European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

GRAPHENE DEVELOPMENTS IN EUROPE

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COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

From science to technology: EU Graphene Flagship

- The Graphene Flagship is a Future and Emerging Technology Flagship by the European Commission

- 10 years & 1000 million Euros
- Started October 1st, 2013
- Led by Chalmers

Why all the hype about graphene?

- Graphene is the first 2D crystal to be demonstrated
- Unprecedented properties
- New physics
- New applications

Talk Content

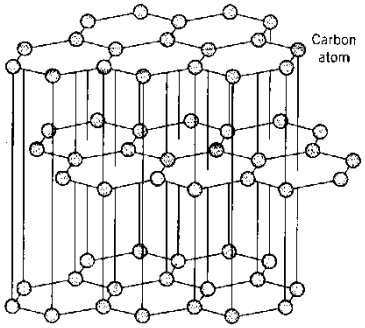
- Graphene as a 2D material
- Graphene Flagship
- Activities at LiU
- Conclusion

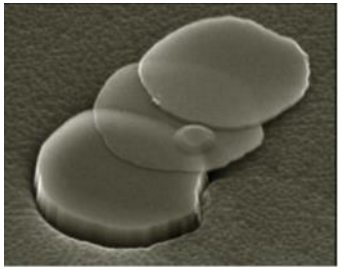
Graphene as a 2D material

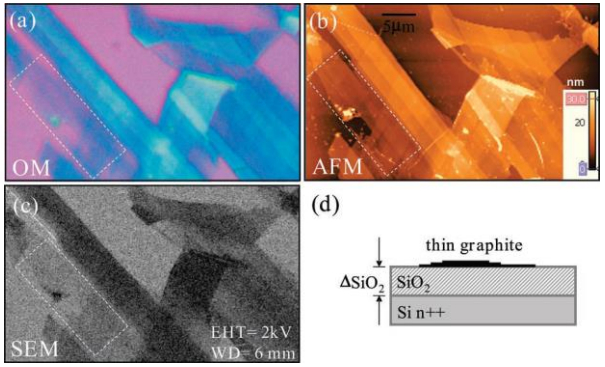
- Graphene is the first 2D crystal to be demonstrated, although being around us

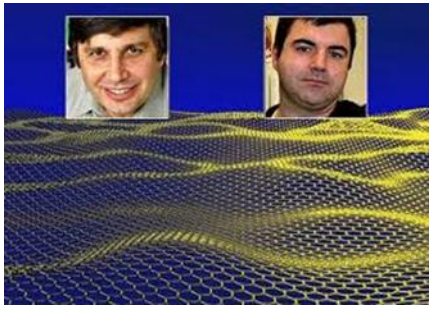
Graphene has always existed as a building block of graphite
=> One millimeter of graphite consists of three million layers of graphene stacked on top of each other.

"…everyone who has used an ordinary pencil has probably produced graphene-like structures without knowing it."
[HTTP//KVA.SE]







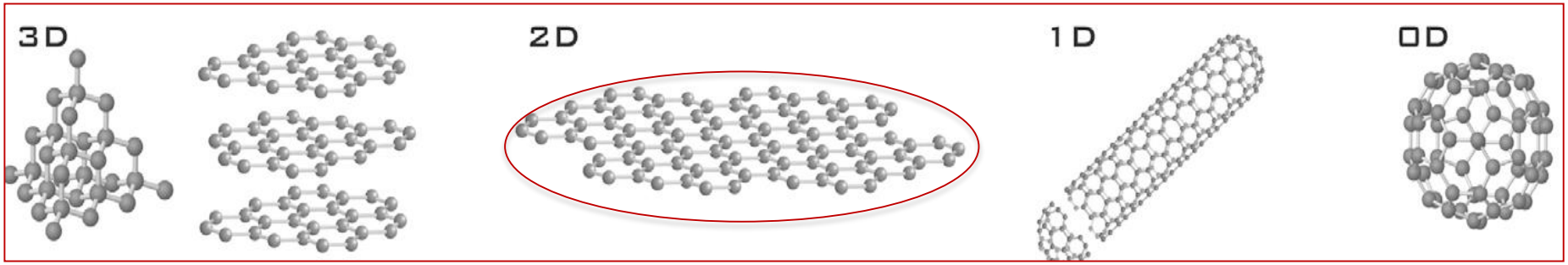


2004

2010

Graphene as a 2D material

- Graphene is the most versatile carbon allotrope



Crystal structures of the different allotropes of carbon. (Left to right) Three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one dimensional nanotubes (1D); and zero-dimensional buckyballs (0D). (*M. Katsnelson, materials today, 10 (1-2) 2007*)

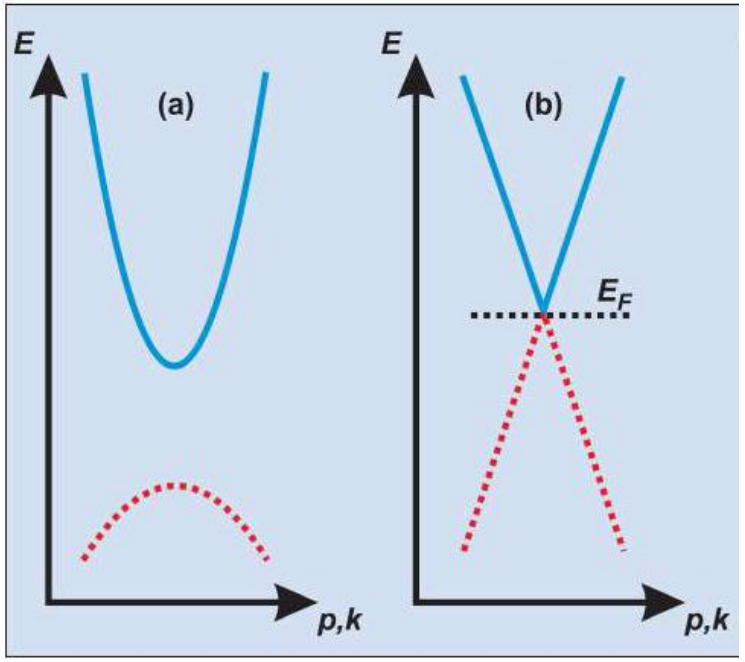
13 October 1867 marks the first recorded discovery of diamonds in the colonial period of South Africa

Smalley et. al. fullerene; 1985

Marita culture
4th millennium B.C.

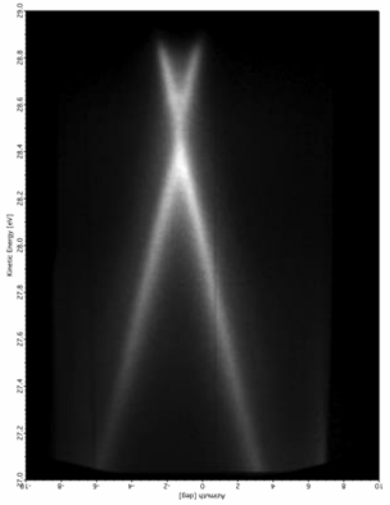
Iijima et al., 1991
Carbon nanotubes

Theoretically predicted



Energy-momentum dispersion

The electronic band structure of graphene was first calculated by Wallace in 1947.



