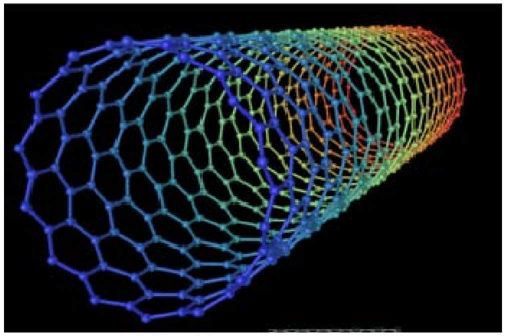
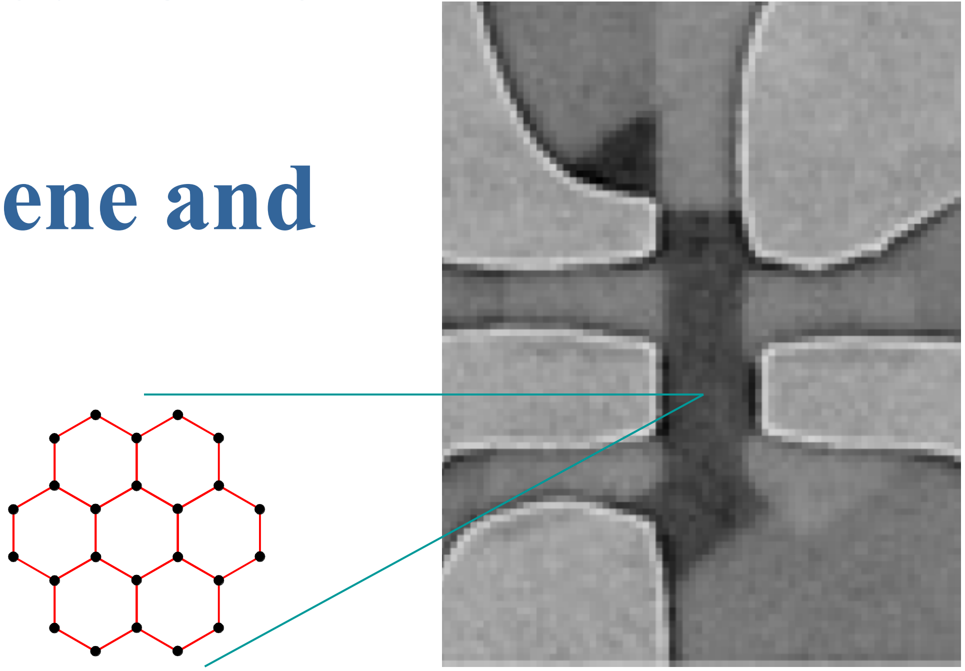
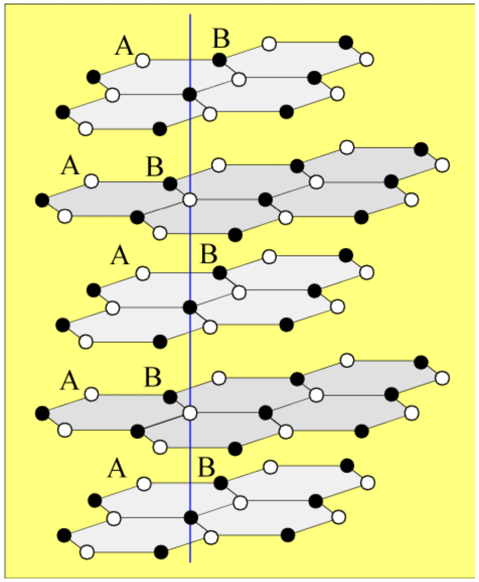
Lectures 15-16

Graphene and carbon nanotubes



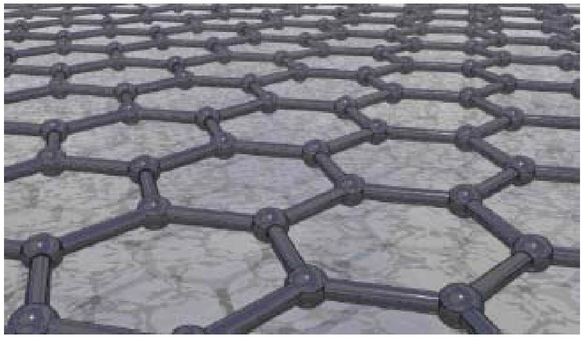


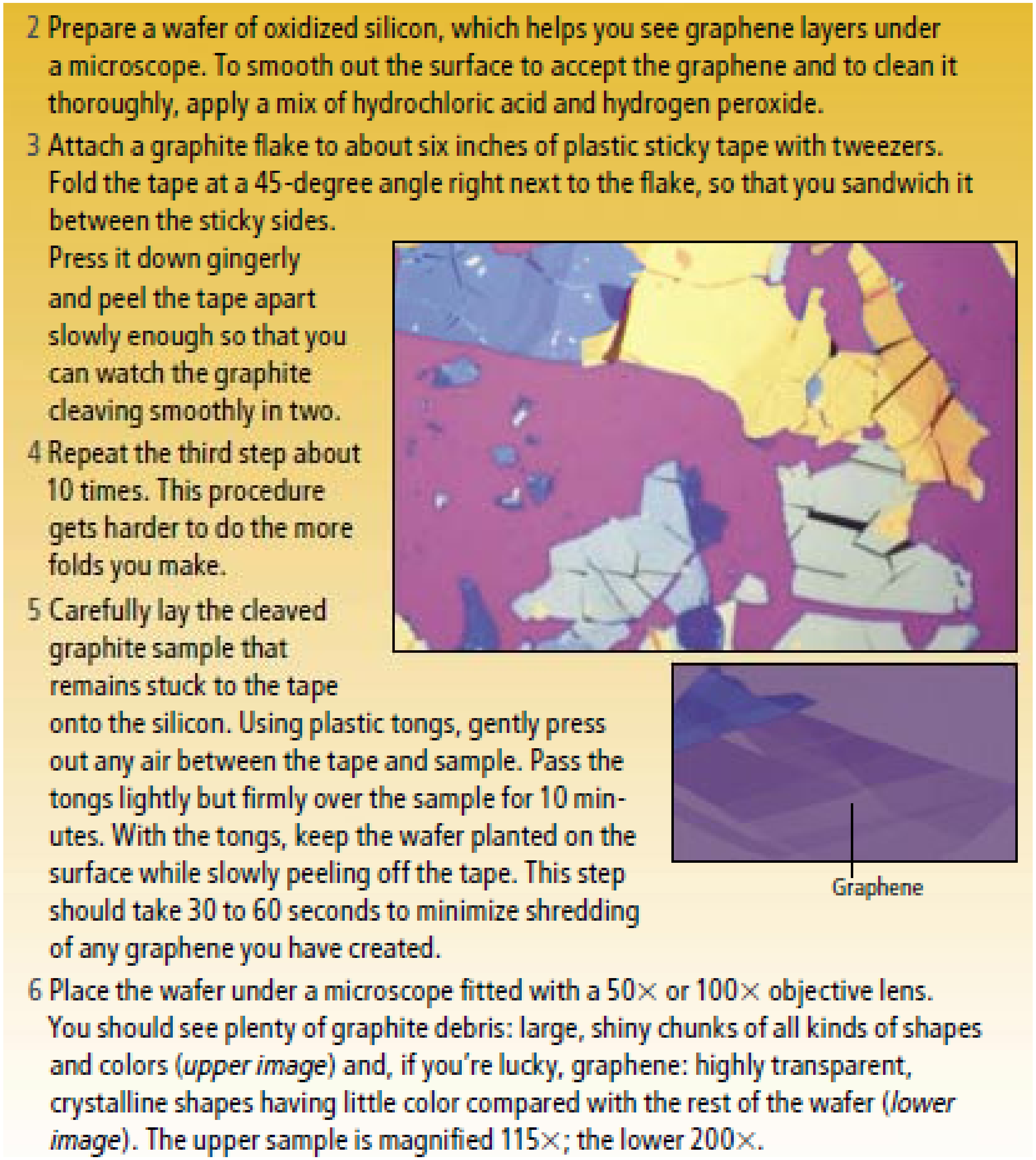
Graphene is atomically thin crystal of carbon which is stronger than steel but flexible, is transparent for light, and conducts electricity (gapless semiconductor).



D.I.Y. Graphene

Geim & Novoselov (Manchester) 2004

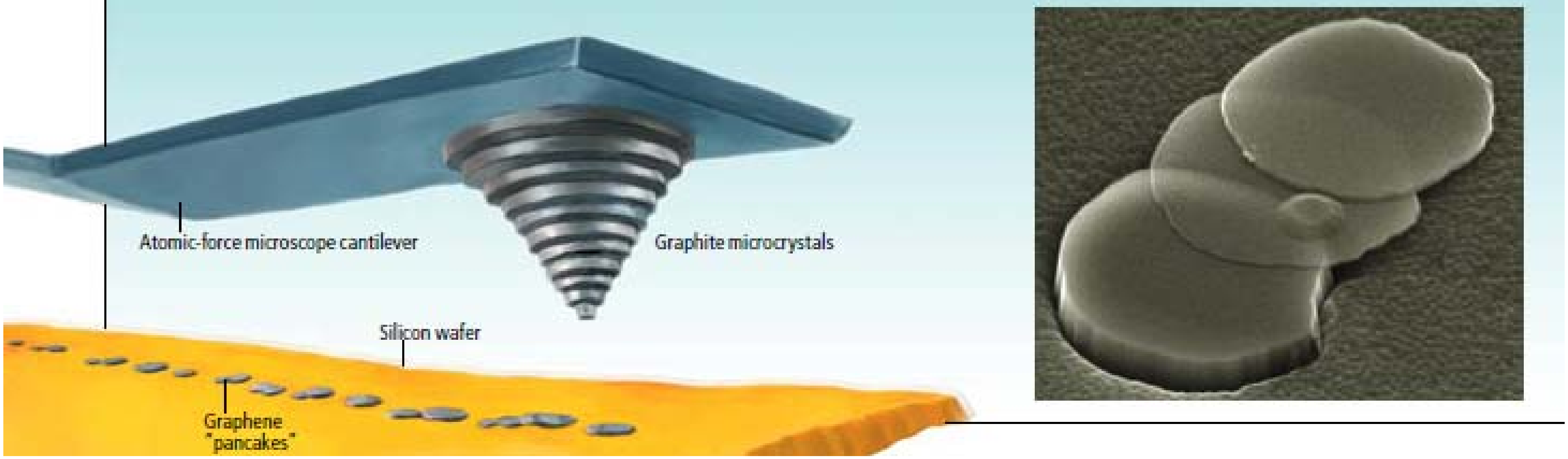




2. Prepare a wafer of oxidized silicon, which helps you see graphene layers under a microscope. To smooth out the surface to accept the graphene and to clean it thoroughly, apply a mix of hydrochloric acid and hydrogen peroxide.
3. Attach a graphite flake to about six inches of plastic sticky tape with tweezers. Fold the tape at a 45-degree angle right next to the flake, so that you sandwich it between the sticky sides. Press it down gingerly and peel the tape apart slowly enough so that you can watch the graphite cleaving smoothly in two.
4. Repeat the third step about 10 times. This procedure gets harder to do the more folds you make.
5. Carefully lay the cleaved graphite sample that remains stuck to the tape onto the silicon. Using plastic tongs, gently press out any air between the tape and sample. Pass the tongs lightly but firmly over the sample for 10 minutes. With the tongs, keep the wafer planted on the surface while slowly peeling off the tape. This step should take 30 to 60 seconds to minimize shredding of any graphene you have created.
6. Place the wafer under a microscope fitted with a 50× or 100× objective lens. You should see plenty of graphite debris: large, shiny chunks of all kinds of shapes and colors (*upper image*) and, if you're lucky, graphene: highly transparent, crystalline shapes having little color compared with the rest of the wafer (*lower image*). The upper sample is magnified 115×; the lower 200×.

