Nanotechnologies and new materials

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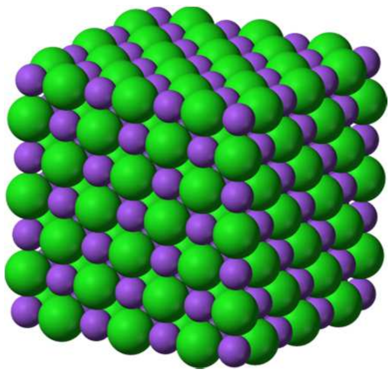
Summary

- 2D materials
- Graphene: Properties
  Exfoliation
  CVD growth - Transfer
  Electronic Structure
- 2D heterostructures
- Conclusions

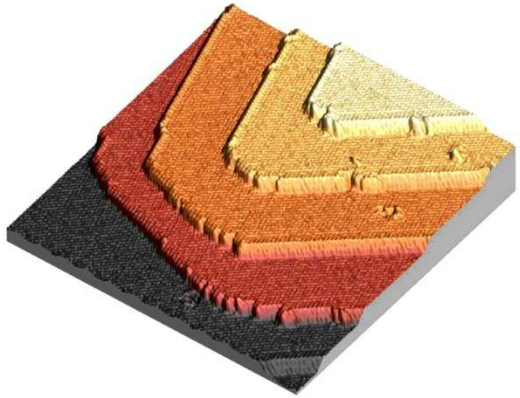
0D, 1D, 2D and 3D materials

3D

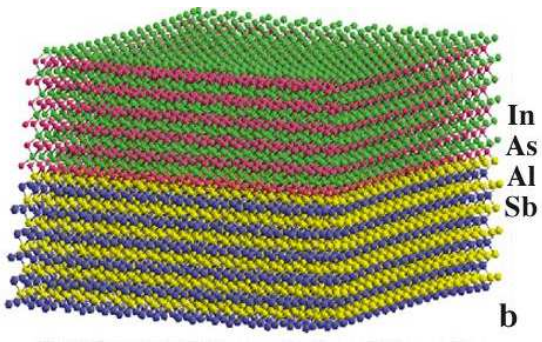


bulk crystals

2D

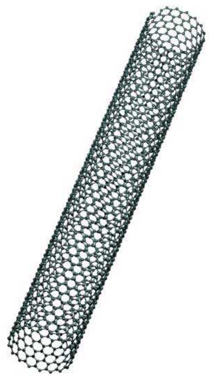


ultra-thin films



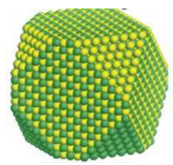
quantum wells

1D



nanotubes
nanowires

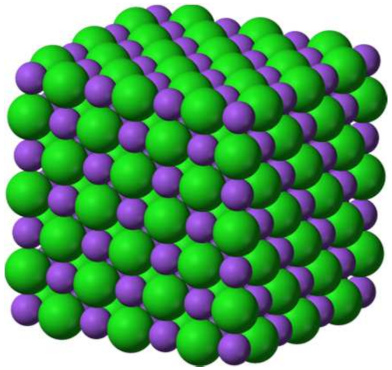
0D



quantum dots

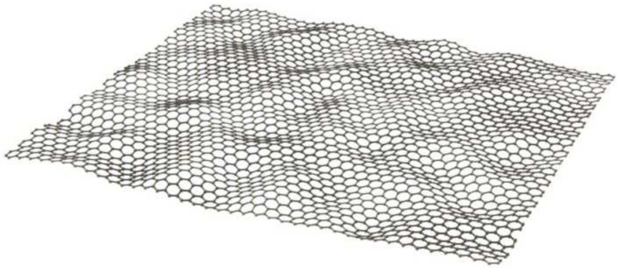
0D, 1D, 2D and 3D materials

3D



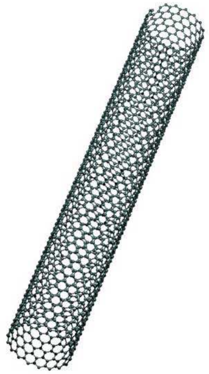
bulk crystals

2D



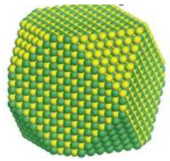
graphene

1D



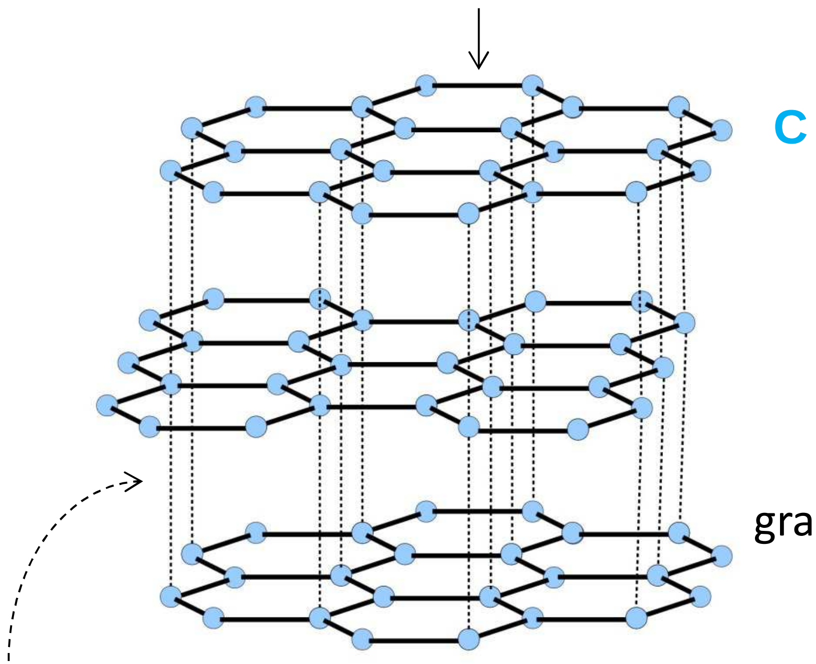
nanotubes
nanowires

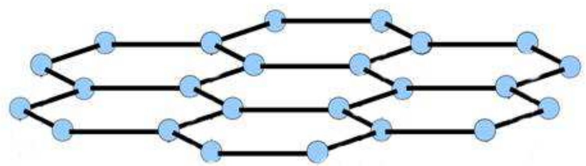
0D



quantum dots

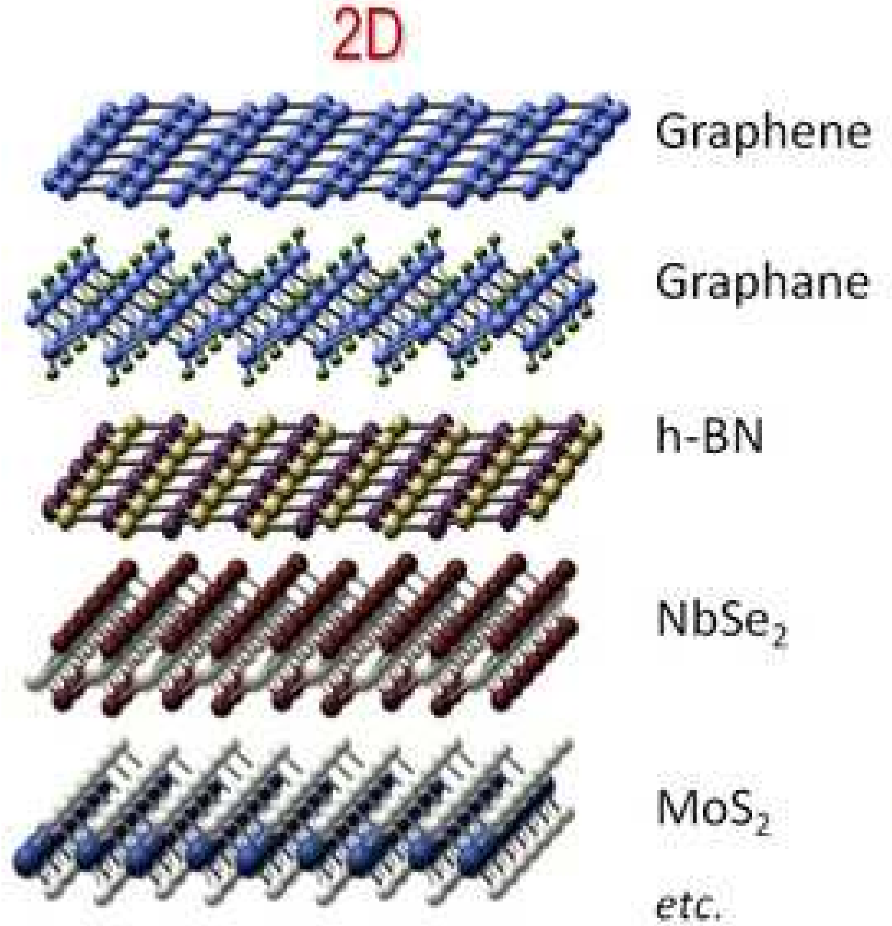
Graphene





graphene

2D Materials

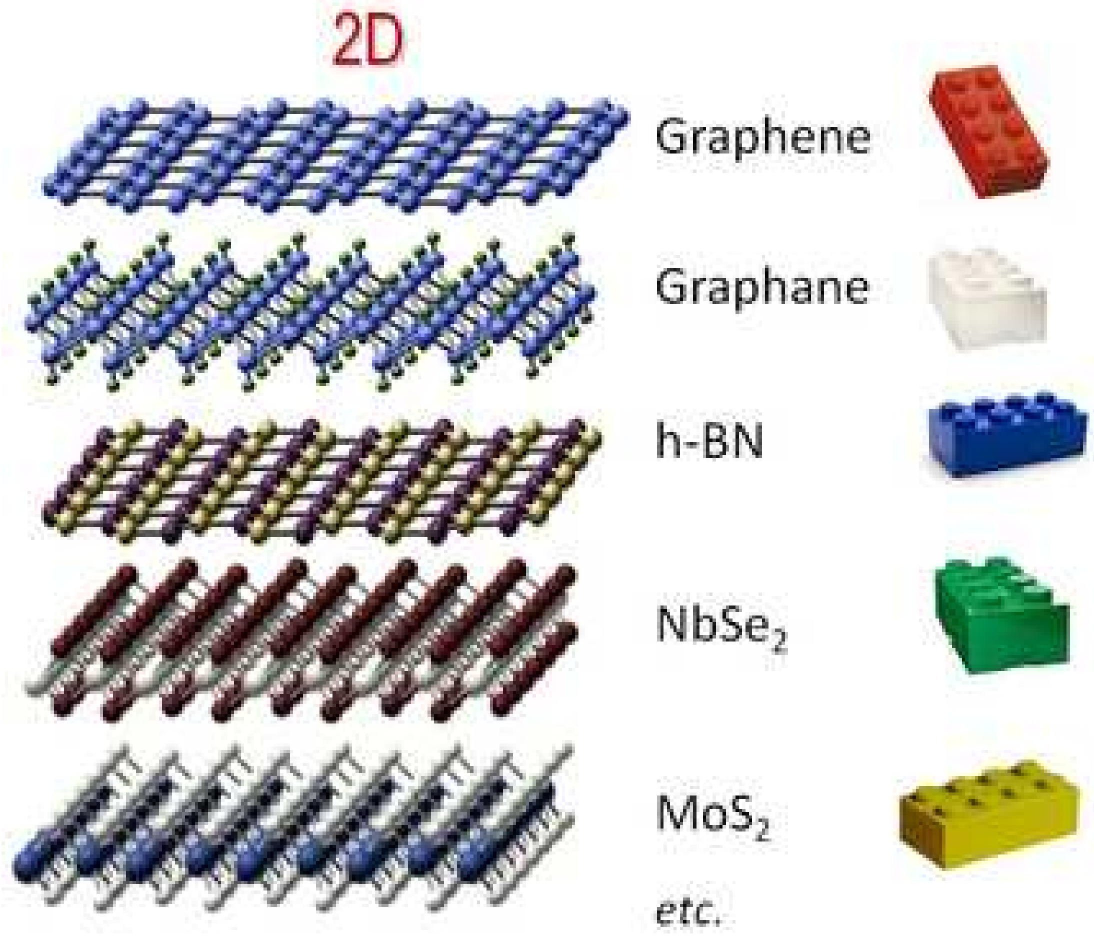


Usually 2D materials have a 3D analog which are lamellar solids

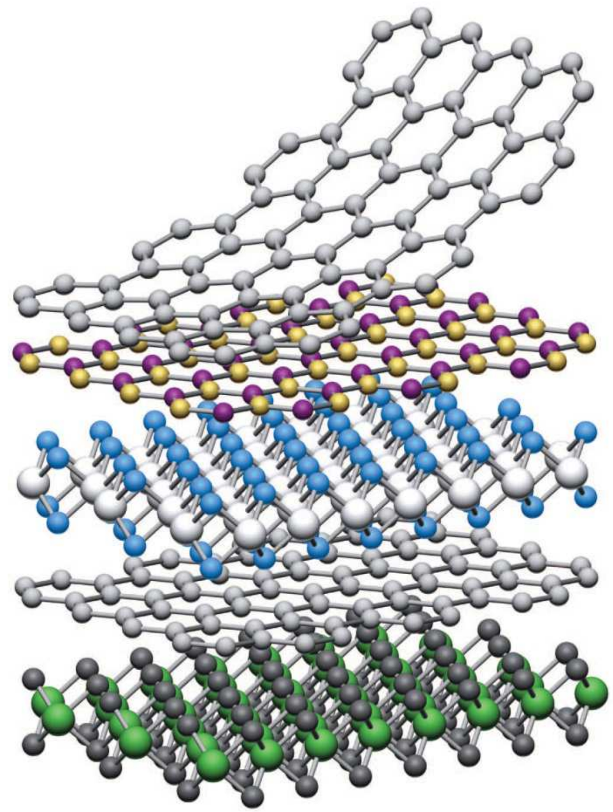
They can be isolated as free-standing one-atom or few-atoms thick layers and can exists without a substrate

They exhibit optical and electronic properties different from their 3D analogs

Materials in the Flatland



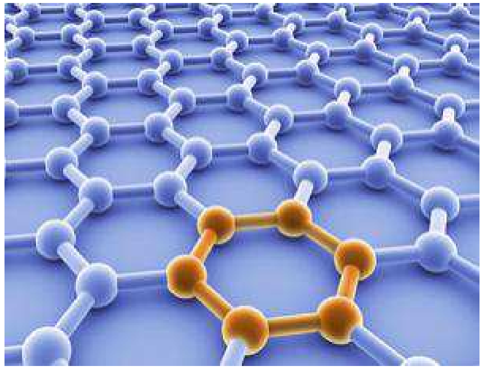
Building blocks

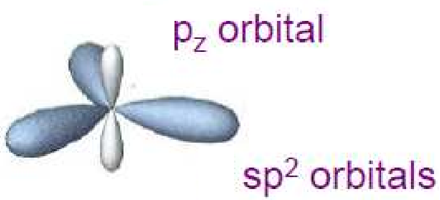


Complex architecture

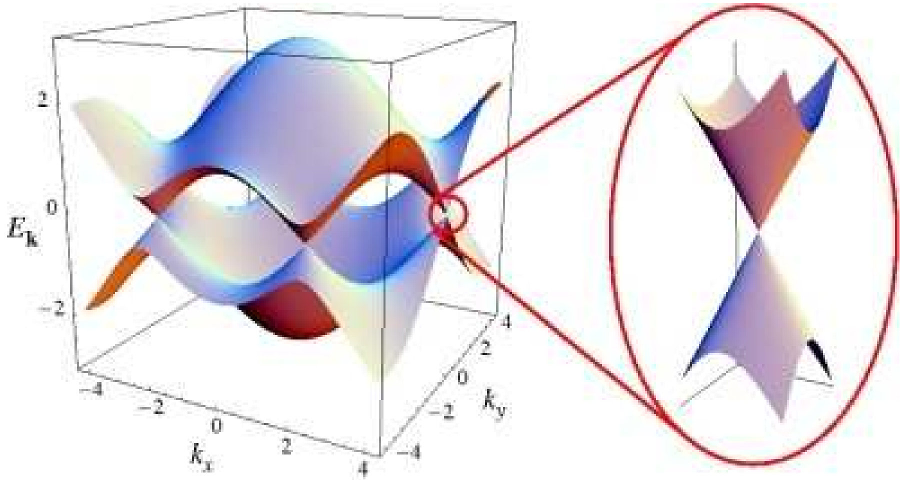
New materials create new challenges in condensed matter research.

