



# Graphene: the Route from Touch Screens to Digital Nanoelectronics

**László Péter Biró**

*Research Institute for Technical  
Physics & Materials Science,  
Budapest, Hungary*

<http://www.nanotechnology.hu/>

# Human History (may be) regarded from the point of view of materials science

- From the Stone Age the development of civilization was made possible by the discovery of new materials and new ways of modifying materials
  - Stone Age (Paleolithic, Neolithic)
  - Bronze Age
  - Iron Age
  - .....
  - Steel Age (end of XIX., first half of XX. cent.)
  - Silicon Age ( IC, PC, mobile phone, etc. end of XX. century, beginning of XXI. century)
  - (**NANO**)CARBON Age?



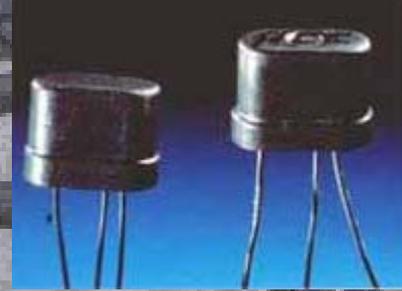
# Electronic history



Electronic tube  
1920



First transistor  
1947



First commercial transistor 1950



Integrated circuit  
1990



Piece of furniture



Portable



Smart & pocket size

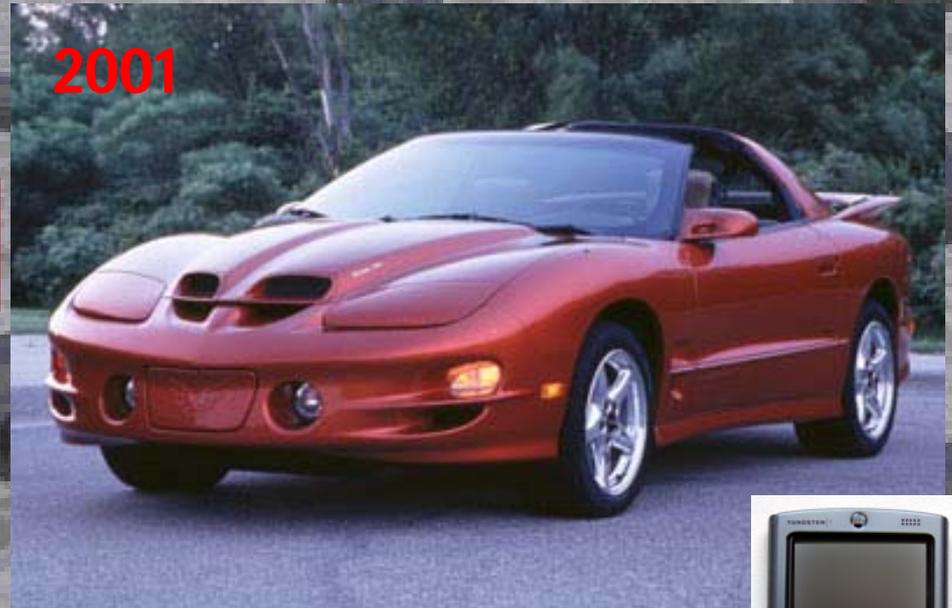
# Technical (r)evolution induced by materials & effects on everyday life

The first car was in fact a chaise without horses ....



1886

Steel



2001



1946

Silicon

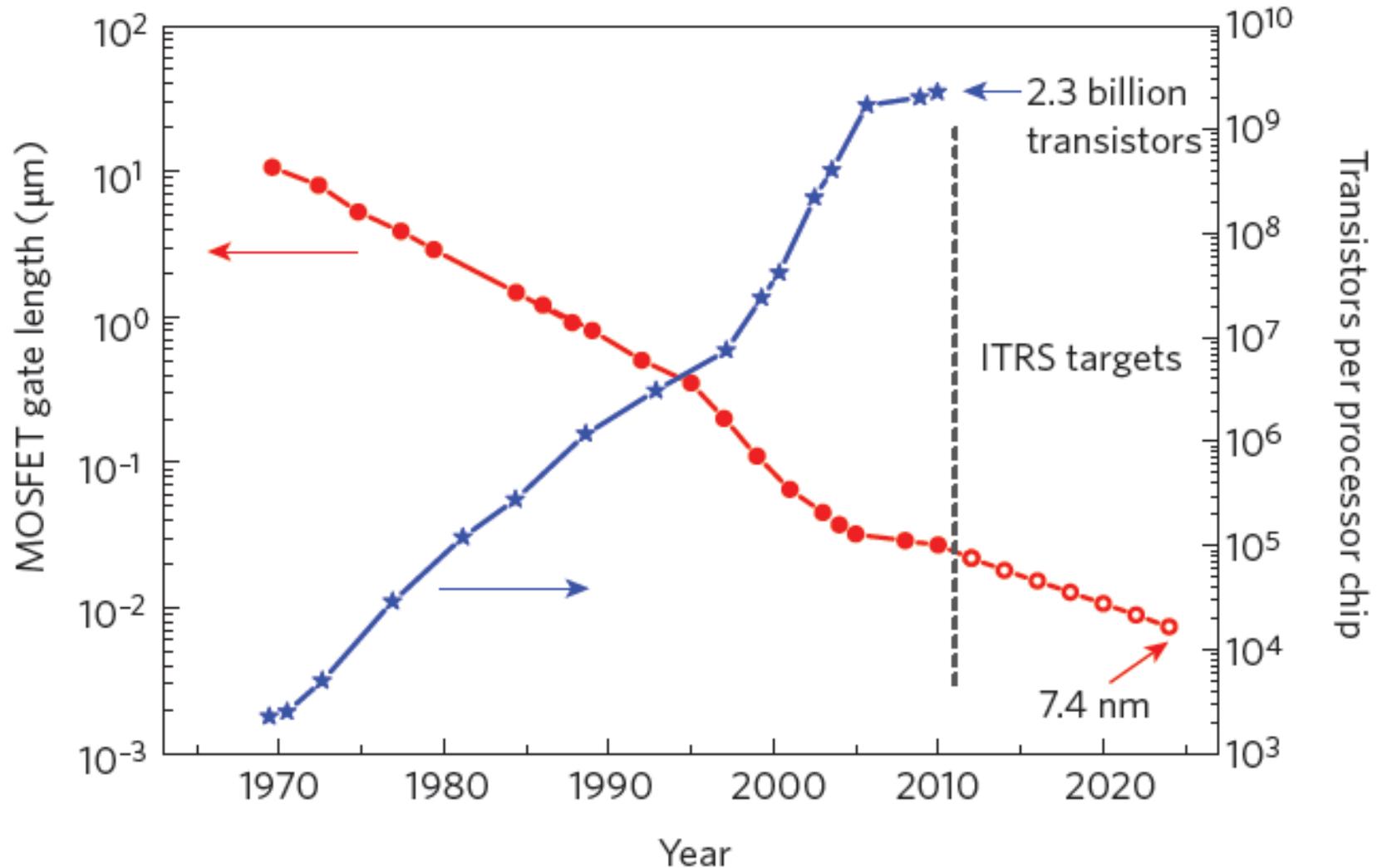
2002



ENIAC, 20.000 electronic tubes ...

# Trends in digital electronics

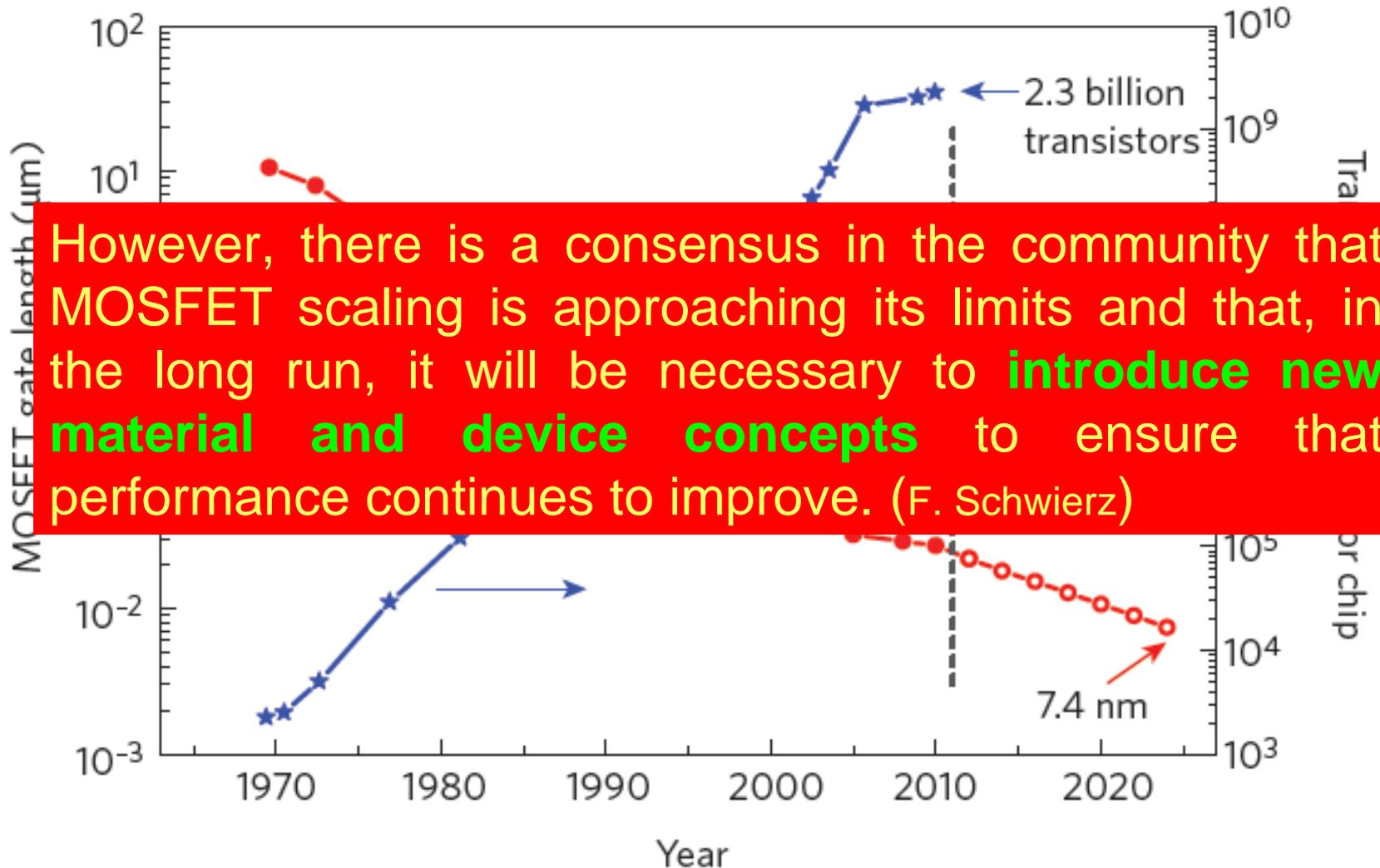
F. Schwierz, Nat. Nanotech. Published online: 30 May 2010  
doi: 10.1038/nnano.2010.89



# Trends in digital electronics

F. Schwierz, Nat. Nanotech. Published online: 30 May 2010

doi: 10.1038/nnano.2010.89



# End of the ROAD(map)

The International Technology Roadmap for Semiconductors<sup>1</sup> (ITRS), which is sponsored by the five leading chip manufacturing regions in the world (Europe, Japan, Korea, Taiwan, and the United States), and has the objective of ensuring cost-effective advancements in the performance of the integrated circuit, has clearly identified an end-of-life for scaled complementary metal–oxide–semiconductor (CMOS) technology around 2022. The causes for the demise of silicon-based

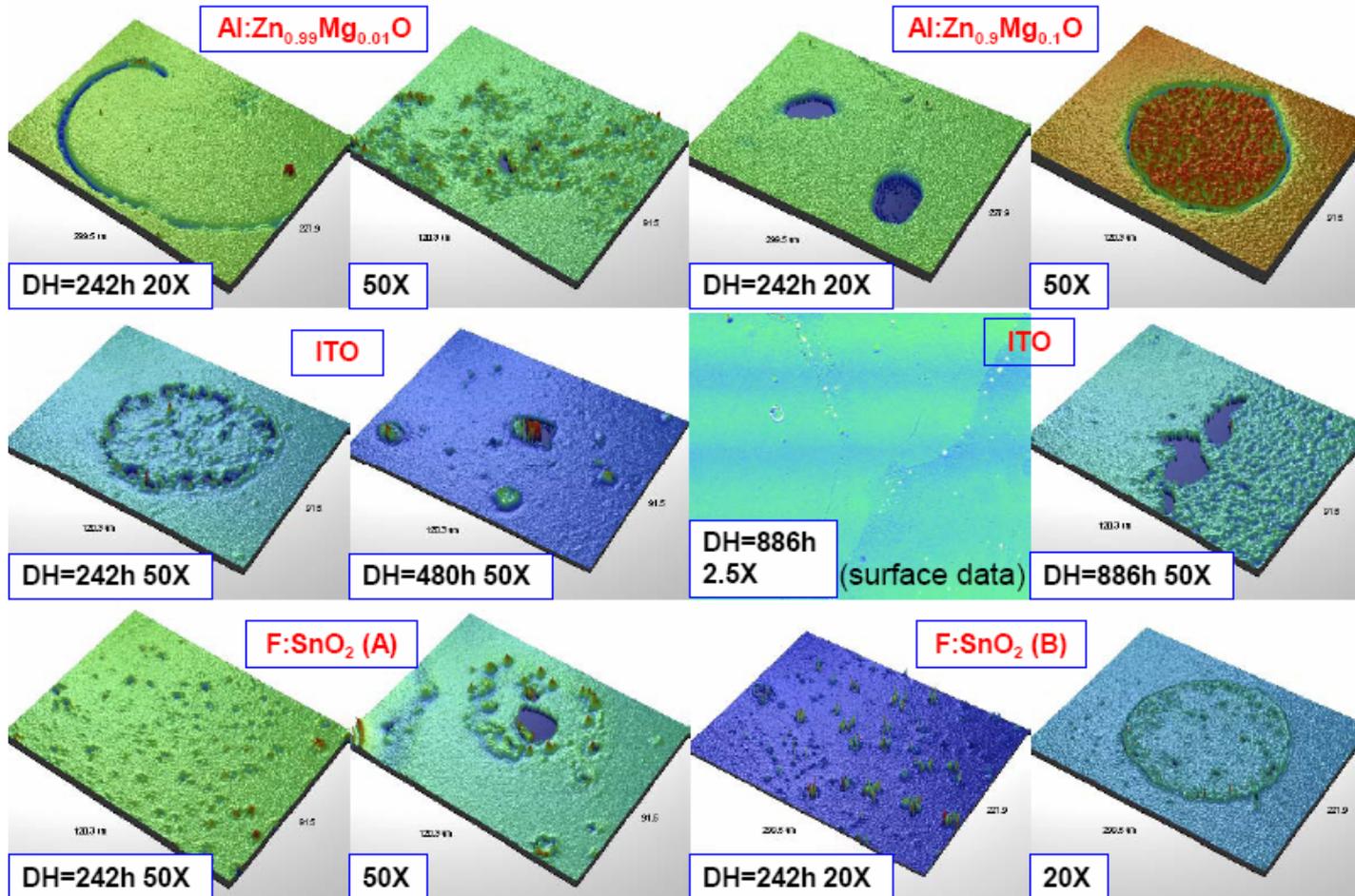


International Technology Roadmap for Semiconductors

<http://www.itrs.net/>

**(NANO)CARBON?**

# Stability Issues of Transparent Conducting Oxides (TCOs) for Thin-Film Photovoltaics



**Indium**  
is  
becoming  
a  
„problem”  
material

From:  
Prof. J.  
Pern,  
NREL

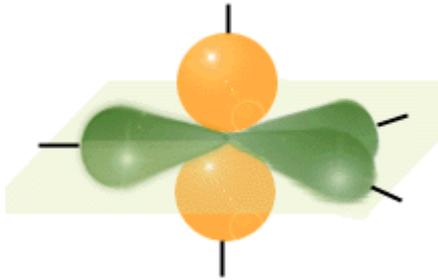
# Graphene vs. Si

- Charge carrier mobility
  - 200.000 cm<sup>2</sup>/Vs (Si: 1400 cm<sup>2</sup>/Vs)
- Charge carrier density
  - $3 \times 10^{12}$  cm<sup>-2</sup> (Si:  $1.3 \times 10^{10}$  cm<sup>-3</sup> intrinsic)
- Current density
  - $2.3 \times 10^9$  A/cm<sup>2</sup> (Si:  $3 \times 10^5$  A/cm<sup>2</sup> on transistor)
- Thermal conductivity
  - 5000 Wm<sup>-1</sup>K<sup>-1</sup> (Si: 163 Wm<sup>-1</sup>K<sup>-1</sup> at room temp.)
  - (heat dissipation on nanoscale is a serious issue!!!)