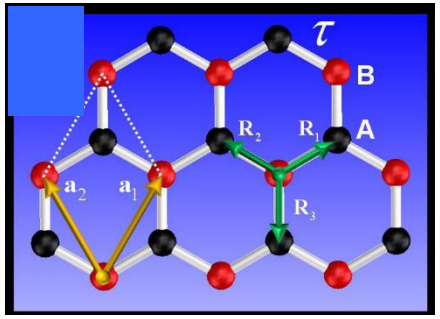
E-k dispersion
ARPES from 1ML graphene on SiC

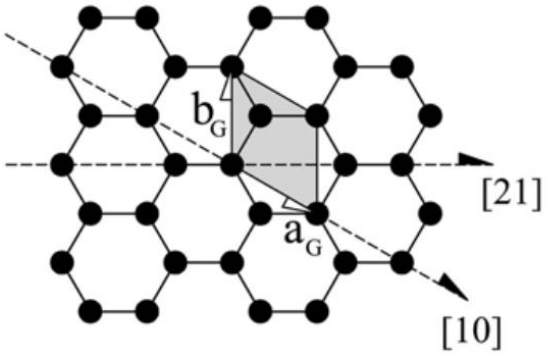
- Parabolic in classical semiconductors
- Linear in graphene – Dirac cone, zero bandgap, ambipolar conductivity

[Semiconductor today 2 (10), 2008, p. 57]

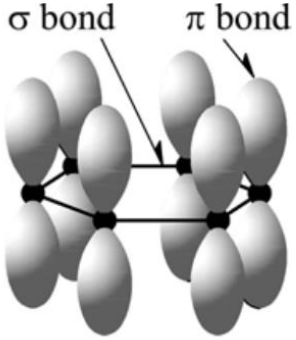
Bonding and crystal structure

• Covalently sp^2 bounded atoms in a 2D honeycomb structure of C atoms => strong bonds with the neighbors; one unbound electron left => conductivity.
Basic lattice structure made up of two interpenetrating hexagonal carbon sublattices, A and B => forming a honeycomb pattern. Sublattice symmetry greatly influences the electronic structure of graphene. BN?
• Unit cell contains two identical carbon atoms (A and B), and is defined by the lattice vectors a_1 and a_2. The distance between honeycombs, $a=a_1=a_2$ is 2.46 Å, A-B distance 1.42Å, strong interatomic bond coupling. Rj -translation vectors





(a)

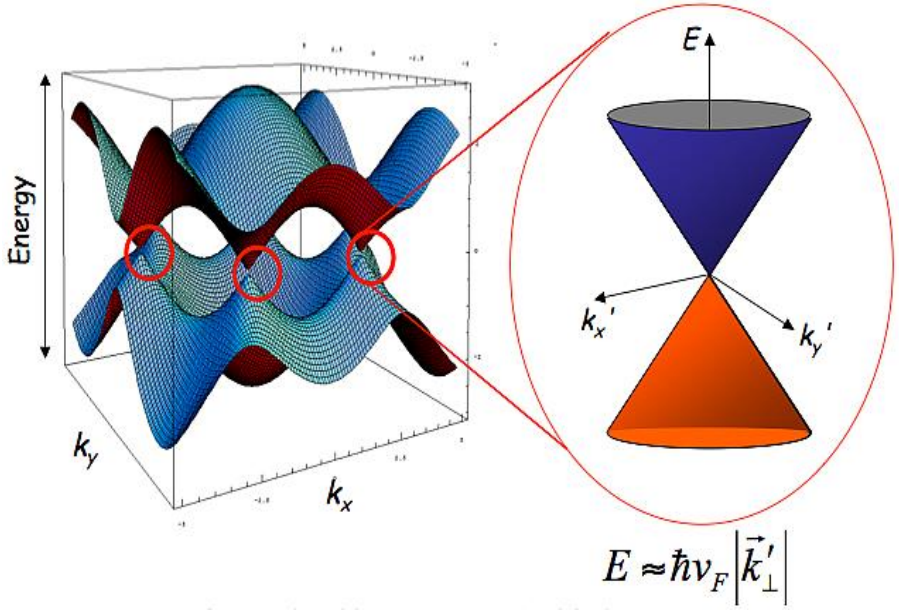


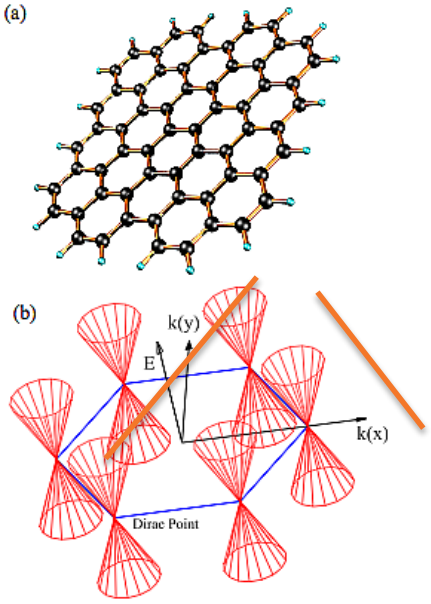
(b)

(a) The unit cell (shaded) containing two carbon atoms is shown along with standard unit cell vectors a_G and b_G. The armchair edge [21] and the zig-zag [10] directions are shown.
(b) Schematic of the in-plane *σ* bonds and the *π* orbitals perpendicular to the plane of the sheets.

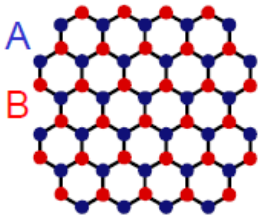
Graphene energy band structure

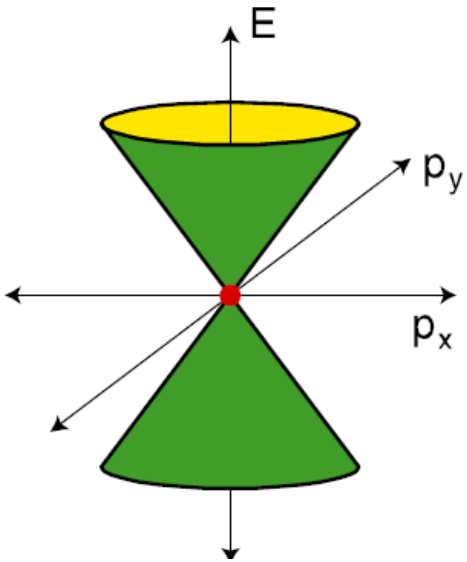
- Linear energy-momentum dispersion - Massless, pseudo-relativistic Dirac fermions
- Ballistic transport at room temperature, and intrinsic mobility μ >10^5 cm^2 $V^{-1}s^{-1}$ (Silicon: 1400 cm^2 $V^{-1}s^{-1}$)
- High thermal conductivity (unlimited heat conduction, diverging with size)
- Transparent, flexible, strong... Nature Communications **5**, 3689 (2014)
- Ambipolar π- bands touch at Dirac points – carrier concentration controlled by bias





Low energy electronic structure





The low energy electronic states in graphene are described by the Dirac equation for particles with

Mass : m=0

"Speed of light" $c = v_F$

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$$ sublattice A / sublattice B

Emergent Dirac Fermions

In a world of paradoxes

Electrons travelling in graphene behave as if they did not have any mass and move ahead at a constant speed of one thousand kilometers per second. This opens up the possibility of studying certain phenomena more easily on a smaller scale, i.e. without the use of a large particle accelerator.

