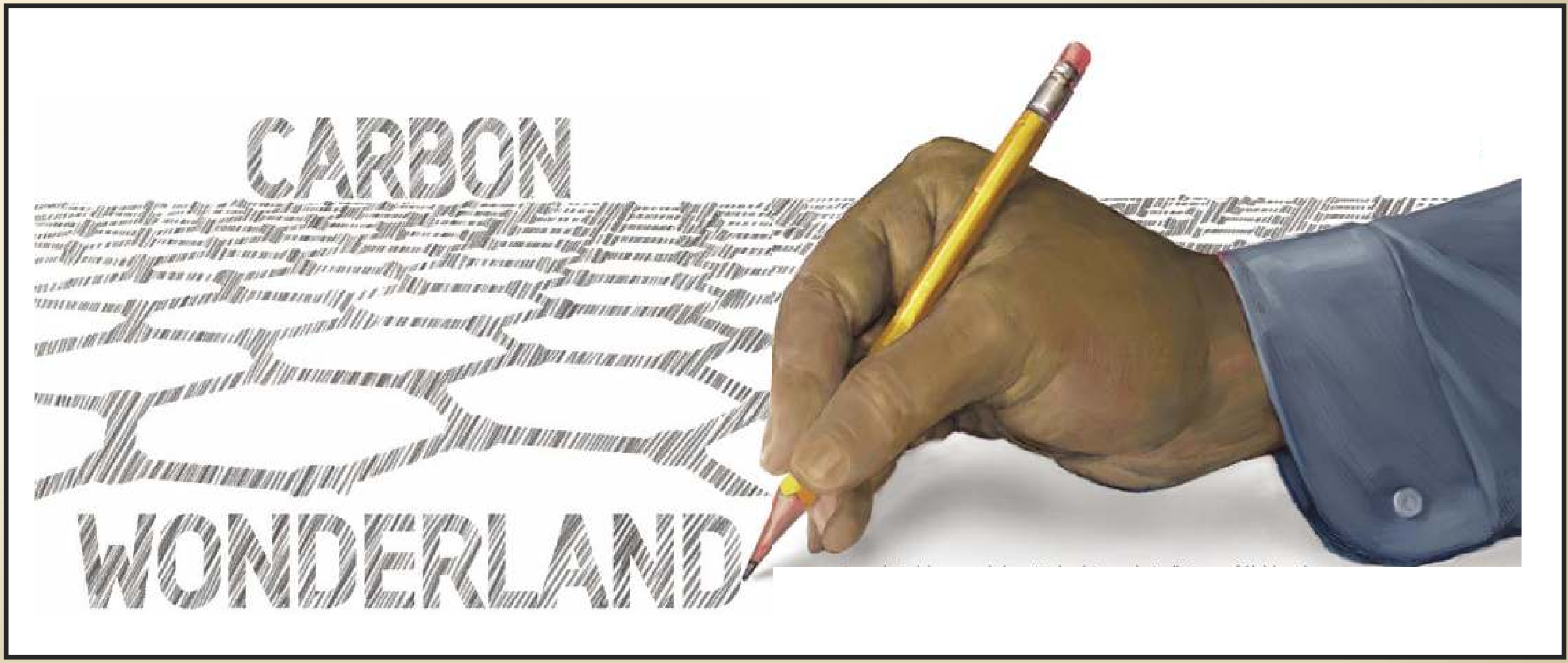
Graphene



Prepared for Solid State Physics II – Pr Dagotto – Spring 2009

Laurene Tetard – 03/23/09

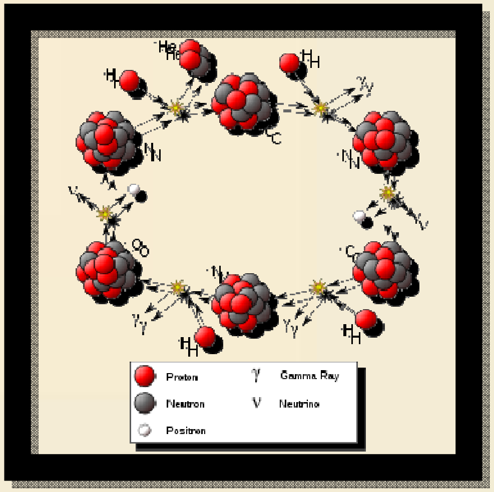
Overview

- Carbon in all its forms
- Background & Discovery
- Fabrication

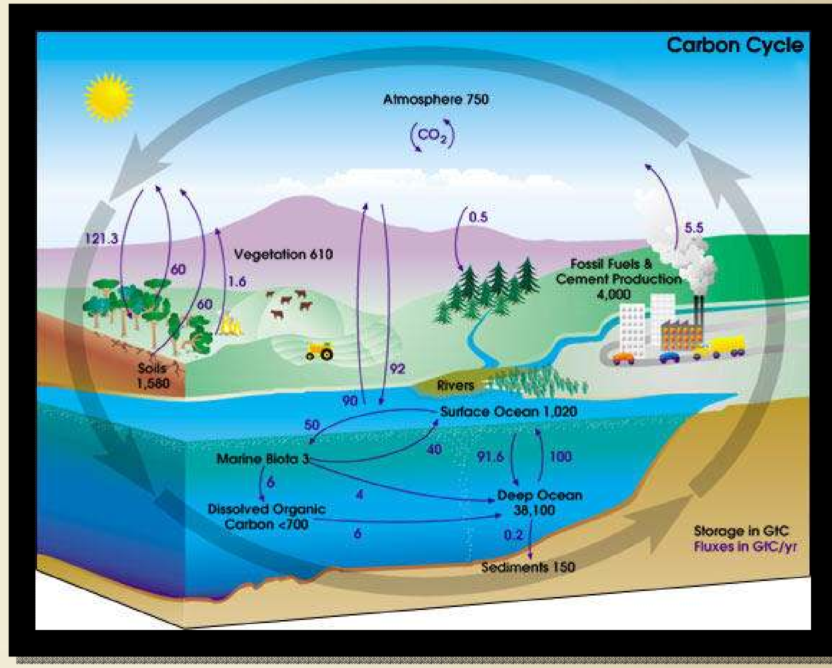
- Important properties
- Overview of current research
- Summary & References