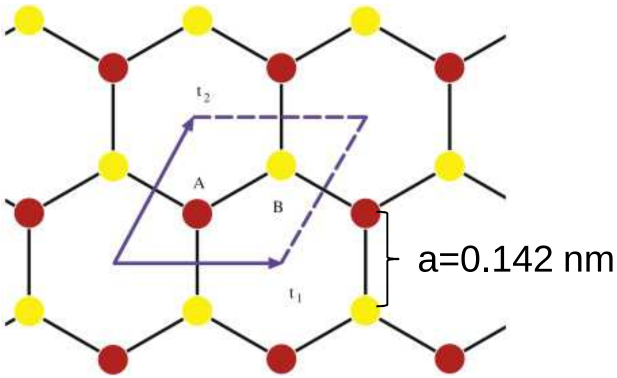
Monolayer graphene properties





semi-metal or zero-gap semiconductor



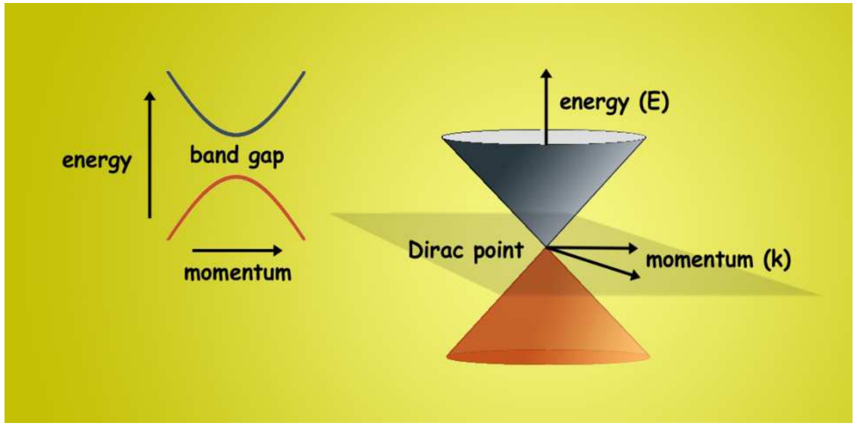


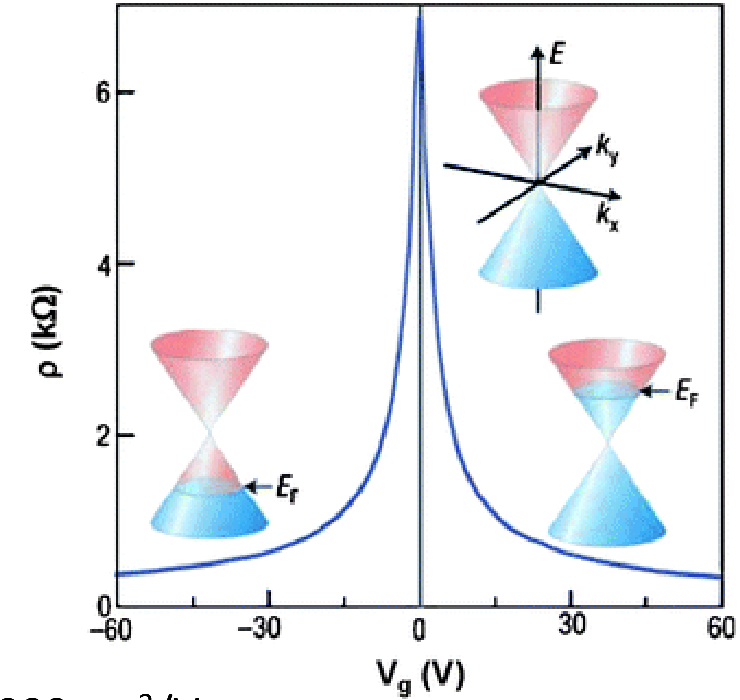
at the Dirac points the dispersion is linear and electrons and holes behave like relativistic particles with Fermi velocity $v_F \sim 10^6$ m/s

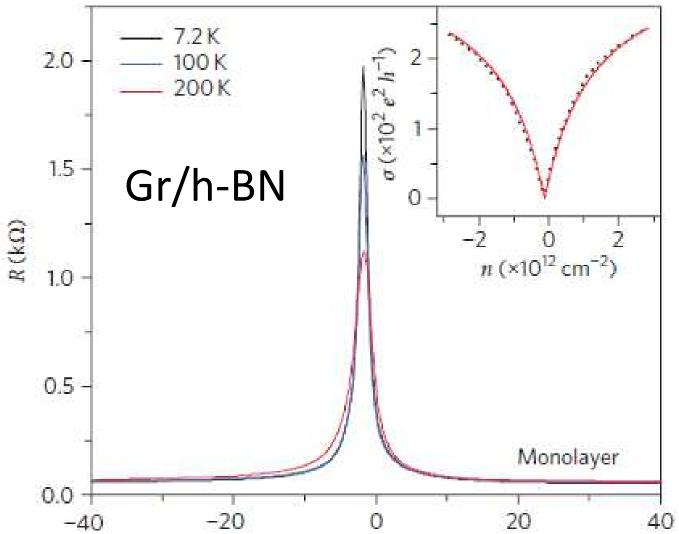
trasport is ambipolar

graphene lacks a bandgap around the Fermi level

Monolayer graphene properties





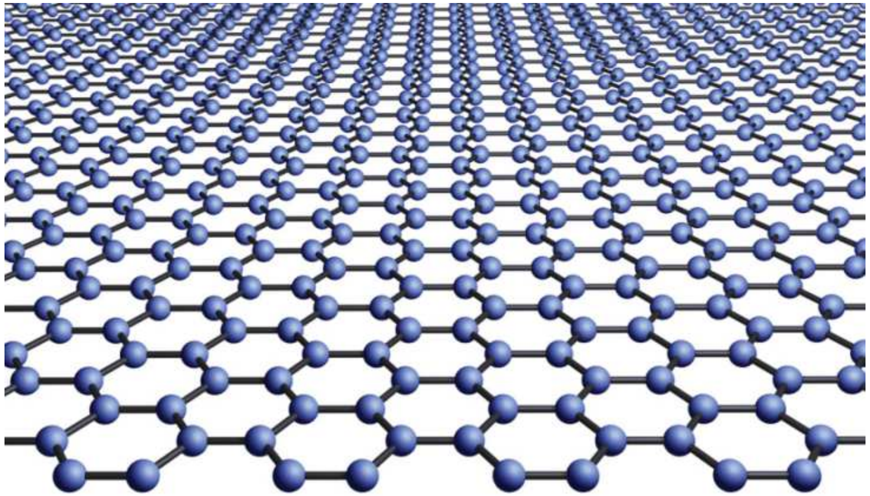


$\mu_C \approx 60.000\ cm^2/Vs$

0.5 μm

Daen Nat. Nanotech. 2010

Graphene properties



Graphene:

is a semimetal but conducts as the best metals

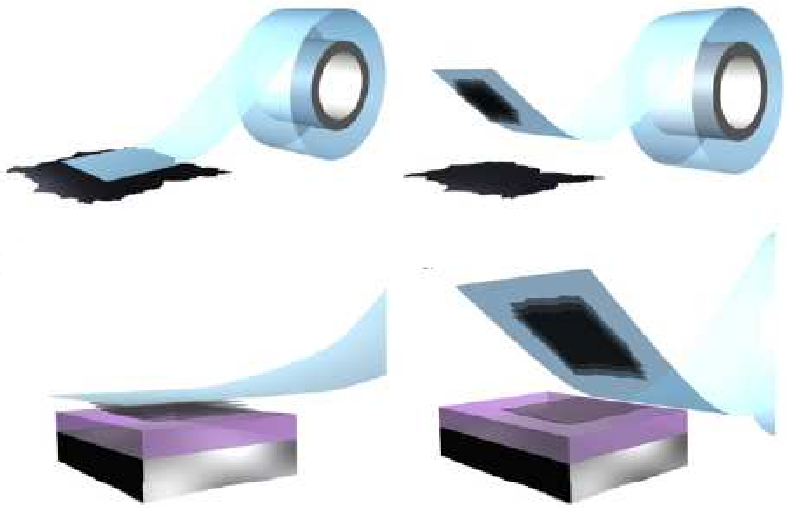
transport can be modulated (it can be switched ON and OFF)

possesses record electron and hole mobilities (>x100 than Si)

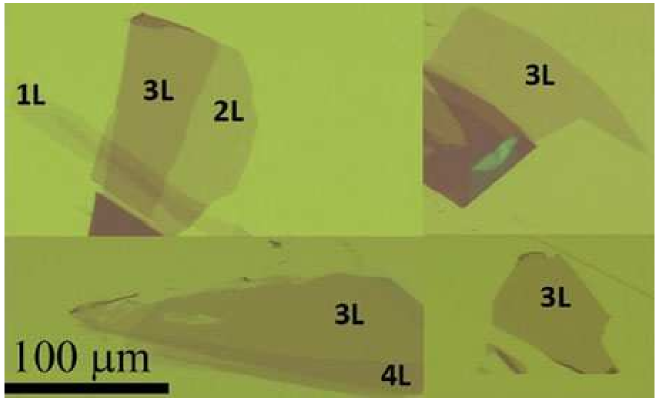
allows very high current densities (~ 4-8 mA/µm, 10^9 A/cm^2)

- is the strongest material (>5x stailess steel and much lighter)
- is flexible
- is a super heat-conductor (>x40 than Si)
- is chemically inert
- is biocompatible

