Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Semester Zimowy 2011/2012

Wykład

Modelowanie Nanostruktur

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Carbon Compounds – Diamonds of the 21st century

- **Carbon nanotubes (CNTs) – geometry, properties, & applications**
- **Electronic structure of graphene**
- **Electronic structure of carbon nanotubes (CNT)**
  - **CNT & graphene based electronics – the future of information technologies ?**

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Modelowanie Nanostruktur, 2011/2012
Jacek A. Majewski

Wykład 6 – *15 XI 2011*

Struktura elektronowa nanorurek

- **Zwiazki wegla**
- **Struktura elektronowa grafenu**
- **Od grafenu do nanorurki**

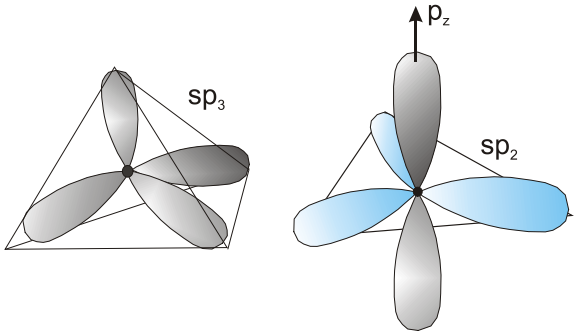
  w przestrzeni prostej i odwrotnej

Allotropes of carbon

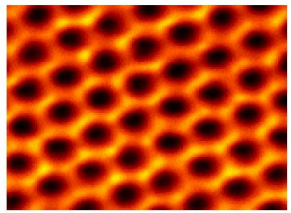
1. diamond
2. graphite
3. fullerene
4. graphene
5. carbon nanotubes
6. carbon nanocoils
7. lonsdaleite "hexagonal diamond"
8. amorphous carbon
9. carbon nanofoam
10. .....

Covalent bonds between carbons

sp^3 and sp^2 hybrids

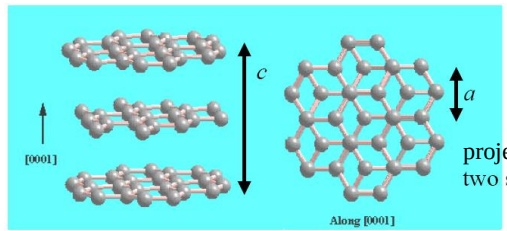


Graphite



STM image

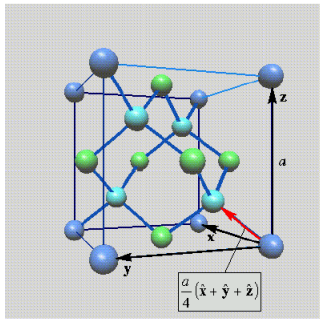
- ***a* = *b*= 0.2456 nm, *c*= 0.6694 nm**
- The carbon-carbon bond length in the bulk form is **0.1418 nm** (shorter and stronger than in diamond**)**
- **The interlayer spacing is *c*/2 = 0.3347 nm**
  - ➡ **weakly coupled 2D planes**
  - ➡ **pencil, lubricant**



projection of two sheets

Diamond

- **Lattice constant** **0.3566 nm at 298 K.**
- **nearest neighbor distance:** **0.154450 nm at 298K.**
- **Atomic weight: 12.01**
- **Atomic radius: 0.077 nm**
- **Number of atoms in a unit cell: 8**

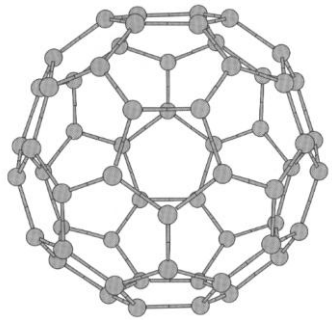


Two fcc lattices shifted by (a/4) [111]

The hardest material !

Fullerenes

The C_{60} cluster



'buckminsterfullerene'

'bucky-ball'

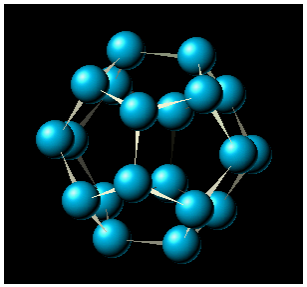
60 carbon atoms formed in

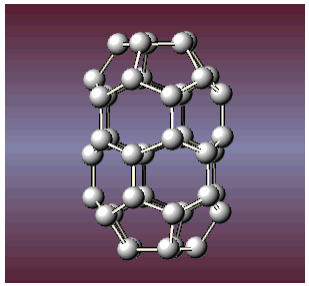
- **12 pentagons**
- **20 hexagons**
- **diameter = 1.034 nm**
- Point group – 120 symmetry operations

Synthesized by R. F. Curl, H. W. Kroto, and R. E. Smalley
Nobel Prize for Chemistry 1996