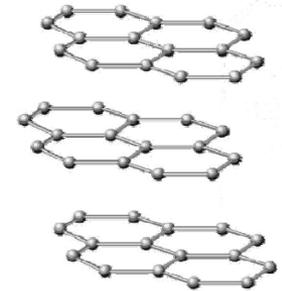
**Transparent & the strongest material known**

# Carbon before 1985

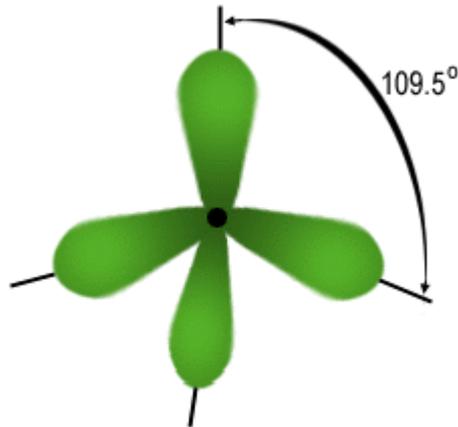
$sp^2$



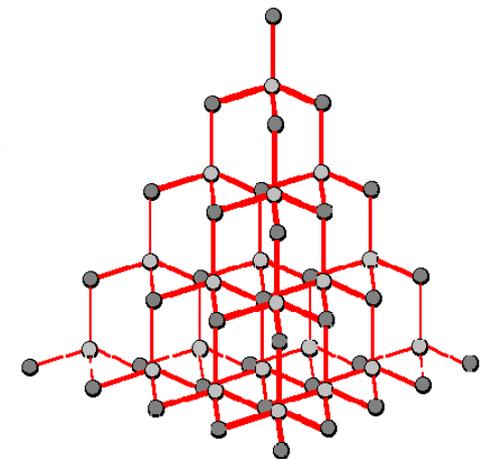
*Graphite*



$sp^3$



*Diamond*

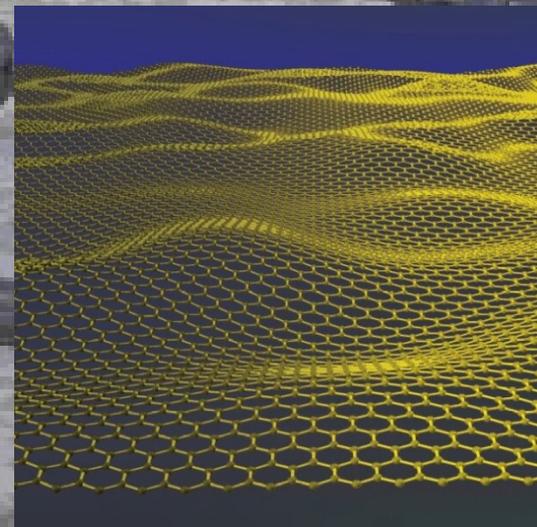
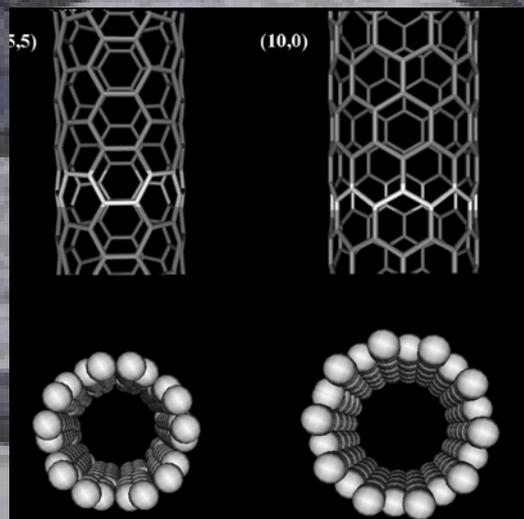
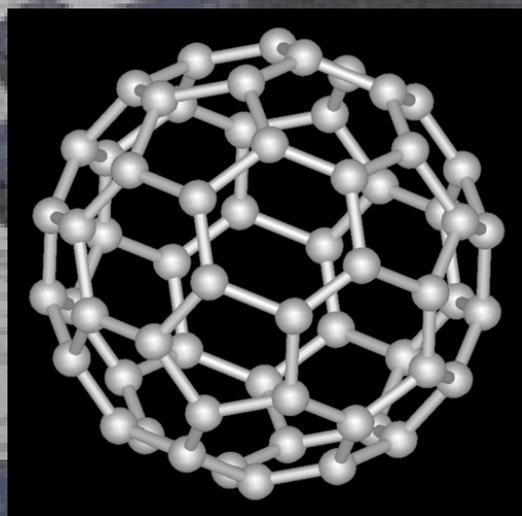


# The family of carbon nanostructures

Fullerene

Carbon nanotube

Graphene



**1985**

H.W.Kroto, R. Smalley &  
R. Curl

**1991**

S. Iijima

**2004**

K. S. Novoselov &  
A. Geim

Nobel Prize 1996

Kavli Prize 2008

Nobel Prize 2010

Graphene



Graphene nanostructures

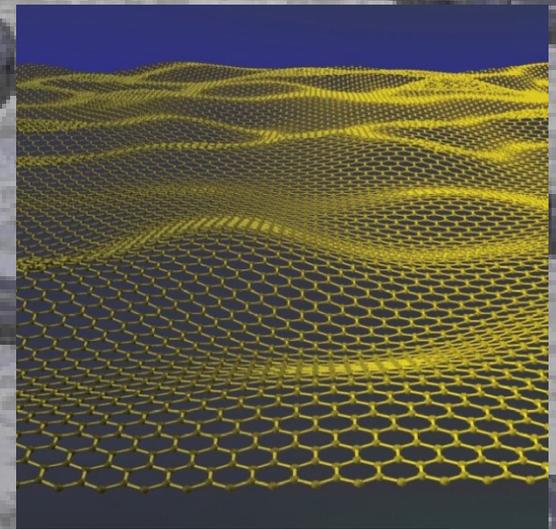


Andre Geim Kostya Novoselov

*“for groundbreaking experiments regarding the two-dimensional material graphene”*

Graphene

Graphene



2004

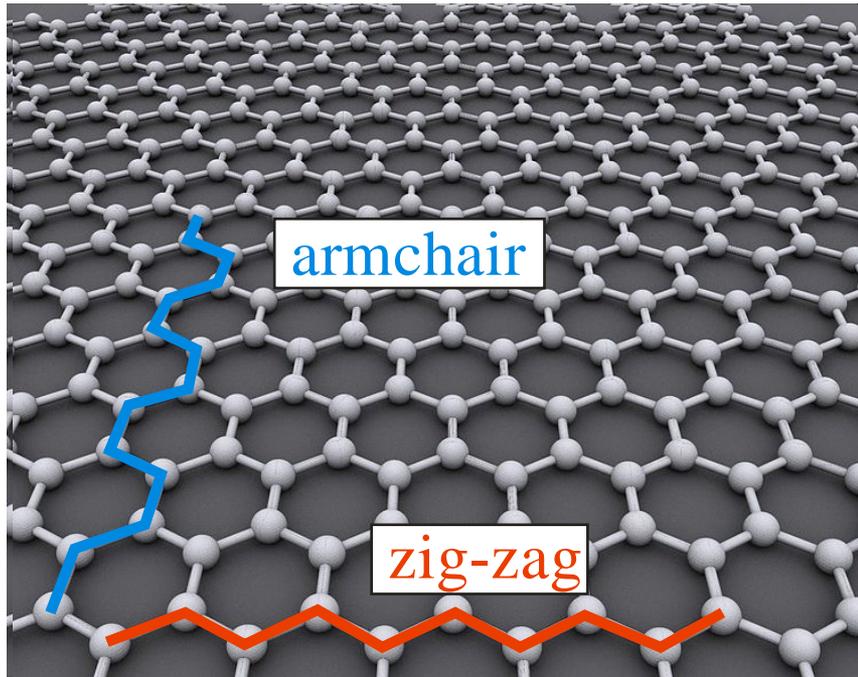


KUNGL.  
VETENSKAPS-  
AKADEMIEN

THE ROYAL SWEDISH ACADEMY OF SCIENCES

THE NOBEL PRIZE IN PHYSICS 2010

# Structure & Electronic structure



<http://en.wikipedia.org/wiki/File:Graphen.jpg>

Single layer graphene	Conventional 2D system
<p>(a) Graphene lattice and 1<sup>st</sup> BZ</p>	<p>(e) Quantum well</p>
<p>(b) Dirac equation</p> $H\Psi = E\Psi$ $H = v_F \mathbf{p} \cdot \boldsymbol{\sigma} \otimes \boldsymbol{\tau}_0$ $\Psi = (\Psi_{AK}, \Psi_{BK}, -\Psi_{BK}^*, \Psi_{AK}^*)$ $E = \hbar v_F (k_x^2 + k_y^2)^{1/2}$	<p>(f) Schrödinger equation</p> $\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(z) \right] \Psi = E\Psi$ $V(z) = \begin{cases} 0 & 0 \leq z \leq d \\ V_0 & \text{otherwise} \end{cases}$ $E = E_n + \frac{\hbar^2}{2m} (k_x^2 + k_y^2)$
<p>(c) Linear E-k dispersion near K (K')</p>	<p>(g) Parabolic sub-bands</p>
<p>(d) Vanished density of states at K (K')</p>	<p>(h) Step-like density of states</p>

Wu, Y. H.; Yu, T.; Shen, Z. X. *J. Appl. Phys.* **2010**, *108*, 071301.

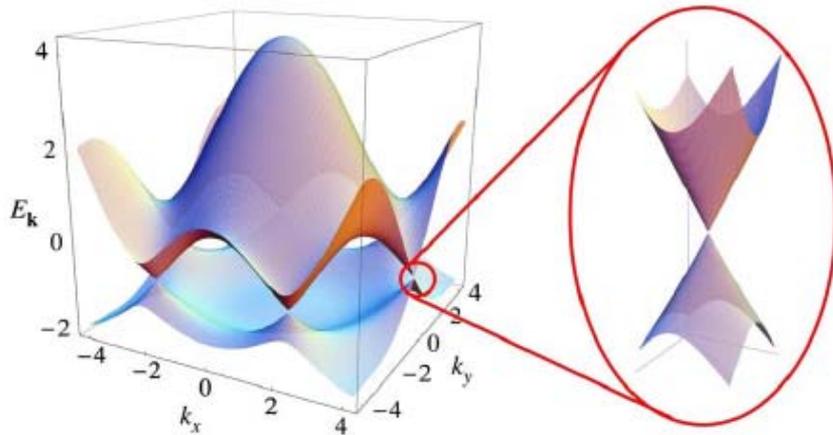
C-C bond shorter than in diamond!

The FIRST truly one single atom thick material!

Different properties along different crystallographic directions.

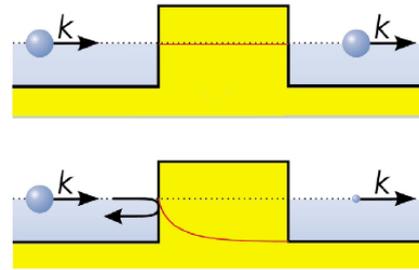
EXTRAORDINARY electronic structure!

# Linear dispersion & Klein tunneling



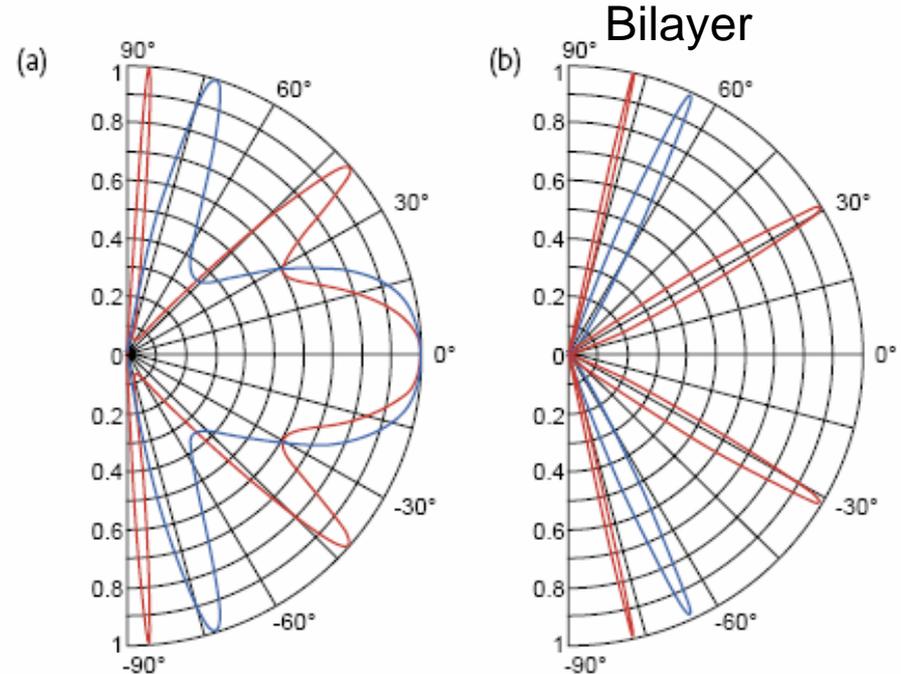
A. H. Castro Neto et al., *Rev. Mod. Phys.* **2009**, 81, 109-162

The charge carriers cannot be confined by electrostatic barriers like in conventional semiconductors



Graphene

Regular material

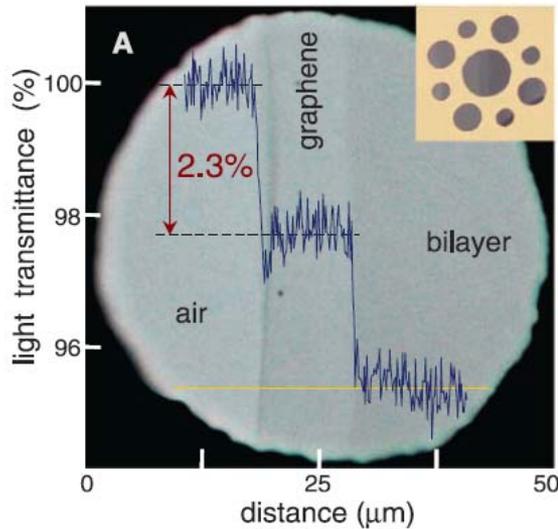


Katsnelson, M. *Materials Today* **2007**, 10, 20-27.