Carbon in all its forms

Carbon



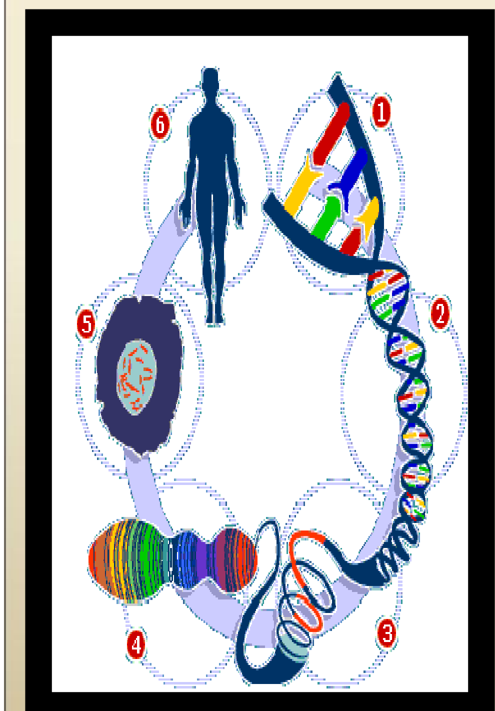
The CNO cycle



The Carbon Cycle

Courtesy NASA. Source: http://earthobservatory.nasa.gov/Library/CarbonCycle/carbon_cycle4.html

DNA - Cell - Human

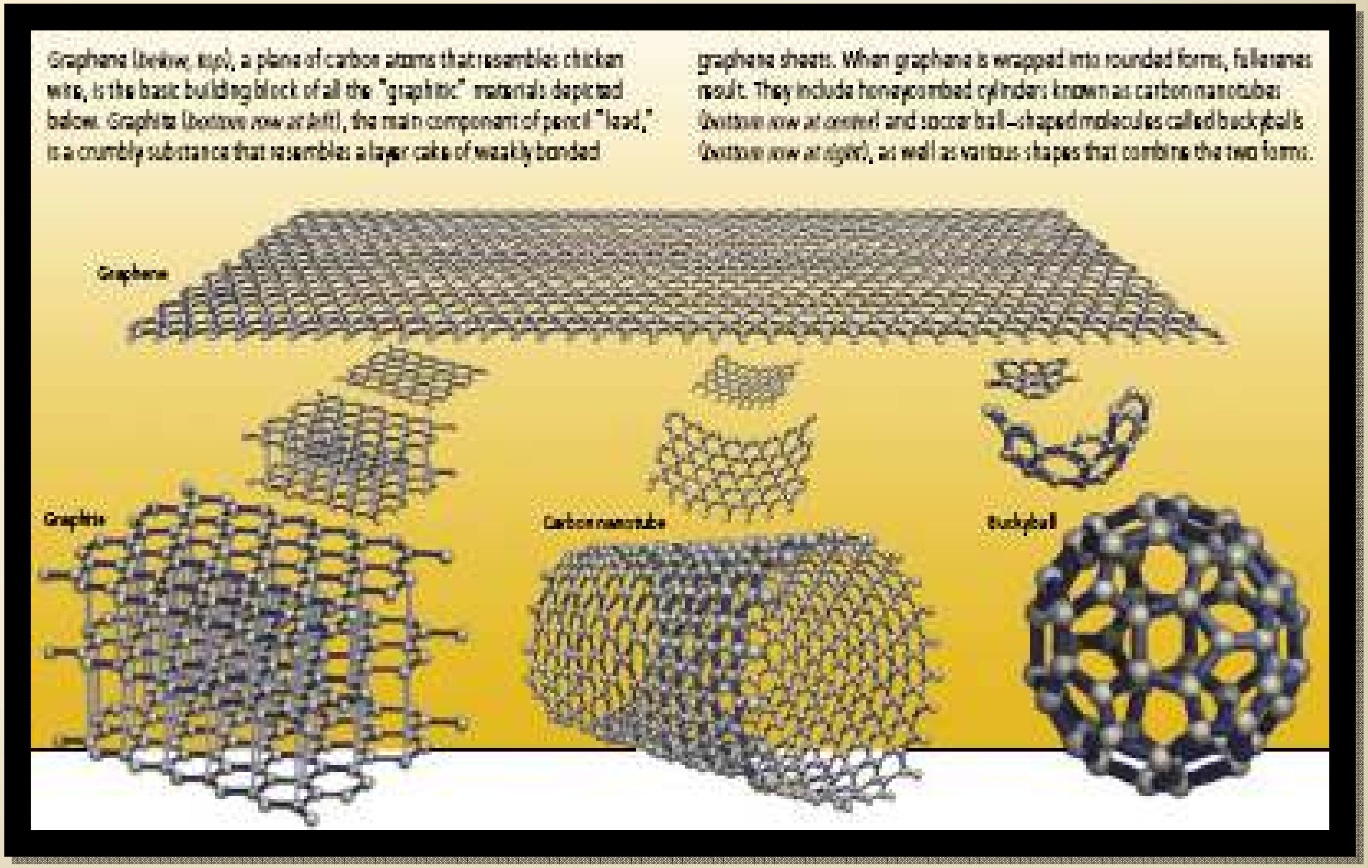


Carbon is very important in Nature

1- it is the 4th most abundant element (after H, He and O),

2- it is part of the very important natural processes (DNA, Cells, photosynthesis, CNO cycle for the formation of stars...)

Carbon in all its forms



Courtesy *Scientific American* April 2008

- The idea of studying carbon in its 2D form is not new. In fact it has been used for decades as a building block to carbon based materials for decades. Graphene has been extensively studied in theory.

Background - Theory

- The successful isolation of a single sheet of graphene contradicts the theory of Landau, Peierles and Mermin who argued that 2D crystals were thermodynamically unstable.
- They formulated a model in which the thermal fluctuations were calculated to have a divergent contribution in the lower dimensional system. The resulting displacement would approach interactomic distances at finite temperature and thus push the system to change its state (to 0D, 1D or 3D structure).