Named after **Buckminster Fuller**
American architect
(living XIX-XX century)

Fullerenes

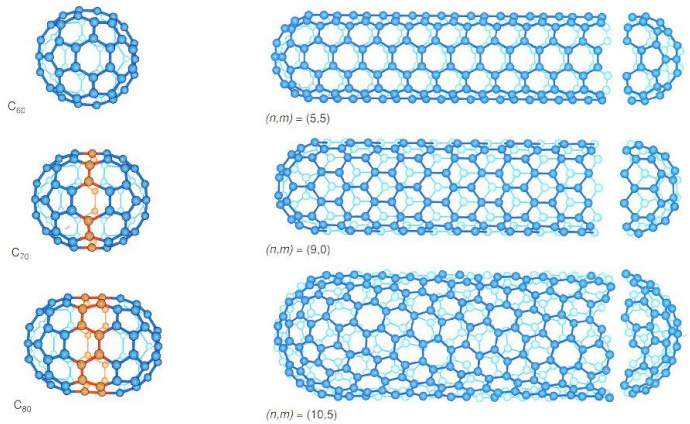




C_{20} C_{40}

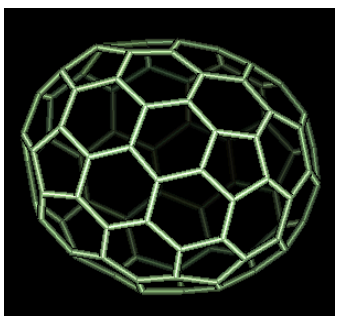
- consists of 12 pentagons
- ideal of dodecahedron

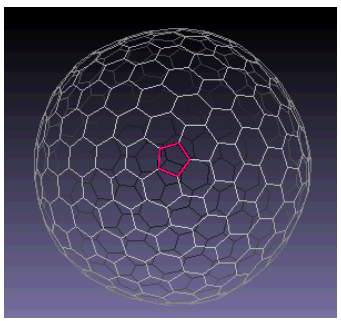
Carbon nanotubes (CNTs)



*S. Iijima, Nature **354**, 56 (1991)*

Fullerenes

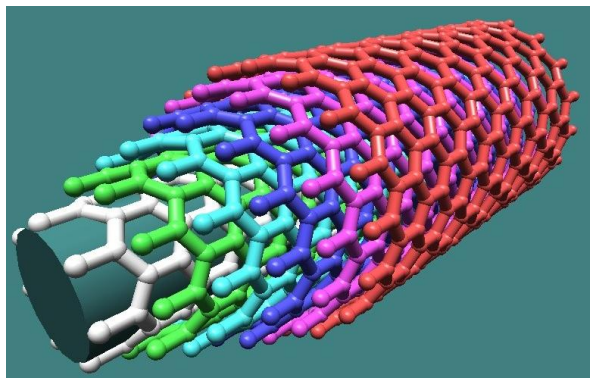




C_{86} C_{540}

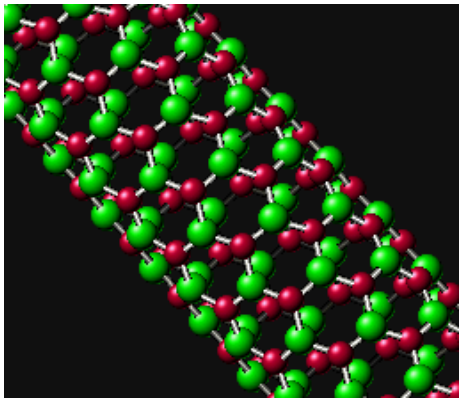
and many more …. (up to C_{980})

Multiple Wall Carbon Nanotubes



*D. Vgarte, Nature **359**, 707 (1992)*

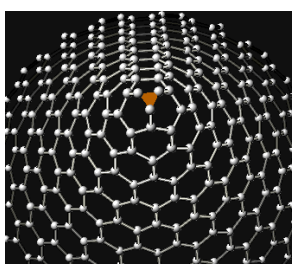
Boron Nitride Nanotubes

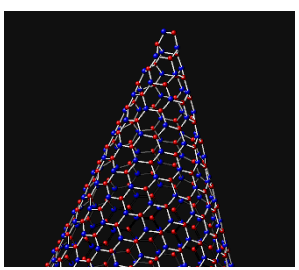


„These nanotubes are so beautiful that they must be useful for something"

