

# GRAPHENE PRODUCTION

*... towards the dream of a flatland*

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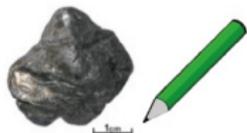


# Outline

- 1 Motivations and theoretical review
  - Introduction and motivations
  - Brief review of theoretical properties
- 2 Growth Methods and Techniques
  - Chemical Vapor Deposition
  - Epitaxial growth by thermal decomposition on SiC
  - C-Si Superlattices Synthesis
  - Graphene at I.N.Ri.M. and applications to Metrology
- 3 Conclusions

# Introduction and motivations

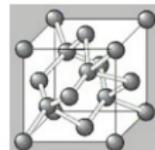
3D



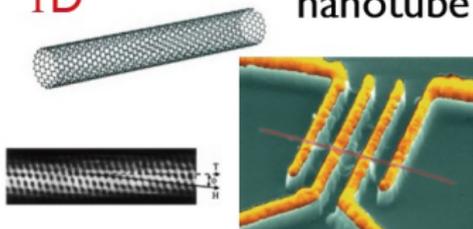
graphite



diamond



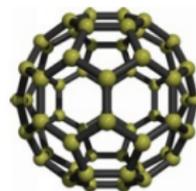
1D



nanotube

0D

fullerene



**2D:** does a single-layer of graphite exist ?

Before 2004 almost anyone (both theorists and experimentalists) was sceptic about the existence of a *truly 2D* (i.e. one atom thick) *system* (mainly because of atomic vibrations)

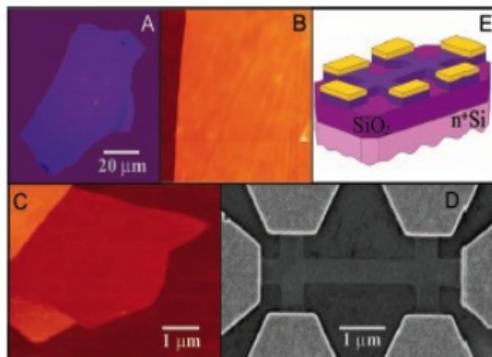
BUT

in 2004, a group from the University of Manchester succeeded in isolating **GRAPHENE** -a single-layer sheet of graphite- on an insulating substrate

## Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,<sup>1</sup> A. K. Geim,<sup>1\*</sup> S. V. Morozov,<sup>2</sup> D. Jiang,<sup>1</sup>  
Y. Zhang,<sup>1</sup> S. V. Dubonos,<sup>2</sup> I. V. Grigorieva,<sup>1</sup> A. A. Firsov<sup>2</sup>

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conduction bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to  $10^{13}$  per square centimeter and with room-temperature mobilities of  $\sim 10,000$  square centimeters per volt-second can be induced by applying gate voltage.



... and, this year, the leaders of that Research Group (*A. Geim* and *K. Novoselov*) have been awarded the Nobel Prize in Physics by the Royal Swedish Academy of Sciences



Photo: Sergeom,  
Wikimedia Commons

**Andre Geim**



Photo: University of  
Manchester, UK

**Konstantin  
Novoselov**

# Why graphene?

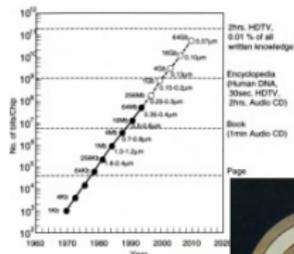
Because it exhibits peculiar properties:

- near ballistic-transport at room temperature
- high charge carriers mobility  $\mu \simeq 2 \cdot 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
- high Fermi velocity  $v_F \simeq c/300 \simeq 10^6 \text{ m/s}$
- a minimum conductivity  $\sigma_{\min} = 4e^2/(\pi h)$ , independent of impurity concentration, at the Dirac point
- a specific anomalous Integer and Fractional Quantum Hall Effect

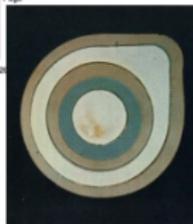


Optimal material for future nano-electronics and nano-devices  
(transistors, spin valves, etc.)  
A promising Si substitute

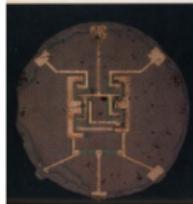
# The development of Si technology - Moore's Law



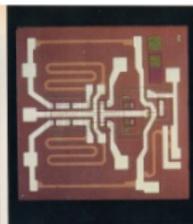
1959  
(1)



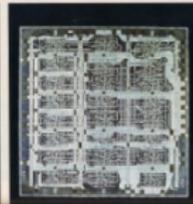
1961  
(4)



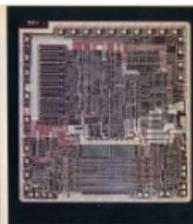
1964 (5)



1968 (180)

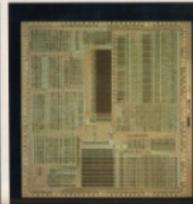


1978



LSI

1985



VLSI

$10^6$   
ULSI

# The potential substitutes of Si

Typical values for c-Si: indirect gap, bandgap = 1.1242 eV,  $\mu \sim 500 - 1200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ,  $\rho = 10^5 \text{ }\Omega\text{cm}$ ,  
 thermal conductivity =  $1.48 \text{ Wcm}^{-1}\text{K}^{-1}$

	YES	NO
<b>GaAs</b>	Direct gap $\mu \sim 4000 - 9000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ $\rho = 10^9 \text{ }\Omega\text{cm}$	Technology
<b>SiC</b>	Bandgap $\sim 2\text{-}3 \text{ eV}$ High temperature operation	Price ( $> 400 \text{ $/wafer}$ )
<b>a-Si:H</b>	Direct gap Bandgap = 1.75 eV High absorption coefficient Cheap	Degradation
<b>Diamond</b>	Bandgap = 5.47 eV $\mu = 2800 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ Thermal conductivity = $25 \text{ Wcm}^{-1}\text{K}^{-1}$	Price Technology
<b>Graphene</b>	Direct gap $\mu \sim 2 \cdot 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ $v_F \simeq 10^6 \text{ m/s}$ Electric-Field Effect at GHz frequencies Electron concentration $\sim 10^{13}/\text{cm}^2$	?? (to be discussed now)

Graphene is NOT the first material that "tries" to supply silicon.