Most potentials one is likely to consider will satisfy (21) for $\lambda = 0$, so the pertinent conditions for the absence of crystalline ordering in two dimensions are

$$\nabla^2 \Phi \sim 1/r^{4+|\epsilon|}, \quad r \to \infty; \qquad (22)$$

$$\Phi(\vec{r}) - \lambda r^2 |\nabla^2 \varphi(\vec{r})| > |A|/r^{2+|\epsilon|},$$

$$r \approx 0, \text{ for some } \lambda > 0 . \qquad (23)$$

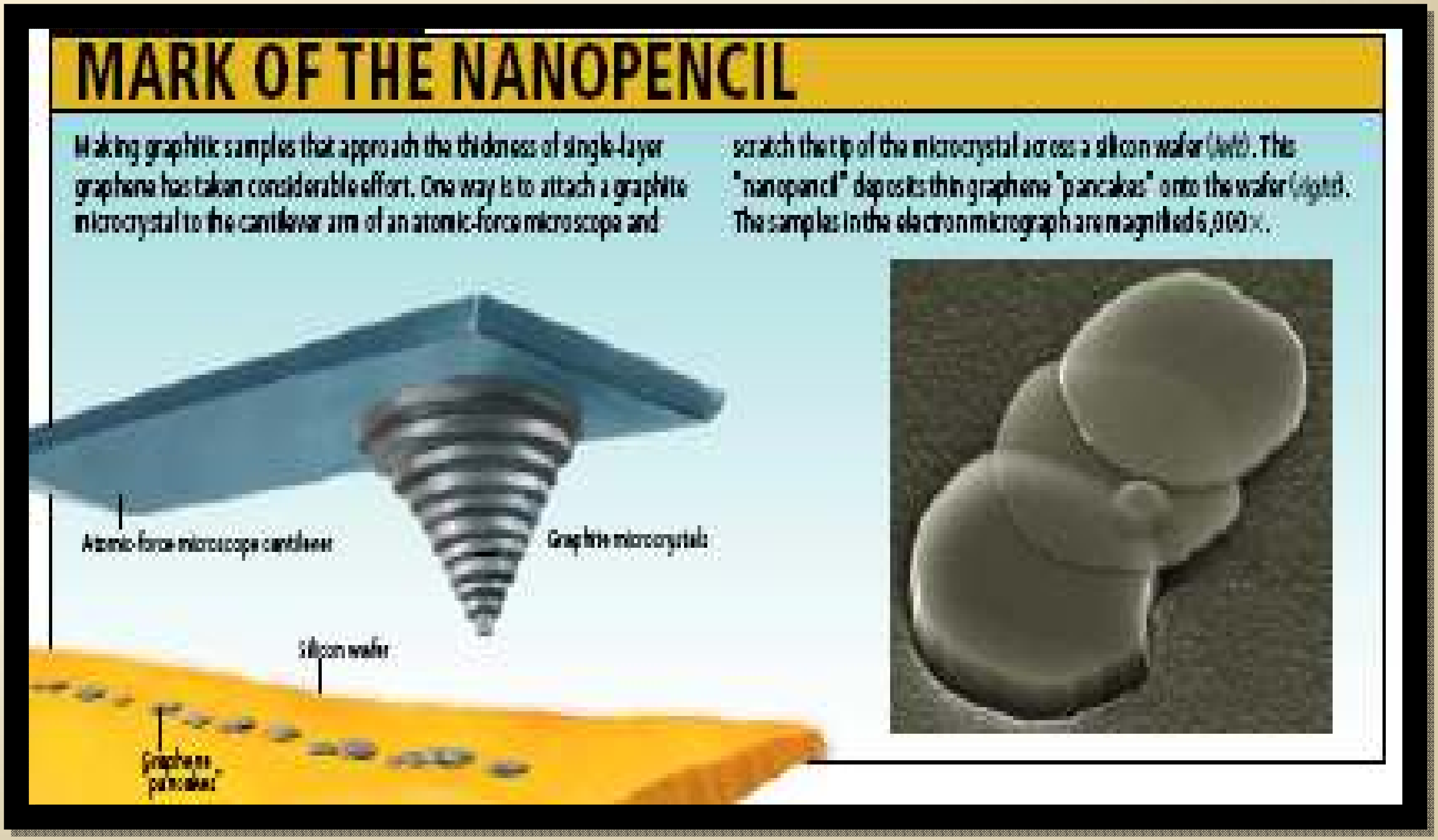
Background - Experimental

- Chemical Exfoliation

It consists in inserting molecules to graphite by chemical treatment to modify the van der Waals forces that hold the single monolayers of carbon together.

NOT VERY SUCCESSFUL: only restacked and scrolled graphene sheets are obtained.

Background - Experimental



Courtesy *Scientific American* April 2008

Discovery

In 2004 Novoselov et al. report the successful isolation and characterization of graphene.

"A **fresh surface** of a layered crystal was rubbed against another surface (virtually any solid surface is suitable), which left a variety of flakes attached to it (the rubbing process can be described as similar to ''drawing by chalk on a blackboard''). Unexpectedly, among the resulting flakes we always found single layers. Their preliminary identification amid thicker flakes and other residue was done in an optical microscope. 2D crystallites become visible on top of an **oxidized Si wafer** (Fig. 1*d), because even a monolayer adds up sufficiently* to the optical path of reflected light so that the interference color changes with respect to the one of an empty substrate (phase contrast). The whole procedure takes literally half an hour to implement and identify probable 2D crystallites." **Novoselov et al., PNAS (2005)**

Localization and Identification of graphene layers obtained by micromechanical cleavage. Optical image (horizontal scale:300microns).

Why did it take so long to isolate and characterize Graphene?

1- this technique forms all kinds of flakes, it is difficult to find the monolayers ,

2- Graphene has no clear signature in TEM ,

3- Graphene is transparent to visible light on most substrate (glass, metals…) : Oxidized Si wafer is the key,

4- For a long time, AFM was the only way to determine the number of layers forming the flake, In addition, AFM has to be operated to its maximum capacity (atomic resolution), which is very difficult.

