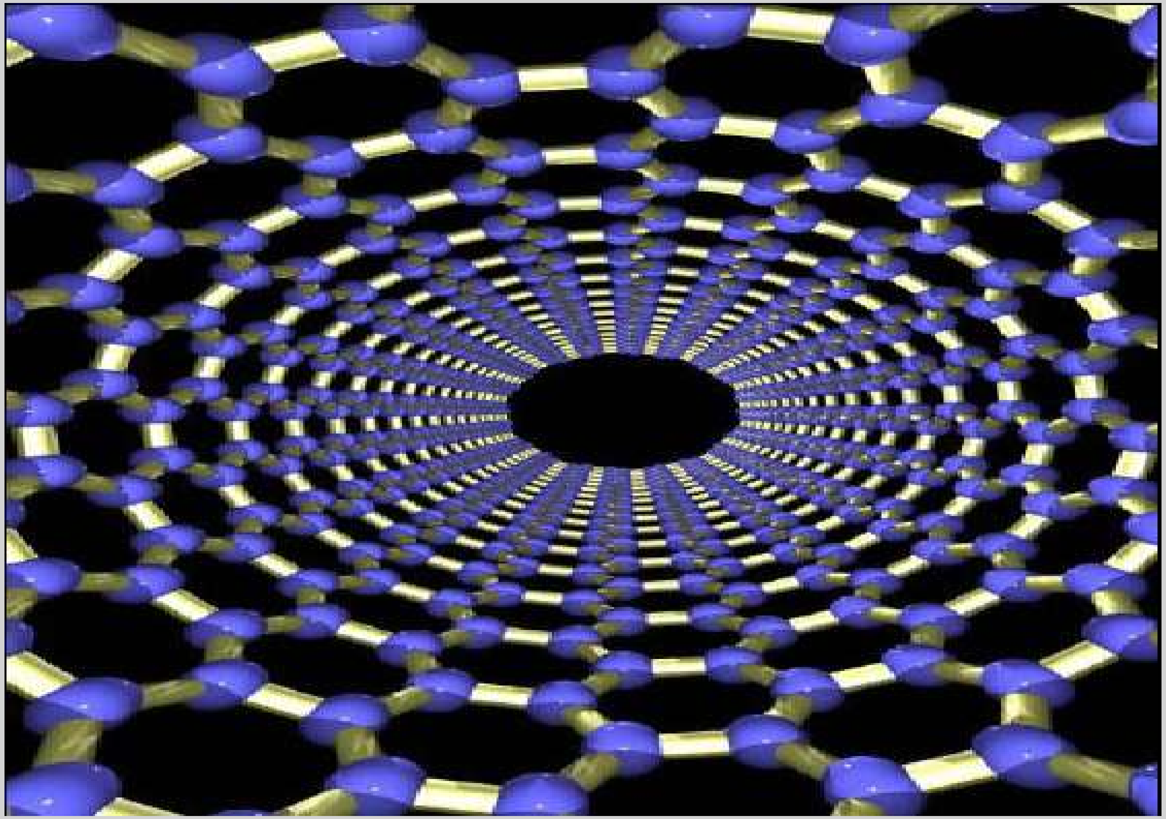
The World of Carbon Nanotubes



Presentation by Jan Felix Eschermann

at JASS05 from March 31st to April 9th, 2005

Outline

- Introduction
- Physical Properties
- Manufacturing Techniques
- Applications
- Outlook

unless stated otherwise all information taken from M.S. Dresselhaus, G. Dresselhaus, Ph. Avouris: Carbon Nanotubes. Springer: Berlin, Heidelberg, New York; year 2000.

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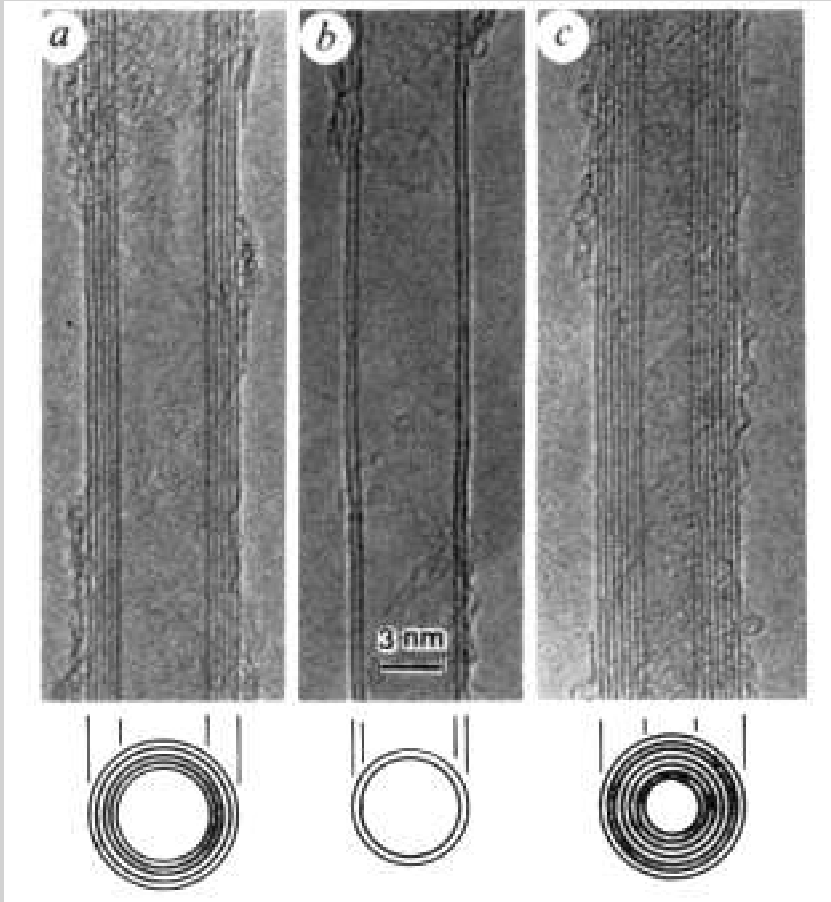
Introduction: History I

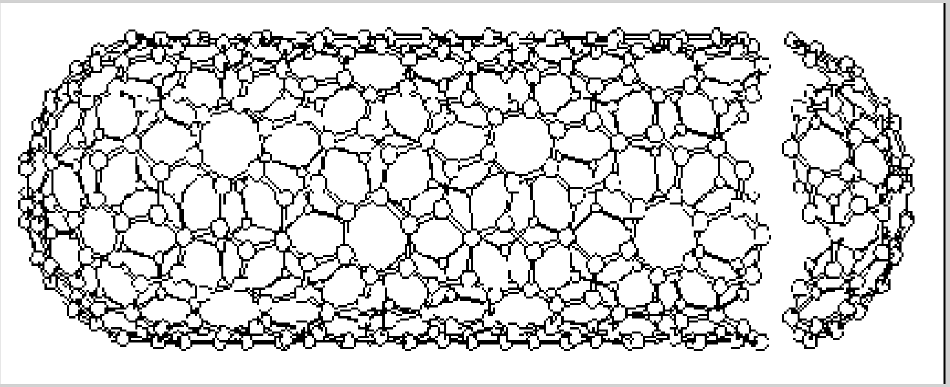
- systematic study of small carbon filaments since 1970s: *"What is the minimum size of a carbon fibre?"* (Kubo, 1977)
- **1991:** CNTs discovered by Iijima at NEC Laboratory in Tsukuba, Japan
- multi wall Nanotubes (MWNT), diameter < 10 nm



TEM images of first CNTs.

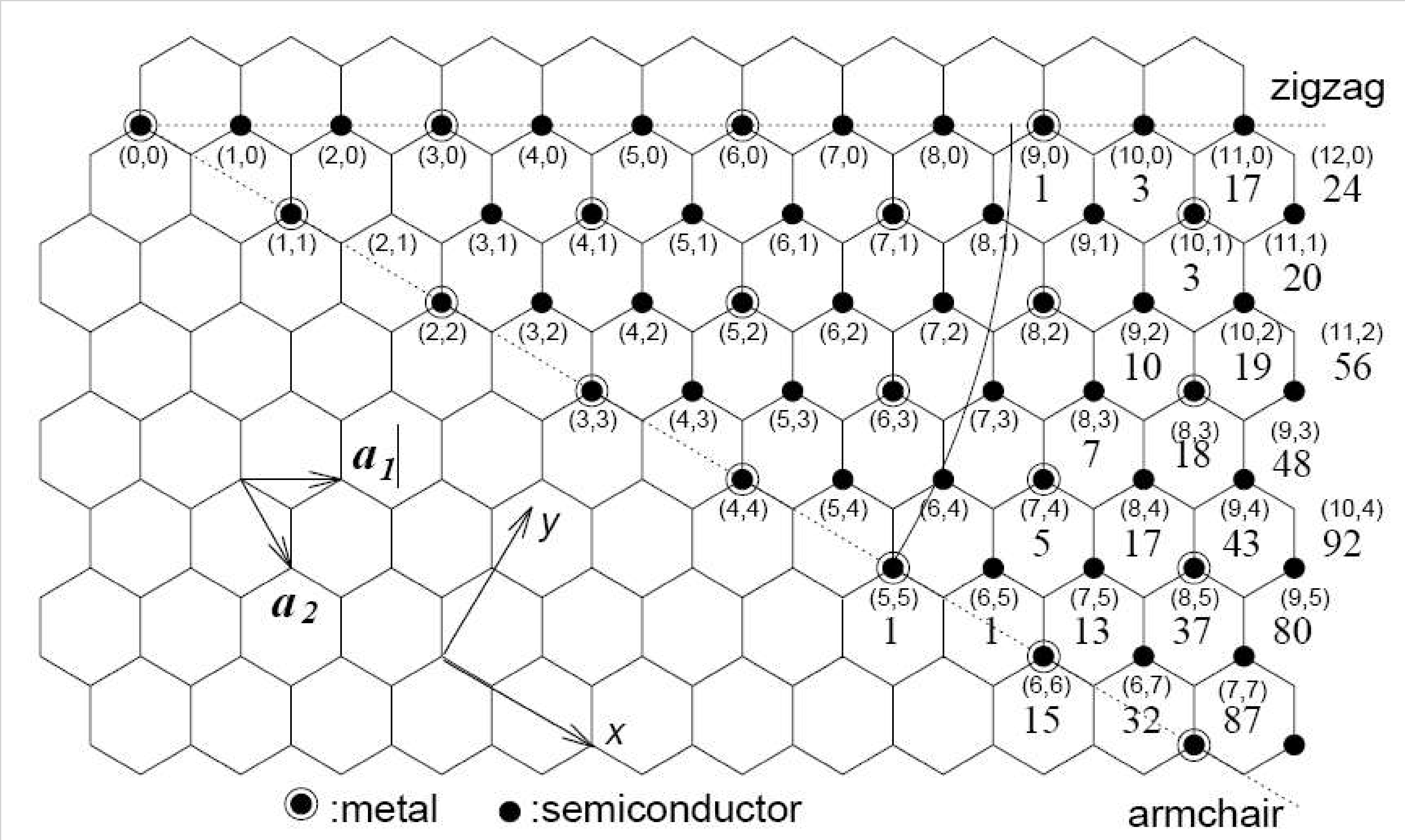
Introduction: History II

- research driven by one-dimensional quantum effects
- **1992:** semiconducting and metallic behavior predicted for single wall nanotubes (SWNT), verified in **1998**
- **1993:** first SWNTs (NEC and IBM Almaden Laboratory, CA)
- more fundamental, important for theoretical studies



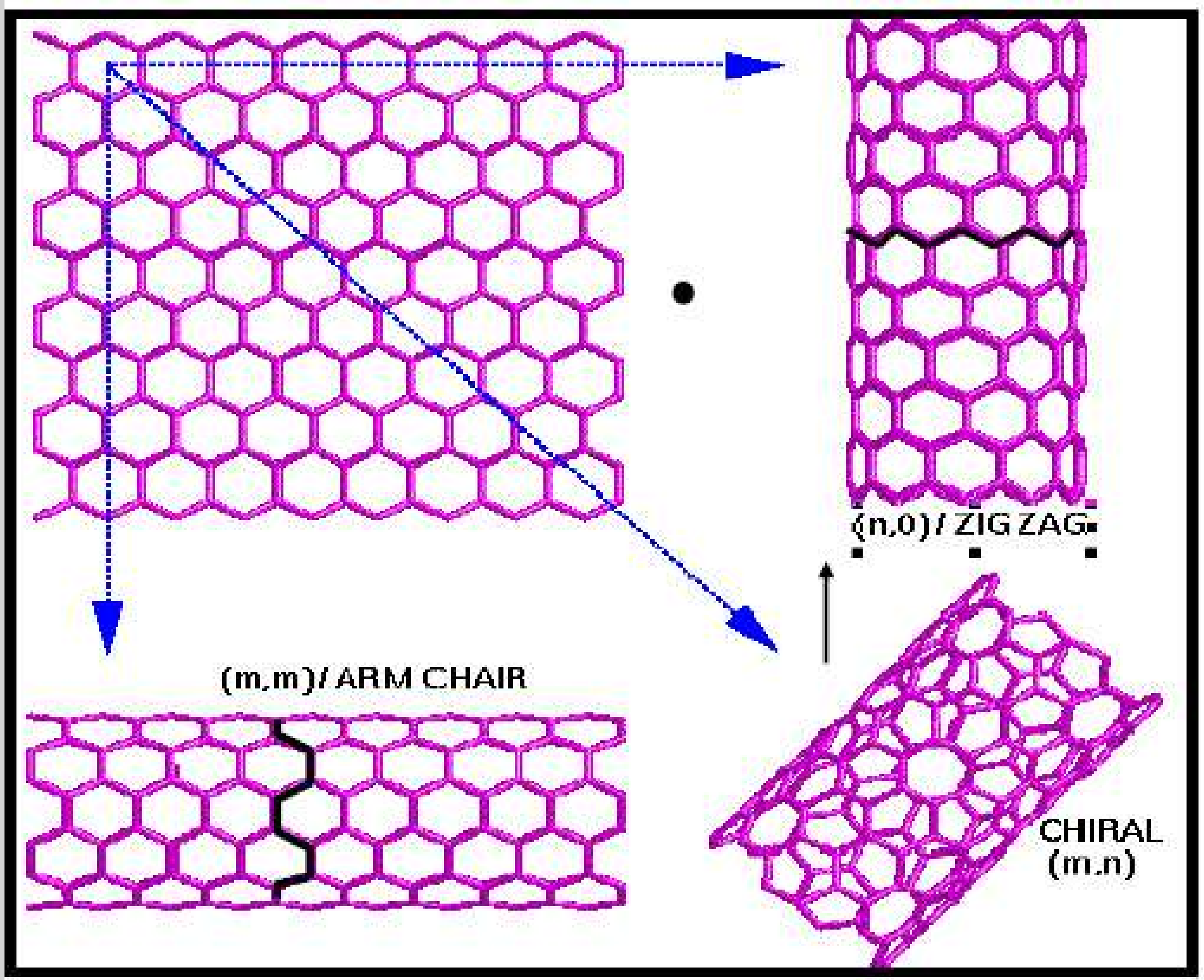
Structure of chiral single wall CNT (IBM Website)

Introduction: From Graphene to CNTs



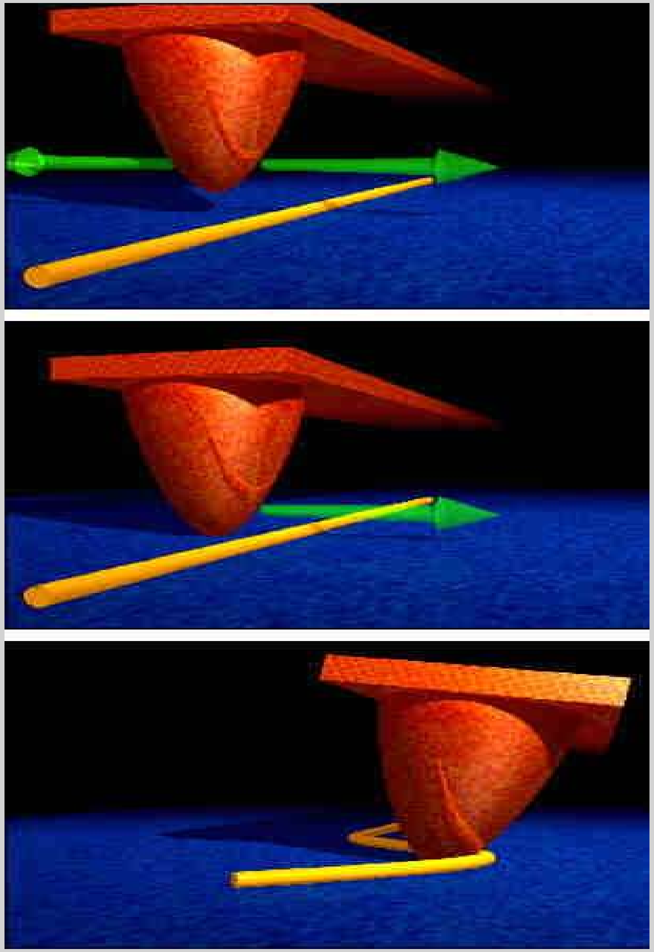
chiral vectors $C = n \cdot a_1 + m \cdot a_2$ for different CNTs → (n,m)

Introduction: Different Types



Introduction: Mechanical Properties

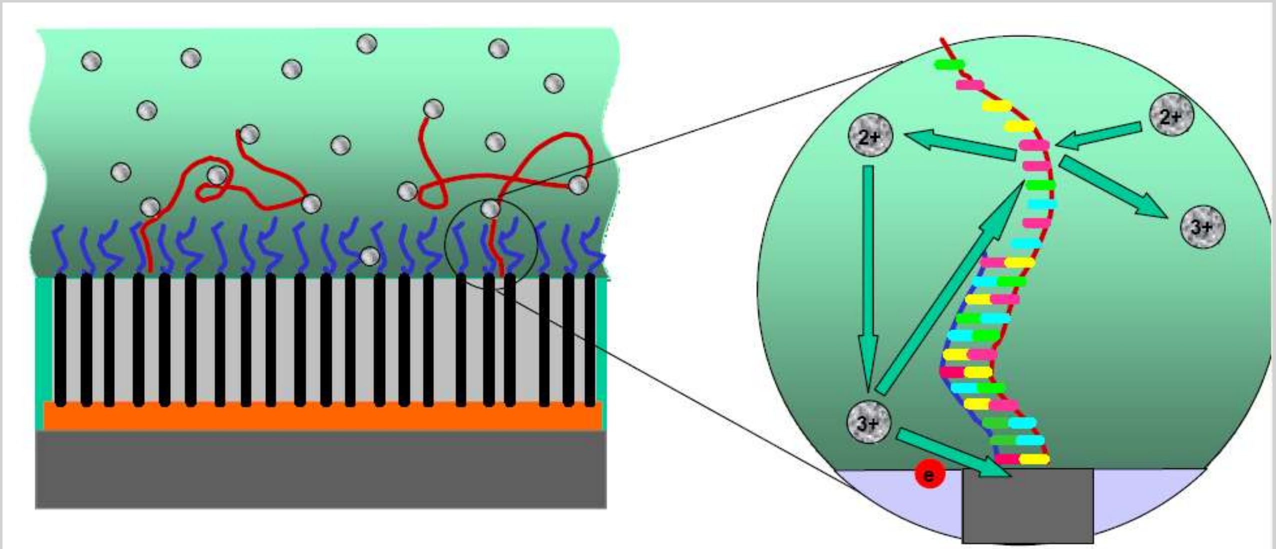
- strongest and most flexible known molecular material
- 10% higher maximum strain than any other material
- Young's modulus of 1TPa (~100 time improvement over steel)