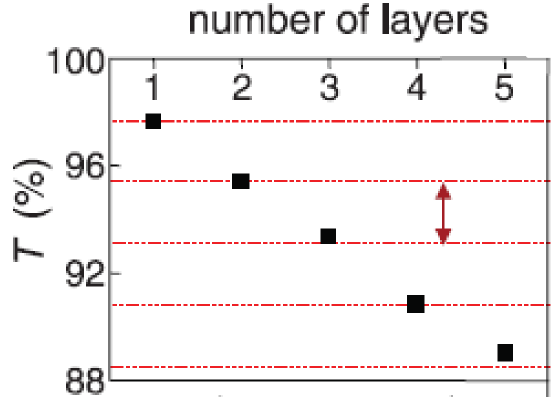
Mechanical exfoliation



Novoselov et al
Phys. Scr. T146 014006 2012



http://emps.exeter.ac.uk/

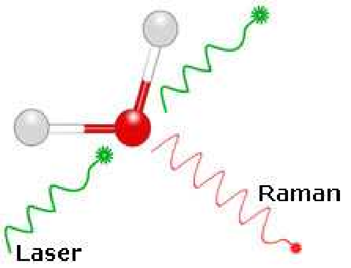


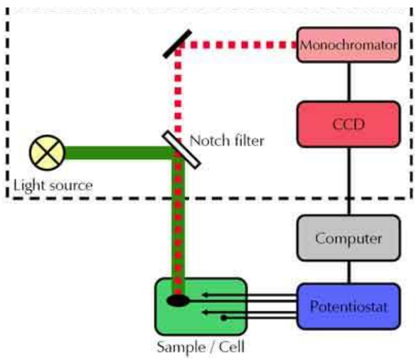
white light

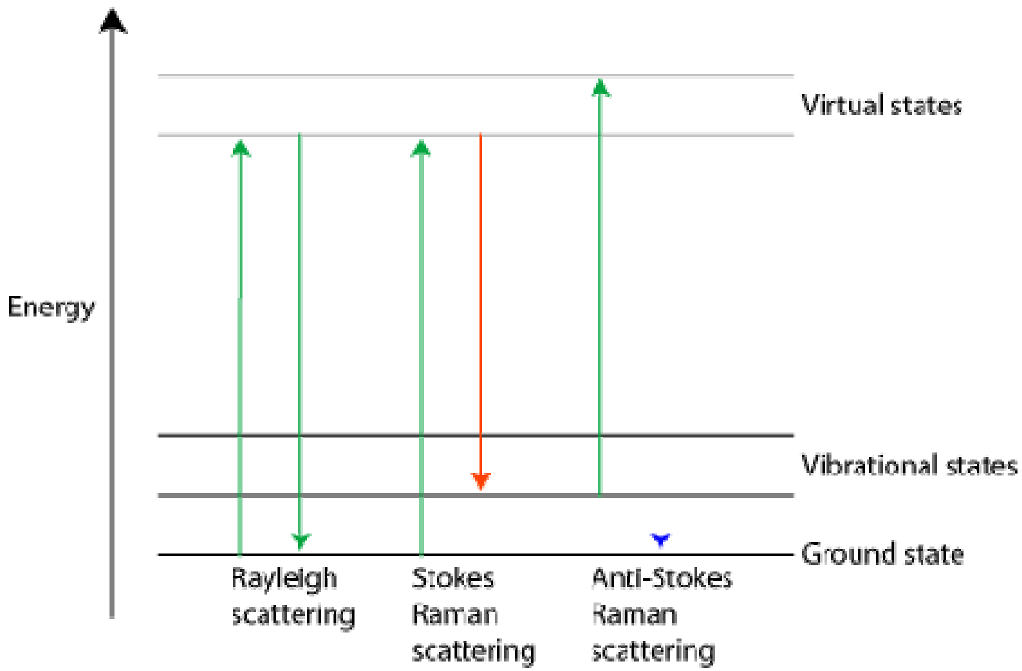
2.3 % ± 0.1

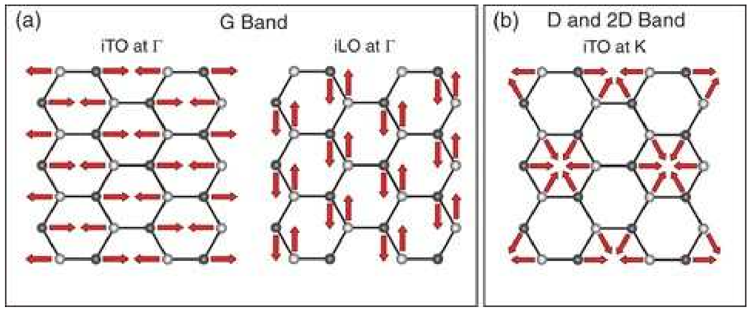
Nair et al. Science 320, 1308 2008

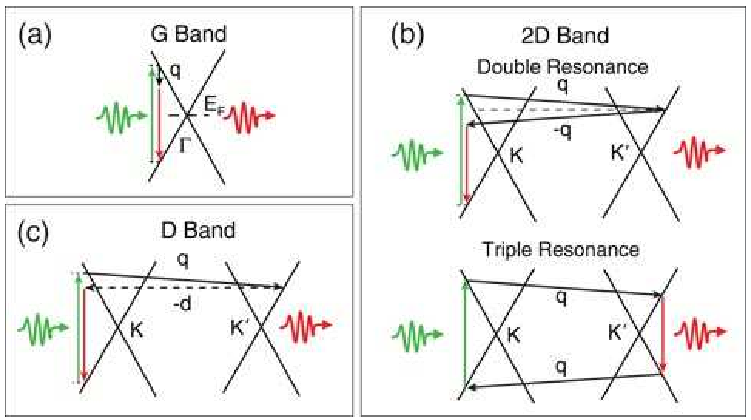
Raman spectroscopy

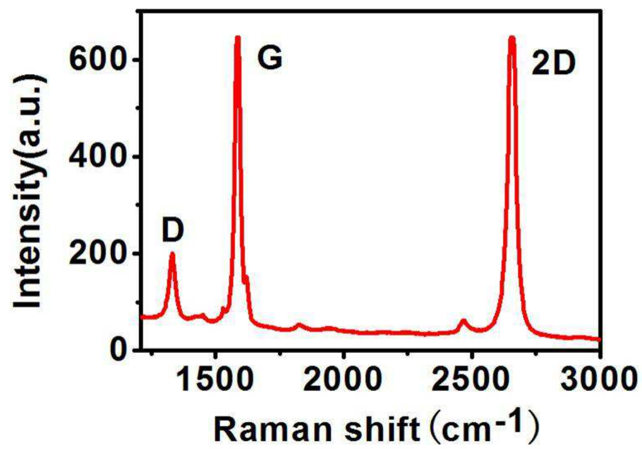




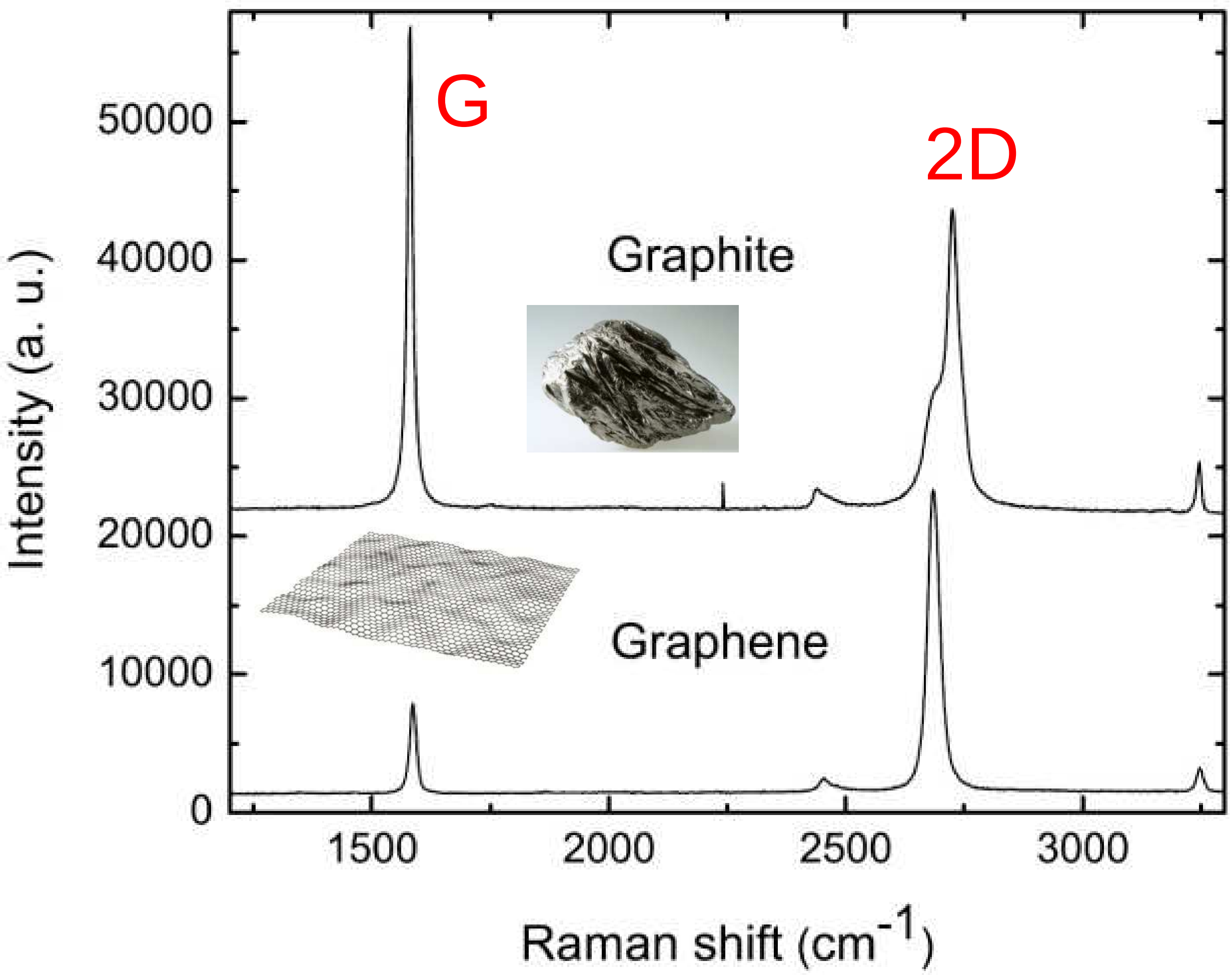




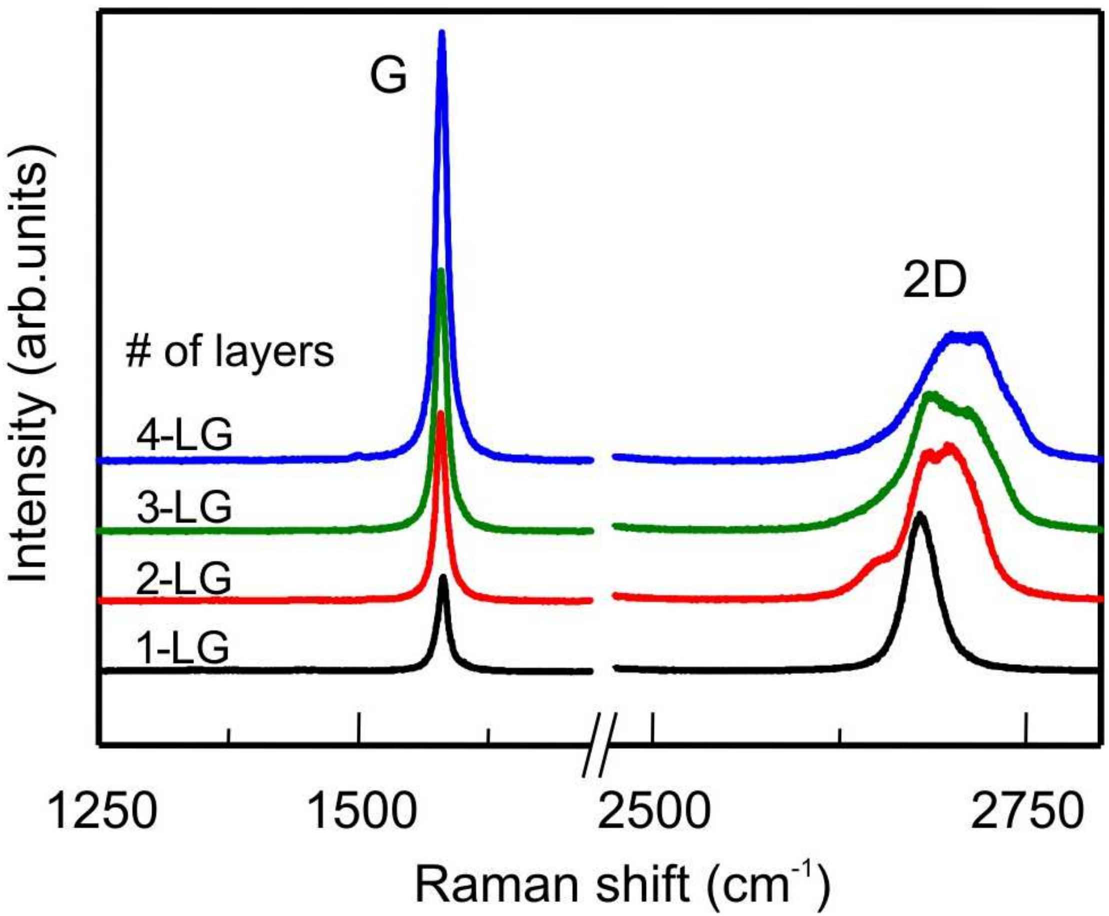




Raman spectroscopy of graphene

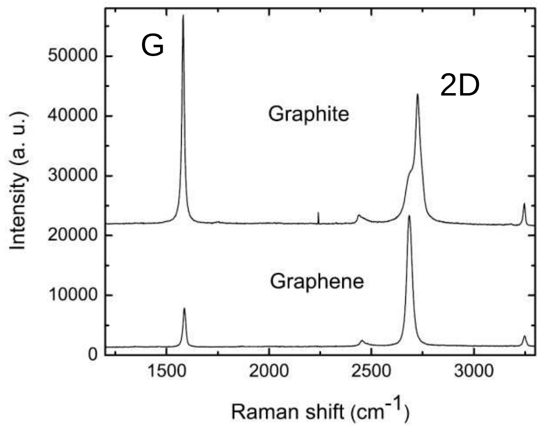


Raman spectroscopy of graphene

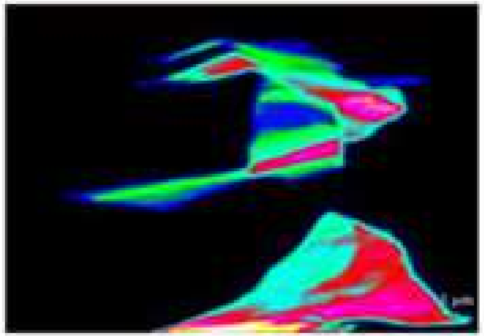


Production of graphene monolayers

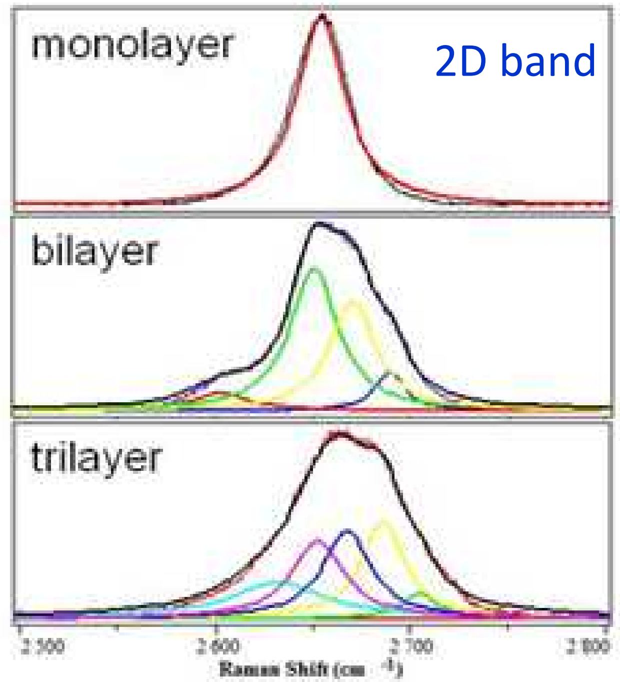
Raman spectroscopy



G band intensity Raman image



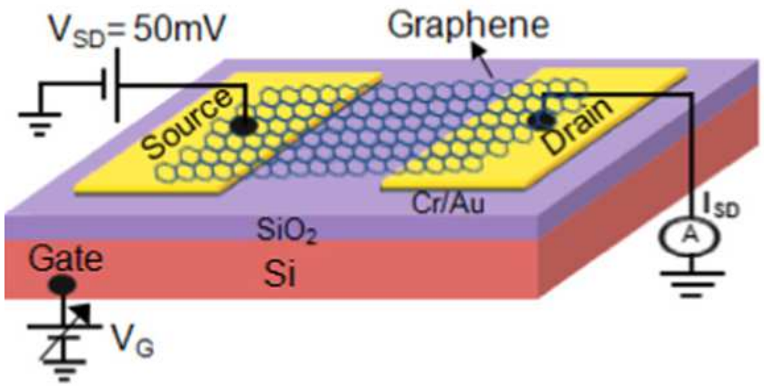
optical image

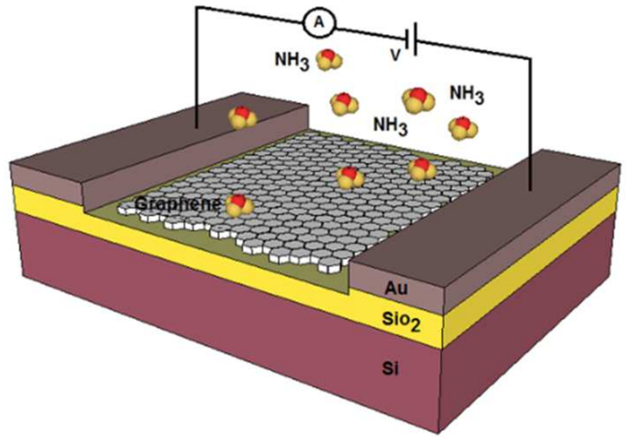


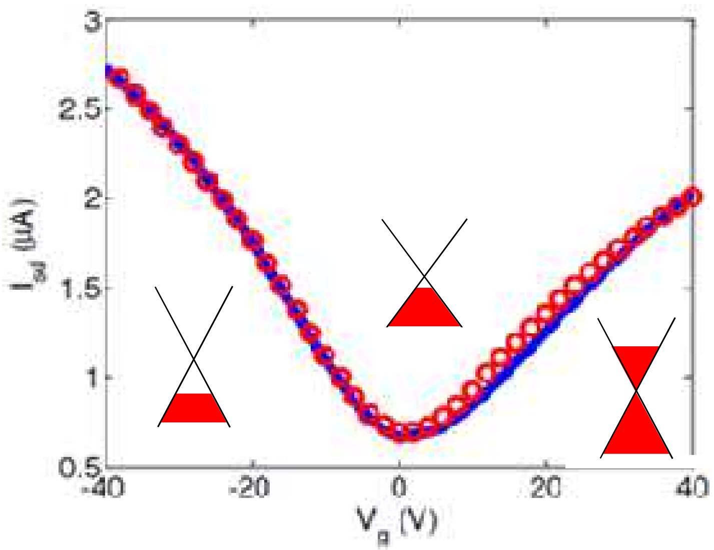
http://www.horiba.com

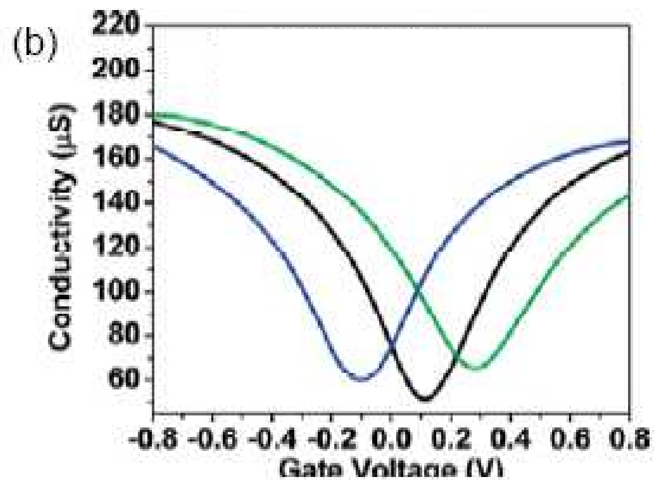
Graphene-based devices

Field effect transistor



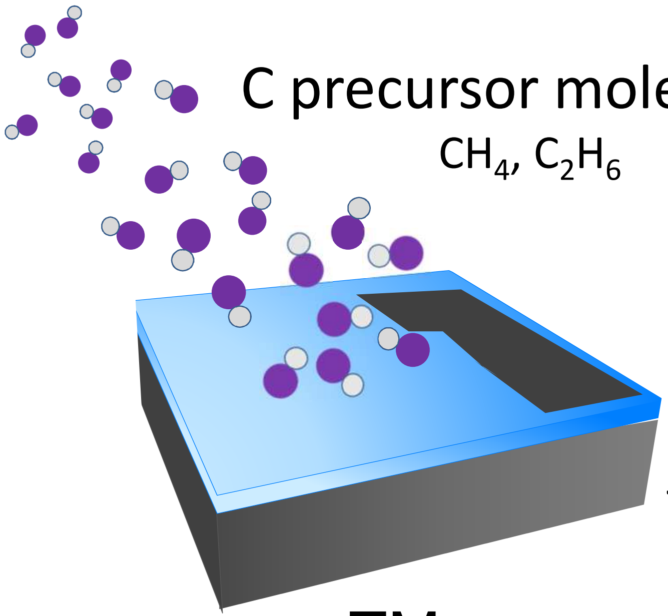


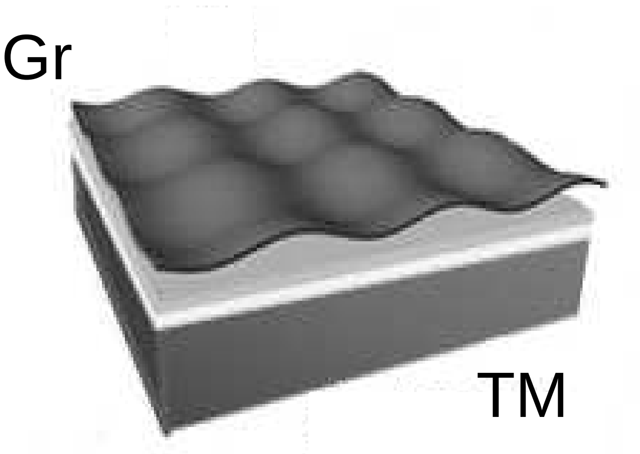




Epitaxial graphene on TM metals

Chemical Vapour Deposition



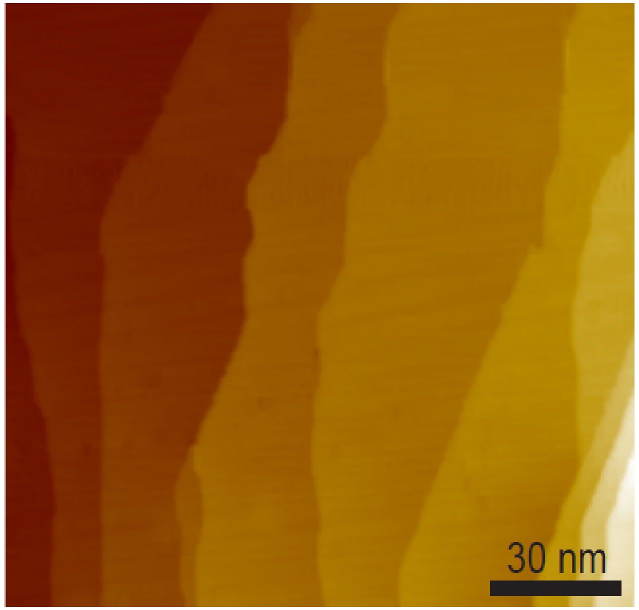


(Ir, Ru, Pt, Re, Rh, Ni, Fe, Cu, PtRh, NiAl, ...)

