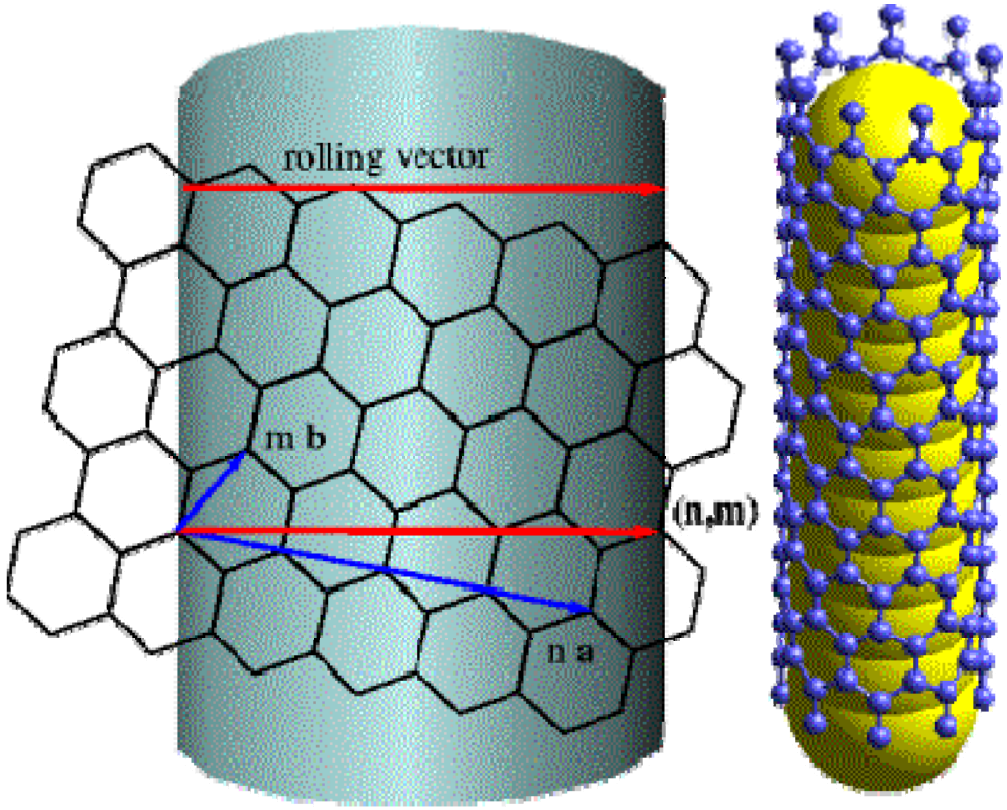


diàmetre ~ 10 nm

- Nanotubs, CNT (MWNT, SWNT)
- diàmetre ~ 1-90 nm
- longitud ~ micres → cm!



Nanotubs de Carboni d'una sola paret: SWNT



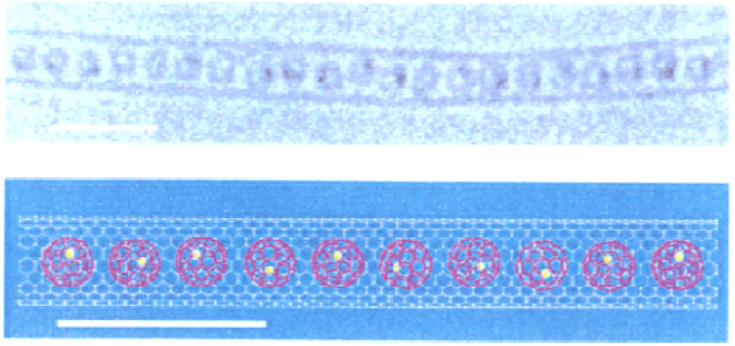
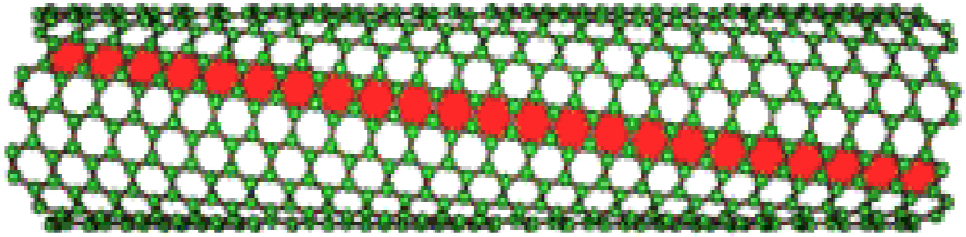
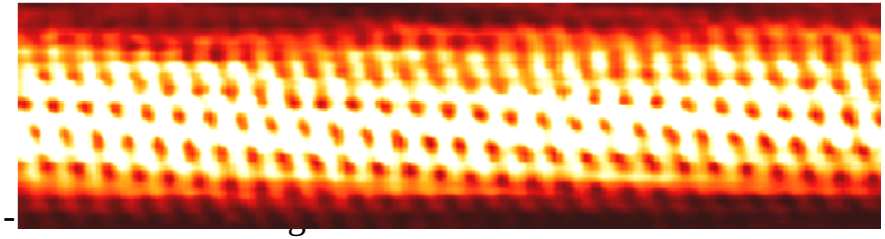
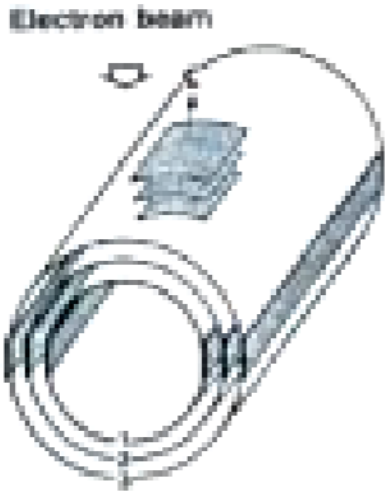


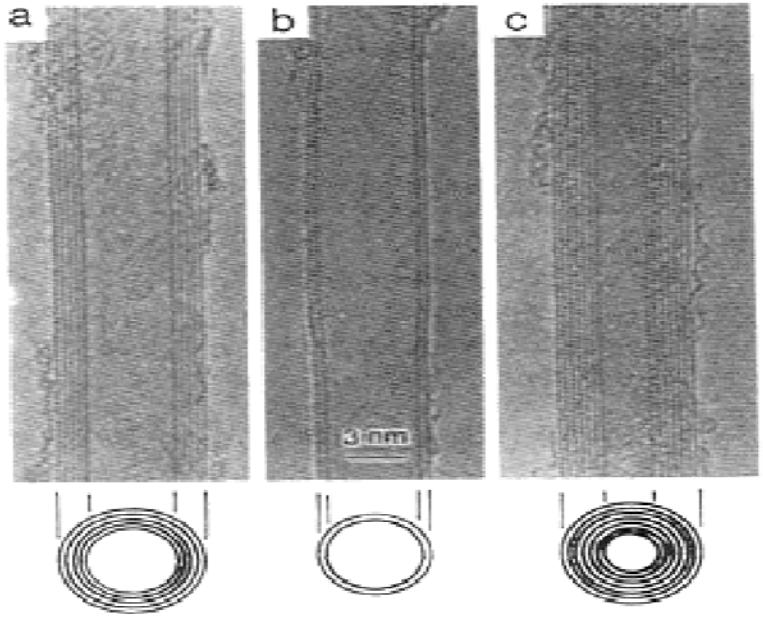
FIGURE 1. A HR image (up) and a schematic model (bottom) of the metallofullerene (empty Gd@C$_{82}$ aligned in SWNT) as an example. The dark spots in the HR image correspond to the encapsulated Gd atoms.

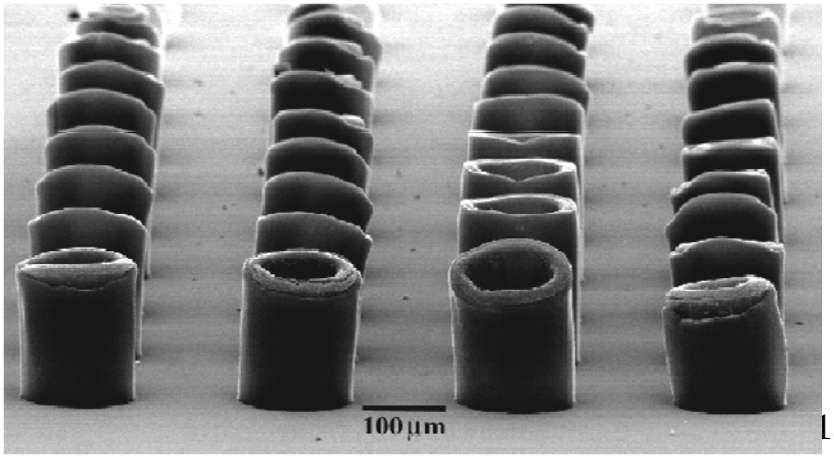


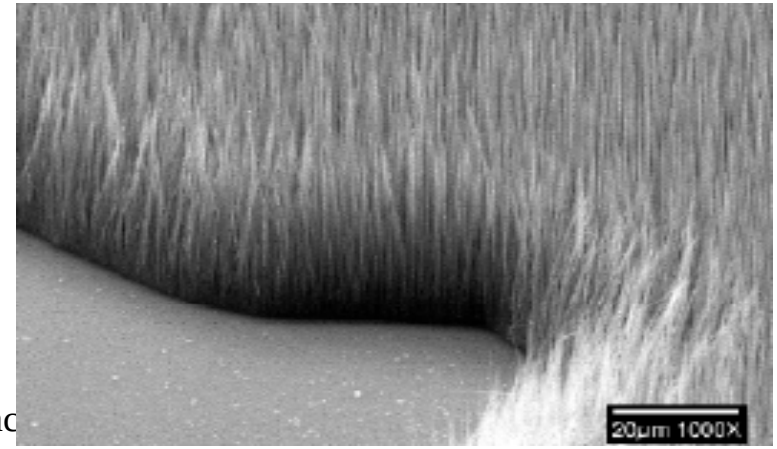


Nanotubs de C de moltes parets: MWCNT









Propietats singulars, úniques

- **SWCNT**
  - **Mecàniques:** mòdul de Young Y =1 – 2 TPa
  - **Elèctriques:** conductivitat σ = 2000 S/cm
  - **Tèrmiques:** gran conductivitat 6000W/mK
  - **CTE:** coeficient de dilatació petit

- Aplicacions: materials més resistents (acer, fibra de C)
- més lleugers
- Bon conductor amb molt poca dilatació
- Materials compòsits amb CNT

3- Fenòmens associats als nanomaterials

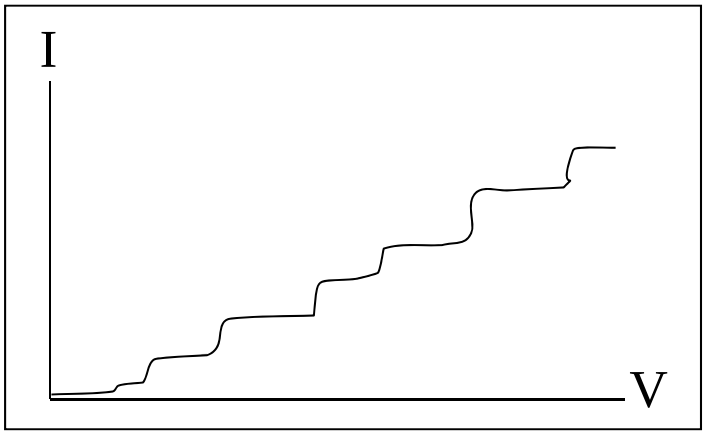
–**Transport de carrega: bloqueig de Coulomb**

–**Els electrons "no xoquen" → R ↓**

–El transport electrònic està quantificat, "a salts":

I(V) escalonada :

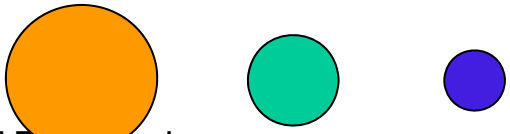
(No llei de Ohm)