CNT deformation with an AFM tip [IBM]

Introduction: Other Properties

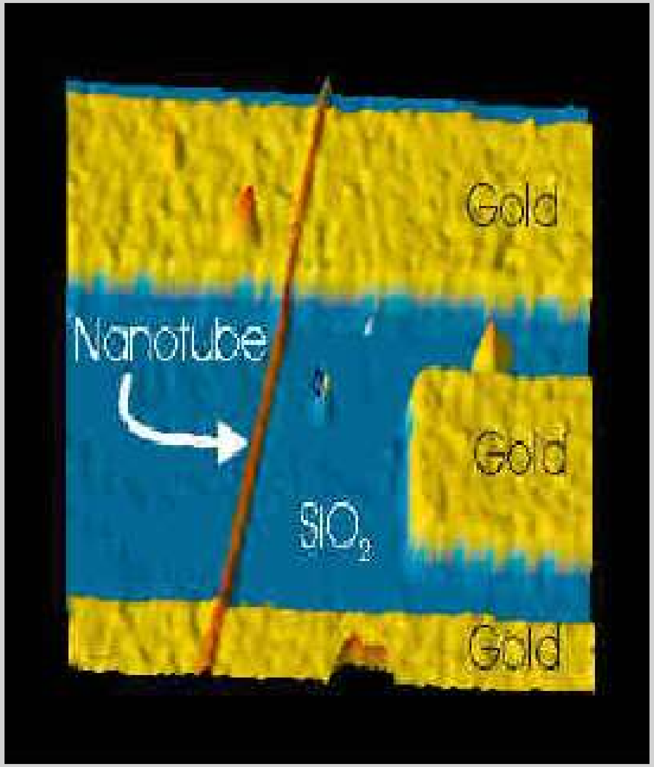
- chemically very stable and functionalizable
- very light weight
- high thermal conductivity



DNA-array with CNTs [NASA]

Introduction: Electrical Properties

- semiconducting or metallic (tunable bandgap)
- very high conductivity
- high current densities possible
- piezoelectric



CNT-transistor [IBM]

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PDMI

Physics: Band Structure I

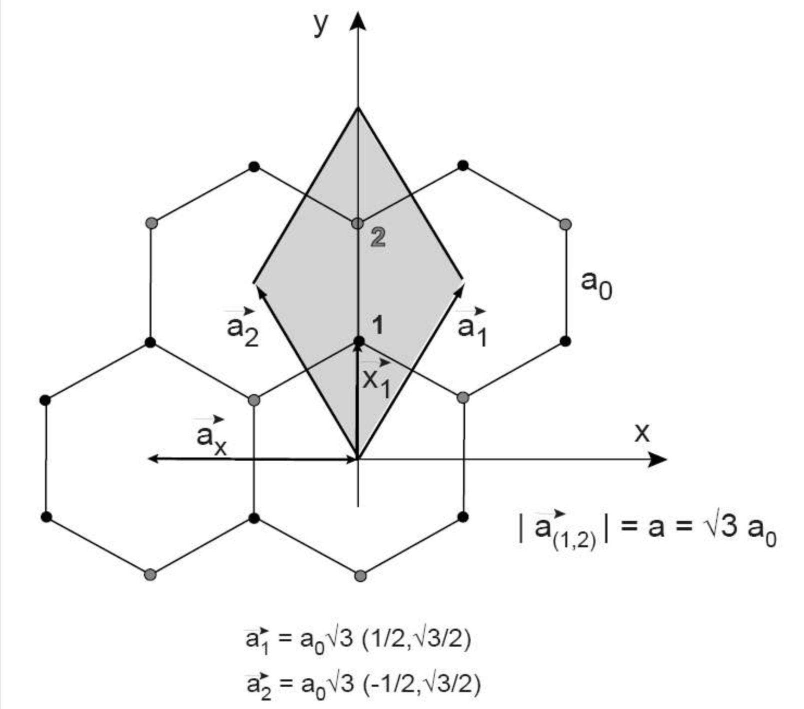
<u>LCAO (linear combination of atomic orbitals) method:</u>

(following an example by Chr. Schönenberger, Uni Basel)

- two-dimensional sheet of graphite
  → 'graphene'
- atomic orbitals → localized
- ansatz wavefunction → Bloch wave

$$\Psi_{\vec{k}} = \sum_{\vec{R} \in G} \exp(i \vec{k} \cdot \vec{R}) \Phi(\vec{x} - \vec{R})$$

G: set of lattice vectors
Φ: atomic wavefunctions



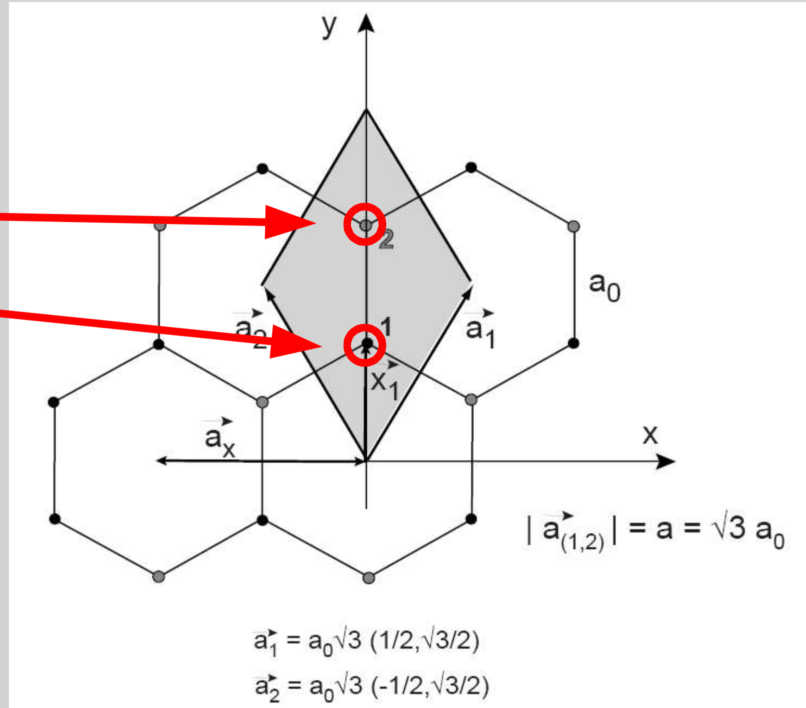
lattice of graphene

Physics: Band Structure II

linear combination:

- only π-bands → p_z orbitals
- 2 atoms in basis

$$\Phi(\vec{x}) = b_1 \Phi_1(\vec{x}) + b_2 \Phi_2(\vec{x})$$



Physics: Band Structure II

linear combination:

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- 2 atoms in basis

$$\Phi(\vec{x}) = b_1 \Phi_1(\vec{x}) + b_2 \Phi_2(\vec{x})$$

Hamiltonian:

- single electron
- atomic potential

$$H = \frac{\vec{p}^{\,2}}{2m} + \sum_{\vec{R} \in G} \left(V_{at}(\vec{x} - \vec{x}_1 - \vec{R}) + V_{at}(\vec{x} - \vec{x}_2 - \vec{R}) \right)$$

kinetic energy

atomic potentials

Physics: Band Structure II

<u>linear combination:</u>

- only π-bands → p_z orbitals
- 2 atoms in basis

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$$\longrightarrow H \Phi_{1,2} = \epsilon_{1,2} \Phi_{1,2} + \left(\sum_{\vec{R} \neq 0} \left(V_{at}(\vec{x} - \vec{x}_1 - \vec{R}) + V_{at}(\vec{x} - \vec{x}_2 - \vec{R}) \right) + V_{at}(\vec{x} - \vec{x}_2) \right) \Phi_{1,2}$$

on site energy

rest of lattice

Physics: Band Structure II

linear combination:

- only π-bands → p_z orbitals
- 2 atoms in basis

$$\Phi(\vec{x}) = b_1 \Phi_1(\vec{x}) + b_2 \Phi_2(\vec{x})$$

Hamiltonian:

- single electron
- atomic potential

$$H = \frac{\vec{p}^{\,2}}{2m} + \sum_{\vec{R} \in G} \left(V_{at}(\vec{x} - \vec{x}_1 - \vec{R}) + V_{at}(\vec{x} - \vec{x}_2 - \vec{R}) \right)$$

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$\varepsilon_{1,2}$: ground energy of orbitals → set to zero

$$\longrightarrow H \Phi_{1,2} = \Delta U_{1,2} \Phi_{1,2}$$

Physics: Band Structure III

Schrödinger equation:

$$H\,\Psi_{\vec{k}} = E(\vec{k})\,\Psi_{\vec{k}} \qquad \Psi_{\vec{k}} = \sum_{\vec{R}\in G} \exp(i\,\vec{k}\cdot\vec{R})\,\Phi(\vec{x}-\vec{R})$$

solution in k-space !!

Physics: Band Structure III

Schrödinger equation:

$$H\Psi_{\vec{k}} = E(\vec{k})\Psi_{\vec{k}} \qquad \Psi_{\vec{k}} = \sum_{\vec{R}\in G} \exp(i\vec{k}\cdot\vec{R})\Phi(\vec{x}-\vec{R})$$

transform into linear system of equations:

$$\langle \Phi_j | \Delta U_j | \Psi \rangle = E(\vec{k})\langle \Phi_j | \Psi \rangle$$

Physics: Band Structure III

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transform into linear system of equations:

$$\langle \Phi_j | \Delta U_j | \Psi \rangle = E(\vec{k}) \langle \Phi_j | \Psi \rangle$$

only consider neighboring atoms:

$$\langle \Phi_1 | \Psi \rangle = b_1 + b_2 \left(\int \Phi_1^* \Phi_2 \right) \left(1 + \exp(-i\,\vec{k}\cdot\vec{a}_1) + \exp(-i\,\vec{k}\cdot\vec{a}_2) \right)$$

$$\langle \Phi_2 | \Delta U_2 | \Psi \rangle = b_1 \left(\int \Phi_2^* \Delta U_2 \Phi_1 \right) \left(1 + \exp(i\,\vec{k}\cdot\vec{a}_1) + \exp(i\,\vec{k}\cdot\vec{a}_2) \right)$$

Physics: Band Structure III

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additional assumptions / definitions:

$$\gamma_0 = \int \Phi_1^* \Phi_2 \in \boldsymbol{R} \ll \gamma_1 = \int \Phi_1^* \Delta U_1 \Phi_2 \in \boldsymbol{R} \qquad \alpha(\vec{k}) = 1 + \exp(-i\vec{k}\cdot\vec{a}_1) + \exp(-i\vec{k}\cdot\vec{a}_2)$$

Physics: Band Structure IV

Final result:

formulation of eigenvalue problem:

$$\begin{pmatrix} E(\vec{k}) & \alpha(\gamma_0 E(\vec{k})-\gamma_1) \\ \alpha^*(\gamma_0 E(\vec{k})-\gamma_1) & E(\vec{k}) \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Physics: Band Structure IV

Final result:

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condition for non-trivial solution:

$$|...|=0$$

Final result:

formulation of eigenvalue problem:

$$\begin{pmatrix} E(\vec{k}) & \alpha(\gamma_0 E(\vec{k})-\gamma_1) \\ \alpha^*(\gamma_0 E(\vec{k})-\gamma_1) & E(\vec{k}) \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

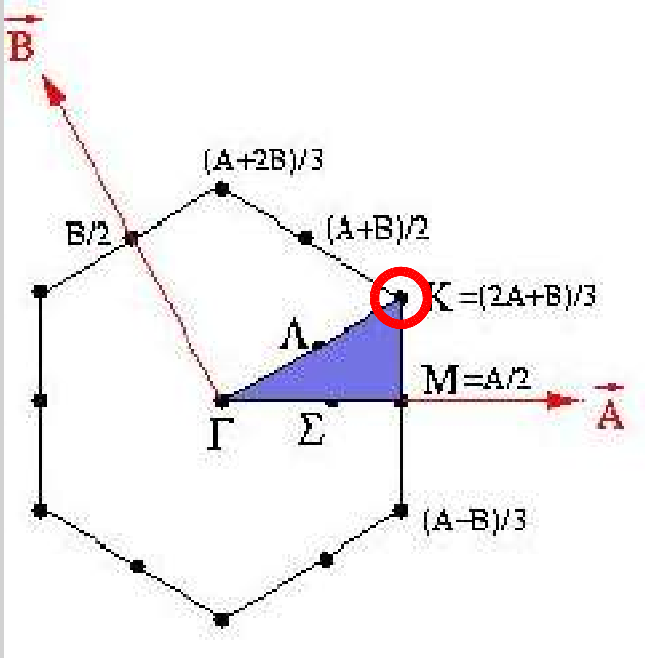
condition for non-trivial solution:

$$|...|=0$$

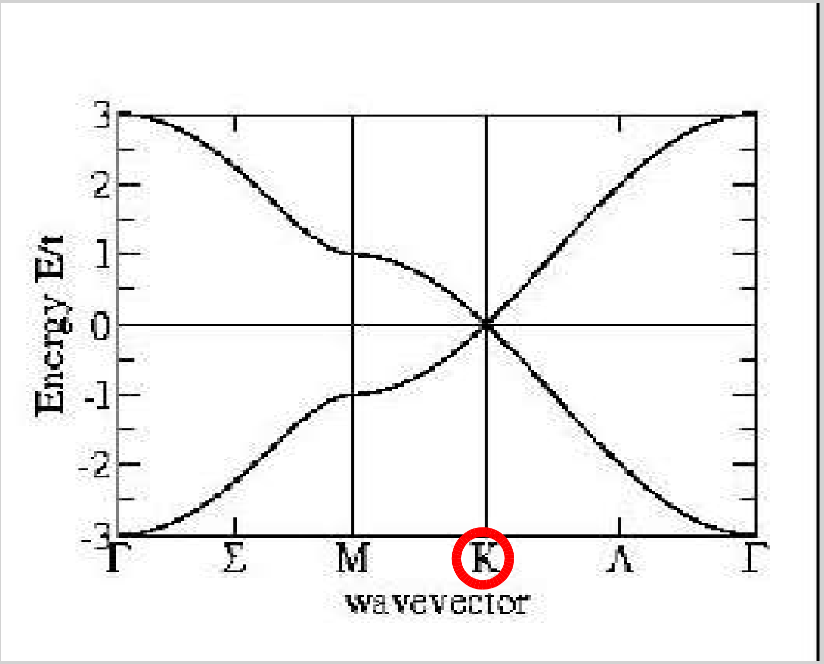
approximation $\gamma_0 \approx 0$:

$$E(\vec{k})=\pm\sqrt{3+2\cos(\vec{k}\cdot\vec{a}_1)+2\cos(\vec{k}\cdot\vec{a}_2)+2\cos(\vec{k}\cdot(\vec{a}_2-\vec{a}_1))}$$

Physics: Bands of Graphene



Brillouin zone



Band structure of graphene

Γ→M: $\varepsilon_{\pm}(k) = \pm \text{ const. } [5 + 4\cos(2\pi\varsigma)]^{1/2}$ $(0 < \varsigma < 1)$

M→K: $\varepsilon_{\pm}(k) = \pm \text{ const. } [3 + 4\cos(2\pi\varsigma/3) - 2\cos(4\pi\varsigma/3)]^{1/2}$

K→Γ: $\varepsilon_{\pm}(k) = \pm \text{ const. } [3 - 4\cos(2\pi\varsigma/3) + 2\cos(4\pi\varsigma/3)]^{1/2}$

Physics: From graphene to CNTs

<u>*periodic boundary condition:*</u>

$$\Psi(z, \varphi) = \Psi(z, \varphi + 2\pi)$$

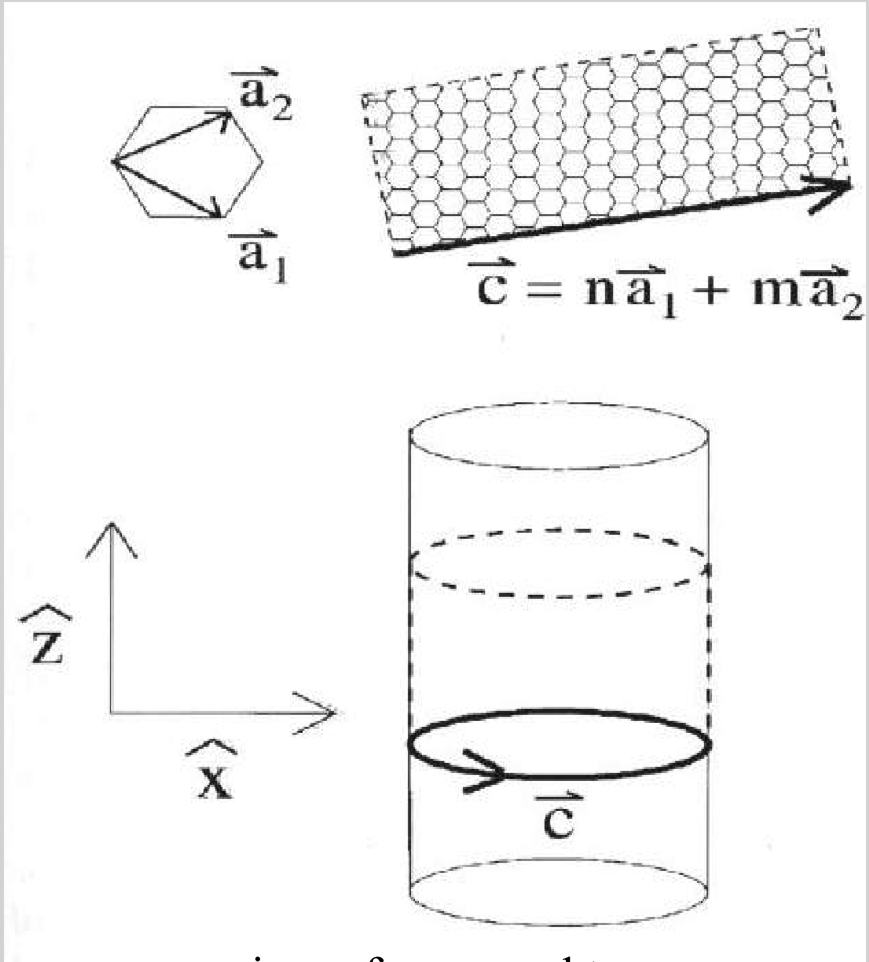
<u>*separation ansatz:*</u>

$$\Psi(z, \varphi) = \exp(i \cdot k_C \cdot \lambda_C(\varphi)) \cdot \chi(z)$$

with: $\vec{\lambda}_C(2\pi) = \vec{C}$

$$\vec{k}_C \cdot \vec{C} = 2\pi \cdot p \quad p \in \mathbb{N}$$

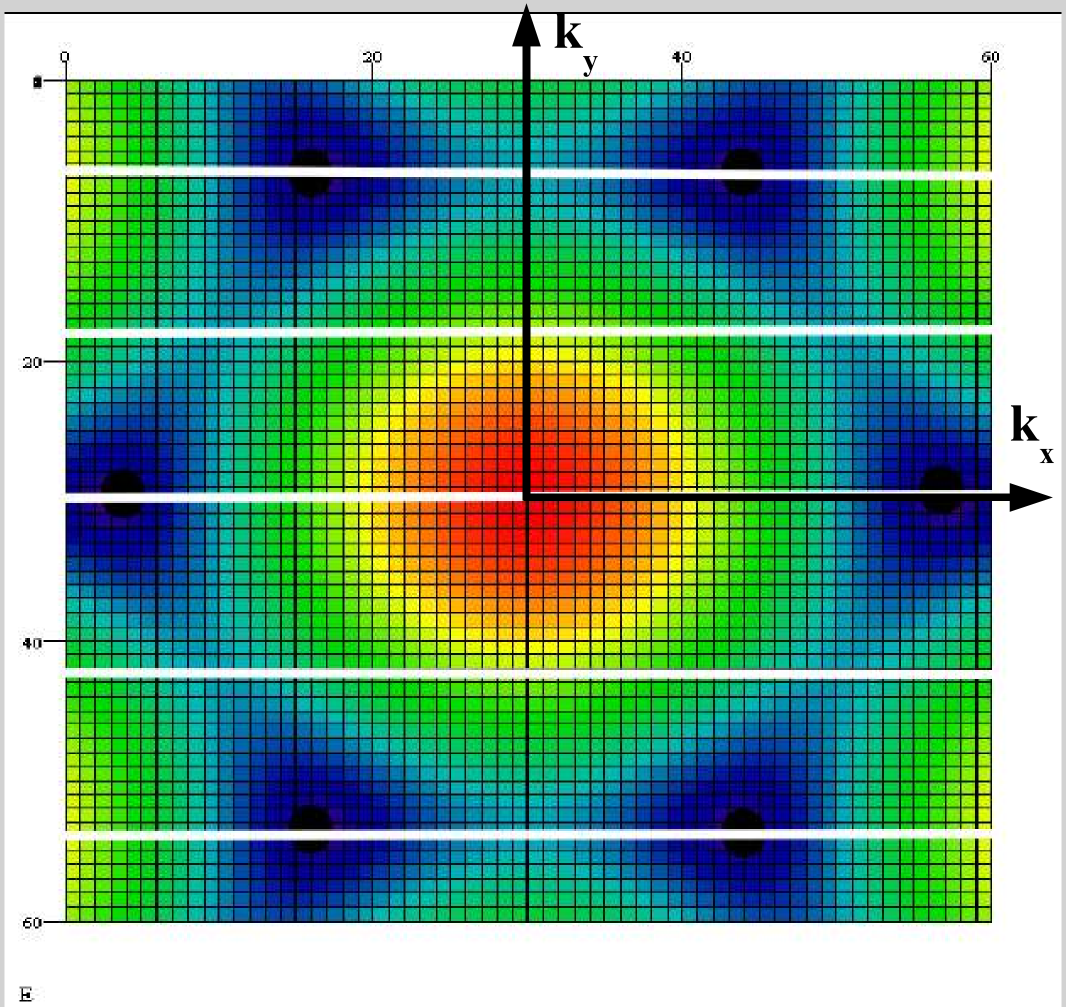
→ line equation in k_x,k_y - coordinates