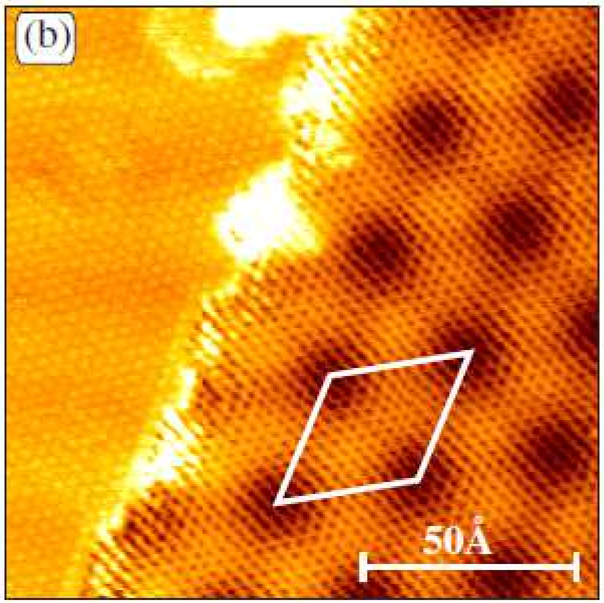
Large area graphene
Self-limiting growth
Low defect density

Epitaxial graphene on TM metals

Scanning Tunneling Microscopy

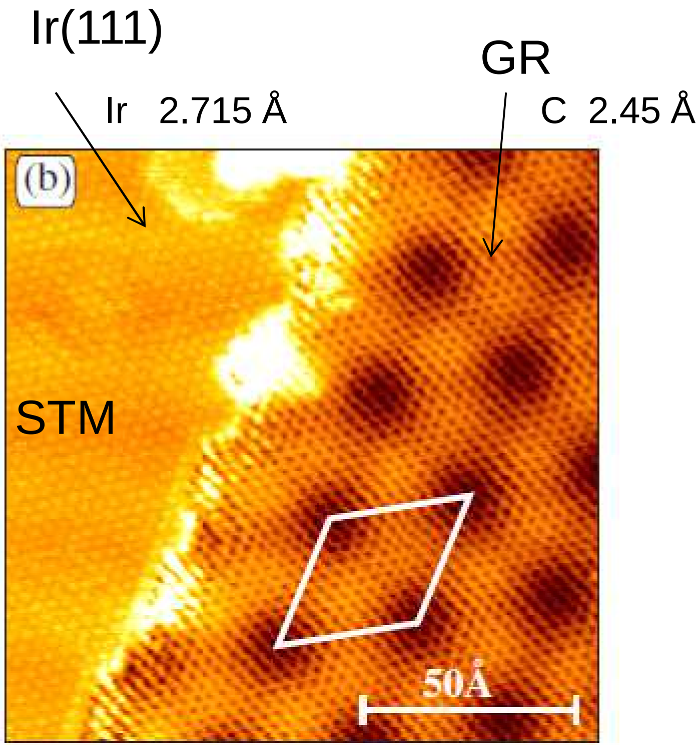


Gr/Ir(111)



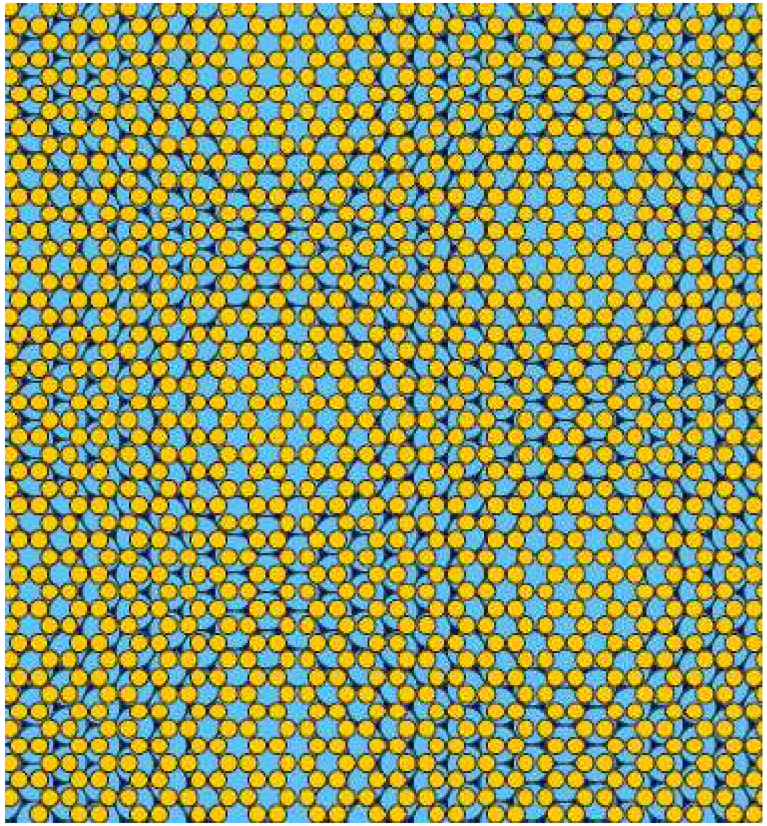
Gr/Ir(111)

Moiré pattern in epitaxial graphene



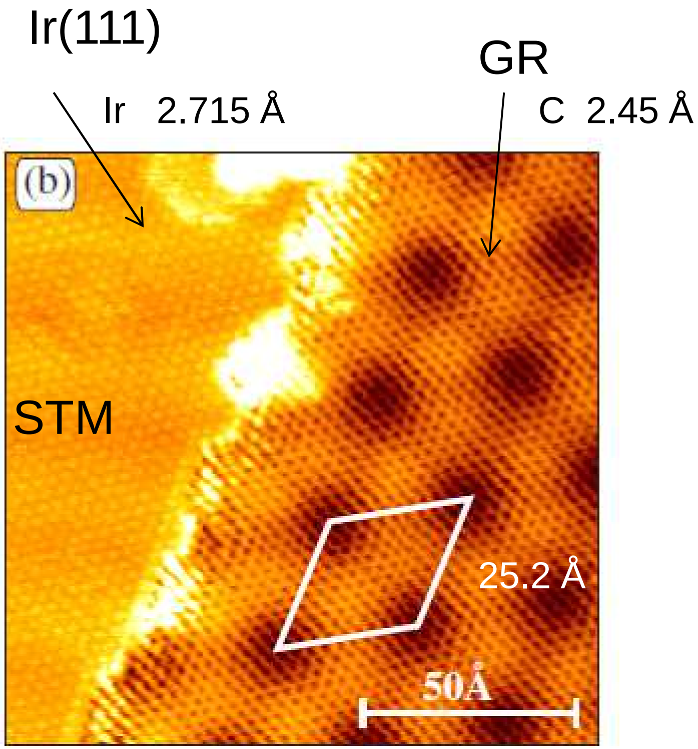
N'Diaye et al PRL 97, 215501 (2006)

Gr/Ir(111)



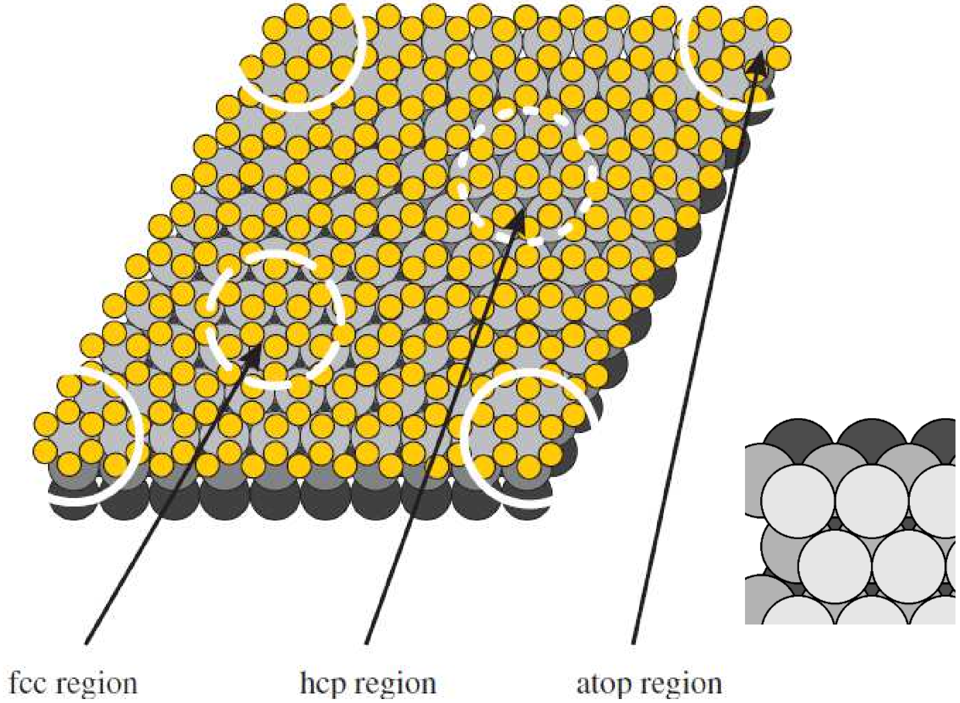
Graphene on Ir(111)

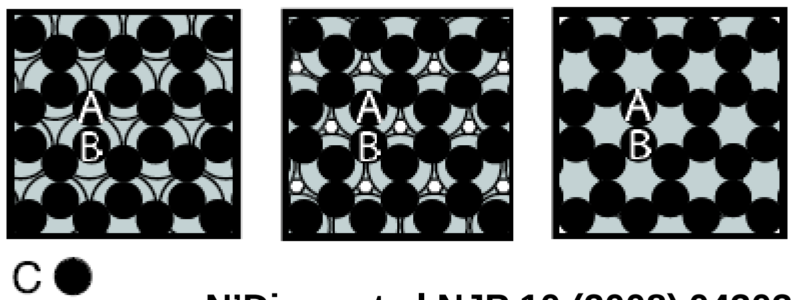
Graphene on Ir(111)



N’Diaye et al PRL 97, 215501 (2006)

9,32x9,32 superstructure

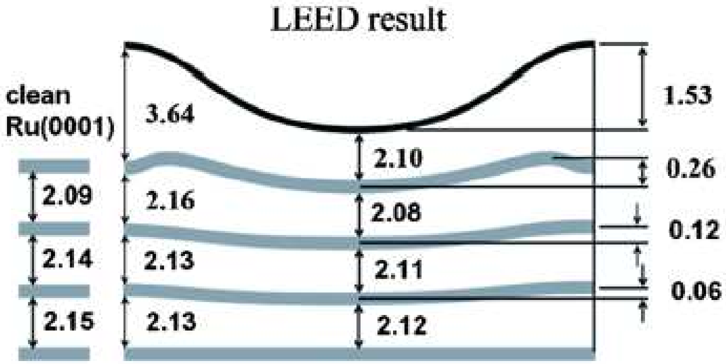




N’Diaye et al NJP 10 (2008) 043033

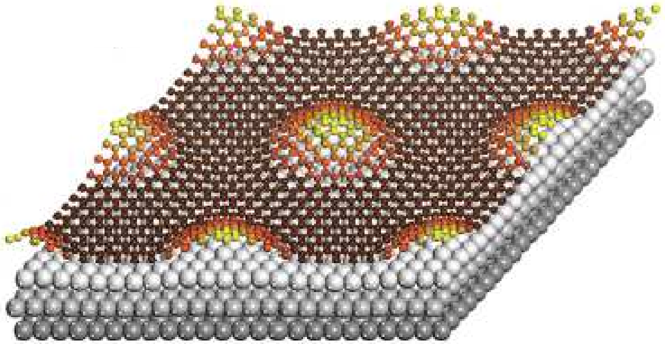
Graphene on TM surfaces

Gr/Ru(0001)



Δh=1.53 Å

minimum Gr-Ru distance=2.1 Å



C(13x13)/Ru(12x12)

Gunther et al. PRL 104 (2010) 136102

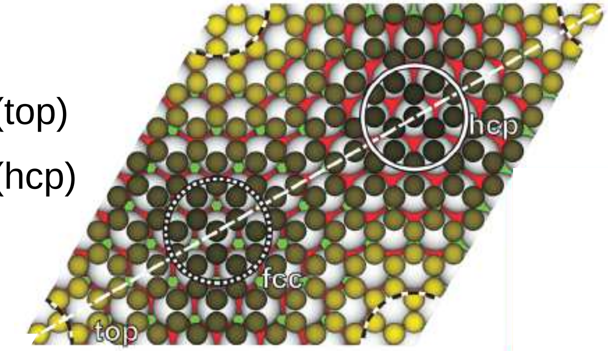
Gr/Ir(111)

DFT

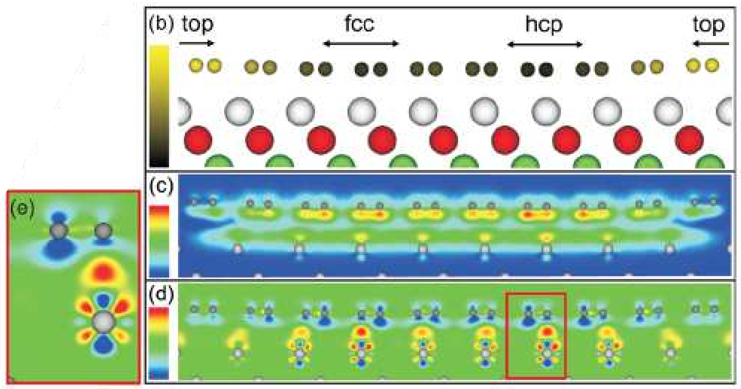
h= 3,62 Å (top)

h= 3,27 Å (hcp)

