# Novel Boron(-Carbon) Nanomaterials: Structure, Properties and Applications

Alexander Quandt,

Institut für Physik, U. Greifswald (D)

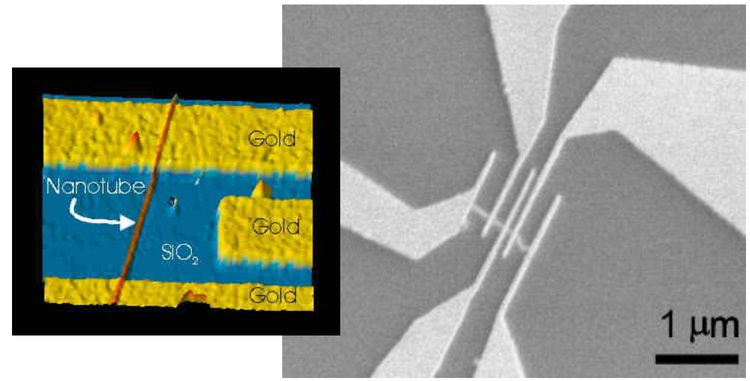
*„New ideas pass through three periods:*

1. *It can‘t be done.*
2. *It probably can be done, but it‘s not worth doing.*
3. *I knew it was a good idea all along“.*

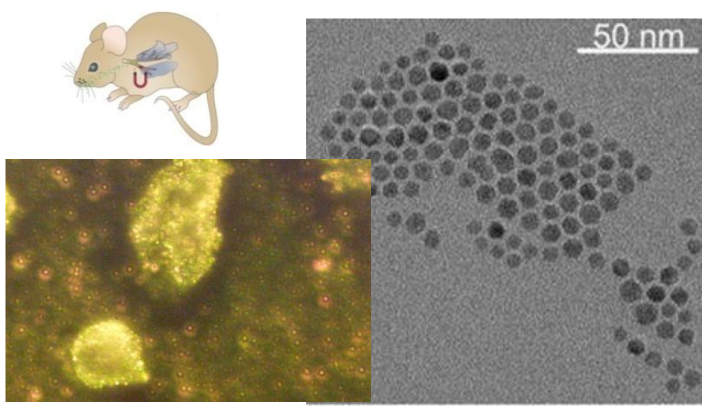
**(Arthur C. Clarke)**

# Survey of this talk :


**Composite Nanomaterials**

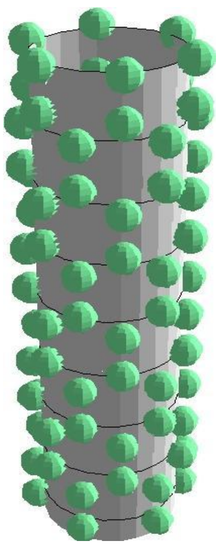



**Nanoelectronics**




**Nanomedicine**

# Materials

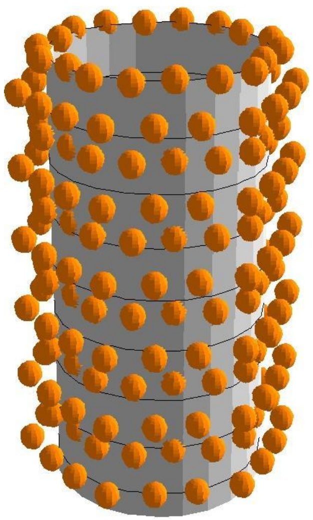


**Carbon Nanomaterials**
**(CNTs, Graphene)**

## PACS 61.48.De

***Structure of carbon nanotubes, boron nanotubes, and related graphitelike systems.***

***(for structure of hollow nanowires, see 61.46.Np)***

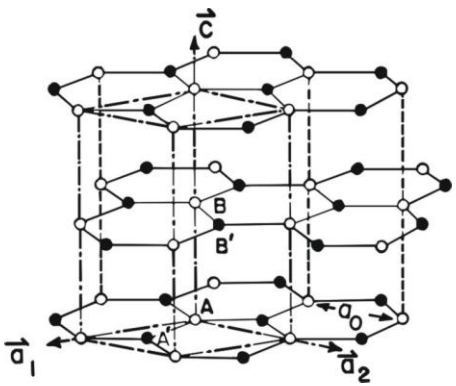


**Boron Nanomaterials**
**(Clusters, BNTs, Sheets)**

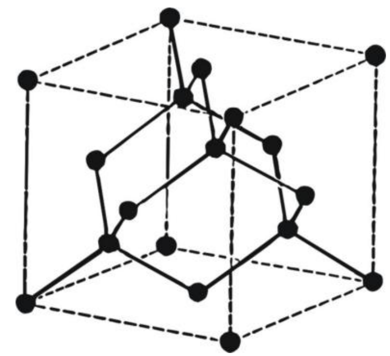
# Carbon

# Carbon chemistry

## • Graphite and diamond :




**Graphite (P6$_3$/mmc, hexagonal)**
**Cohesive energy : 7.4 eV/atom (sp$^2$)**
**Band gap : -0.04 eV (semimetal)**
**Hardness : 0.5 9**

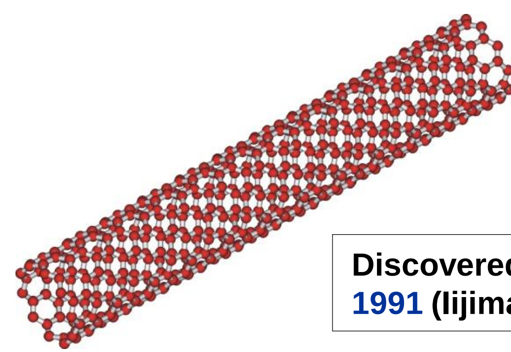


**Diamond (Fd3m, cubic)**
**Cohesive energy : 7.2 eV/atom (sp$^3$)**
**Band gap : 5.47 eV (insulator)**
**Hardness : 10**