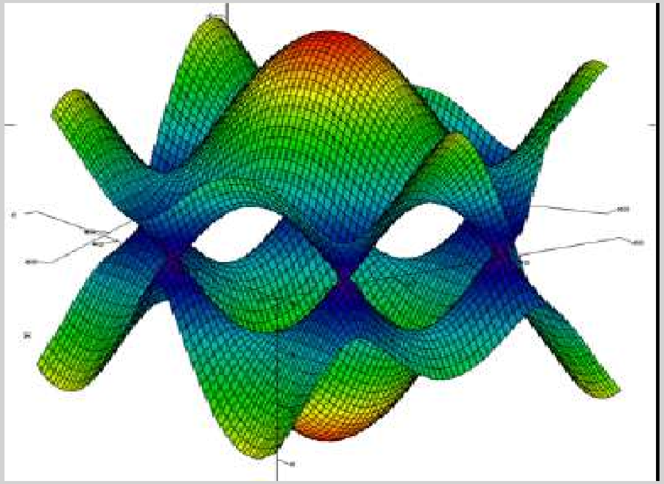


circumference vektor

Physics: k-vectors I

armchair nanotube (n,n):

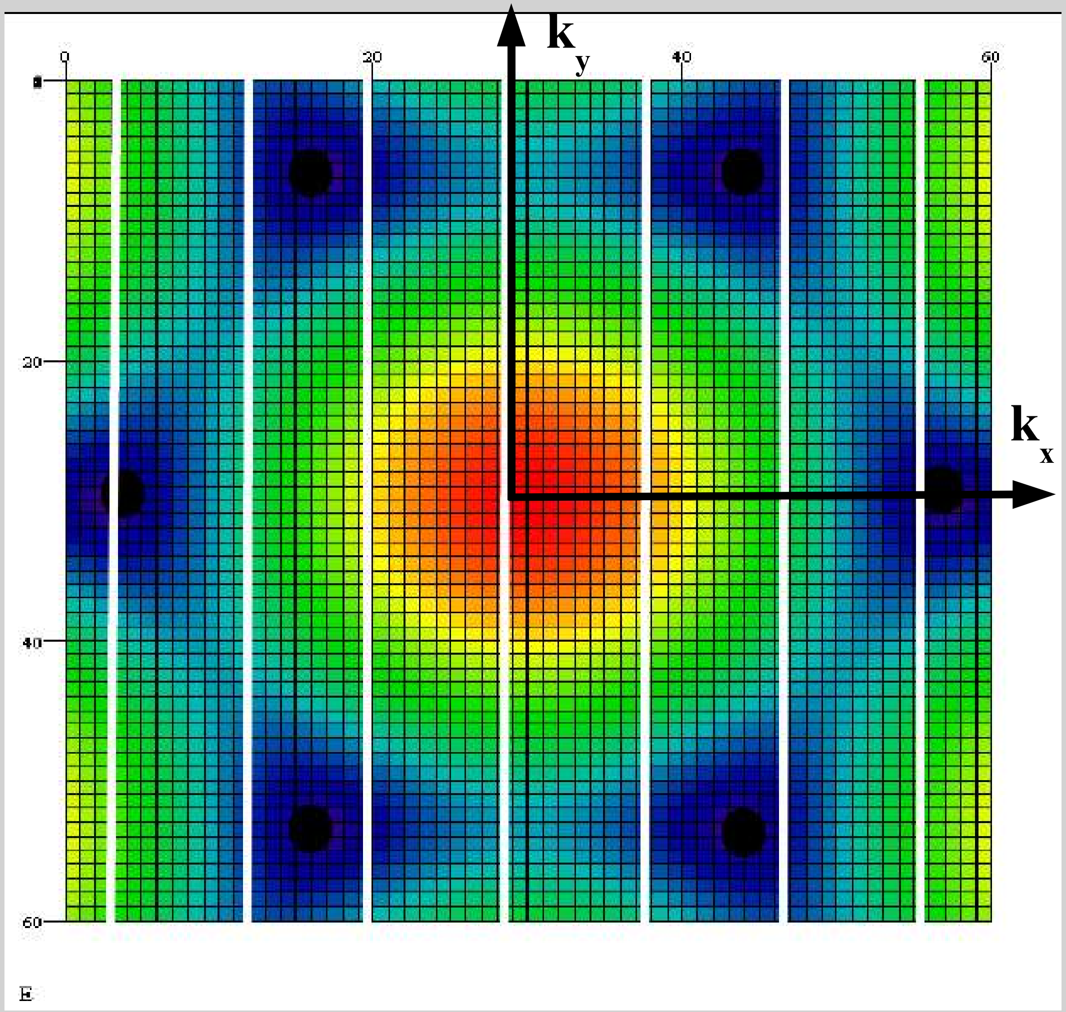


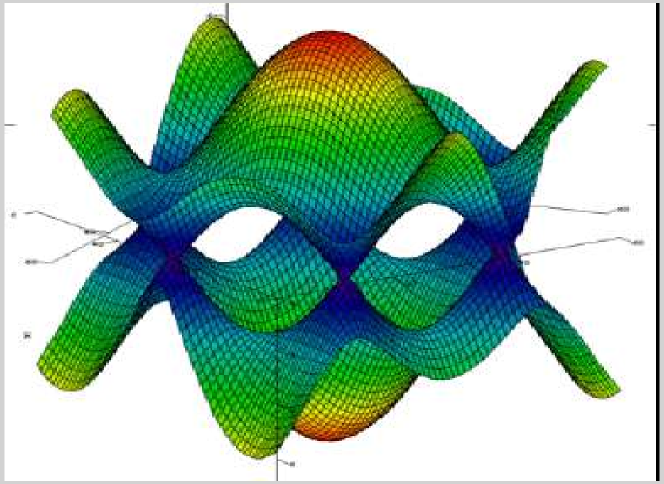


always metallic !!

Physics: k-vectors II

<u>zigzag nanotube (n,0):</u>

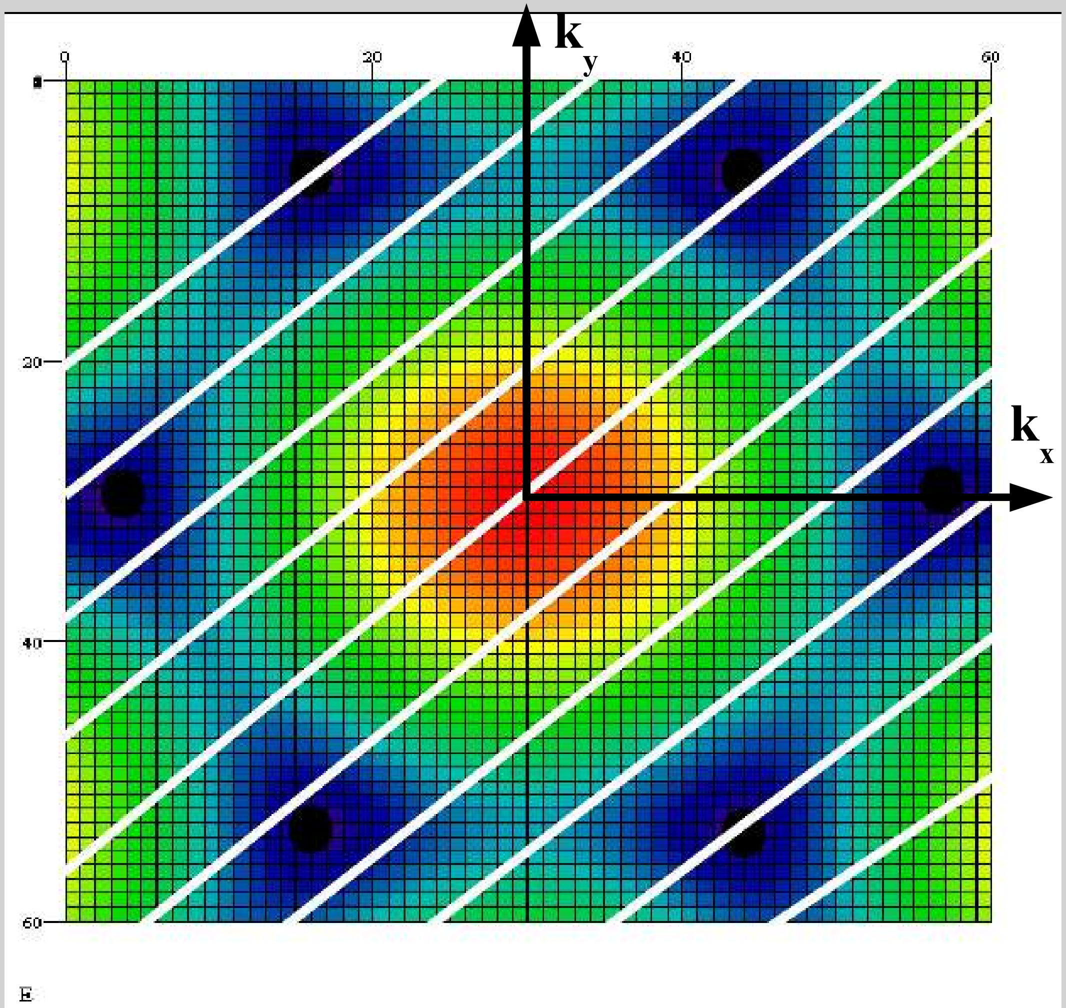


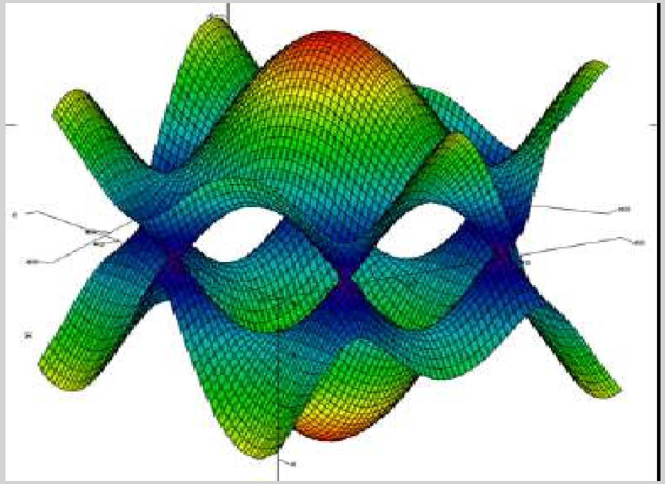


metallic only if
n = 3i !!

Physics: k-vectors III

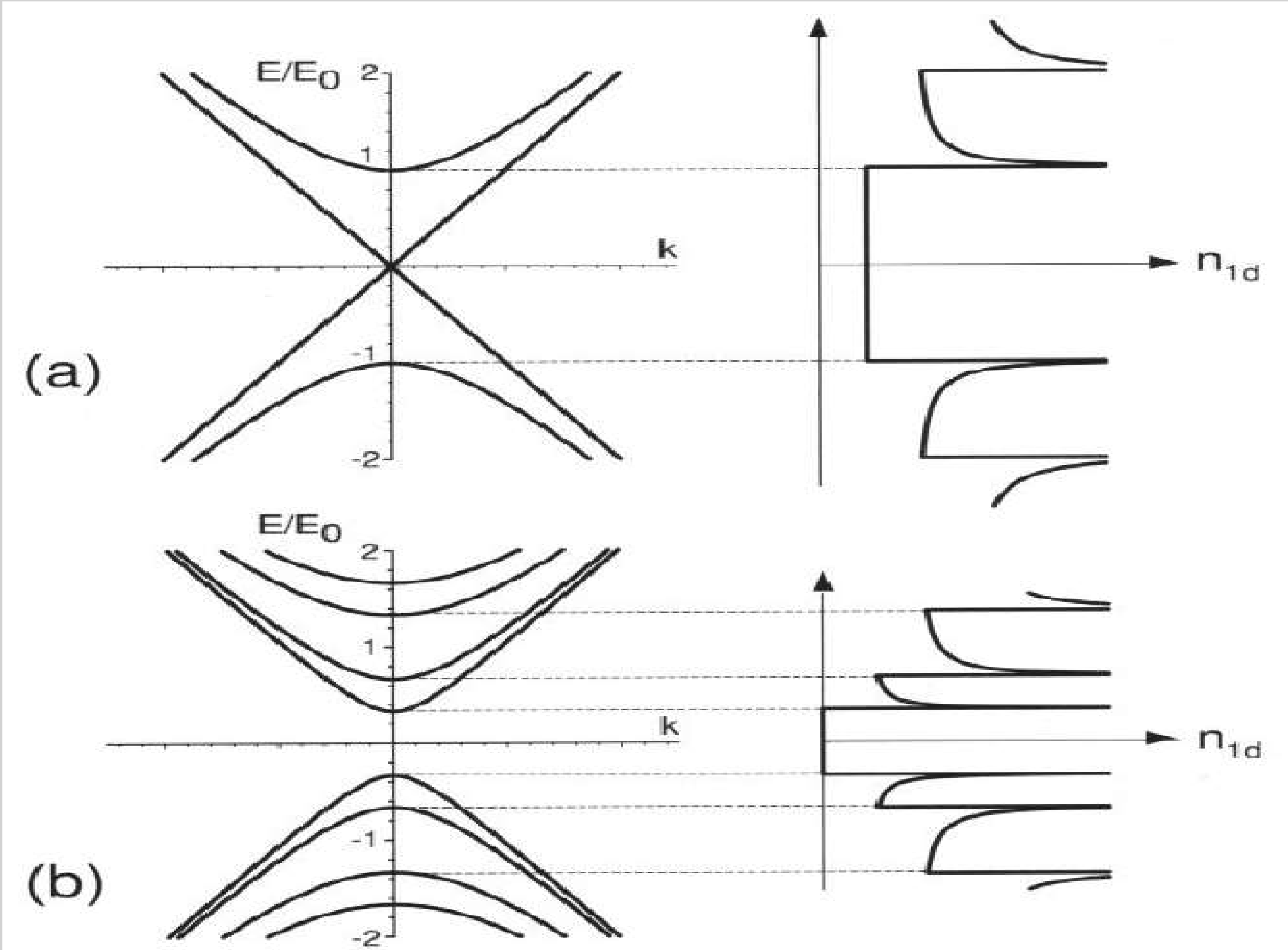
chiral nanotube (n,m):





metallic only if
m - n = 3i !!

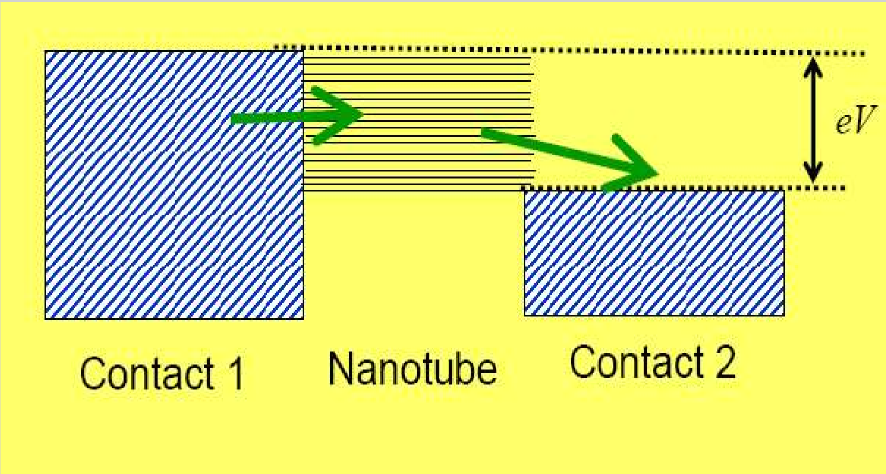
Physics: Bands and DOS



(a) metallic nanotube (linear dispersion)
(b) semiconducting CNT (E_g fewer than 1 eV)

Physics: Transport Behavior I

- 1D – Transport
- ballistic (only elastic scattering)
- geometry independent conduction



Transport through states [Csaba, TUM]

Landauer formula:

$$G = \frac{4e^2}{h}$$

Physics: Transport Behavior II

<u>Metallic CNT vs. Copper</u>

resistivity [Ωm]:

CNT	$2.55\cdot10^{-7}$
Cu	$1.7\cdot10^{-8}$

(CNT: 5nm diameter, 1µm long)

max. current densitiy [A/mm²]:

CNT	$\approx 2.5\cdot10^{7}$
Cu	$\approx 10...10^{2}$

[Cornell University]

Physics: Transport Behavior III

Semiconducting CNT vs. Si

intrinsic hole density [cm^{-3}]:

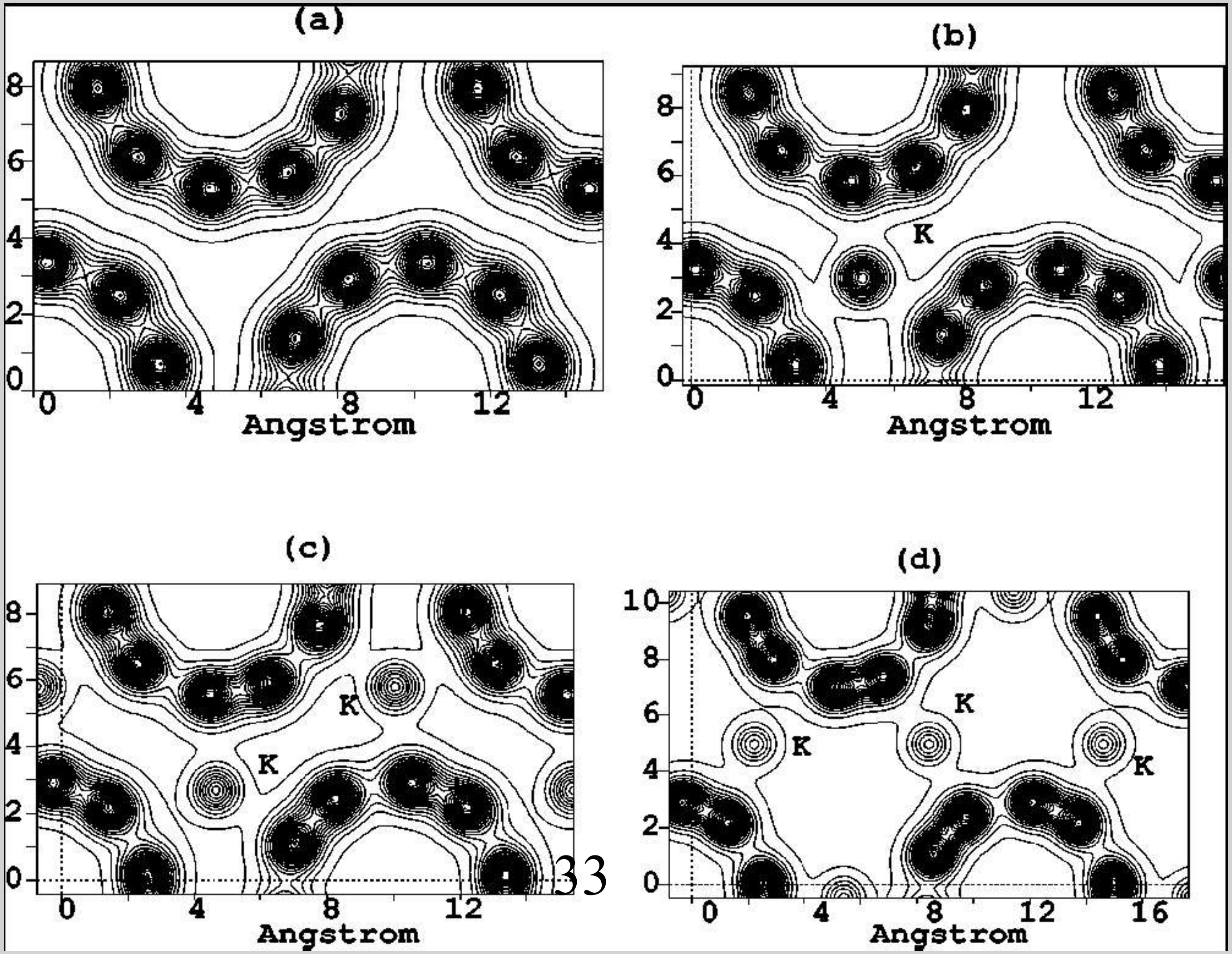
CNT	$\approx 10^{20}$	[Rakitin et al., Brown University, RI]
Si	$\approx 10^{10}$	

(room temperature)

hole mobility [cm²/Vs]:

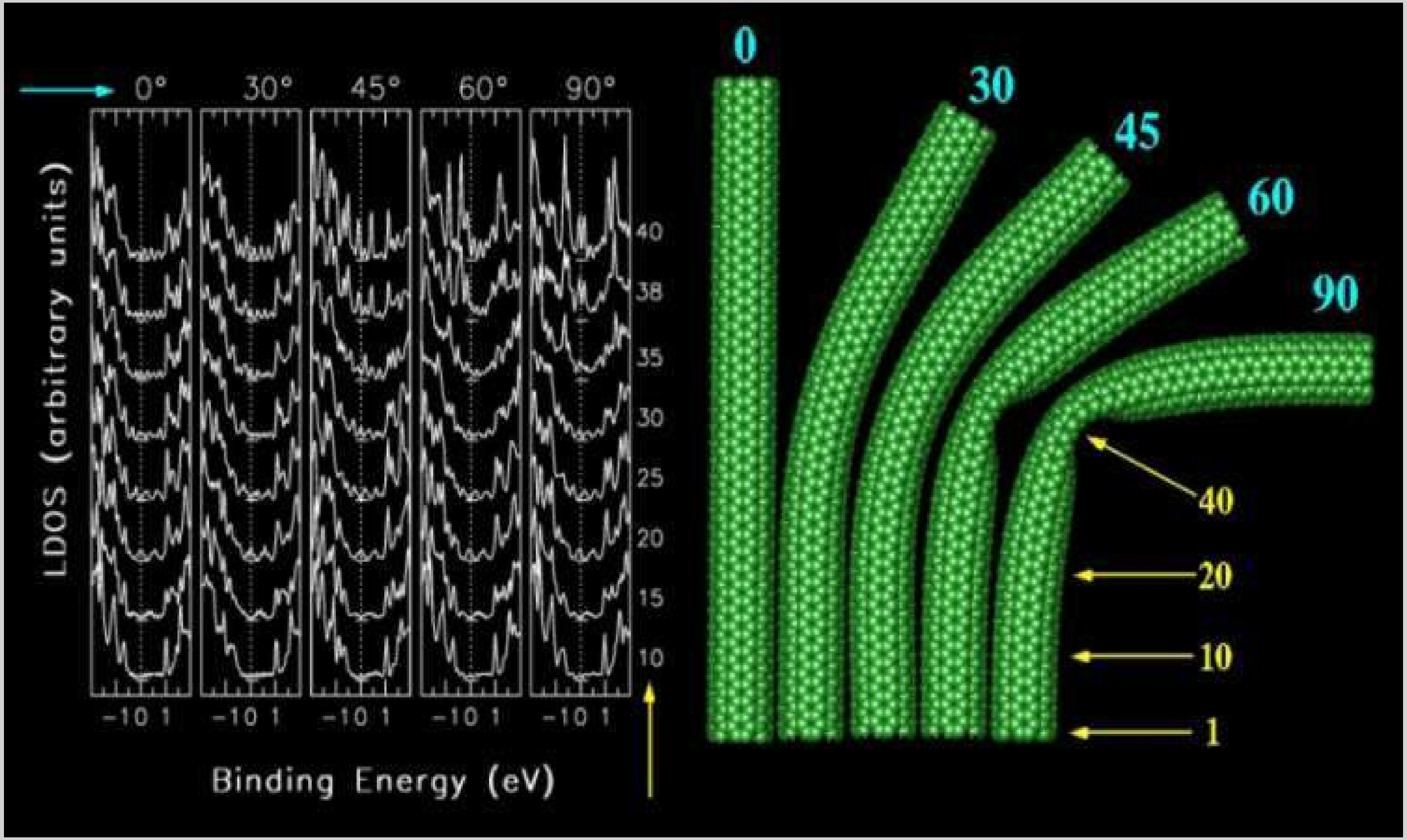
CNT	$\approx 10^{3} \ldots 10^{4}$	[MRS Bulletin (2004)]
p-Si	$\approx 3 \cdot 10^{3}$	($N_A = 10^{16}$ cm^{-3})

Physics: Doping with Potassium



charge densities in increasingly doped CNT-bundles
[Jo, Kim, Lee; Sungkyunkwan University,Korea]

Physics: LDOS vs. Bending



Simulation on bending effects [IBM]

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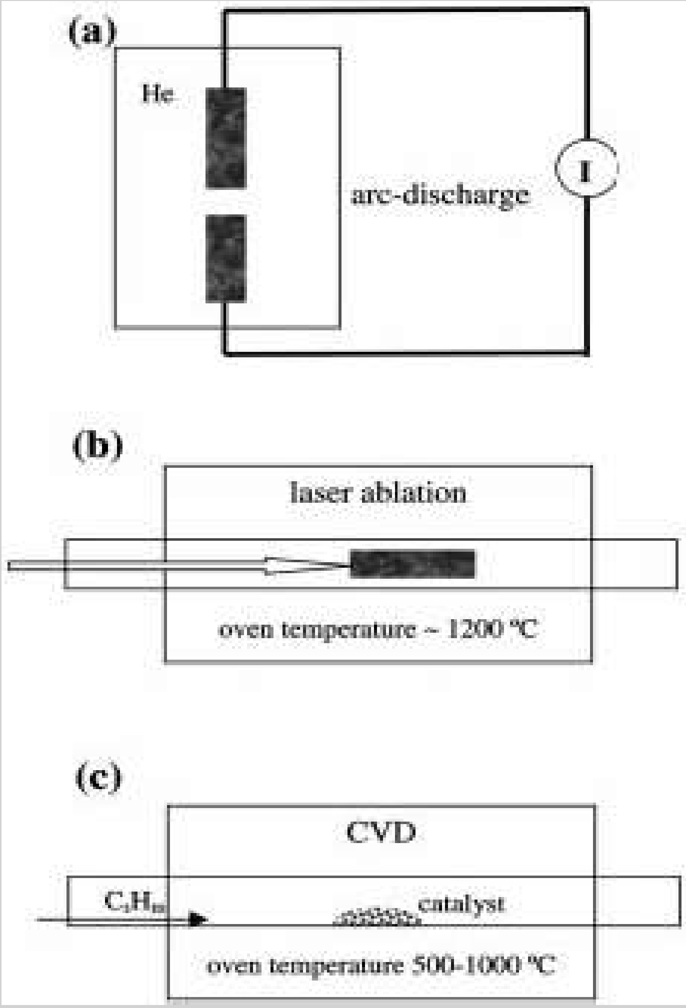
Manufacturing: Overview

(a) arc discharge

(b) laser ablation

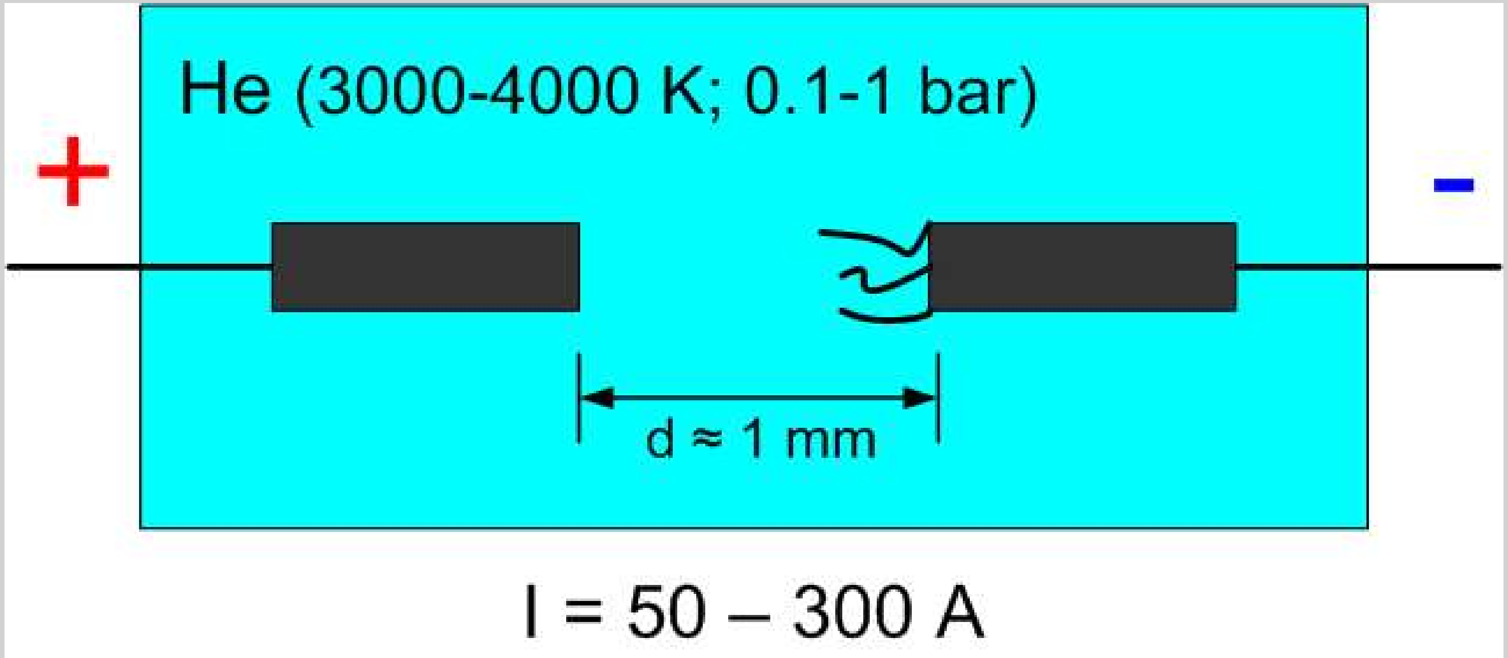
(c) CVD (chemical vapor deposition)



Schematic setups for nanotube growth

Manufacturing: Arc Discharge

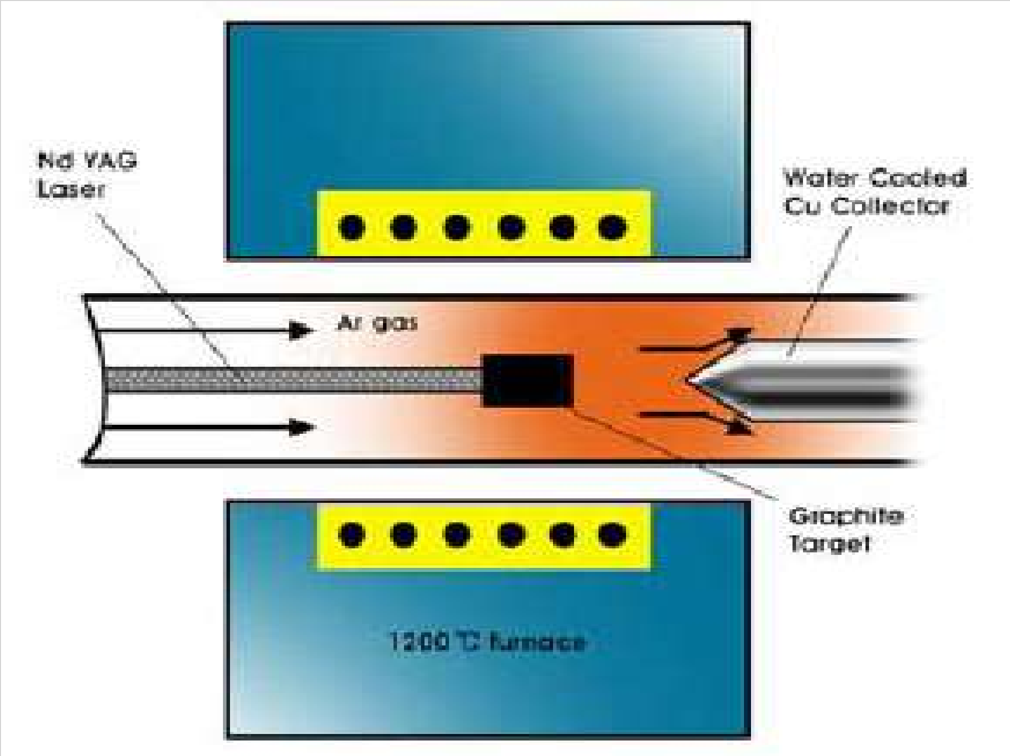
setup and parameters



- high quality
- good yield → cheap
- MWNT and SWNT
- BUT: unclean (amorphous C)

Manufacturing: Laser Ablation

setup and parameters

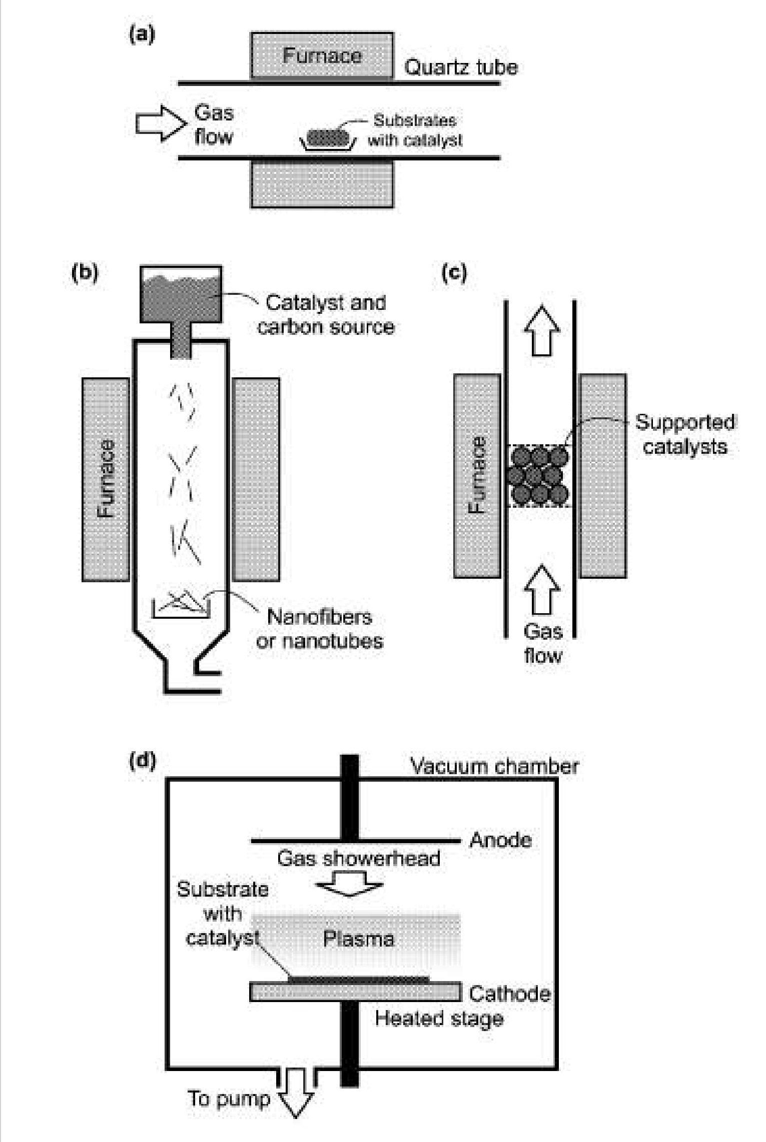


- good control
- no electric fields
- high yield of SWNT
- BUT: expensive

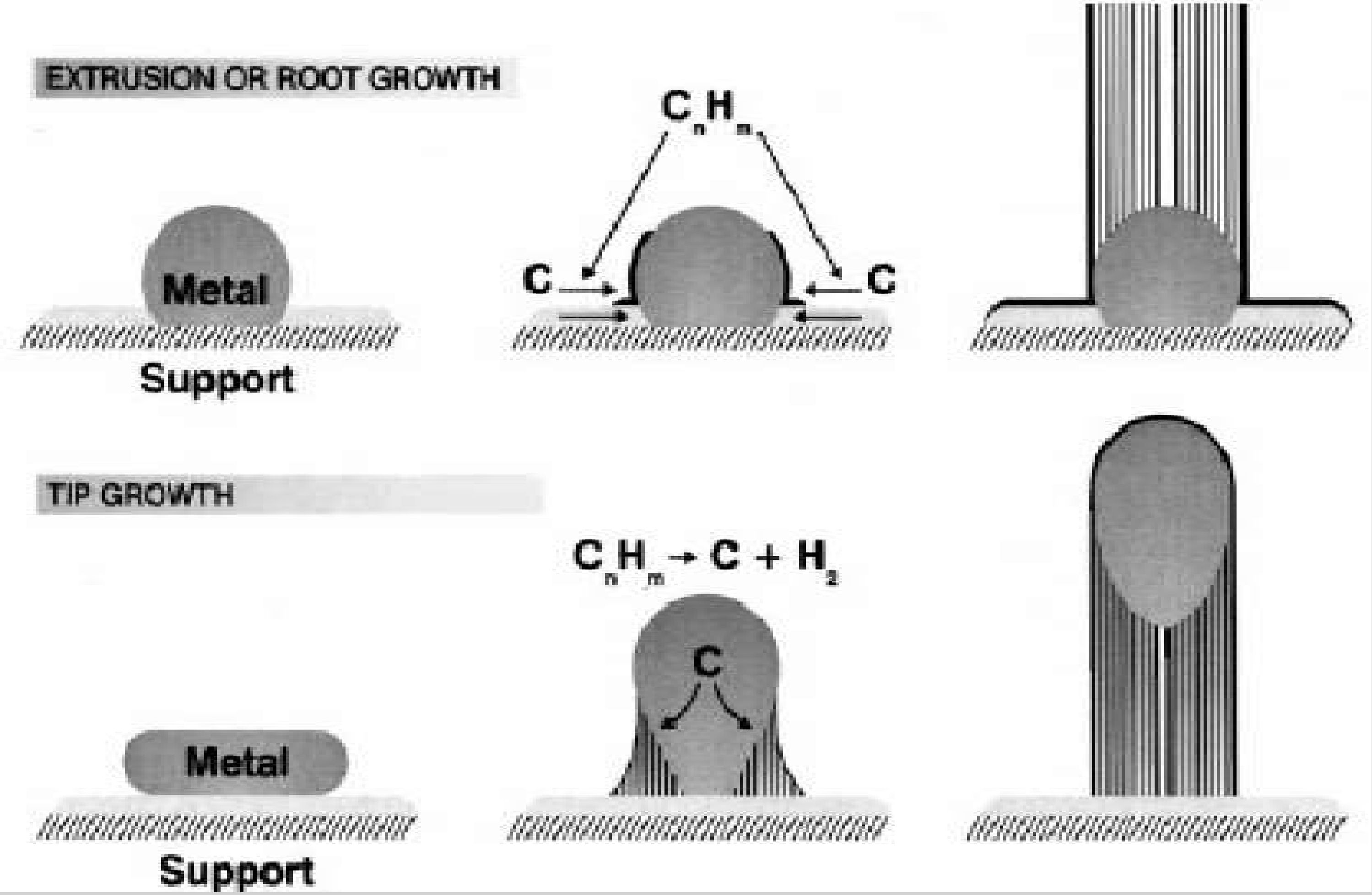
Manufacturing: CVD I

<u>variety of setups</u>
(Univ. of Cambridge, UK)