NOTE: This discovery is not limited to Graphene. BN, MoS_2, $NbSe_2$, $Bi_2Sr_2CaCu_2O_x$, were also reported.

Fabrication

The obstacles encountered for carbon nanotubes were a good learning to identify the upcoming challenges that graphene will face.

1- mechanical cleavage is a research grade procedure, need for a large scale production (high throughput)

2- identify to what extend the structure can be controlled (ex: edge effects, number of layers, sizes…)

3- applications

NOTE: Graphene is a strong material

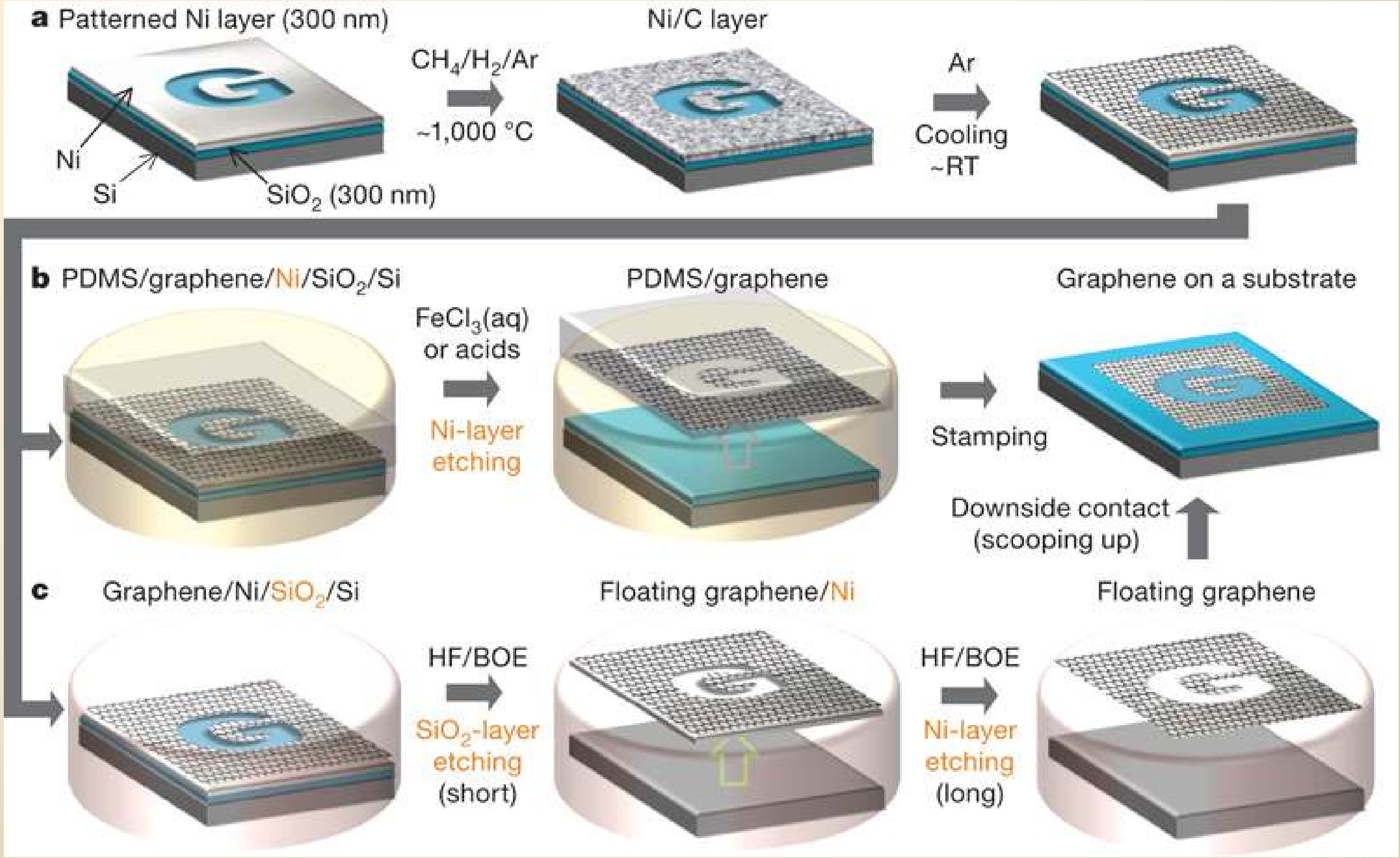
Possible routes

- Chemical exfoliation of graphite through oxidation and then dispersion in water down to single graphene sheets
- Thermal exfoliation of graphite oxide.

  - chemical vapor deposition (CVD) of hydrocarbons deposited on a metal substrate

  - thermal decomposition method : semiconducting SiC substrate heated to over 1200°C until the silicon begins to evaporate, at which point the remaining carbon on top of the substrate nucleates into graphitic film
- Liquid-phase exfoliation of graphite
- Expandable graphite powders

Synthesis, etching and transfer processes for the large-scale and patterned graphene films.



KS Kim *et al. Nature* **000**, 1-5 (2009) doi:10.1038/nature07719

nature

Metallic or Semiconductor?

nature materials

ARTICLES

PUBLISHED ONLINE: 15 FEBRUARY 2009 | DOI: 10.1038/NMAT2378

The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons

Kyle A. Ritter[1,2]* and Joseph W. Lyding[1,3]