There are a lot of examples of materials with transport properties better than Si: Amorphous-Si, SiC, GaAs, diamond, ...  
All of them failed to be good competitors of Si-based commercial devices

### A CHALLENGE ARISES

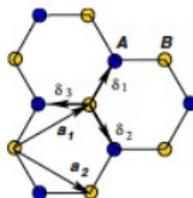
**Produce graphene on large-scale area substrates using high reproducible techniques (without affecting its remarkable properties)**

only in this way graphene can be thought of as a real Si substitute

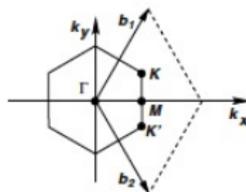
## Brief review of theoretical properties

- Graphene is the 2D allotropic form of carbon (from which the other  $dD$  -  $d = 0, 1, 3$ - allotropic forms can be derived)
- Carbon atoms (electronic configuration  $1s^2 2s^2 2p^2$ ) in graphene are arranged in a honeycomb lattice (with carbon-carbon distance  $a \simeq 1.42 \text{ \AA}$ ) because of  $sp^2$  hybridization of the  $n = 2$  orbitals
- 3 of the 4 valence electrons per atom fill this hybrid orbitals and are involved in  $\sigma$ -bond (thus explaining the robustness of graphene lattice structure) - the electron left in  $2p_z$  orbital is responsible for  $\pi$ -bond and conductivity in graphene

- The hexagonal lattice is equivalent to two inter-penetrating triangular Bravais lattices  $\Rightarrow$  the basis of the crystal structure contains 2 inequivalent carbon atoms A and B



- A and B correspond to 2 *special* points in the first Brillouin zone, called **Dirac points**:  $\mathbf{K}$  and  $\mathbf{K}'$



- The tight-binding Hamiltonian for  $\pi$ -electrons in graphene is given by (considering only nearest-neighbors hopping and  $\hbar = 1$ ):

$$\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} \left( \hat{a}_{\sigma,i}^\dagger \hat{b}_{\sigma,j} + \hat{b}_{\sigma,j}^\dagger \hat{a}_{\sigma,i} \right)$$

where  $t \approx 2.8$  eV is the hopping energy,  $\langle i, j \rangle$  are nearest-neighbors sites and  $\hat{a}_{\sigma,i}$  ( $\hat{a}_{\sigma,i}^\dagger$ ) annihilates (creates) an electron of spin  $\sigma$  ( $\sigma = \uparrow, \downarrow$ ) at position  $\mathbf{R}_i$  on sublattice A (an equivalent definition holds for  $\hat{b}_{\sigma,j}$ ,  $\hat{b}_{\sigma,j}^\dagger$  on sublattice B)

- The energy bands deriving from it are<sup>1</sup>:

$$E_{\pm}(\mathbf{k}) = \pm \sqrt{3 + f(\mathbf{k})}$$

with  $f(\mathbf{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right)$

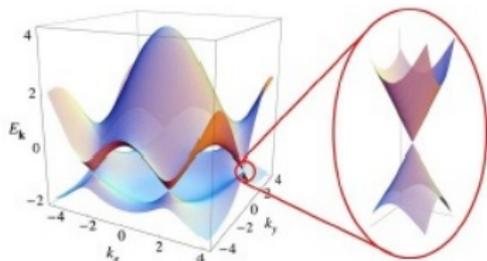
<sup>1</sup>Wallace, *Phys. Rev.* **71**, 622(1947); Castro Neto et al., *Rev. Mod. Phys.* **81**, 109(2009)

- Expanding the dispersion relation around the Dirac points we obtain the following fundamental **linear** relation ( $\mathbf{k} = \mathbf{K} + \mathbf{q}$  with  $\|\mathbf{q}\| \ll \|\mathbf{K}\|$ ):

$$E_{\pm \mathbf{q}} \approx \pm v_F \|\mathbf{q}\| + O \left[ (\|\mathbf{q}\| / \|\mathbf{K}\|)^2 \right]$$

with  $v_F = 3ta/2 \simeq c/300 \simeq 10^6$  m/s *independent* from momentum or energy (as opposed to the behaviour in metals)

- The bands meet each other at the Dirac points in a linear way  
 $\Rightarrow$  graphene is a zero-gap semiconductor



- The same spectrum is obtained diagonalizing the following 2D Dirac Hamiltonian for massless fermions (holding around  $\mathbf{K}$  and  $\mathbf{K}'$ ):

$$\hat{H}_{\mathbf{K}/\mathbf{K}'} = \pm v_F (\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{k}})$$

where  $\hat{\mathbf{k}} = -i\nabla$  is the momentum operator and  $\hat{\boldsymbol{\sigma}} = (\sigma_x, \sigma_y)$  are Pauli matrices representing pseudo-spin



This fact:

- 1 makes the electronic behaviour of graphene quite unique (electrons behave like massless Dirac fermions with  $v \neq c$ )
- 2 explains the remarkable properties of this material
- 3 makes possible to investigate relativistic effects in condensed-matter systems

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## Main production methods of graphene

A lot of techniques have been developed since 2004 up to now:

- ▶ micromechanical exfoliation of graphite, by using adhesive tape
- ▶ liquid-phase chemical exfoliation
- ▶ carbon nanotubes unzipping
- ▶ Chemical Vapor Deposition, by thermal decomposition of a Carbon precursor, on a catalyst substrate
- ▶ epitaxial growth, by thermal decomposition, on SiC (or on Ni/SiC, its improved version)
- ▶ C-Si Superlattices synthesis (until now developed only in a theoretical framework)

Substrate	Growth condition (gas, T, exposure)	Experimental technique	Edges	Comment ( $a_c = 0.245$ nm)					
Metals	Pt(111)	Benzene ( $C_6H_6$ ), T = 1000 K. 1-5L: non-graphitic film; >5L: full coverage	STM, LEED, AES	Hexagonal arrangement beyond edges					
		Ethylene ( $C_2H_4$ ), T = 800 K. 5L exposure (if T > 1000 K: graphitic island)	LEED, STM	No clear hexagonal arrangement; No growth over the edges	$a_{Pt} = 0.278$ nm $a_{Moire} = 2.2$ nm				
		HOPG on 1ML graphitic film	AFM, PCM	Continuous film from upper terrace to lower terrace	0.738 nm < a < 2.1 nm				
	Pt(755)	Chemical vapor deposition	LEED, XPS, ARUPS	Formation of large sheet					
	Ni(111)	Chemical vapor deposition	LEED, AES vibrational spectro		Evidence of Fuchs-Kliewer phonons				
	Ni(110)	Carbon monoxide (CO), T = 600 K. 90000L exposure	SEELFS		Graphitic layer on [110] faces				
	Ru(001)	Ethylene ( $C_2H_4$ ), T = 1270 K. T-dependent solubility gradient	LEEM, SEM, $\mu$ -Raman, AES, electrical	No growth "uphill" over the edges	$a_{Ru} = 0.271$ nm a = 0.145 nm (1st layer)				
Carbides	nH-SiC (n = 1, 2, ...)	Si sublimation, T ~ 1670 K.	LEED, X-ray, STM	Formation of large continuous sheet over terraces	Growth on each facet				
						TiC(111)	Chemical Vapor Deposition on faceted surface, T = 1770 K	XPS, ARUPS, LEED	No edge-localized state
						TiC(410)	Chemical Vapor Deposition on platelets surface, T = 1770 K	XPS, ARUPS, LEED	No growth over the edges
						TaC(111)	Ethylene ( $C_2H_4$ ), T = 1570 K. 10000L exposure, T = 1270 K	AES, LEED, STM	Coverage is interrupted at terrace interface