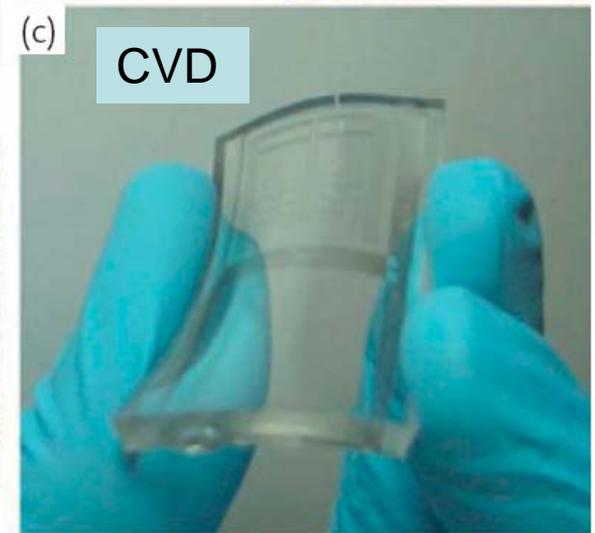
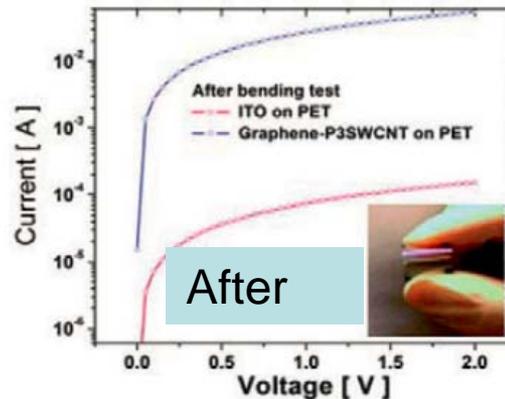
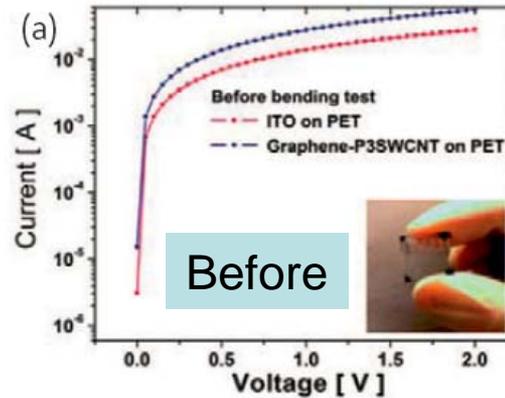
$$p = 1 \times 10^{12} \text{ cm}^{-2}$$

$$p = 3 \times 10^{12} \text{ cm}^{-2}$$

# Transparent & flexible material



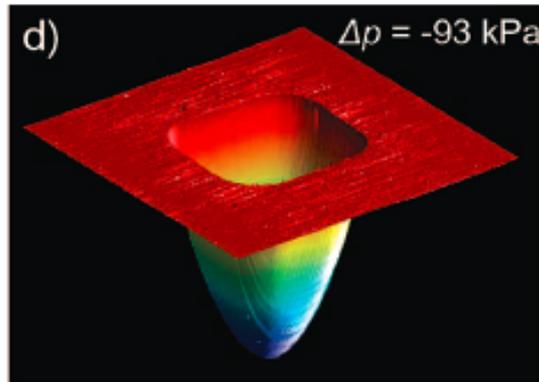
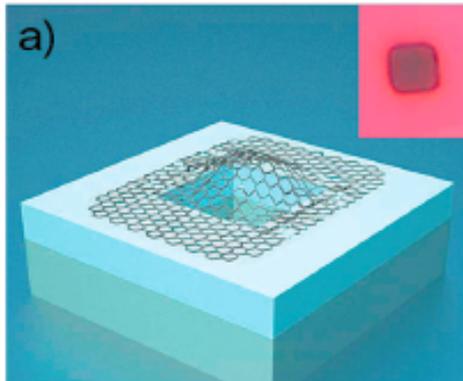
Nair, R. R. et al. *Science* **2008**, 320, 1308.



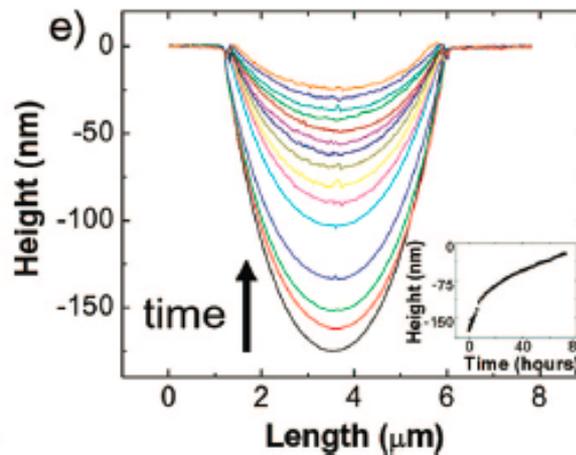
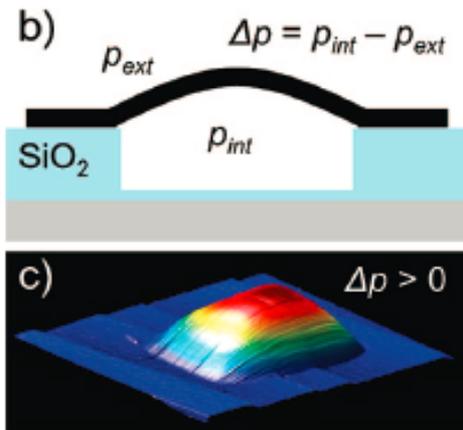
Bending graphene  
vs. ITO on PET

Wassei, J. K.; Kaner, R. B. *Materials Today* **2010**, 13, 52-59.

# Highly stretchable material, impermeable to gases



AFM image  $\Delta z =$   
175 nm



AFM linecuts in  
time (3 days!)

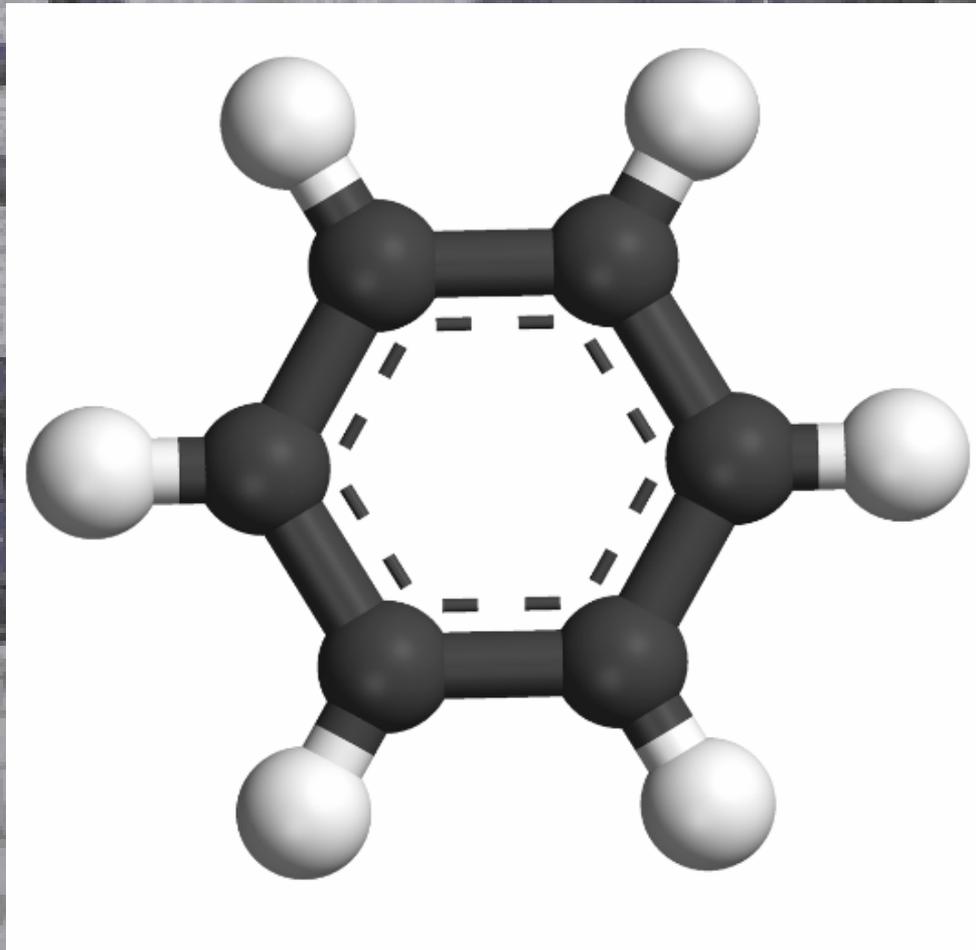
Bunch, J. S. et al, *Nano Lett.* 8 (2008) 2458 .

# Properties & Applications

Linear dispersion

High mobility

Unique optical properties



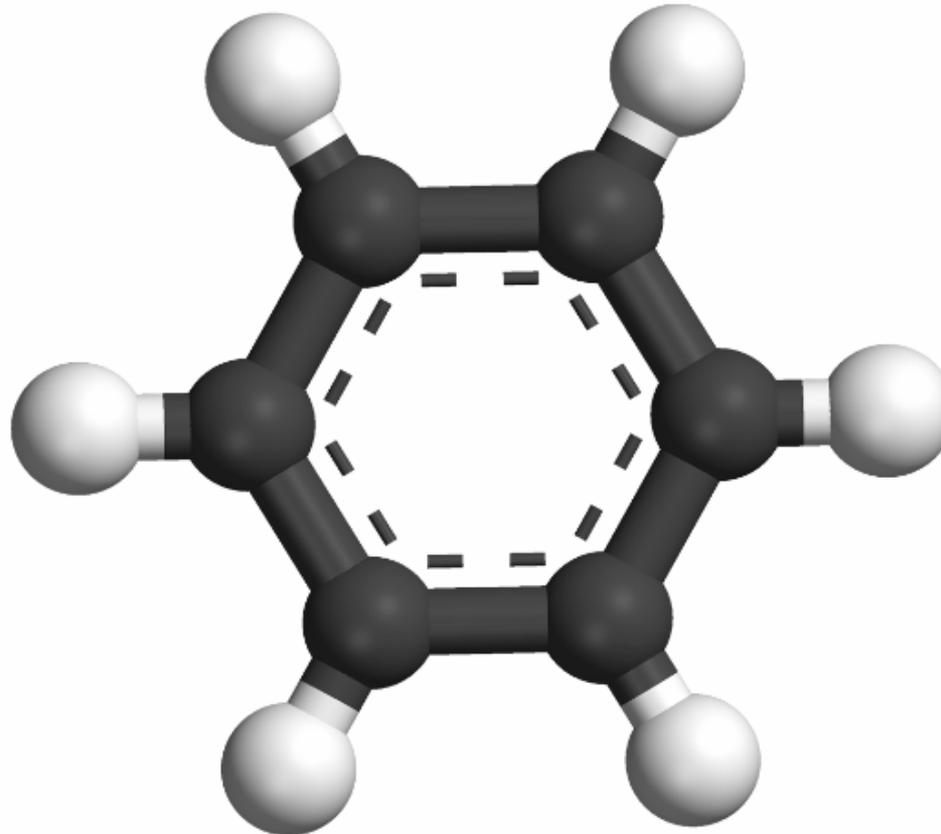
One atom thin

High strength

Highly stretchable

# Properties & Applications

## Quantum Hall Effect & Spintronics



Linear dispersion

Transistors

High mobility

Photovoltaics

Unique optical properties

Transparent & flexible conductors

One atom thin

Membranes, ultracapacitors

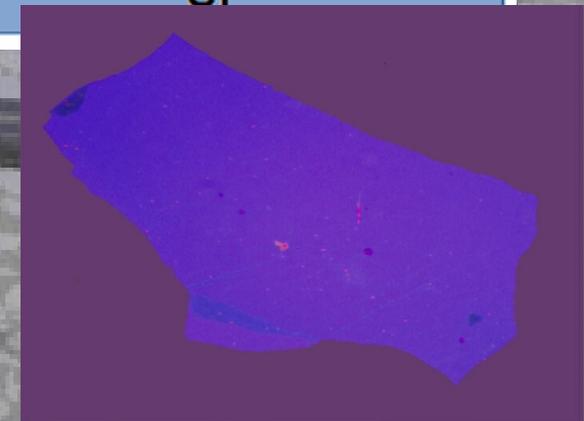
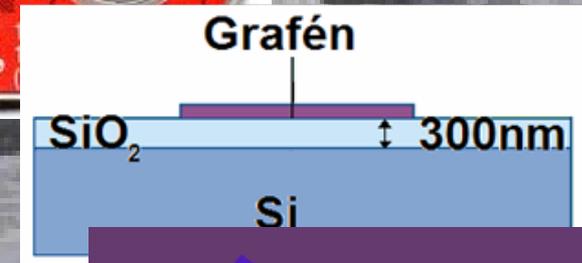
High strength

Composites

Highly stretchable

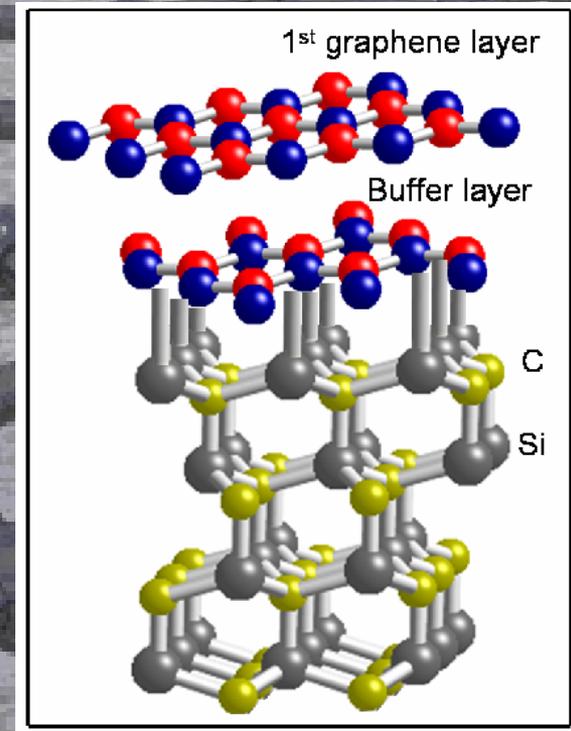
# Production of graphene

- Micromechanical cleavage 
- Epitaxy on SiC
- **CVD (Ni, Pt, Rh, Cu)**
- Chemical exfoliation (G-O, **oxigene removal!**)
- CNT „unzipping”
- and many other exotic methods ....