## • Fullerenes and nanotubes :

*C60-molecule*

**Discovered in 1985**
**(Curl, Kroto, Smalley)**
**Nobel Prize**
**Chemistry 1996**

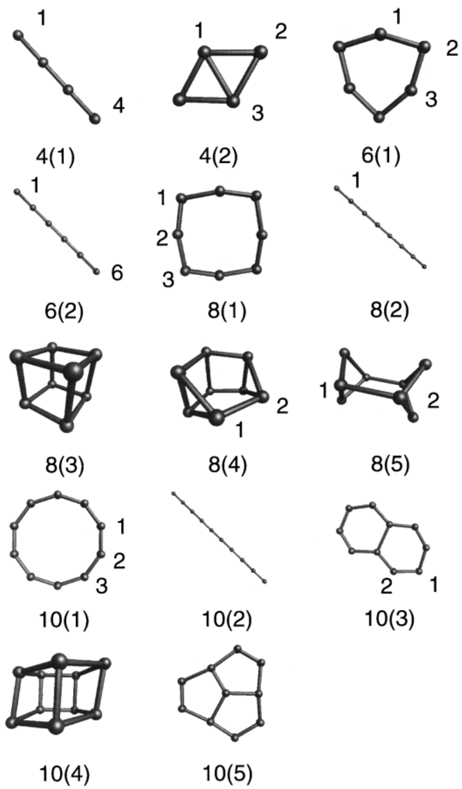


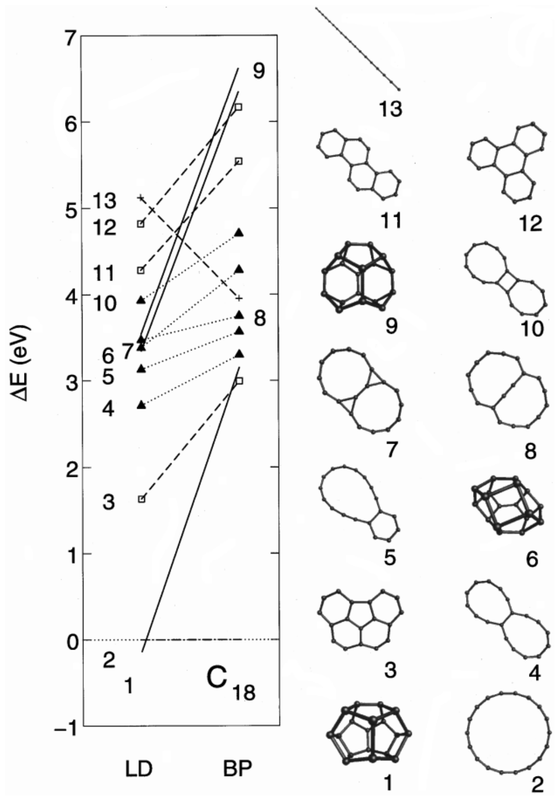
**Discovered in 1991 (Iijima)**

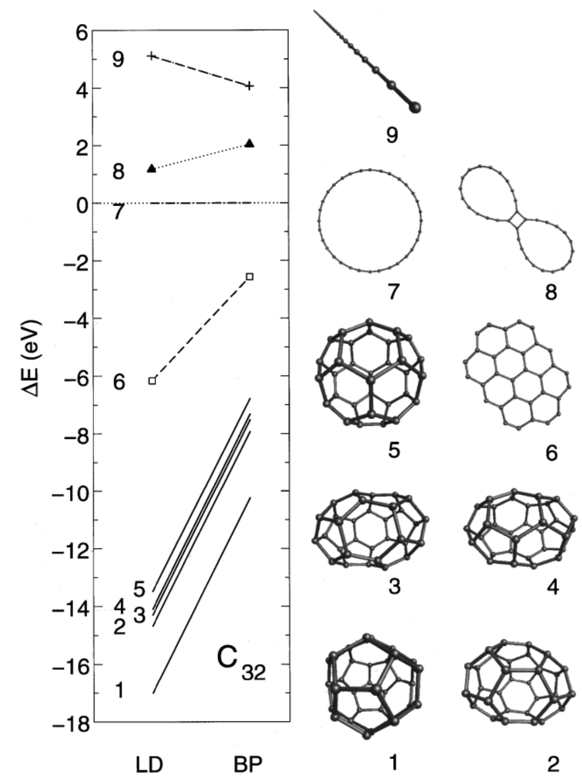
*Carbon nanotube*

# Carbon clusters

**See:** *R. O. Jones, J. Chem. Phys. 110, 5189 (1999); R. O. Jones & G. Seifert, PRL 79, 443 (1997).*




**$C_4$-$C_{10}$: Chains, rings.**

**$C_{18}$: Cages, rings.**

**$C_{32}$: Cages, graphitic.**

**Slow transition : chains, rings, cages, graphitic ….**

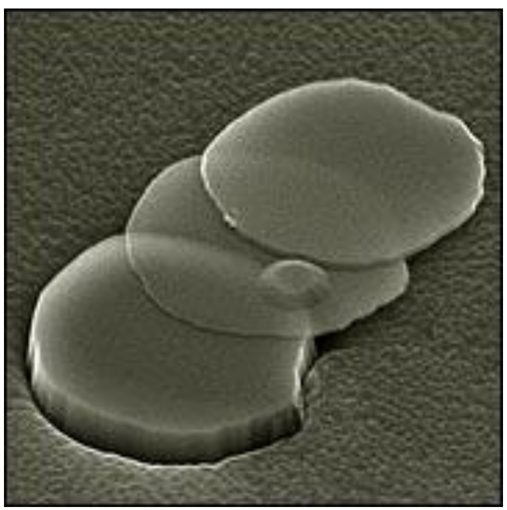
# Graphene (*K. S. Novoselov, Science 306, 666 (2004)*)

- **Old idea:**

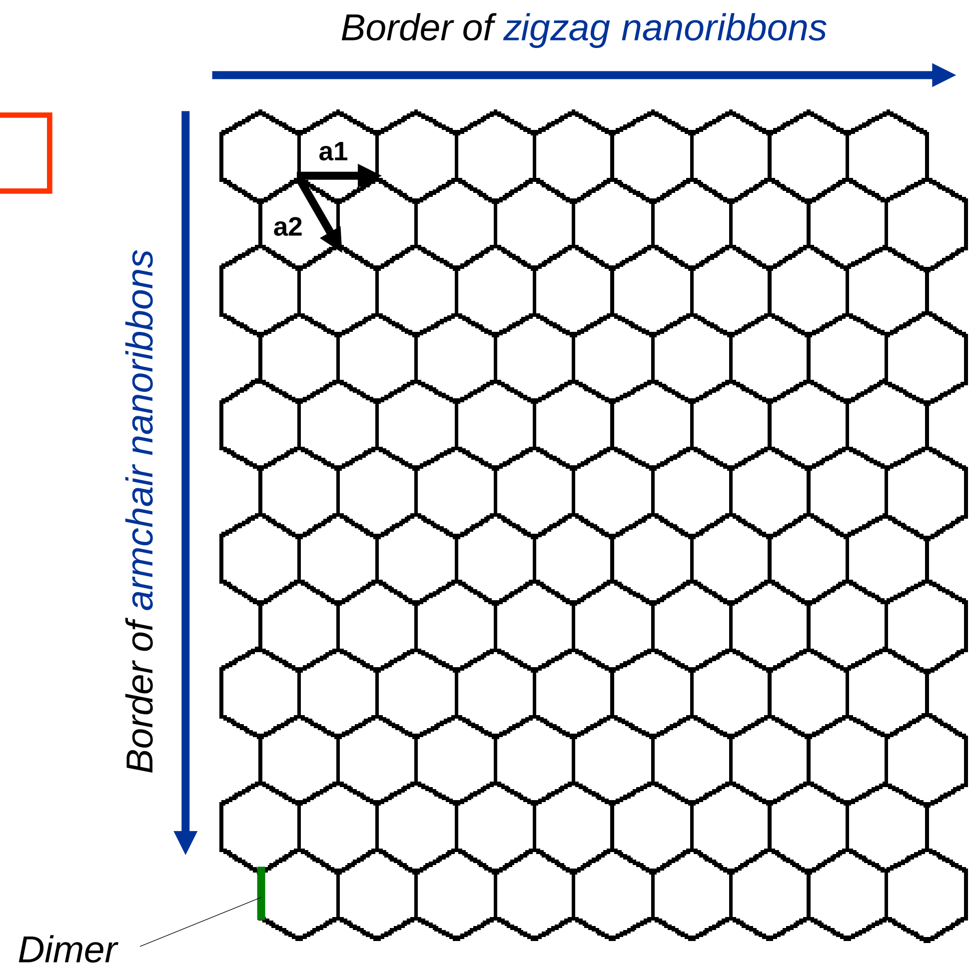
**Isolate a single layer of graphene !**

- **Solution:**

**Starting from graphite, peel off layers one by one using adhesive tape until one layer is left.**



*Multi-layered graphene*

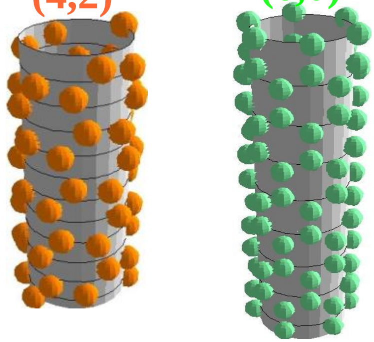


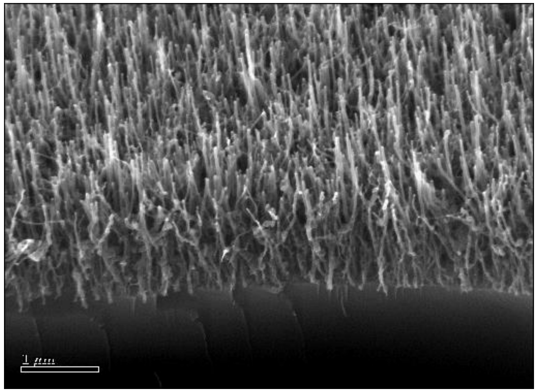

**Graphene sheet/nanoribbons**

# Carbon nanotubes

- **Cut & Paste :**

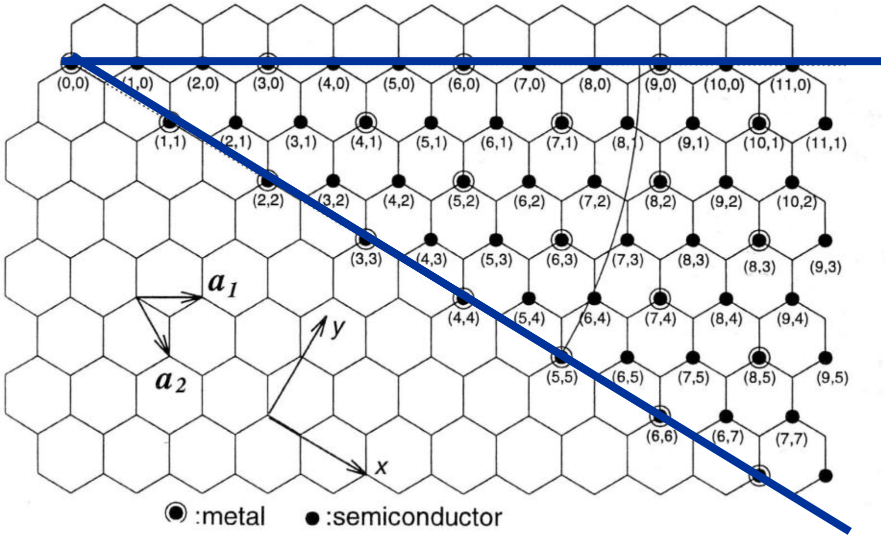
**Cut a rectangular sheet (n,m) out of bulk graphene, paste it, and attach similar segments periodically.**