Graphene from a nanopensil

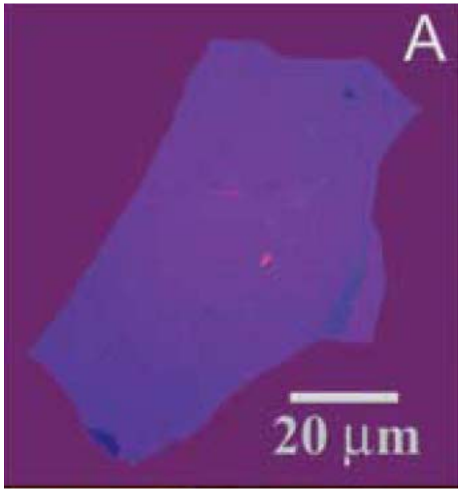
Kim (Columbia Univ) 2005

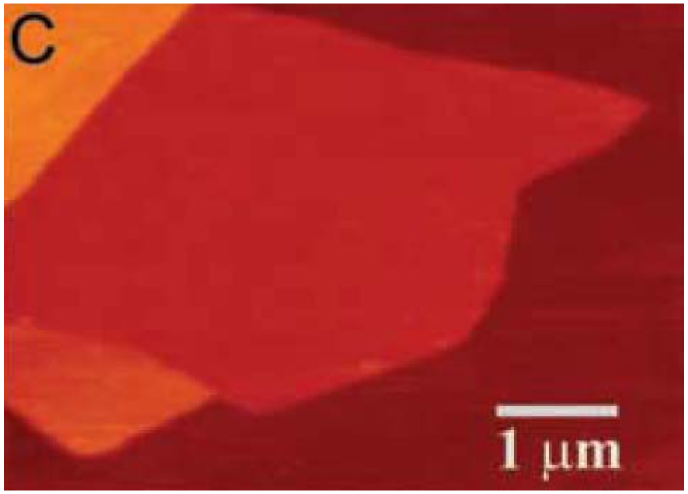


Making graphitic samples that approach the thickness of single-layer graphene has taken considerable effort. One way is to attach a graphite microcrystal to the cantilever arm of an atomic-force microscope and scratch the tip of the microcrystal across a silicon wafer (*left*). This "nanopencil" deposits thin graphene "pancakes" onto the wafer (*right*). The samples in the electron micrograph are magnified 6,000×.

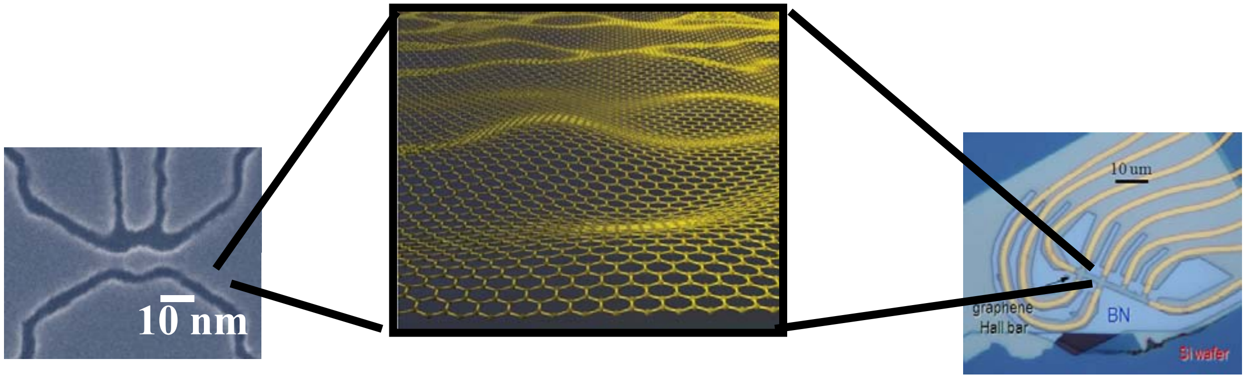
Ultra-thin graphitic films mechanically exfoliated from bulk graphite

Novoselov & Geim (Manchester)
Science 306, 666 (2004)



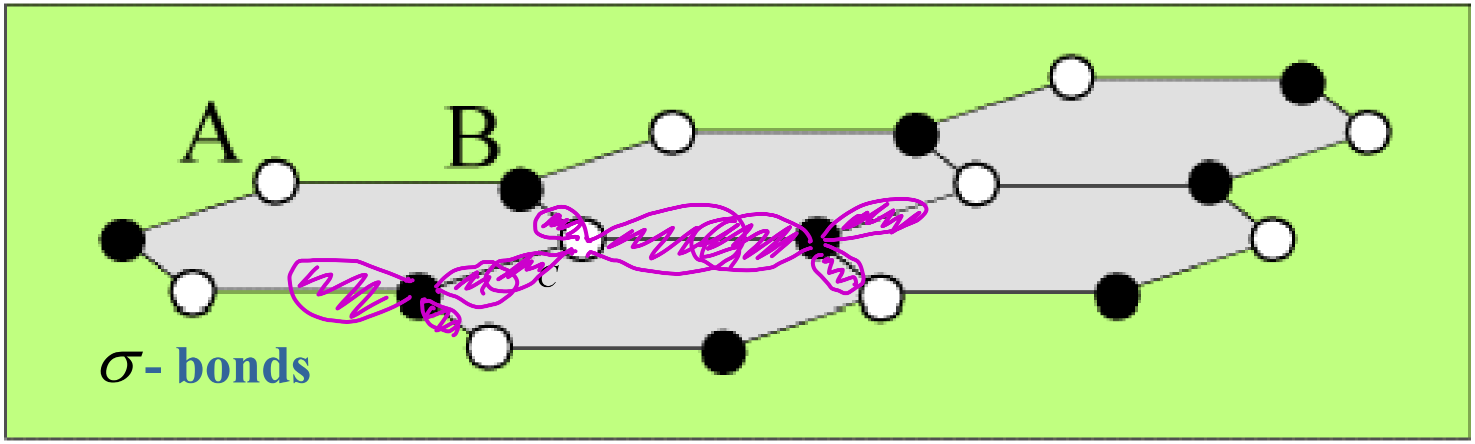


Geim & Novoselov - Nature Materials 6, 183 (2007)
Geim & MacDonald, Physics Today 60, 35-41 (2007)
Geim & Kim, Scientific American 90-97 (April 2008)

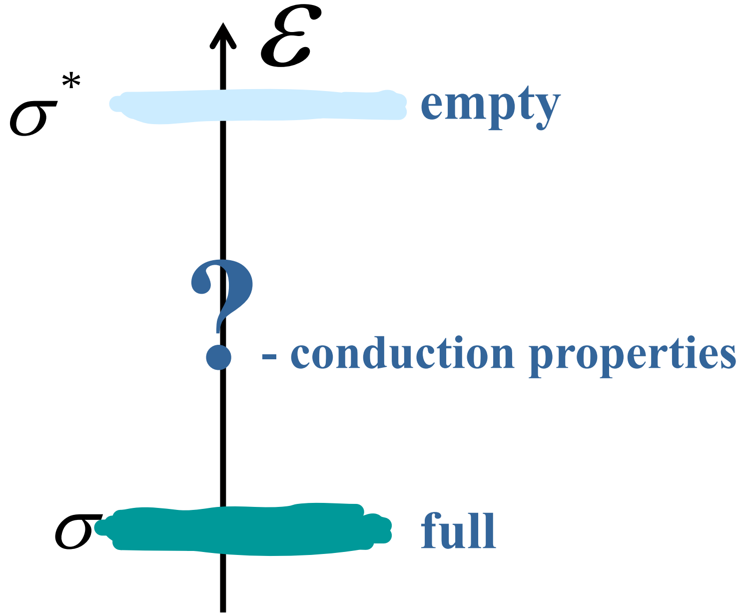


Carbon has 4 electrons in the outer s-p shell

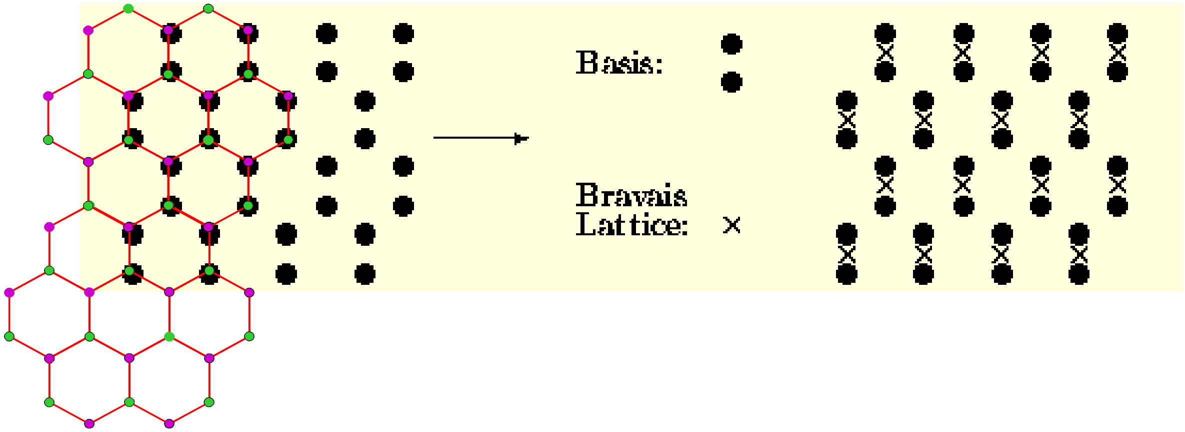
sp^2 hybridisation forms strong directed bonds which determine a honeycomb lattice structure.



Strong sp^2 hybridised bonds make graphene mechanically strong. It takes 48,000 kN·m·kg^{-1} (compare to best steel's 154 kN·m·kg^{-1}). Also, it is chemically resilient.