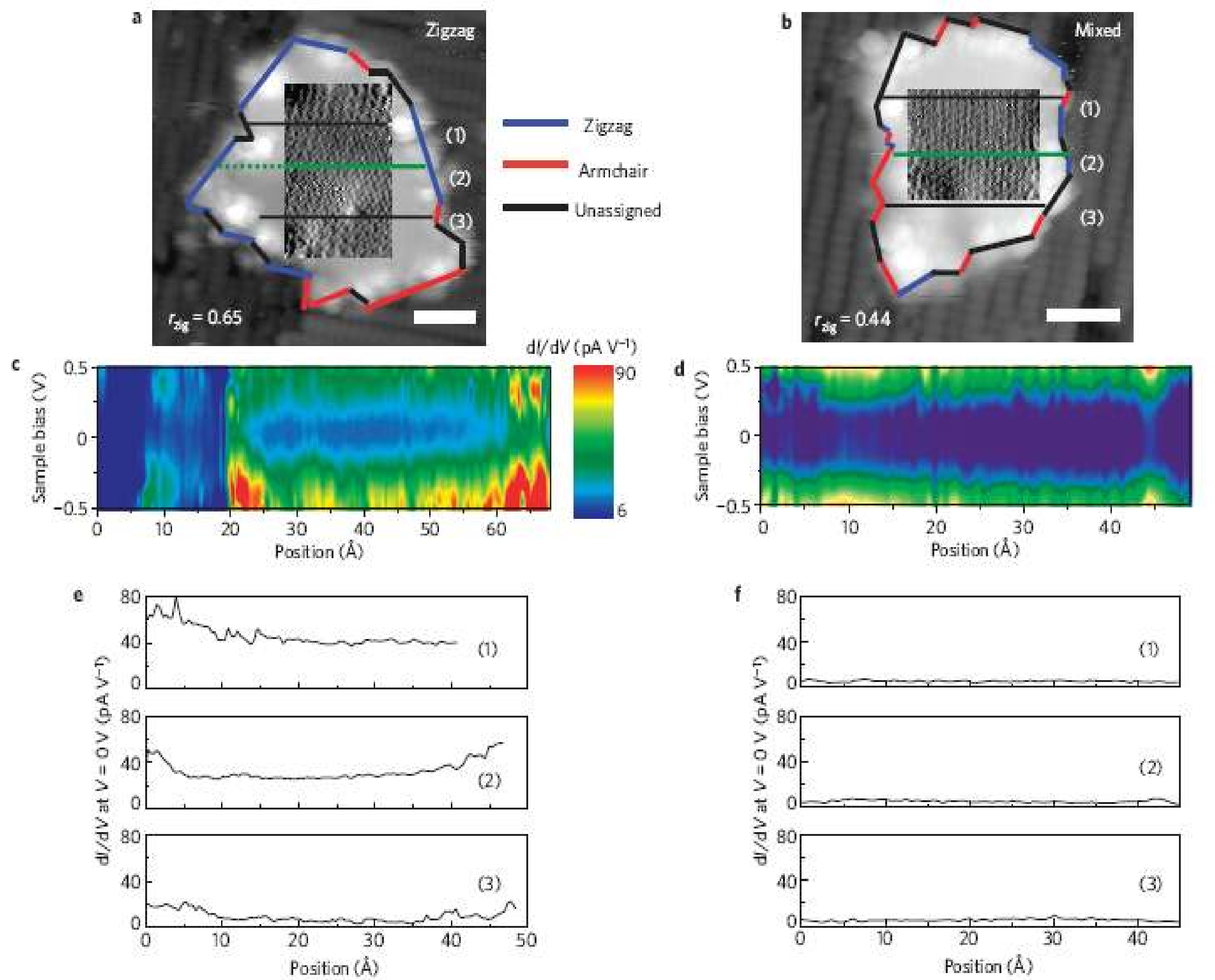


Figure 4 | Comparison of a zigzag- and mixed-edge GQD using spatially resolved tunnelling spectroscopy. a, Predominantly zigzag-edge GQD from the E_g–L plot in Fig. 2, which exhibits metallic character. The fraction of zigzag edges (r_{zig}) is 0.65. **b**, STM topograph of a 5 nm GQD with a mixture of both zigzag and armchair edges (r_{zig} = 0.44). Although zigzag edges are present, they are shorter than the sample in **a**. **c**, $dI/dV - V$ spectra, obtained with 0.42 Å spatial resolution, plotted as a function of position across the green line in **a**. **d**, $dI/dV - V$ spectra, obtained with 0.60 Å spatial resolution, plotted as a function of position across the green line in **b**. **e**, Constant voltage, dI/dV versus position contours corresponding with the three numbered lines in **a**. In general, we observe an increase in the differential conductance at the edges oriented along the zigzag direction. The spatial decay of the zigzag edge states into the graphene interior prevents the observation of the expected 0.15 eV energy gap for this ≈8 nm sample. Line (2) is plotted along the solid green line in **a** and does not include the dotted green line, which delineates the low conductance region at the left edge of the spectra map in **c**. **f**, Constant voltage, dI/dV versus position contours recorded along the three lines in **b**. In contrast to the zigzag GQD, the differential conductivity does not increase near the edges of the mixed-edge GQD and the magnitude of the differential conductivity is substantially lower than the zigzag GQD. The scale bars in **a** and **b** represent 2 nm. STS setpoint: −2 V, 0.1 nA.

Characterization

nature materials
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PUBLISHED ONLINE: 8 FEBRUARY 2009 | DOI: 10.1038/NMAT2382

Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide

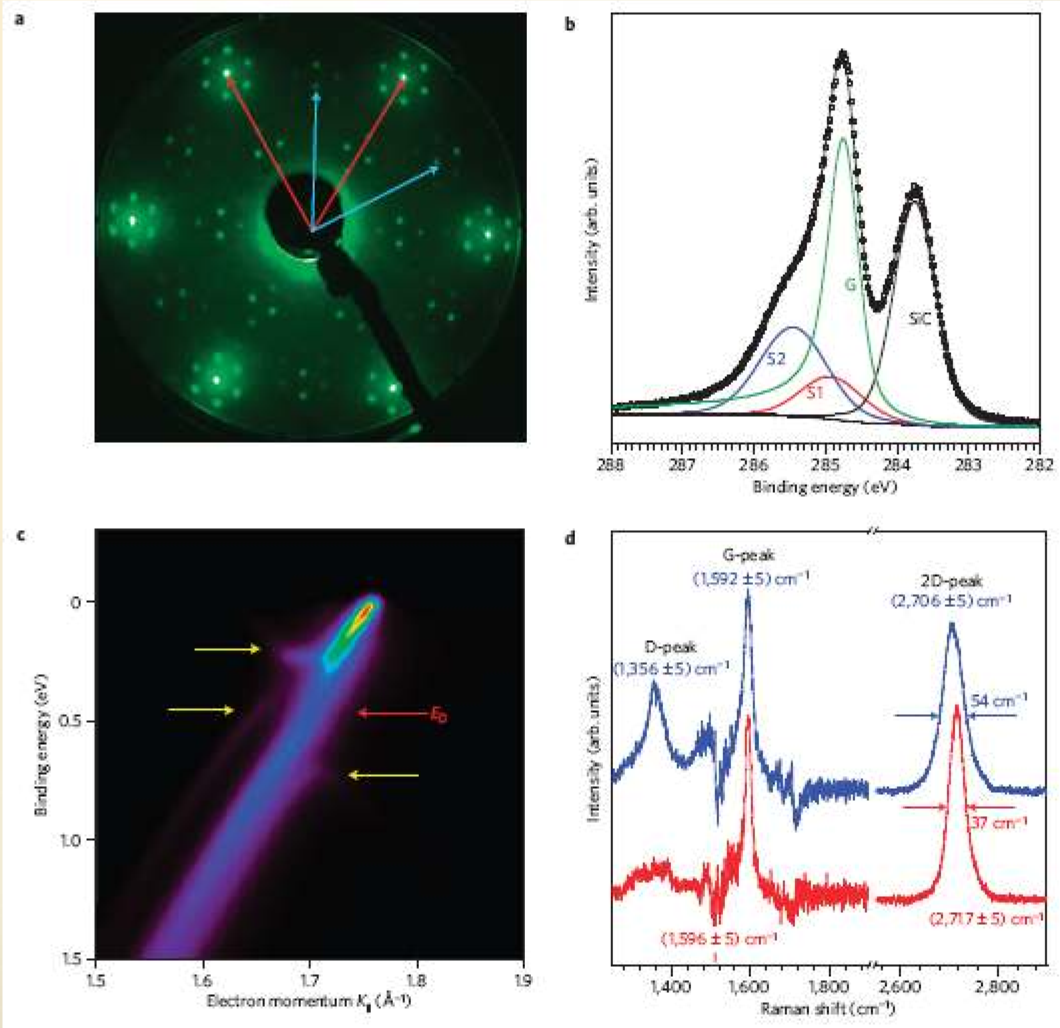
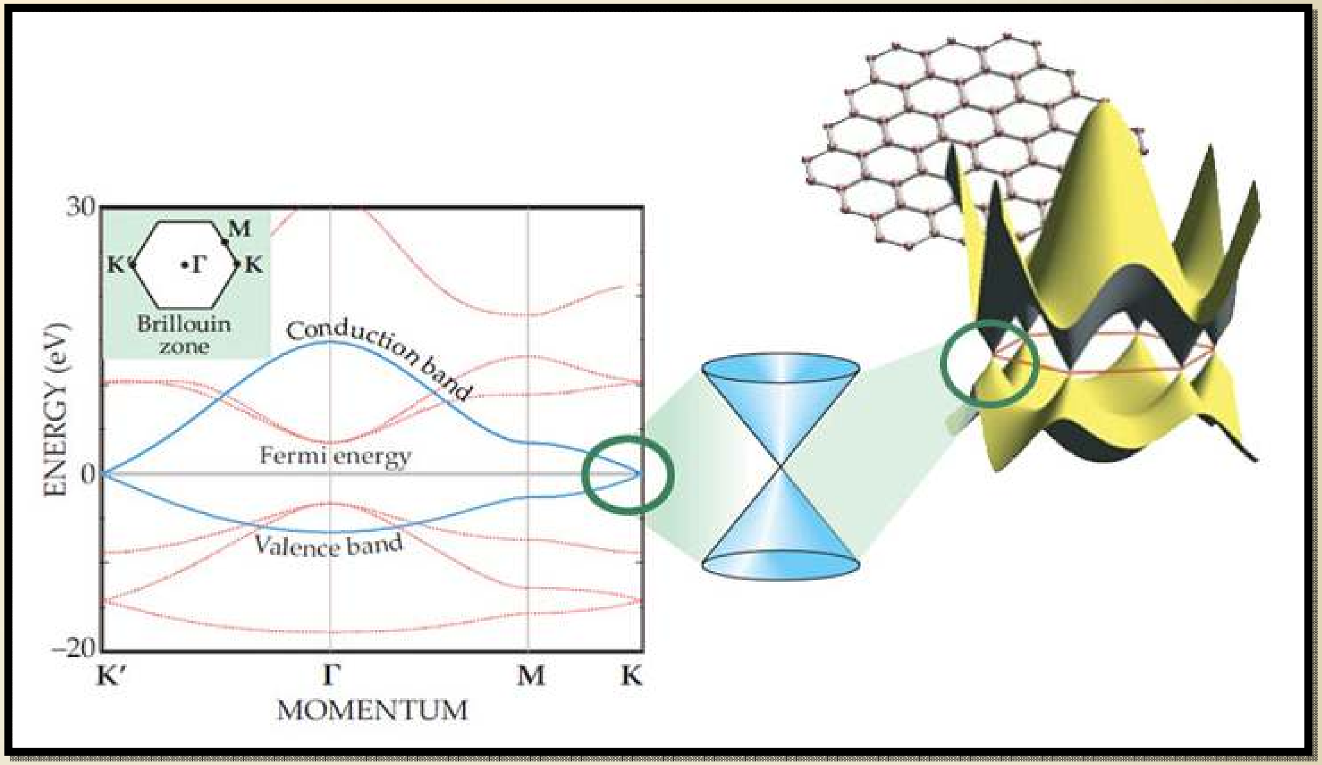


Figure 2 | Atomic and electronic structure of *ex-situ*-grown monolayer graphene. a, LEED pattern at 74 eV showing the diffraction spots due to the SiC(0001) substrate (blue arrows) and the graphene lattice (red arrows). The extra spots are due to the $(6\sqrt{3} \times 6\sqrt{3})$ interface layer. **b**, C1s core-level spectrum measured at a photon energy of 700 eV. The spectrum contains contributions from the SiC substrate (marked SiC), the $(6\sqrt{3} \times 6\sqrt{3})$ interface layer (marked S1 and S2) and from the graphene layer (G) residing on top of the interface layer. **c**, π-bands probed by ARPES in the vicinity of the K-point of the hexagonal Brillouin zone measured along the Γ K-direction. The position of the Dirac energy (E_D) at 0.45 eV below the Fermi energy is consistent with previous reports on UHV-grown graphene on SiC(0001). Faint features marked by yellow arrows signal the presence of small regions of bilayer graphene in agreement with the LEEM results. **d**, Comparison of Raman spectra of Ar-grown (red) and UHV-grown (blue) epitaxial graphene on 6H-SiC(0001). The spectra of the D- and G-line shown here are corrected for the emission of the substrate by subtraction of a reference spectrum[26] (see Supplementary Information).