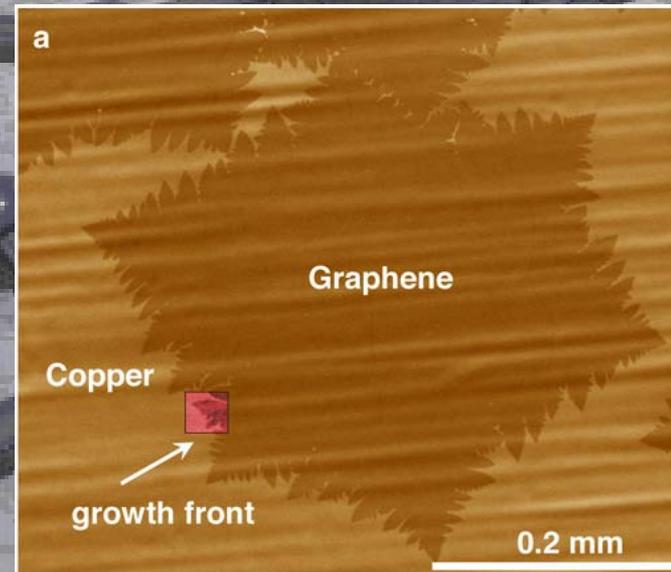
# Production of graphene

- Micromechanical cleavage 
- Epitaxy on SiC
- **CVD (Ni, Pt, Rh, Cu)**
- Chemical exfoliation (G-O, **oxigene removal!**)
- CNT „unzipping”
- and many other exotic methods ....



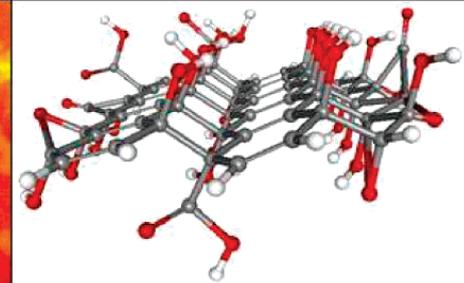
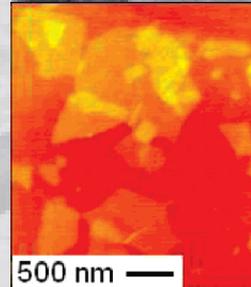
# Production of graphene

- Micromechanical cleavage 
- Epitaxy on SiC
- **CVD (Ni, Pt, Rh, Cu)**
- Chemical exfoliation (G-O, **oxigene removal!**)
- CNT „unzipping”
- and many other exotic methods ....



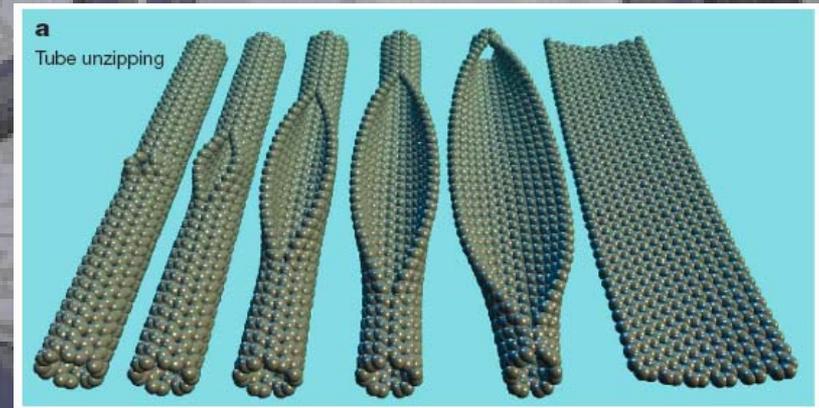
# Production of graphene

- Micromechanical cleavage 
- Epitaxy on SiC
- **CVD** (Ni, Pt, Rh, **Cu**)
- Chemical exfoliation (G-O, **oxigene removal!**)
- CNT „unzipping”
- and many other exotic methods ....

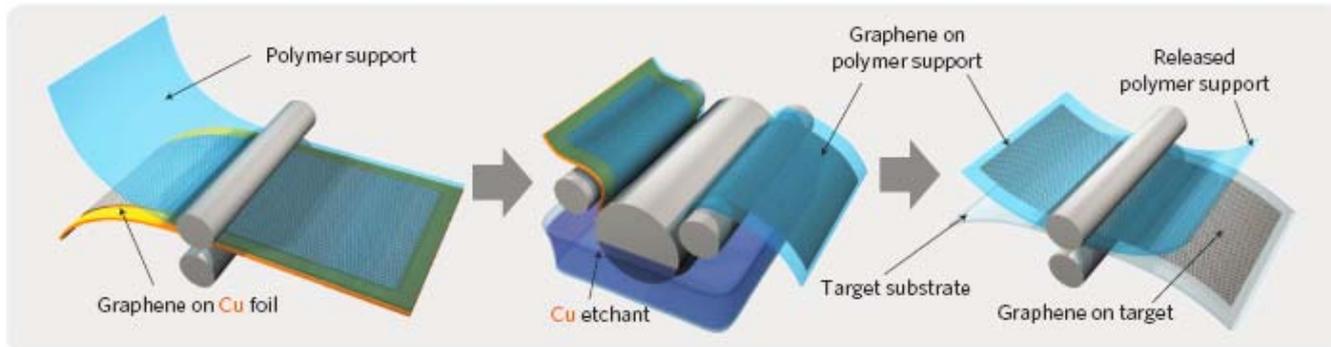


# Production of graphene

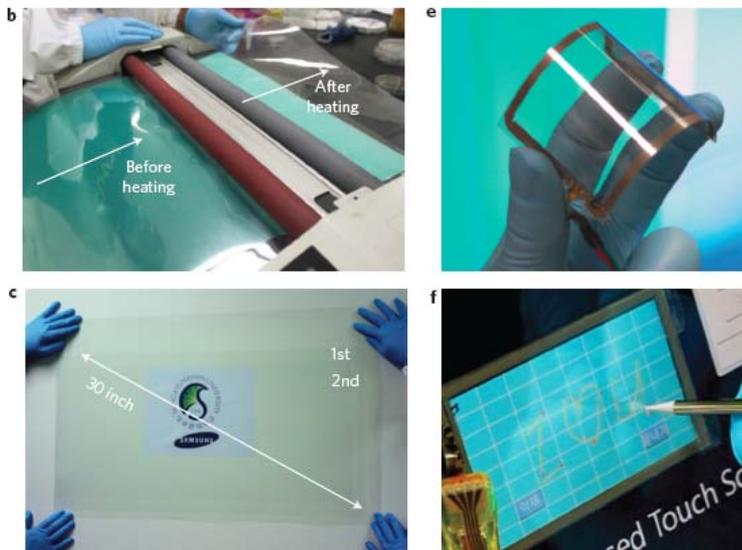
- Micromechanical cleavage 
- Epitaxy on SiC
- CVD (Ni, Pt, Rh, Cu)
- Chemical exfoliation (G-O, **oxigene removal!**)
- CNT „unzipping”
- and many other exotic methods ....



# „Roll-to-roll” large size CVD graphene



**Figure 1 | Schematic of the roll-based production of graphene films grown on a copper foil.** The process includes adhesion of polymer supports, copper etching (rinsing) and dry transfer-printing on a target substrate. A wet-chemical doping can be carried out using a set-up similar to that used for etching.

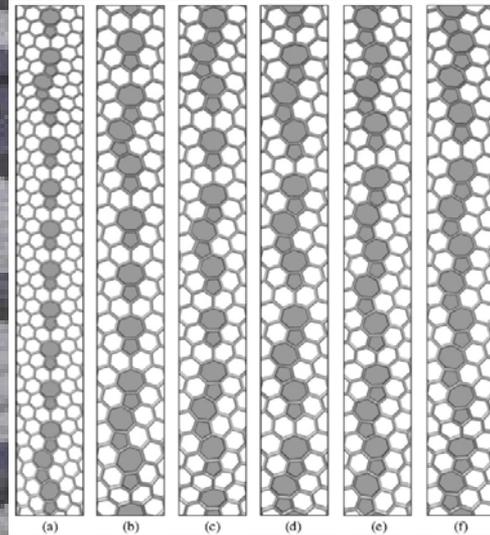


Bae, S. et al., *Nature Nanotechnology* **2010**, 5, 574 .

The quality of the material is well suited for transparent conducting & flexible electrodes => **market ready!**

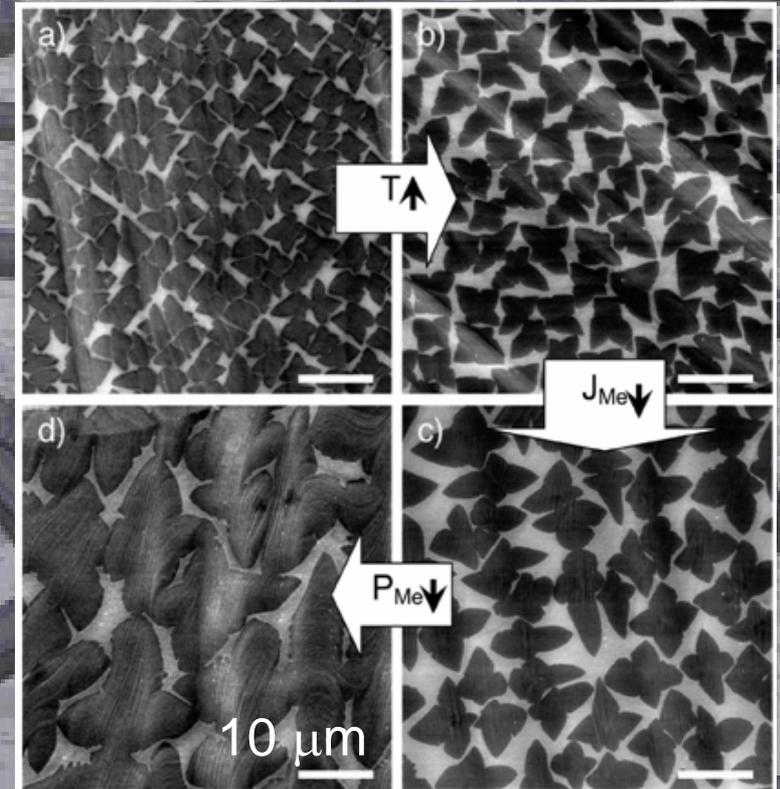
# Grain boundaries in CVD grown graphene

Liu, T.-H., et al.,  
*Carbon* **2011**, *49*,  
2306



The grain boundaries decrease the very high mobility values by 10 – 100 times.

The grain structure must be revealed for the optimization of the growth conditions.



Li, X. et al. *Nano Letters* **10** (2010) 4328.

Random nucleation =>  
many grain boundaries

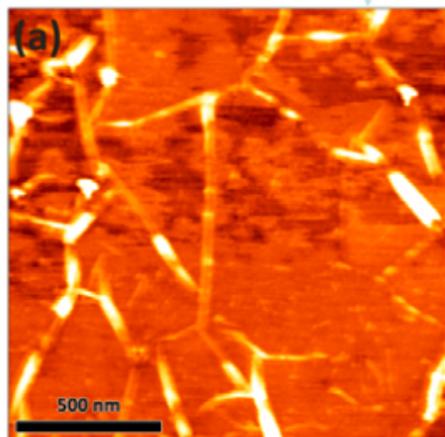
# Characterization of grain structure by AFM



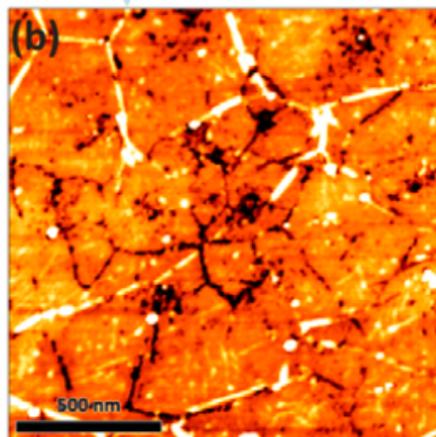
CVD graphene transferred to mica

Heat for 30 minutes at 500°C in air.

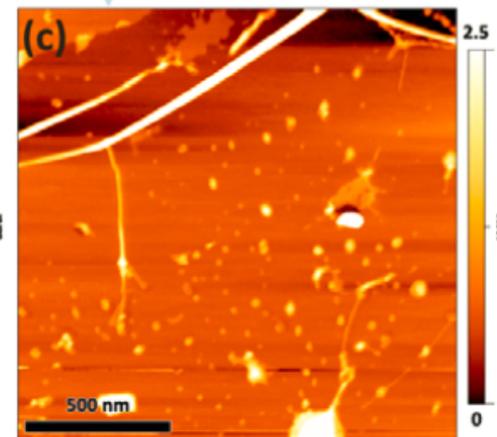
Graphene exfoliated onto mica



CVD graphene, after transfer



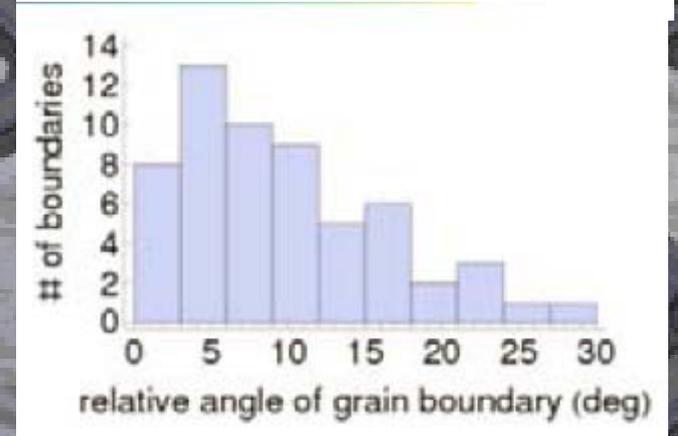
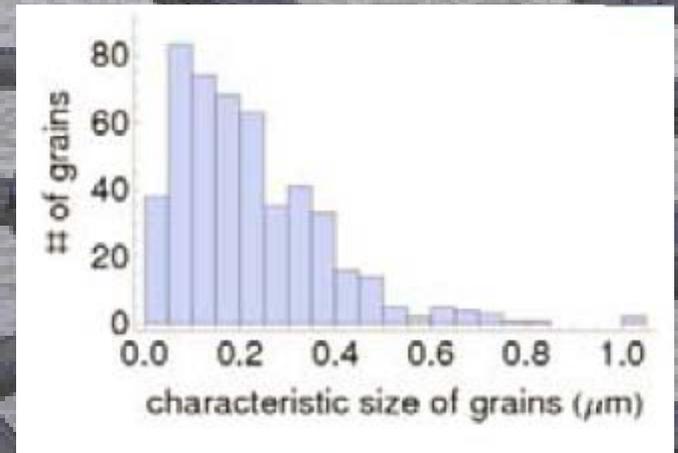
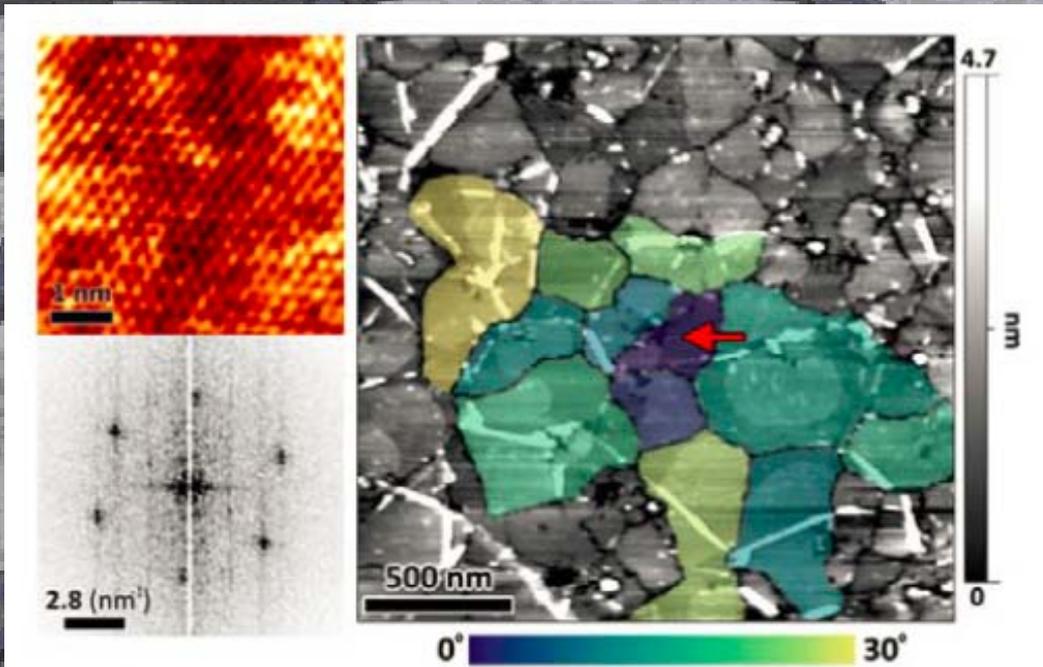
CVD graphene, after oxidation