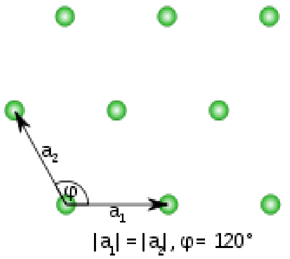


strong covalent bonds

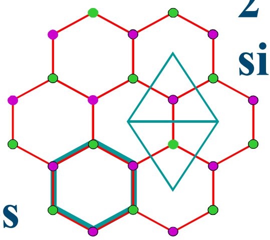


hexagonal Bravais lattice

$$R_{n_1 n_2} = n_1 \vec{a}_1 + n_2 \vec{a}_2$$



unit cell – can be chosen differently

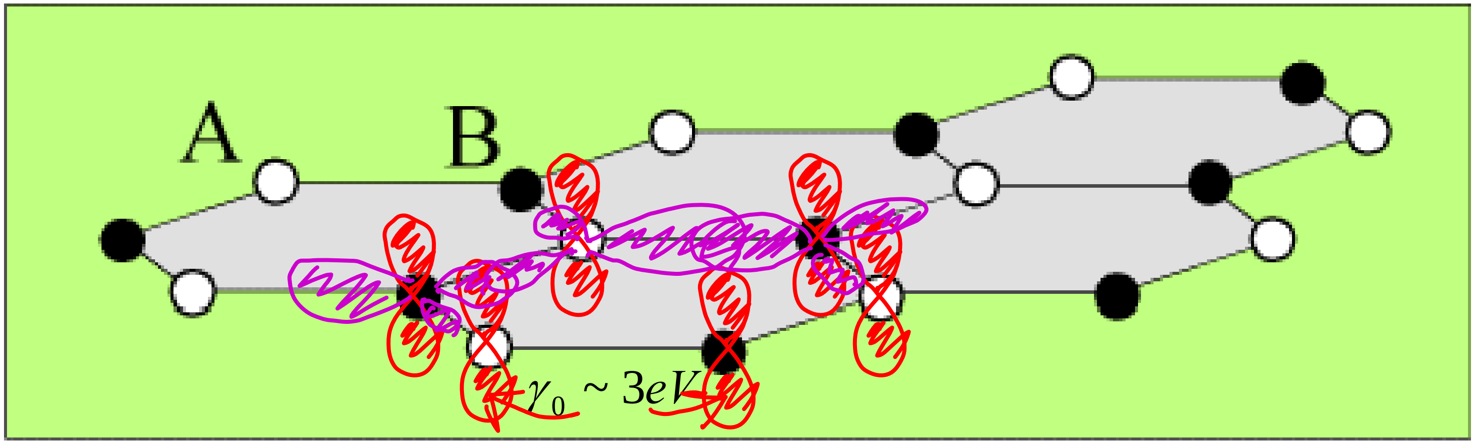


2 full sites

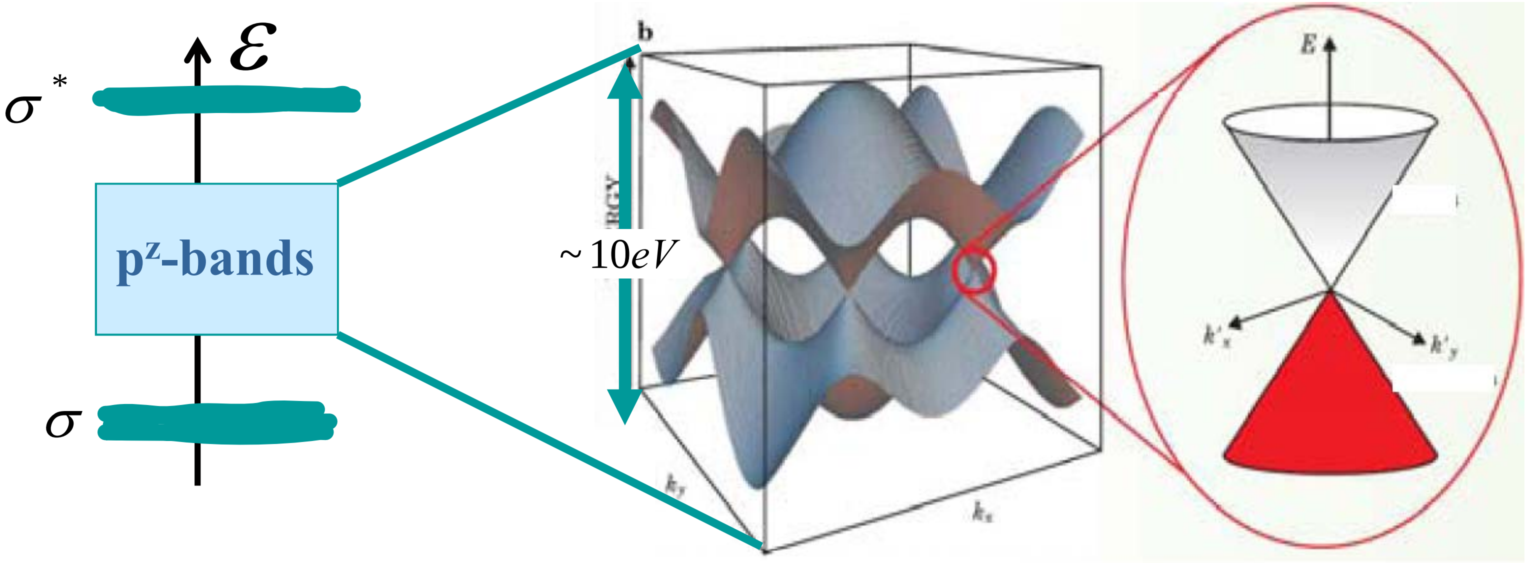
6 x 1/3 sites

Carbon has 4 electrons in the outer s-p shell

sp^2 **hybridisation forms strong directed bonds which determine a honeycomb lattice structure.**



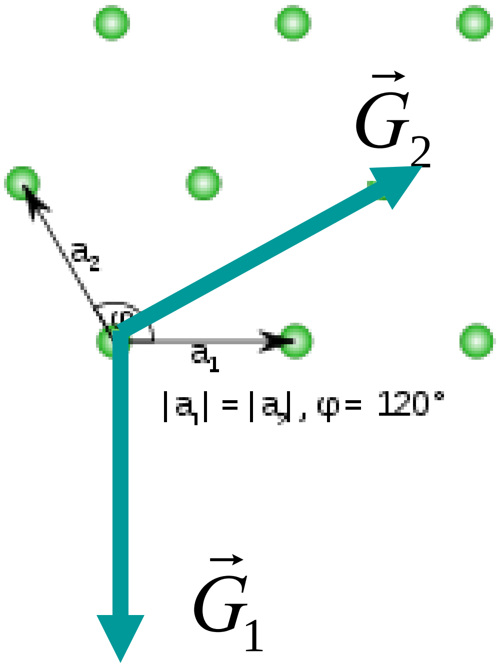
$p^z(\pi)$ **orbitals determine conduction properties of graphite**



Bragg scattering conditions

$$e^{i\vec{G}\cdot\vec{R}_{n_1 n_2}} = 1$$

$$\vec{G}\cdot\vec{R}_{n_1 n_2} = 2\pi M$$



Reciprocal lattice

$$\vec{G}_{N_1 N_2} = N_1\vec{G}_1 + N_2\vec{G}_2$$

$$\vec{G}_1 \perp \vec{a}_1; \qquad |\vec{G}_1| = \frac{2\pi a_1}{S_{unitcell}}$$

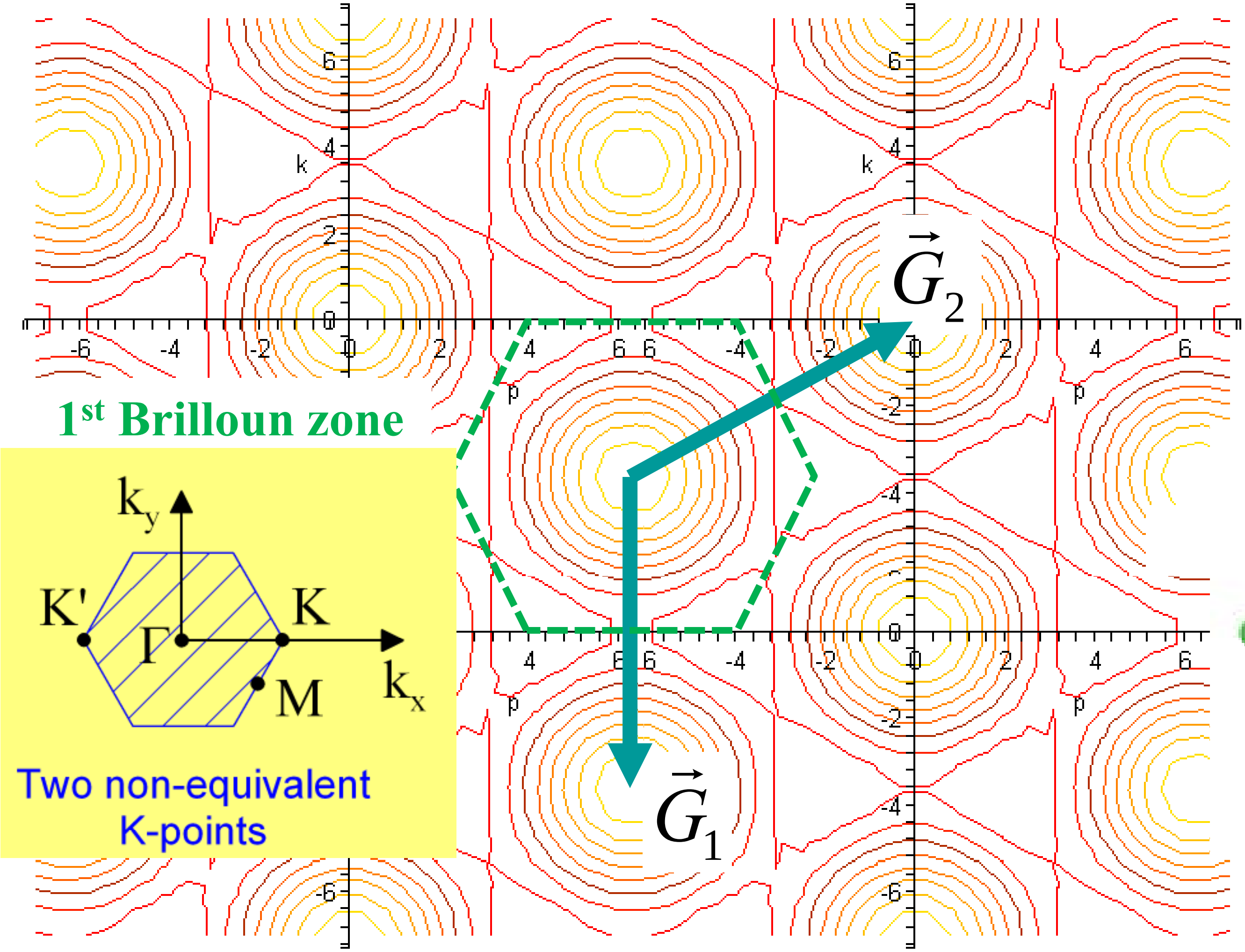
$$\vec{G}_2 \perp \vec{a}_2; \qquad |\vec{G}_2| = \frac{2\pi a_2}{S_{unitcell}}$$