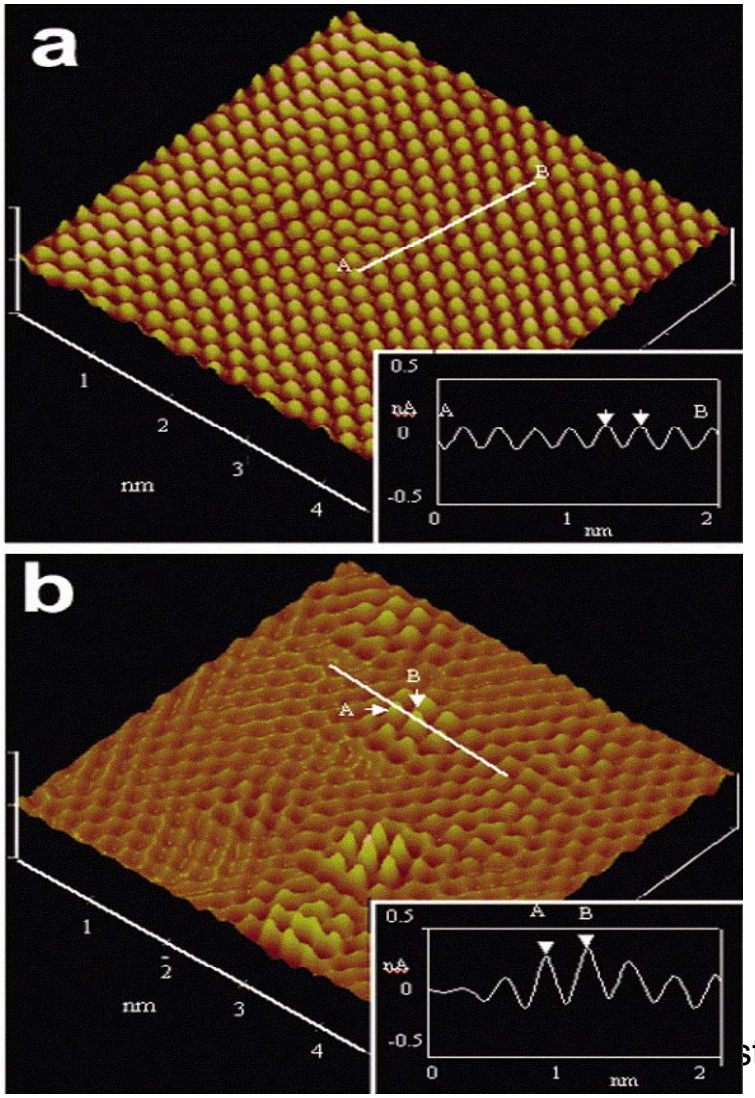
–El color depén de la mida!

en nanopartículas coloidals

en nanoclusters d'or



3- HRTM: Microscòpia Electrònica d'alta Resolució



- Segons la física quàntica:
- de Broglie: $E = hf$

$p = h/\lambda$

$$E = eV = p^2/2m = (h/\lambda)^2/2m$$

$$\lambda = h/(2meV)^{1/2}$$

$\downarrow \lambda \Longleftrightarrow \uparrow V$

4- Tècniques d'obtenció

Descàrrega per arc

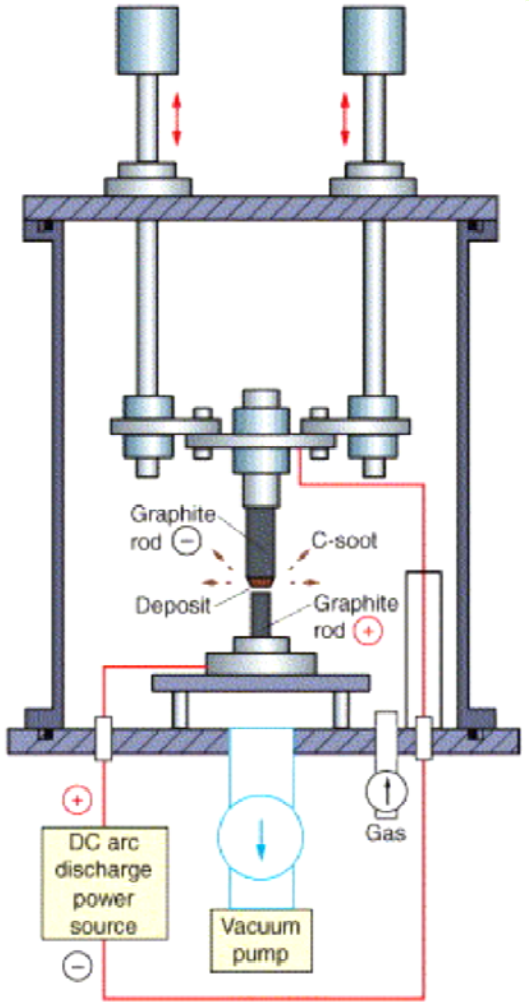


Fig. 1. Schematic diagram of CNT formation apparatus by the arc-discharge

CVD: Dipòsit químic en fase vapor

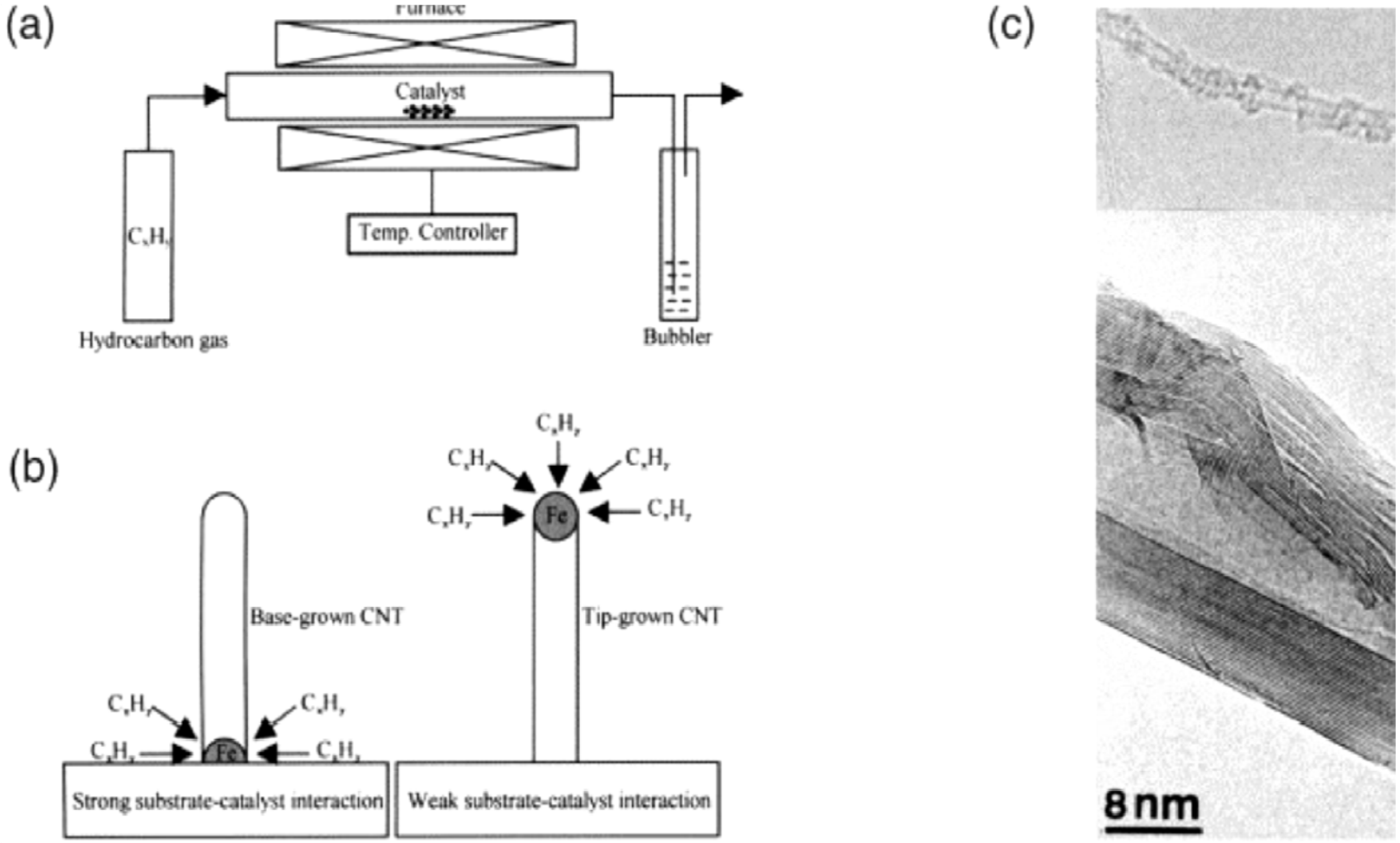


Fig. 6. (a) Schematic diagram of a CVD setup. (b) Probable models for CNT growth. (c) An example of a SWNT and a MWNT grown from camphor via CVD.

Obtenció en un forn làser

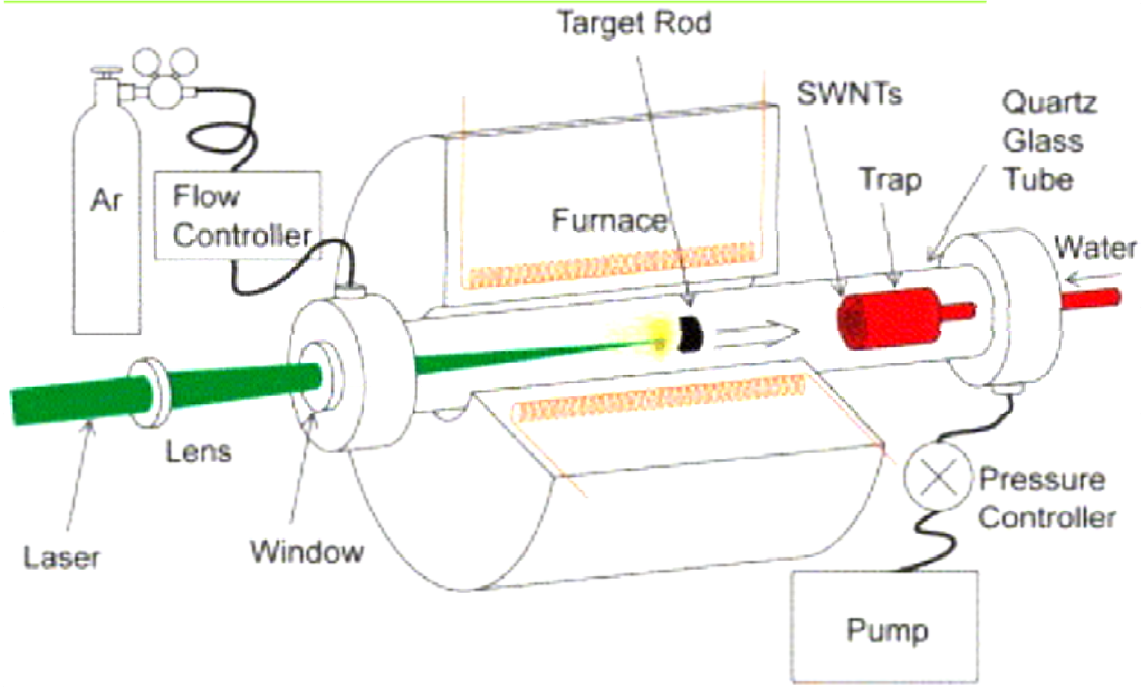
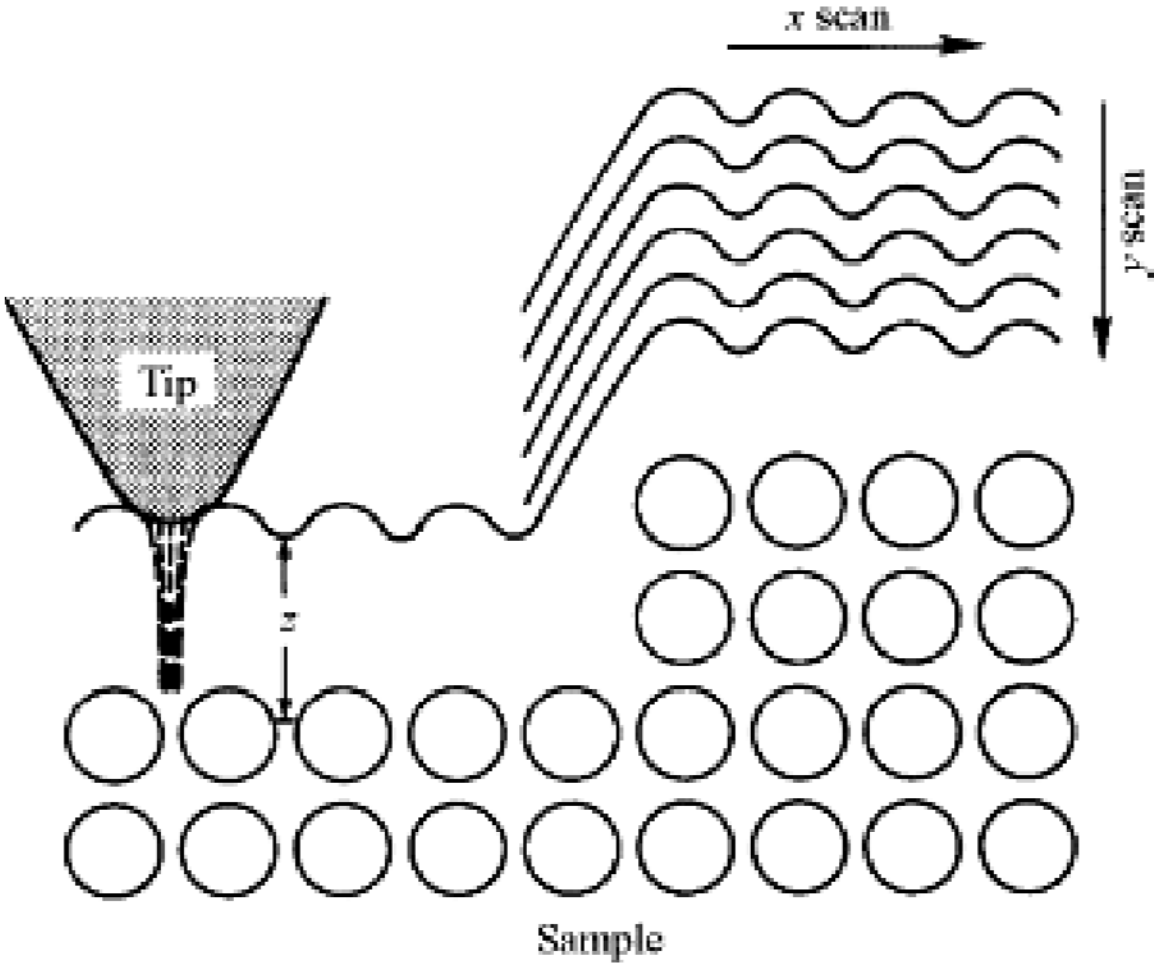


Fig. 5. Schematic diagram of the laser-furnace apparatus.