- horizontal (most common)
- vertical (mass production)
- plasma enhanced (PECVD)



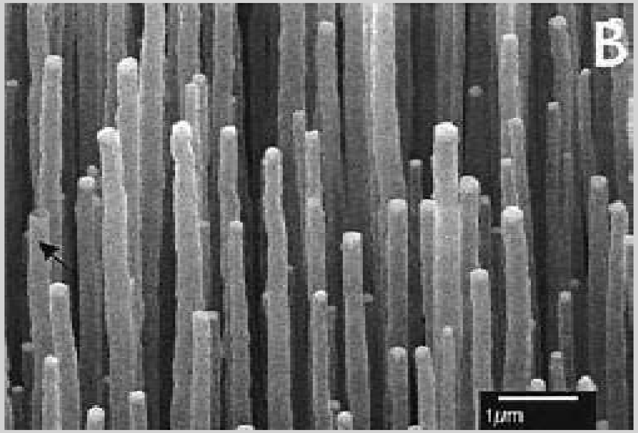
Manufacturing: CVD II

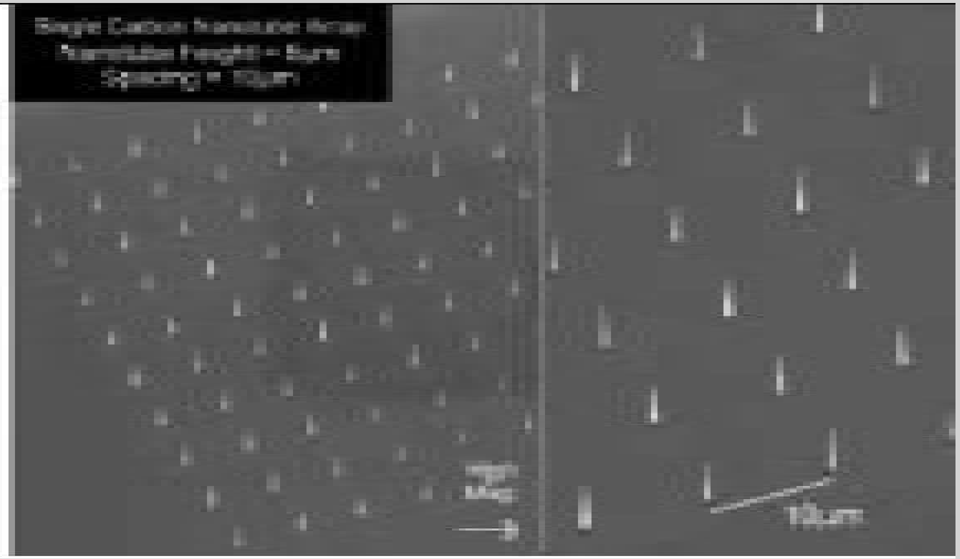


tip- and base-growth in the presence of catalyst (Fe, Co, Ni)

Manufacturing: CVD III

- SWNTs and MWNTs
- patterned growth
- aligned CNTs
- batch process → cheap and fast





Manufacturing: Summary

<u>Techniques differ in:</u>

- Types of Nanotubes
- Catalyst used
- Yield
- Purity

Manufacturing: Purification

- thermal oxidation
- annealing
- micro filtration
- magnetic separation (catalyst)
- selective functionalisation

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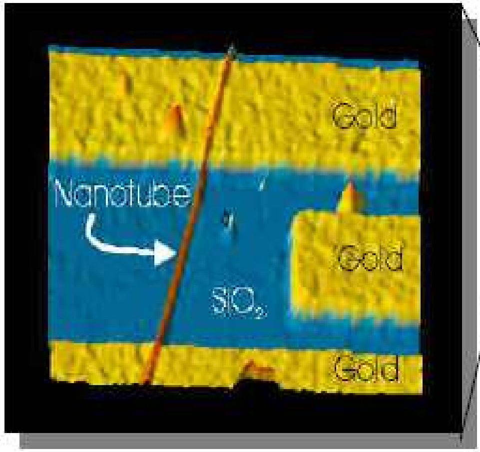
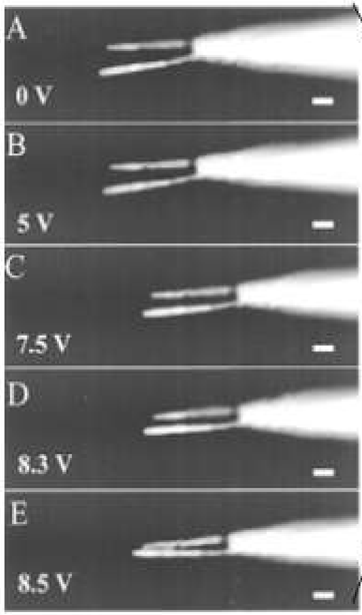
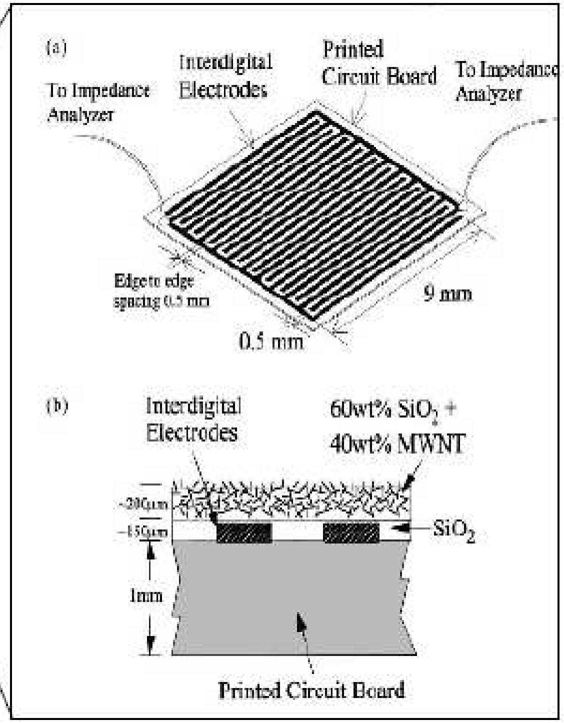
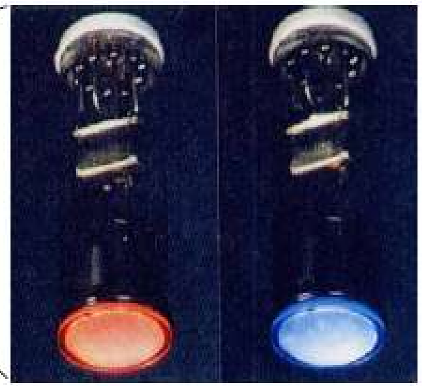
Applications: Overview (Prof. Lugli, TUM)





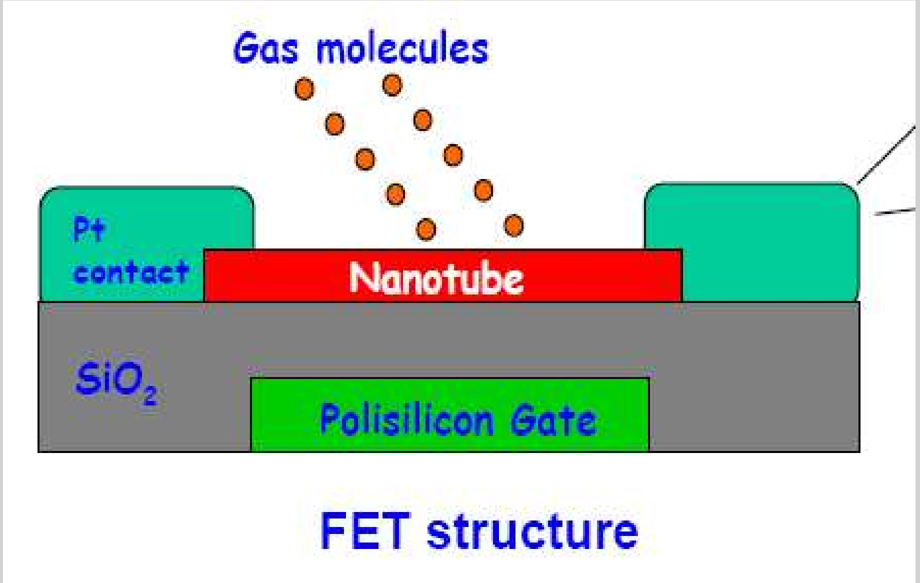
- Field Effect Transistors
- Sensors and Actuators
- Interconnects
- Hydrogen storage
- Fuel cell components
- Reinforcing agents
- Molecular tweezers
- Field Emission





Applications: Chemical Sensors I

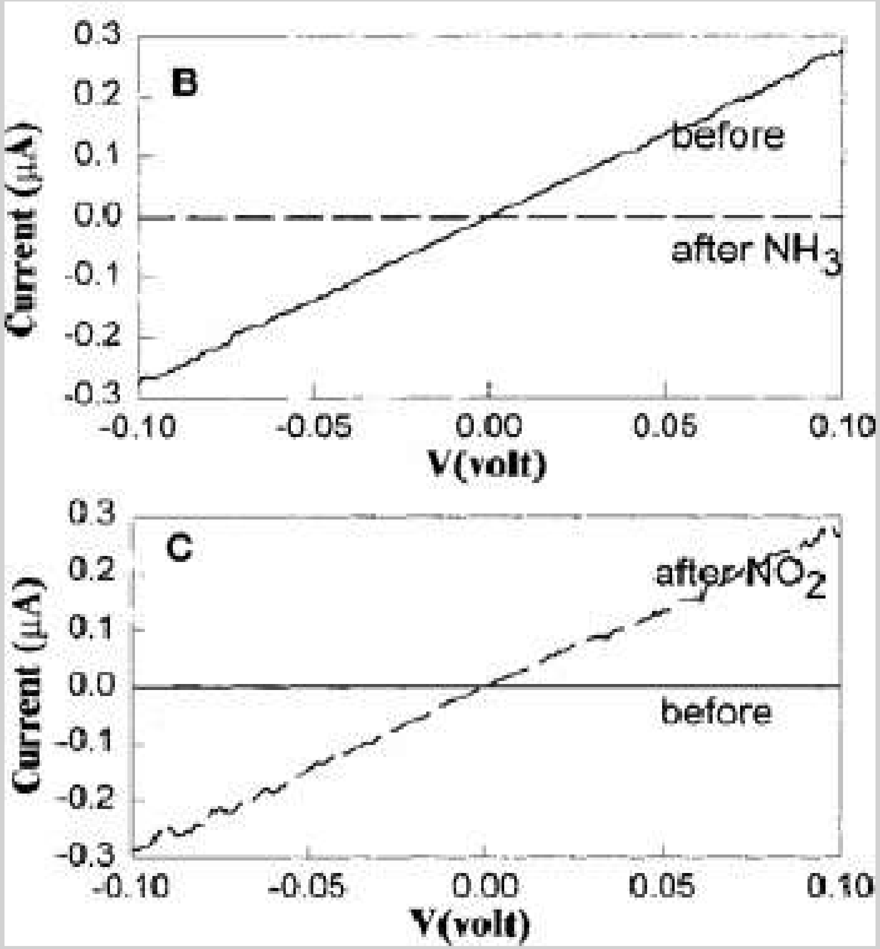
- FET-structure
- semiconducting SWCNT
- depletion / accumulation of carriers



CNT based gas-sensor

Applications: Chemical Sensors II

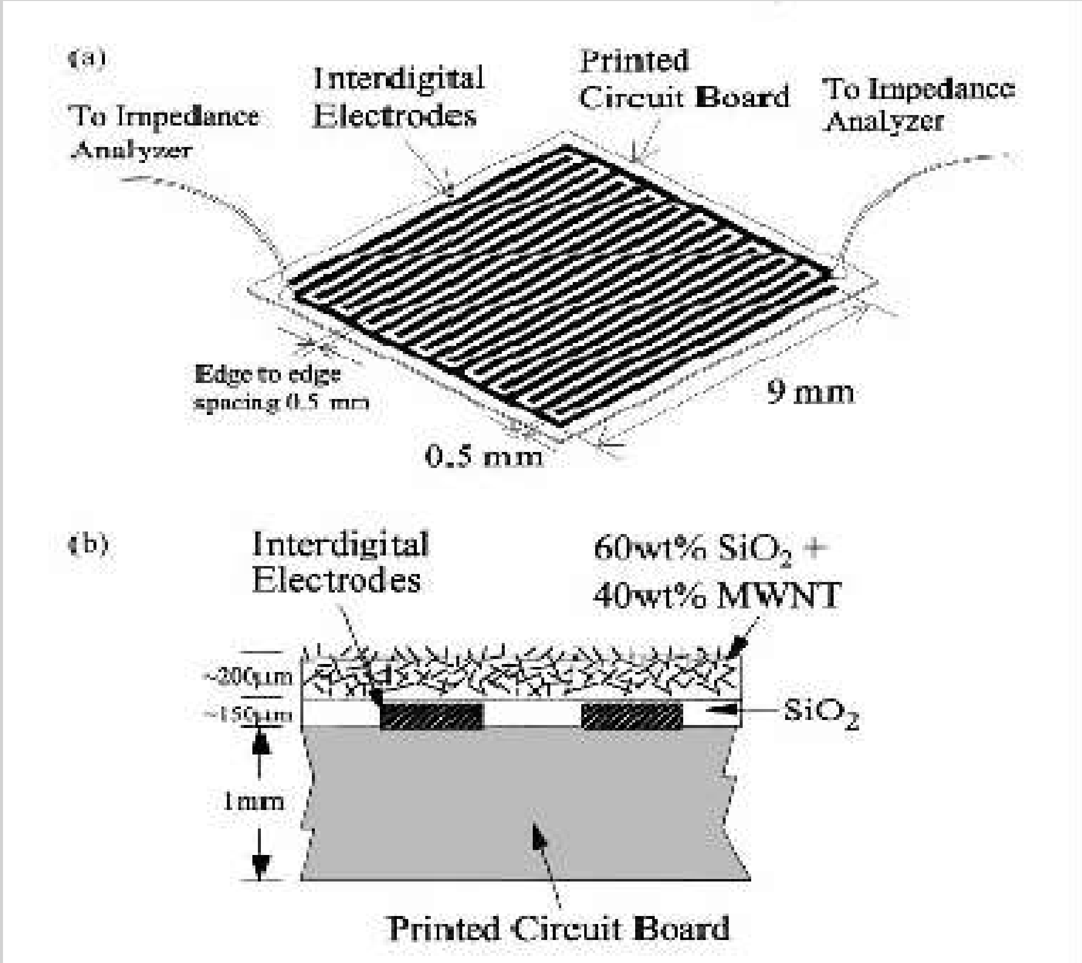
- O_2, NH_3, NO_2
- high sensitivity (ppm)
- medical and industrial applications



I-V-plots of gas sensors

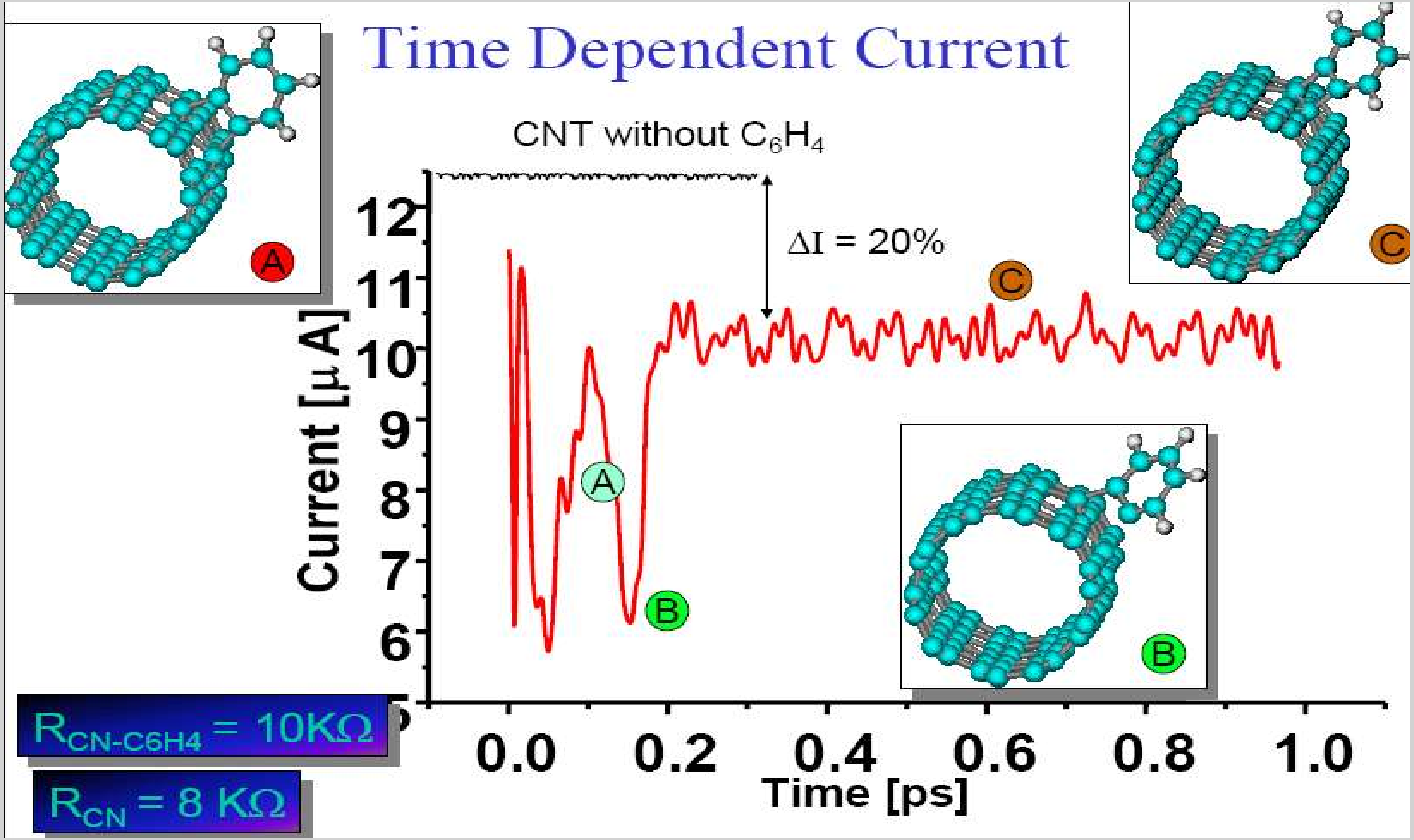
Applications: Chemical Sensors III

- interdigital structure
- MWNTs
- impedance measurement



MWNT gas sensor [Varghese, Sensors and Actuators (2001)]