Hexagonal Bravais lattice determines a hexagonal reciprocal lattice, with

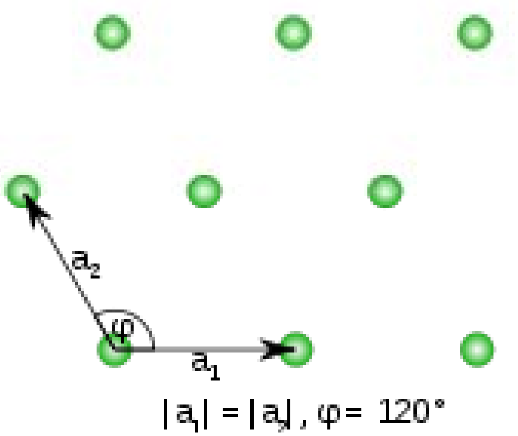
$$|\vec{G}_1| = |\vec{G}_2| = \frac{2\pi a}{a^2\sqrt{3}/2} = \frac{4\pi}{\sqrt{3}a}$$

Reciprocal lattice

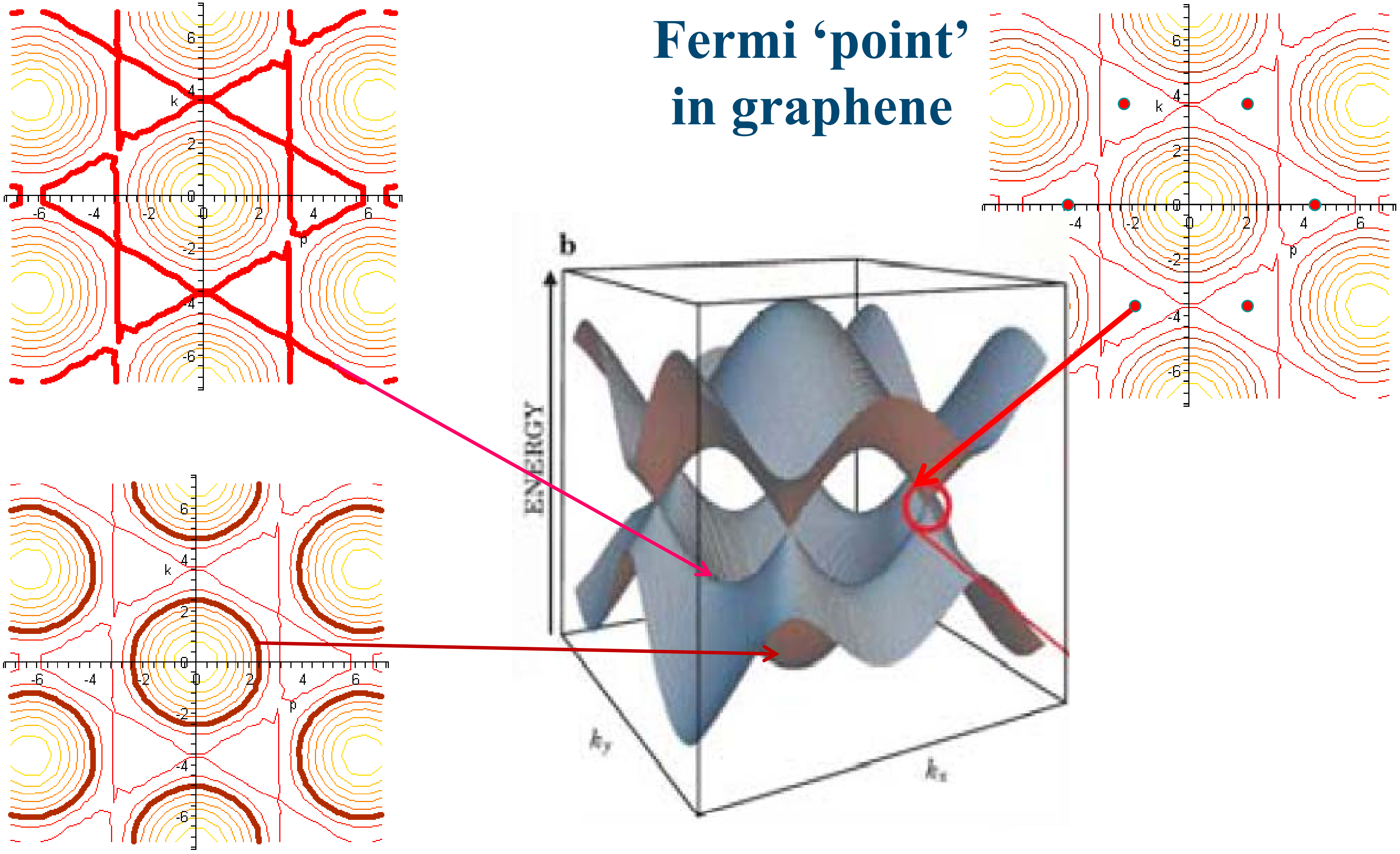
$$\varepsilon(\vec{k}+\vec{G}_{N_1N_2}) = \varepsilon(\vec{k}) \qquad \vec{G}_{N_1N_2} = N_1\vec{G}_1 + N_2\vec{G}_2$$



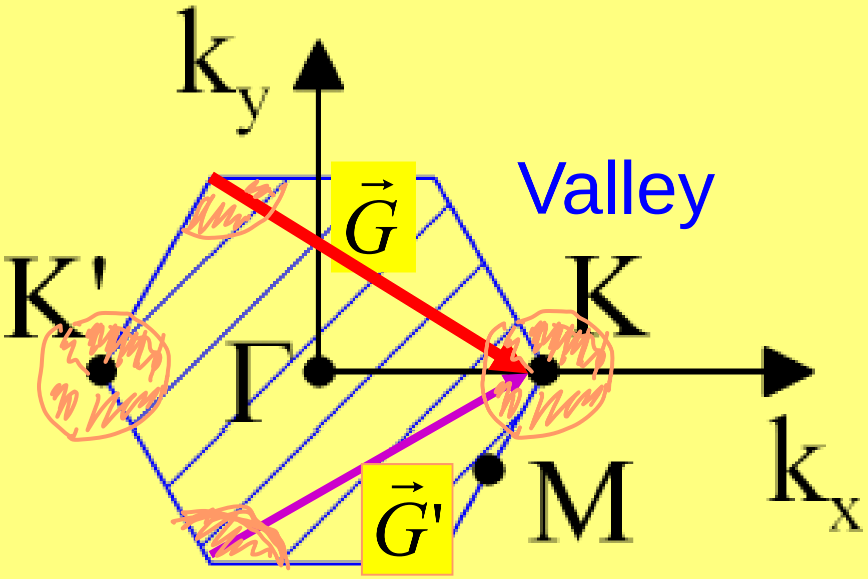
Hexagonal reciprocal lattice corresponding to the hexagonal Bravais lattice



Fermi 'point' in graphene

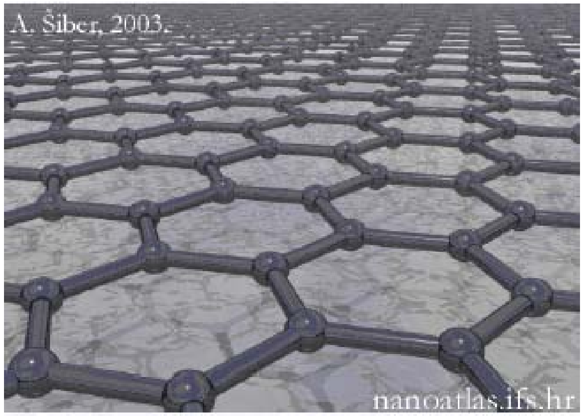


Brillouin zone

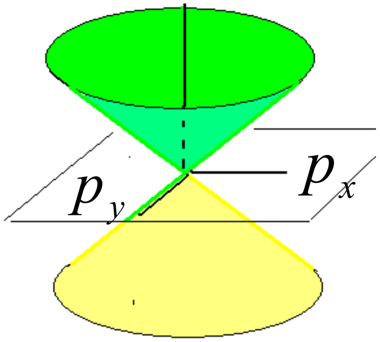


Two non-equivalent K-points

Graphene (monolayer of graphite) is an atomically thin zero-gap two-dimensional semiconductor with linear dispersion of conduction and valence band electrons.



$$\varepsilon^{cond} = vp = v\sqrt{p_x^2 + p_y^2}$$



Electronic dispersion in the vicinity of the corner of the Brillouin zone: the same in both valleys.

$$\varepsilon^{val} = -vp = -v\sqrt{p_x^2 + p_y^2}$$

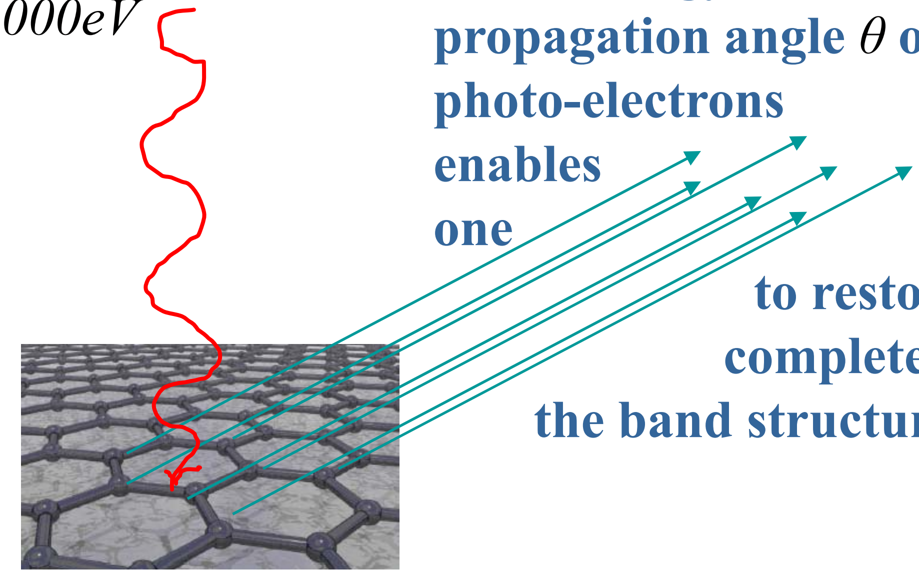
high-energy photon

$\hbar\omega \sim 100\text{-}1000 eV$

$$p_{\|} = \sqrt{2mE}\cos\theta$$

$$\hbar\omega + \varepsilon(p_{\|}) - A = E$$

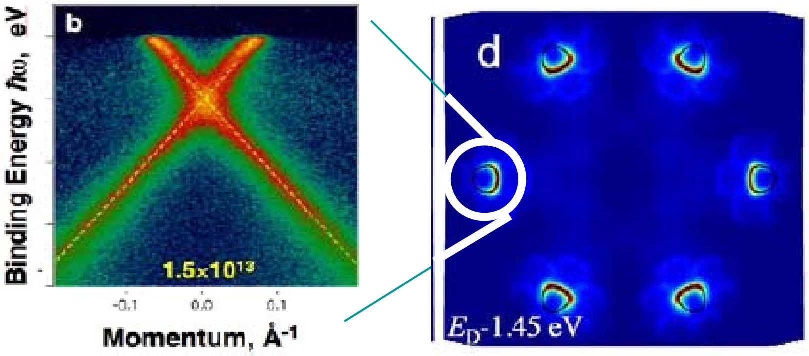
work function



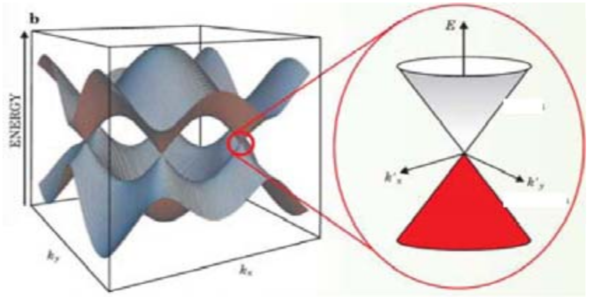
Simultaneous detection of the energy, E and propagation angle θ of photo-electrons enables one to restore completely the band structure.