Δh=0.35 Å



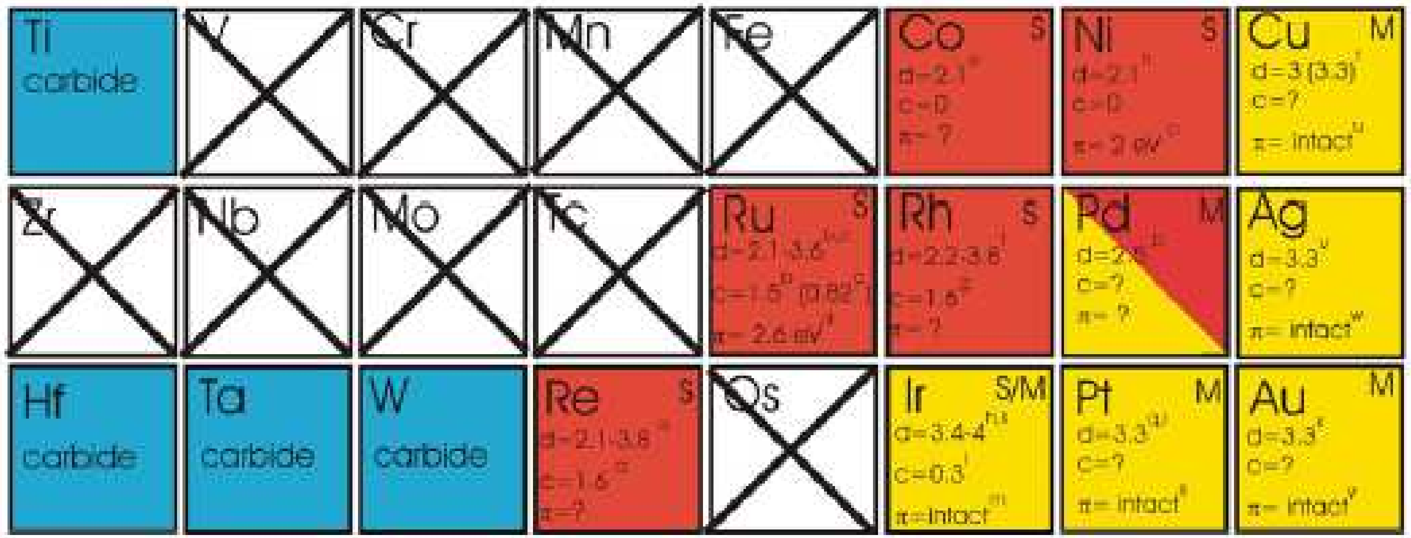
C(10x10)/Ir(9x9)



SW Δh=0.6±0.1 Å; Δh=1.0±0.2 Å

Busse et al. PRL 107 (2011) 036101

Interaction between TM metals and graphene



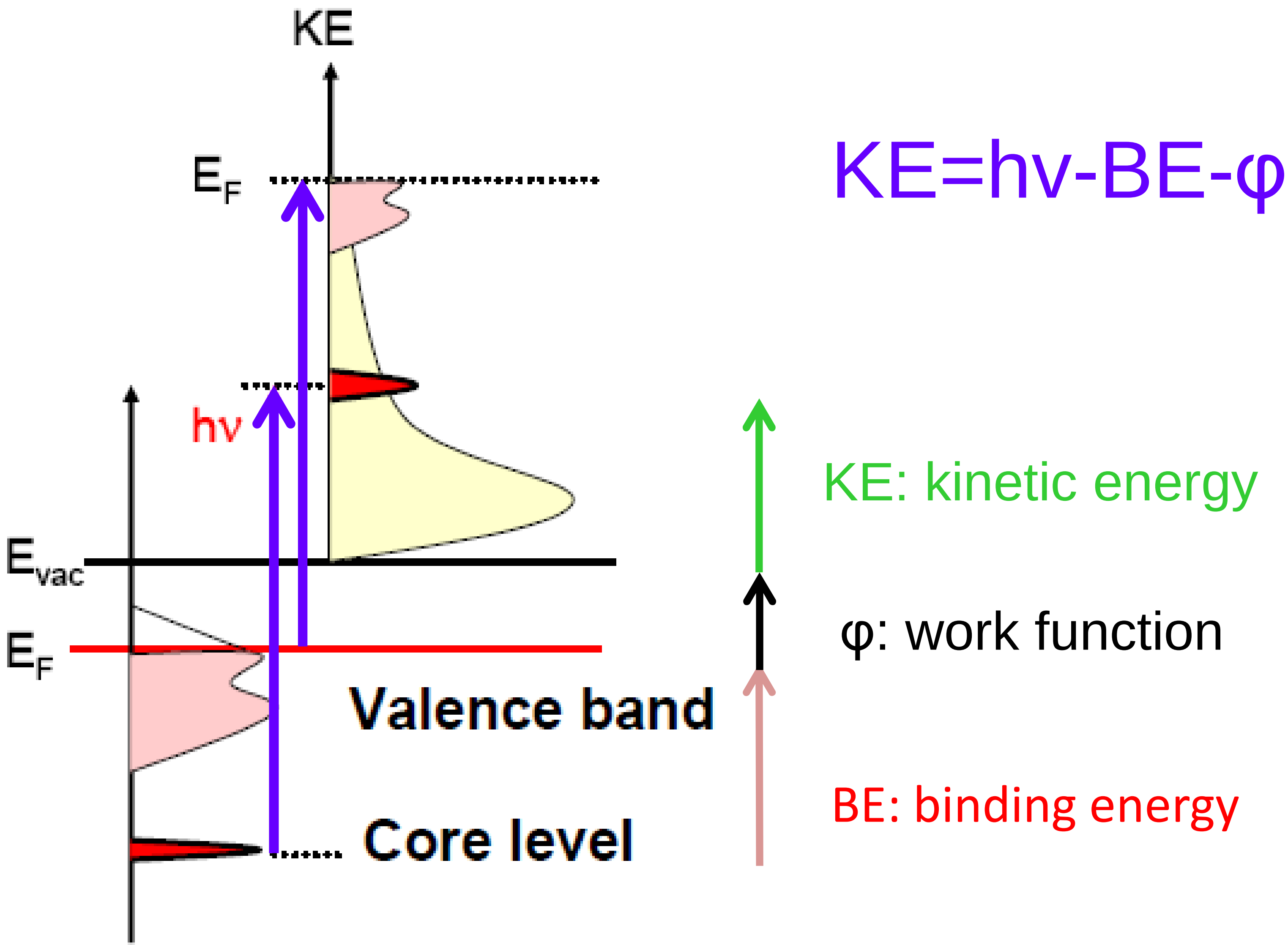
Gr may grow on the bulk carbide

strongly interacting with Gr

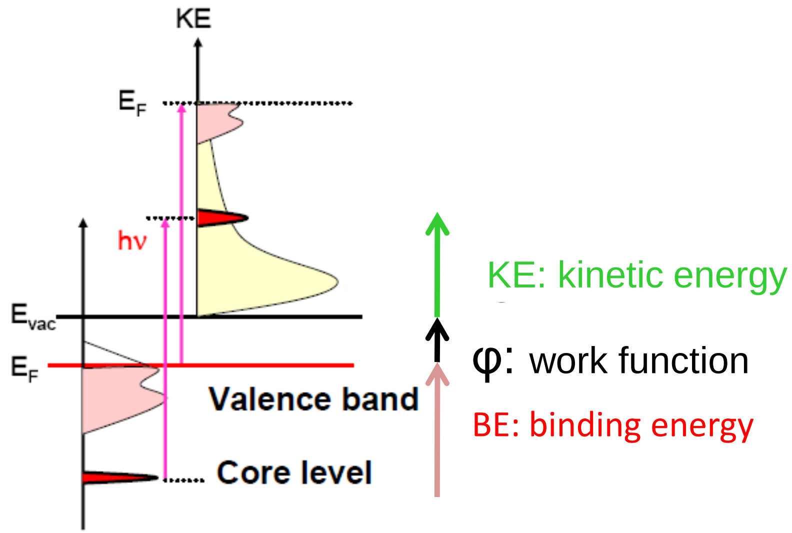
weakly interacting with Gr

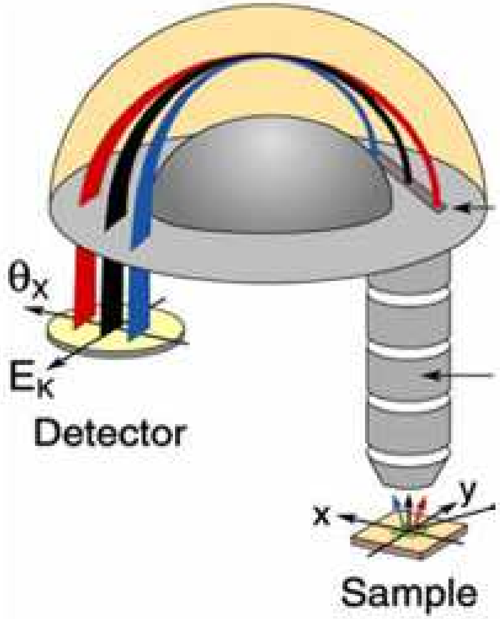
Batzill Surf. Sci. Rep. 67 (2012) 83

Angle resolved photoelectron spectroscopy (ARPES)

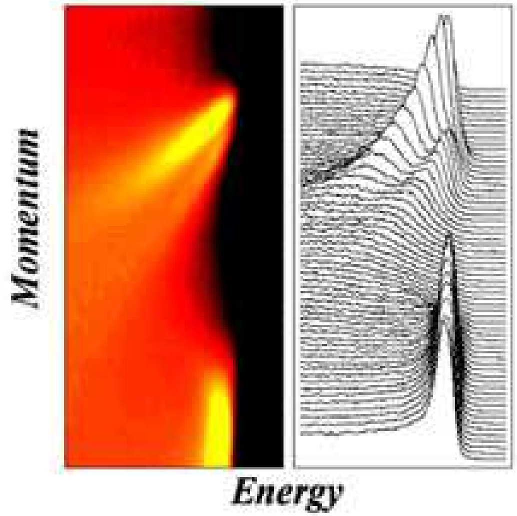


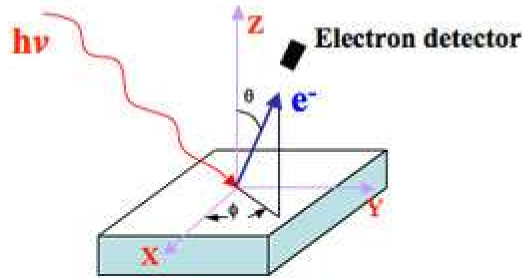
Angle resolved photoelectron spectroscopy (ARPES)



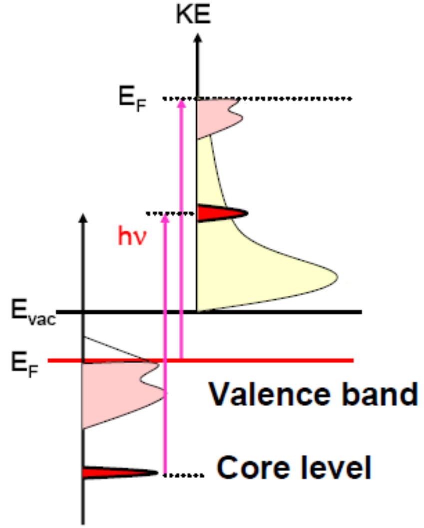


KE=hν-BE-φ





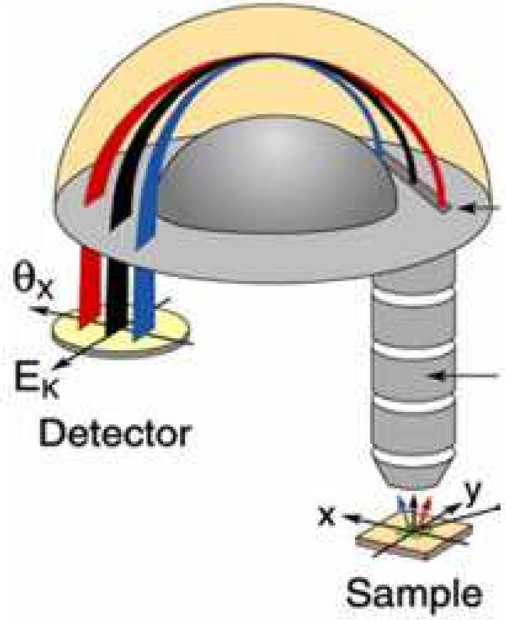
Angle resolved photoelectron spectroscopy (ARPES)



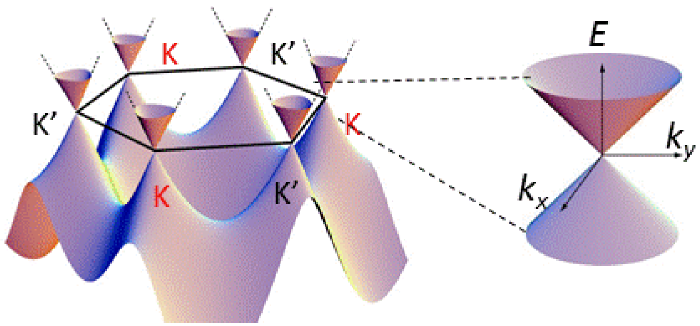
KE: kinetic energy

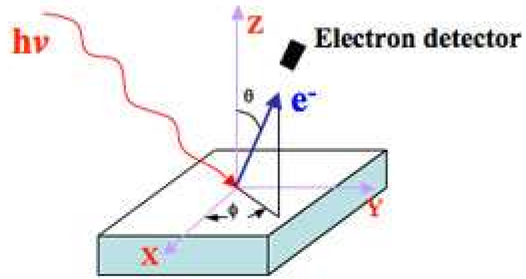
φ: work function

BE: binding energy

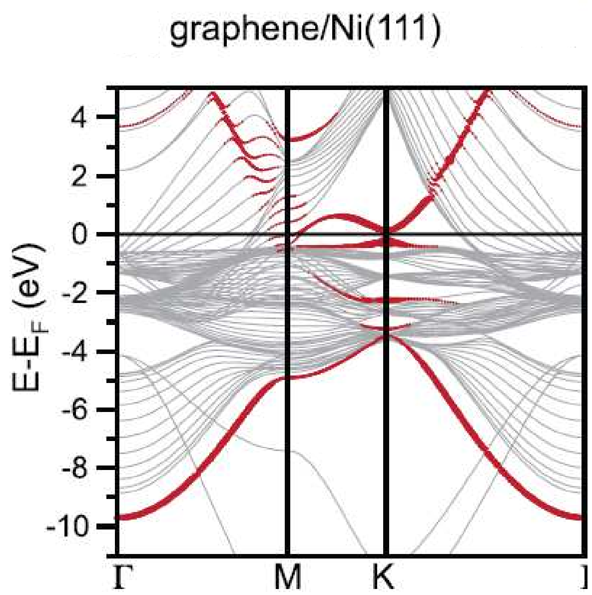


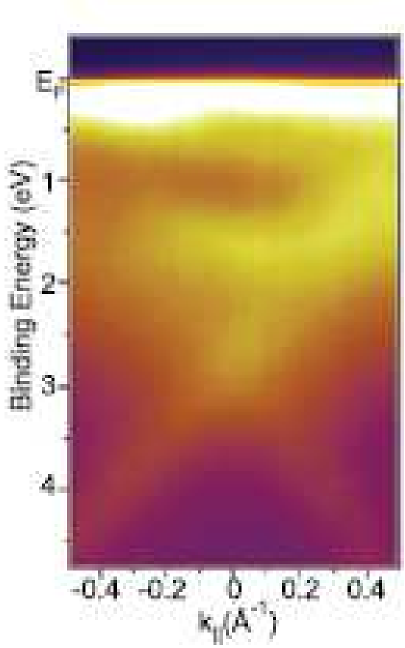
$$KE = h\nu - BE - \varphi$$

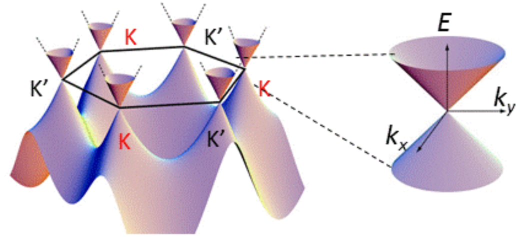




Graphene/Ni(111)