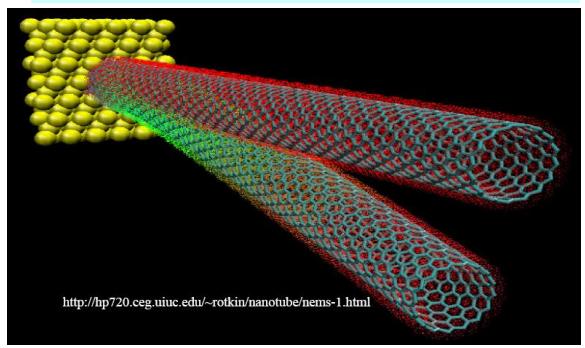
R. Smalley

Carbon (Boron Nitride) Nanocoils





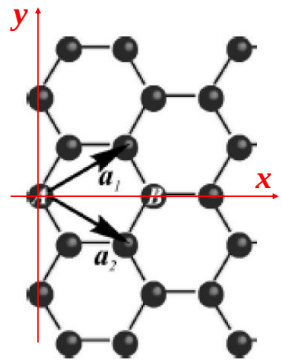
CNTs – Mechanical Properties



Mechanical strength – graphite-like strong bonds
-- no dangling bonds
-- no weakly bound sheets

Graphene:
a sheet of carbon atoms

Graphene – a single sheet of C atoms



- Two unit-cell vectors:

$$\vec{a}_1 = a(\frac{\sqrt{3}}{2}, \frac{1}{2})$$

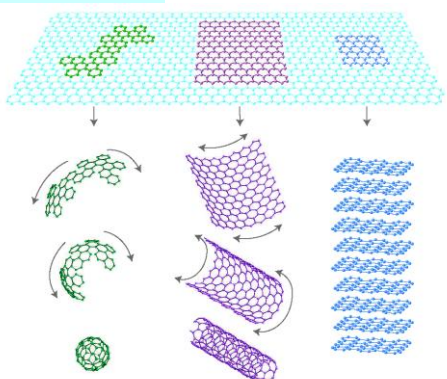
$$\vec{a}_2 = a(\frac{\sqrt{3}}{2}, -\frac{1}{2})$$

- Two non-equivalent atoms A and B in the unit cell (two sublattices)

$$a = \sqrt{3}d, d = 0.14nm$$

What is graphene?

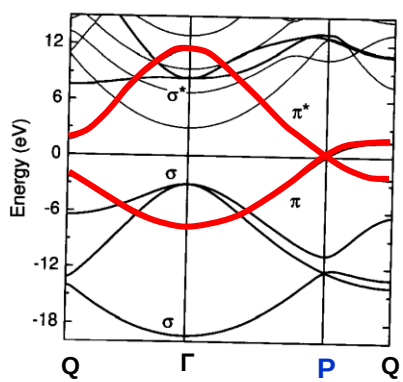
- 2-dimensional hexagonal lattice of carbon
  - sp^2 hybridized carbon atoms
    Among strongest bonds in nature

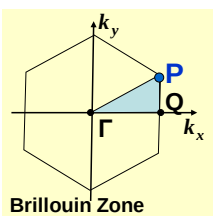


- Basis for:

C-60 (bucky balls) nanotubes graphite

Electronic band structure of graphene

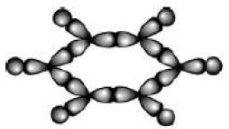




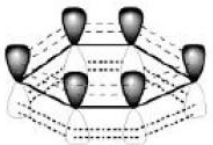
The band structure was calculated with a first-principles method

M. Machon, *et al.*, Phys. Rev. B **66**, 155410 (2002)

Tight-binding description of graphene



σ bonds – not considered in this model



π bonds considered

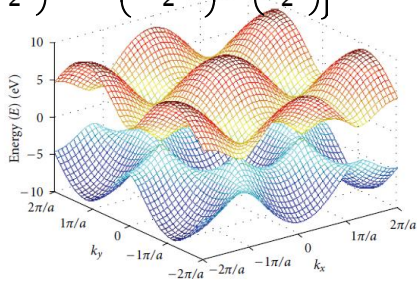
- **One p_z orbital pro atom**
- **Only couplings between nearest neighbors taken into account**

Dispersion relations for graphene

$$\varepsilon = \alpha \pm \beta\sqrt{3+\cos\left(\frac{a}{2}\left(\sqrt{3}k_x+k_y\right)\right)+2\cos\left(\frac{a}{2}\left(\sqrt{3}k_x-k_y\right)\right)+2\cos\left(ak_y\right)}.$$

$$\alpha=\varepsilon_p=0 \qquad \beta\equiv t$$

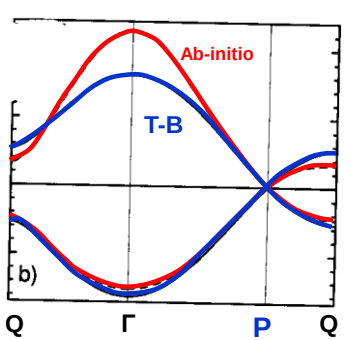
$$\varepsilon(\vec{k})=\pm t\left\{1+4\cos^2\left(\frac{k_y a}{2}\right)+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\right\}^{1/2} \quad \begin{matrix}\alpha=\varepsilon_p=0\\ \beta=t\end{matrix}$$