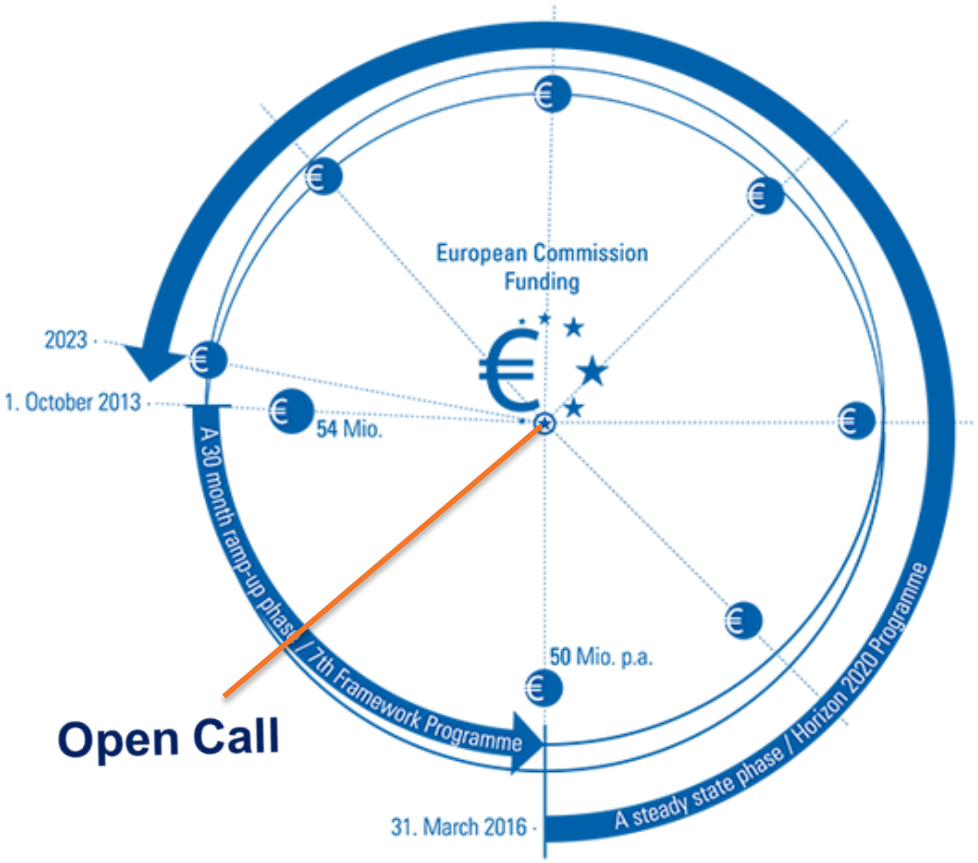
Unique material properties

- One atom thick - the thinnest material
- Mechanically the strongest - about 200 times the strength of structural steel
- As a conductor of electricity it performs as well as copper. The sheet conductivity of a 2D material is given by $\sigma = enμ$. The mobility is theoretically limited to $μ = 200{,}000\ cm^2V^{-1}s^{-1}$ by acoustic phonons at a carrier density of $n = 10^{12}\ cm^{-2}$. The 2D sheet resistivity, also called the resistance per square, is then 31 Ω.
- As a conductor of heat it outperforms all other known materials. The thermal conductivity of graphene is dominated by phonons and has been measured to be approximately 5000 $Wm^{-1}K^{-1}$. Copper at room temperature has a thermal conductivity of 401 $Wm^{-1}K^{-1}$. Thus graphene conducts heat 10 times better than copper.
- It is almost completely transparent, it absorbs only 2.3% of the light intensity, independent of the wavelength. Suspended graphene does not have any color.
- So dense that not even helium, the smallest gas atom, can pass through it.

FLAGSHIP Mission:

Bring graphene disruptive technologies *from European laboratories to Europeans*

Time line & initial consortium



Initial consortium enlarged by Open Call

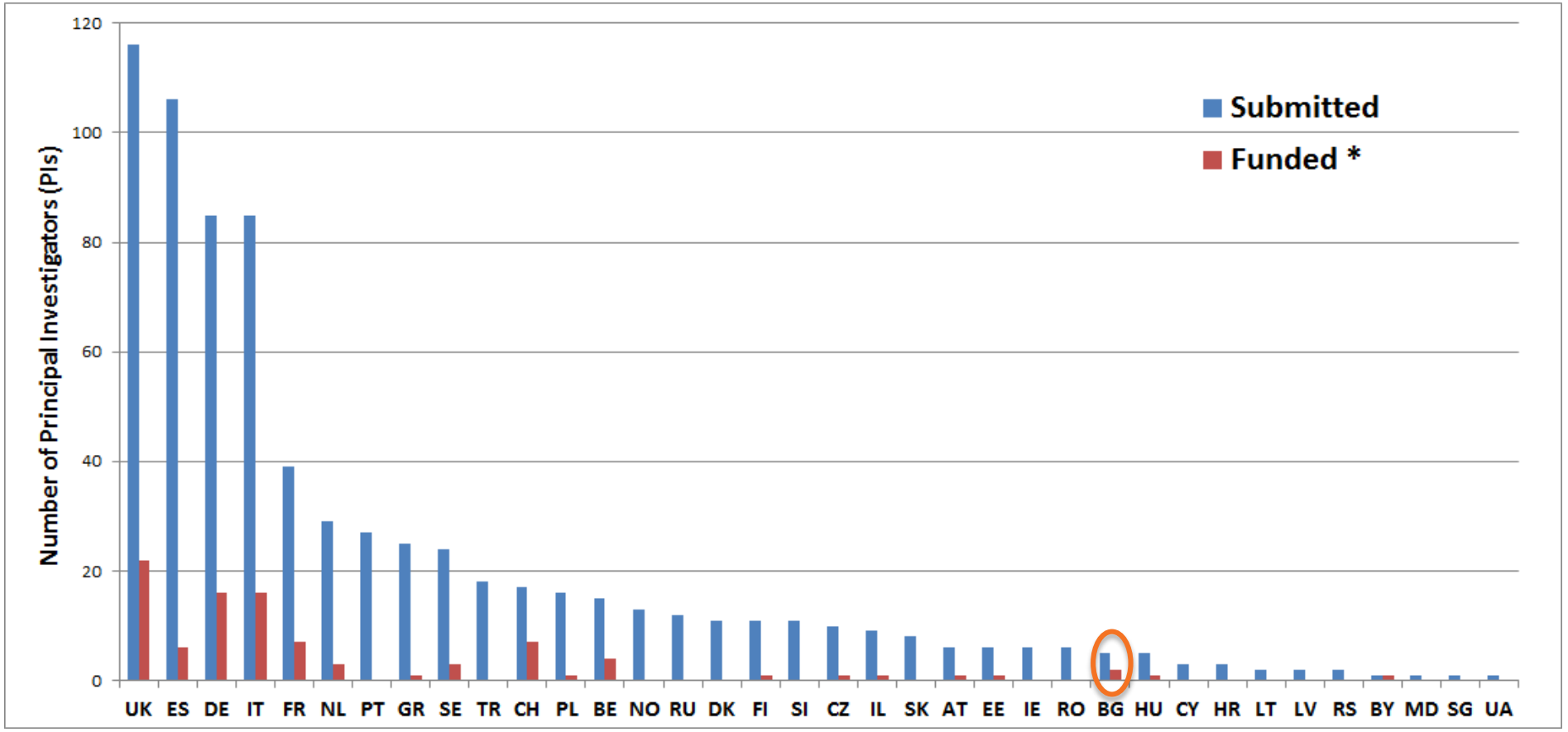
The Graphene Flagship is divided into two separate phases:

1st- a 30 month ramp-up phase under the 7th Framework Program (October 1, 2013 – March 31, 2016) with a total EC funding of 54 millions euro.
2nd- a steady state phase under the Horizon 2020 Program (April 1, 2016 – 2023) with expected EC funding of 50 millions euro per year (Graphene Core project).

Initial consortium: 75 partners from 17 countries
Led by Chalmers (Sweden)
Kick off 11 October 2013

Open call – time line&statistics by country

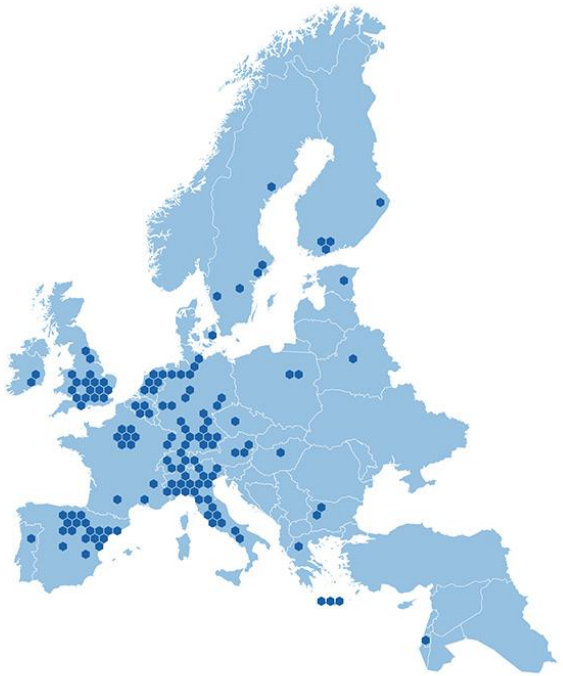
25 NOV 2013 – call opens;
05 FEB 2014 – call deadline;
JUNE 2014 - Recommendations on new beneficiaries from the GRAPHENE Executive Board to the European Commission;
AUTUMN 2014 - Accession of new beneficiaries