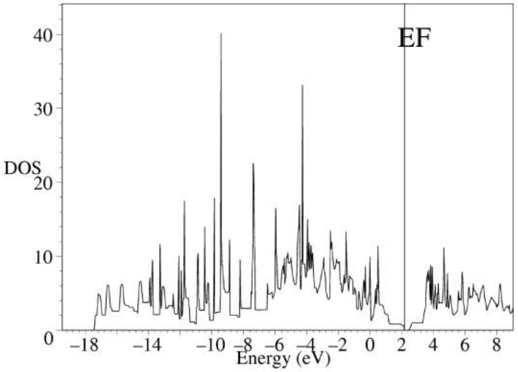


*CNT-forest*

- **Electronic properties :**



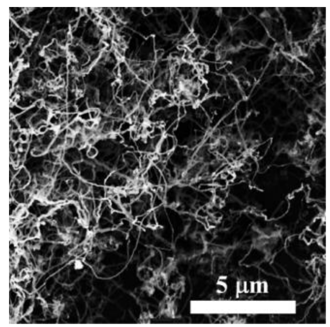




*DOS of (6,6)-nanotube*

**Electronic properties depend on the chirality of the tubes, on mechanical deformations etc. Hard to control experimentally !**

# Composite Nanomaterials

B



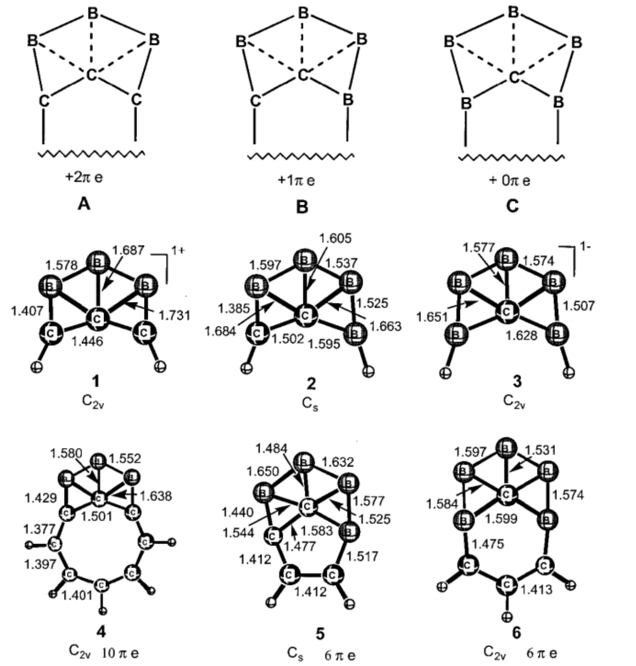

*Boron doped multiwalled carbon nanotubes*

C

# Electron deficient (ED) elements

• **ED element has more stable orbitals than electrons in its valence shell.**

| LMNt | $Be$ | $B$ | $C$ |
|---|---|---|---|
| Atom. config | $1s^2 2s^2$ | $1s^2 2s^2 2p^1$ | $1s^2 2s^2 2p^2$ |
| Coordination (**solids**) | **8** (bcc)<br>**12** (hcp) | **6** ($\alpha$-$B$) | **3** (graphite)<br>**4** (diamond) |
| ED ? | yes | yes | no |




- **Characteristics :**

1. **Ligancy of ED atom higher than the number of valence electrons, and even higher than the number of stable orbitals.**
2. **ED atom causes adjacent atoms to increase ligancy to value greater than the orbital number.**

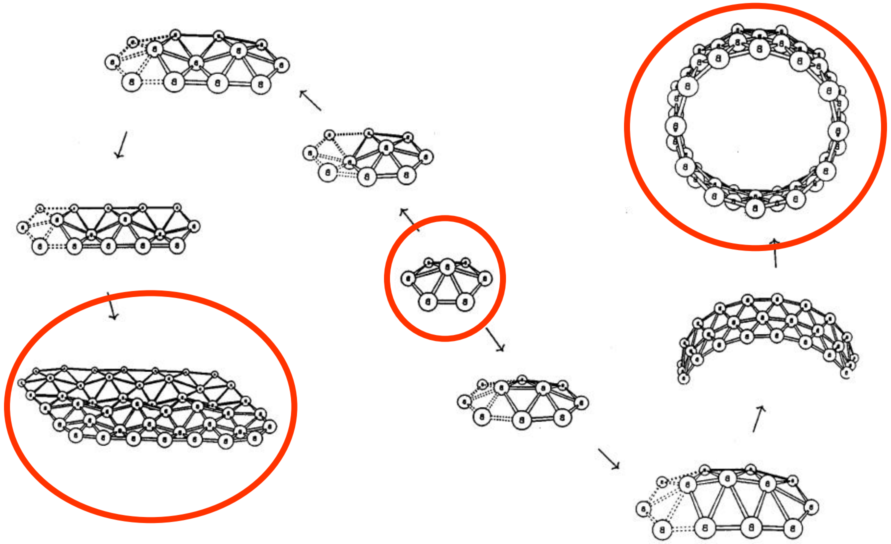
*See: L. Pauling, Nature of the Chemical Bond.*

**Aromatic BC clusters with hypercoordinated carbon :**

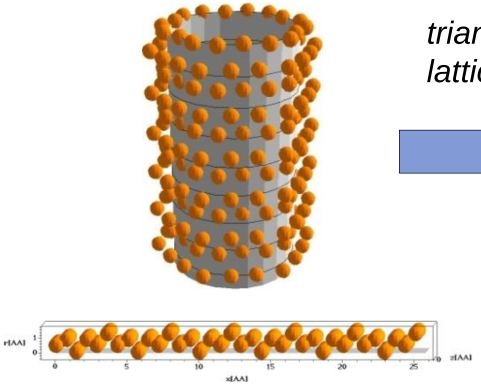
*Wang & Schleyer, Science 292, 2465 (2001).*