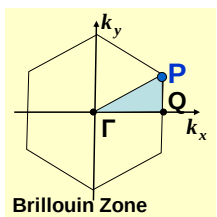


Tight-binding description of graphene

- $\begin{vmatrix} \varepsilon_p-\varepsilon(\vec{k}) & H_{AB}(\vec{k}) \\ H^*_{AB}(\vec{k}) & \varepsilon_p-\varepsilon(\vec{k}) \end{vmatrix}=0 \quad \Rightarrow \quad \varepsilon(\vec{k})$
- $H_{AA}=H_{BB}=\varepsilon_p$
- $H_{AB}(\vec{k})=\sum_{\vec{R}_n} exp(i\vec{k}\cdot\vec{R}_n)<\varphi_A(\vec{\tau}_A)|\hat{H}|\varphi_B(\vec{\tau}_B+\vec{R}_n)>$
- $H_{AB}(\vec{k})=t[1+exp(i\vec{k}\cdot\vec{a}_1)+exp(i\vec{k}\cdot\vec{a}_2)]$
- $\varepsilon_p=0$ (zero of energy)
- $\varepsilon(\vec{k})=\pm t\left(H_{AB}(\vec{k})H^*_{AB}(\vec{k})\right)^{1/2}$

Nearest-neighbors tight-binding electronic structure of graphene



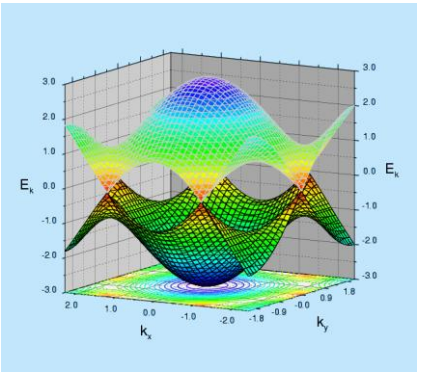


Hopping parameter

t = -2.7 eV

Tight-binding band structure of graphene

$$\varepsilon(\vec{k}) = \pm t\left\{1 + 4\cos^2\left(\frac{k_y a}{2}\right) + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\right\}^{1/2}$$



⟹ **Graphene is semi-metallic**

Energy gap is equal zero only in one k-point (P-point)

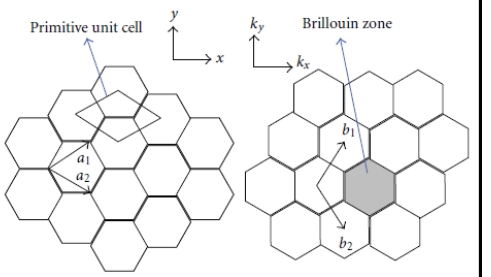
Reciprocal lattice of graphene

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2 \times \vec{z}_0}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{z}_0)}, \qquad \vec{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right),$$

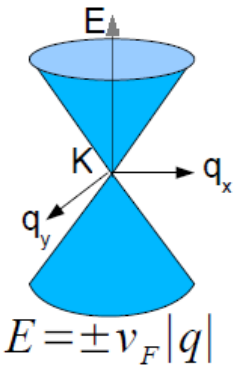
$$\vec{b}_2 = 2\pi\frac{\vec{z}_0 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{z}_0 \times \vec{a}_1)}, \qquad \vec{b}_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}\right).$$

$$\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right),$$

$$\vec{a}_2 = a\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right),$$



Massless 2D Dirac Fermions



$$E = \pm v_F |q|$$

"light cone"

$$H_K = \begin{pmatrix} 0 & v_F(q_x - iq_y) \\ v_F(q_x + iq_y) & 0 \end{pmatrix}$$

- q = K - k
- 2x2 structure from 2 site unit cell => pseudo spin

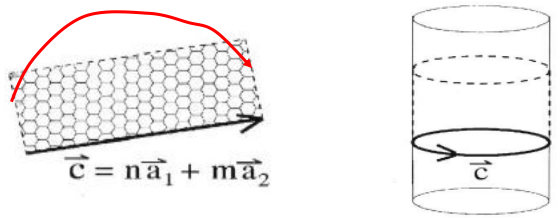
$$H_K = v_F(\sigma_x \quad \sigma_y)\begin{pmatrix} q_x \\ q_y \end{pmatrix}$$

Pseudo spin is projected on momentum
- σ parallel q <=> electron
- σ antiparallel q <=> hole

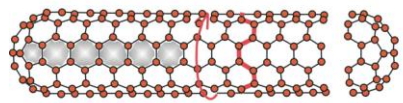
Carbon nanotubes:
geometry & electronic structure