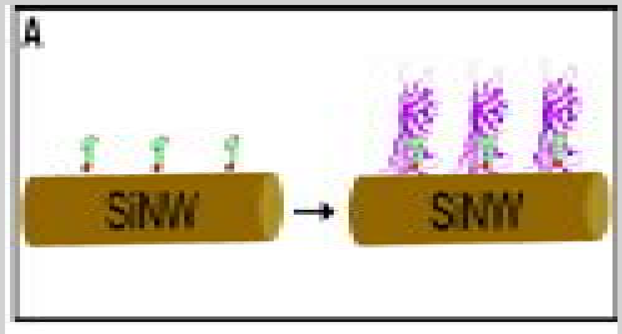
Applications: Chemical Sensors IV



Molecular Dynamics simulation of CNT-C_6H_4 interaction [Lugli, TUM]

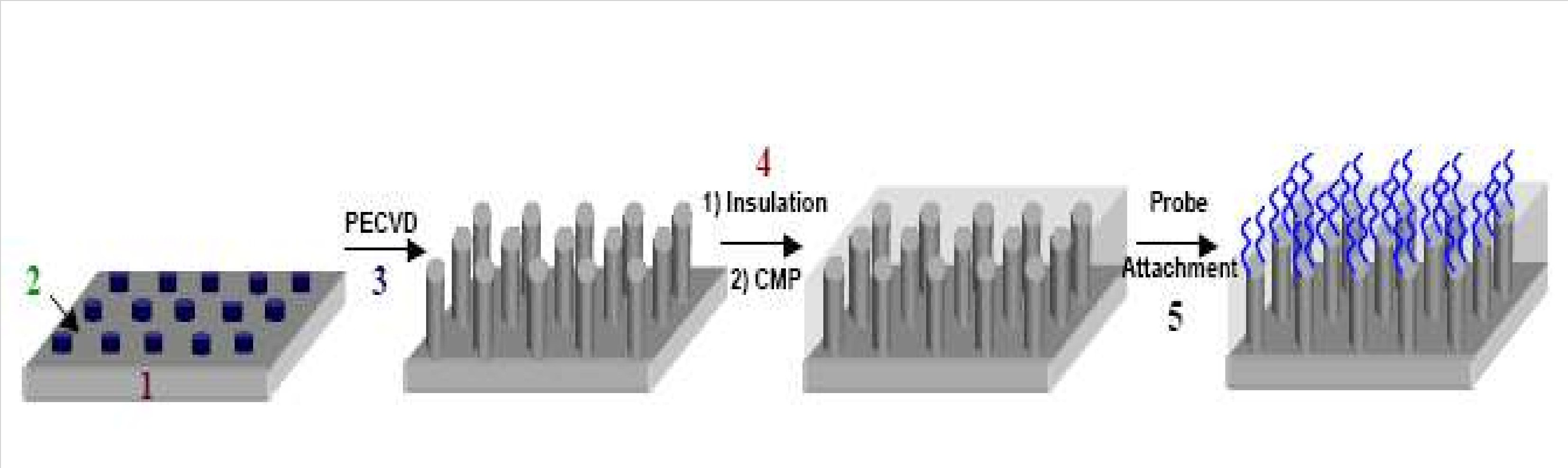
Applications: Nanowire Biosensor

- principle as chemical sensors
- CNTs functionalized with Biotin
- electrochemical gating



Si nanowire sensor [Cui et al., Science (2001)]

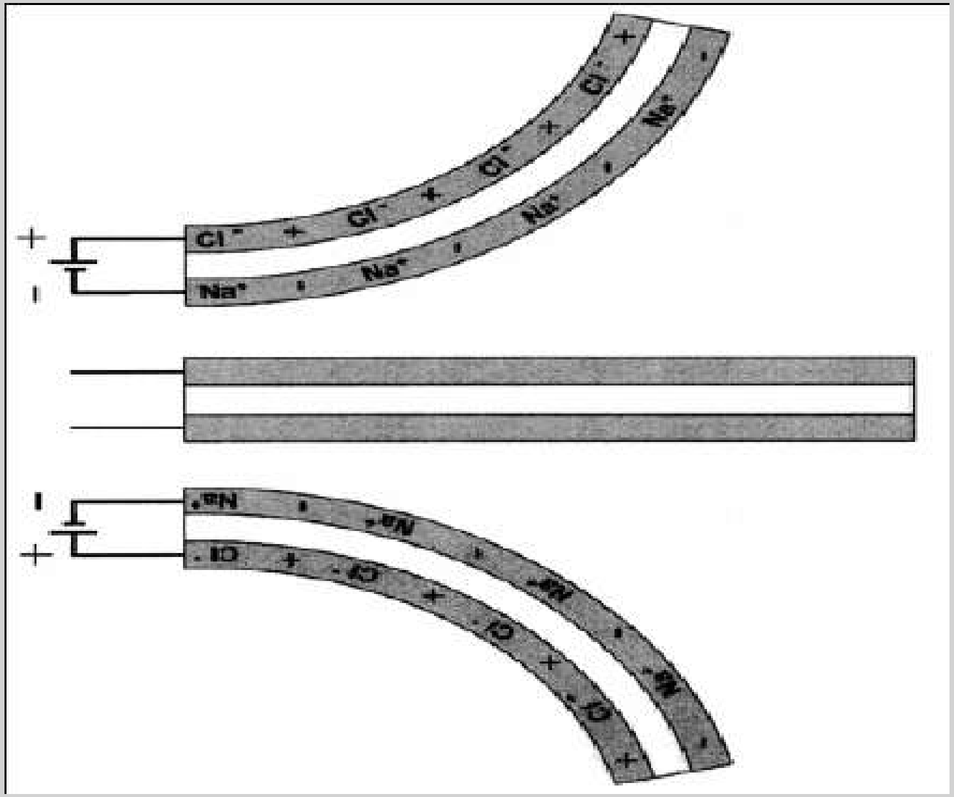
Applications: CNT-DNA-Array



Nanotube-DNA-Chip [Cassell, NASA (2004)]

Applications: Electromechanical actuator

- CNTs in NaCl solution
- principle:
  - differential charging when voltage applied
  - covalent bonds changed
- operation:
  - deflection up to 1 cm
  - dynamic up to 15 Hz



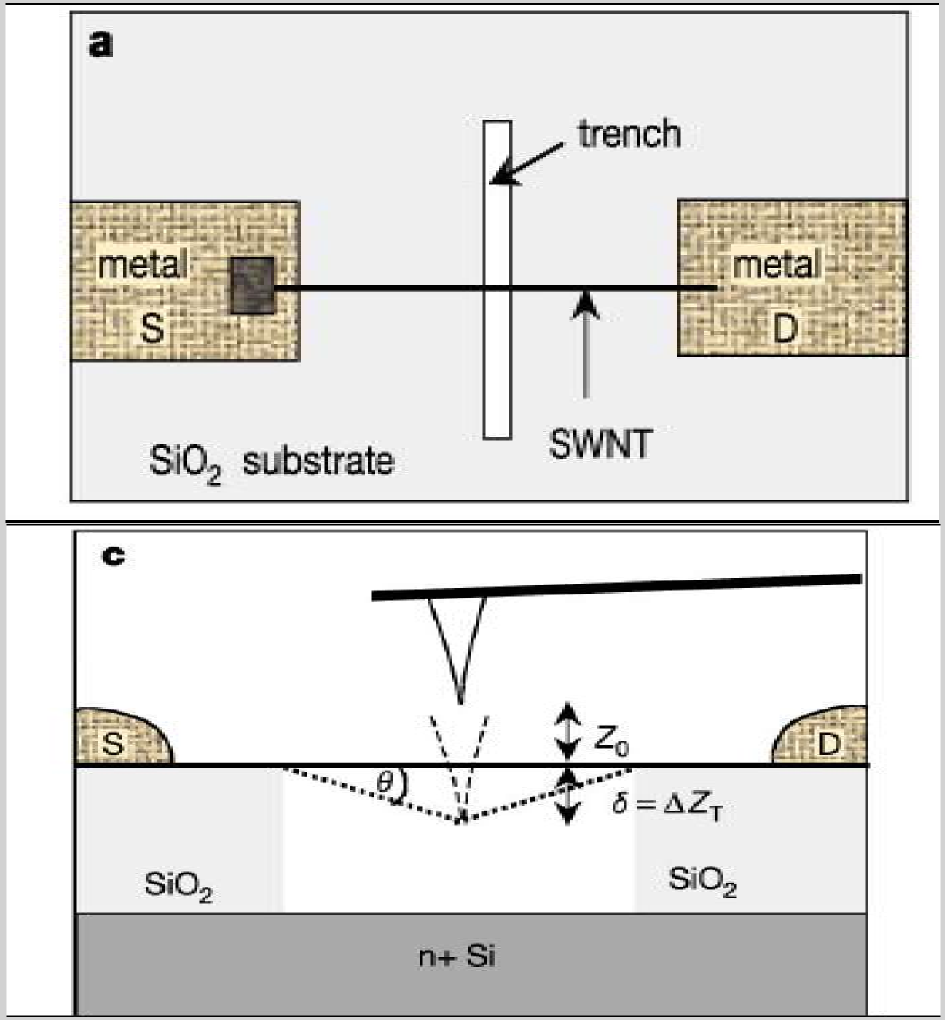
nanotube cantilever [(Baughman et al., Science (1999)]

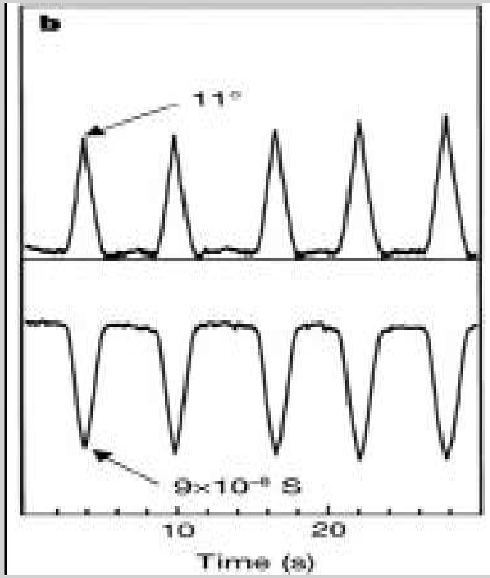
Applications: Deformation Sensor

- CNT-bridge over trench
- deformation:

  → weaker π delocalisation

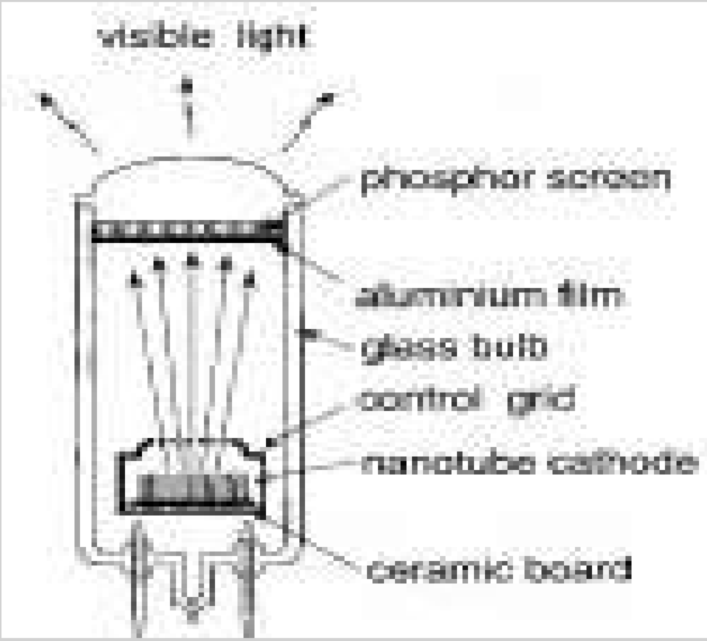
  → lower conductance





setup (a,c) and measurement response (b) of a CNT deformation sensor

Applications: Field Emission

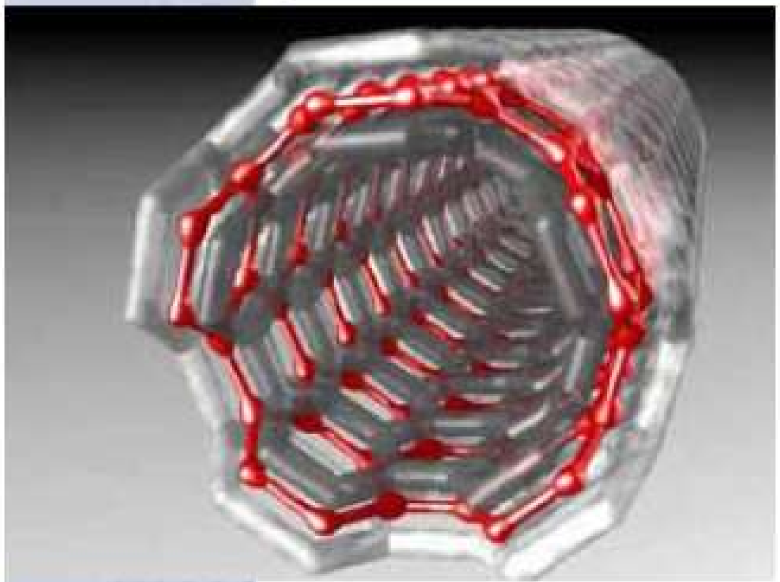


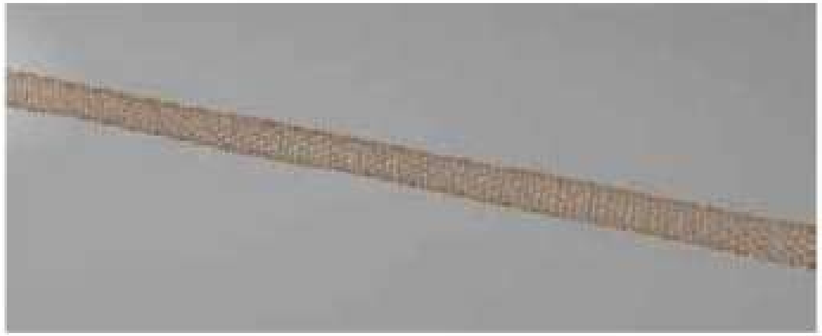
CNT - 'light bulb'

field emission display [Samsung]

Applications: Interconnects

Nanotubes – Interconnects of the Future?

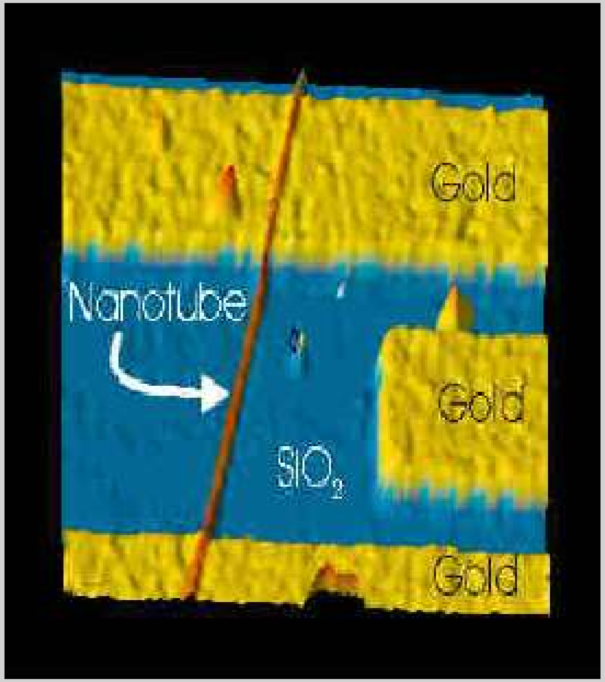


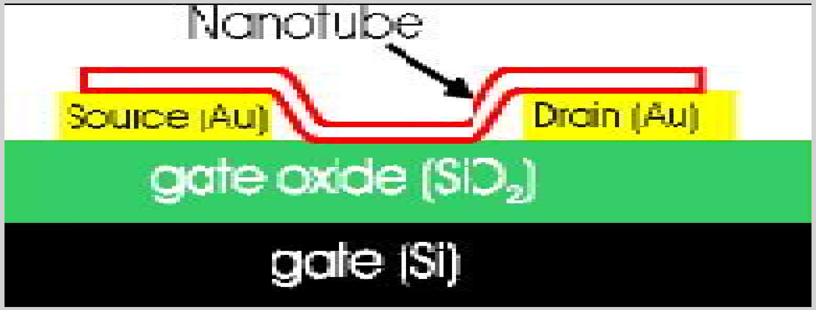


- ⇒ **Ultra high current densities: 10^{10} A/cm^2** (Copper 10^7 A/cm^2)
- ⇒ **No electromigration**
- ⇒ **Low resistance due to ballistic transport** (factor 15 compared to copper)
- ⇒ **No diffusion barrier necessary**