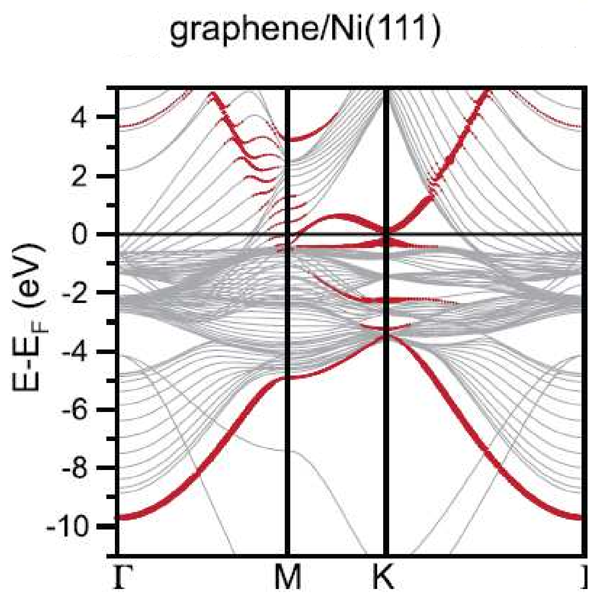


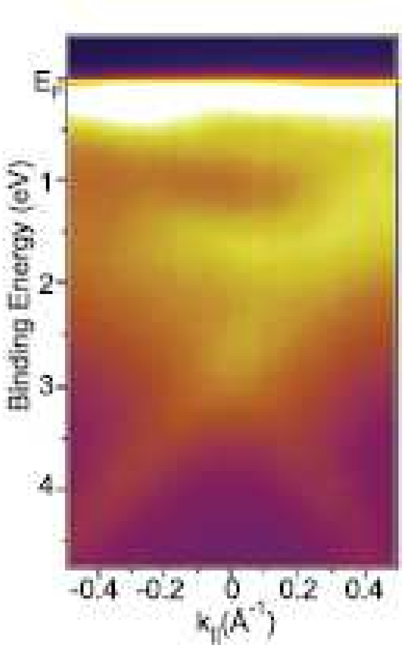


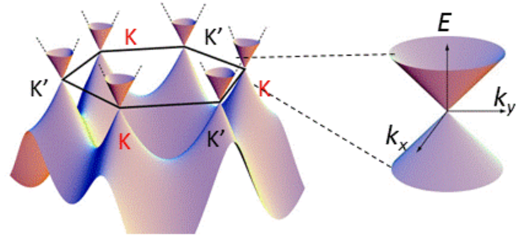


Voloshina New J. Phys. 13(2011) 113028

Graphene/Ni(111)



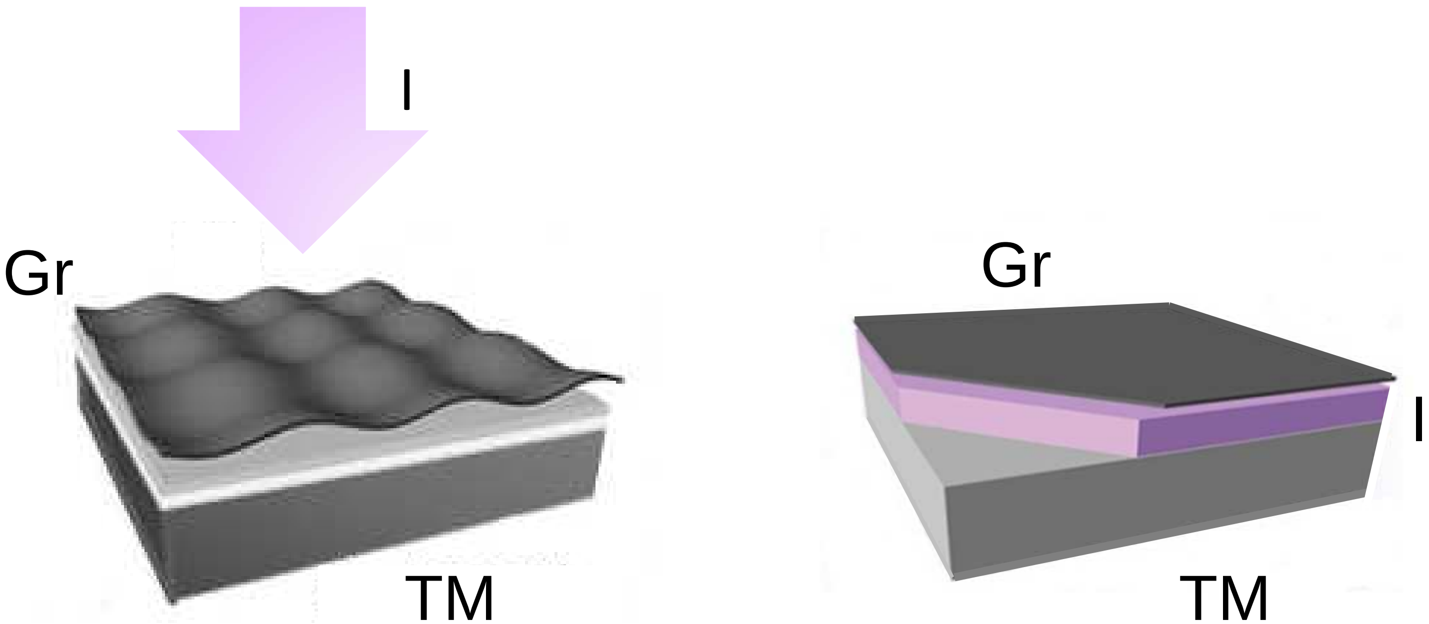




No Dirac cones: the interaction between graphene and the Ni(11) substrate is too strong

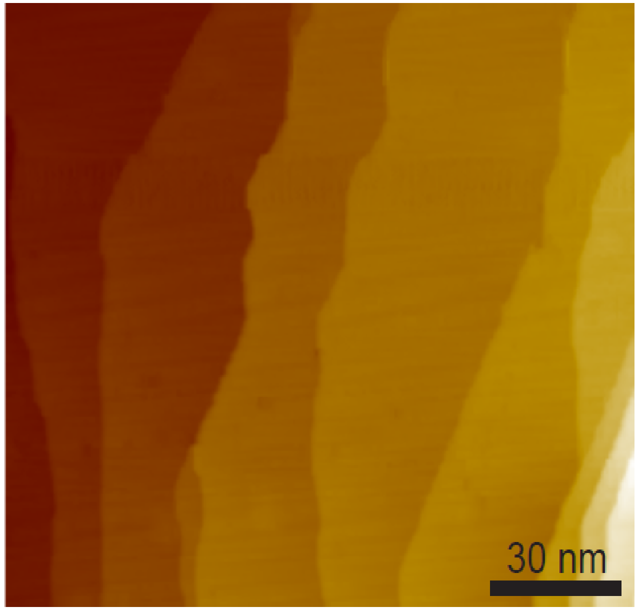
Voloshina New J. Phys. 13(2011) 113028

Intercalation of below epitaxial graphene

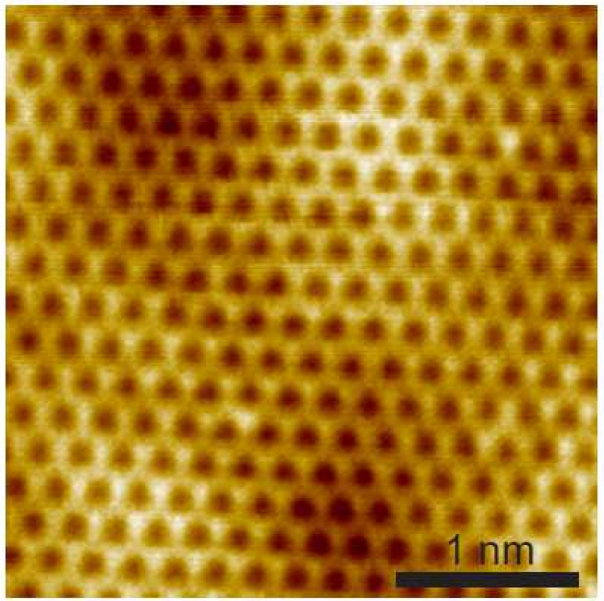


Decoupled graphene

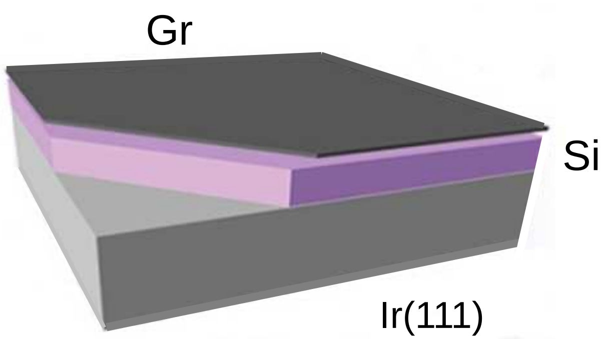
Scanning Tunneling Microscopy



Gr/Ir(111)

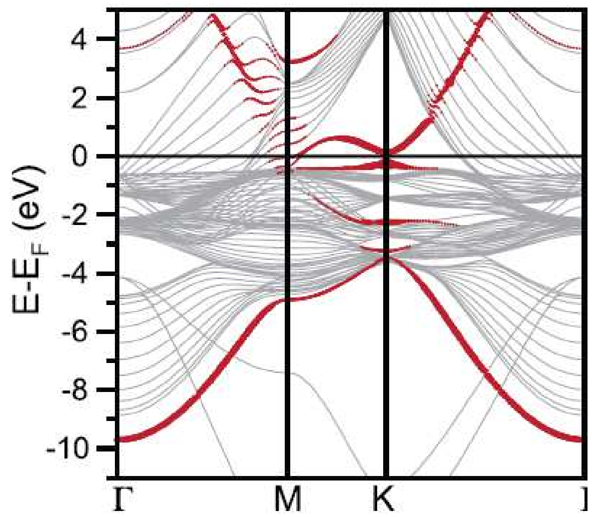


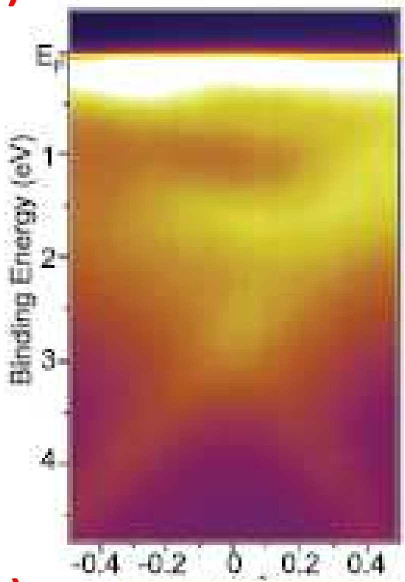
Gr/Si/Ir(111)



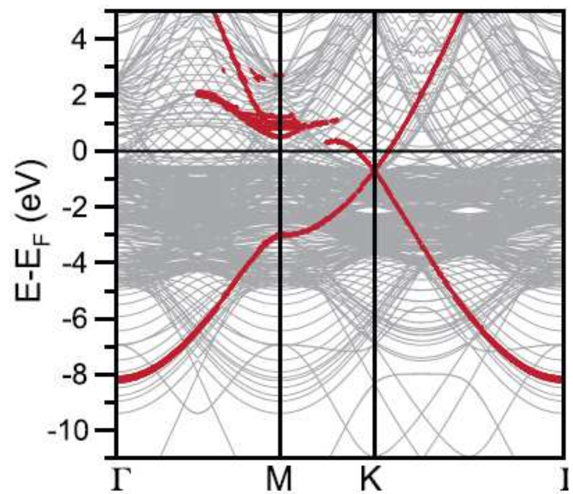
Decoupled graphene/Ni(111): Au intercalation

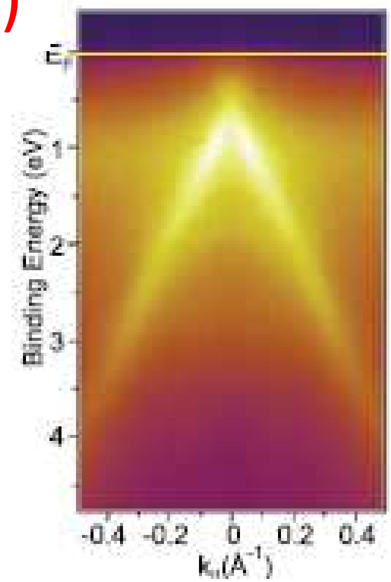
graphene/Ni(111)

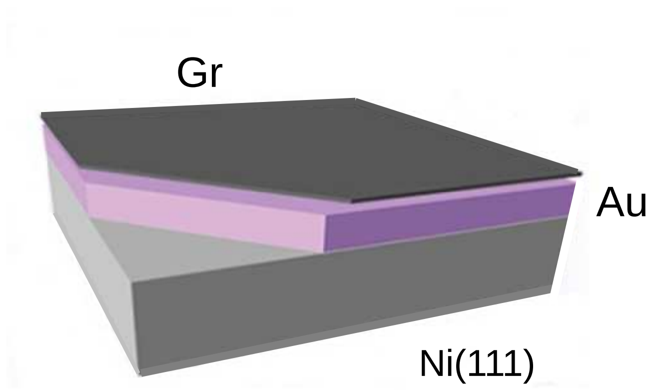




graphene/Au/Ni(111)



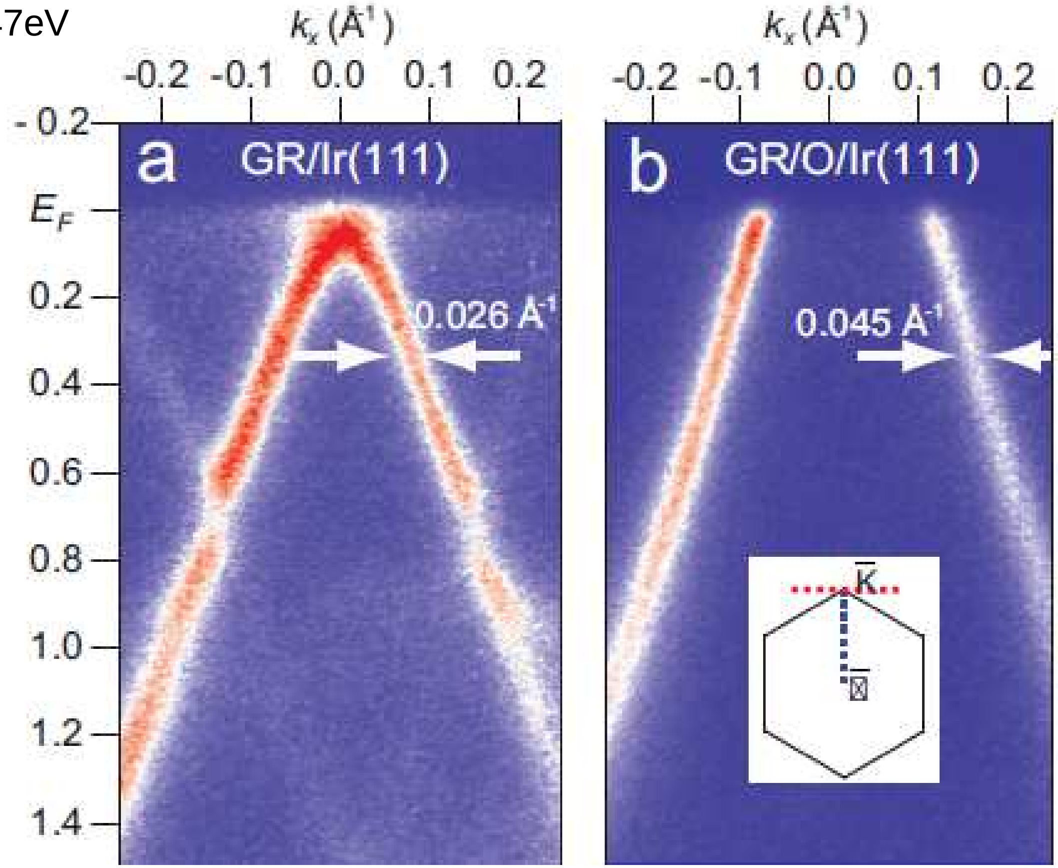


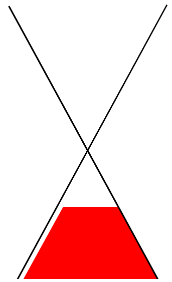


Voloshina New J. Phys. 13(2011) 113028

Decoupling of Gr from the Ir(111) substrate by O intercalation

ARPES hν=47eV

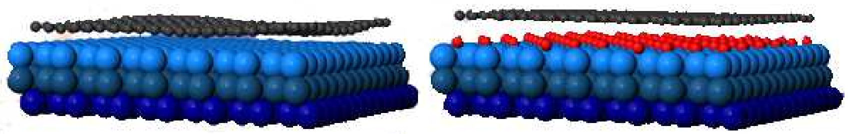




hole doping

E_D=-0.067 eV

E_D=-0.64 eV



Larciprete et al *ACS Nano 6,* 9551 (2012)

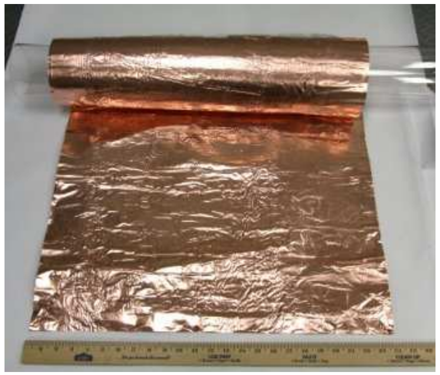
What we have learned :

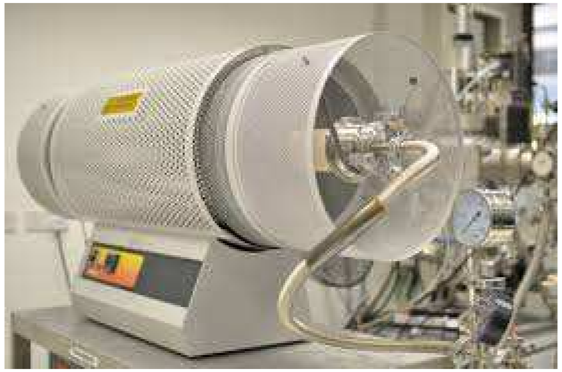
- Graphene grows on reactive TM metal crystals
- The intercation with the metal substrate changes the electronic structure of graphene
- Graphene can be decoupled from the substrate
- Atoms in contact to graphene might induce doping

If we want to move to technology……..