*Exner & Schleyer, Science 290, 1937 (2000).*

# Boron Sheets and Boron Nanotubes

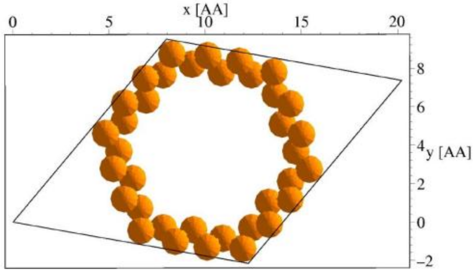


**Stable planar boron sheets and tubular boron clusters obtained from pyramidal $B_7$ subunits.**

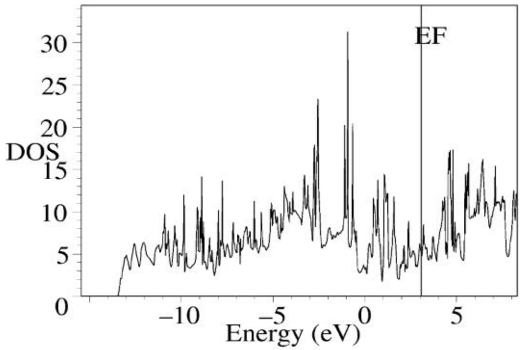



**puckered tube**

*triangular lattice*




**unit cell**




**Boron nanotubes and boron sheets should always be metallic !**

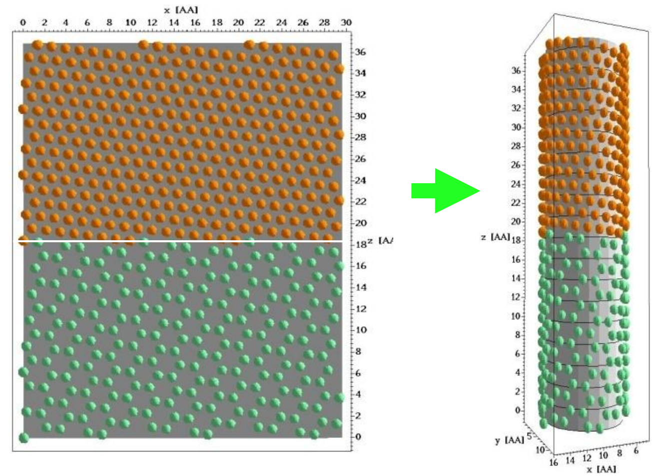
# Nanotubular heterojunctions

- **Basic questions :**

**Compatibility of different nanotubular systems ?**

**Structural paradigm for nanojunctions, interfaces, sublithographic patterning**

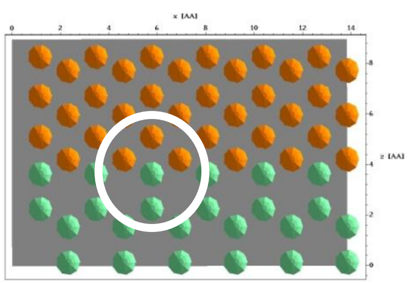
**.....**



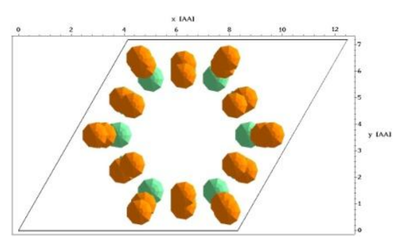
*Boron*

*Carbon*

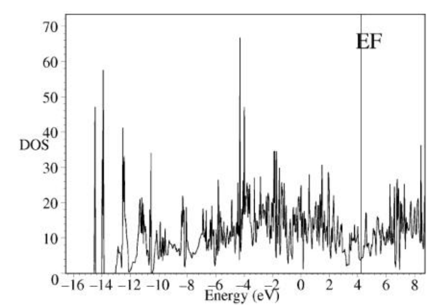
- **Model junctions :**



*Local chemistry of stable junctions.*



*Unit cell of BC bundle*

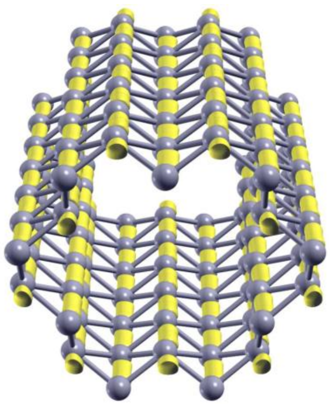



*DOS of BC-heterojunction*

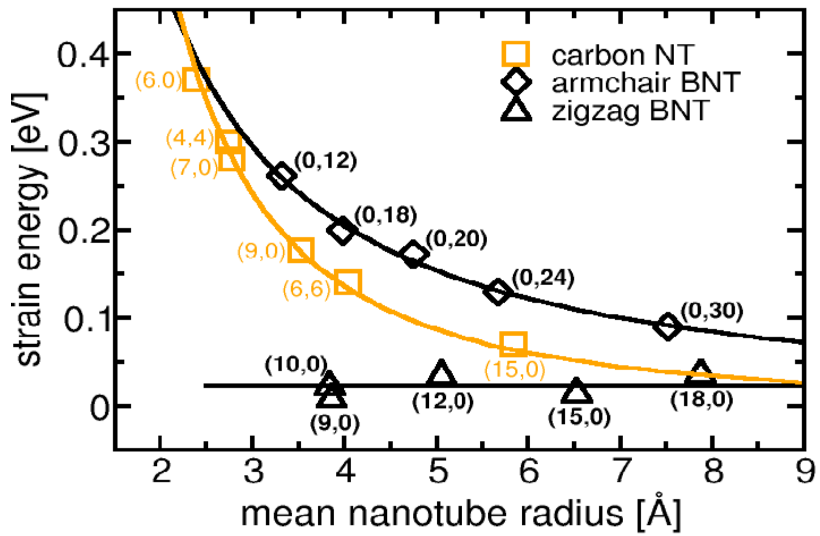
(*J. Kunstmann and A. Quandt, J. Chem. Phys. 121, 10680 (2004)*)

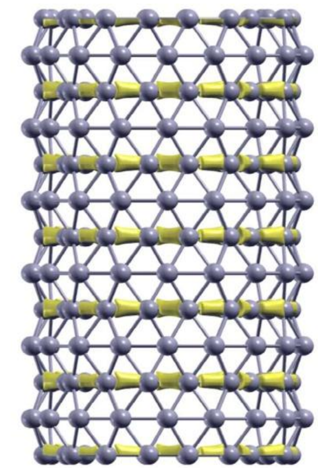
# Structure control/Layout

(*J. Kunstmann, A. Quandt, I. Boustani, Nanotechnology 18, 155703 (2007)*)



zigzag BNT



armchair BNT

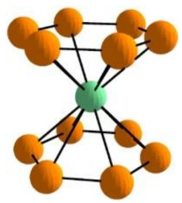
**Strain energy of CNTS depends on radius.**

**Strain energy of BNTs depends on radius and chiral angle !**

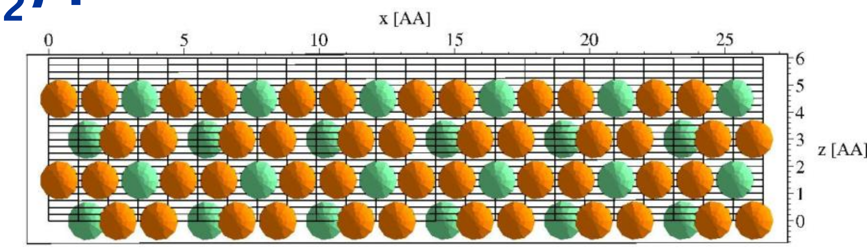
**Thus : use short segments of BNTs to grow specific CNTS.**

# Metal-boron nanotubes

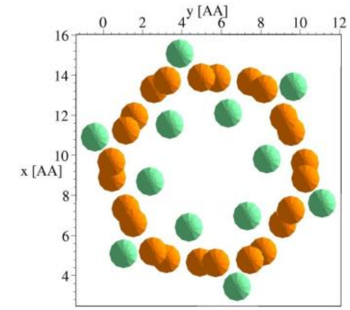
## • Structure ($AlB_2$) :



B : honeycomb lattice
Al : center of hexagons, between boron sheets



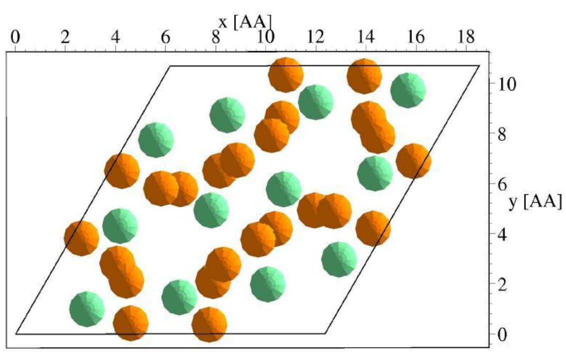

puckered $AlB_2$-sheet, reference structure for at least 22 compounds of type $MeB_2$, comprising sp-, d-, and f-metals Me.




(6,6) nanotube

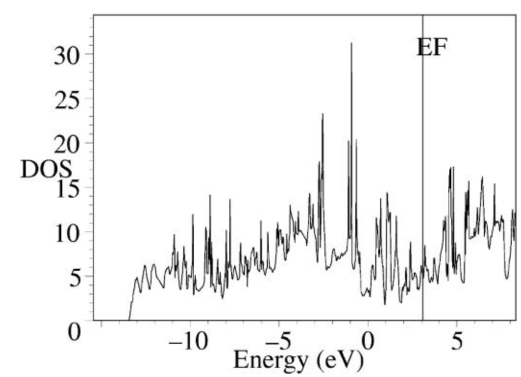
## • Properties :

*Theory : A. Quandt, A. Y. Liu and I. Boustani, PRB 64, 125422 (2001).*




*unit cell of (6,6) nanotube bundle*

- **Twisted in a gear-like fashion.**
- **small 0.23 eV/atom instability w.r.t. crystalline $AlB_2$ (0.14 eV/atom for (6,6) carbon nanotube !)**
- **metallic.**




*DOS of (6,6) nanotube*

# Other composites


# Nanotube composites

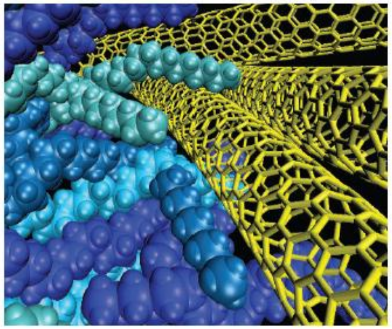
**„Nanophase materials – metals or ceramics with very small grain sizes – have been fairly disappointing.“**

**• small grains should result in harder metals. They turn out to be harder, but also more brittle.**
**• ceramics with very small grains would be much stronger, which has not really been demonstrated, yet.**

**„…. Yet there is reason to expect that nanometre-scale composite materials might turn out to be better than conventional composites“.**

Paul Calvert, *A recipe for strength*, Nature 399, 210 (1999).