Angle-resolved photo-emission spectroscopy (ARPES) of heavily doped graphene synthesized on silicon carbide

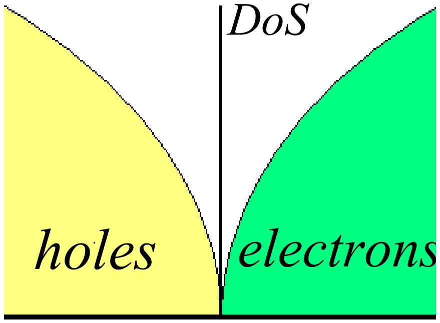
A. Bostwick *et al* – Nature Physics, 3, 36 (2007)



Graphene: gapless semiconductor

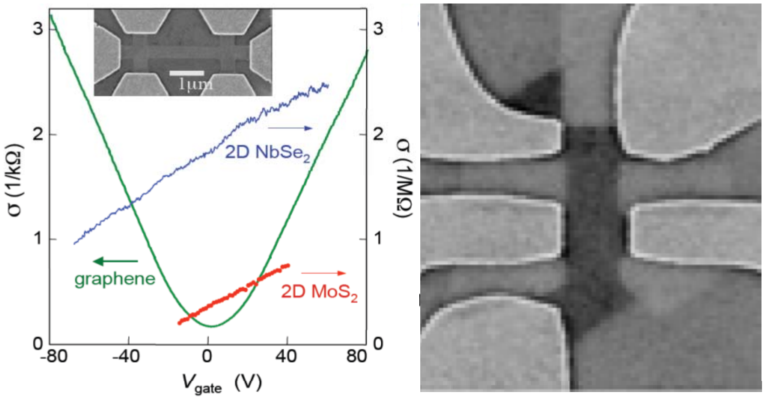


Wallace, Phys. Rev. 71, 622 (1947)



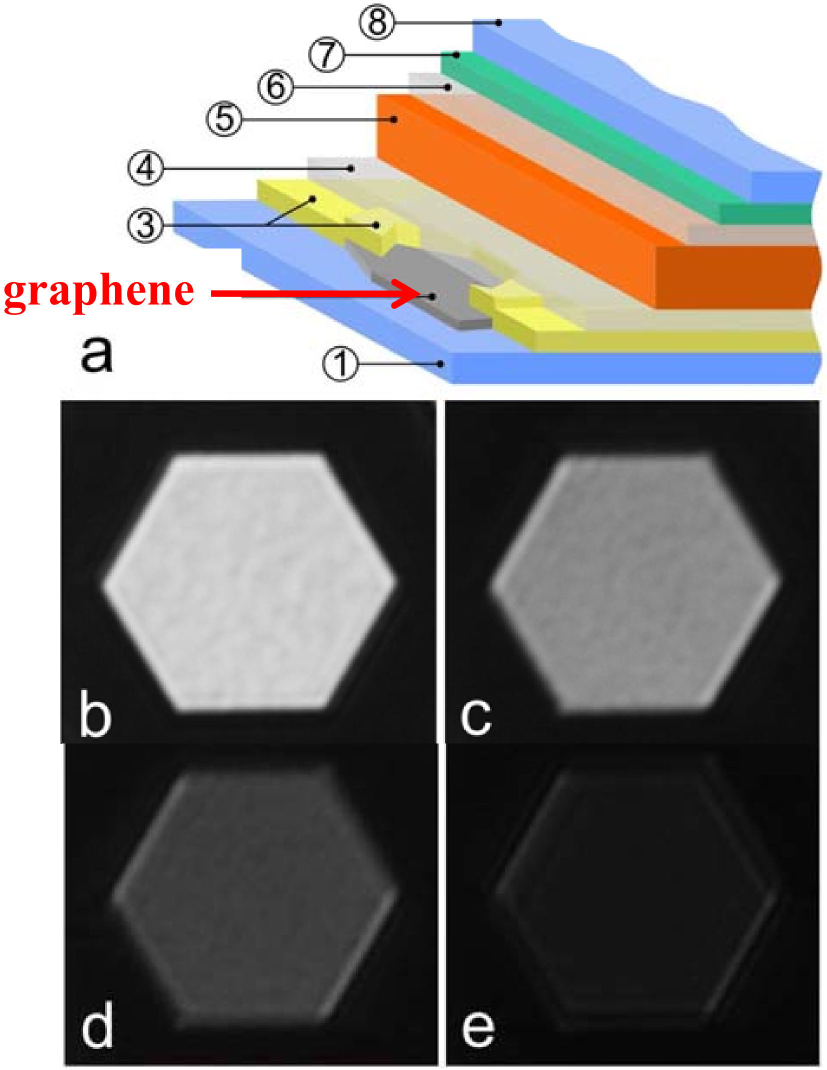
$$n_{carriers} \propto V_{gate}$$

Graphene-based field-effect transistor: GraFET



Geim and Novoselov, Nature Mat. 6, 183 (2007)

Graphene-based pixels

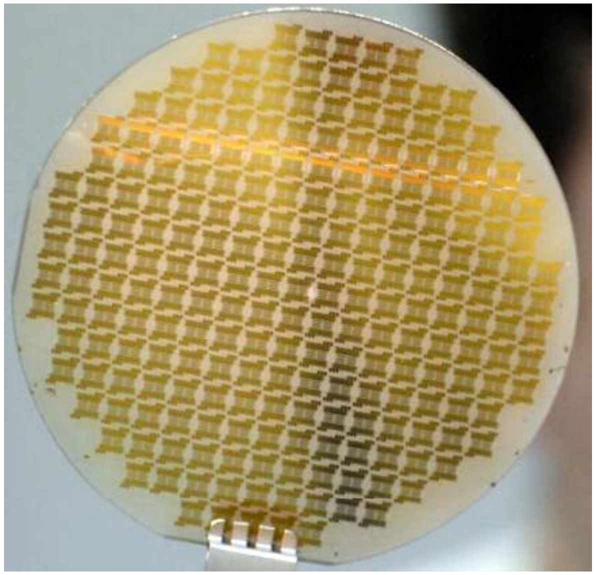


Blake (Graphene Industries Ltd), *et al*
Nano Lett. 8, 1704, (2008)

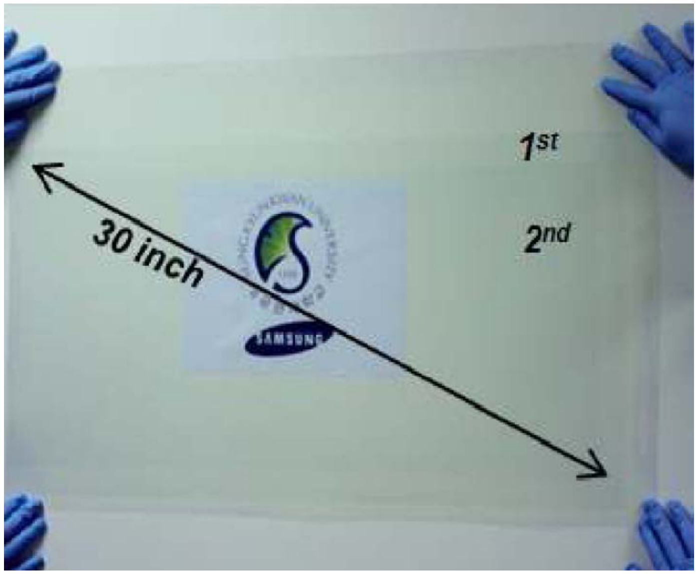
When embedded in polymers, graphene reinforces them, remains conducting and, since it's thin, it is highly transparent.
Thus, it is an ideal material to make flexible liquid crystal screens

or to be used in conducting coating.

Graphene: state of the art in applicaitons

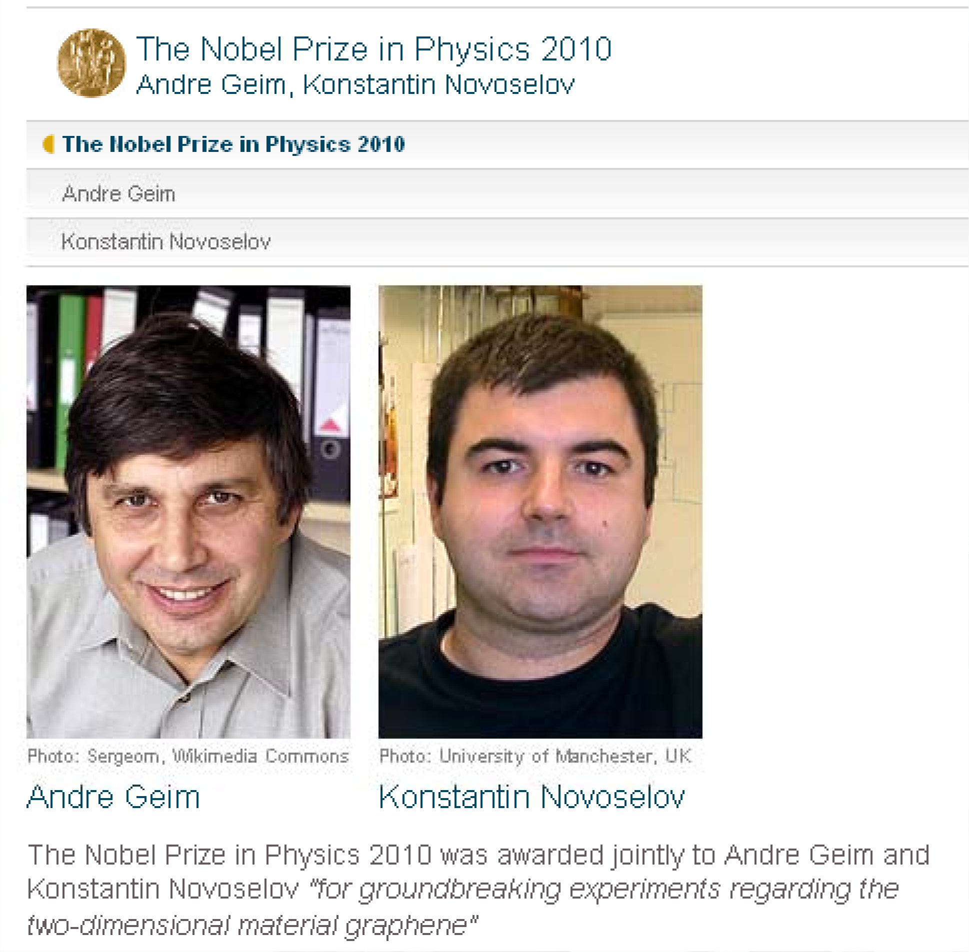


G sublimated on inch-size SiC is used for manufacturing THz circuits. IBM & HRL (USA)



G grown on copper and transferred into various media is used for flexible optoelectronics, LCD displays, touch screens. (Samsung)

G exfoliated from bulk graphite into suspensions is used to enhance mechanical properties of light-weight materials (for aerospace and medical implants).