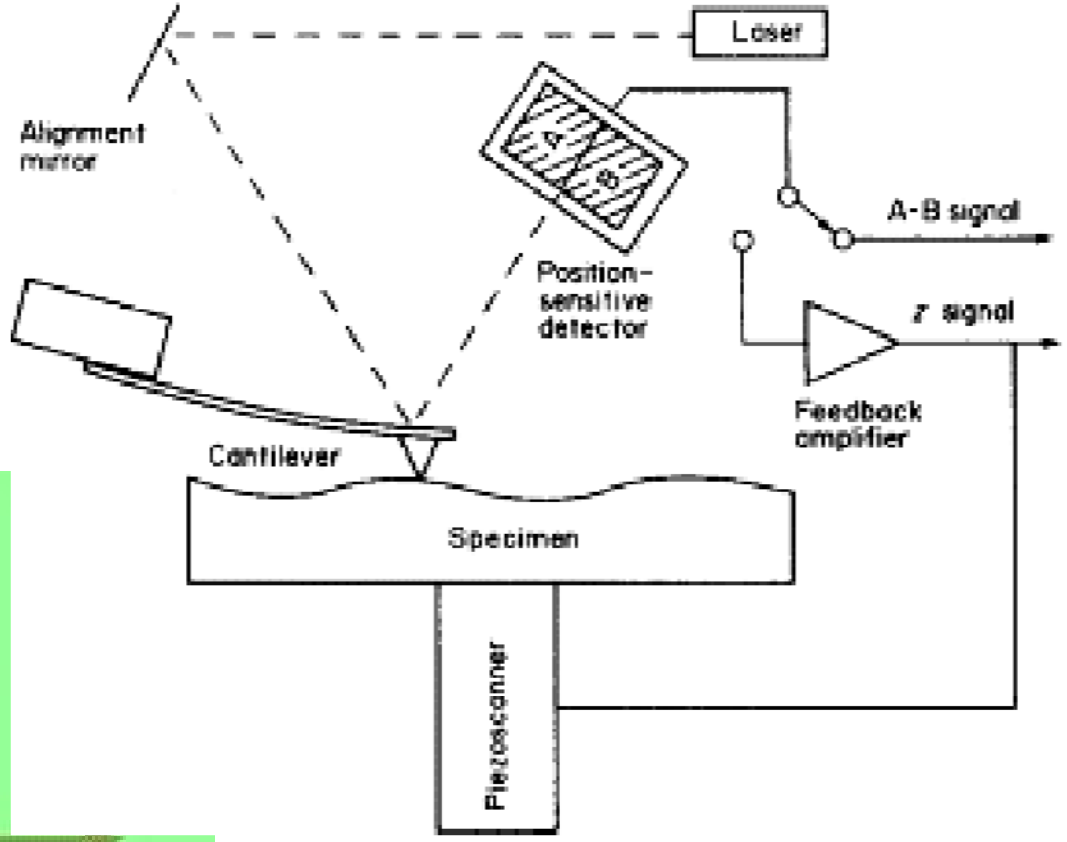
- Tècniques d'observació i de caracterització

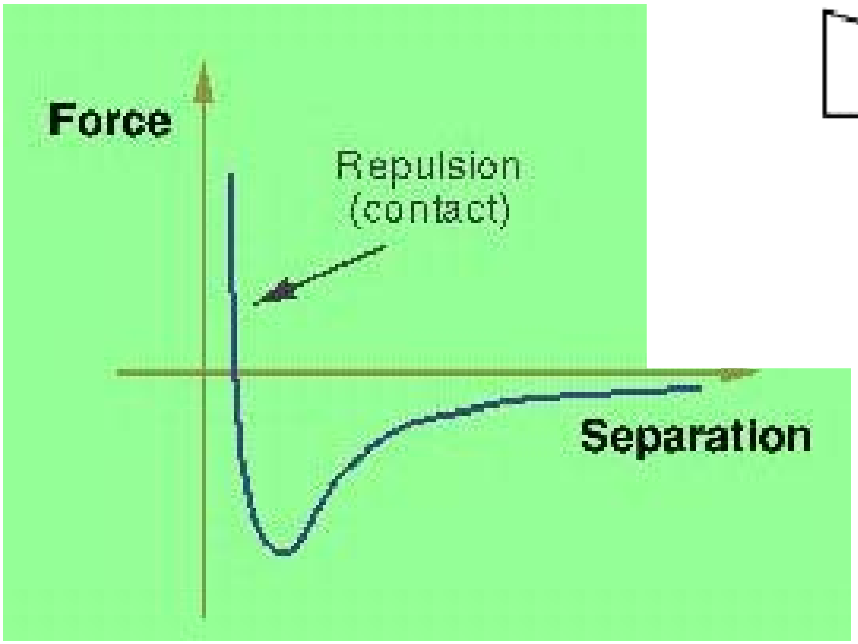
- Microscòpia electrònica:
  - TEM (per transmissió), SEM (d'escombrada)
  - HTRM (d'alta resolució)
  - Difracció d'electrons
- Difracció de raigs x
- Espectroscòpia òptica, UV, IR
- Sincrotró
- Espectroscòpia Raman
- AFM, STM
- Ressonància magnètica

AFM
Microscòpia de Força Atòmica



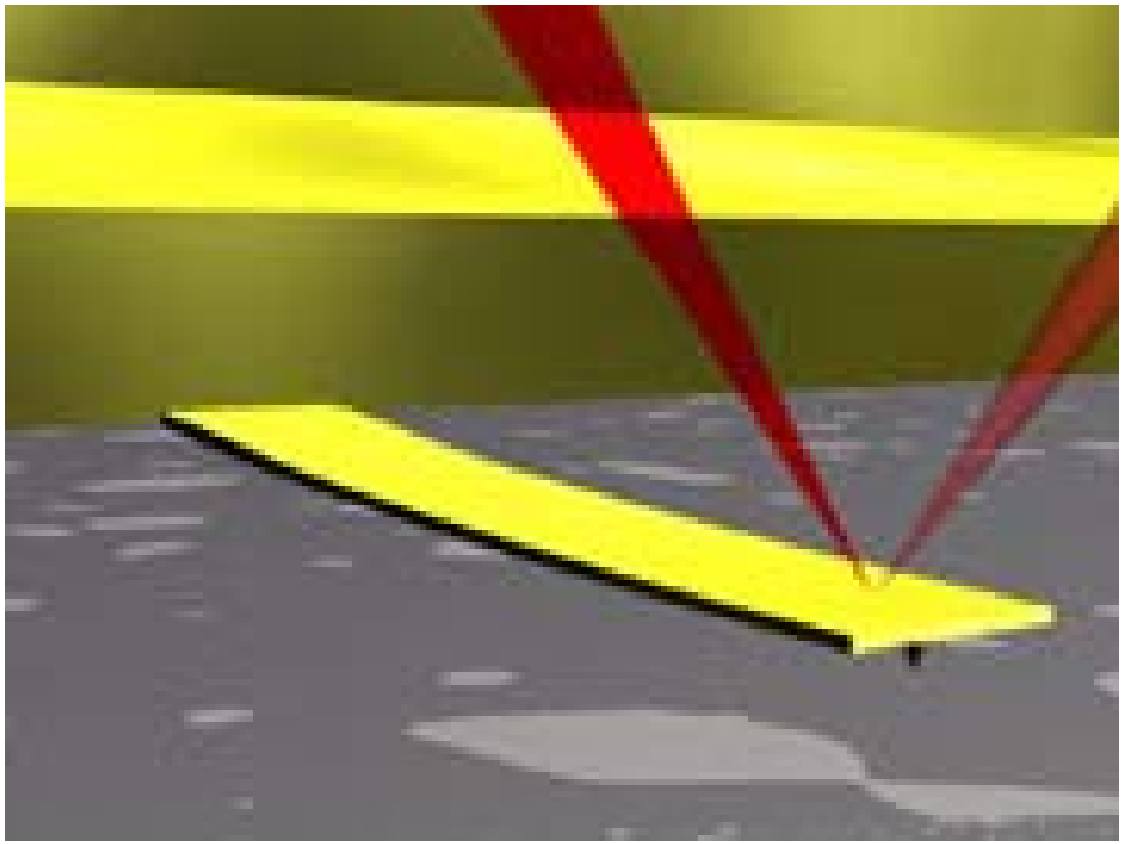
AFM


Laser
Alignment mirror
A
B
A-B signal
Position-sensitive detector
z signal
Feedback amplifier
Cantilever
Specimen
Piezoscanner

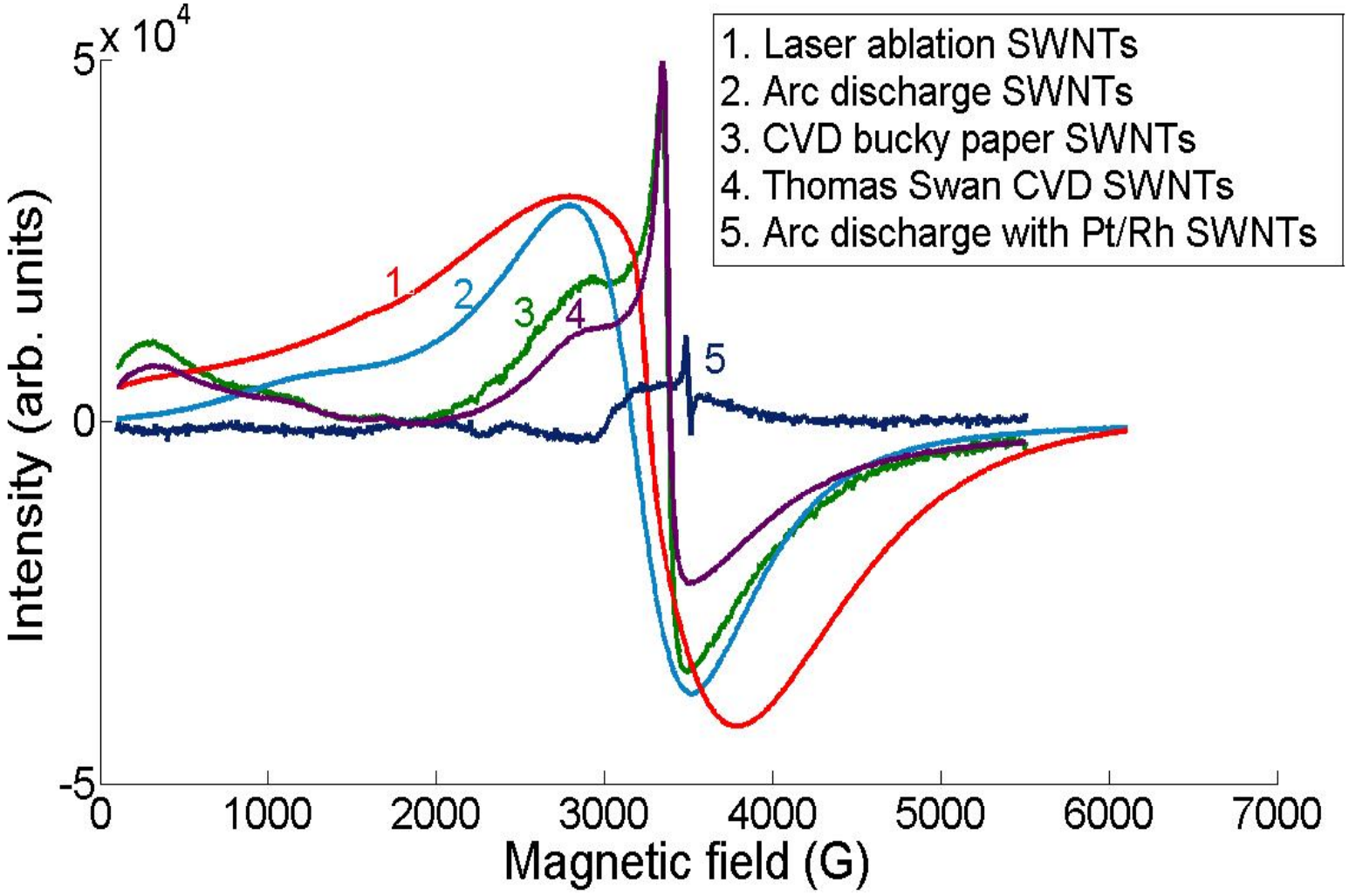

Force
Repulsion (contact)
Separation

AFM
Microscòpia de Forces Atòmiques

- La punta registra la topografia



ESR spectra of SWCNTs obteined by different methods



Aplicacions

- Dispositius electrònics
- Pantalles: “displays”
- Sensors, biosensors
- muscles artificials
- “Nanocompòsits”