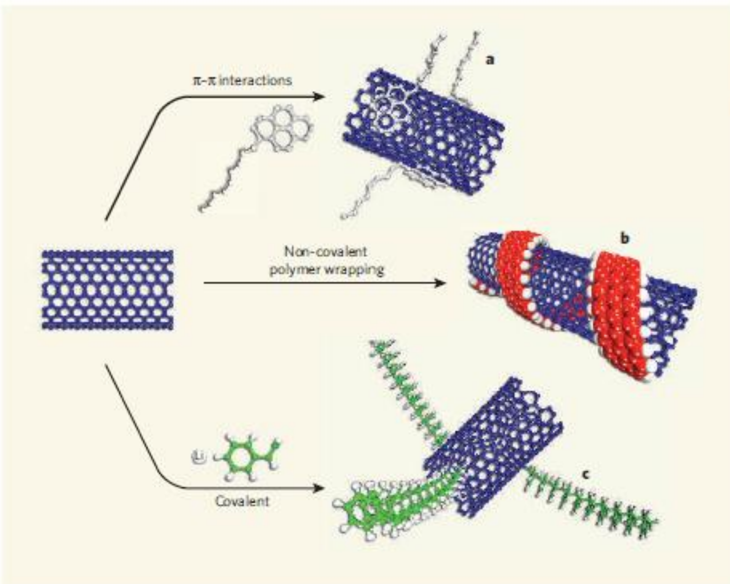
## • The idea:



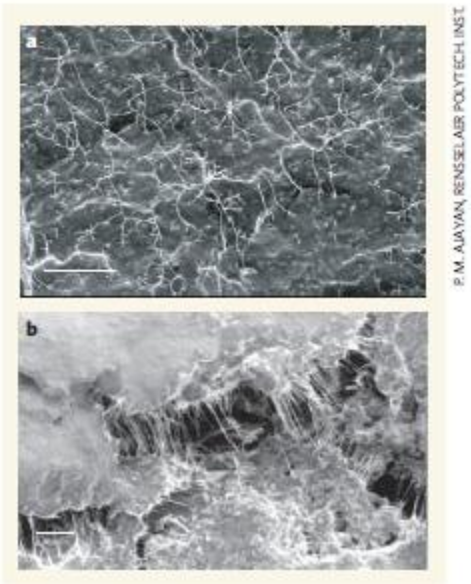
**• soft matrix (polymer) + stiff, load bearing filler (fiber).**
**• search for fibers with high aspect ratio (length to width) → nanotubes (aspect ratios of 1000 or more).**
**• fibers may add new properties to polymer matrix, like thermal and electrical conductivity.**

**see:** P. M. Ajayan and J. Tour, *Nanotube composites*, Nature 447, 1066 (2007)

# Problems & Solutions




**Three roads to bind CNTs inside a polymer matrix. Major problems: create strong but flexible bonds, bundles must be broken to disperse individual CNTs.**




**Typical problems:**

1. **Pull out of single CNTs, f.e. during fracture.**
2. **Percolation: In order to achieve conductivity, it is necessary to create a network of conducting CNTs.**

**Boron nanotubes are:**

**a) Always metallic.**

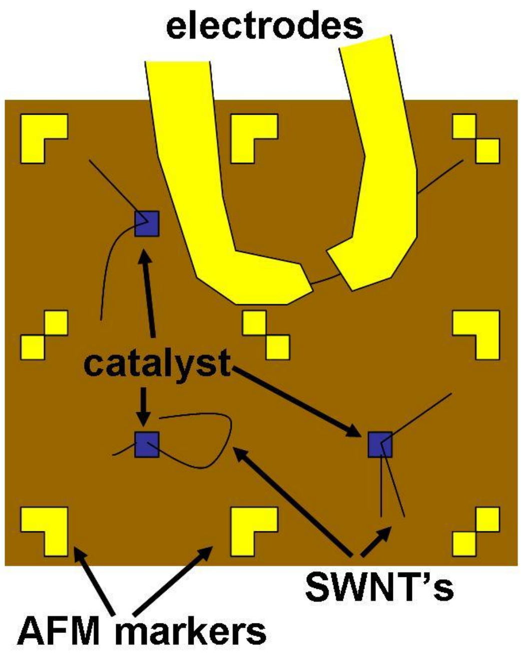
**b) Mechanically strong (armchair) .**

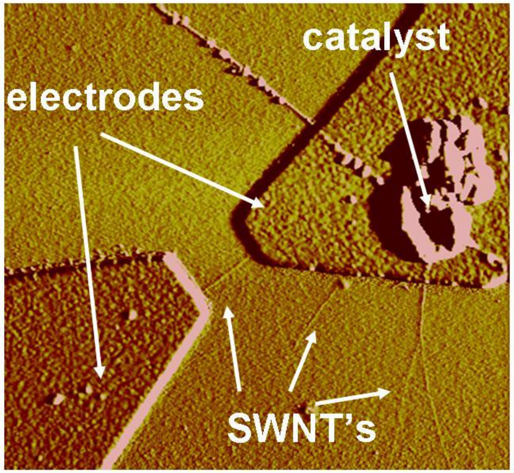
**c) Show strong, but flexible type of bonding. More suitable for polymers.**

**See:** *Kunstmann & Quandt, Phys. Rev. B 74, 035413 (2006).*

**Examine BNT-polymer composites and B(-C)NT-polymer composites !**

# Nano-Electronics

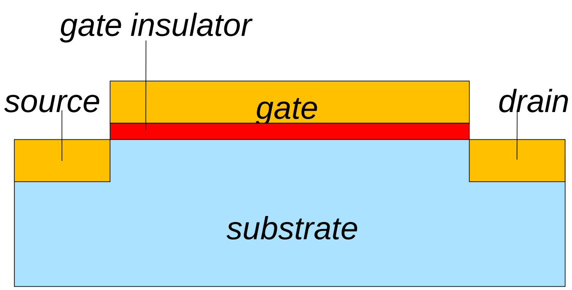


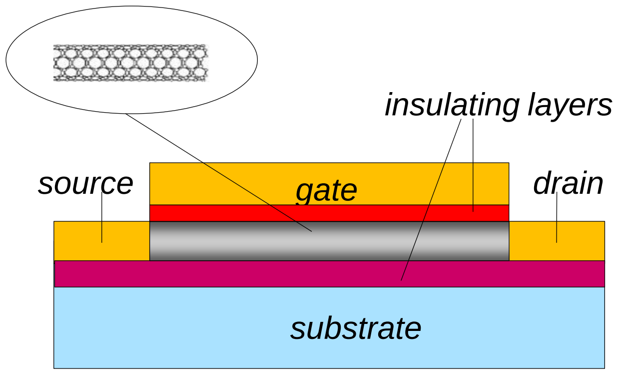
# MOSFETs & TubFETs

A. Quandt, M. Ferrari, G. Righini, *Towards Integrated Nanoelectronic and Photonic Devices*, in press (2009).

- **Basic layout**:




**MOSFET**




**TubFET**

- **FET design problems**:

RC circuit model: $C_g$ (gate capacitance), $R$ (resistance for gated current)

$\Rightarrow$ discharge times: $\tau = RC_g = \dfrac{L^2}{\mu V_{gs}}$ ($\sim$ switching)

$V_{gs}$ (gate voltage), $L$ (gate length), $\mu$ (mobility of carriers)

$\Rightarrow$ Dynamic switching energy: $E = \dfrac{1}{2}(C_g + C_w)V_{gs}^2$ ($\sim$ power consumption)

$C_w$ (effective capacitance of wiring)

**Smaller gate length ↔ increase doping to switch off the device.**
**Higher mobility ↔ straining of substrate.**
**Higher gate voltage ↔ leakage currents, large power consumption.**

## • Advantages/disadvantages of CNT channels:

**Pro:**

- *small (1-2 nm) and atomically smooth.*
- *very high carrier mobilities.*
- *small gate voltage.*
- *low channel capacitance.*
- *tunable gap (~1/diameter).*

*See: P. Avouris, Physics Today 62, 34 (2009).*

**Con:**

- *problematic layout: mixtures of metallic/semiconducting CNTs.*
- *disturbing Schottky barriers between CNTs and metallic contacts.*

**Solution: Employ BNTs !!!**
**(~ structure control, junctions)**

## • Bandwidth problems:

Delays caused by charging of wiring:

$\Rightarrow$ characteristic times: $\tau = RC_w \sim \frac{L^2}{A}$ $\quad (L\ (A):$ length (area) of wire$)$

$\Rightarrow$ Estimated band width: $B \sim \frac{1}{\tau} \approx 10^{16}\frac{A}{L^2}$ bit/s $\quad$ (changes with aspect ratio $\frac{L}{\sqrt{A}}$)

## • Challenges:

1. **Develop reliable FET technology (substrates, channels, wires …) below 42 nm gate length (state of the art).**
2. **Supply fast and integrated global interconnects.**

# Graphene nanoribbons

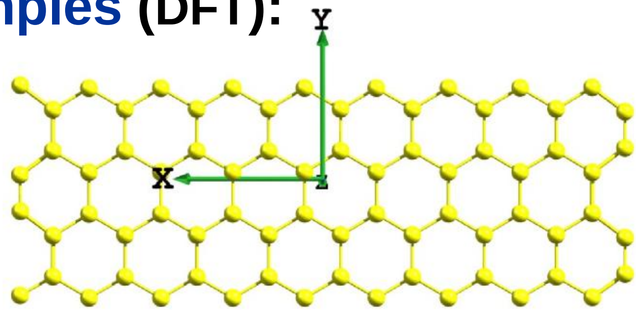
*A. Quandt, C. Özdogan, J. Kunstmann, H. Fehske, Nanotechnology 19, 335707 (2008).*