Properties at room temperature



Graphene is a semi-metal or zero-gap semiconductor.

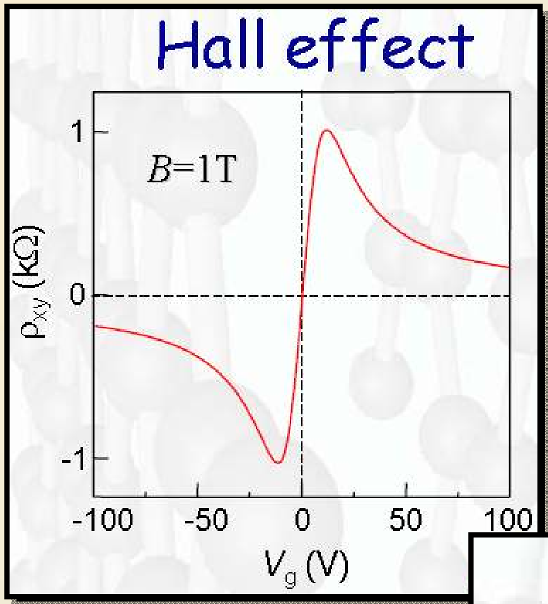
Its linear behavior at E<1ev near the six carbon sites of the Brillouin Zone is very special.

At these particular points (Dirac points) the charge carriers behave like relativistic particles.

They are massless Dirac fermions (1/300 of the speed of light).

Electric transport at room temperature

At the ambient, Ballistic transport at submicron scale

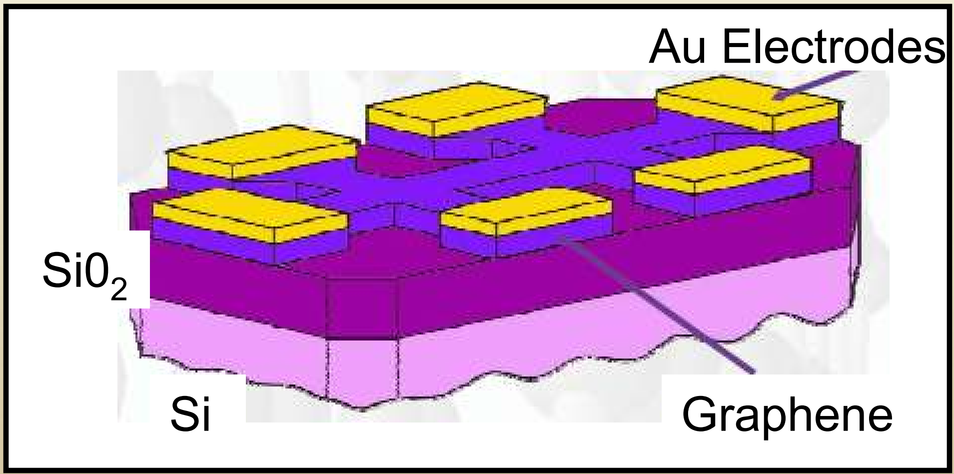


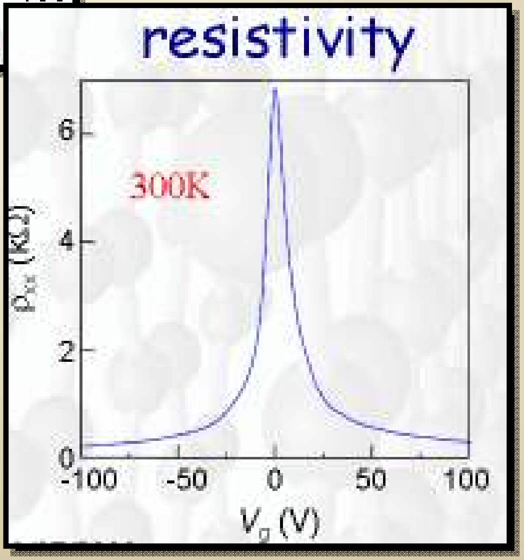
FOR FREE STANDING Graphene:

-mobility is nearly independent of temperature between 10 K and 100 K

-mobility = 200,000 $cm^2V^{-1}s^{-1}$ at a carrier density of 10^{12} cm^{-2}

-Resistivity : 10^{-6} $\Omega\cdot cm$





Electric Field Effect – Quantum Hall effect

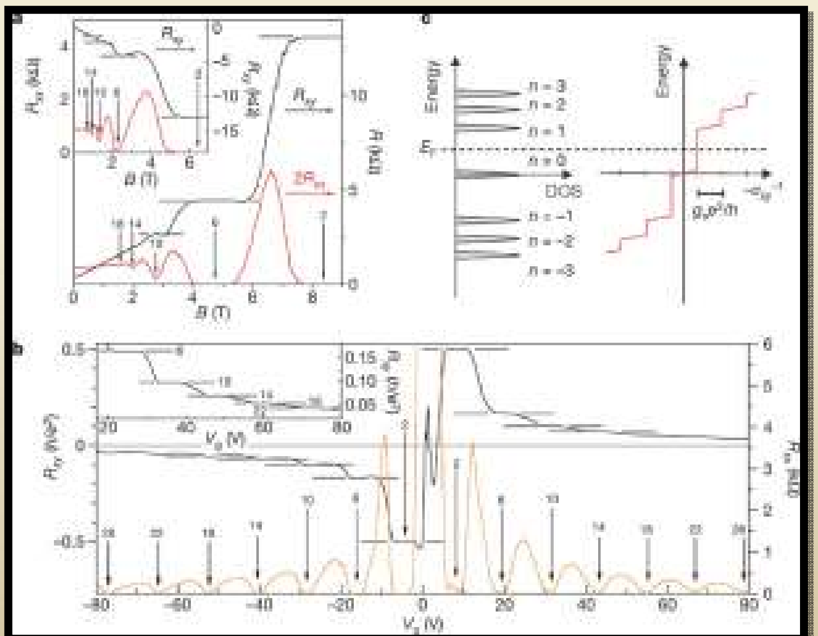
$$\sigma = \nu \frac{e^2}{h},$$

Hall conductivity

"filling factor"