	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed, SiO <sub>2</sub> thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (not suitable for large-scale production)
Epitaxial growth	Most even films (of any method) Large scale area	Difficult control of morphology and adsorption energy High-temperature process
Graphene oxide	Straightforward up-scaling Versatile handling of the suspension Rapid process	Fragile stability of the colloidal dispersion Reduction to graphene is only partial

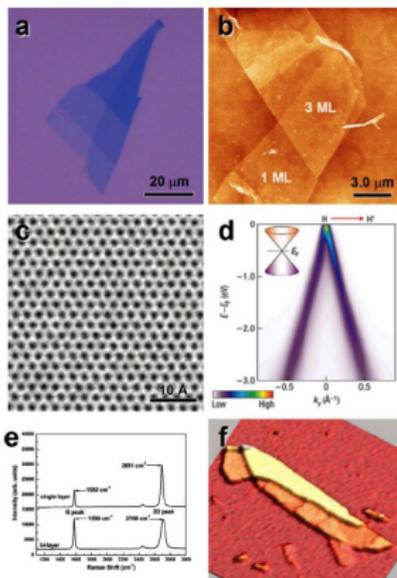
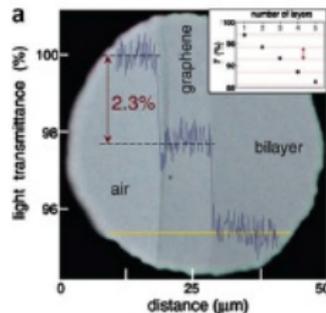
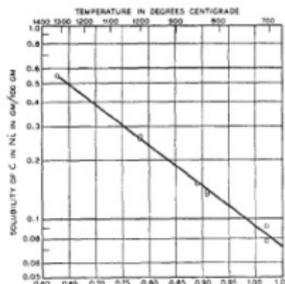


Fig. 3 - Major techniques for graphene characterization. (a) optical microscopy, (b) atomic force microscopy (AFM), (c) transmission electron microscopy (TEM), (d) angle-resolved photoemission spectroscopy (ARPES), (e) Raman scattering and (f) Rayleigh scattering. Adapted with permission from (a) [23], copyright 2008 American Chemical Society, (b) [27], MacMillan Publishers Ltd: Nature Physics, copyright 2006, (c) [41], copyright 2007 American Chemical Society, (f) [42], copyright 2007 American Chemical Society.

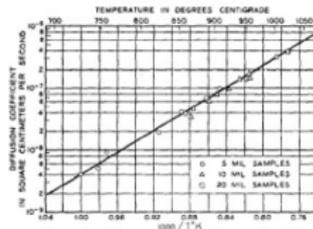


# CVD Method

- CVD method is known from '70s and it's based on C-atoms solid solubility in the metallic catalyst used as substrate (usually deposited over a SiO<sub>2</sub>/Si sample<sup>2</sup>)



$$\ln S = 2.480 - 4,880/T$$



$$\ln D = 0.909 - (20,200/T)$$

- Thermal decomposition of a hydrocarbon (usually methane or ethylene, although acetylene -allowing for lower temperature synthesis on Ni- has been recently proposed<sup>3</sup>) or carbon oxide precursor provides C-atoms that freely diffuse inside the catalyst

<sup>2</sup>Lander et al., *Jour. Appl. Phys.* **23**, 1305(1952)

<sup>3</sup>Nandamuri et al., *Nanotech.* **21**, 145604(2010)

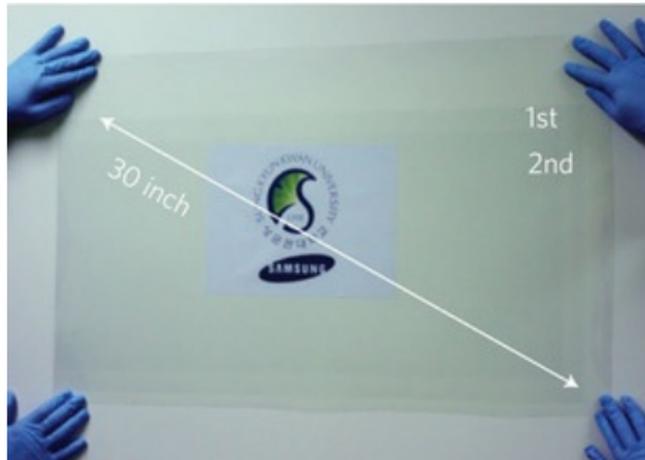
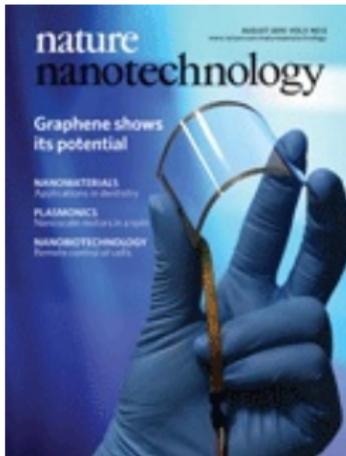
- During the subsequent cooling-down process of the sample, C-atoms exceeding their solid solubility in the catalyst start to segregate on the sample surface forming graphene
- Graphene can be transferred to other substrates using chemical etching (typically using HCl solutions)

It's important that **graphene grows** during the **cooling-down** process and **not** during the **CVD heating** (to avoid formation of bad quality graphene)

The use of CVD method applied to many different catalysts has been reported in literature:

- 1  $Ru(0\ 0\ 0\ 1)$ : Martocchia et al., *Phys. Rev. Lett.* **101**, 126102(2008), Sutter et al., *Nat. Mater.* **7**, 406(2008)
- 2  $Pt(1\ 1\ 1)$ : Sasaki et al., *Phys. Rev. B* **61**, 15653(2000), Nakagoe et al., *Surf. Sci.* **514**, 414(2002), Starr et al., *Surf. Sci.* **600**, 2688(2006)
- 3  $Ir(1\ 1\ 1)$ : Coraux et al., *Nano Lett.* **8**, 565(2008)
- 4  $Co(0\ 0\ 0\ 1)$ : Vaari et al., *Catal. Lett.* **44**, 43(1997)
- 5  $Ni(1\ 1\ 1)$ : Gamo et al., *Surf. Sci.* **374**, 61(1997), Tanaka et al., *Surf. Rev. Lett.* **10**, 697(2003), Obratsov et al., *Carbon* **45**, 2017(2007), Reina et al., *Nano Lett.* **9**, 30(2009), Kim et al., *Nature* **457**, 706(2009), Nandamuri et al., *Nanotech.* **21**, 145604(2010), Liu et al., *Thin Sol. Films* **518**, S128(2010)