- Graphene grows on reactive TM metal ~~crystals~~
- The intercation with the metal substrate changes the electronic structure of graphene weakly interacting metal
- Graphene can be decoupled from the substrate
- Atoms in contact to graphene might induce doping

It is convenient to switch to a cheap substrate
polycrystalline copper foils **WEAKLY reactive**

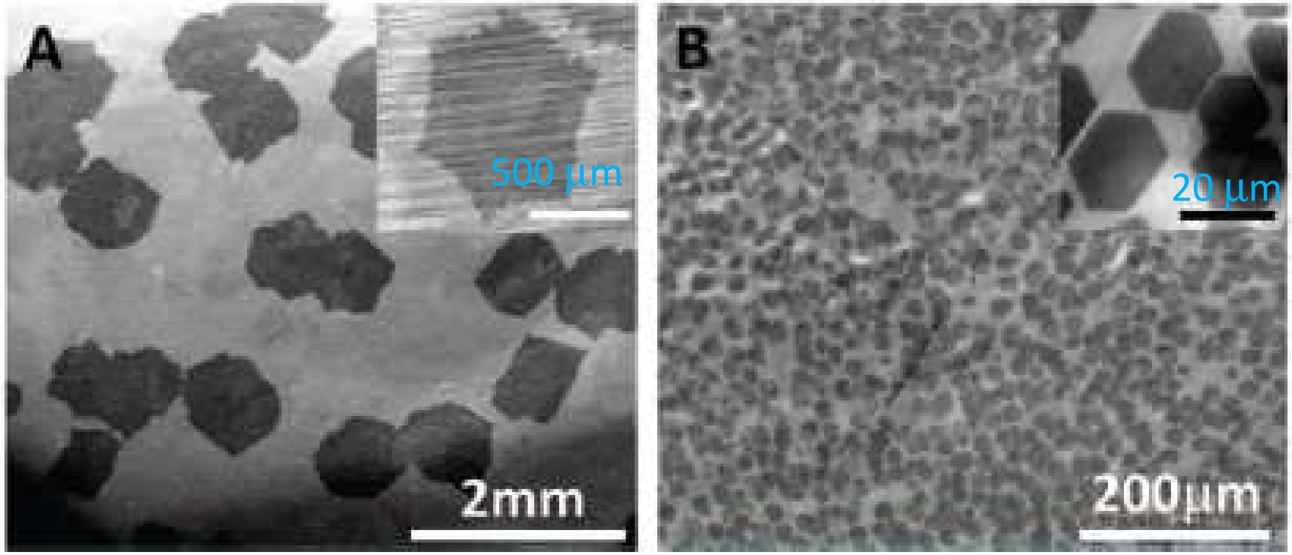




and use furnaces to grow large area graphene

Graphene growth on copper

oxygen-rich Cu   oxygen-free Cu



SEM

150 min   50 min

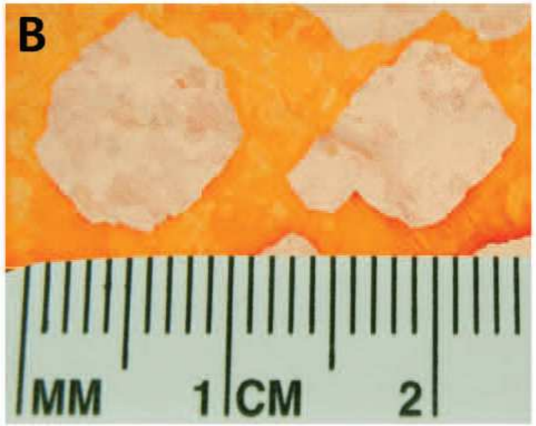
p_{CH4}=1x10^{-3} torr p_{H2}=0.1 torr

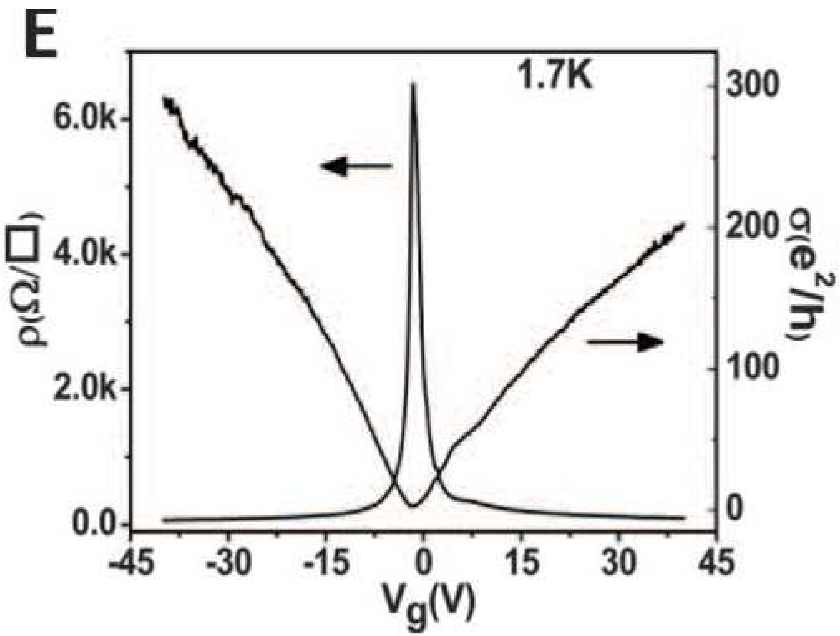
Hao et al. Science 2013

Low domain density Dendritic edges	High domain density Sharp edges

Graphene growth on copper

Carrier mobility 40.000-65.000 cm^2/Vs (1.7 K)
15.000-30.000 m^2/Vs (RT)

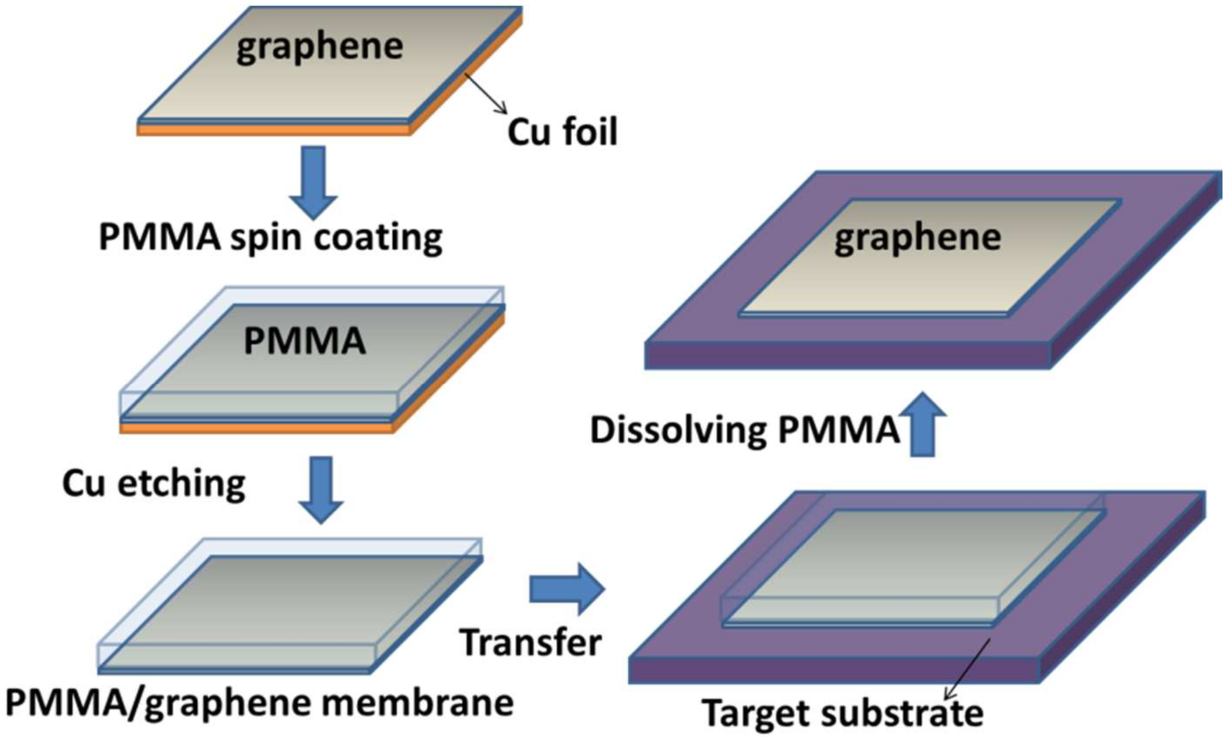




Hao et al. Science 2013

Electrical quality of large Gr domains is comparable to that of exfoliated graphene

Transfer of large area graphene

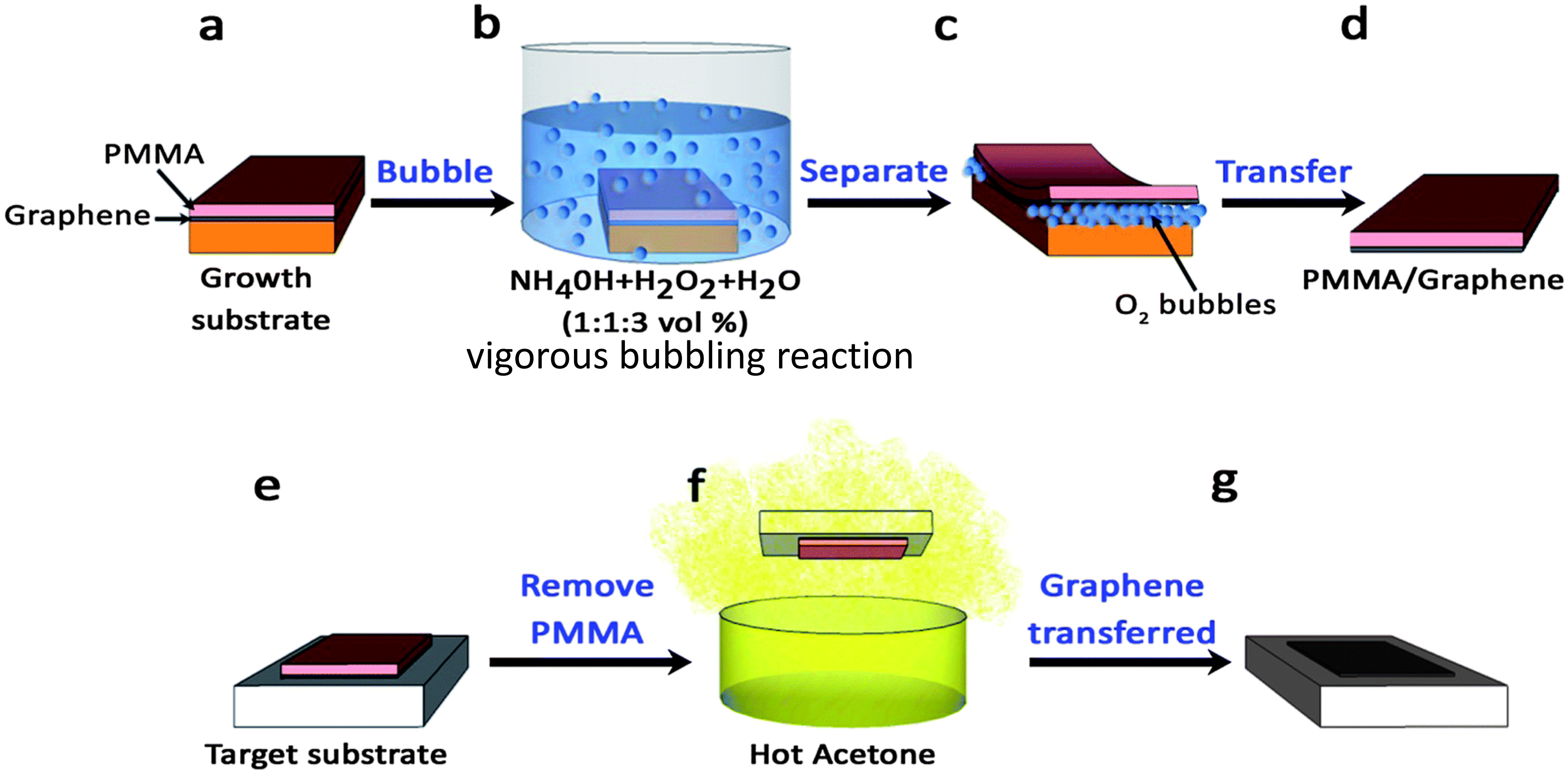


Ajay Kumar[1] and Chee Huei Lee[2]

Drawbacks:
Structural defects , cracks, polymer residuals.