GRAPHENE FLAGSHIP

Graphene Flagship Consortium

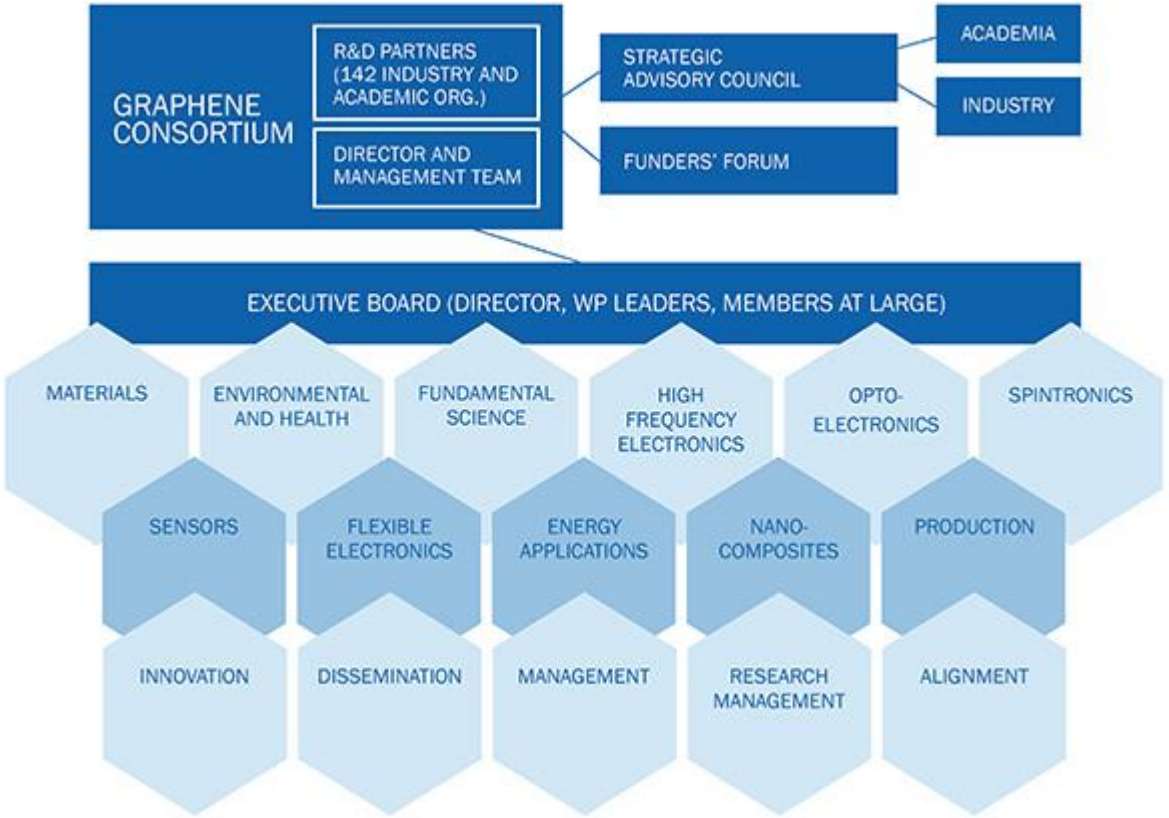
Today, the Graphene Flagship coordinates 142 academic and industrial research groups in 23 countries, and consists of a number of associated members (not funded).



The Graphene Flagship is implemented as 16 work packages , 11 on specific science and technology topics and five on operative management aspects => LiU is involved in WP Materials.

European Commission

Management & Work packages



Decision-making in the Graphene Flagship is the responsibility of:

- The Executive Board, composed of the Work Package Leaders and four members-at-large (elected by the General Assembly)
- The General Assembly, comprising one representative for each partner institution

Strategic Advisory Council (SAC)

SAC established during the pilot phase and continues to be an integral part of the Graphene Flagship.

- It consists of scientific and technological experts and its key tasks are to advise on strategic research decisions.
- advise on issues pertaining to handling and protection of intellectual property and requirements on the Graphene Flagship implementation implied by an efficient IPR management
- facilitate contacts to related national and international research programs
- to act as ambassadors for the Graphene Flagship

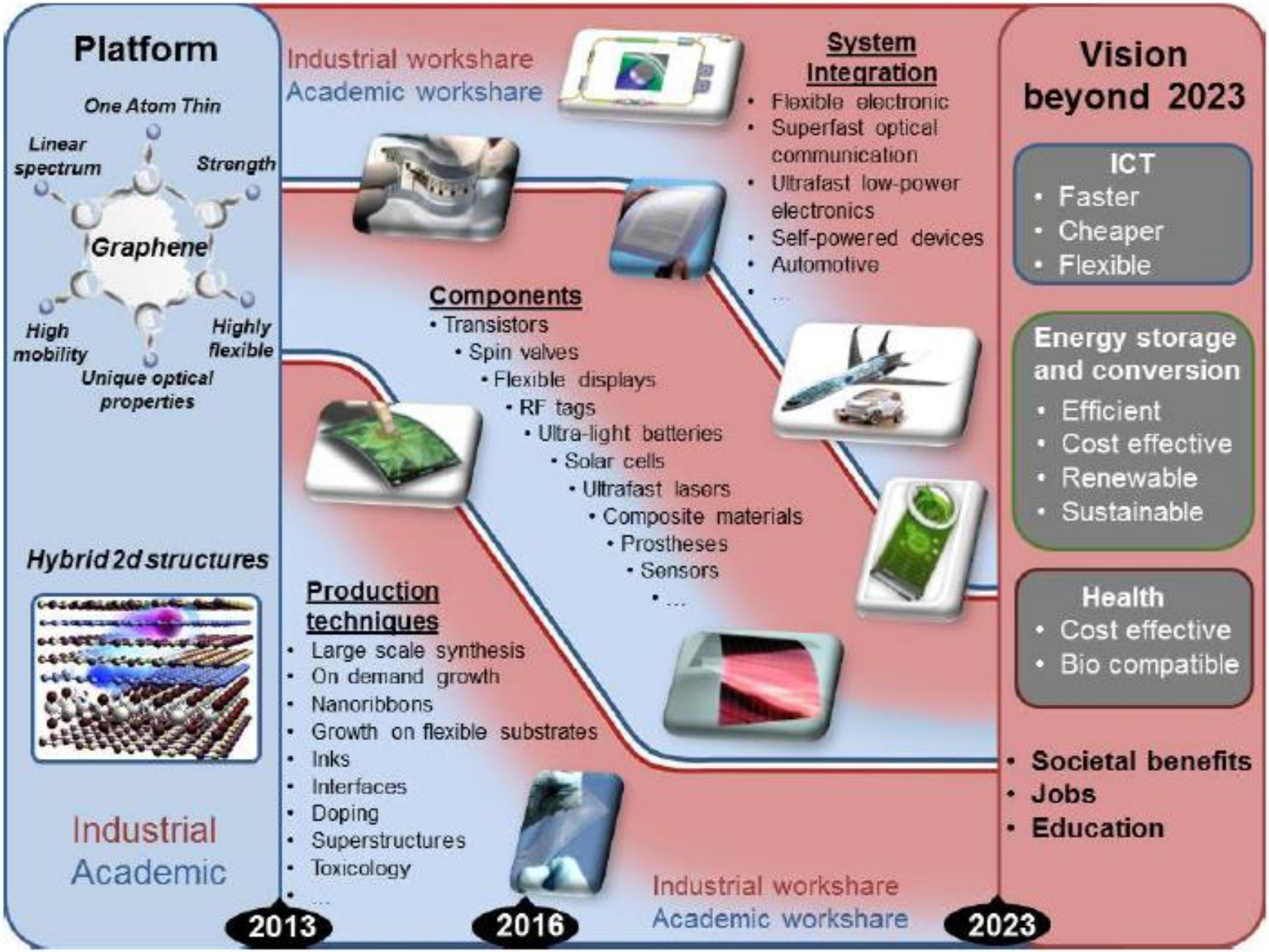
The Chairman of the Strategic Advisory Council is Professor Sir Andre Geim, University of Manchester, Manchester, UK.