... and, on August 2010, graphene conquered the cover of *Nature Nanotechnology* thanks to a Korean Research Group<sup>4</sup> that succeeded in producing a 30-inch  $\approx 75$  cm sheet by means of CVD growth on Copper sample and roll-to-roll transfer on a target substrate



<sup>4</sup>Bae et al., *Nature Nanotech.* **5**, 574(2010)

## An example: graphene on Ni/SiO<sub>2</sub>/Si substrate

3 key parameters control *growth* and *number* of graphene layers:

- ★ CVD growth temperature;
- ★ growth-exposure time;
- ★ post-growth cooling-down rate

recent experiments show that the last one is the **most important** factor in determining the final quality of the layer; the product of the first two parameters determines the supply rate of C-atoms in Ni

**CHALLENGE:** optimize the parameters for a fixed experimental setup

We report the results of a recent experiment described in “Liu et al., *Thin Sol. Films* **518**, S128(2010)” - it’s a good example of a standard experimental setup and procedure for a CVD growth on Ni

## TECHNICAL DETAILS

### ▪ Ni film deposition and annealing

- Substrate: Si/SiO<sub>2</sub> wafer of 1-in. diameter
- Film thickness: 500 nm
- Annealing temperature: 1000 °C
- Annealing pressure: 200 Torr
- Annealing time: 30 to 60 min
- Annealing gas flow: 200 sccm H<sub>2</sub> + 400 sccm Ar

### ▪ CVD growth and post-growth cooling

- Growth pressure: 200 Torr
- Growth gas flow: 500 sccm H<sub>2</sub> + 50 sccm of 5% diluted CH<sub>4</sub> in Ar
- Post-growth cooling gas flow: 500 sccm H<sub>2</sub> + 2000 sccm Ar

a longer Ni-annealing time enhances the crystallization degree and the size of Ni grains

## RESULTS

Best choice of the parameters:

- growth temperature: 900 °C
- growth time: 50 s
- cooling rate: 25 °C/min (fastest possible in an hot-wall system as the one used in this experiment - *presumably BETTER if faster*)

Average dimension of graphene flakes:  $100 \mu\text{m}^2$  → the **usual size** obtained by means of this method is in fact **1 ~ 20  $\mu\text{m}$**

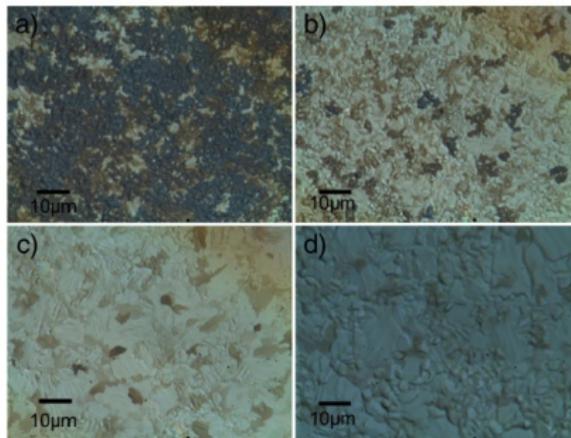
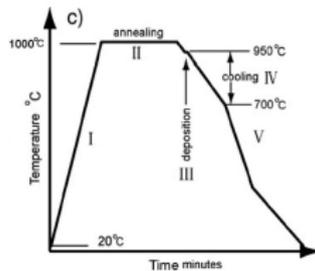
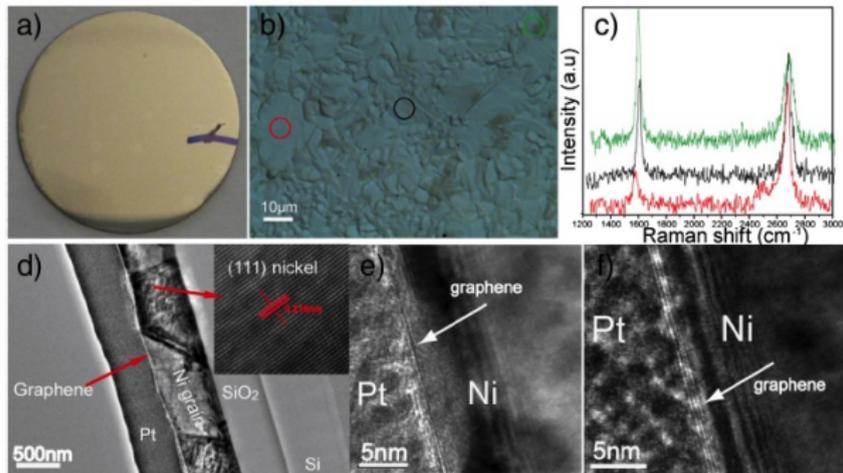
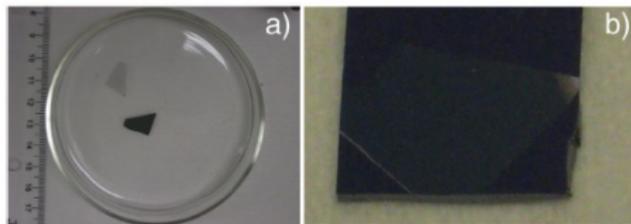


Fig. 5. Optical micrographs of samples grown with different cooling rate: a) 7 °C/min, b) 10 °C/min, c) 17 °C/min, and d) 25 °C/min. The temperature range of controlled cooling is from 950 °C to 700 °C inside the CVD system, which is followed by exposing the sample to room ambient with rapid cooling from 700 °C to 300 °C in 5 min. Annealing condition: 1000 °C, H<sub>2</sub>/Ar = 200:400 sccm, 30 min, 200 Torr. Decomposition condition: 950 °C, dilute CH<sub>4</sub>, 5% in Ar with 500 sccm H<sub>2</sub> at 200 Torr.



**Fig. 2.** a) The optical digital image of an 1-in. diameter sample after graphene growth. b) Optical micrograph of the nickel surface after graphene growth c) The Raman spectra corresponding to the three circles in b). d) Low resolution XTEM of graphene on nickel with HRTEM shown in the inset. XTEM images of a single layer graphene region and a three-layer graphene region are shown in e) and f), respectively.