Nanotube = rolled graphene sheet

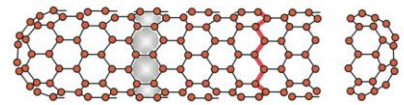
Nanotube is specified by chiral vector: $\vec{C}_h(n,m) = n\vec{a}_1 + m\vec{a}_2$



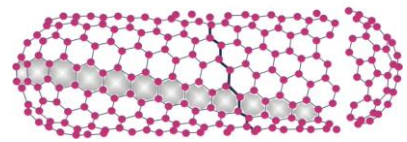
Structure of Carbon Nanotubes



Carbon nanotube of type chair (5,5)



Carbon nanotube of type zigzag (9,0)

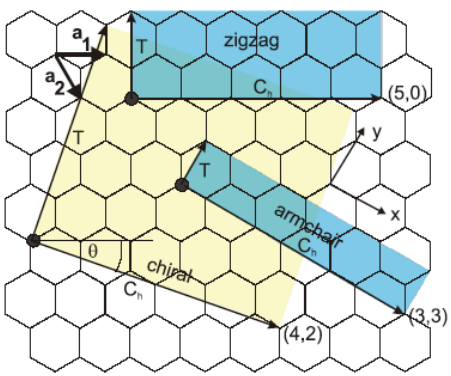


Chiral (10,5) carbon nanotube

Structure of Carbon Nanotubes

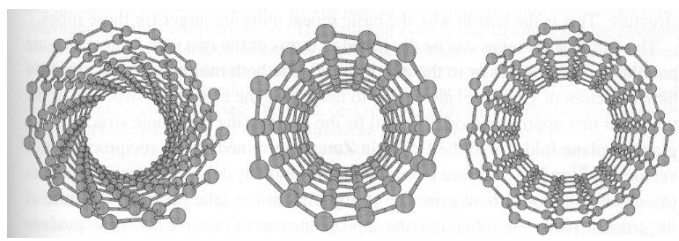
The chiral vector: $\vec{C}_h(n,m) = n\vec{a}_1 + m\vec{a}_2$

$m < n$



- *(n,0)* – zig-zag
- *(n,n)* – armchair
- *(n,m)* – chiral $m \neq n$

Perspective view of nanotubes



(8,4) chiral tube (7,0) zig-zag tube (7,7) armchair tube

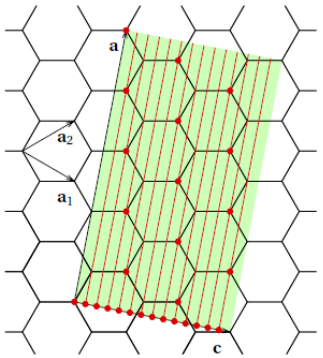


Figure 2: Unit cell of the (2,1) tube (green area) with indicated graphene basis lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Projecting the unit cell of the (2,1) tube on the **c** axis yields $q = 14$ projected origins of graphene unit cells which yields the smallest physical real space period in **c** direction to be $\frac{\|\mathbf{c}\|}{q}$.

Which CNTs are metallic? Which semiconducting?

- $E_{GAP} = 0 \Leftrightarrow H_{AB}(\vec{k}) = 0$

  $E_{GAP} = 0 \Leftrightarrow 1 + exp(i\vec{k}\cdot\vec{a}_1) + exp(i\vec{k}\cdot\vec{a}_2) = 0$

  We get two possible conditions

  $\vec{k}\cdot\vec{a}_1 = 2\pi\left(\frac{1}{3} + l\right)$ and $\vec{k}\cdot\vec{a}_2 = 2\pi\left(\frac{2}{3} + l'\right)$

  or

  $\vec{k}\cdot\vec{a}_1 = 2\pi\left(\frac{2}{3} + l\right)$ and $\vec{k}\cdot\vec{a}_2 = 2\pi\left(\frac{1}{3} + l'\right)$

  l, l', l'' – integers

- Due to the periodicity condition

  $\vec{k}\cdot\vec{C}_h(n,m) = \vec{k}\cdot(n\vec{a}_1 + m\vec{a}_2) = 2\pi l''$

  $2\pi n\left(\frac{1}{3} + l\right) + 2\pi m\left(\frac{2}{3} + l'\right) = 2\pi l'' \rightarrow \frac{n+2m}{3} = l$

  or

  $2\pi n\left(\frac{2}{3} + l\right) + 2\pi m\left(\frac{1}{3} + l'\right) = 2\pi l'' \rightarrow \frac{2n+m}{3} = l'$

Electronic structure of CNT – Zone-folding Approximation

Graphene – infinite plane in 2D

For CNTs, we have a structure which is

- macroscopic along the tube direction,
- but the circumference is in atomic scale