Exfoliated graphene, after oxidation

1. STEP: Reveal the grain boundaries by selective oxidation (negative comparison exfoliated graphene)

# Characterization of grain structure by AFM



2. STEP: Analyze the grain size and the relative angle of grain boundaries by atomic resolution AFM images

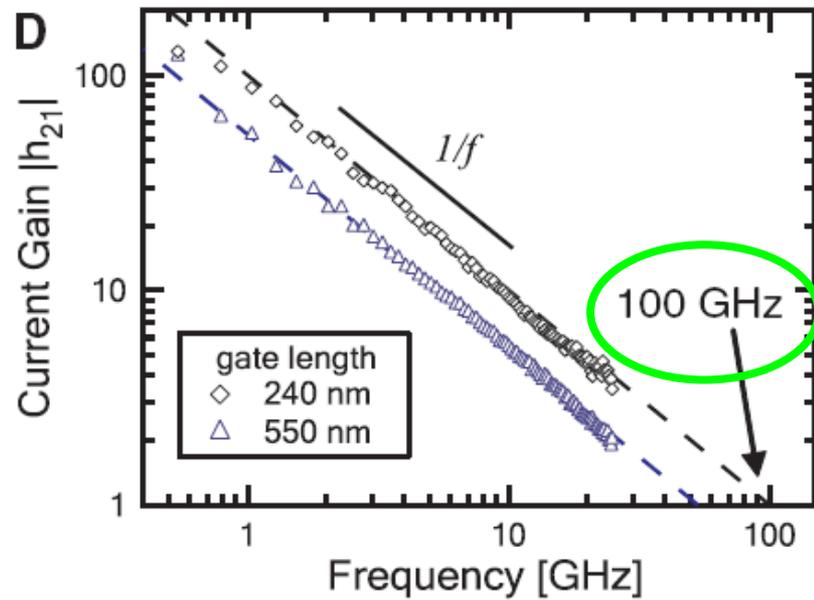
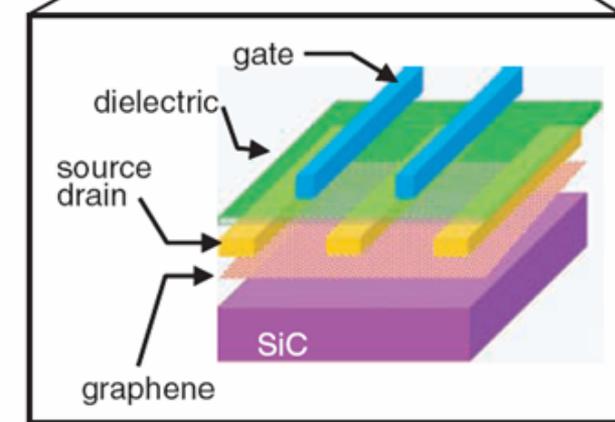
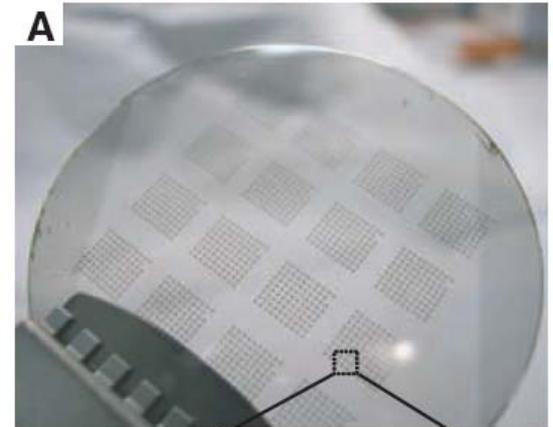
# Application in high speed nanoelectronics

## 100-GHz Transistors from Wafer-Scale Epitaxial Graphene

Y.-M. Lin,\* C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, Ph. Avouris\*

662

5 FEBRUARY 2010 VOL 327 SCIENCE



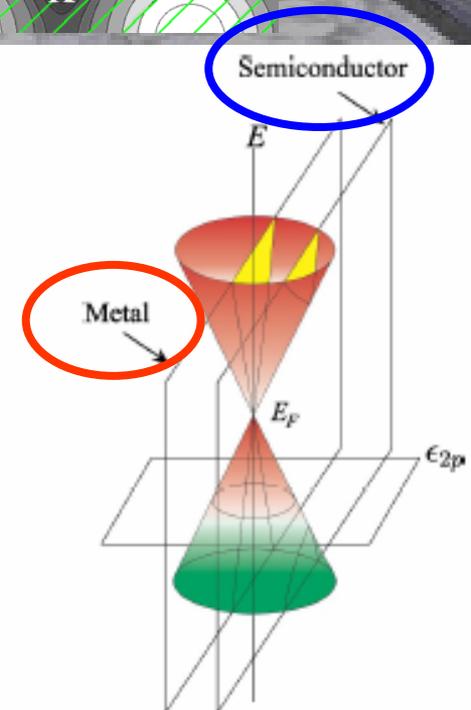
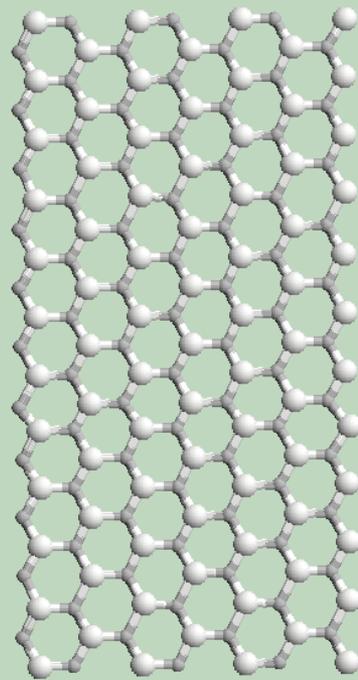
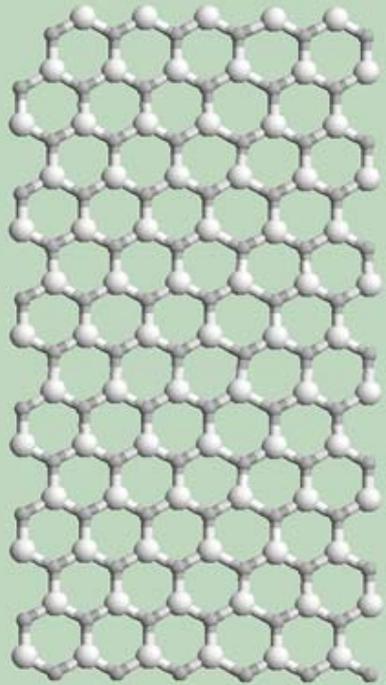
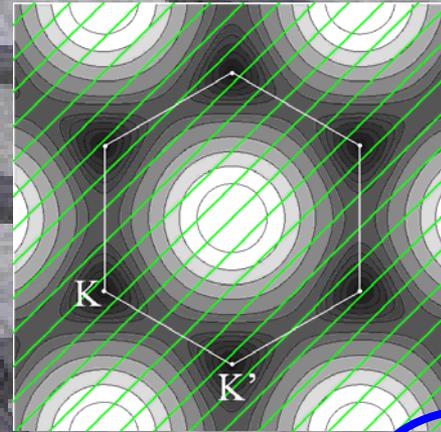
**NO** „switched off” state => **NO** DIGITAL applications

# The electronic structure has to be reengineered – Badgap induced by confinement

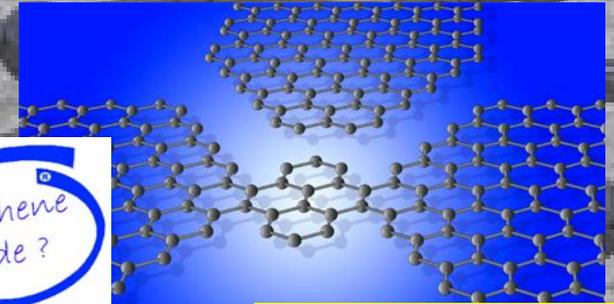
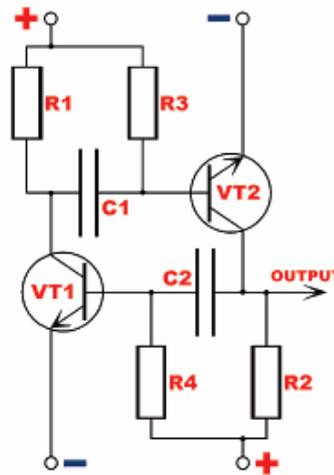
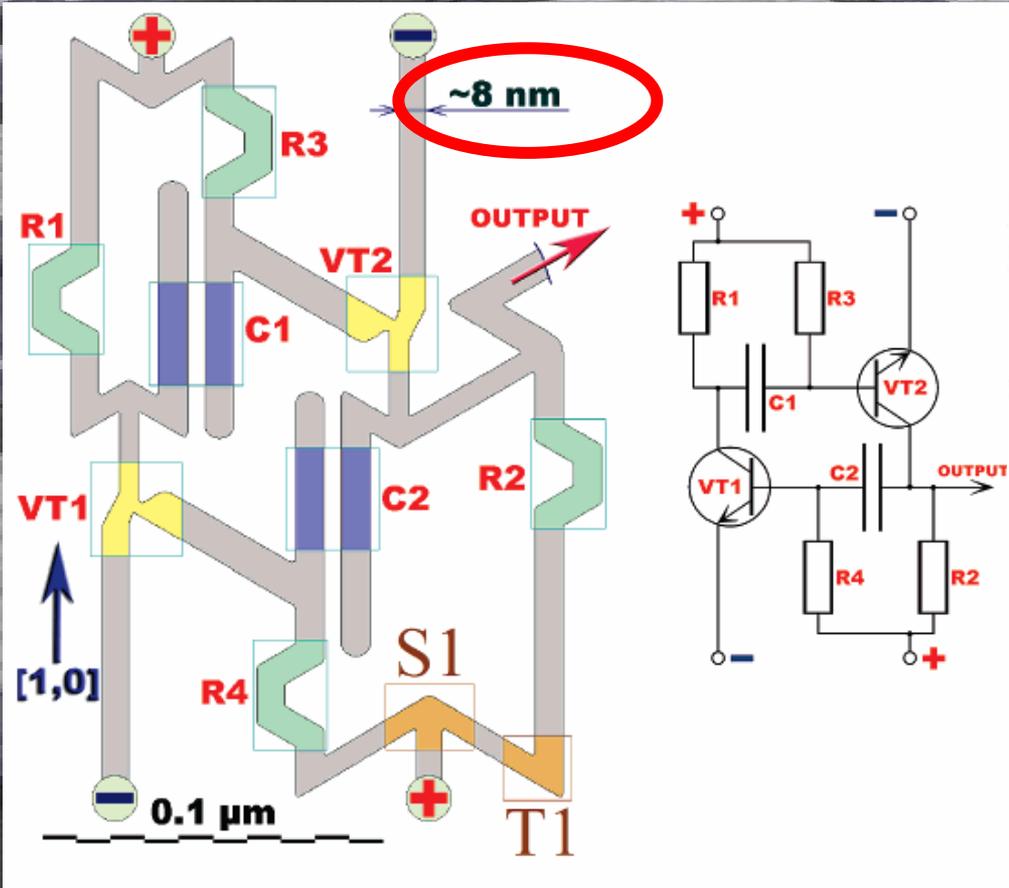
Graphene nanoribbons

Armchair

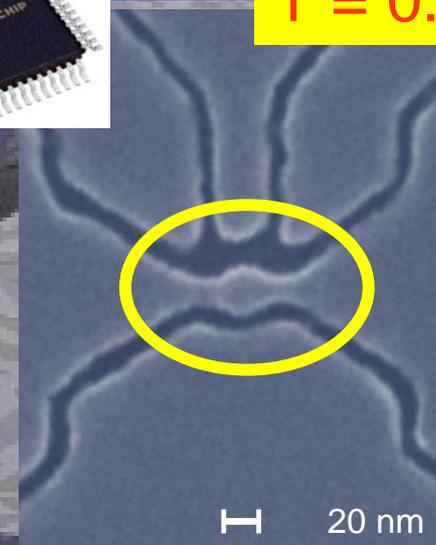
Zigzag



# ALL GRAPHENE nanoelectronics



T = 0.3 K !!!

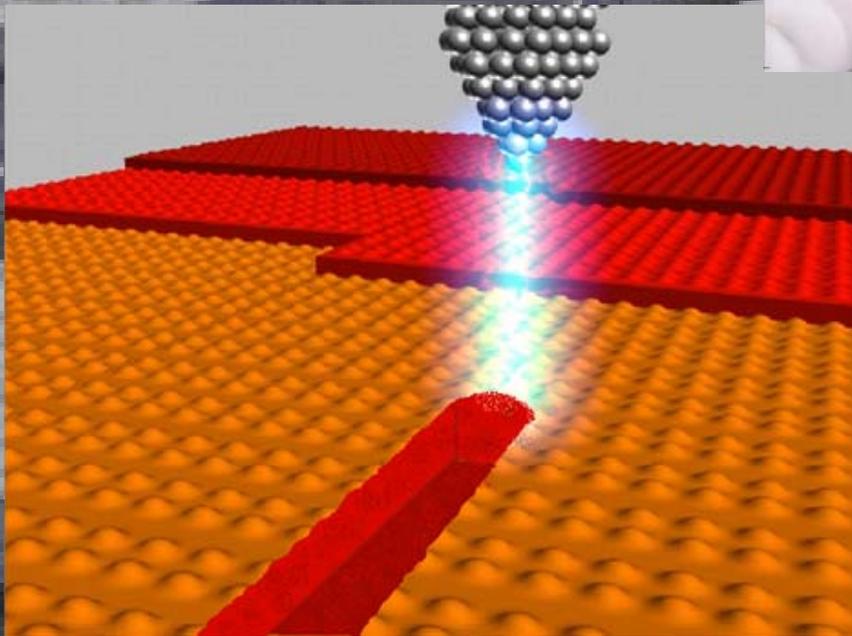
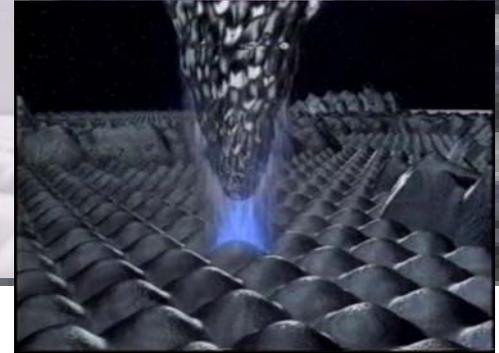
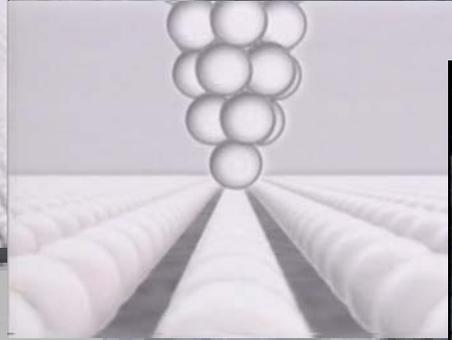
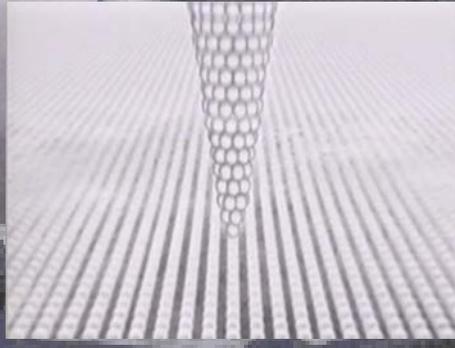