## ADVANTAGES (same for all metallic catalysts employed as substrates)

- easy transfer of graphene to other substrates (a transfer-independent low temperature  $\sim 650$  °C- CVD growth on patterned Fe films has also been proposed<sup>5</sup>, in order to obtain top-gated Field Effect graphene-based Transistors);
- not very high temperatures (i.e.  $\sim 1000$  °C) needed during the process;
- possibility of growing quite large single-layer graphene flakes with high reproducibility;
- possibility of a direct optical investigation of the sample during the growth process.

<sup>5</sup>Kondo et al., *Appl. Phys. Exp.* **3**, 025102(2010)

## DISADVANTAGES

- interfacial interactions and presence of substrate changing graphene properties w.r.t. the free-standing case (in particular electronic and magnetic properties: induced magnetism of C-atoms of graphene layer grown over Ni has been experimentally observed<sup>6</sup> - this effect is less pronounced for graphene grown on Ir(1 1 1) and is expected to be more pronounced on Fe/Ni(1 1 1) surfaces<sup>7</sup>);
- best reported sheet resistance of graphene grown on Ni ( $\sim 280 \Omega\text{cm}^{-2}$ )<sup>8</sup> not as low as in commercial ITO transparent transistors ( $\lesssim 100 \Omega\text{cm}^{-2}$ ) - a great improvement has been observed in graphene sheet grown on Cu ( $\sim 125 \Omega\text{cm}^{-2}$ )<sup>9</sup>;
- difficulty to obtain truly single-layer graphene flakes.

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<sup>6</sup>Weser et al., *Appl. Phys. Lett.* **96**, 012504(2010)

<sup>7</sup>a theoretical study of structural and magnetic properties of the graphene/Fe/Ni(1 1 1) system, based upon DFT *ab initio* calculations within the GGA-PBE framework, has been made by Sun et al., *Jour. Phys. D* **43**, 385002(2010)

<sup>8</sup>Kim et al., *Nature* **457**, 706(2009)

<sup>9</sup>Bae et al., *Nature Nanotech.* **5**, 574(2010)

## Brief digression: the role of interfacial interactions

- The presence of the substrate changes substantially the structural and magnetic properties of graphene → need for a transfer of graphene in order to plenty exploit its properties
- In particular interactions' strength and graphene electronic properties depend on metallic substrate: the last one changes graphene  $E_F$  level or, equivalently, graphene doping level ( $p$ - or  $n$ -type). Moreover, different bonding distances  $d$  between graphene and metallic substrate have been theoretically evaluated and experimentally measured:
  - Ni:  $d \approx 2.01 \text{ \AA}$
  - Pt:  $d \approx 3.31 \text{ \AA}$  (for  $\theta = 30^\circ$ )
  - Ru:  $2.13 \text{ \AA} \leq d \leq 3.78 \text{ \AA}$  (surface corrugation)

As an example, a dependence between the thermoelectric potential (i.e. the offset voltage  $V_t(I = 0)$  observed in  $I - V$  curves of graphene/metal system) and the substrate properties has been reported<sup>10</sup>

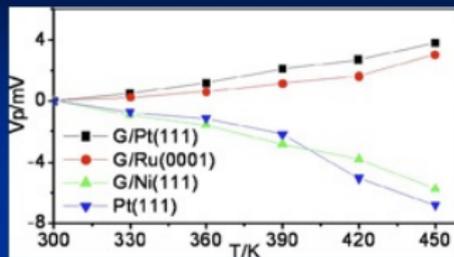


the values of the Seebeck coefficient  $S \equiv V_t/\Delta T$  are different for free-standing and on metallic substrate grown graphene

the largest value of  $S$  for free-standing in-plane graphene measured up to now and reported in “Dragoman et al., *Appl. Phys. Lett.* **91**, 203116(2007)”, is:  
 $S \sim 30 \text{ mV/K}$

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<sup>10</sup>Gao et al., *Appl. Phys. Lett.* **96**, 053109(2010)



Metal substrate	Ni	Pt	Ru
Properties			
<b>Sign of <math>V_t</math></b>	Negative	Positive	Top: positive Bottom: negative
<b>Electron flux</b>	From Ni to graphene	From graphene to Pt	From top to bottom graphene region (surface corrugation)
<b>Graphene doping type</b>	<i>n</i> - type	<i>p</i> - type	Top: <i>p</i> - type Bottom: <i>n</i> - type
<b><math>E_F</math> level</b>	Above Dirac point	Below Dirac point	Top: above Dirac point Bottom: below Dirac point

## Epitaxial growth by thermal decomposition on SiC

- The Epitaxial Growth of graphene on SiC(0 0 0 1) is the most used, first developed and best known method in order to produce graphene<sup>11</sup>
- Graphene flakes grow on top of a SiC substrate heated up to an annealing temperature  $T_a > 1000$  °C: at  $T_a$  surface Si coverage start to decrease  $\Rightarrow$  surface changes from Si-rich to C-rich
- Graphene do NOT grow directly on top of the bulk-truncated SiC(0 0 0 1) surface BUT on a  $6\sqrt{3} \times 6\sqrt{3}R30^\circ$  reconstructed buffer layer

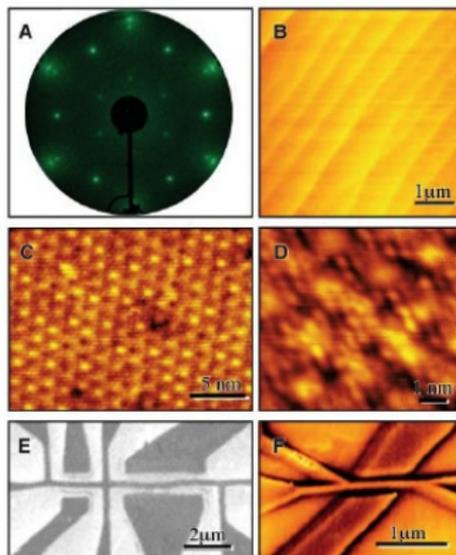
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<sup>11</sup>Berger et al., *Jour. Phys. Chem. B* **108**, 19912(2004), Berger et al., *Science* **312**, 1191(2006), de Heer et al., *Sol. State Commun.* **143**, 92(2007), for a theoretical study Kageshima et al., *Appl. Phys. Exp.* **2**, 065502(2009)

## Quality and number of layers controlled by:

- 1 time used for the heating process
- 2 heating temperature
- 3 SiC face used for the growth (Si-truncated  $\Leftrightarrow$  several layers, C-truncated  $\Leftrightarrow$  few layers)