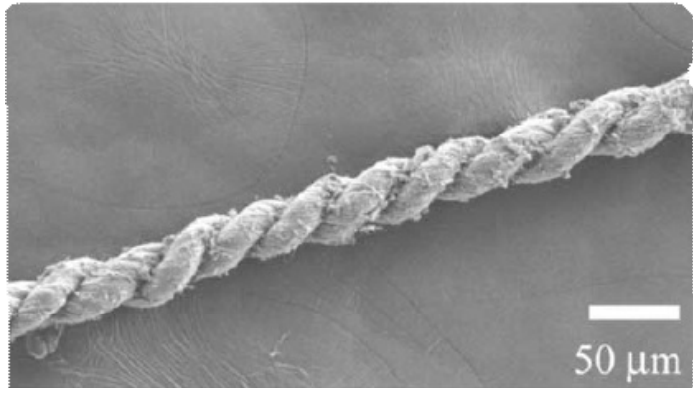
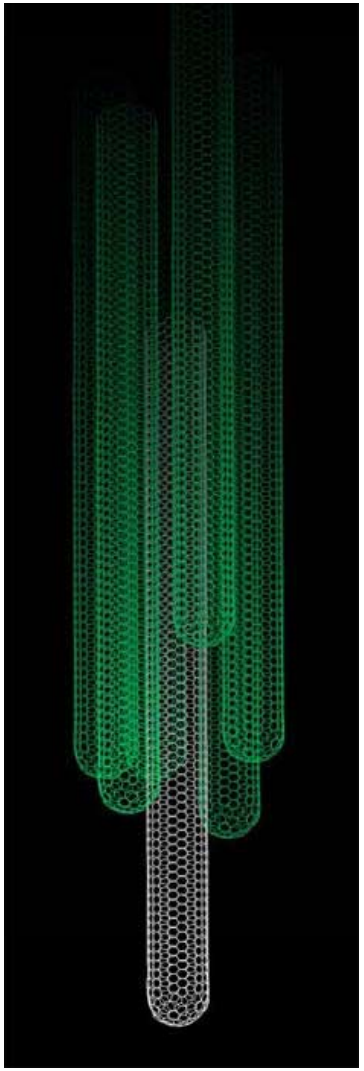
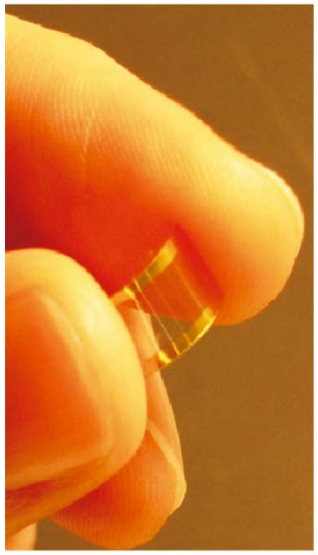


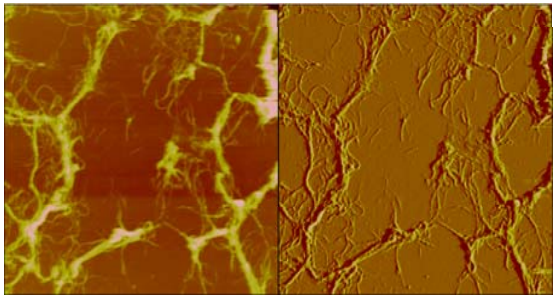
Fig. 14. Micrographs showing the exceptional flexibility of carbon nanotube-based fiber [78].

The Space Elevator Project

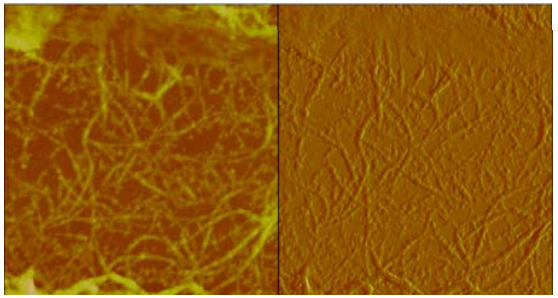


Elèctrodes transparents CNT-Polímer (AFM)

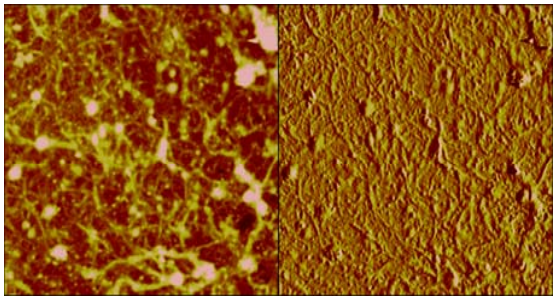




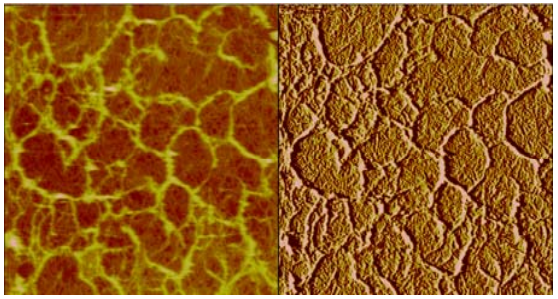
a 15.0µm x15µm



b 5.00µmx5.00 µm



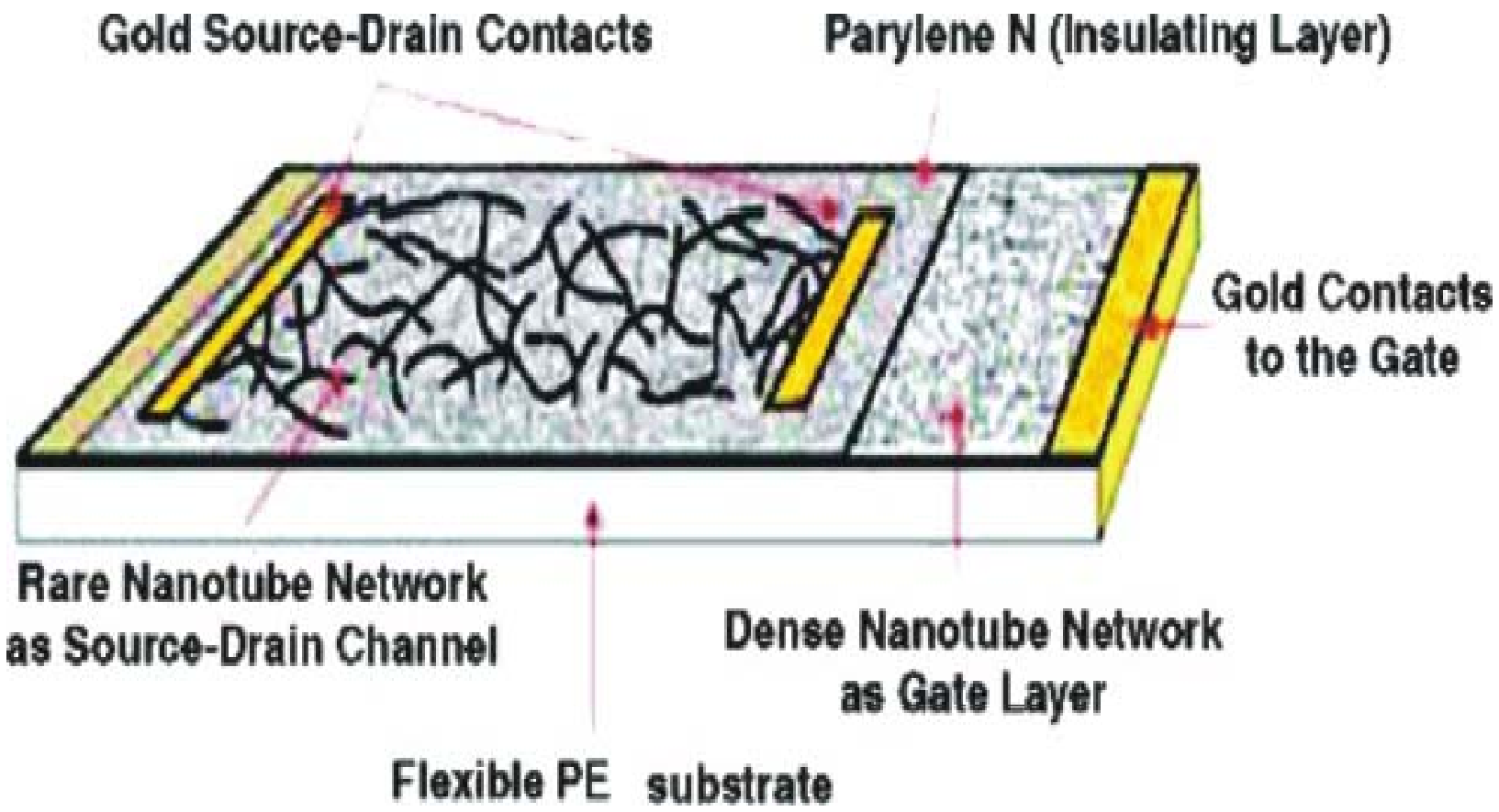
c 15.0 µm x 15.0 µm



d 50.0µm x50.0 µm

Transparent and flexible carbon nanotube transistor

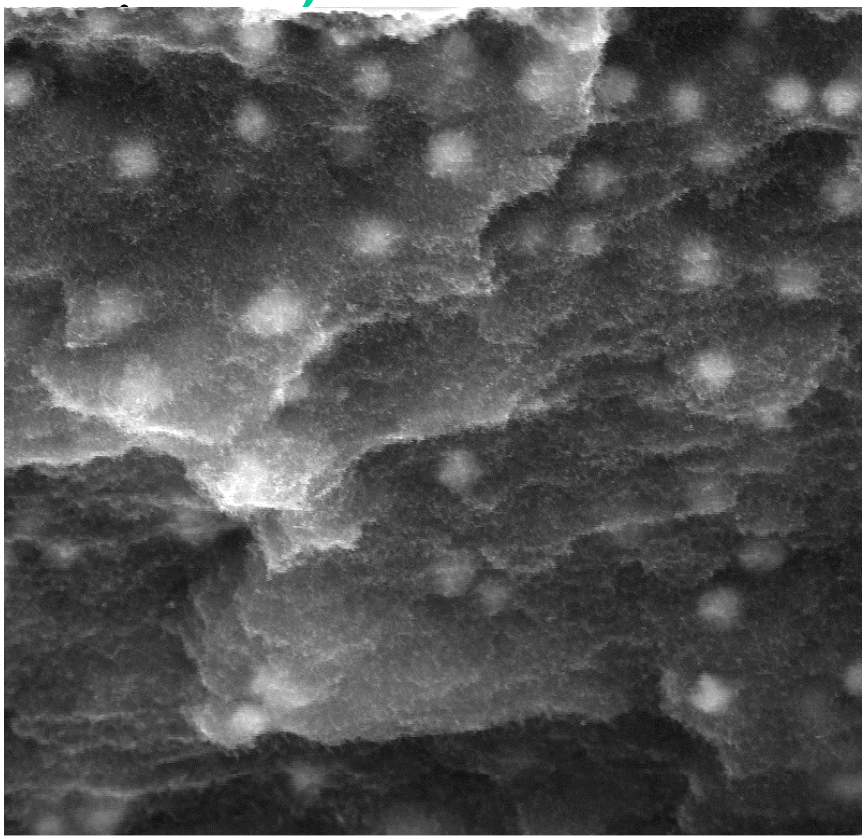
-E. Artukovic, M. Kaempgen, D.S. Hecht, S. Roth, G. Grüner, *NanoLetters, 5, 757 (2005)*


Gold Source-Drain Contacts
Parylene N (Insulating Layer)
Gold Contacts
to the Gate
Rare Nanotube Network
as Source-Drain Channel
Dense Nanotube Network
as Gate Layer
Flexible PE substrate