Dr. Silvia Lazcano
Airbus
Madrid, Spain

Dr. Tapani Ryhänen Nokia
Research Center
Espoo, Finland

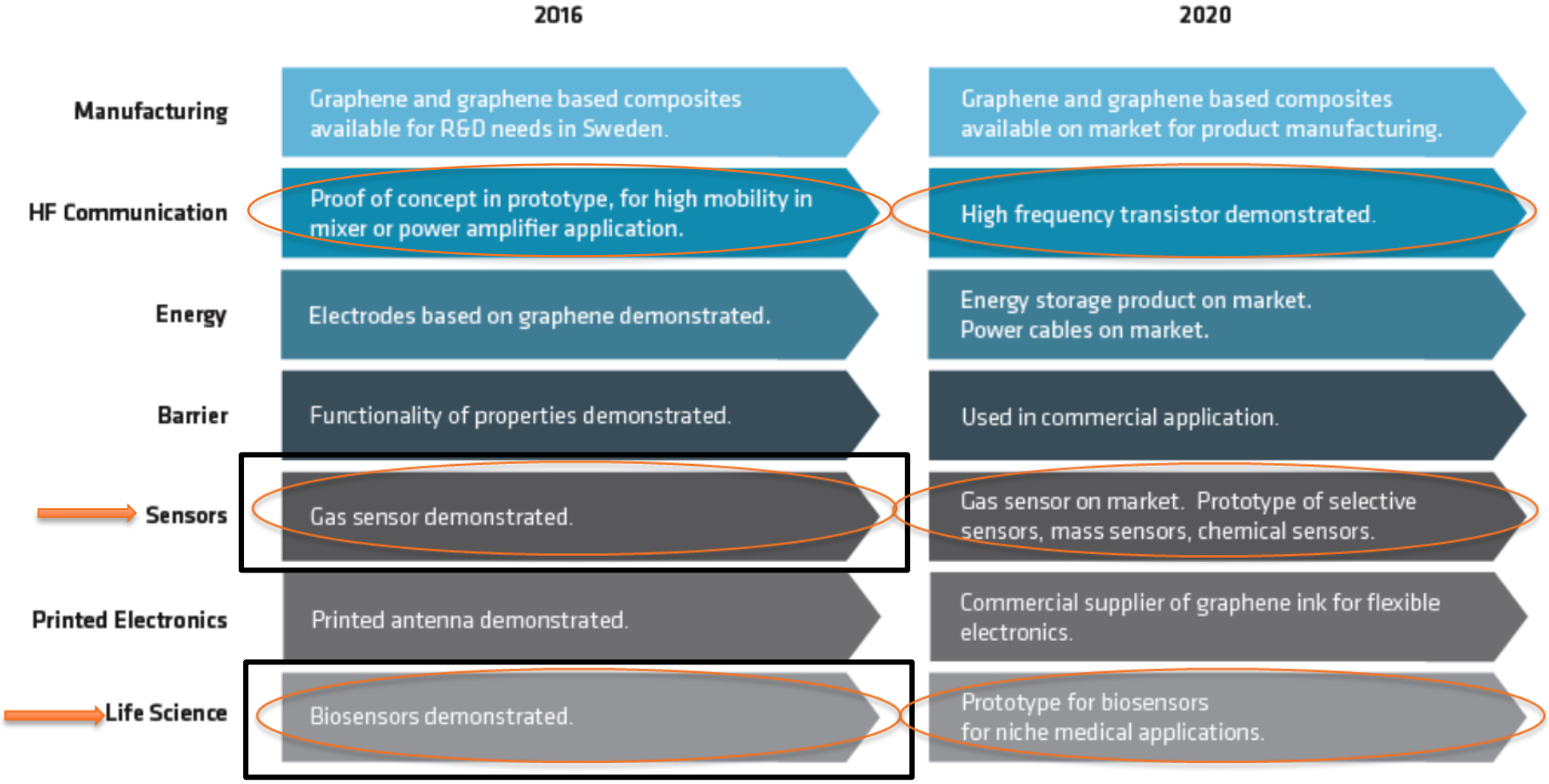
Dr. Norbert Wagner
BASF
Ludwigshafen, Germany

Graphene Roadmap

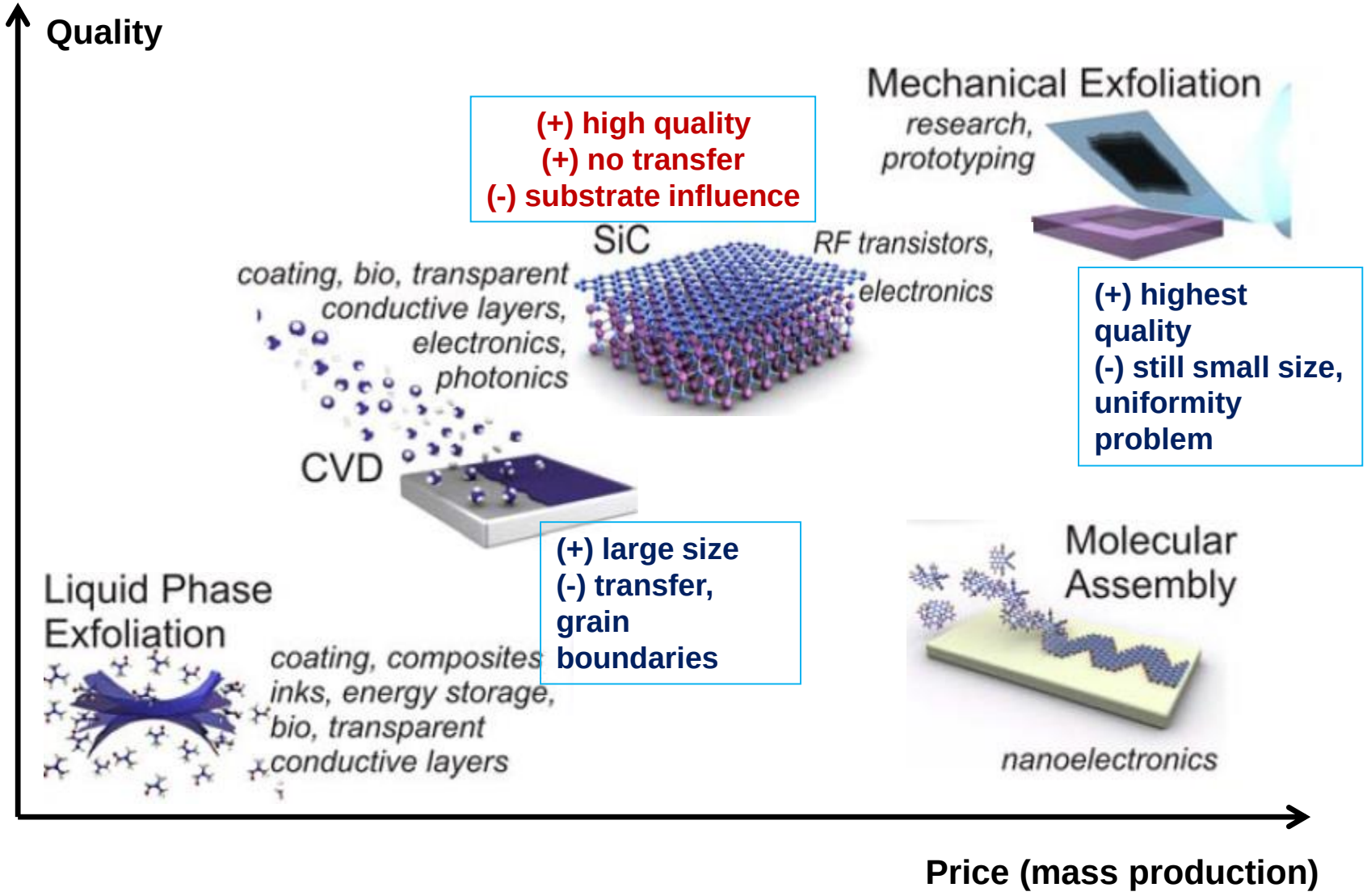


R&D towards Applications

Areas of strength in Sweden - 43% related to LiU graphene



Graphene fabrication



Why Graphene sensors?