**Fig. 1.** Production and characterization of EG. (A) LEED pattern (71 eV) of three monolayers of EG on 4H-SiC(0001) (C-terminated face). The outermost hexagon (spots aligned on the vertical) is graphene  $1 \times 1$  diffraction. Bright sixfold spots aligned on the horizontal are SiC  $1 \times 1$ . The smallest hexagon is the result of a  $\sqrt{3} \times \sqrt{3}$  reconstruction of the interfacial layer, as are the spots lying just inside the graphene pattern. Graphene thickness is determined via Auger spectroscopy (attenuation of Si peaks). (B) AFM image of graphitized 4H-SiC, showing extended terraces. STM studies indicate that the graphite is continuous over the steps (1). (C) STM image of one monolayer of EG on SiC(0001). Tunneling conditions (tip bias  $-0.8$  V, current  $100$  pA) preferentially image structure beneath the graphene layer. Two interface corrugations are apparent, with periods  $6 \times 6$  ( $1.8$ -nm triangular superlattice) and  $\sqrt{3} \times \sqrt{3}$  (smaller spots with  $0.54$ -nm spacing) relative to the SiC surface unit cell. (D) STM image of interface reconstruction beneath one monolayer of graphene on SiC(0001) obtained after lithography. General features are as seen in (C). (E) SEM of patterned EG. Dark regions are the EG (still coated with electron-beam resist). (F) EFM of another patterned EG sample, showing a horizontal ribbon (bright contrast) with tapered voltage contacts left and right, which is flanked by diagonally oriented side gates above and below the ribbon. Contrast is obtained through electrostatic forces between the probe and the graphene structure to which potentials are applied, thus allowing functioning devices to be measured.



## PROBLEMS

- graphene difficult to transfer (strong cohesive strength and high chemical stability of graphene/SiC structures)
- high temperatures needed for the process ( $\sim 1300$  °C in UHV conditions,  $\sim 1650$  °C in 900 mbar-Ar atmosphere)
- strong metallic character shown by graphene (due to an heavily doping from the substrate)



*Better to deposit a thin metallic film over SiC samples (allowing lower graphitization temperature and higher possibility of transfer)*

## Example: EG on Ni/SiC

We report the results of the experiment described in “Juang et al., *Carbon* **47**, 2026(2009)”

- 1 rapid heating up to  $T_r \approx 750 \text{ }^\circ\text{C}$
- 2 formation of Nickel Silicide/Carbon mixed solid phase and diffusion of C atoms inside Ni bulk
- 3 **graphitization during the cooling-down process**

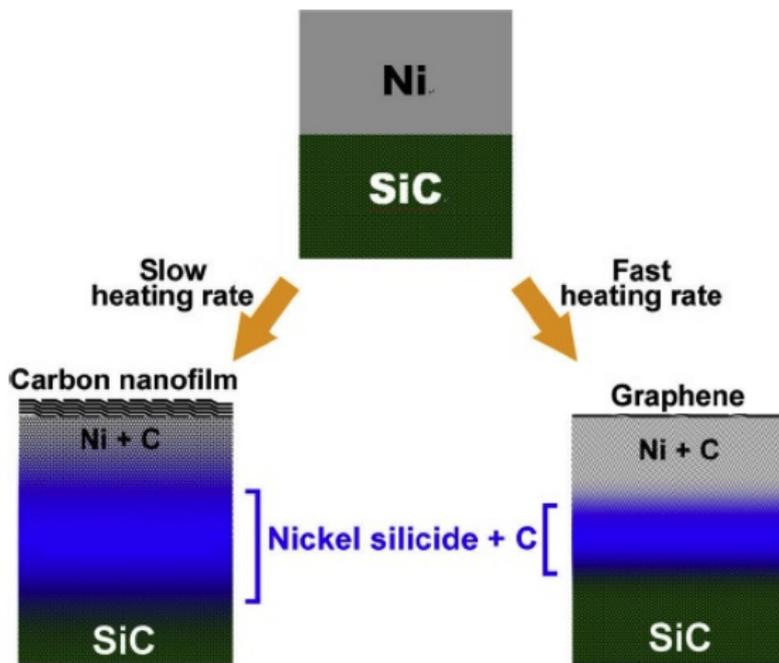
▪ Ni film deposition and rapid heating

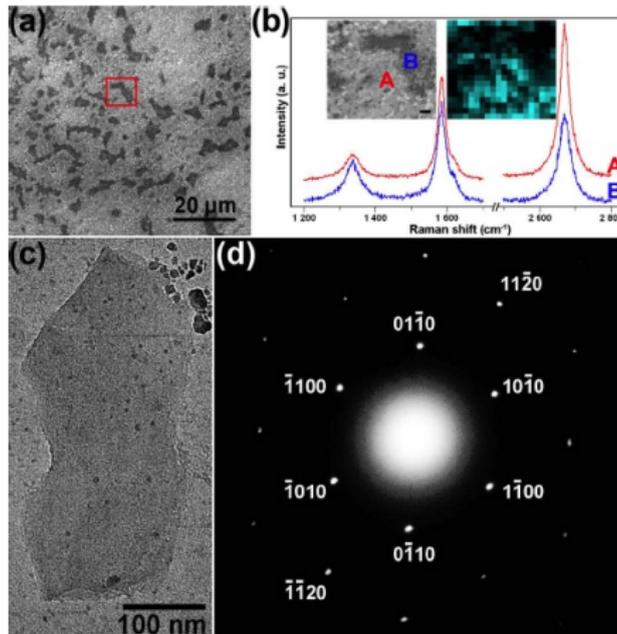
- Substrate: single-crystalline 6H-SiC(0 0 0 1) or 3C-SiC coated Si
- Film thickness: 200 nm (patterned or non-patterned)
- Heating rate: 17 °C/s or 25 °C/s → to be optimized
- Heating process pressure:  $10^{-7}$  Torr

▪ Graphene growth and post-growth cooling

- Process temperature for mixed  $\text{Ni}_2\text{Si}/\text{C}$  mixed phase formation: 750 °C
- Post-growth cooling rate: initially 10 - 20 °C/s (obtained switching off the heater)

# The key parameter: **HEATING RATE**

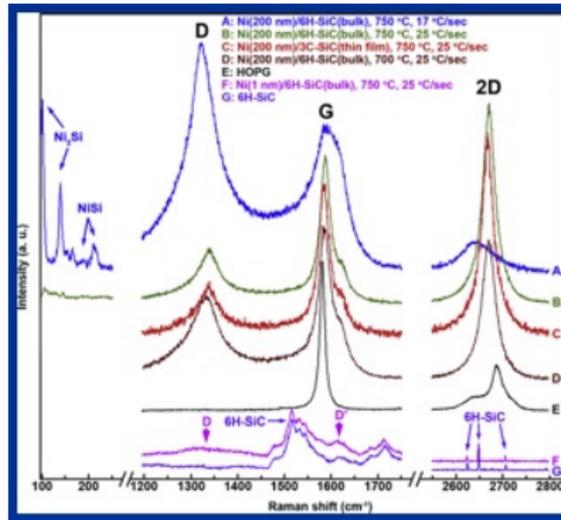




## RESULTS

Average dimension of graphene flakes:  $\lesssim 1 \text{ mm}$

## Critical comparison of Raman spectra from different samples:



- Comparison of A and B samples: FASTER HEATING RATE improves crystalline size and single-layer nature
- Comparison of A or F and B samples: Ni rich supporting layer necessary for synthesis of layers with higher graphitization degree → Ni<sub>2</sub>Si layers NOT helping in graphene synthesis
- Comparison of B and C samples: graphene synthesis process has NO SELECTIVITY for the type of SiC substrate

## ADVANTAGES

- possibility of obtaining graphene flakes larger than in CVD method;
- increased possibilities of graphene transfer w.r.t. EG on SiC;
- not so high temperatures needed during the process;
- freedom of choosing SiC substrate (single-crystalline 6H-SiC or 3C-SiC coated Si).