Quantum Hall Effect requires to work at sufficiently strong B-fields.
In such a case, Landau levels $E_n = \hbar\omega_c(n + 1/2)$
Are highly degenerated. As a consequence the free electrons of the system occupy only a few number of energy levels.

It can be measured at room temperature !!!



Vol 438|10 November 2005|doi:10.1038/nature04235 **nature**

LETTERS

Experimental observation of the quantum Hall effect and Berry's phase in graphene

Yuanbo Zhang[1], Yan-Wen Tan[1], Horst L. Stormer[1,2] & Philip Kim[1]

Figure 2 | Quantized magnetoresistance and Hall resistance of a graphene device. a, Hall resistance (black) and magnetoresistance (red) measured in the device in Fig. 1 at $T = 30$ mK and $V_g = 15$ V. The vertical arrows and the numbers on them indicate the values of B and the corresponding filling factor ν of the quantum Hall states. The horizontal lines correspond to $h/e^2\nu$ values. The QHE in the electron gas is shown by at least two quantized plateaux in R_{xy}, with vanishing R_{xx} in the corresponding magnetic field regime. The inset shows the QHE for a hole gas at $V_g = -4$ V, measured at 1.6 K. The quantized plateau for filling factor $\nu = 2$ is well defined, and the second and third plateaux with $\nu = 6$ and $\nu = 10$ are also resolved. b, Hall resistance (black) and magnetoresistance (orange) as a function of gate voltage at fixed magnetic field $B = 9$ T, measured at 1.6 K. The same convention as in a is used here. The upper inset shows a detailed view of high-filling-factor plateaux measured at 30 mK. c, A schematic diagram of the Landau level density of states (DOS) and corresponding quantum Hall conductance (σ_{xy}) as a function of energy. Note that, in the quantum Hall states, $\sigma_{xy} = -R_{xy}^{-1}$. The LL index n is shown next to the DOS peak. In our experiment the Fermi energy E_F can be adjusted by the gate voltage, and R_{xy}^{-1} changes by an amount $g_s e^2/h$ as E_F crosses a LL.

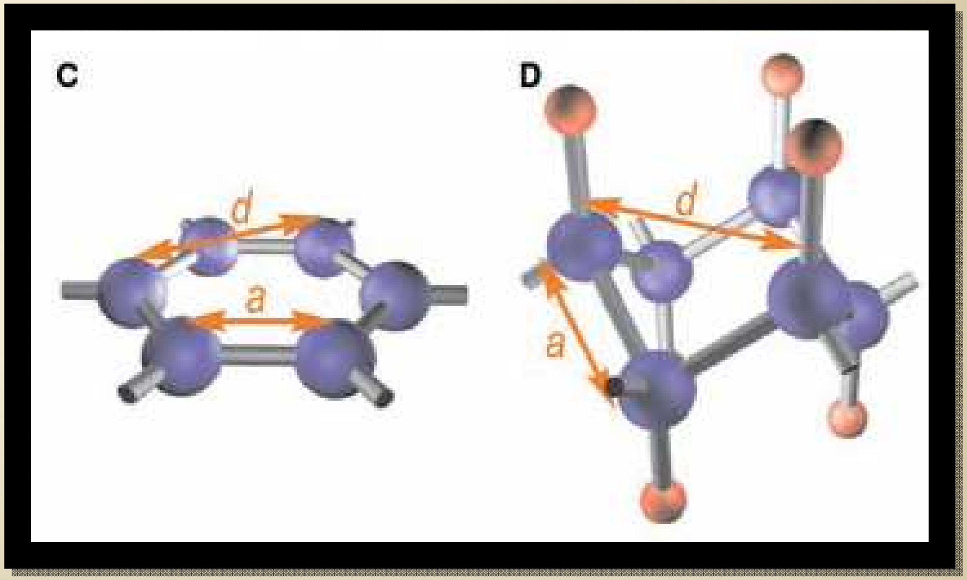
Brief Overview of the Current Research

- Graphene oxide

Tunable electrical conductivity and optical transparency with the level of oxidation

Appications: sensors, membrane based NEMS devices, transparent conductors for optoelectronic new materials

- Graphane



Courtesy *Nature Magazines* 2009

- Spintronics
- Novel materials
- Transistors…

Important names in the current research

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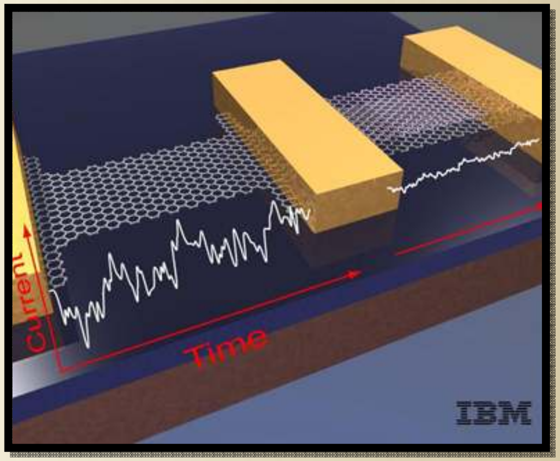

P. Kim

Associate Professor of Physics at Columbia University – Quantum thermal and electrical transport processes in nanoscale materials.

K. Novoselov

Royal Society Research Fellow in School of Physics & Astronomy at
the University of Manchester