- Ulra-high sensitivity necessary for Air Quality Monitoring
- Low density of states near the Dirac point (E_D) – small changes in the number of charge carriers result in large changes in the electronic state
- Every atom at the surface – ultimate surface to volume ratio - 1 gram of graphene is sufficient to cover a football field.
- Low mass, low noise
- **Has potential as a low noise, ultra-sensitive transducer.**

❑ WHO: **100.000** premature annual deaths in Europe due to household pollution

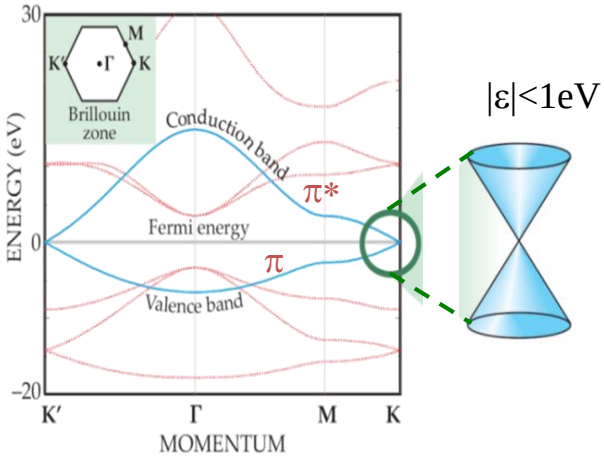
People spend more than 85% of time indoor

→ Prolonged exposure
Threshold for health effects lower

Applications where ultra-high sensitivity is required:

❑ Air quality control: Monitoring of highly toxic gases in normal living environments (indoor and outdoor)
- VOCs (formaldehyde, benzene, naphthalene…)
- NOx

❑ Liquid phase: Early detection of disease biomarkers, biological threats

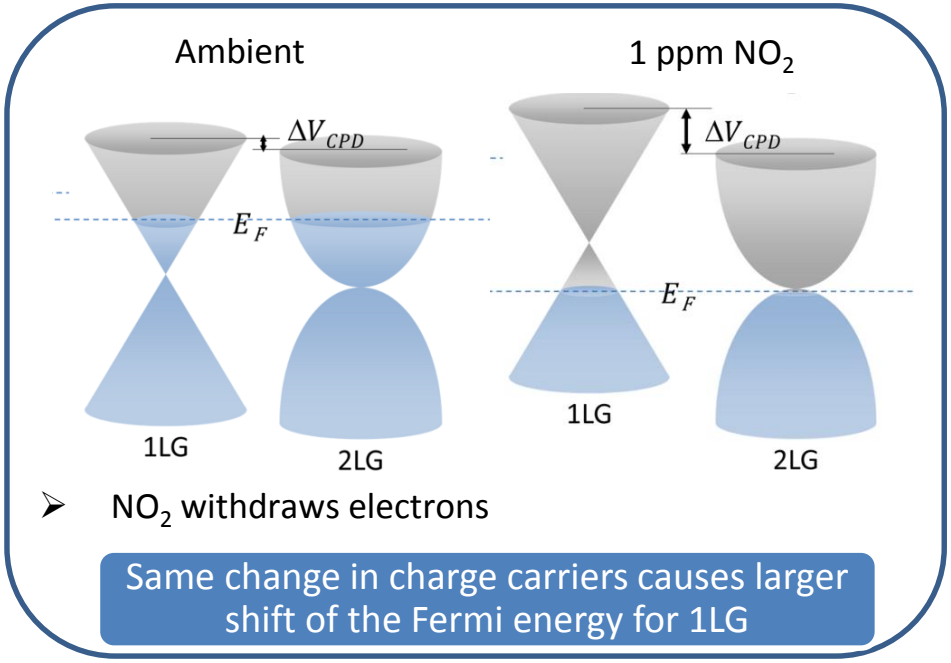


cost
EUROPEAN COOPERATION IN SCIENCE AND TEC

Reproducibility is an issue that partly arises from the graphene synthesis

Different sensitivity for 1LG and 2LG

ΔS depends on thickness due to differing band structures for 1LG, 2LG... MLG

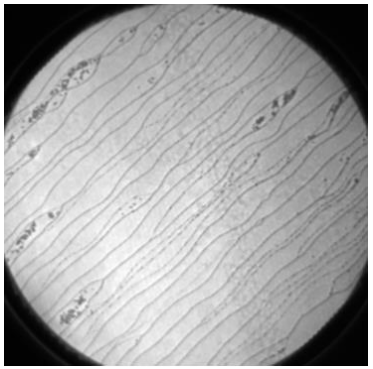


- NO_2 withdraws electrons

Same change in charge carriers causes larger shift of the Fermi energy for 1LG

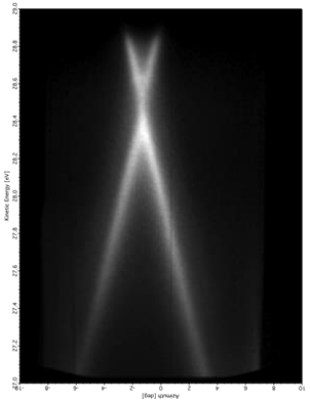
R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS Nano 7 (5), pp 4647–4656 (2013)

Uniform 1LG leads to very reproducible sensor characteristics

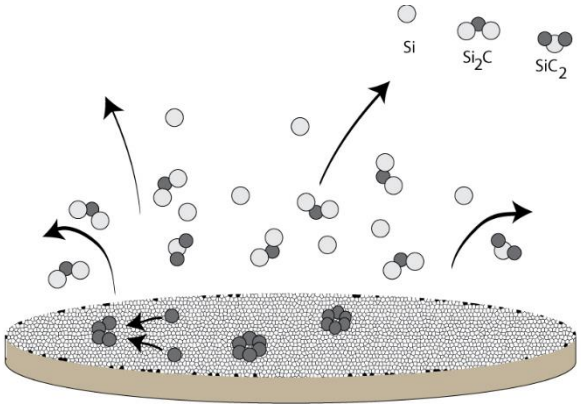


LEEM:~50μm² area 1 ML graphene on SiC

ARPES: E-k spectrum

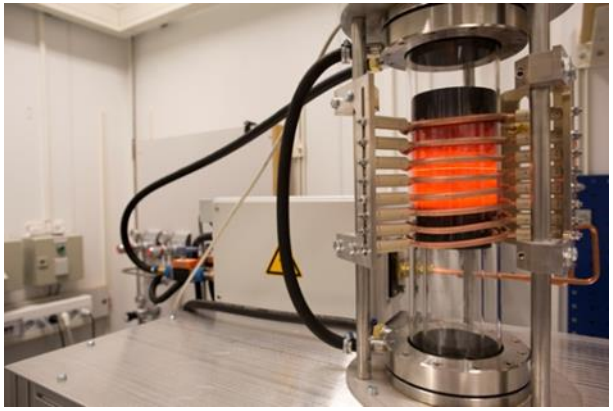


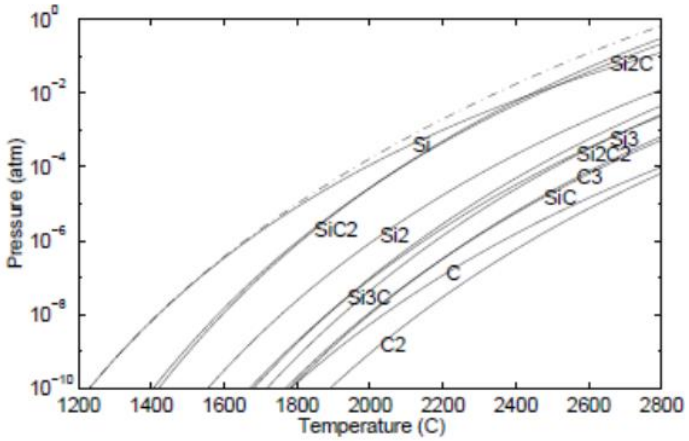
Controlled graphene synthesis

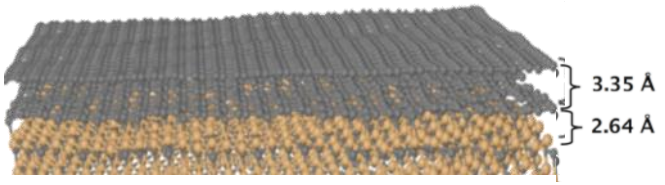


↑↑ T ↑↑

- Thermal decomposition of SiC at high temperature (T ~2000C) in Ar atmosphere





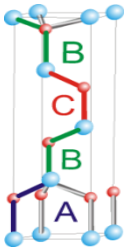


- G formation sensitive to T
- Thickness uniformity depends on substrate surface
- SiC wafer is not only a substrate, but also the precursor