➡ **Periodic boundary conditions in the circumferential direction**

➡ **The allowed electronic states are restricted to k-vectors that fulfill the condition**

$$\vec{k}\cdot\vec{C}_h(n,m) = 2\pi l$$

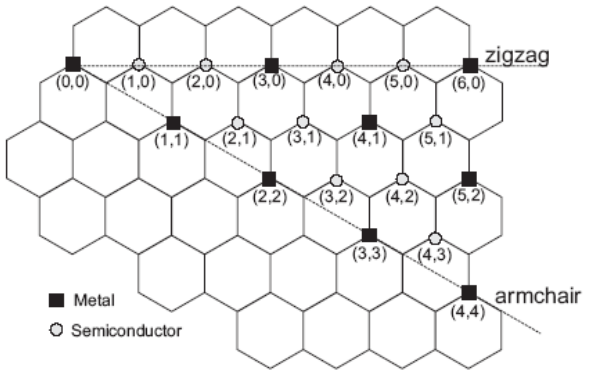
- **P-point belongs to allowed k-vectors → CNT is metallic**
- **P-point does not belongs to allowed k-vectors → CNT is semiconducting**

Which CNTs are metallic? Which semiconducting?

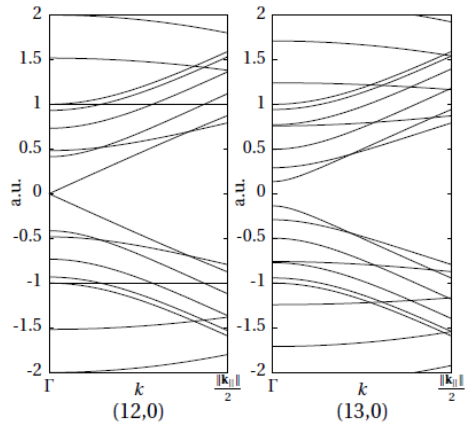
Nanotube (*n*,*m*) is metallic $\Leftrightarrow$ $\frac{n+2m}{3} = l$, $\frac{2n+m}{3} = l'$ $\Leftrightarrow$ $n - m = 3l$

- **Nanotube is a metal if *n*-*m* is multiple of three**
- **Otherwise CNT is a semiconductor**
- **All armchair (*n*=*m*) CNTs are metallic**

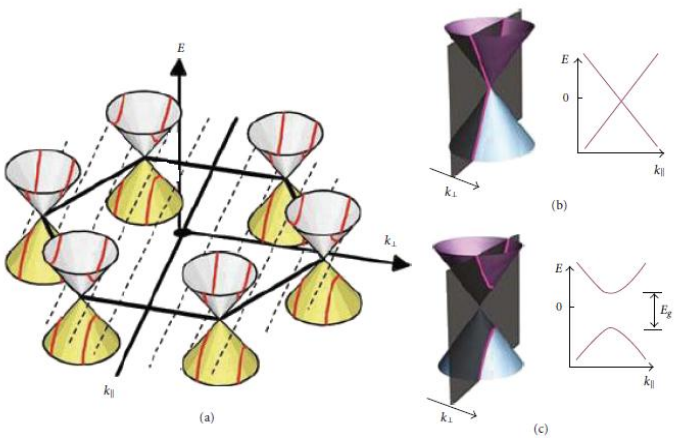
Metallic and semi-conducting CNTs



Metallic and semi-conducting CNTs – Band Structure

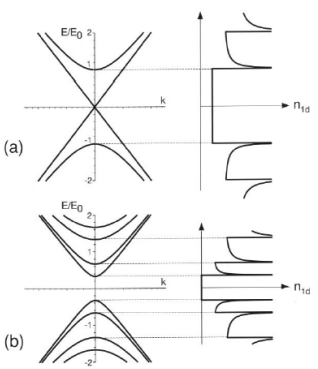


Metallic and semi-conducting CNTs

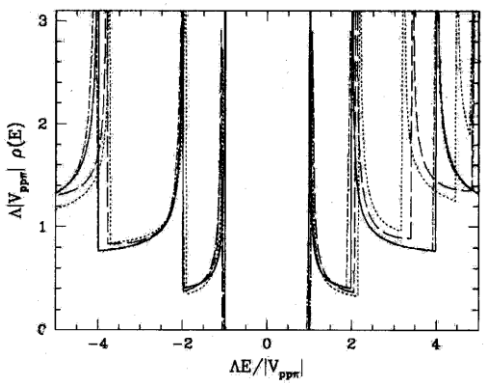


CNTs – band structure & density of states

- Metallic SWNT: constant DoS around *E=0*, van Hove singularities at opening of new subbands
- Semiconducting tube: gap around *E=0*
- Energy scale in SWNTs is about 1 *eV*, effective field theories valid for all relevant temperatures



Electronic density of states for (16,0), (13,6), (21,20) nanotubes



Pronounced 1D-behavior !

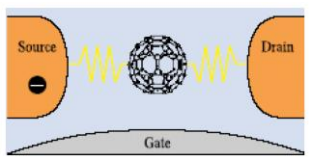
CNT & graphene based FETs - the future of nanoelectronics?