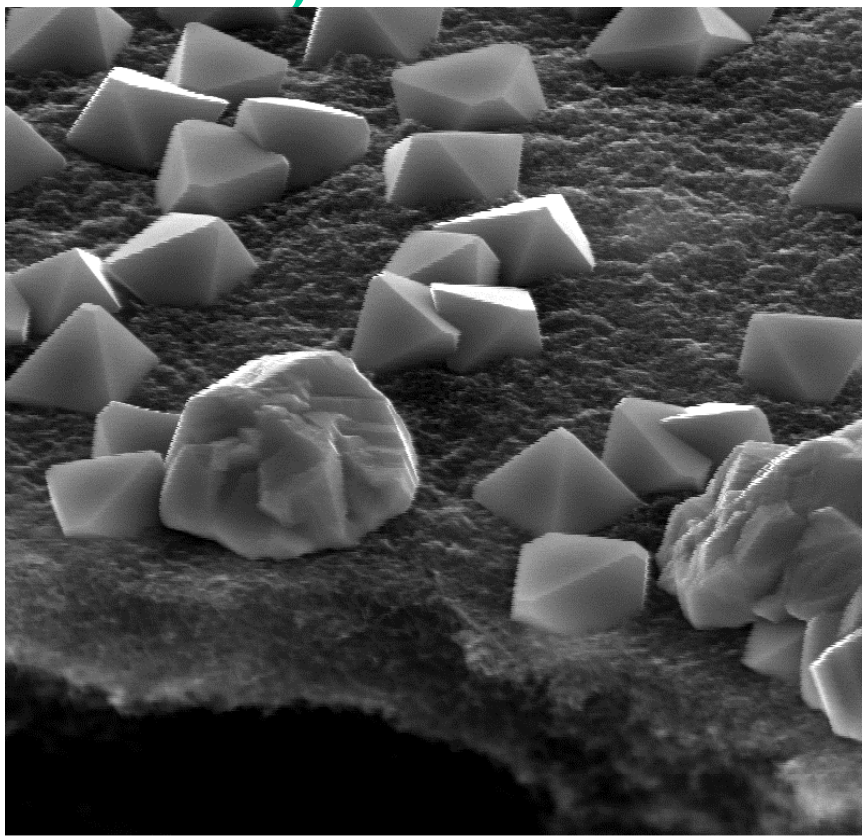
Nanotubs de Carboni - Cu

SEM a 75º de CNT-Cu,

a) 31%w Cu



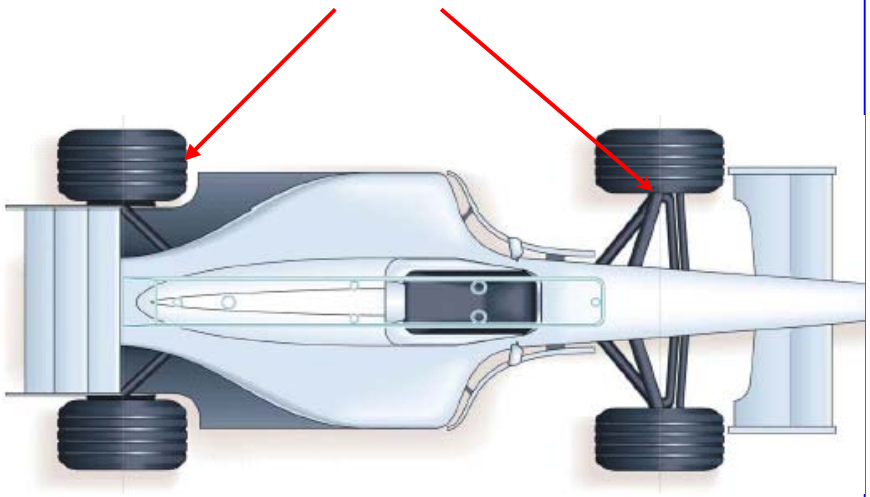
b) 39%w Cu



Materials per a Fórmula 1

- *a. CNT in the spring suspensions*
- *b. Bodyworks*
- *c. Engine*

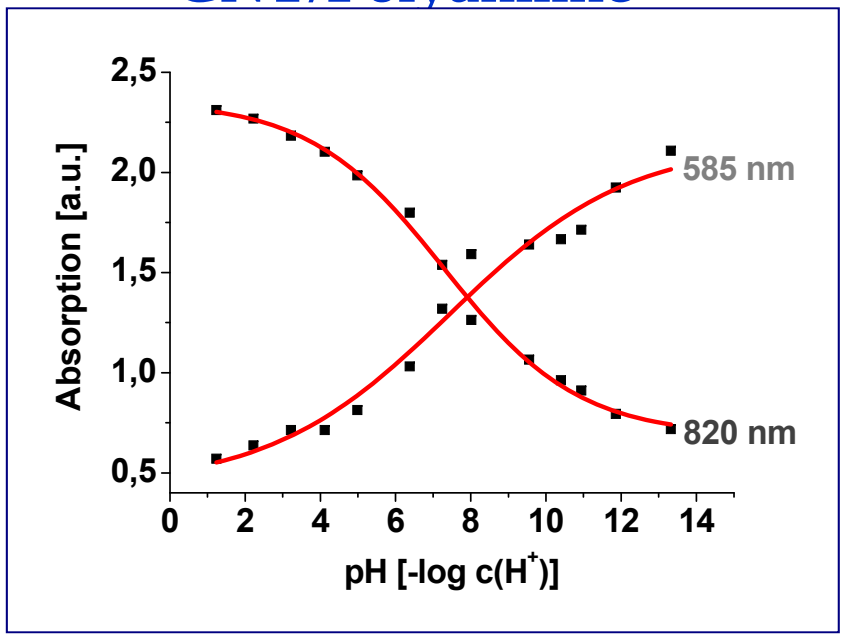
The idea is to make a substitution of the Carbon in the actual Titan/carbon matrix, and replace it by CNT to make an alloy of Ti-CNT.



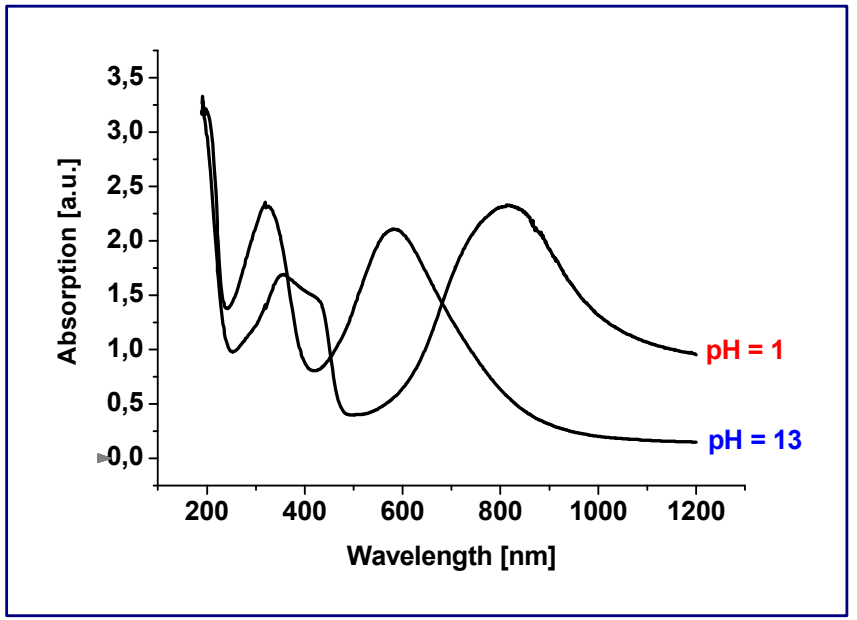
Increase mechanical resistance with less material → weight and section size.

CNT-polyaniline sensor

- **Optical pH response of CNT/Polyaniline**



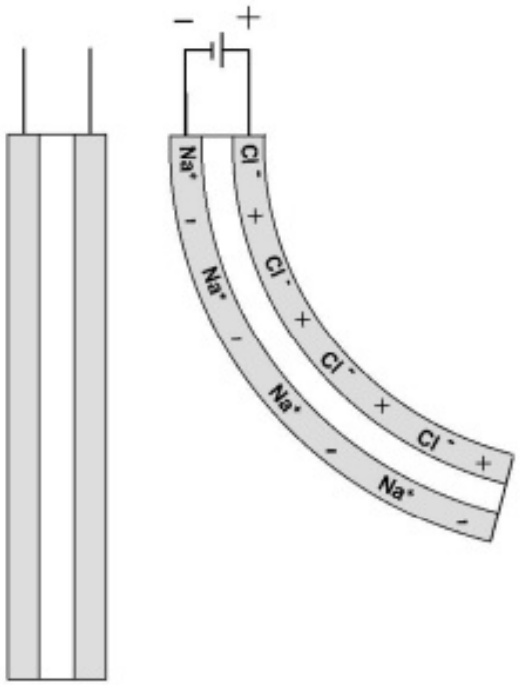
- the absorption and
- the colour change with pH
- It could be used as a sensor just by the colour changes

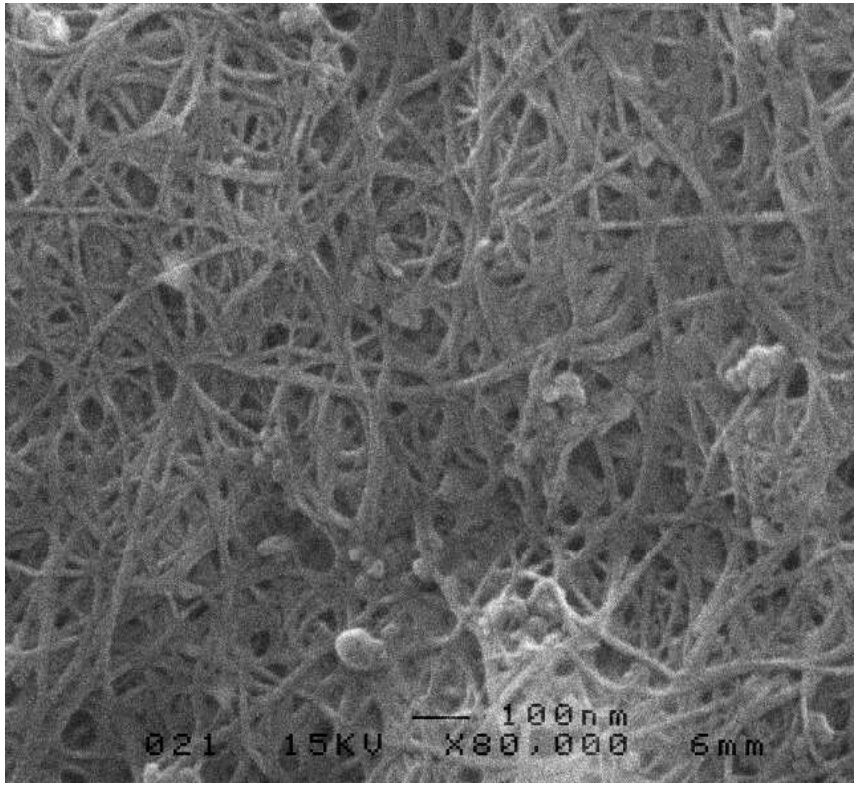


M. Kaempgen, S. Roth; *J. Electroanalytical Chem., 586, 72 (2006)*

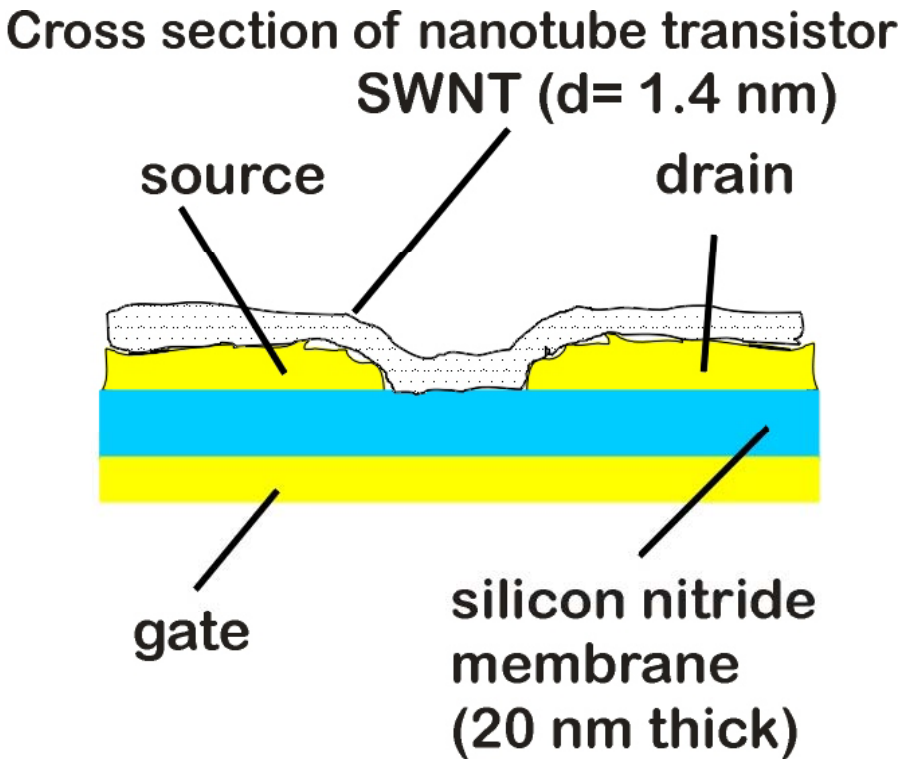
Actuadors: muscles artificials

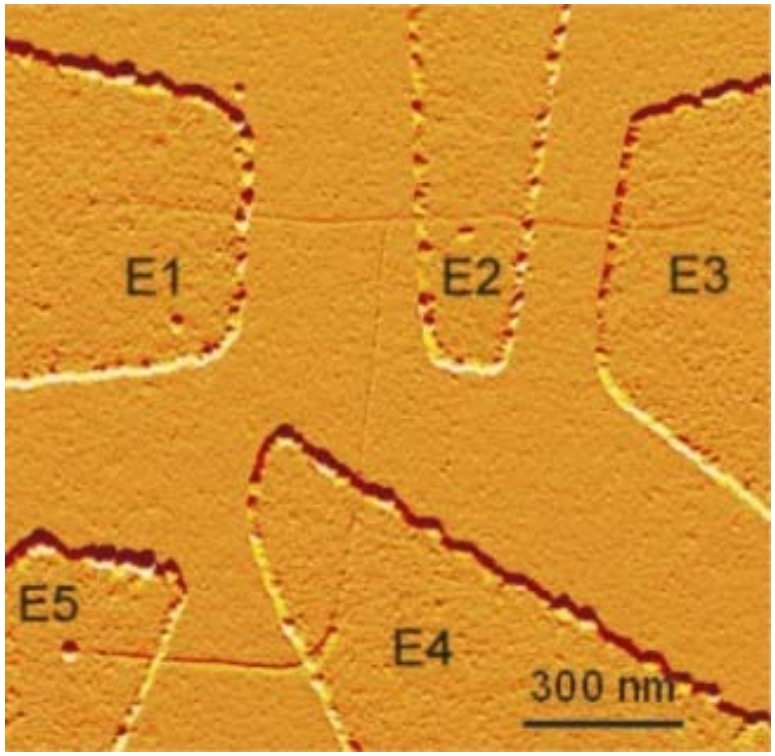
fets amb bucky-paper de CNT, una fibra, o amb un sol nanotub