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

Photo: Sergeom, Wikimedia Commons

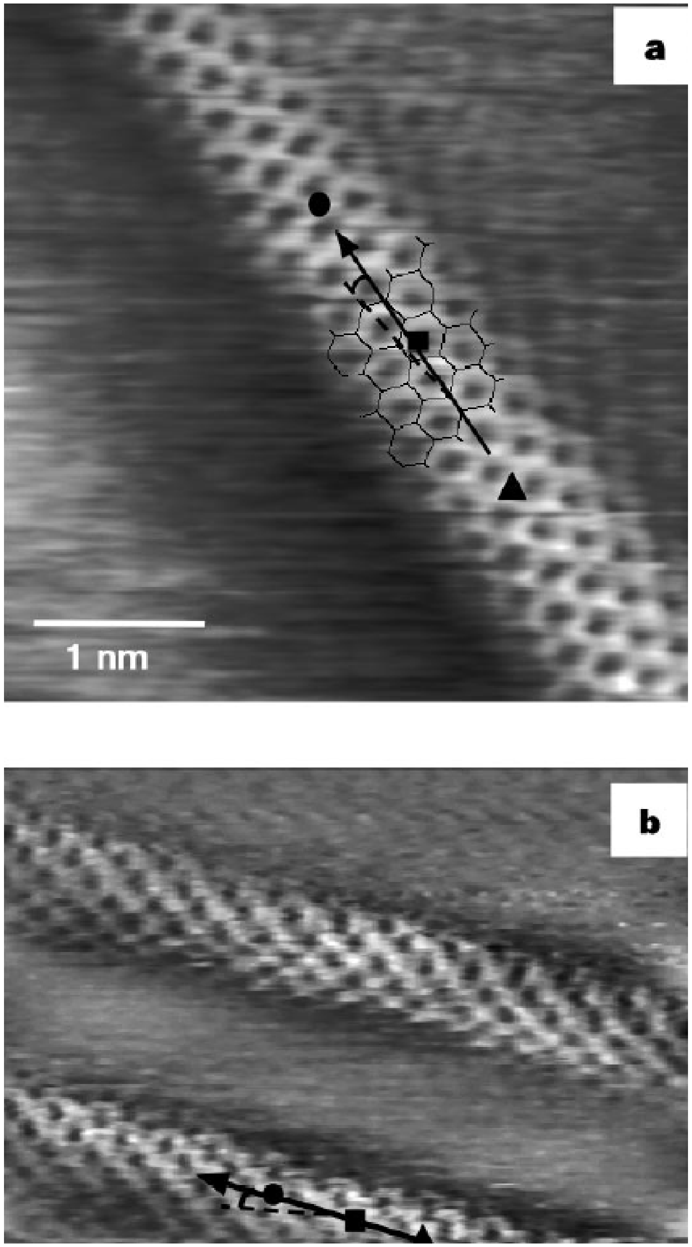
Andre Geim

Photo: University of Manchester, UK

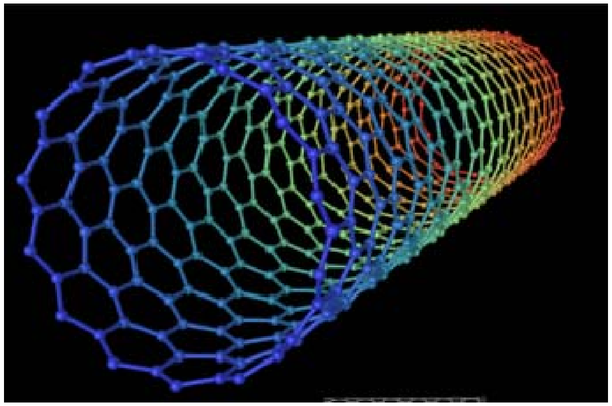
Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

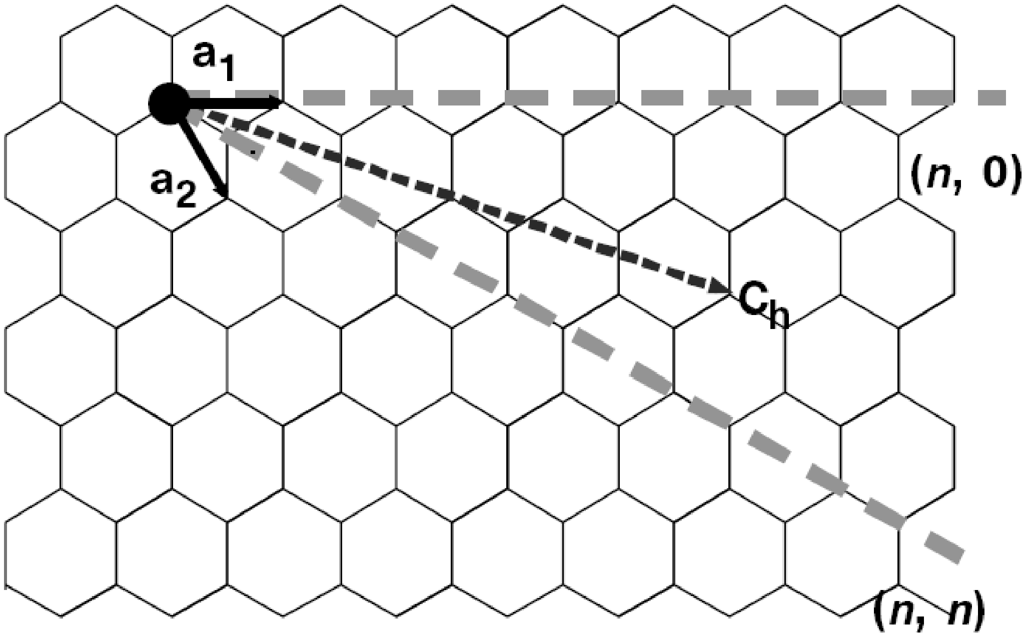
Carbon nanotubes



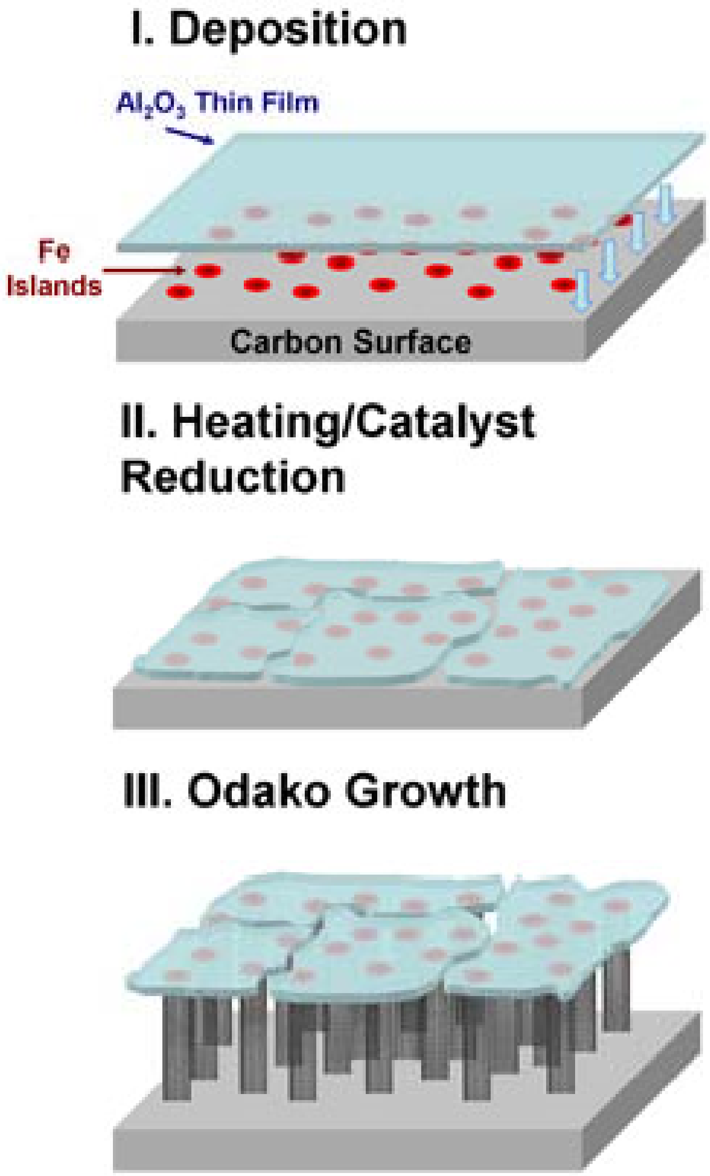
STM images of carbon nanotubes
T.W. Odom, J.-L. Huang, P.Kim, C.Lieber, Nature 391 (1998)



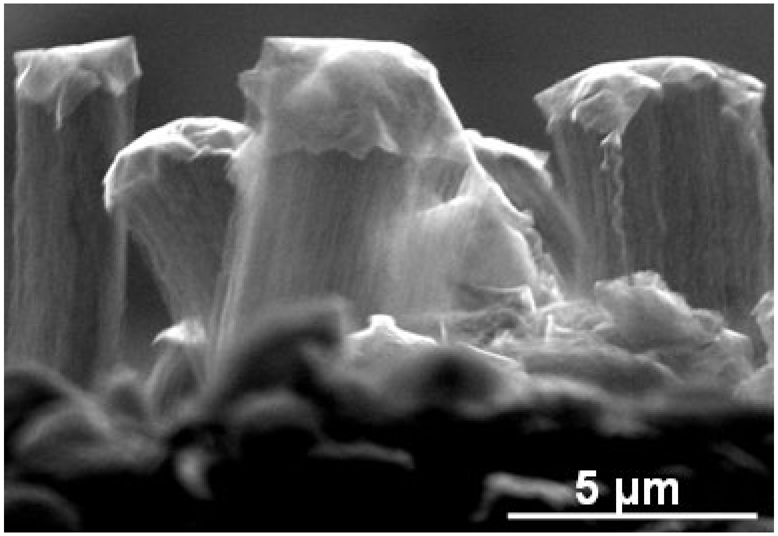
Iijima 1991
Smalley 1993



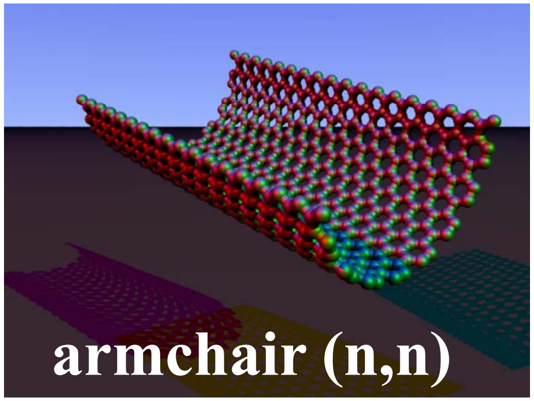
Nanotubes growth

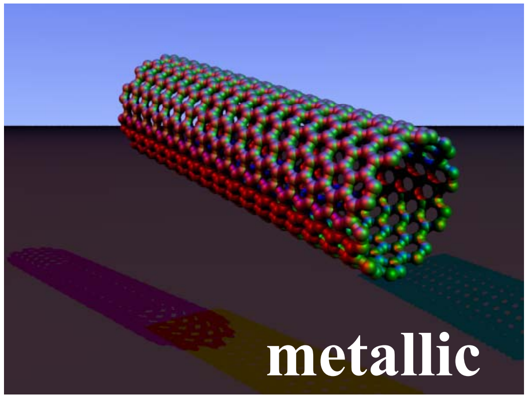


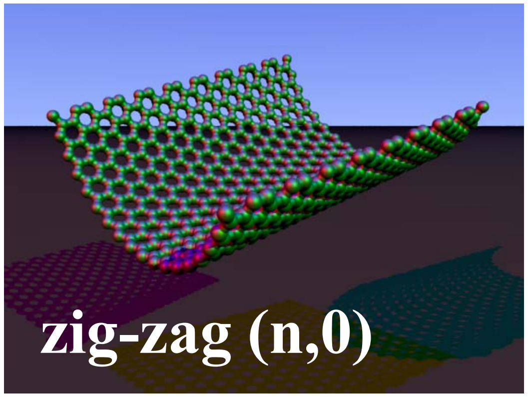
Single-walled nanotubes grow from iron "islands" deposited between a carbon substrate and the aluminum oxide catalyst.