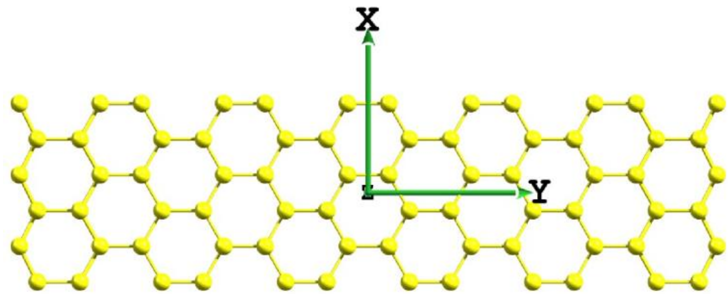
- **Electronic properties of graphene nanoribbons (TB theory):**

**All zigzag nanoribbons are metallic.**

**Armchair nanoribbons are either metallic or semiconducting, depending on the number of dimers across the width of the ribbons.**

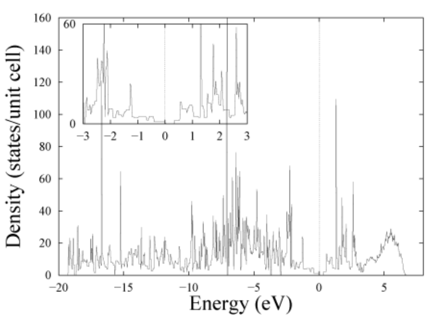
- **Examples (DFT):**

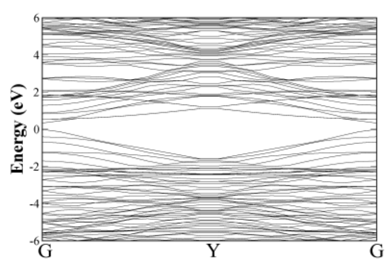


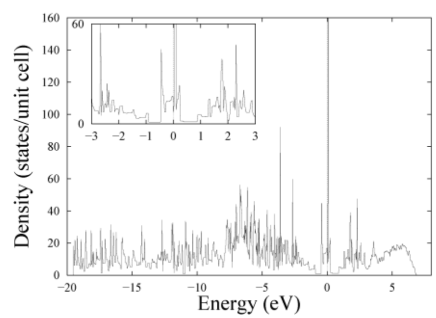



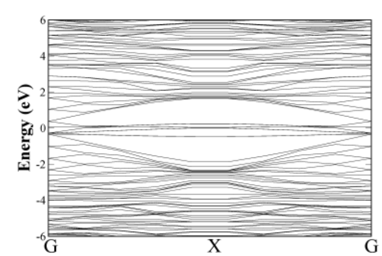

**Armchair graphene nanoribbon**

**Zigzag graphene nanoribbon**



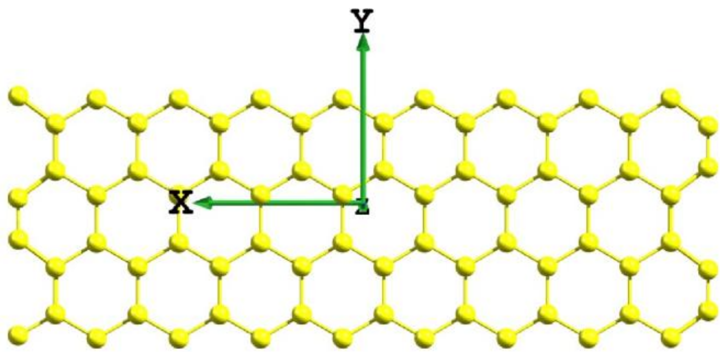



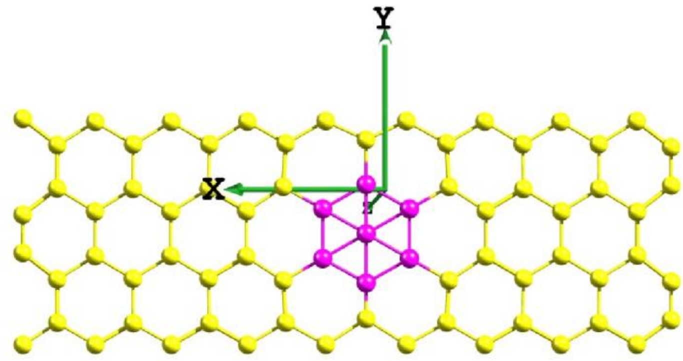
# Functionalizing graphene

**Nanowires and devices at the ultimate size limit of nanotechnology ?**

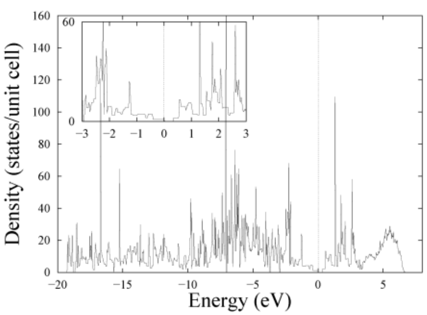
- **Insert alternating chains of boron clusters :**

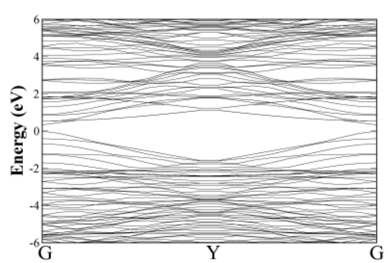


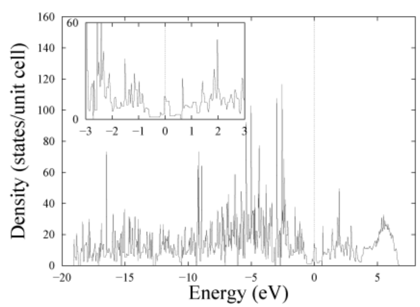

**Armchair graphene nanoribbon**

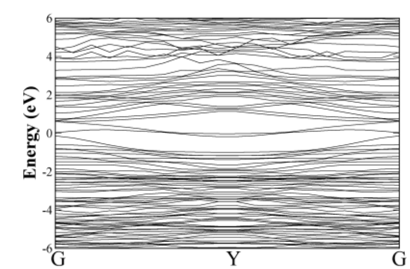



**$B_7$ doped armchair nanoribbon**



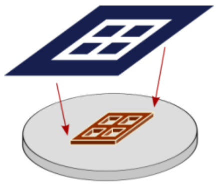




**See:** *A. Quandt, C. Özdogan, J. Kunstmann, H. Fehske, Nanotechnology 19, 335707 (2008).*

# Diverging technologies ?

- **Top down design for integrated devices using lithographic techniques:**



**Rayleigh limit:**

$\Delta x = \kappa\lambda/\mathrm{NA}$

$\Delta x$ : lateral optical resolution

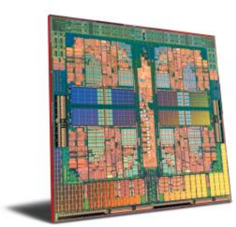
$\lambda$ : wavelength of irradiating light

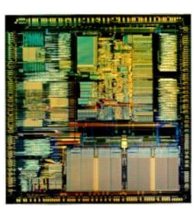
$\kappa$ : process factor $\approx 0.25$

NA : numerical aperture $\approx 1.5$ (immersion techniques)

## Electronics:

*Electron currents, wavelength within Å range.*

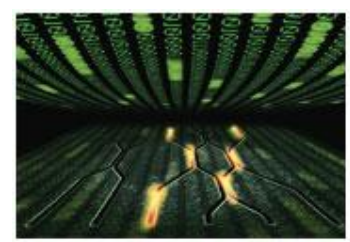




*Processors: 42 nm technologies and smaller using extreme UV lithographic techniques.*

## Photonics:

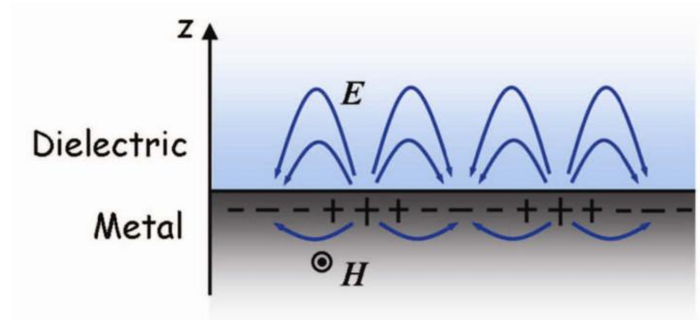
*Photon streams, 850/1300/1550 nm wavelength.*



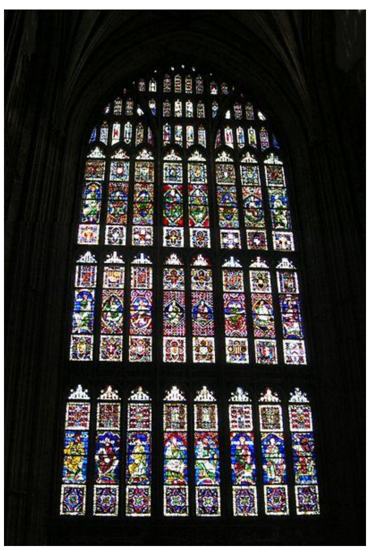
*Integrated optical devices should be large enough to interact with technical (IR) photon streams (>850 nm).*