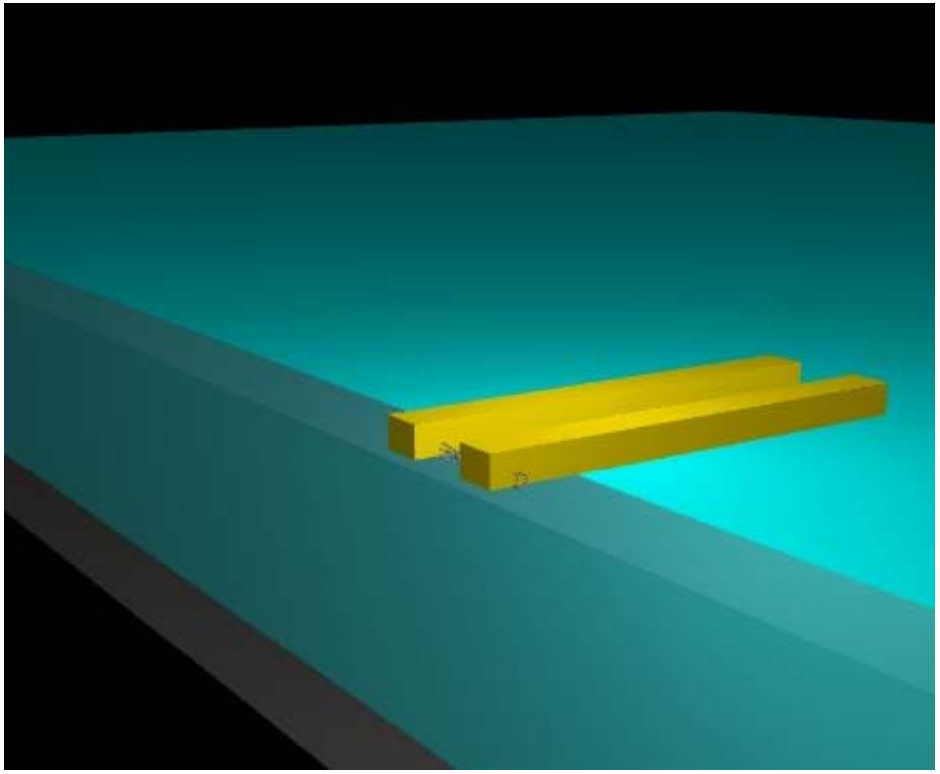


Transistors de CNT





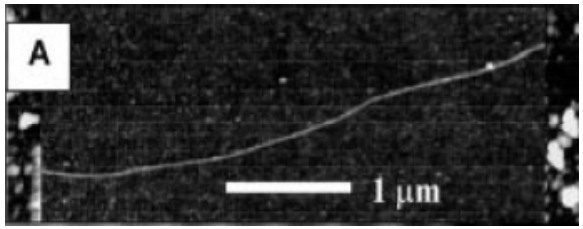
Un sol Nanotub per mesurar nanoforces

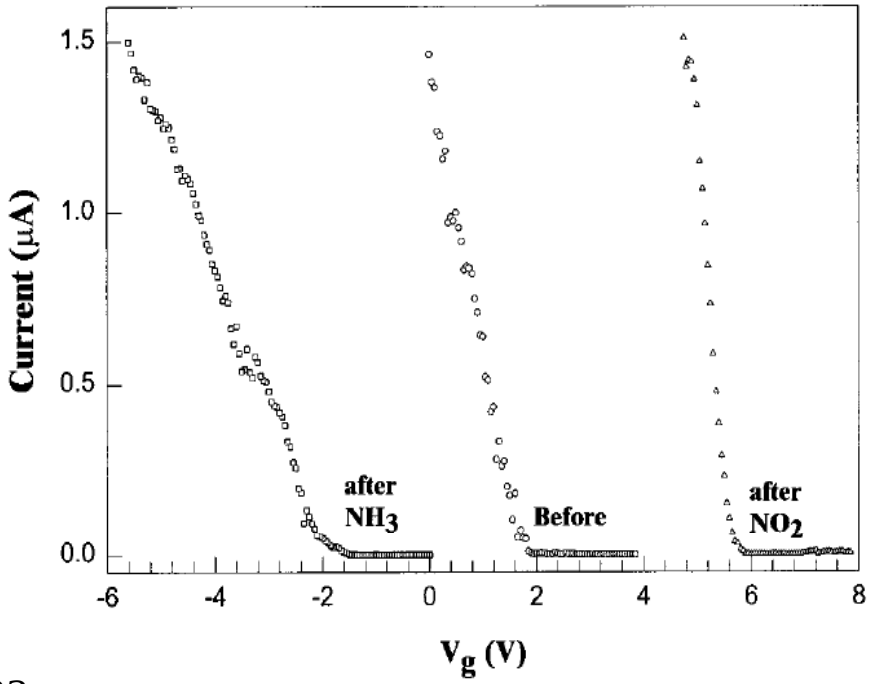


Carbon nanotubes gas sensors

Gas sensor demonstrators utilizing SWCNTs have been fabricated & tested

It was shown that SWCNT can detect NO_2 & NH_3 gases (J. Kong & al; Science **287** (2000) 222)





*Images from: J. Kong & al; Science **287** (2000) 622.*

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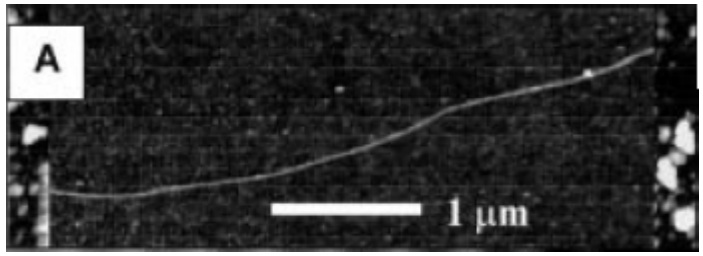
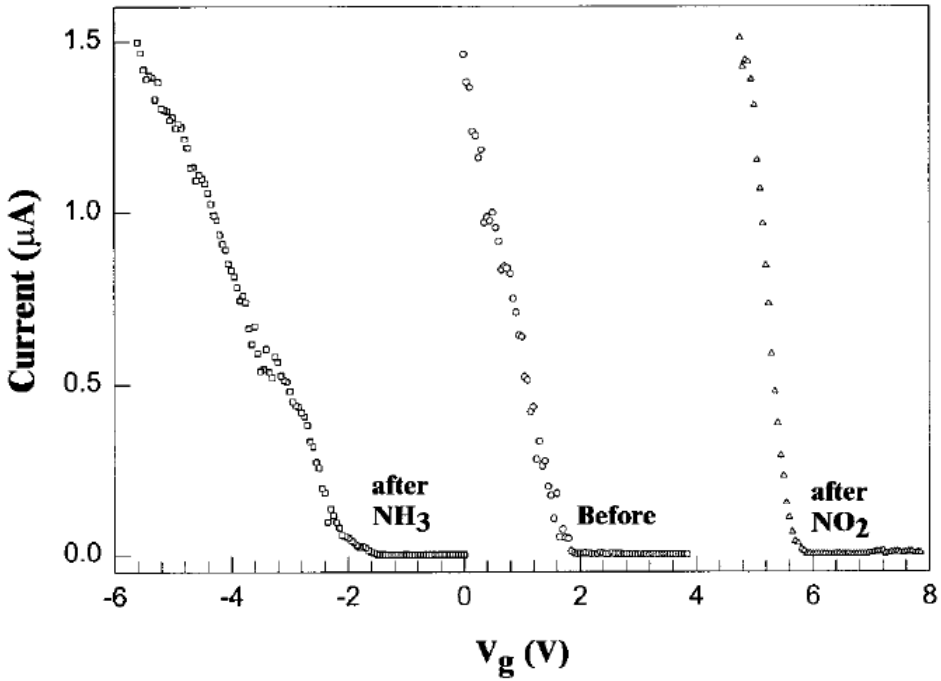
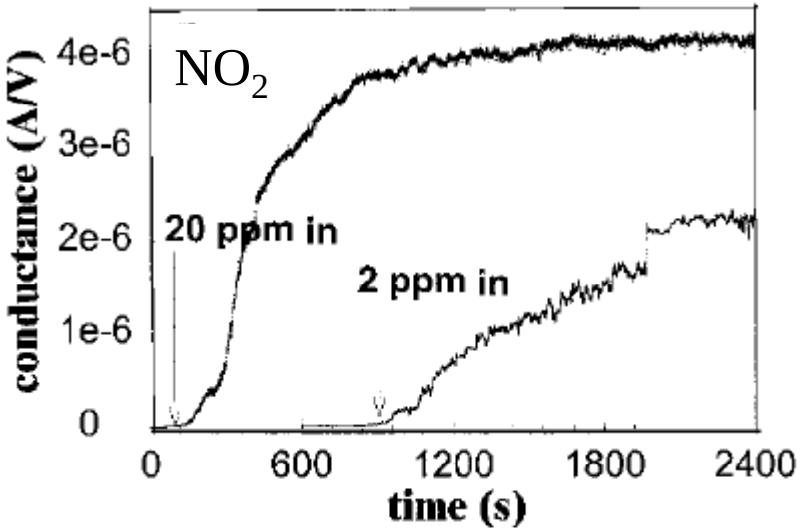
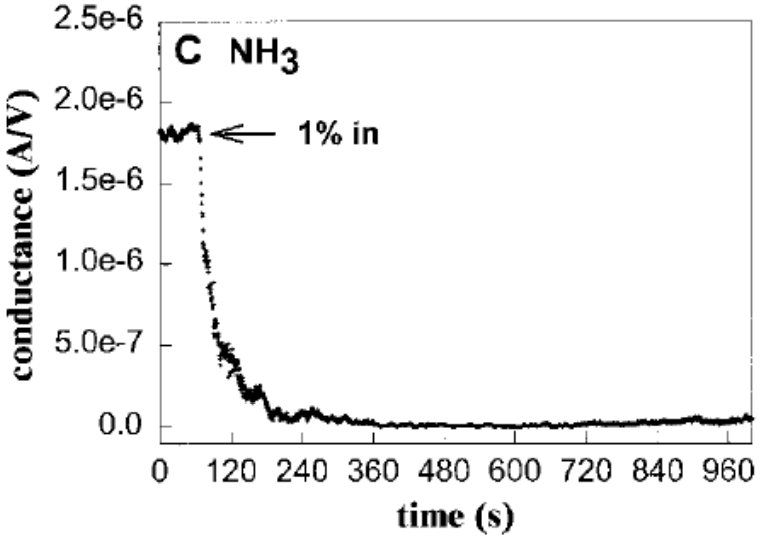
Carbon nanotubes gas sensors









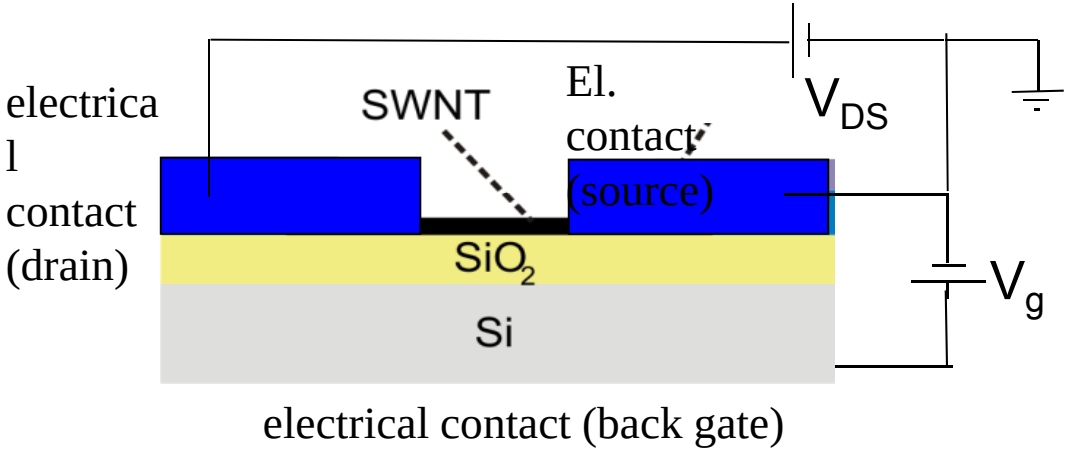
1st NO_2 & NH_3 CNT sensor

J. Kong & al; Science **287** (2000) 222

Carbon nanotubes gas sensors

Our choice: gas sensor based on CNFET

Sketch of gas sensors based on a field effect transistor (FET) configuration with as-grown individual Single Wall Carbon Nanotube (SWNT) as the active channel.