SET

Areshkin, D. A.; White, C. T. *Nano letters* **2007**, *7*, 3253

Ponomarenko, L.. *Science* **2008**, *320*, 356-

# STM lithography

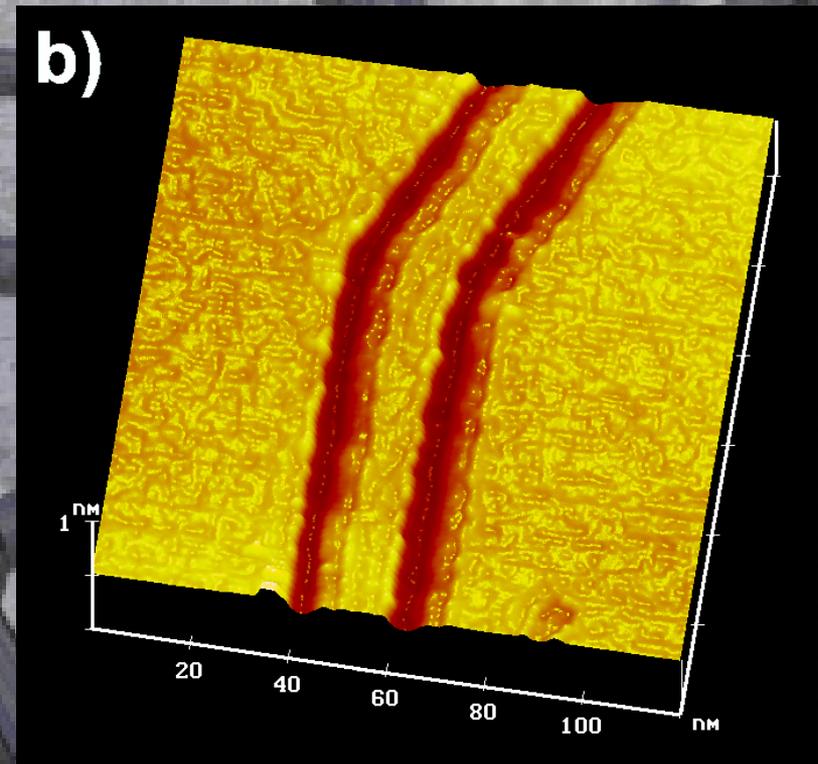
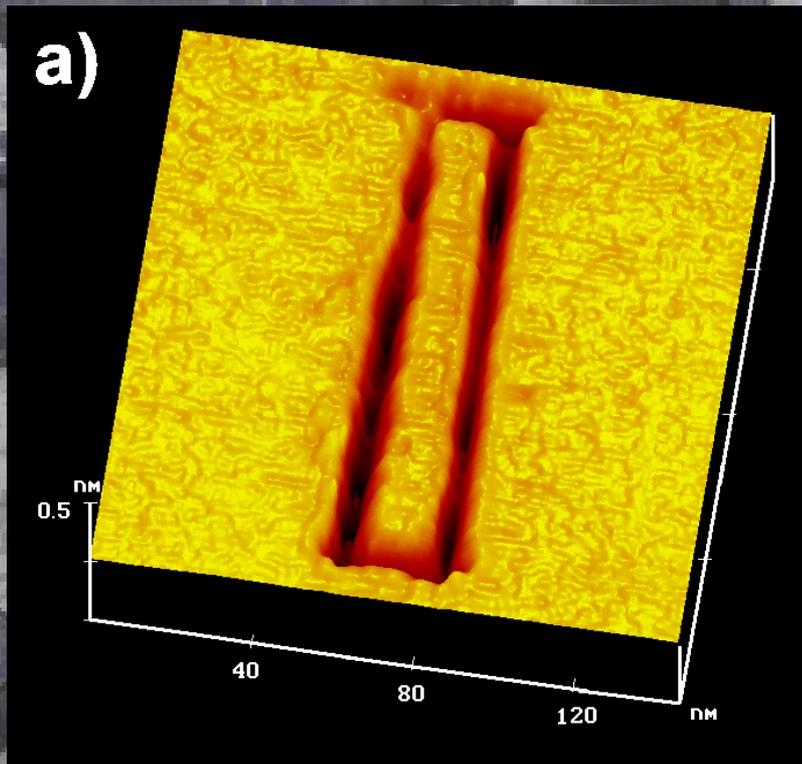


- Local modification of sample surface
- Atomically precise tip positioning
- Atomic resolution imaging

**To solve:**

- Control the etching process, realize the first true nanometer precision lithography

# Graphene nanoribbons created by STM lithography



*L. Tapasztó et al. Nature Nanotechnology, 4, 937 (2008)*

nature  
nanotechnology

VOLUME 4 JULY 2008  
www.nature.com/naturenanotechnology

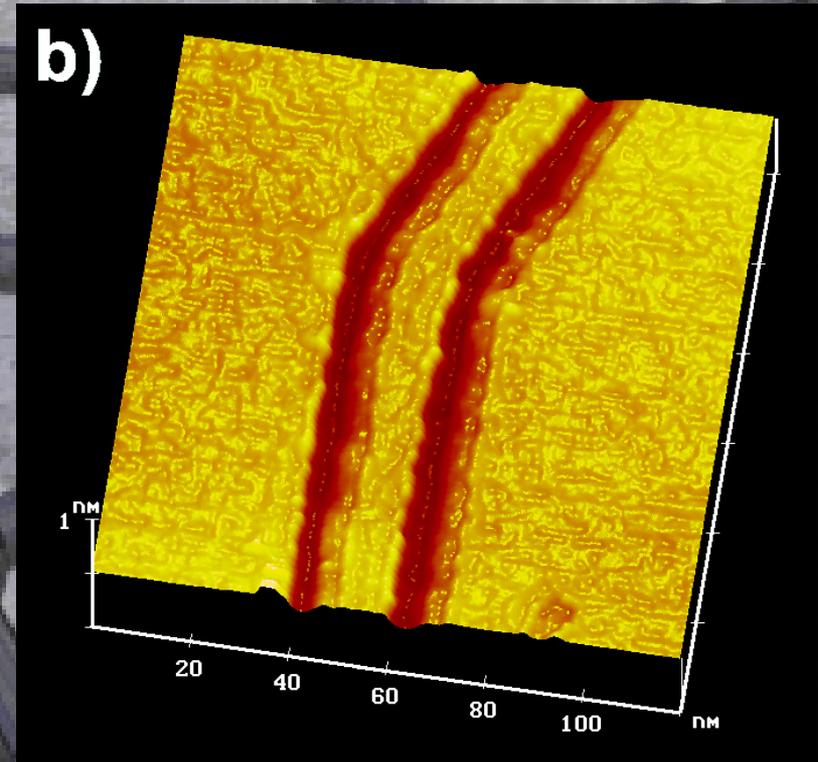
Tailor-made graphene  
nanoribbons

NANOTECHNOLOGY  
Are carbon nanotubes safe?

DATA STORAGE  
The ferroelectric approach

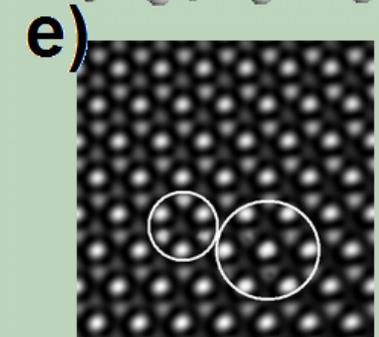
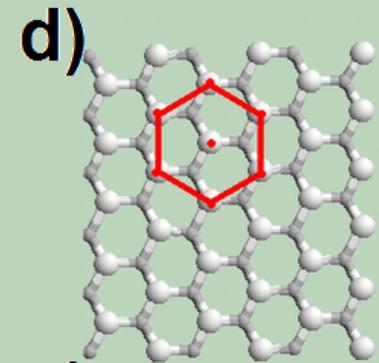
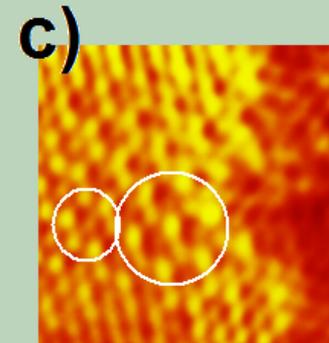
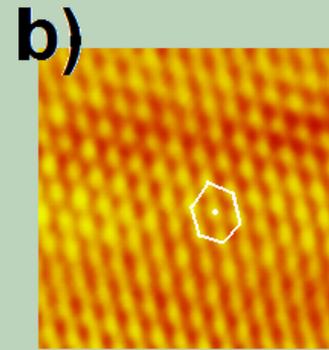
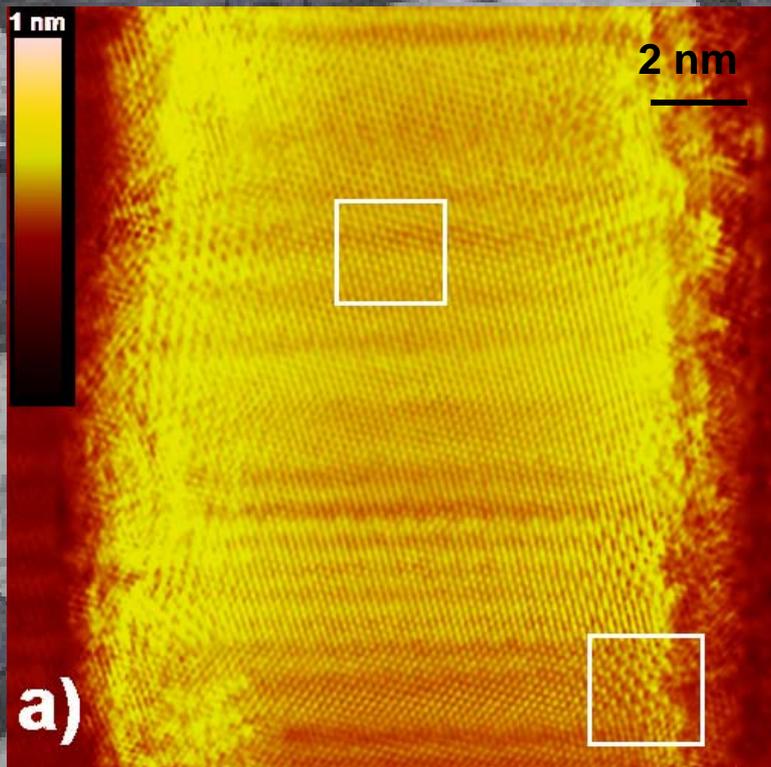
NANOELECTRONICS  
Ions get in on the act

ions created by  
graphy

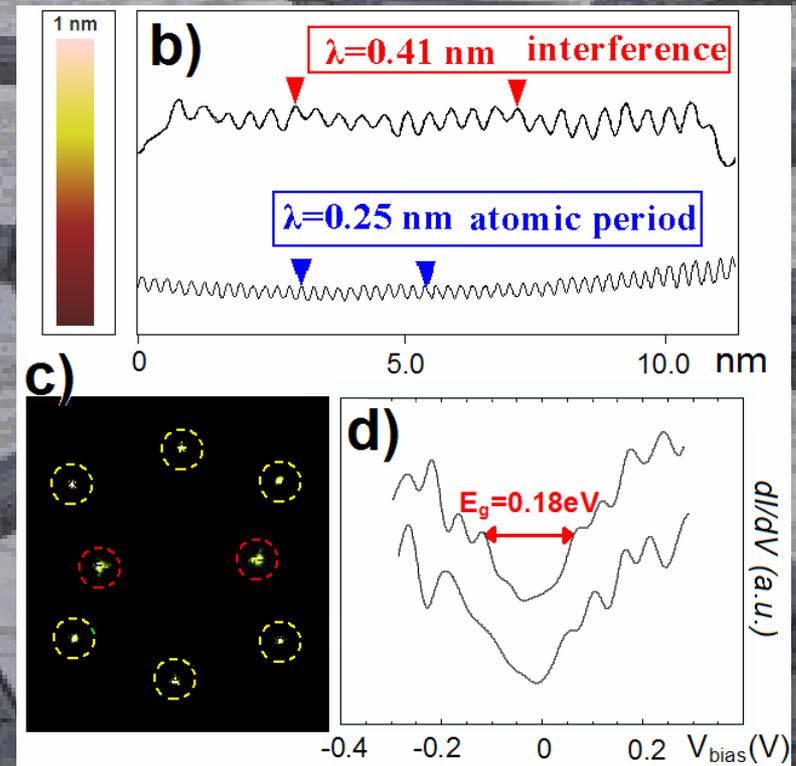
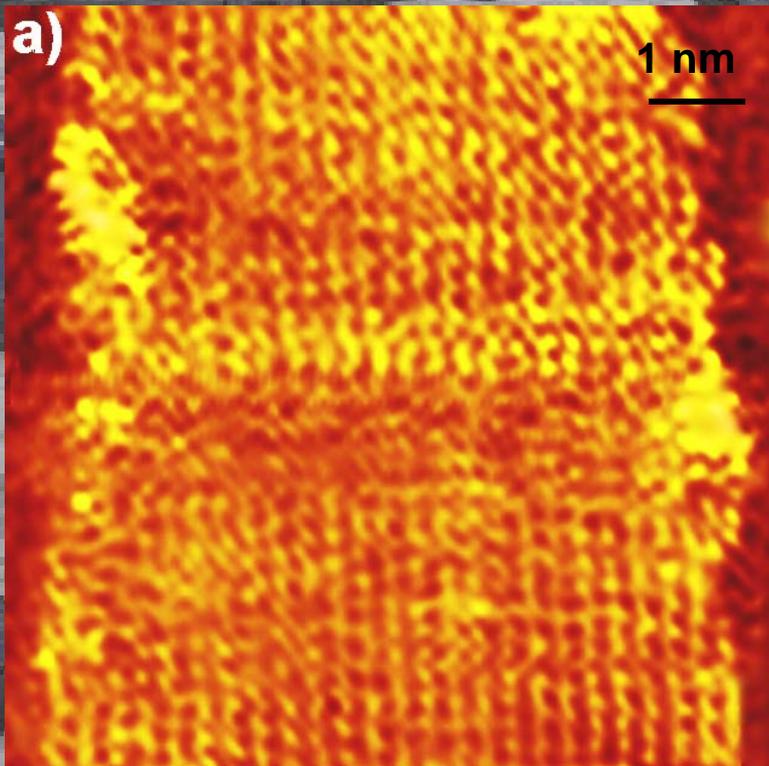