G.S. Düsberg, CPR NP
305. Heraeus Seminar
Nov. 2003

Applications: CNT-MOSFET I

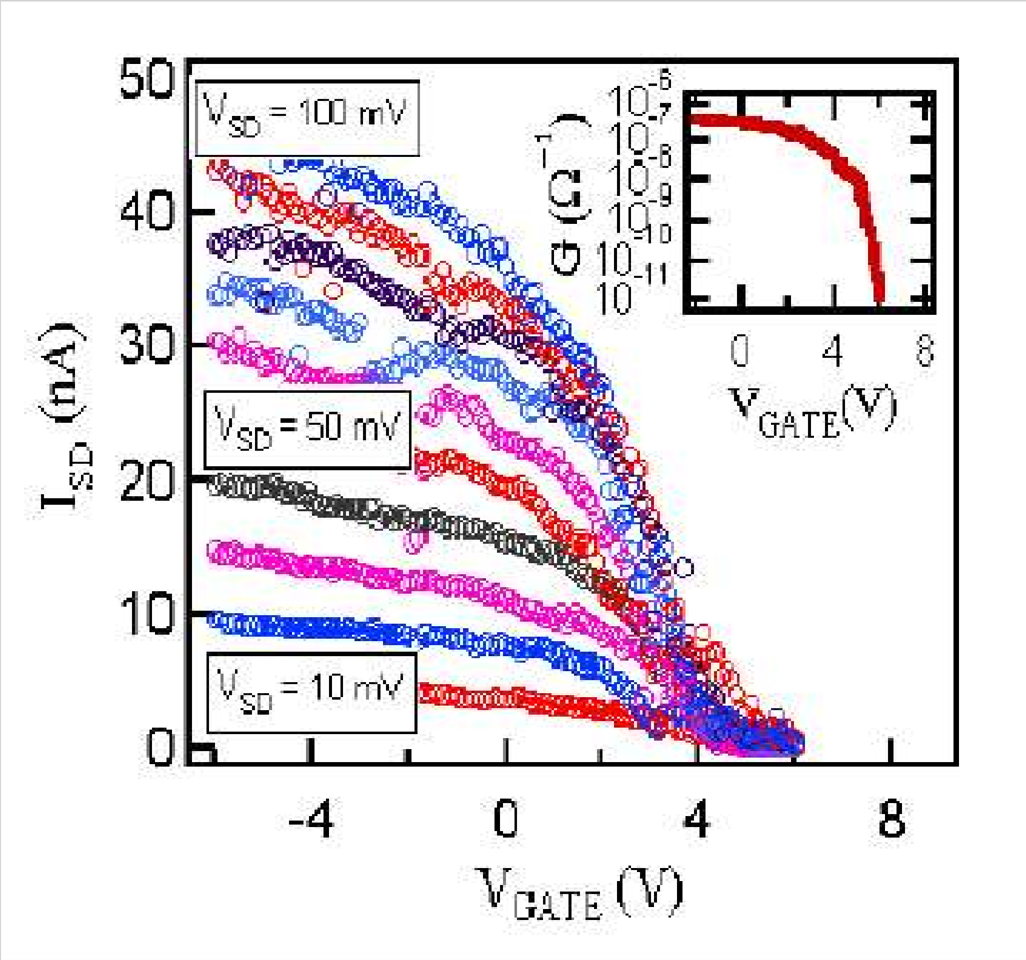




schematic and AFM picture of CNFET [IBM]

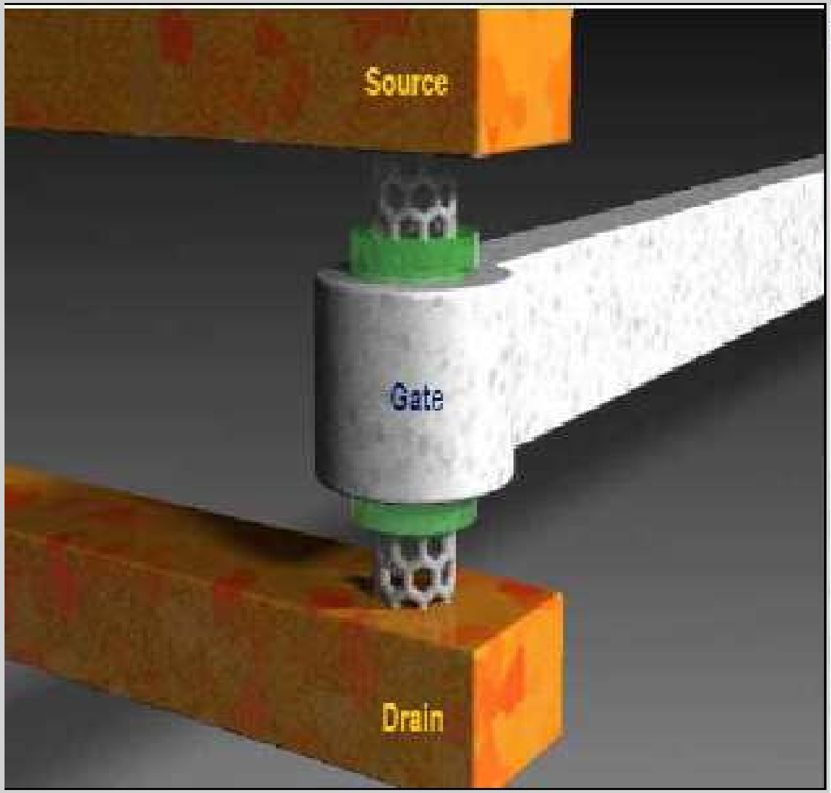
Applications: V_G-I_{SD}-Diagram

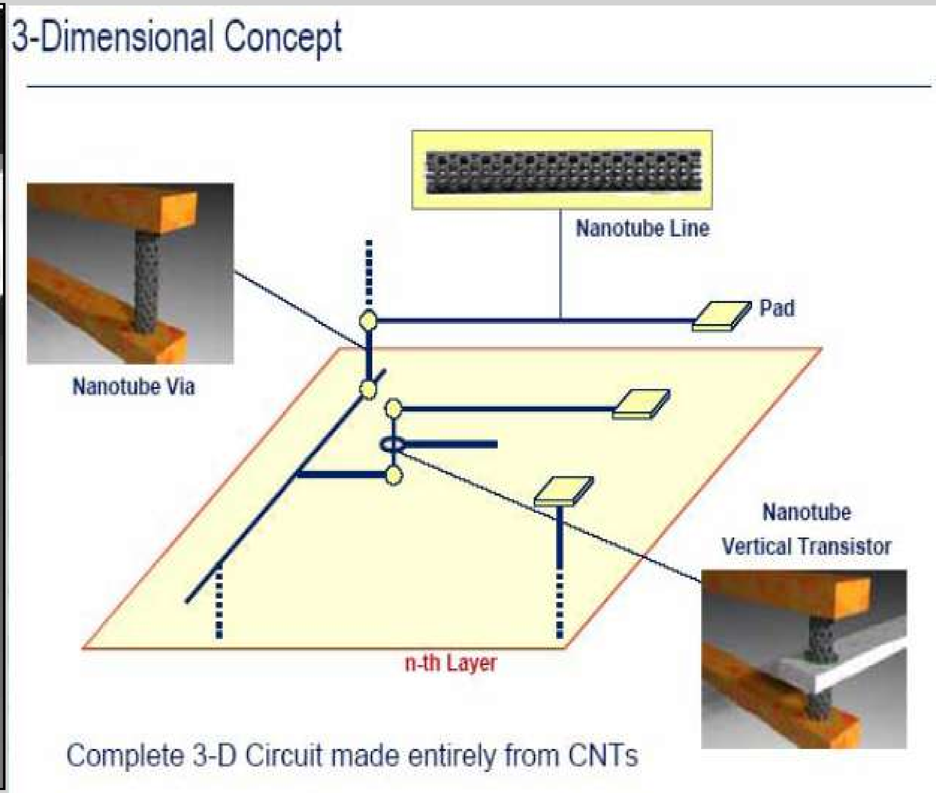
- intrinsically p-type
- low currents (nA)
- quite noisy
- CMOS compatible



V-I-plot of CNFET [IBM]

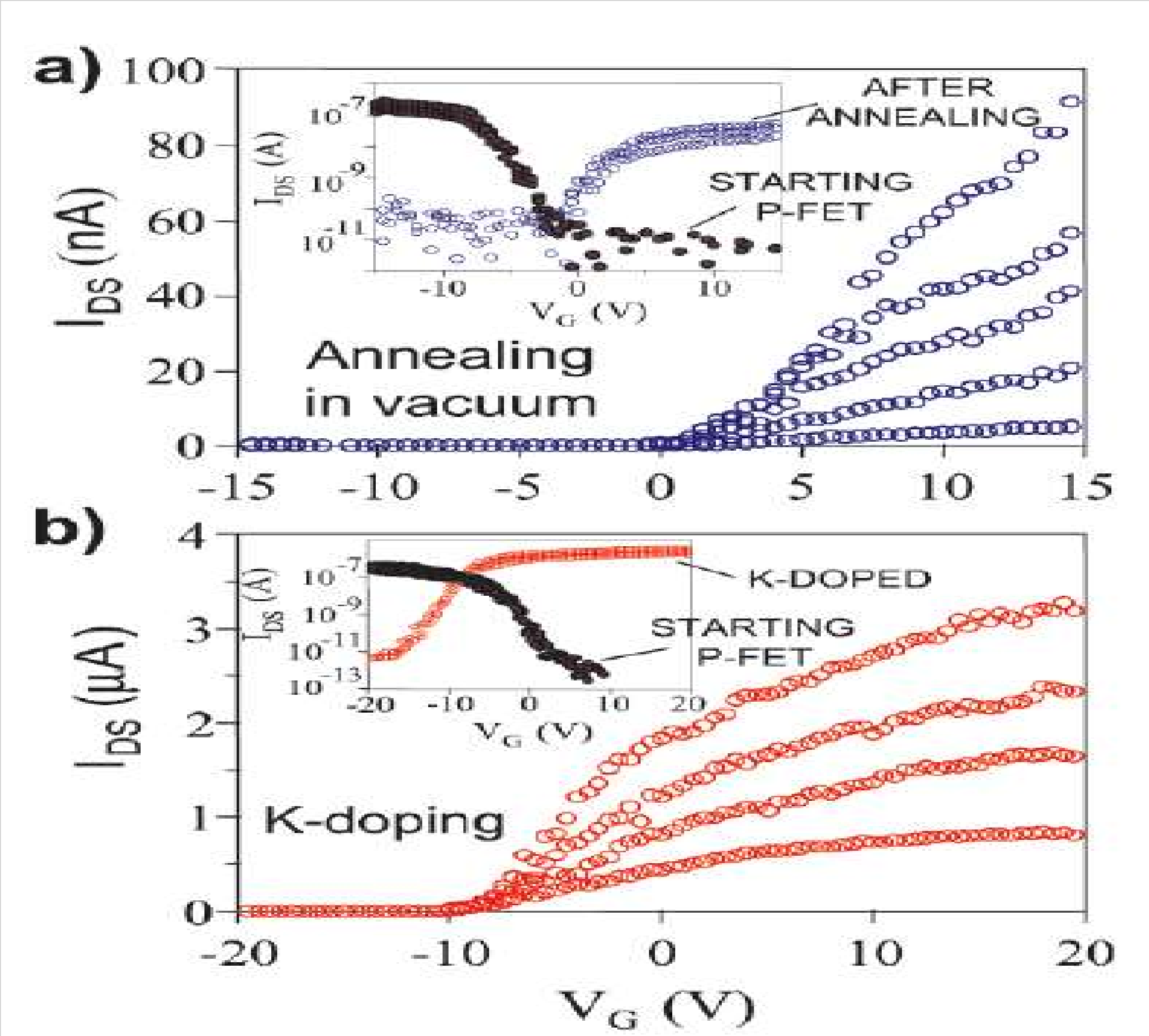
Applications: CNT-MOSFET II





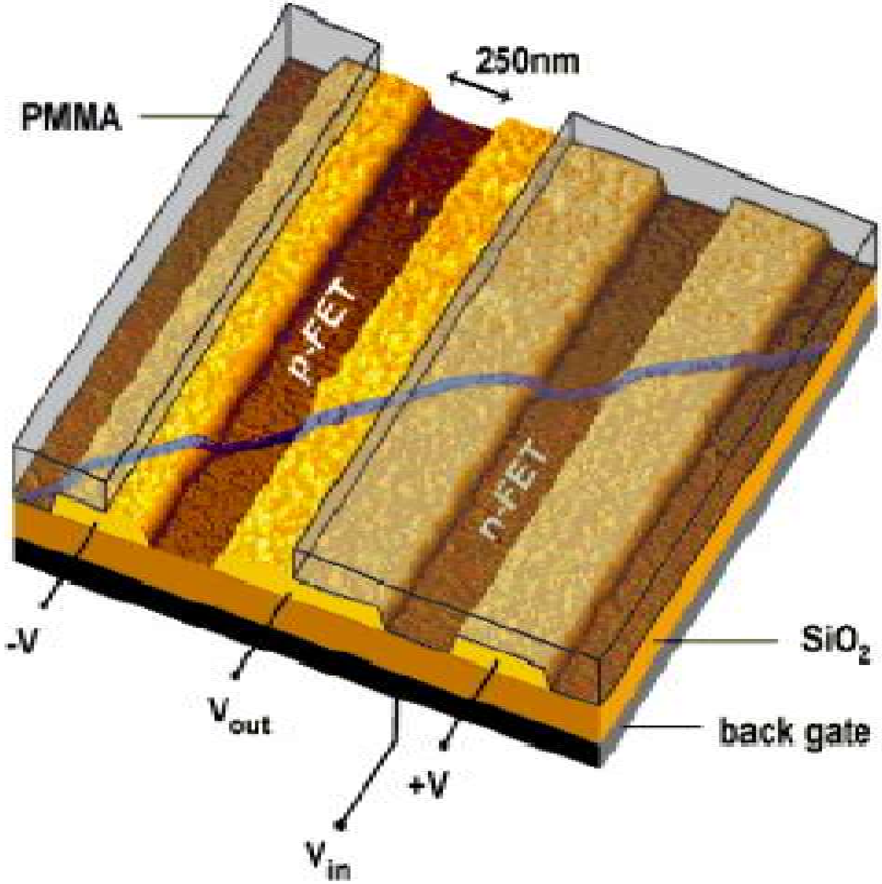
vertical CNFET and circuit architecture [Infineon]

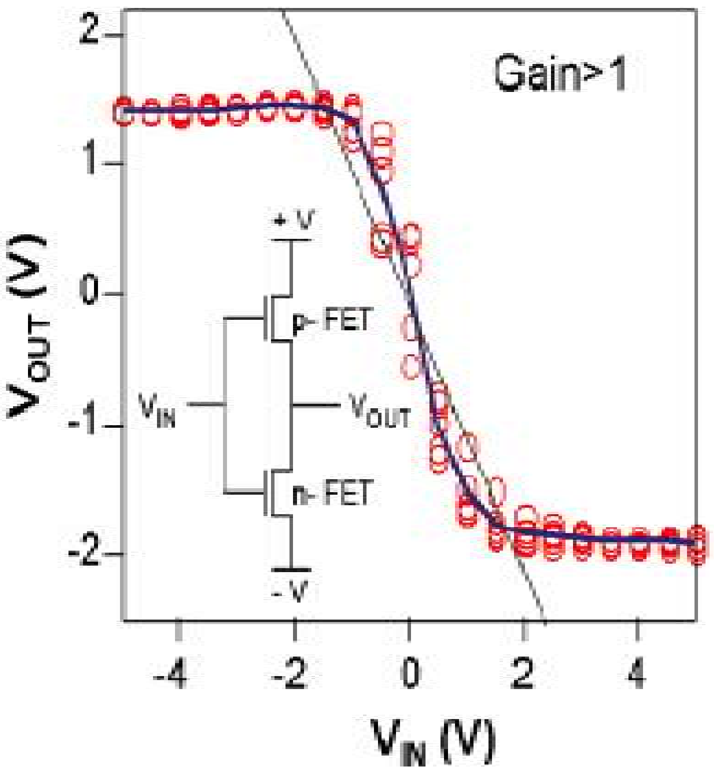
Applications: n-Type CNTs



n-type CNTs by annealing (a) / K-doping (b) [IBM]

Applications: CNT-Inverter



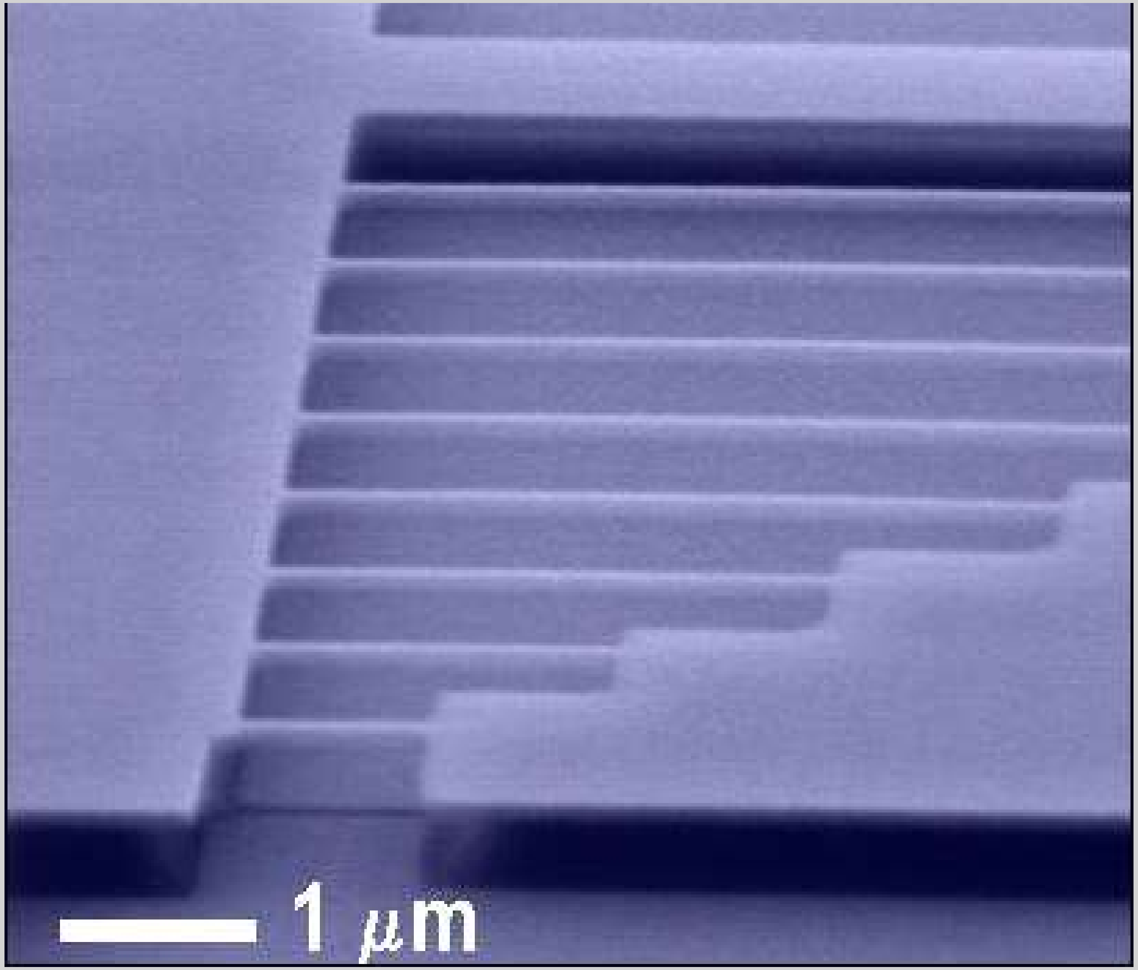


n-FET and p-FET are made from *same* nanotube [IBM, 2001]

Outline

- Introduction
- Physical Properties
- Manufacturing Techniques
- Applications
- Outlook

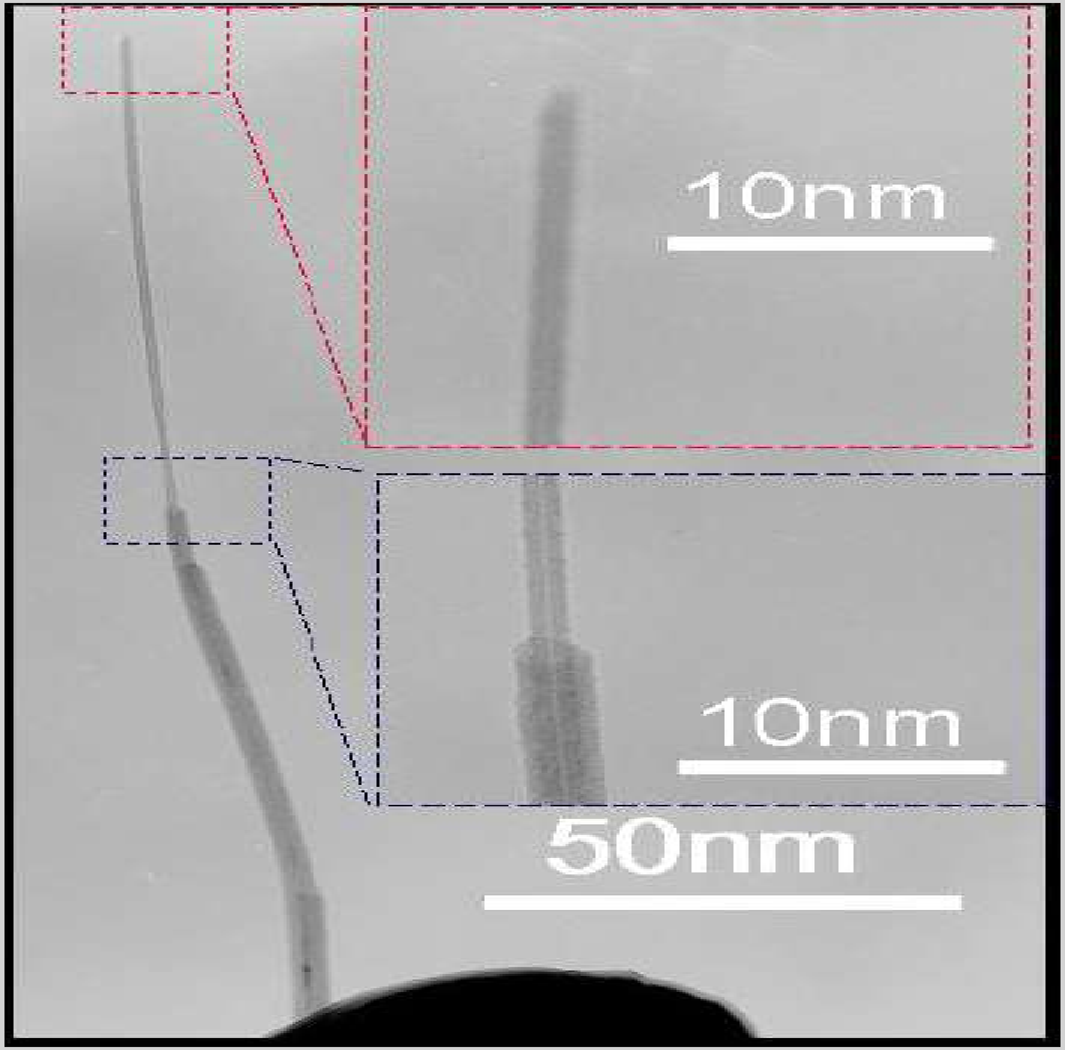
Outlook: Nano-Resonators



Silicon resonators

CNT based NEMS ?