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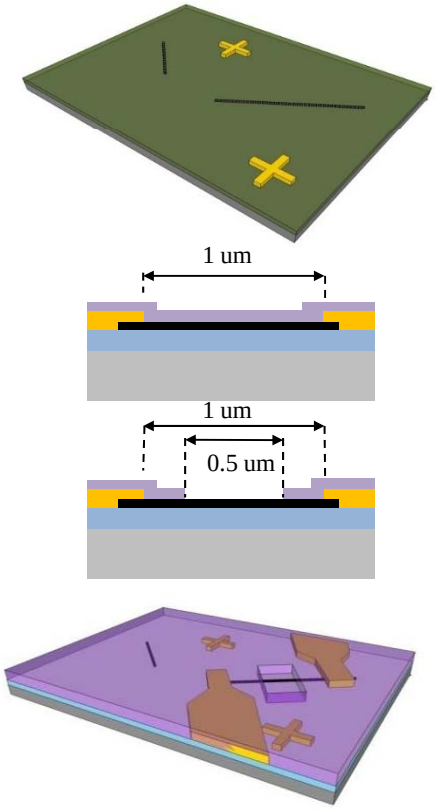
Fabrication of CNFET devices

1/

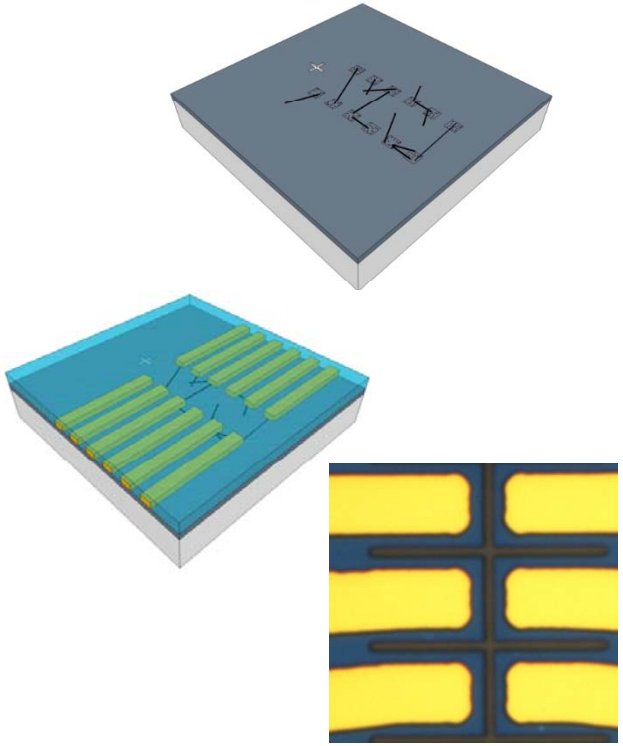
SWCNT FETs fabricated by e-beam lithography.



Moritz Mattmann & Wei Liu
NMS ETH Zurich

2/

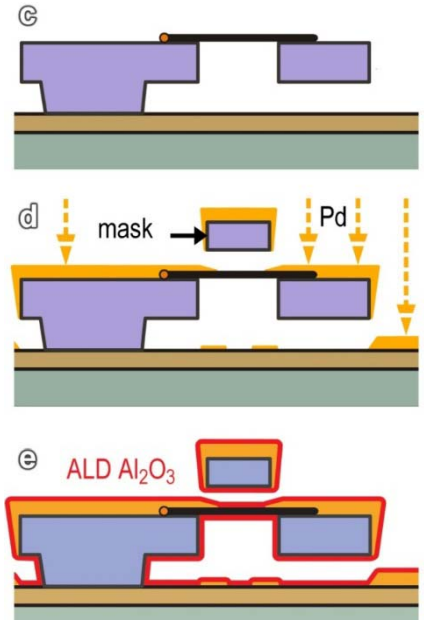
SWCNT FETs multi device array fabricated by photolithography.



Lukas Durrer & Kiran Chkkadi;
NMS ETH Zurich

3/

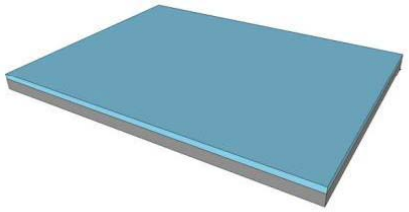
Suspended SWCNT



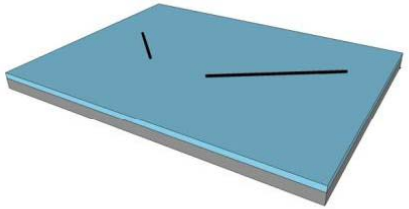
M. Muoth et al., pss (b)
248 (2011) 2664
MNS ETH Zurich

ETH Zurich

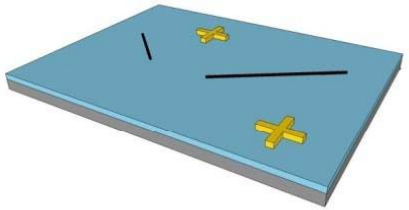
1/ Fabrication of CNFET devices by e-beam lithography



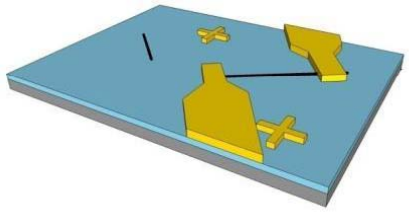
1) Highly doped Si substrate with 100 nm SiO_2.



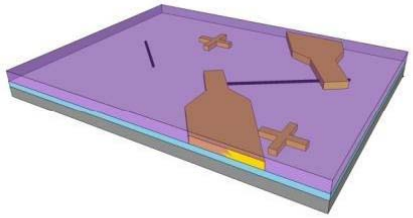
2) Synthesis of SWCNTs on SiO_2 from Ferritin based catalysts in CVD process.



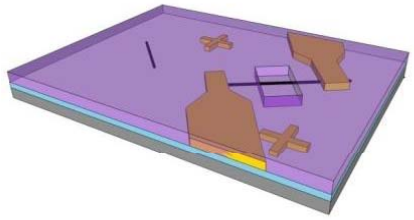
3) Deposition of metal markers and localization of SWCNTs by AFM.



4) Deposition of metal leads to electrically contact SWCNTs.



5) Passivation of the device by ALD Al_2O_3.

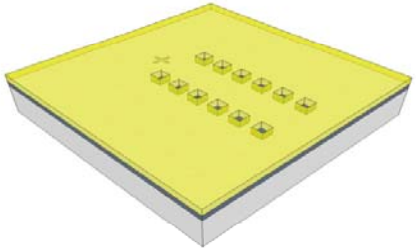


6) HF or H_3PO_4 wet etching.

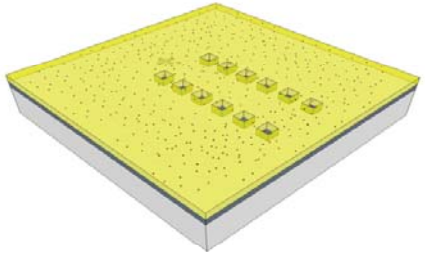
M. Mattmann, MNS ETH Zurich

ETH Zurich

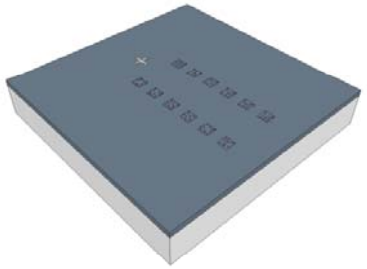
2/ Fabrication of CNFET devices by photolithography at MNS ETH Zurich



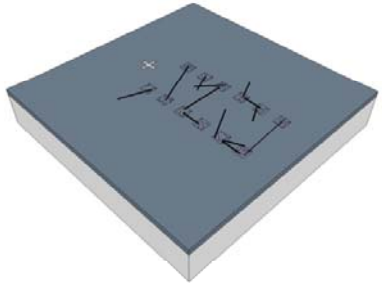
Islands
in photoresist



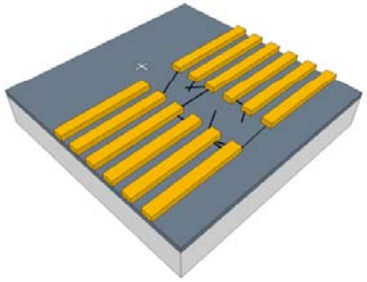
Deposition of ferritin



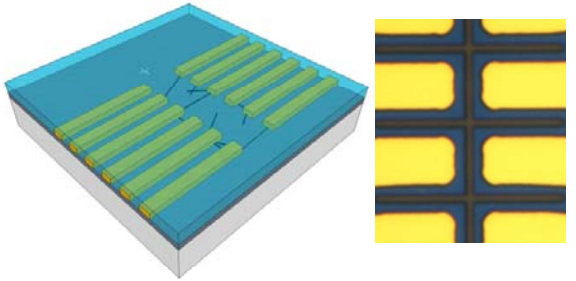
Lift off photoresist



SWCNTs growth



Deposition of electrodes



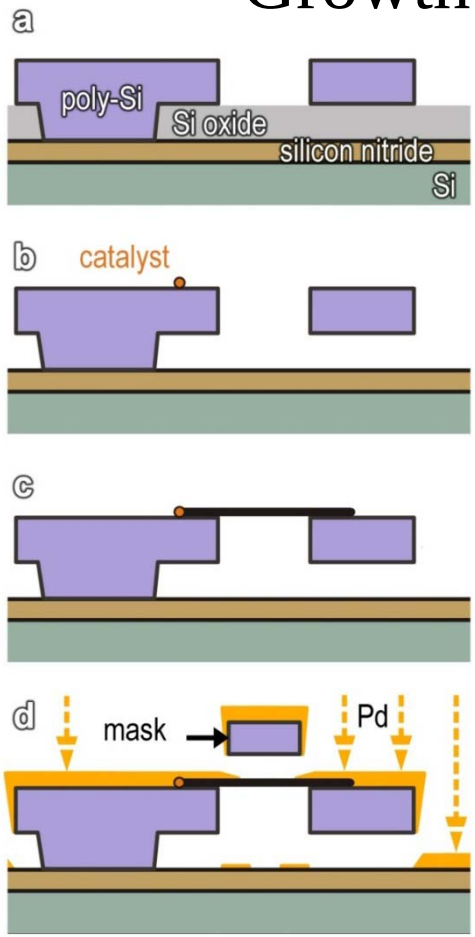
ALD of passivation
layer (Al_2O_3)