=> careful control of process parameters needed

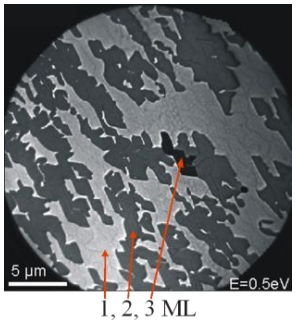
Graphene thickness uniformity

4H-SiC

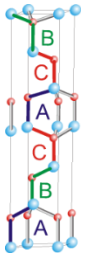


60%
1ML

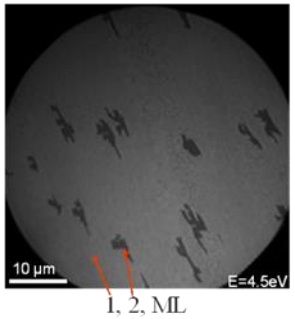
LEEM



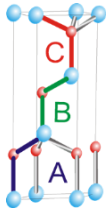
6H-SiC



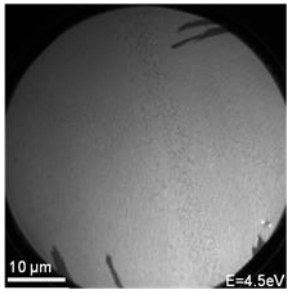
90%
1ML



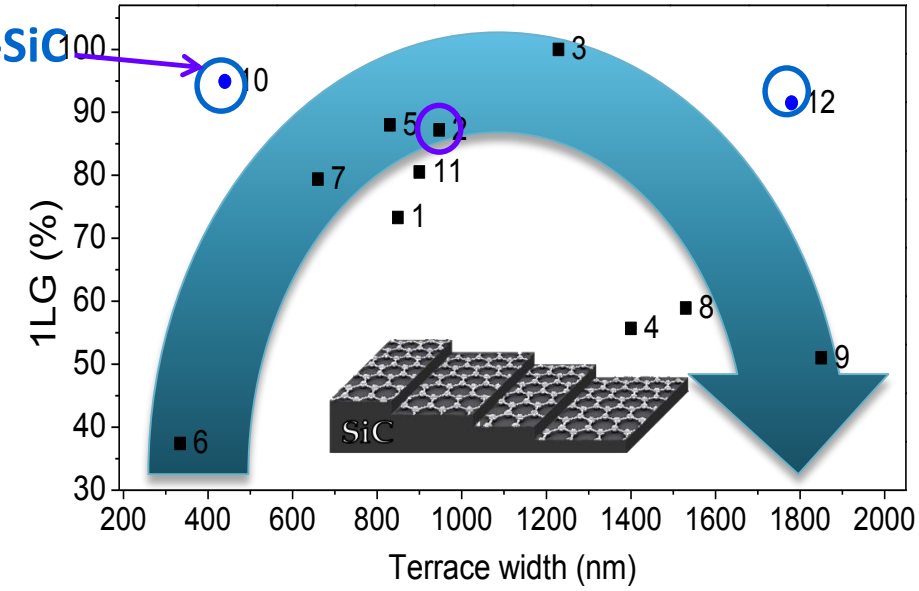
3C-SiC



98%
1ML



3C-SiC



SKPM

- **There is an optimal terrace width (TW) for 1ML graphene; 700nm 1200 >TW > 700 nm for hexagonal polytypes.**
- **Bilayer graphene growth starts at step edges; many step edges → many nucleation sites; Island growth in the absence of steps**
- **3C-SiC – higher 1LG % for lower terrace width , 1LG % independent of terrace width.**
- **3C-SiC is a preferable substrate, but a number of obstacles exist**

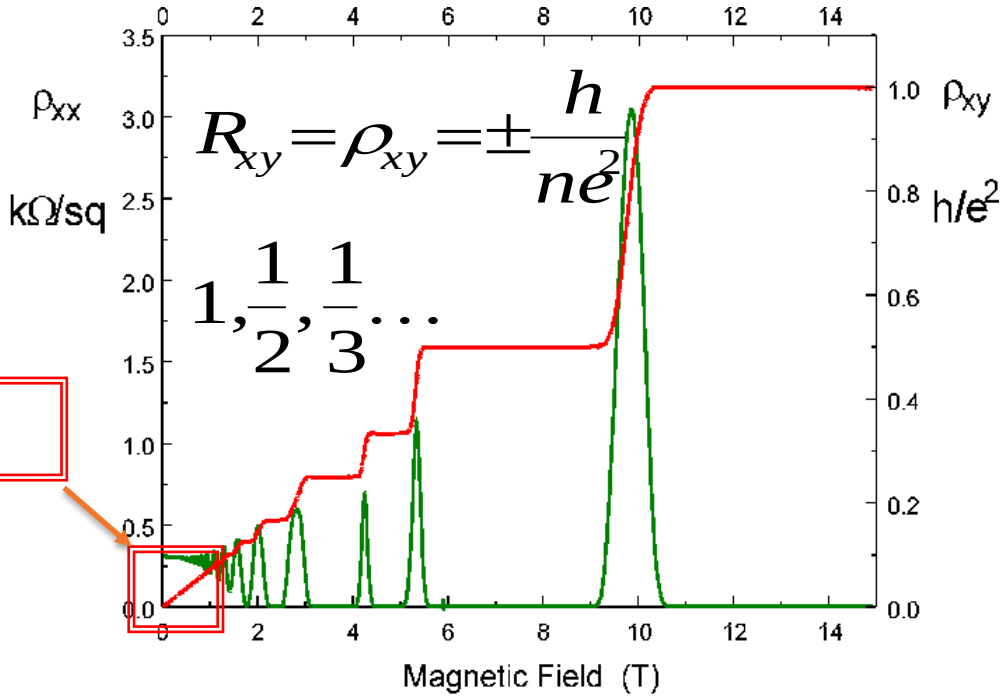
Yazdi G.R et al (2013) Carbon, 57, p. 477

Eriksson J. at al (2012) APL, 100 (24)

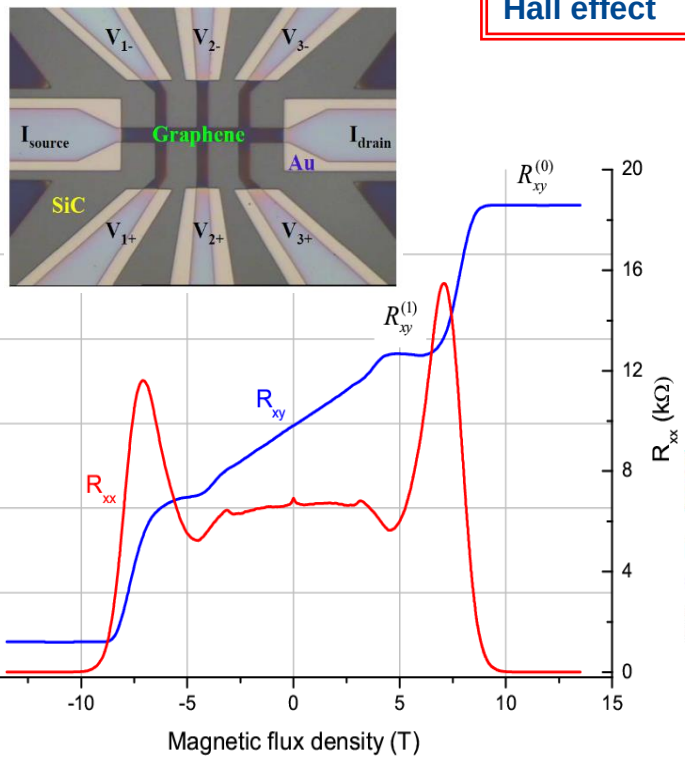
ML Graphene - QHE

Quantization of transverse (Hall) resistance in rational fractions of the resistance quantum and vanishing longitudinal resistance of 2DEG. *Von Klitzing, Dorda & Pepper, 1980*

Observable only in ML graphene



Classical Hall effect



$$R_K = h/e^2 = 25\,812.807\,557(18)\,\Omega$$


nature nanotechnology LETTERS

PUBLISHED ONLINE: 17 JANUARY 2010 | DOI: 10.1038/NNANO.2009.474

Towards a quantum resistance standard based on epitaxial graphene

Alexander Tzalenchuk[1]*, Samuel Lara-Avila[2], Alexei Kalaboukhov[2], Sara Paolillo[3], Mikael Syväjärvi[4], Rositza Yakimova[4], Olga Kazakova[1], T. J. B. M. Janssen[1], Vladimir Fal'ko[5] and Sergey Kubatkin[2]