# Plasmonics

*Lycurgus cup (400 AD).*




*Surface plasmon-polaritons (SPP) are TM light waves trapped on dielectric/metal interfaces, due to interaction with free electrons of the conductor.*



$$k_{SPP} = k_0 \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} = k'_{SPP} + i k''_{SPP} \text{ as } \epsilon_m = \epsilon'_m + i\epsilon''_m$$

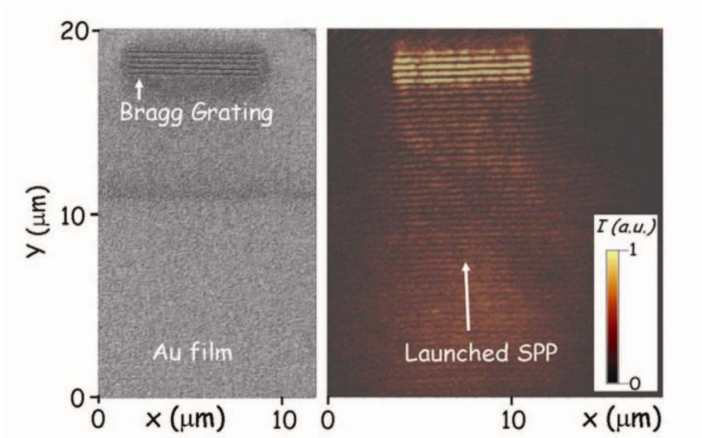
Note that $k_0 = \omega/c$. For small $\epsilon''_m$ and $\epsilon'_m < -\epsilon_d$:

$$k'_{SPP} = k_0 \sqrt{\frac{\epsilon_d \epsilon'_m}{\epsilon_d + \epsilon'_m}} > k_0 \text{ (extra momentum, evanescent)}$$

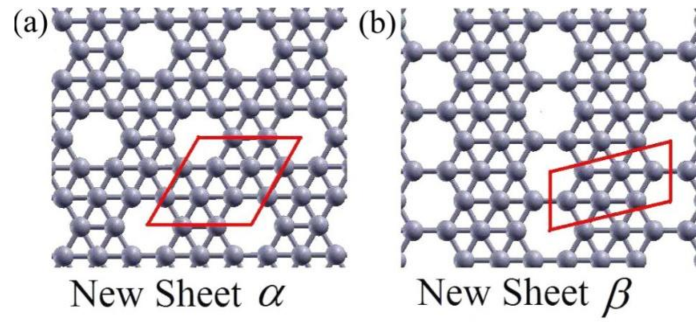
$$\delta_{SPP} \equiv \frac{1}{2k''_{SPP}} = \frac{1}{k_0}\left(\frac{\epsilon_d + \epsilon'_m}{\epsilon_d \epsilon'_m}\right)^{3/2} \frac{(\epsilon'_m)^2}{\epsilon''_m} \text{ (propagation length)}$$

*For a **review** see: Barnes et. al., Nature 424, 824 (2003), or: Maier & Atwater, J. Appl. Phys. 98, 011101 (2005).*

# How to generate an SPP …




*Photon-STM picture of surface plasmon-polariton wave (SPP) scattered at surface Bragg grating.*
***From**: Zia et. al., Materials Today 9, 20 (2006).*




Injection (supply additional momentum, as $k'_{SPP} > k_0$ …):
Light with $\vec{k}_0$ hits metal surface with grating under angle $\theta$
$\Rightarrow \vec{k}_{SPP} = \vec{k}_{0,\|}(\theta) + \vec{G}$ (resonance condition)
($\vec{G}$ is a reciprocal lattice vector of the grating)

Silver/air interfaces (example):
$\Rightarrow$ Propagation length $\delta_{SPP} \approx 1mm$ for $1.5\mu m$ IR injection!

Theory (see: Meyer & Atwater …) predicts longer propagation lengths for certain SPP modes in extremely thin metallic films.

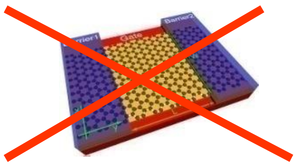
Determine ε(ω) for free standing or suspendend B(-C) nanomaterials (ab initio).

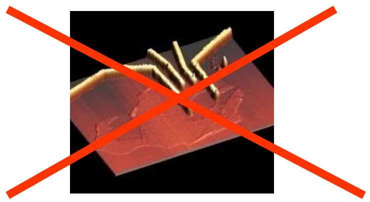
Afterwards, it will be sufficient to use classical electrodynamics in order to design suitable plasmonic devices.

Eberlein et. al., *Plasmon Spectroscopy of Free Standing Graphene Films,* PRB 77, 233406 (2009):
**Red shift of in-plane π →π* plasmon peaks of bulk graphite towards the visible range (4.7 eV)!**

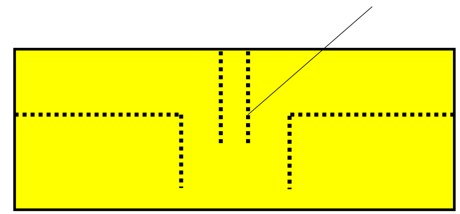
# Novel concepts & layout strategies

• **Novel graphene based nano-electronics :**



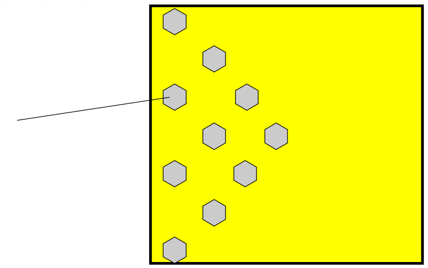


**Bulky concepts**



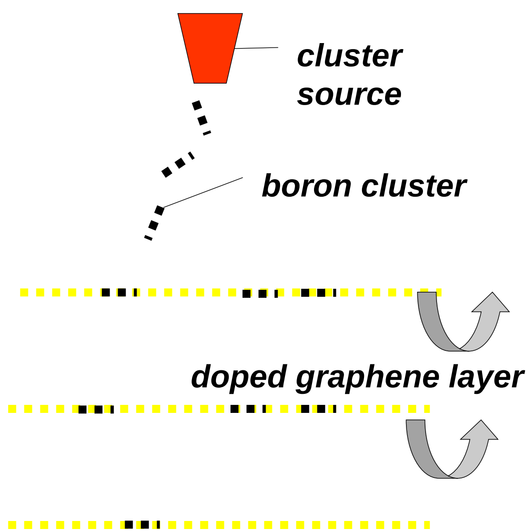

***Semicond.* graphene nanoribbon**

**Integrated electronic devices**



***Metallic* graphene nanoribbon**

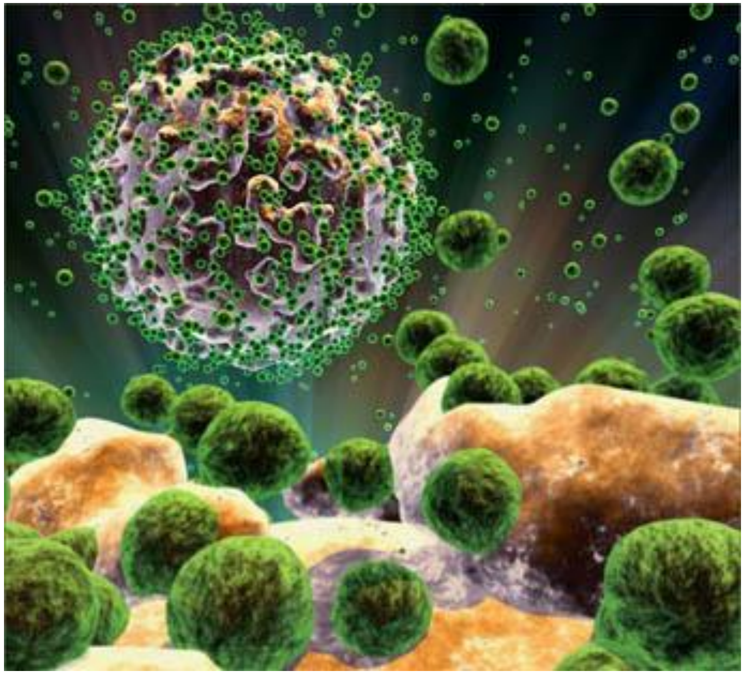
**Refractive/plasmonic elements**




## Use existing technologies:

- **Implantation of boron clusters is standard procedure for silicon based integrated circuits ( ~42 nm).**
- **First step: put graphite into the same machines!**
- **Peel off single boron doped layers the standard way and analyze them.**
- **Depending on intensity of cluster beam, neighboring layers may contain copies of roughly the same pattern.**
- **Gradual improvements : speckle patterns of large boron islands, dotted lines, dotted devices, ….**