K. Chikkadi, et al., Procedia Engineering **47** (2012) 1374 – 1377

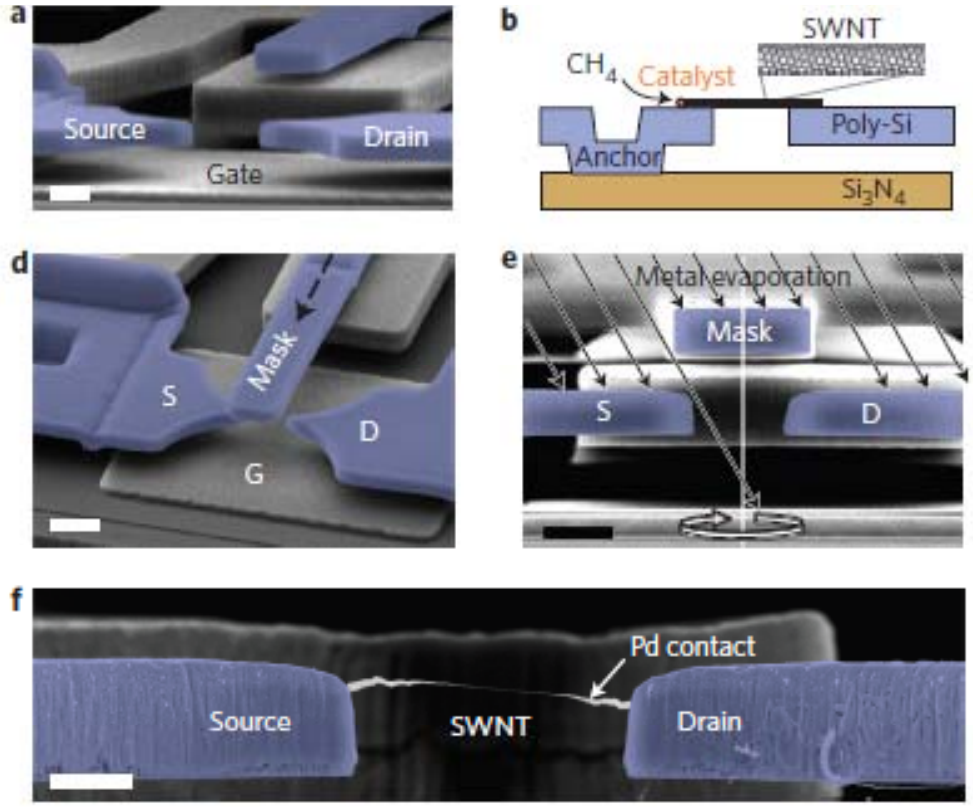
ETH Zurich

3/ Fabrication of CNFET devices / resist residual contamination free process

Growth of suspended SWCNT @ MEMS



M. Muoth et al., pss (b) **248** (2011) 2664

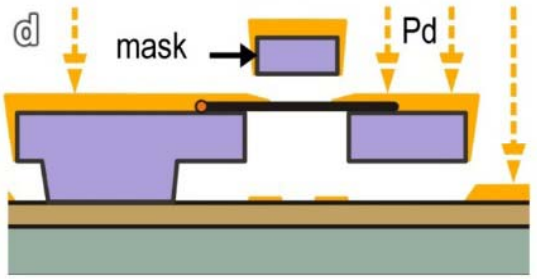


M. Muoth et al.; Nature Nanotechnology **5** (2010) 589

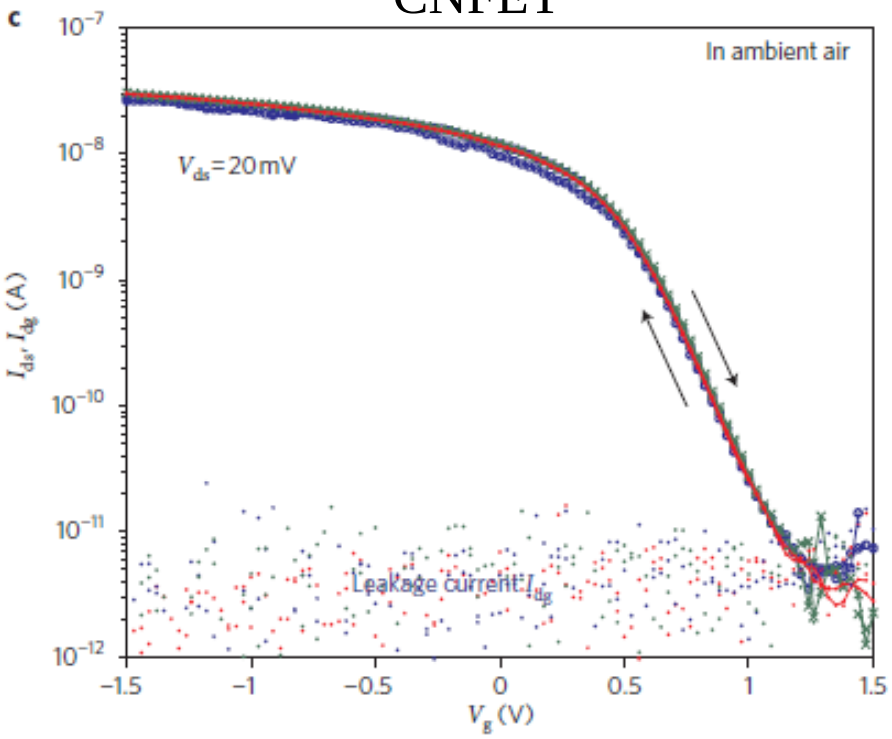
ETH Zurich

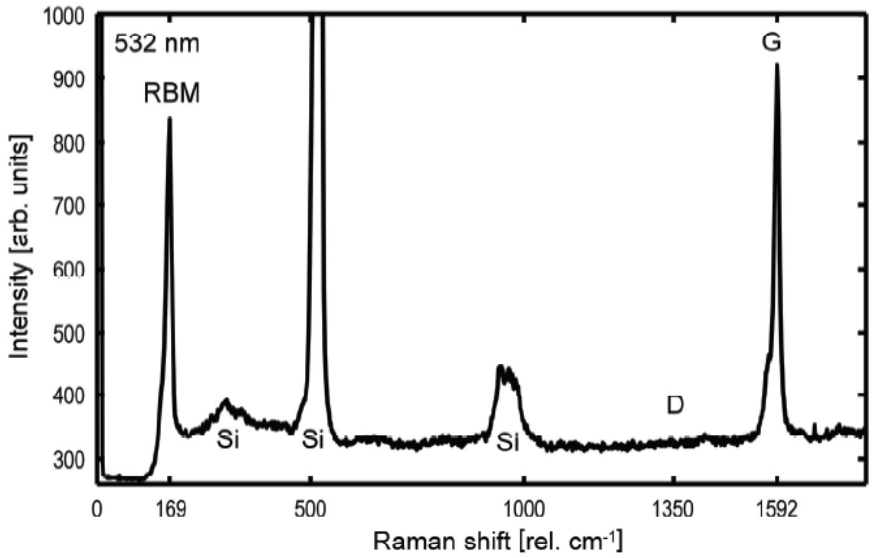
3/ Fabrication of CNFET devices / resist residual contamination free process

Growth of suspended SWCNT @ MEMS



CNFET





M. Muoth et al.; Nature Nanotechnology; **5** (2010) 589

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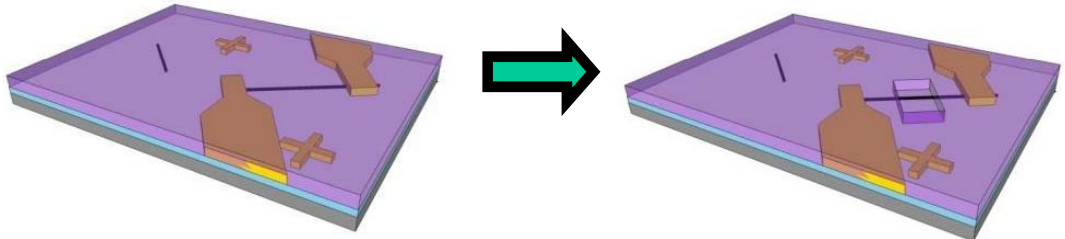
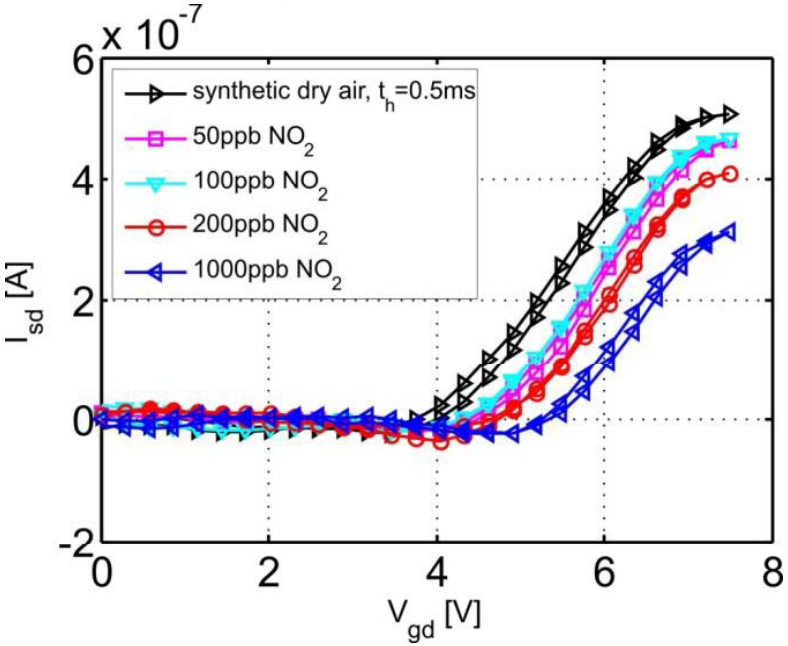
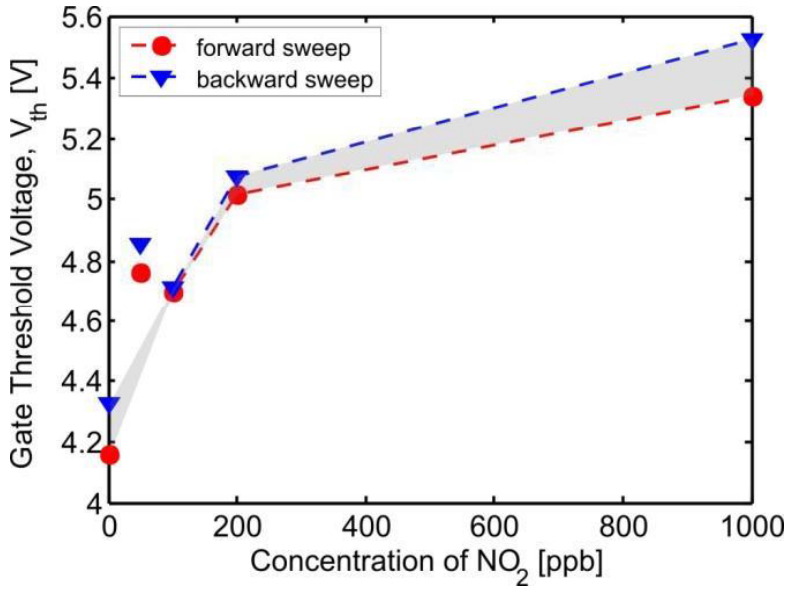
NO_2 gas sensors based on individual SWCNT FET

NO_2 detection in dry air





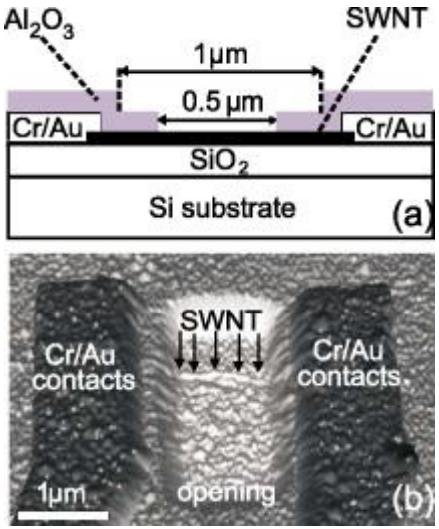


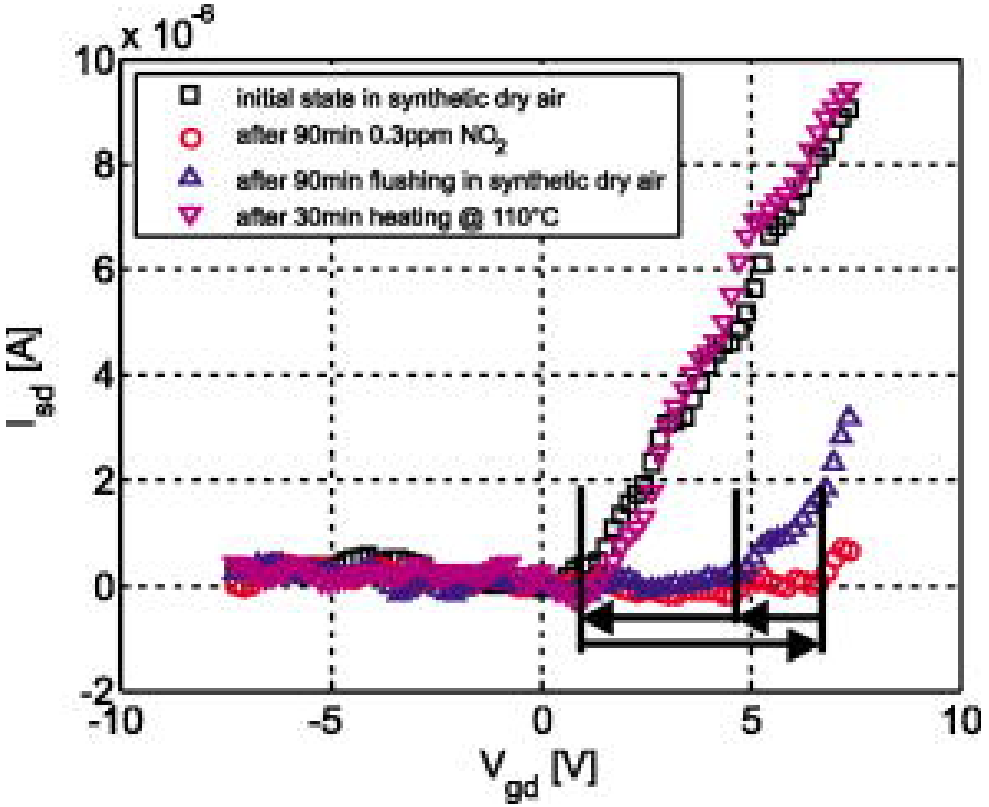
- Positive shift of the gate threshold upon exposure to NO_2.

Mattmann *et al.* Nanotechnology 2010; **21:** 185501.

ETH Zurich

Recovery of partially passivated CNFET NO_2 sensor





Sensor recovery after 30min @ 110°C.

Mattmann *et al.*, *Appl. Phys. Lett.* 94, 183502 (2009)

Col·laboradors

- **Departament de Física Aplicada, Campus Nord**
  - Jordi Pérez-Puigdemont
  - Jordi Figueras
  - Aida Abiad-Monge
- **Max-Planck-Institut fkf, Stuttgart**
  - U.Dettlaff-Veglikovska
  - M. Kaempgen
  - S. Roth
- **ETH Zurich**
  - Miroslav Haluska

Departament de Física Aplicada

Thank you for your attention!

GRACIES!