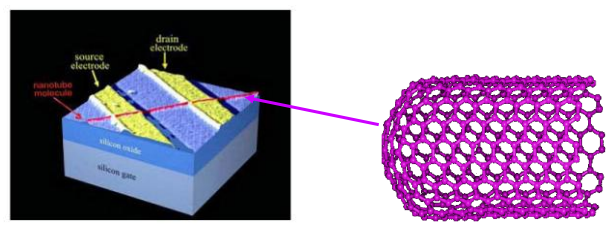
CNTs – Ideal 1D Quantum Wires

- Transverse momentum quantization:
  - $k_y = 0$ is only allowed mode,
  - all others more than 1eV away (ignorable bands)
- 1D quantum wire with two spin-degenerate transport channels (bands)
- Massless1D Dirac Hamiltonian
- Two different momenta for backscattering

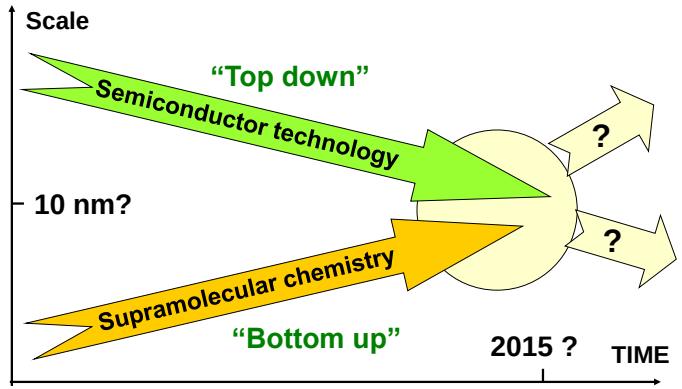
$$q_F = |E_F| / v_F < k_F = |\vec{K}|$$

Molecular Electronics with fullerenes and Transistors based on CNTs



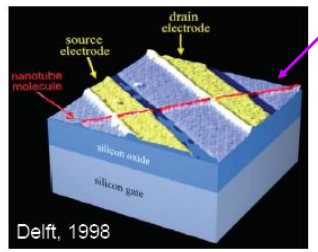


Electronics based on semiconductor nanostructures and large molecules

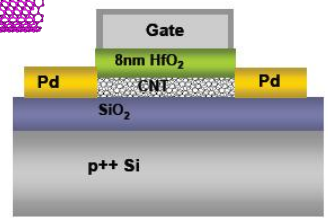


CNTFETs: 1998 - 2004

Back gate transistor



Top gate transistor



Delft:
Tans, et al., Nature, **393**, 49, 1998

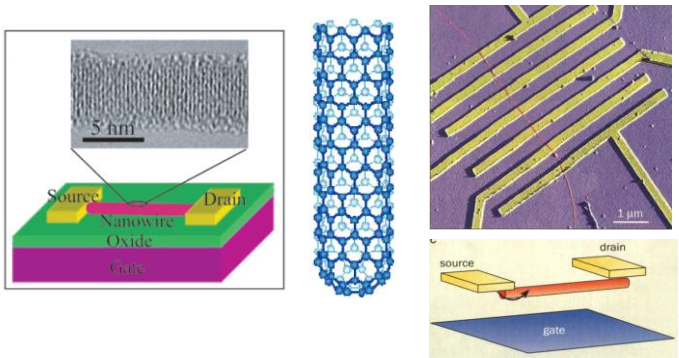
IBM:
Martel et al., APL, **73**, 2447,1998

Javey, et al., *Nano Letters*, **4**, 1319, 2004

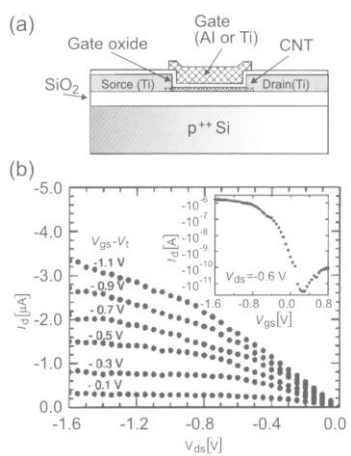
Semiconductor nano-wires & carbon nanotubes

Field Effect Transistor based

on silicon nano-wire **& carbon nanotube**



CNTFETs – Isolated Top Gate Devices



Schematic cross section of a top gate CNTFET

Output characteristics of a p-type device with Ti gate and a gate oxide thickness of 15 nm.