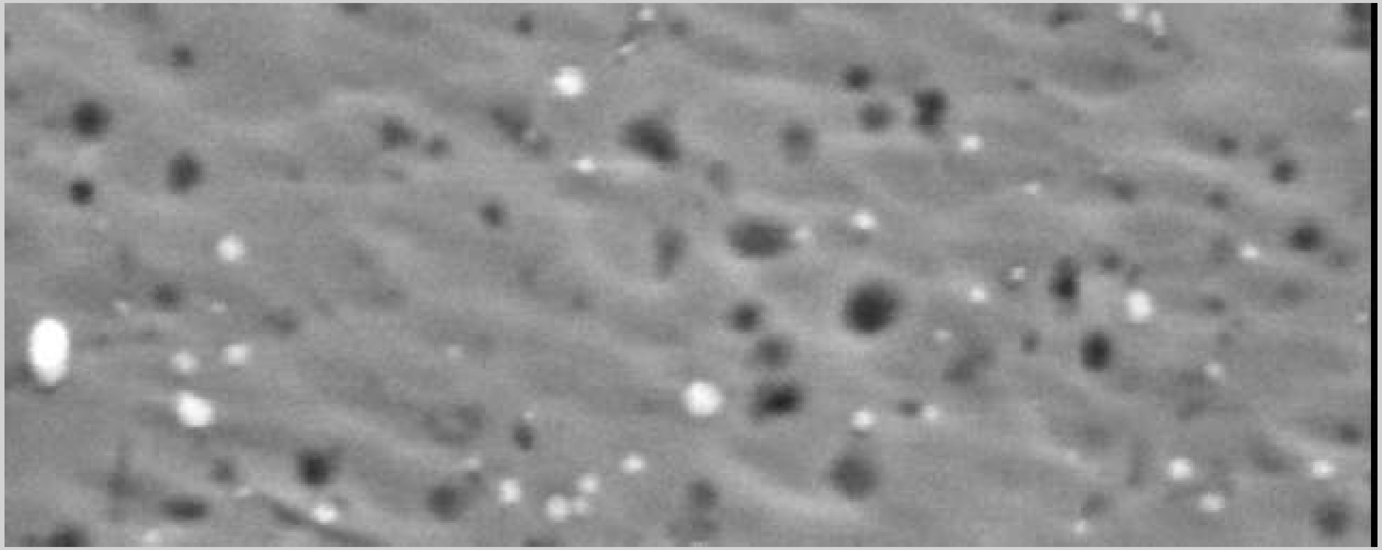
Outlook: Telescoping CNTs



Nanoprobes?
(Temperature, DNA-Hybridisation)

Improved field emitters?

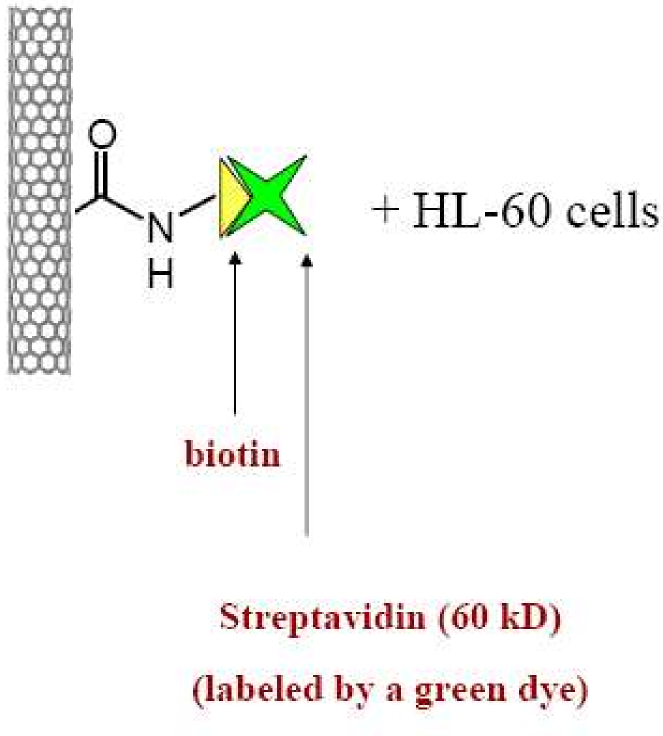
Outlook: Membranes

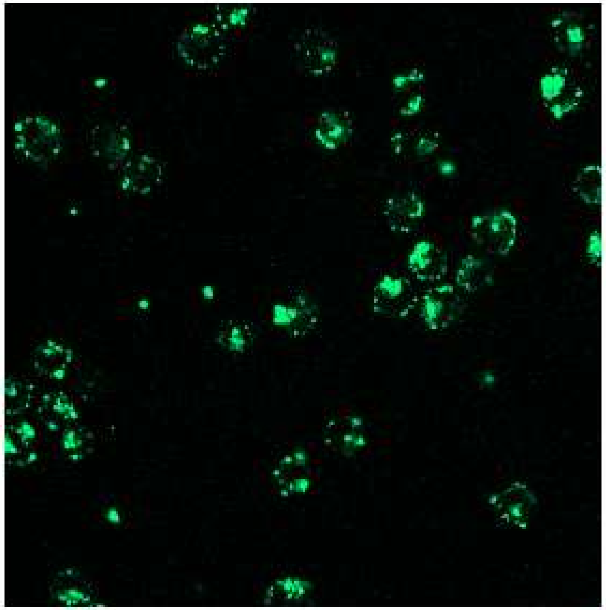


CNT in Si_3N_4 membrane

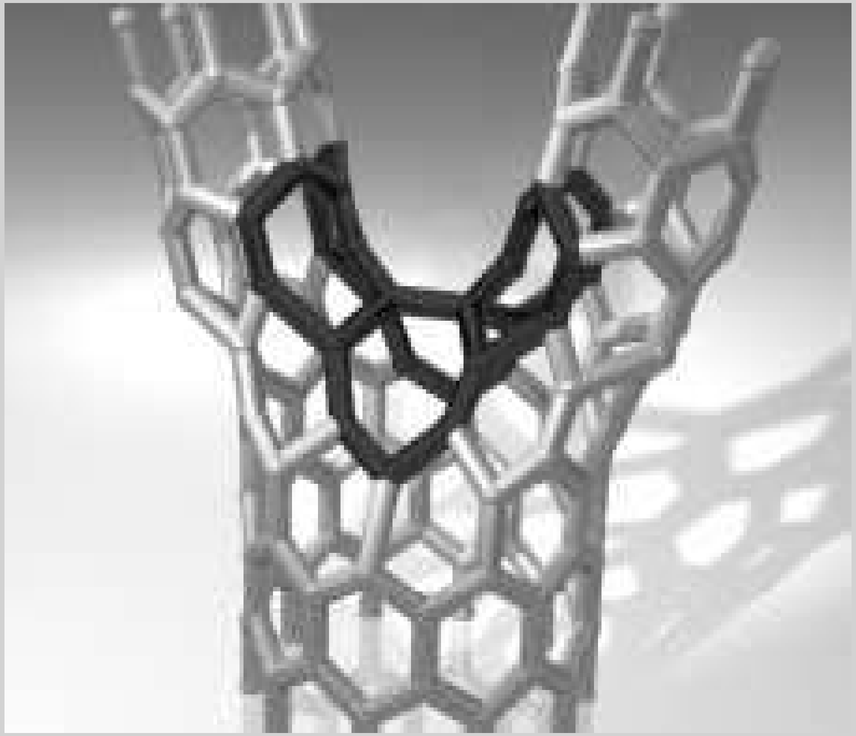
Nanofluidics?

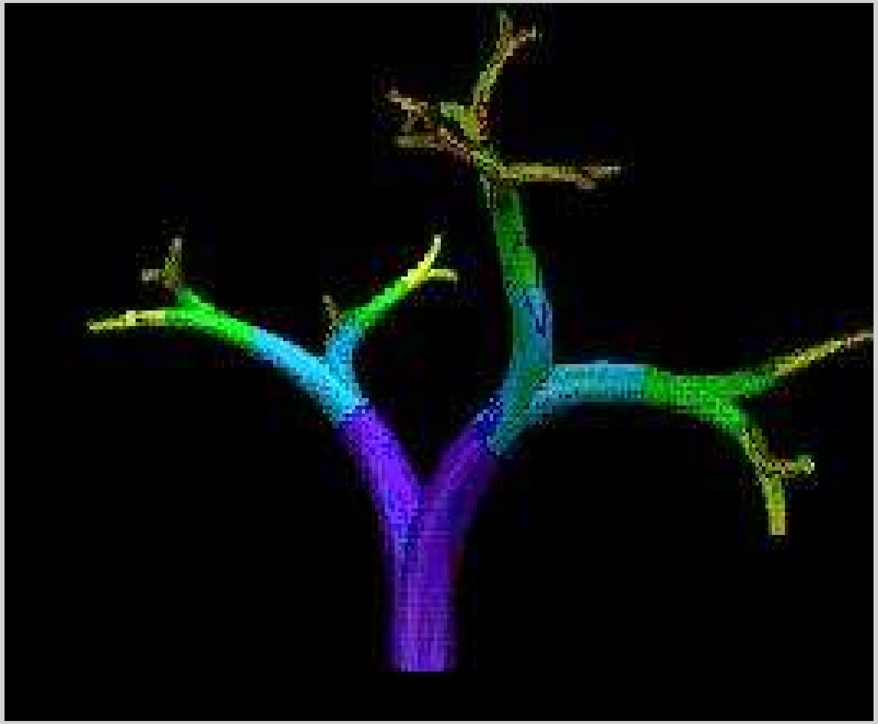
Outlook: Molecular Transporters [Stanford]





Outlook: Y-junctions

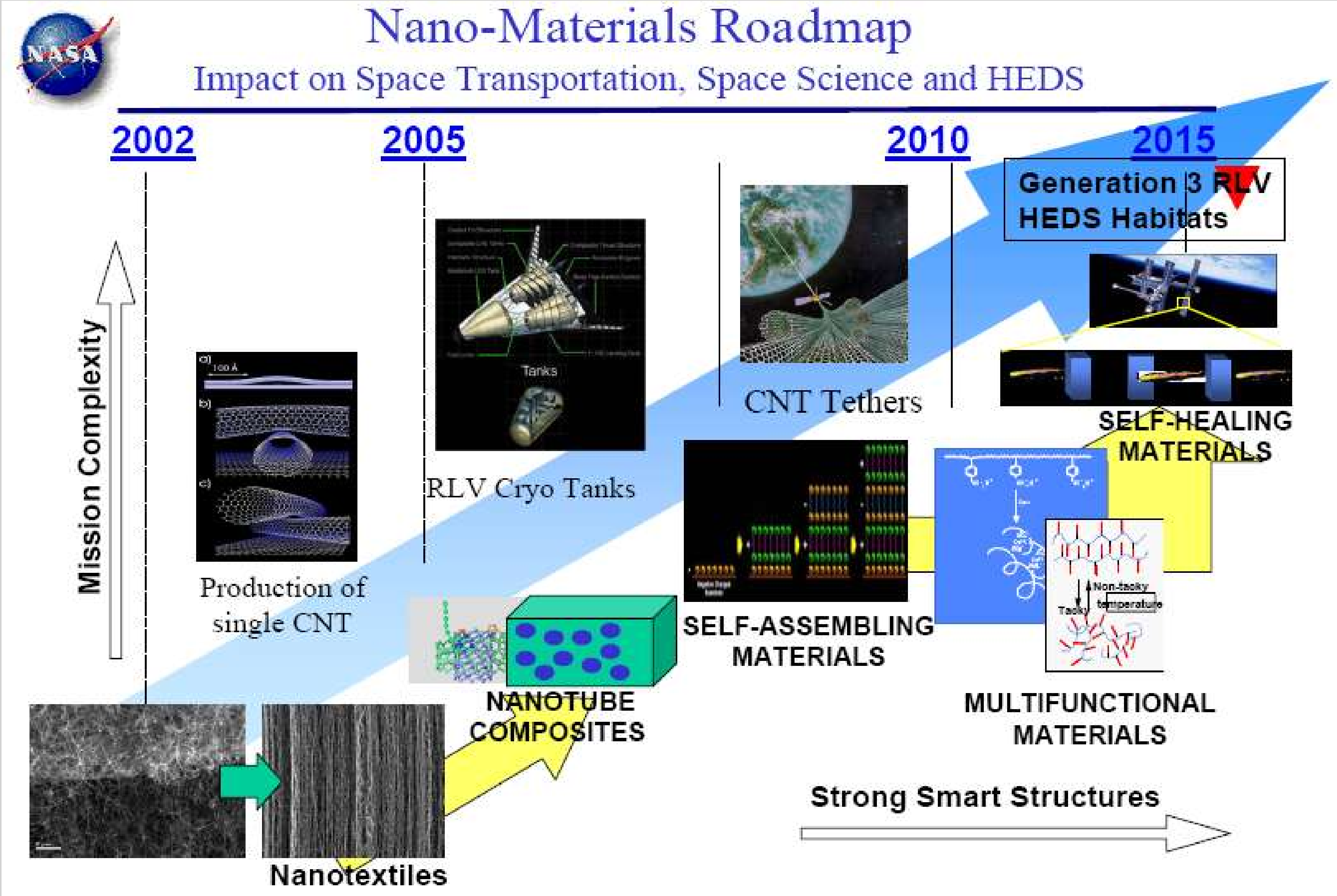




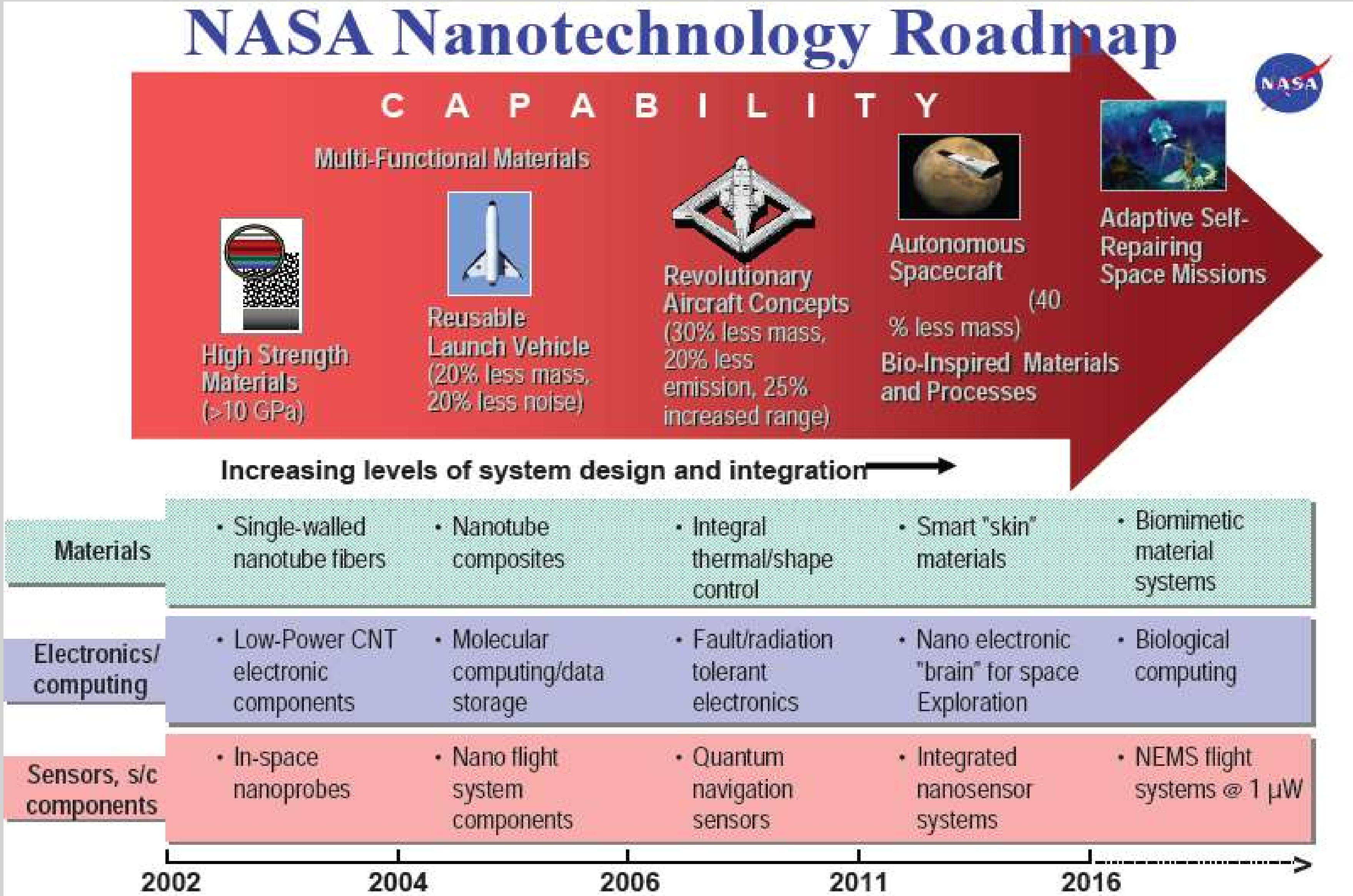
CNT y-junction and dentrite

CNT-Networks?

Outlook: NASA roadmap I



Outlook: NASA roadmap II



Thank you for your attention!!

Спасибо!!

Danke für eure Aufmerksamkeit!!