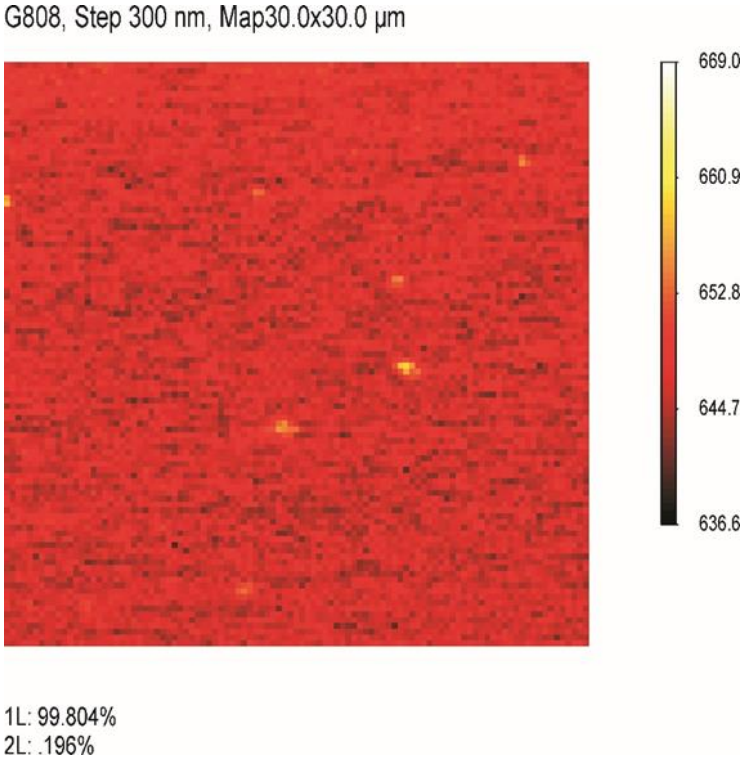
"We report a quantum Hall resistance quantization accuracy of three parts per billion in monolayer epitaxial graphene at 300 mK, four orders of magnitude better than previously reported."

ECHNOLOGY

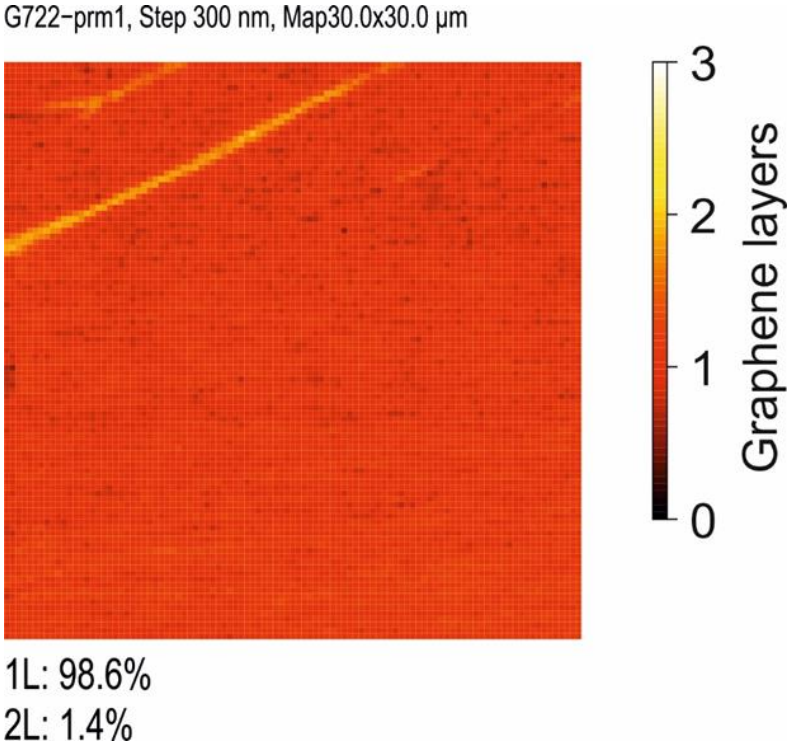
Towards sensor applications

- Graphene thickness uniformity improvement and sample size increase

7 x 7 mm^2



20 x 20 mm^2



Uniform 1LG leads to reproducible ultra-sensitive sensors

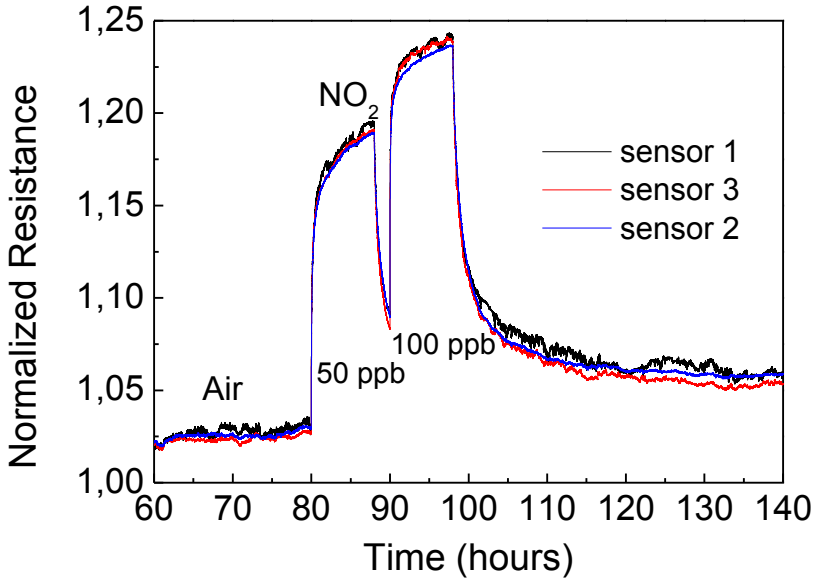
1LG is more sensitive to NOx than 2LG or MLG

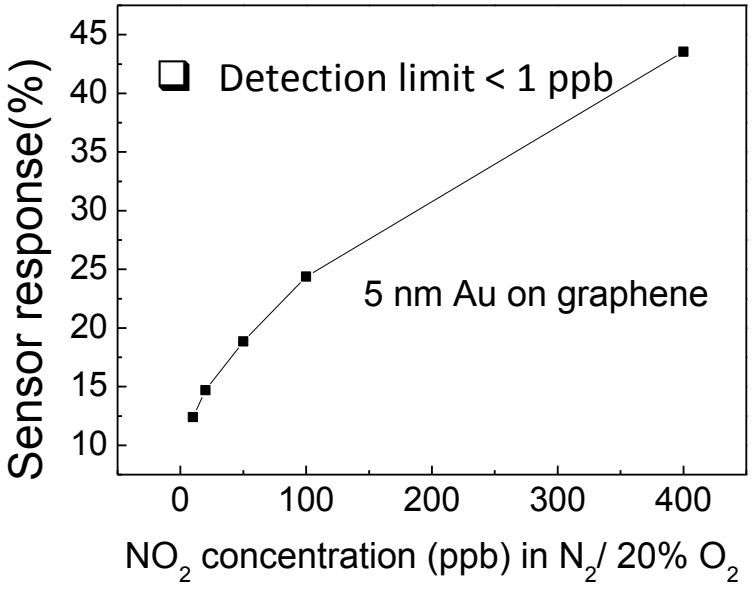
Uniform 1LG required for maximum sensitivity and reproducibility

Different sensors fabricated on 100% 1LG show identical response

Epitaxial graphene on SiC enables **highly reproducible** sensor fabrication

NO_2 response





NO_2 sensing interesting for:

- Emission control (few ppm)
- Air quality control (few ppb)

Air Qality: WHO limit levels for NO_2

- Hourly average < 100 ppb
- Yearly average < 20 ppb

Conclusion

- Graphene can be produced by different methods, in different amount and quality that are suited for different applications.
- Graphene epitaxially grown on SiC via thermal decomposition is the most suitable for electronic devices, including high sensitivity sensors, and can be fabricated on 4 inch-6 inch SiC wafers.
- Graphene has reached a maturity needed to process pilot devices.
- Beyond graphene research area has emerged within which hybrid layered structures can be engineered.

Acknowledgements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Thank you for your attention!