*L. Tapasztó et al. Nature Nanotechnology, 4, 937 (2008)*

# Atomic resolution STM imaging of GNRs

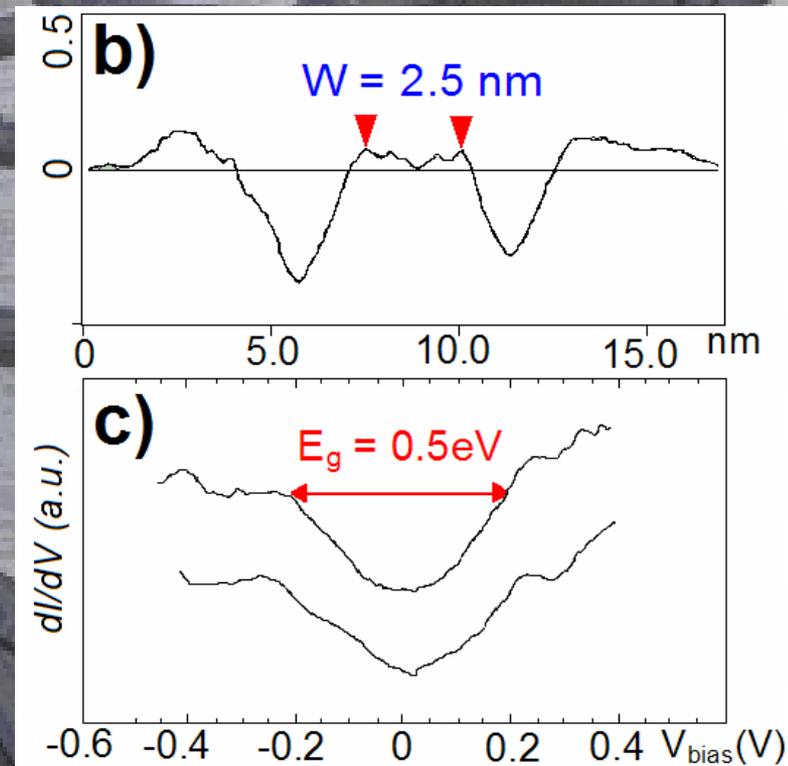
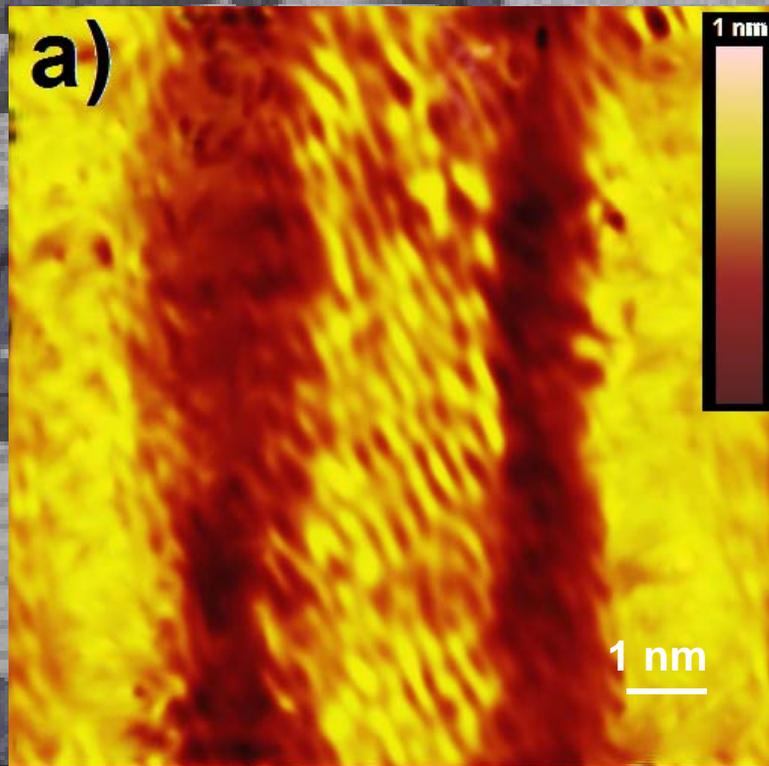


# Electron standing waves at room temperature



$$E_g (W) = \pi \hbar v_0 / W \approx (2eV \cdot nm) / W$$

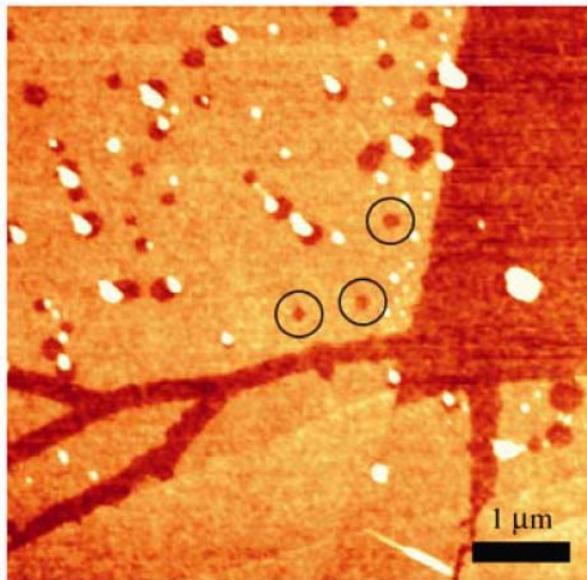
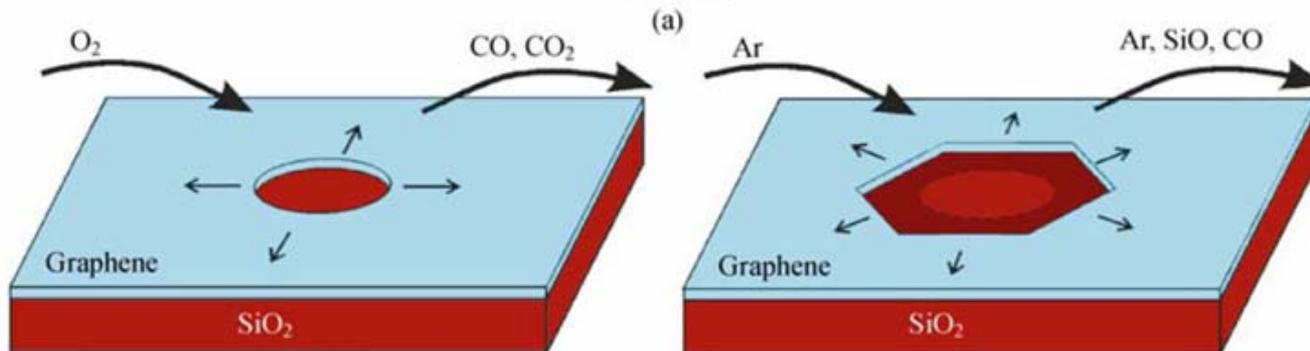
# STILL the best lithographic resolution today



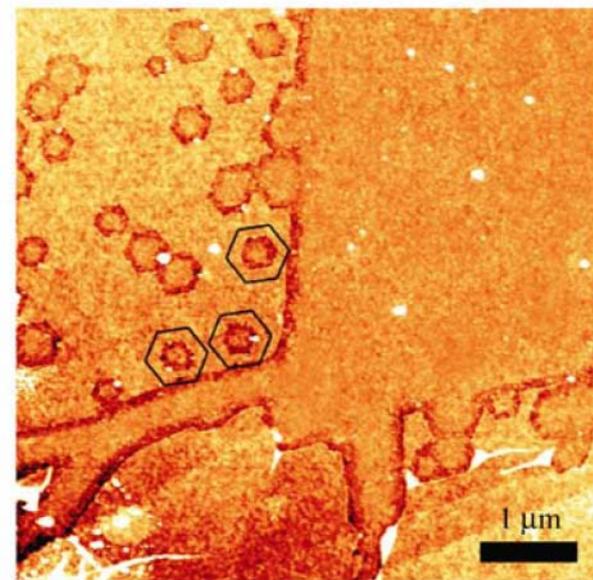
*L. Tapasztó et al. Nature Nanotechnology, 4, 937 (2008)*

$E_g = 0.5 \text{ eV}$  allows room temperature operation!

# Atomically perfect zigzag edges by: Carbothermal Etching (CTE)

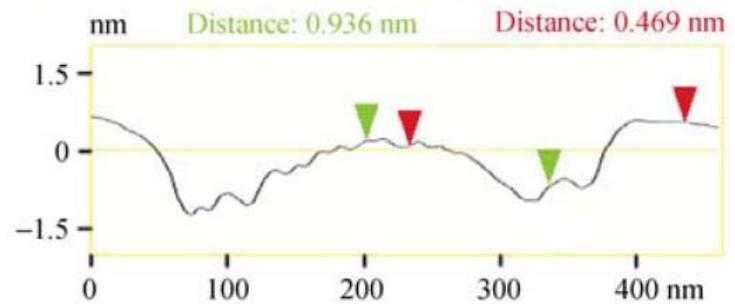
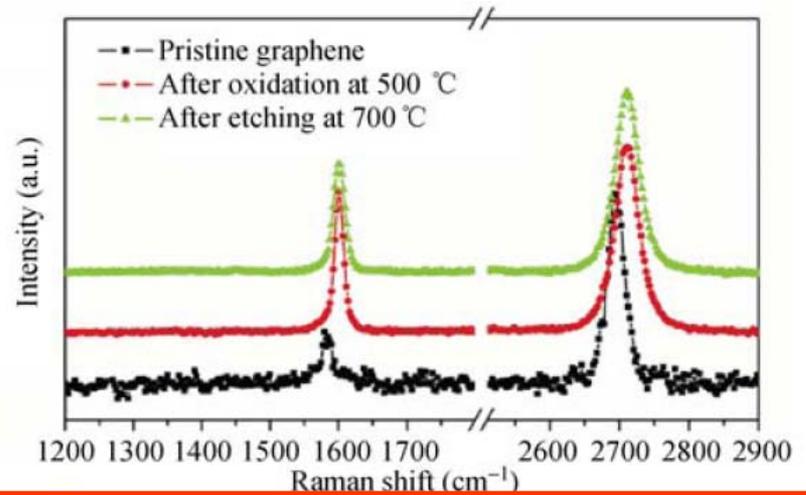
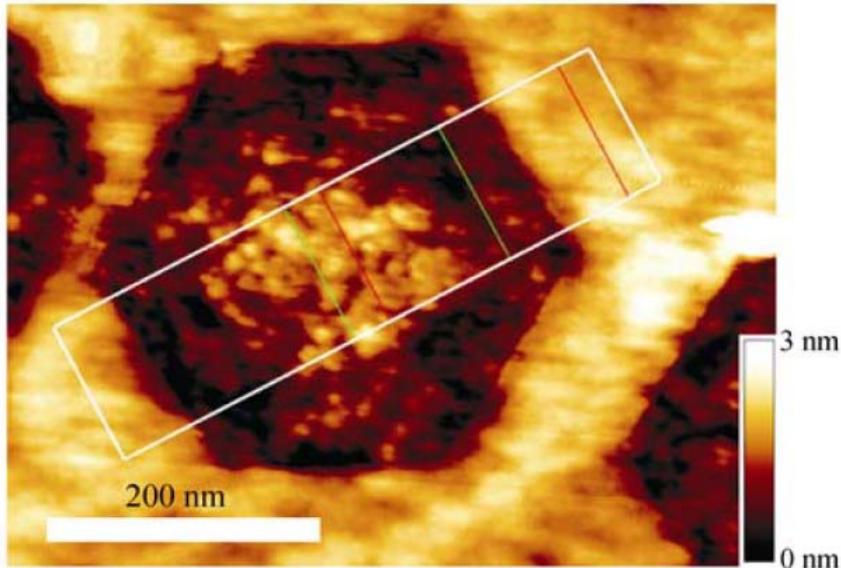


(a)

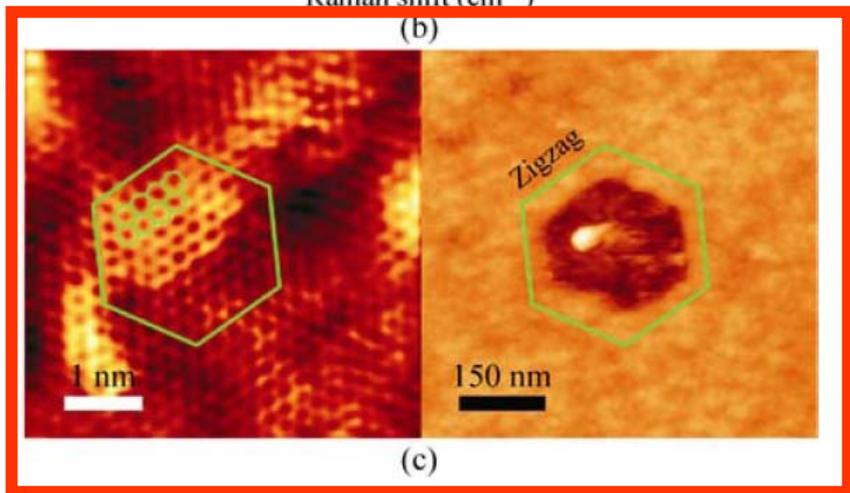


(b)

# Edge orientation by STM

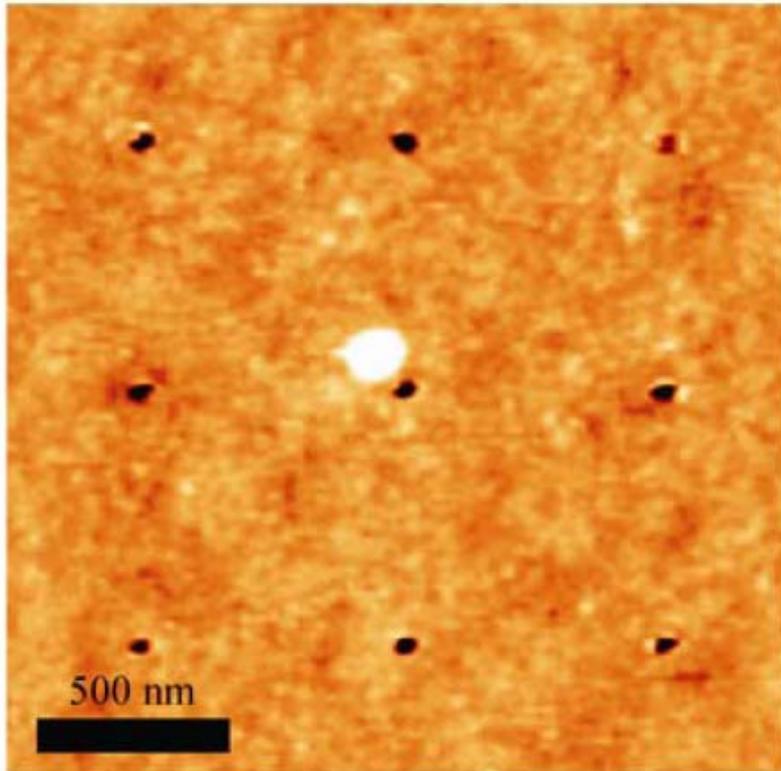


(a)