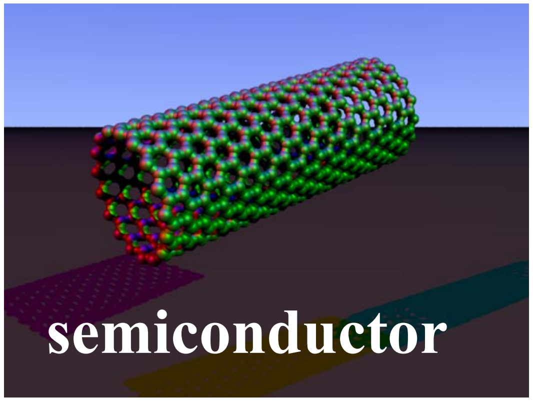


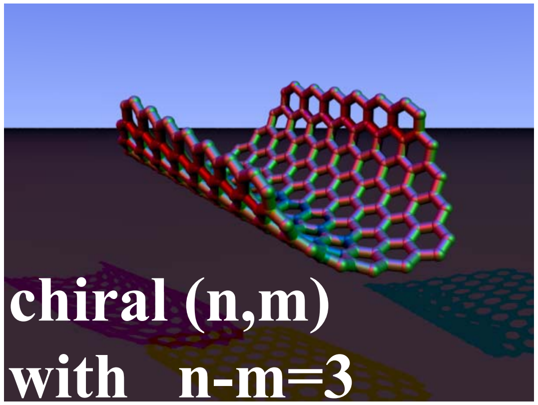
Nanotube types

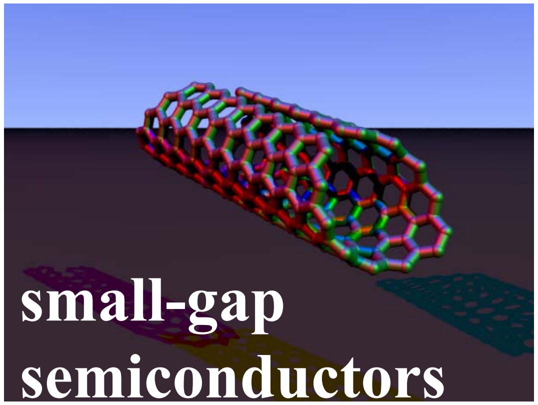

armchair (n,n)

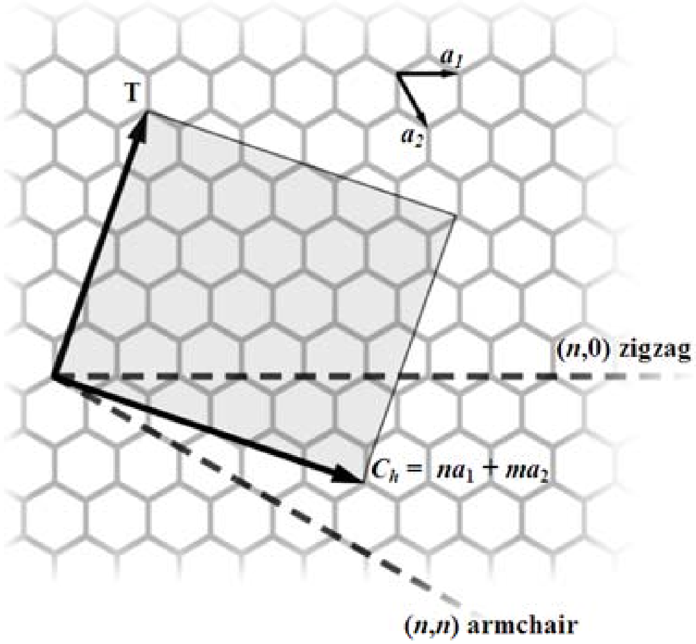

metallic


zig-zag (n,0)


semiconductor


chiral (n,m)
with n-m=3


small-gap
semiconductors



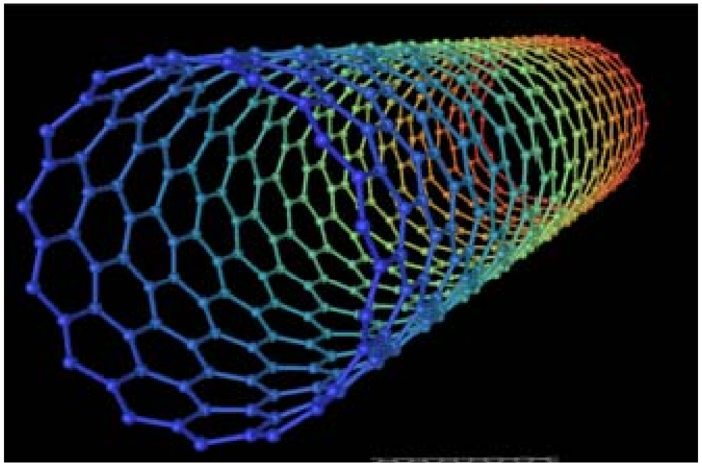
Metallic nanotubes (n,n)

$$\psi(y=0)=\psi(y=L_\perp)$$

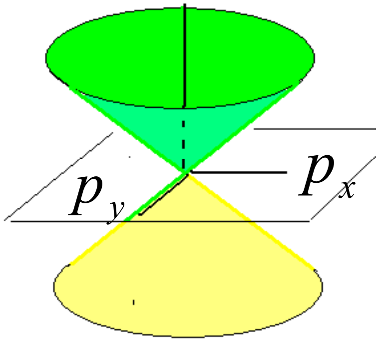
$$\psi \sim \frac{1}{\sqrt{L_\perp}}e^{i2\pi y/L_\perp}$$

perimeter, 2πr

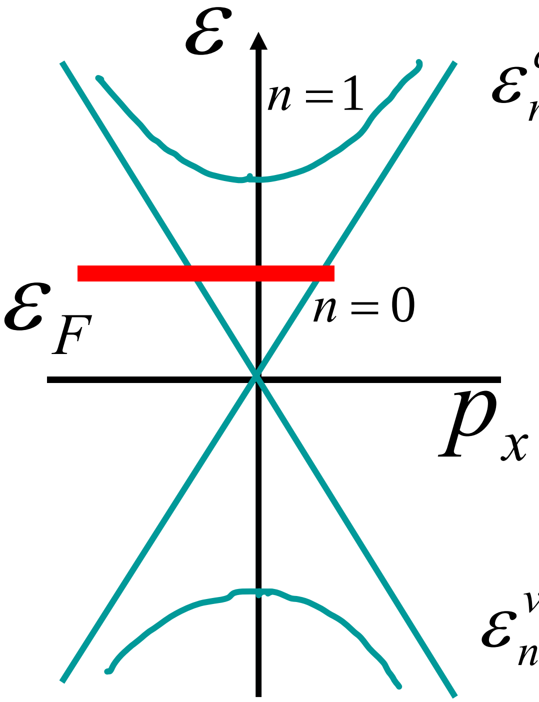
$$p_y = \frac{2\pi\hbar}{L_\perp}M$$



$$\varepsilon^{cond} = v\sqrt{p_x^2+p_y^2}$$



$$\varepsilon^{val} = -v\sqrt{p_x^2+p_y^2}$$

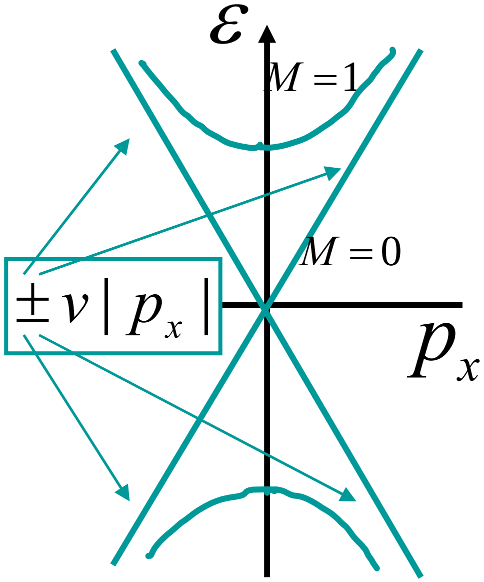


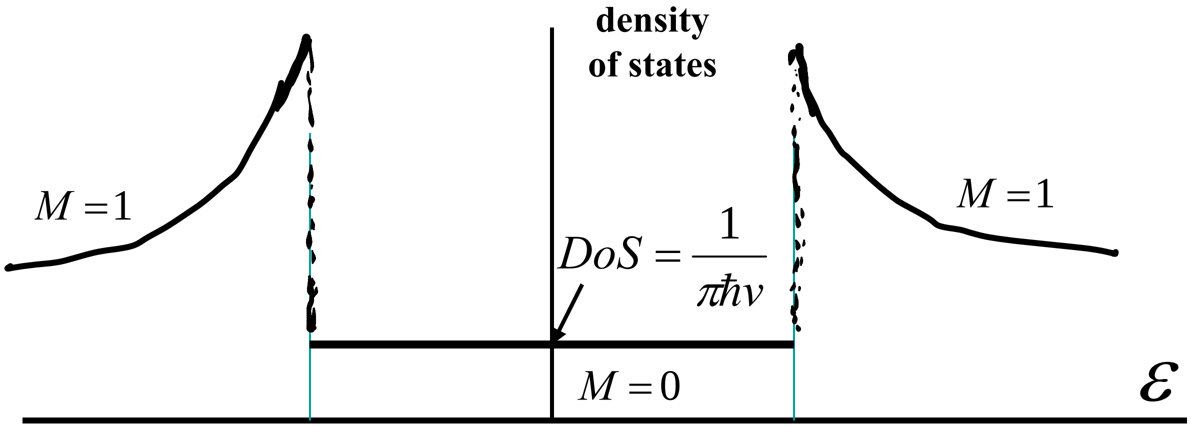
$$\varepsilon_n^{cond} = v\sqrt{p_x^2+\frac{h^2M^2}{L_\perp^2}}$$