S. J. Wind et al., Appl. Phys. Lett. **80**, 3817 (2002)

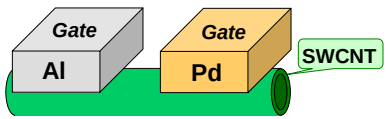
Comparison of Si-MOSFETs with up-scaled CNT-MOSFETs

	p-type CNFET	Ref. 59	Ref. 60
Gate length (nm)	260	15	50
Gate oxide thickness (nm)	15	1.4	1.5
V_t (V)	–0.5	~ –0.1	~ –0.2
I_{ON} (μA/μm) ($V_{ds} = V_{gs} - V_t \approx$ -1 V)	2100	265	650
I_{OFF} (nA/μm)	150	< 500	9
Subthreshold slope (mV/dec)	130	~ 100	70
Transconductance (μS/μm)	2321	975	650

- **CNTs devices show competitiveness to state-of-the-art Si-MOSFETs !**
- **CNT-MOSFET shows unprecedented values for transconductance and maximum current drive**

Integrated circuit built on single nanotube

- Metals with different work functions as the gates

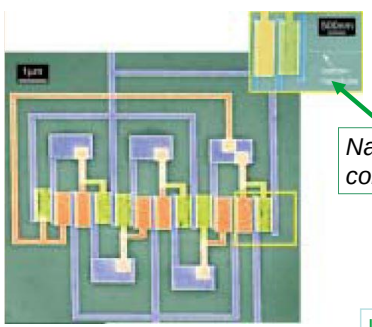


- The difference in the two work functions shifts the characteristics to give a **p-/ n-FET** pair

n-type FET + p-type FET = Inverter

- In this way, five inverters involving ten FETs were arranged side-by-side on a single, 1.8 μm long SWNT.
- Inverter works at a frequency of **52 MHz**, ~100 000 times faster than previous circuits built by connecting separate nanotube transistors.
- This improvement is a result of our compact design, which eliminates parasitic capacitance contributions to a large extent

Integrated circuit built on single nanotube



Nanotube covered by the contact and gate electrodes.

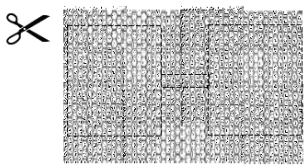
Ring oscillator circuit built on a single carbon nanotube consisting of five CMOS inverter stages.

IBM T. J. Watson Research Center, the University of Florida, and Columbia University [Chen *et al*., Science(2006) 311, 1735].

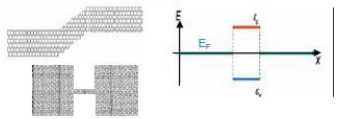
Graphene for devices

Graphene's advantage: cut-a-structure

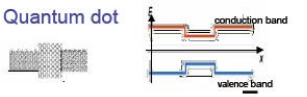
Seamless connection between graphene components



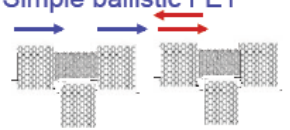
Semiconducting strip



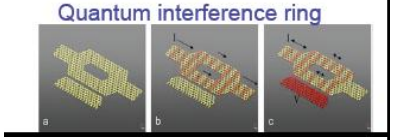
Quantum dot



Simple ballistic FET



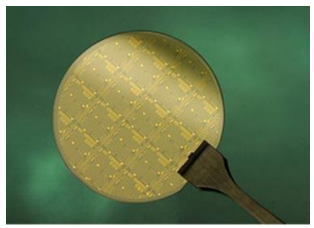
Quantum interference ring



Epitaxial graphene based devices

On May 21, 2009,, HRL laboratories said that it had made devices from single-layer graphene on 2 inch diameter 6H-SiC wafers with much-improved performance figures.

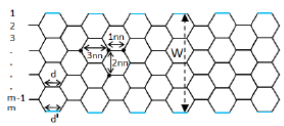
"They have world-record field mobility of approximately 6000 cm^2/Vs, which is six to eight times higher than current state-of-the-art silicon n-MOSFETs,"



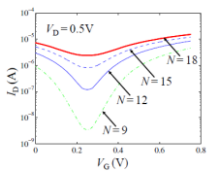
IEEE Electron Devices Lett. **30**, 650-652 (2009)

Graphene Nanoribbon FETs (GNR FETs)

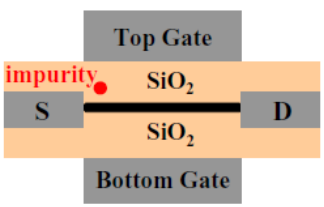
The schematic sketch of an GNR



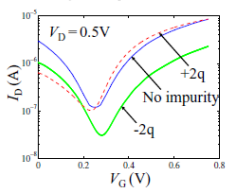
I-V characteristics for different GNR widths



Scheme of GNR FET



I-V characteristics for n=12 GNRs with charge impurities



Summary

- Fascinating world of carbon compounds
- Electronic structure of graphene & CNTs
- Are carbon compounds based devices the future of information technologies?

It's not clear yet, but

- Carbon compounds definitely changed the way of thinking about materials science

Jacek A. Majewski, University of Warsaw

When it happens?

The Shockley Building

Thank you