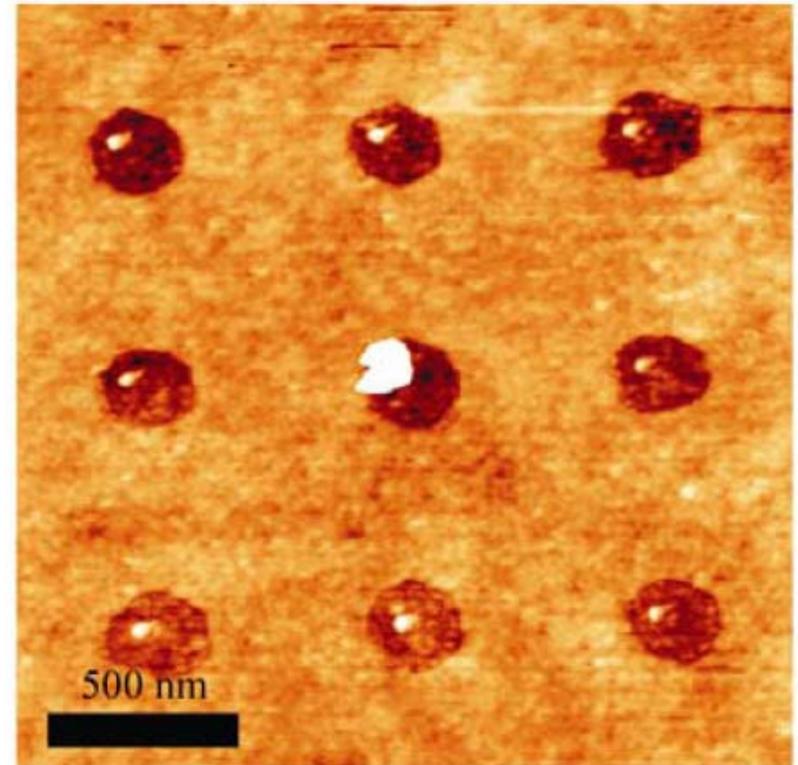


(c)

# Starting point fixed by AFM indentation

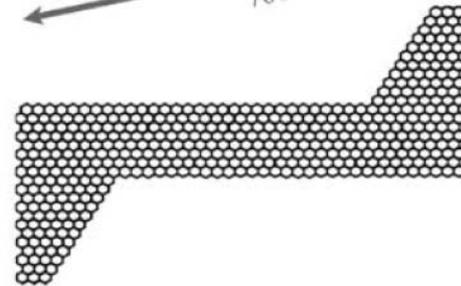
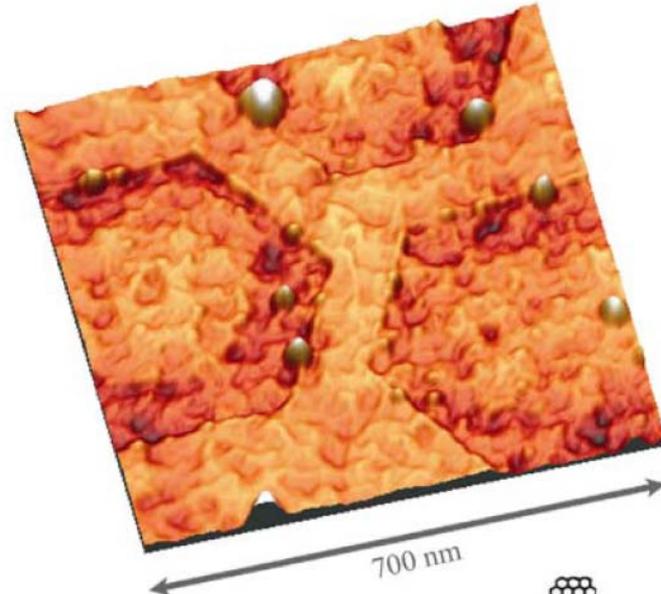
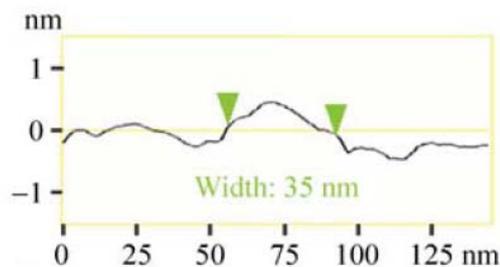
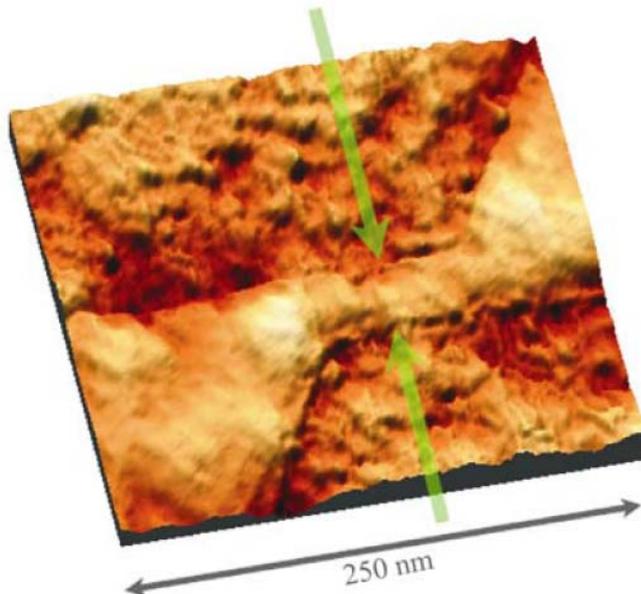


(a)



(b)

# Nanoarchitectures: graphene nano-Y Junction



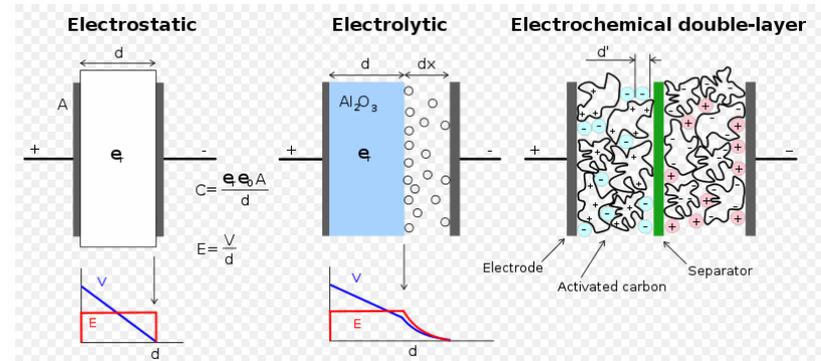
# Further applications



[http://en.wikipedia.org/wiki/File:Maxwell\\_MC\\_and\\_BC\\_ultracapacitor\\_cells\\_and\\_modules.jpg](http://en.wikipedia.org/wiki/File:Maxwell_MC_and_BC_ultracapacitor_cells_and_modules.jpg)

## Graphene-Based Ultracapacitors

Meryl D. Stoller, Sungjin Park, Yanwu Zhu, Jinho An, and Rodney S. Ruoff\*



Nano Letters 8 (2008) 3498

## Supercapacitors (Ultracapacitors?)

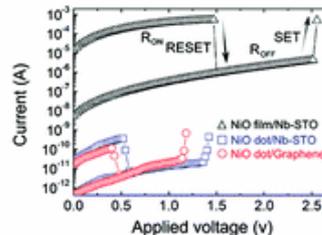
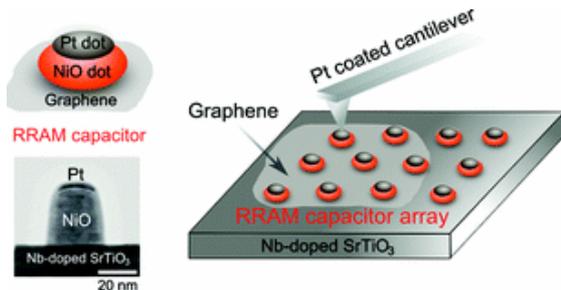
Electronic two-terminal bistable graphitic memories

Nature Materials 7 (2008) 966

YUBAO LI<sup>1\*</sup>, ALEXANDER SINITSKII<sup>1\*</sup> AND JAMES M. TOUR<sup>1,2†</sup>

## NiO Resistive Random Access Memory Nanocapacitor Array on Graphene

ACS Nano, 2010, 4 (5), pp 2655

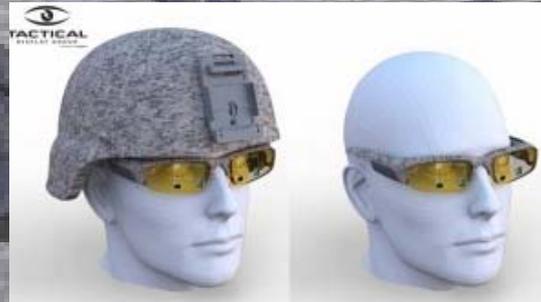


## Memory devices

# FLEXIBLE (Transistors + memory + energy source) = WEARABLE (nano)Electronics



<http://www.crunchwear.com/cute-circuit-galaxy-led-dress/>



**Augmented-reality-holographic sunglasses**

<http://www.crunchwear.com/vuzix-and-darpa-team-up-to-create-augmented-reality-holographic-sunglasses/>



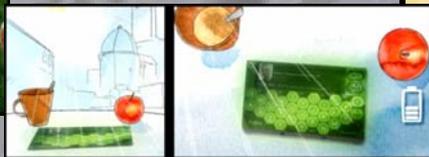
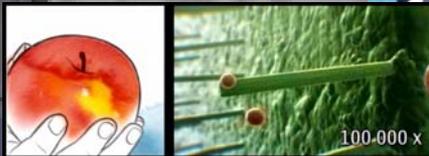
**Solar Soldier system to take the weight off infantry soldiers**

<http://www.gizmag.com/solar-soldier-power-system-for-infantry/18140/>

# NOKIA

# Μορφή

Morph is a concept demonstrating some of the possibilities nanotechnologies might enable in future communication devices



## Let's stop here

...



<http://www.gizmag.com/body-to-body-networks/16769/>

# Summary

- Graphene is the first of the family of single atom (molecule) thin materials
- It has many extraordinary properties
- It has short range application possibilities in flexible flat screens and photovoltaic devices
- It has long range perspectives to replace silicon in nanoelectronic devices – bandgap reengineering needed – atomic precision nanolithography
- Flexible and wearable electronics from power source to fast logic and memory

# Acknowledgments

- Funding: In Hungary OTKA-NKTH: K67793 „Nanoarchitectures from nanostructures”



Korean-Hungarian Joint Laboratory  
for Nanosciences

- **MFA:** P. Nemes-Incze, G. Dobrik, P. Vancsó, G. I. Márk, Z. Vértesy, Z. E. Horváth, L. Tapasztó,
- **KRIS:** K. J. Yoo & C. Hwang

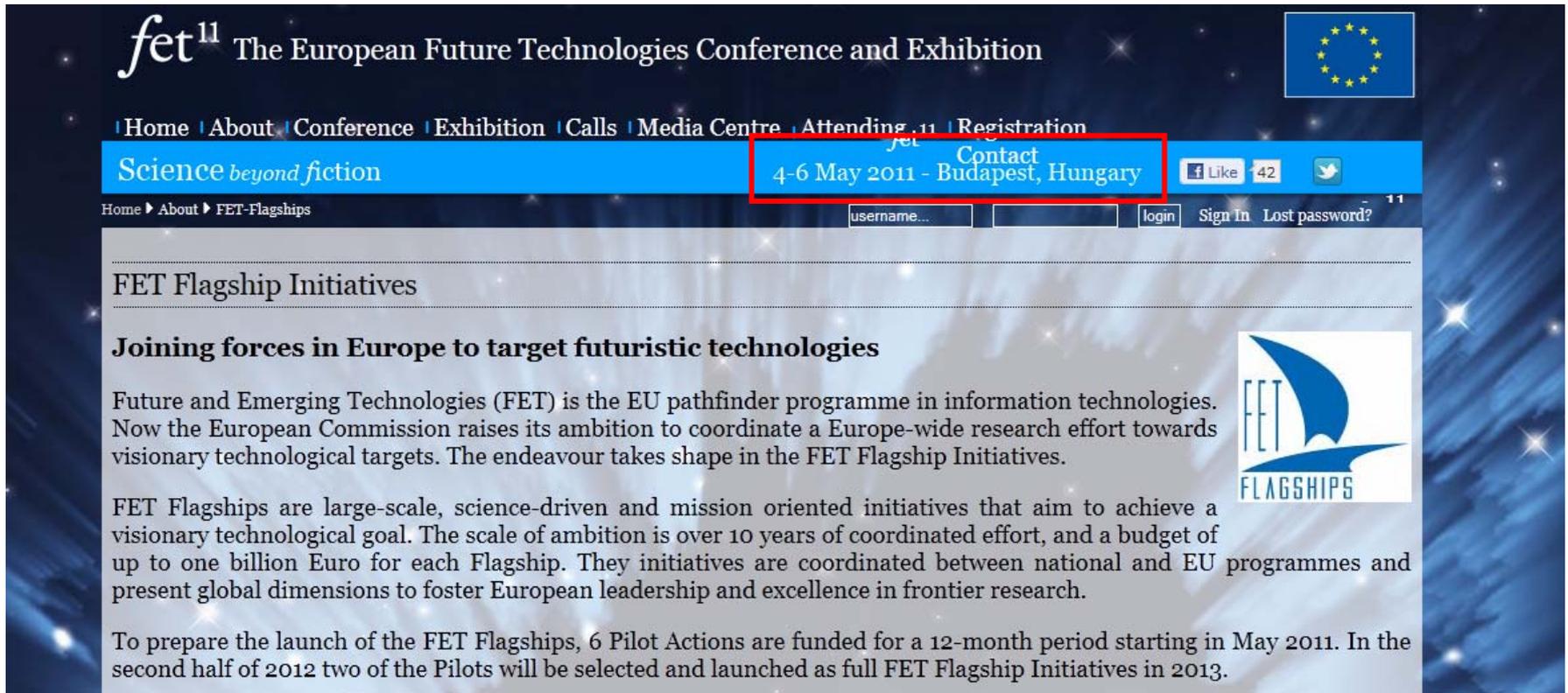
*fet*<sup>11</sup> The European  
Future Technologies  
Conference and Exhibition

4-6 May 2011  
Budapest, Hungary

Science  
*beyond fiction*

**Thank you for your attention!**

# Graphene „FLAGSHIP” – EU-FP7



**fet<sup>11</sup>** The European Future Technologies Conference and Exhibition

Home | About | Conference | Exhibition | Calls | Media Centre | Attending | Registration | Contact

Science *beyond fiction* 4-6 May 2011 - Budapest, Hungary

Home | About | FET-Flagships

## FET Flagship Initiatives

### Joining forces in Europe to target futuristic technologies

Future and Emerging Technologies (FET) is the EU pathfinder programme in information technologies. Now the European Commission raises its ambition to coordinate a Europe-wide research effort towards visionary technological targets. The endeavour takes shape in the FET Flagship Initiatives.

FET Flagships are large-scale, science-driven and mission oriented initiatives that aim to achieve a visionary technological goal. The scale of ambition is over 10 years of coordinated effort, and a budget of up to one billion Euro for each Flagship. They initiatives are coordinated between national and EU programmes and present global dimensions to foster European leadership and excellence in frontier research.

To prepare the launch of the FET Flagships, 6 Pilot Actions are funded for a 12-month period starting in May 2011. In the second half of 2012 two of the Pilots will be selected and launched as full FET Flagship Initiatives in 2013.



The six FET Flagship Pilot Actions to be launched are:

- [FuturICT - The FuturICT Knowledge Accelerator and Crisis-Relief System: Unleashing the Power of Information for a Sustainable Future](#)
- [Graphene - Graphene Science and technology for ICT and beyond](#)
- [Guardian Angels - Guardian Angels for a Smarter Planet](#)
- [HBP - The Human Brain Project](#)
- [ITFoM - IT Future of Medicine: a revolution in healthcare](#)
- [RoboCom - Robot Companions for Citizens](#)