## DISADVANTAGES

- interfacial interactions and presence of substrate changing graphene properties w.r.t. the free-standing case (problem reduced in the case of simple SiC substrate);
- substrate quite expensive;
- difficulty in obtaining truly single-layer and good quality graphene domains.

## C-Si Superlattices Synthesis

- Superlattices are man-made periodic solid structure (proposed in '70s<sup>12</sup>) exhibiting unique properties
- Graphene/Silicon (C-Si) superlattices could be synthesized *stacking Si and graphene layers on top of each other*, by means of the *Molecular Beam Epitaxy (MBE)* technique  $\Rightarrow$  this type of growth improves the precision of the method
- This kind of superlattice can both preserve intrinsic properties of pristine graphene and be enough rigid for electronic device applications

*The structure has been only theoretically modelled<sup>13</sup> using the DFT/LDA framework*

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<sup>12</sup>Esaki et al., *IBM Res. Dev.* **14**, 61(1970)

<sup>13</sup>Zhang et al., *Nanoscale Res. Lett.* **5**, 805(2010)

## STRUCTURAL PROPERTIES

- 1 Chemical formula of the superlattice:  $\text{SiC}_2 \Rightarrow$  Si atoms sit at the hollow site of graphene in an equilateral triangular lattice (configuration of highest symmetry and lowest mismatch between in-plane lattice constants possible)

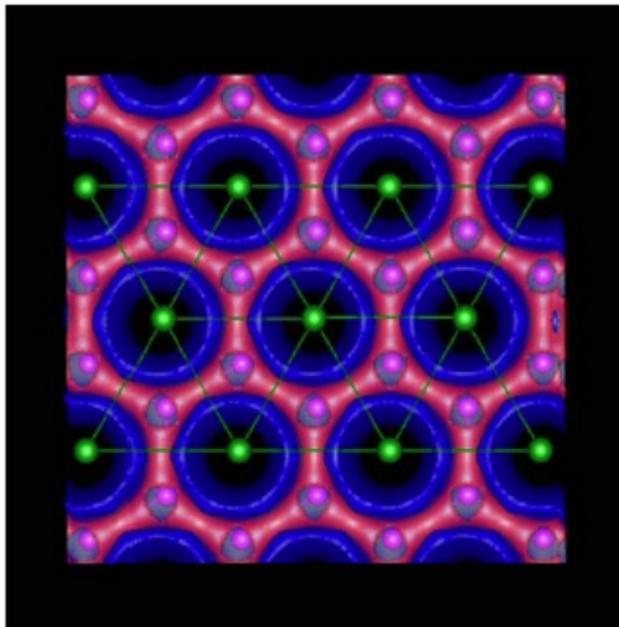
$$a_{\text{Si}} = 2.4271 \text{ \AA} \quad (a_{\text{AB}} = 2.4395 \text{ \AA} \text{ and } a_{\text{AA}} = 2.43927 \text{ \AA})$$

- 2  $a_{\text{gr}} = 2.43935 \text{ \AA}$  (mismatch: 0.5%)

$$a_{\text{gr/Si}} = 2.4363 \text{ \AA}$$

- 3  $c_{\text{gr/Si}} = 7.2662 \text{ \AA}$  ( $c_{\text{AB}} = 6.6589 \text{ \AA}$  and  $c_{\text{AA}} = 7.2324 \text{ \AA}$ )

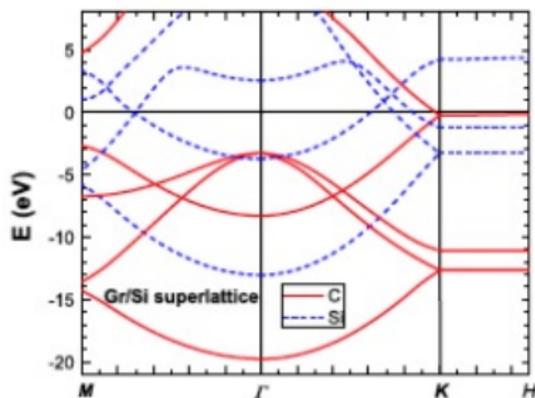
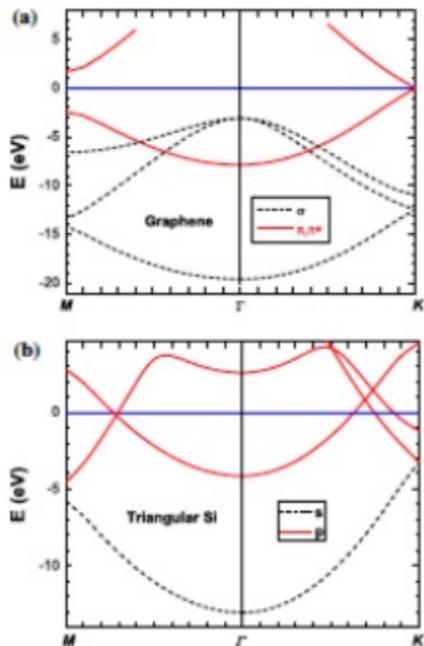
- 4 binding energy of the superlattice:  $E_{\text{b}} = 35.1 \text{ meV/atom}$  (stronger than in AB graphite  $-E_{\text{b}} = 24.4 \text{ meV/atom}$ - and AA graphite  $-E_{\text{b}} = 15.0 \text{ meV/atom}$ )



## ELECTRONIC PROPERTIES

There are 3 important features in the band structure of the superlattice:

- 1 dispersion curves can be divided into 2 groups - from graphene- and from Si-sheet  $\Rightarrow$  relatively weak coupling
- 2 dispersion curves of graphene-type are *still linear near the Dirac point  $\mathbf{K}$*  as in pristine graphene
- 3  $E_F$  level moves upward of 234 meV w.r.t. the Dirac point and downward w.r.t. the Si Fermi level  $\Rightarrow$  electron transfer from Si to graphene ( $n_{\text{el.transf.}} \sim 4 \times 10^{-3}$  e/Si)