# Nanomedicine



# What is Nanomedicine ?

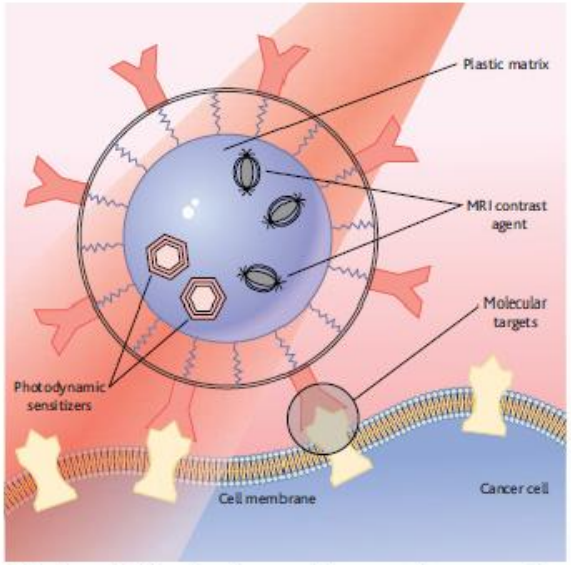
**„Nanomedicine can be defined as the monitoring, repairing, construction and control of human biological systems at the cellular level by using materials and structures engineered at the molecular level.“**

*M. Kralj & K. Pavelic, EMBO reports 4, 1008 (2003).*

## • Tasks and examples:

1. **Drug delivery:** liposomes, polymer nanoparticles, nanosuspensions (accelerated distribution).
2. **Drugs and therapy:** fullerenes and dendrimers (unique medical effects due to structure).
3. **In Vivo imaging:** contrast agents like superparamagnetic iron oxide nanoparticles for MRI.
4. **In Vitro diagnostics:** novel sensors based on nanotubes, nanowires, cantilevers or AFMs.
5. **Biomaterials:** self-assembling and biocompatible nanomaterials for dental fillers, implant coatings and bone substitution. Smart materials that stimulate growth and differentiation.
6. **Active implants:** nanomaterials that protect implanted devices and increase their biocompatibility.

*After: Wagner et. al., Nature Biotechnology 24, 1211 (2006).*




**Triple threat.** Multifunctional nanoparticles can combine tumor-seeking sensors, imaging agents, and toxins that kill cancer cells.

**From:** *R. Service, Nanotechnology Takes Aim at Cancer, Science 310, 1132 (2005)*

# Boron Neutron Capture Therapy (BNCT)

**Reviews**: *S. C. Mehta and D. R. Lu, Pharmaceutical Research 13, 344 (1996).*
*R. F. Barth et. al., Clin Cancer Res 2005:11, 3987 (2005).*

## Short history:

*1930* — *first recognitions of the potential of BNCT*

*1951-1961* — *(unsuccessful) clinical trials as Brookhaven National Labs, using boric acid and an inappropriate neutron source.*

*after 1961* — *development and application of novel agents dubbed BSA and BPA. Successful treatment of more than 100 patients.*

**Worldwide interest in BCNT, with research groups in the US, Europe, Japan and Australia. Development of novel drugs that are able to enter the nucleus of the tumor cells.**

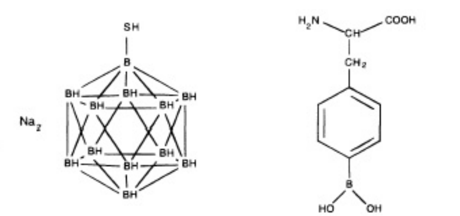


Fig. 2. Compounds in clinical use for BNCT: (a) borocaptate sodium (BSH) and (b) p-boronophenylalanine (BPA).

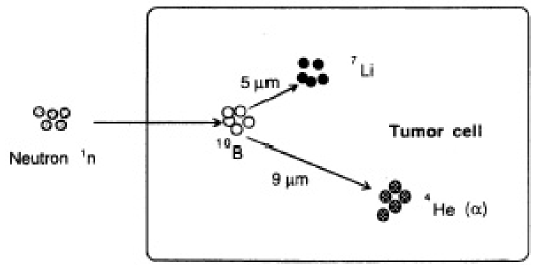
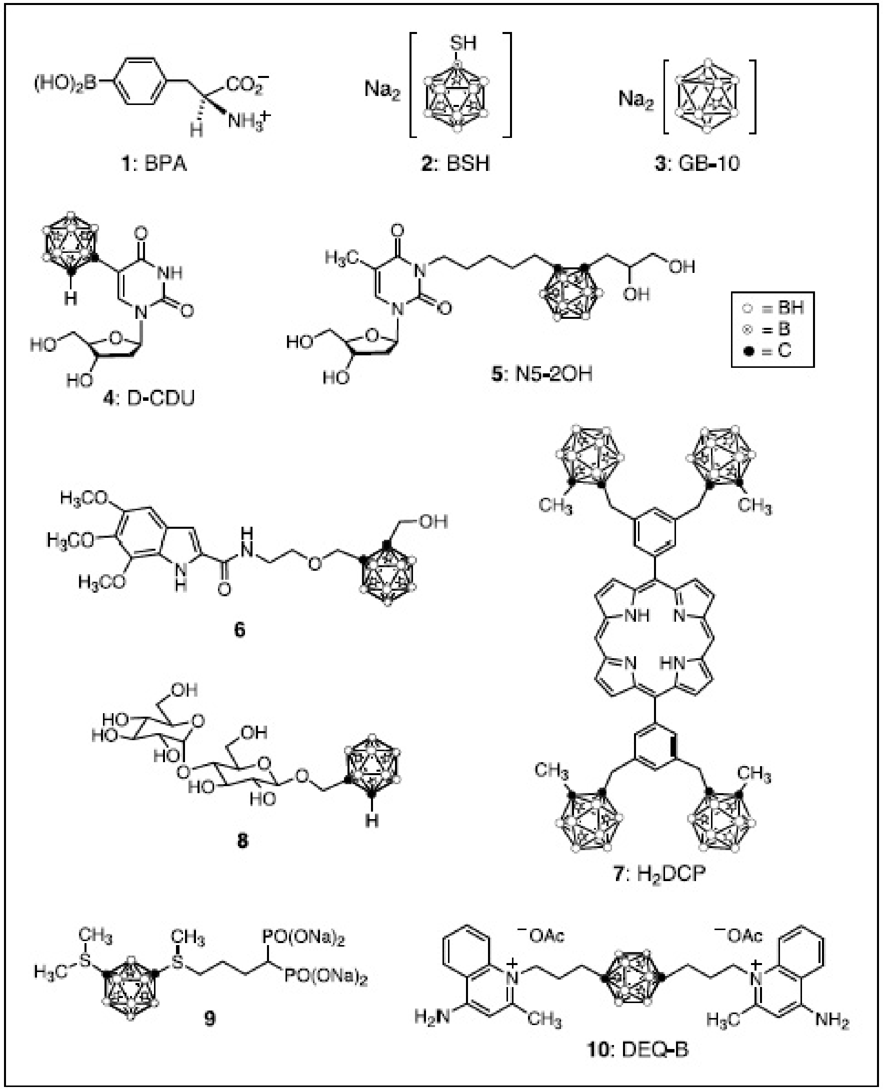


Fig. 1. Schematic representation of boron neutron capture therapy.

- **Dual therapy: boron carrying agent + neutron beam.**
- **Nuclear reaction of $^{10}$B (20% of natural boron) with low energy neutrons.**
- **The nuclear fragments and the radiation kill cells only on the length scale of one cell diameter, such that healthy tissue will be largely preserved.**

# Challenges for Nanotechnology:




1. **Enrichment of $^{10}$B (promising approach using Ru nanoparticles:** Yinghuai et. al., J. Am. Chem. Soc. 129, 6507 (2007)**).**
2. **Development of smart and detectable agents for targeted delivery of $^{10}$B to the tumor cells.**

- **What is a good B delivery agent?**

*a. Low systematic toxicity and low normal tissue uptake. High tumor uptake.*
*b. Concentrations around ~20 µg $^{10}$B/g tumor (i.e. $10^9$ atoms/cell).*
*c. Rapid clearance from blood and normal tissues. Persistance in tumor during BNCT.*

**Better boron delivery agents on the basis of small boron clusters, fullerenes, sheets or fullerenes ???**

# Summary

# Various B(-C) nanomaterials were recommended for:

- **Improved composite nano-materials (strong, conductive).**
- **Novel electronic and optical nano-devices.**
- **Novel medical therapies to cure (deadly) diseases.**
- ....

*„If we have learned one thing from the history of invention and discovery, it is that in the long run – and often in the short one – the most daring prophecies seem laughably conservative".*

**(Arthur C. Clarke)**

# Thanks to

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