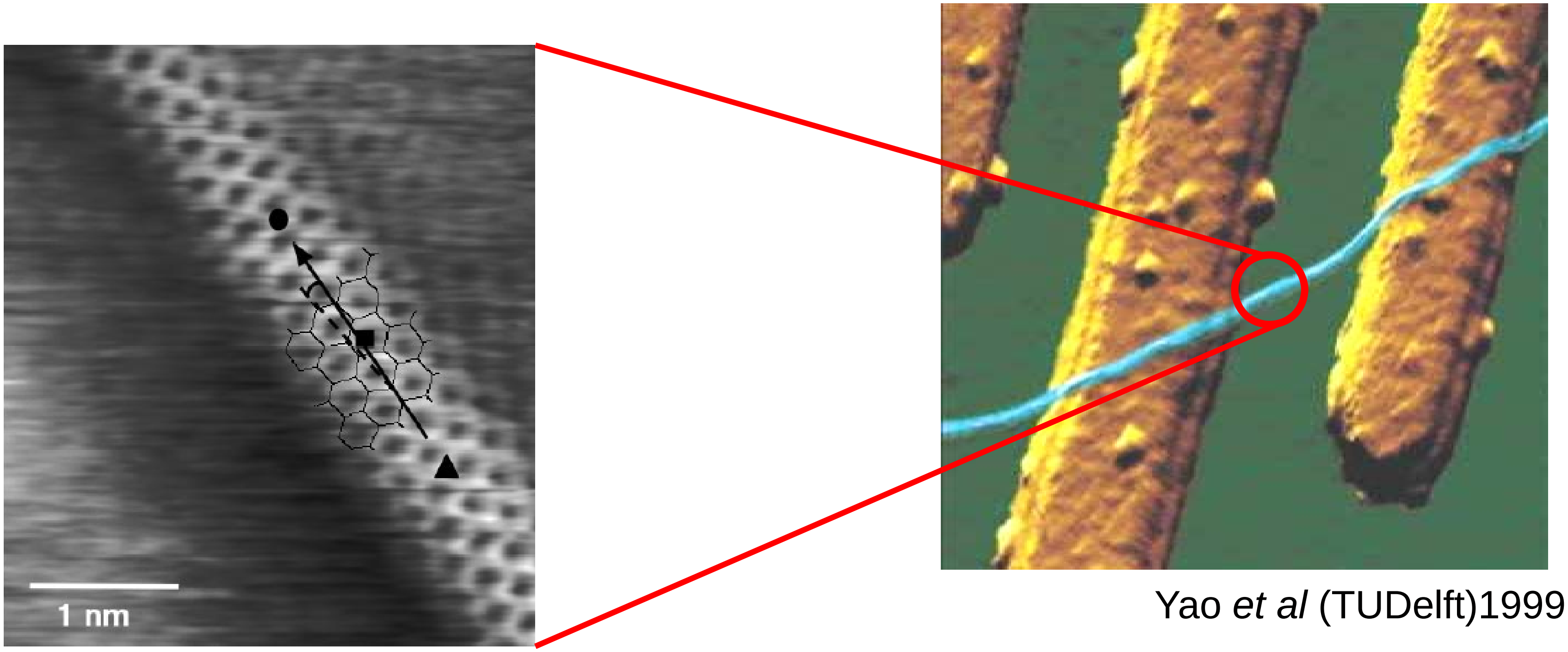
$$n=0,1,2,3,....$$

$$\varepsilon_n^{val} = -v\sqrt{p_x^2+\frac{h^2M^2}{L_\perp^2}}$$

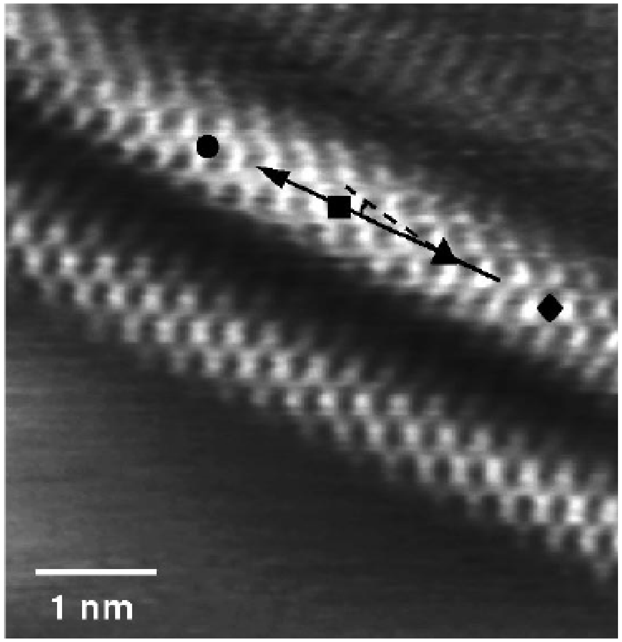
Metallic nanotubes (m,m') with m=m' truly 1D conductors







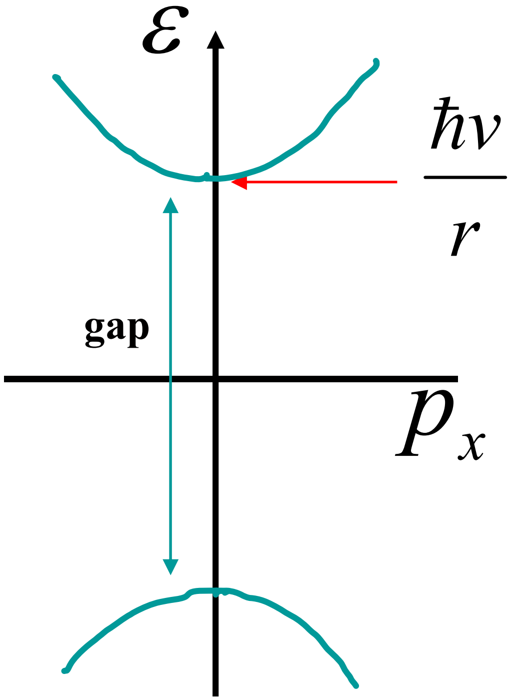
Yao *et al* (TUDelft)1999

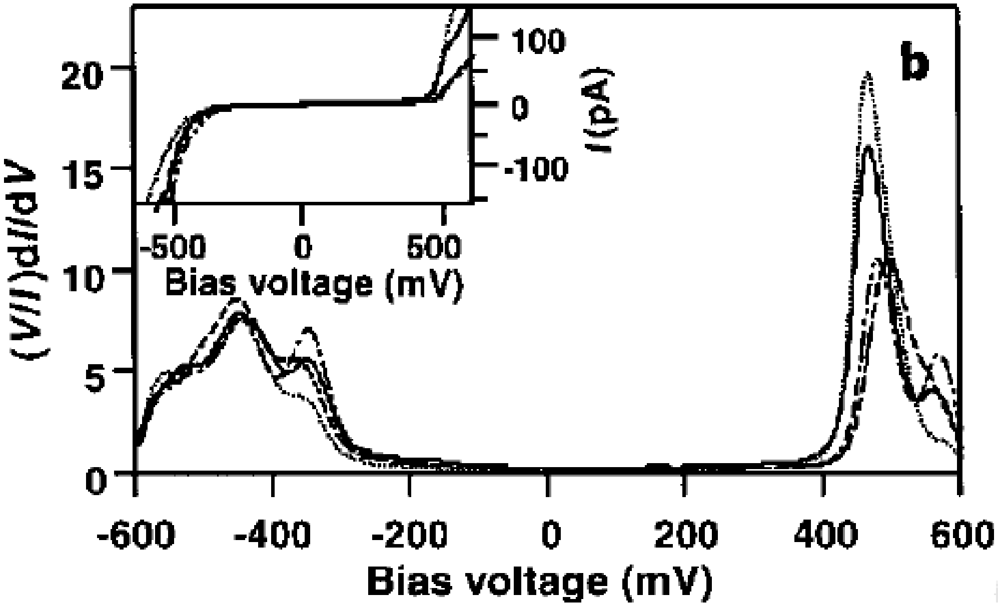


Semicondutor-type nanotubes

(different n and m)

Depending on how the carbon sheet is rolled into a nanotube, the resulting nanotube may have a gap in the electron spectrum. A gap in the nanotube spectrum is determined by its radius *r*, which offers a direct root towards engineering semiconductor wires with a prescribed band gap, for use in electronic and optoelectronic devices.





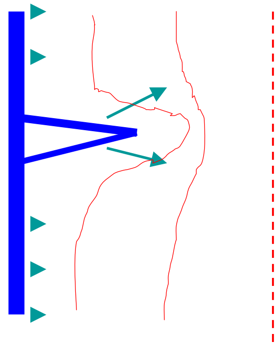
tunnelling current

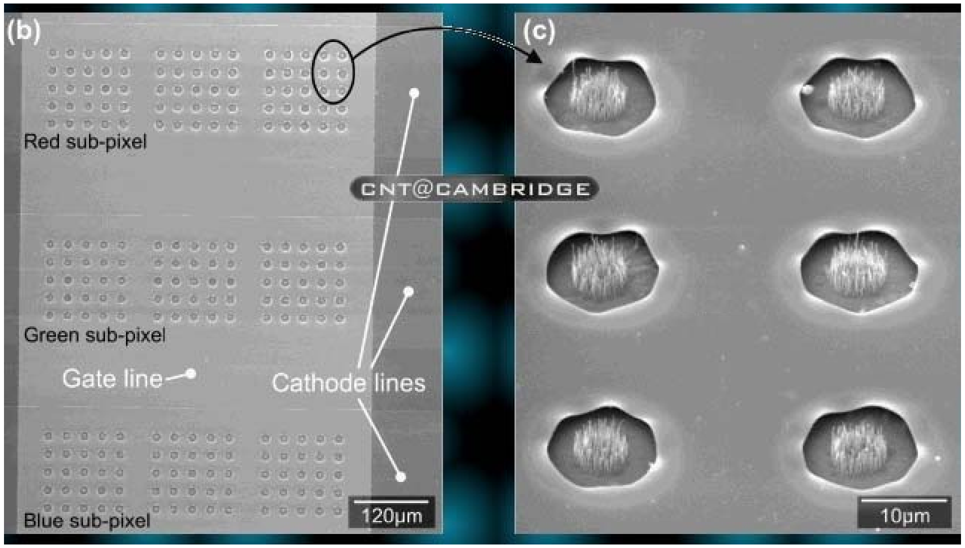
T.W. Odom, J.-L. Huang, P. Kim, C. Lieber, Nature 391 (1998)

Potential applications of carbon nanotubes:

In surface tunnelling microscopy – used as a tip.

Make excellent tips for field-effect electron guns for plasma.





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Northwest
Doctoral Training Centre
in Nanoscience

- Initial training designed to demonstrate the breadth and potential of nanoscience, before focusing on one specific area of the subject.
- Research and training in fundamental nanoscience,
practical nano-engineering, and nanotechnology in medicine.
- Interdisciplinary PhD projects which span from development and studies (exp and th) of fundamental properties of new materials and structures to making devices for applications in electronics and medicine.
- Development of skills in nanofabrication, low-temperature physics, materials science and data storage, synthetic chemistry, cell &tissue biology, biophysics, nanophotonics and materials science – this will be your choice!