## CONCLUSIONS

- C-Si superlattices show enough mechanical robustness to match the standards of nano-electronics (more than IGCs)
- linear electronic band structure near Dirac points still present
- no need for graphene transfer (as far as nano-electronic applications are concerned)
- C-Si superlattices show unique properties both in layer thickness and chemical bonding
- layer by layer growth makes possible to replace Si sheet with other species (BN, SiO<sub>2</sub>, P, ...) and to improve the precision of the method and the quality of graphene sheet

## CHALLENGE

Prepare it experimentally and compare the results

## Graphene at I.N.Ri.M. - Turin

What we are trying to do in graphene research at I.N.Ri.M.:

- CVD growth by means of a RT-CVD system (*faster cooling-rate*  $\Rightarrow$  *hopefully higher quality of graphene*)
- C-Si superlattice synthesis by means of an MBE system
- theoretical and experimental investigation of optical properties



Figure: Deposition of Ni-films system at I.N.Ri.M.



**Figure:** RT-CVD system at I.N.Ri.M. - highest temperature reached: 1300 °C,  
fastest cooling-rate: 300 °C/min



Figure: MBE system at I.N.Ri.M.

# A possible application to Metrology

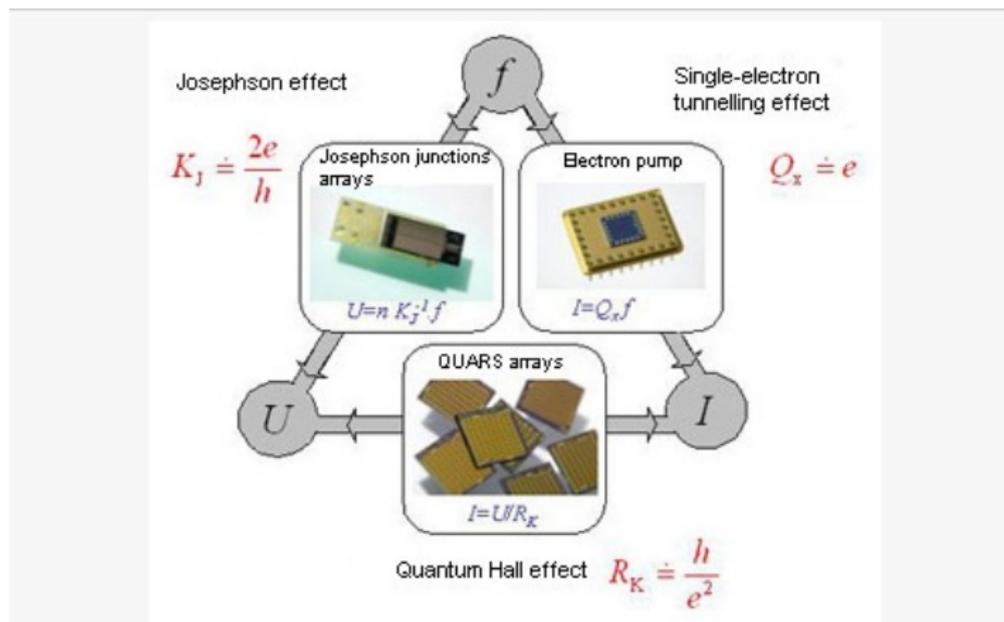


Figure 1 : The metrological triangle with the three material standards linked to the three quantum effects: Josephson, quantum Hall and single-electron tunnelling.

# Possible to use graphene for setting new Metrological Standards?

## LETTERS

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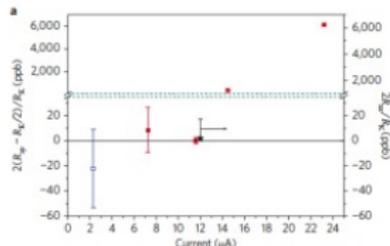
nature  
 nanotechnology

## Towards a quantum resistance standard based on epitaxial graphene

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

The quantum Hall effect<sup>1</sup> allows the international standard for resistance to be defined in terms of the electron charge and Planck's constant alone. The effect comprises the quantization of the Hall resistance in two-dimensional electron systems in rational fractions of  $R_H = h/e^2 = 25\,812.807\,557(18)\ \Omega$ , the resistance quantum<sup>2</sup>. Despite 30 years of research into the quantum Hall effect, the level of precision necessary for metrology—a few parts per billion—has been achieved only in silicon and *ii-v* heterostructure devices<sup>3–6</sup>. Graphene should, in principle, be an ideal material for a quantum resistance standard<sup>7</sup>, because it is inherently two-dimensional and its discrete electron energy levels in a magnetic field (the Landau levels)<sup>8</sup> are widely spaced. However, the precisions demonstrated so far have been lower than one part per million<sup>9</sup>. Here, 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. Moreover, by demonstrating the structural integrity and uniformity of graphene over hundreds of micrometres, as well as reproducible mobility and carrier concentrations across a half-centimetre wafer, these results boost the prospects of using epitaxial graphene in applications beyond quantum metrology.

relativistic (Dirac) electrons<sup>8</sup>. This last feature of charge carriers in graphene is manifested most spectacularly through an unusual sequence of the quantum Hall effect (QHE) plateaux<sup>10</sup>. The QHE is a result of the Landau level quantization of the energy spectrum of two-dimensional electrons. In the quantum Hall regime the current is carried by a quantum state, spreading through the whole sample, and the sequence of plateaux in the transverse resistance  $R_{xy}$  is determined by the topological (Berry) phase acquired by the charge moving in the magnetic field. This phase is zero in conventional materials, where  $R_{xy} = \pm h/mv^2$  ( $m$ -integer  $\geq 1$ ); it is equal to  $2\pi$  in bilayer graphene<sup>11,12</sup>, leading to a sequence of QHE plateaux at  $R_{xy} = \pm (h/4e^2)/(n+1)$  ( $n \geq 0$ ), and it is  $\pi$  in the monolayers<sup>13</sup>, which determines the QHE sequence  $R_{xy} = \pm (h/4e^2)/(n+1/2)$  ( $n \geq 0$ ), currently regarded as a smoking gun for the sample to



# Outline

- 1 Motivations and theoretical review
  - Introduction and motivations
  - Brief review of theoretical properties
- 2 Growth Methods and Techniques
  - Chemical Vapor Deposition
  - Epitaxial growth by thermal decomposition on SiC
  - C-Si Superlattices Synthesis
  - Graphene at I.N.Ri.M. and applications to Metrology
- 3 Conclusions

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- CVD method and superlattice synthesis seem to be nowadays the most promising techniques for reaching this aim
- If this is the case, maybe we are entering a new transistors' and nano-electronics' era

*... thank you!*