Additional processing: vacuum annealing, substrate treatment,…

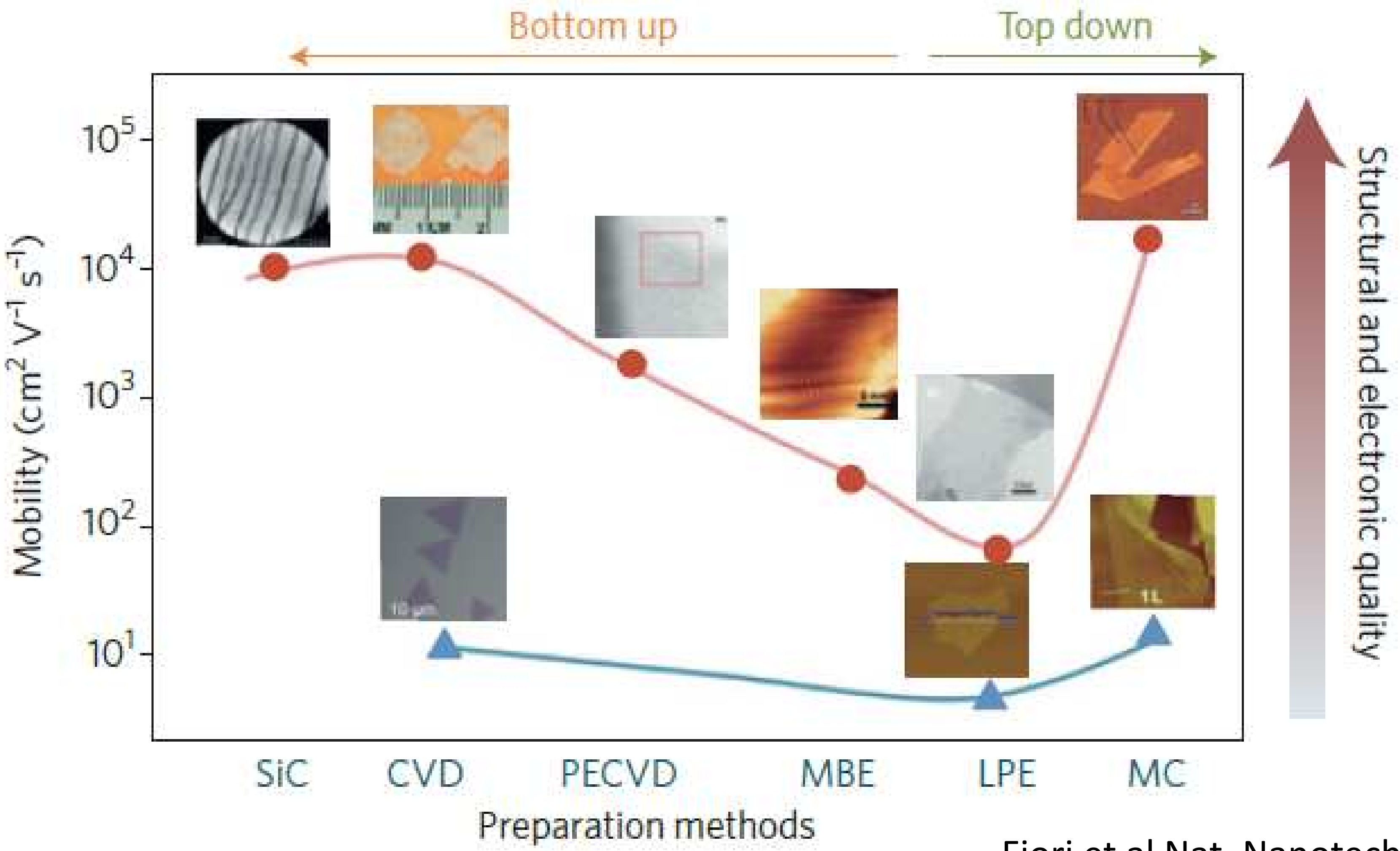
Transfer of large area graphene



vigorous bubbling reaction

Gorantla, *Nanoscale*, 2014,6, 889

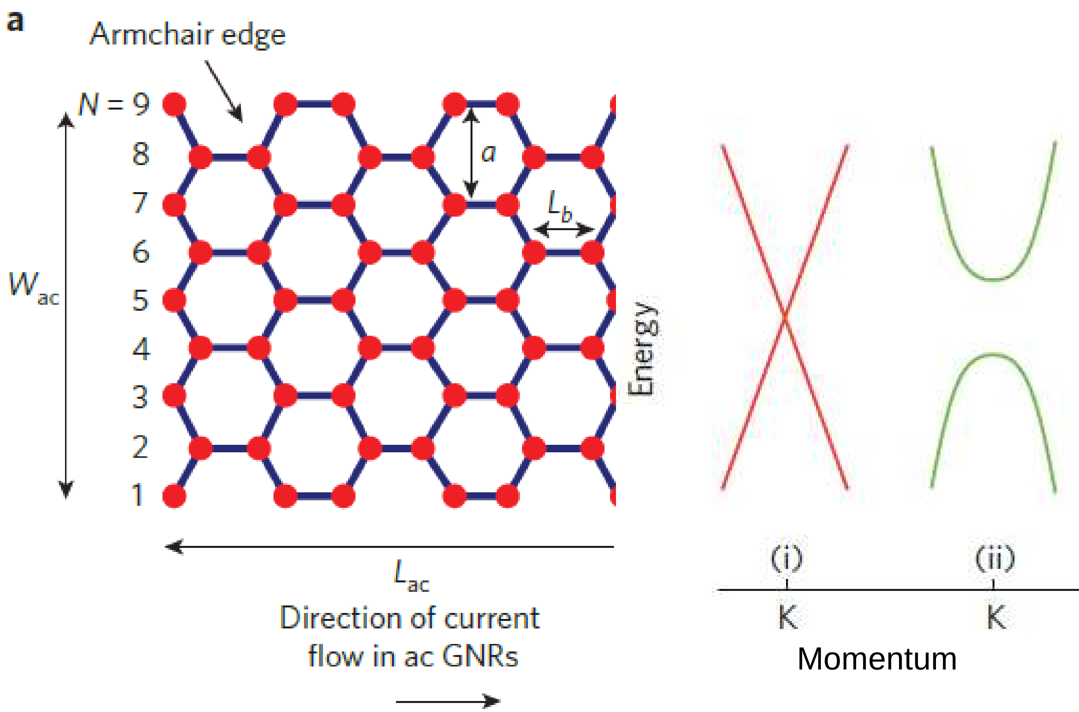
Mobility of 2DMs vs. preparation methods



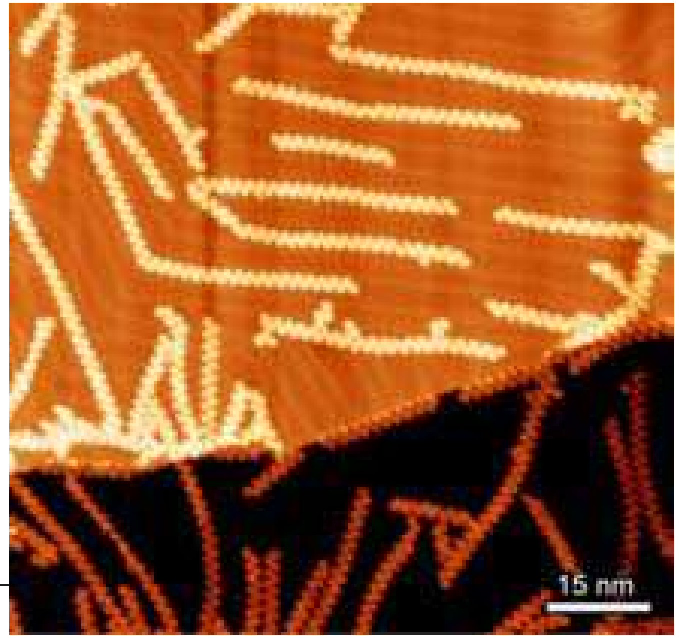
Fiori et al Nat. Nanotech 2014

Graphene grown at high T has a higher mobillity than that grown at lower T.

Graphene nanoribbons



Schwiertz Nat. Nanotech. 2010



1 nm wide, 50 nm long

J. Cai *et al, Nature*, 2010

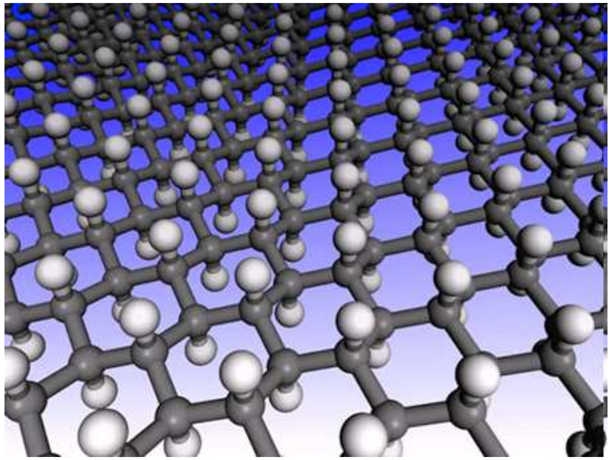
E_{gap}~1.38/W eV

carrier mobilities 50-200 cm^2 /Vs

relative increase in edge scattering events of charge carriers in the GNRs.

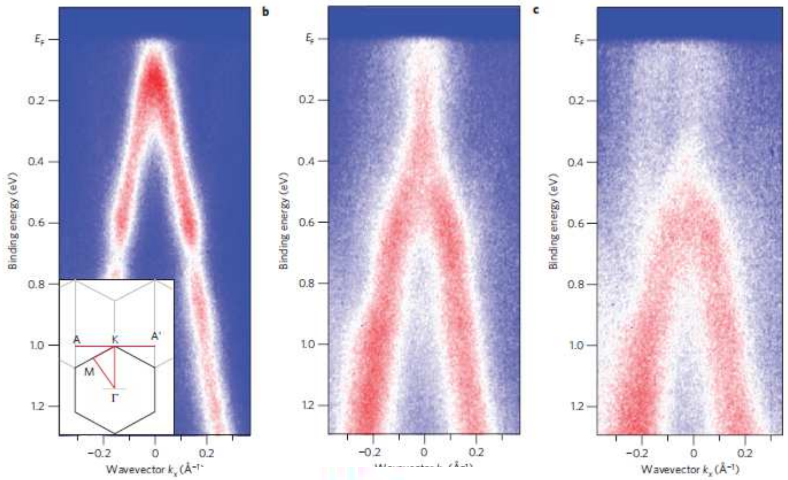
Graphane (CH)n

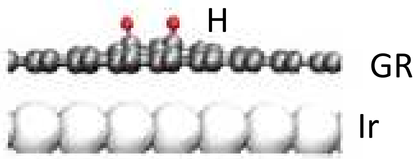
sp^3 bonds



graphane is a 2-D analog of cubic diamond

DFT calculations reveal that fully hydrogenated graphene is a wide-bandgap semiconductor, whereas half-hydrogenated graphene has a bandgap of 0.43 eV

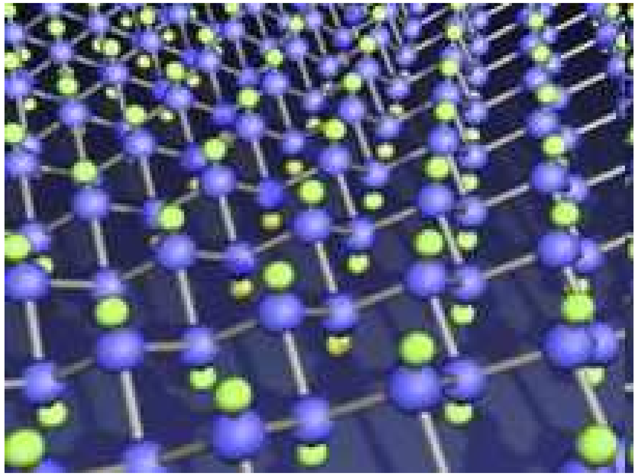




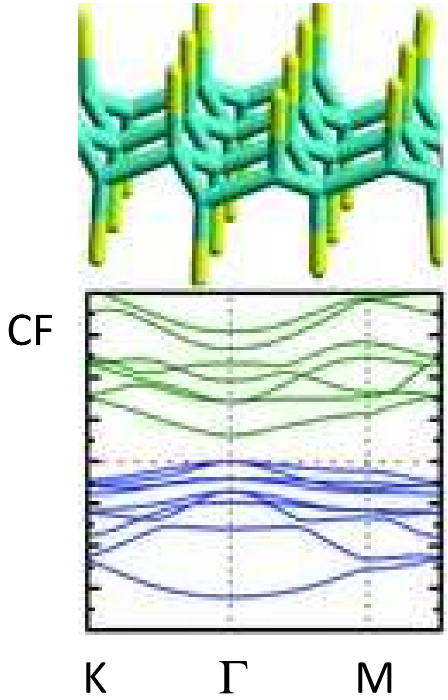
Balog et al. Nature mat. 9 (2010) 315

graphene hydrogenated from either one or both sides rapidly lost H at moderate *T,* which casts doubts that it could be used in applications where stability is required

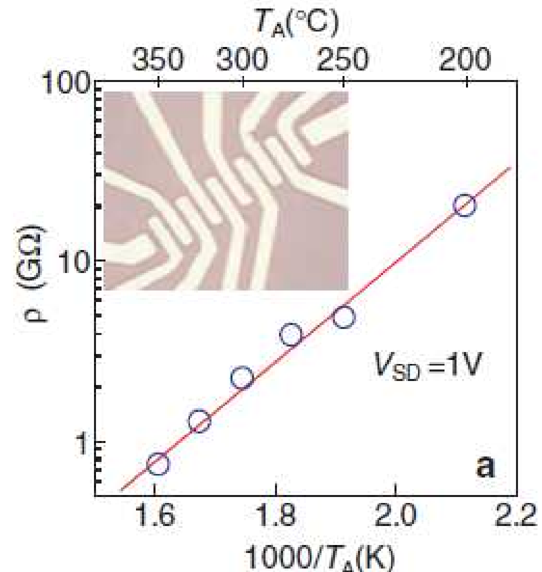
Fluorographene: the world's thinnest insulator



FG can be seen as a 2D analogue of Teflon, which is a fully fl fuorinated 1D carbon chain, or as a 2D counterpart of graphite fluoride.

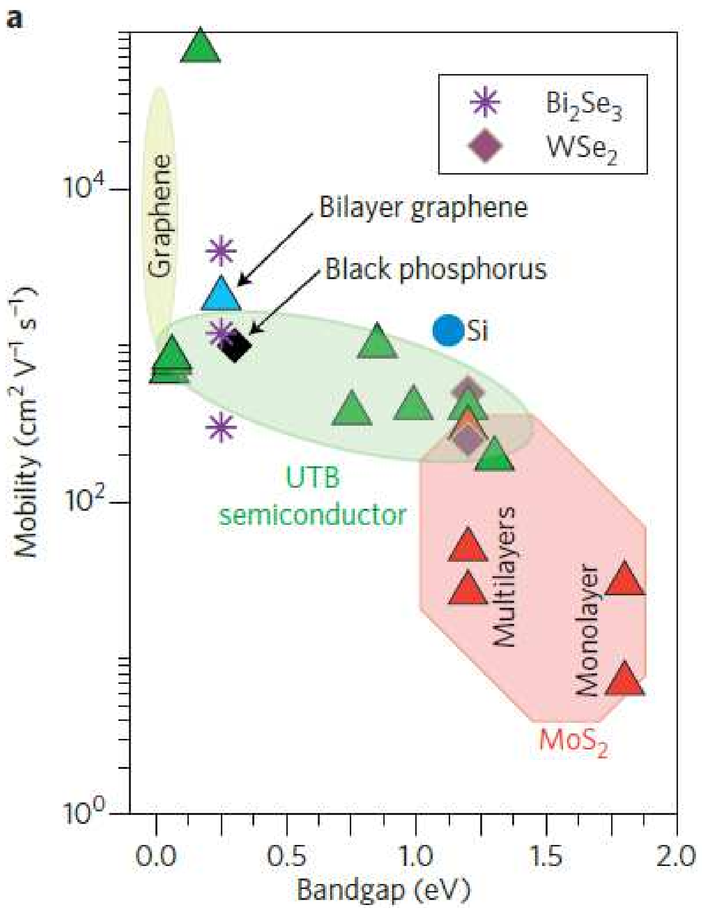


Zboril et al Small, Nov. 2010



Geim et al, Small Nov. 2010

2D materials



Fiori et al Nat. Nanotech 2014

- New materials

2D layers of IV group elements:

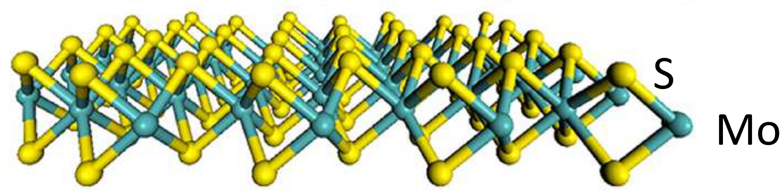
silicene, germanene, stannene

- Materials already known in their 3D form

Nitrides **h-BN**

Transition metal dichalcogenides (**MoS_2, WS_2**…)

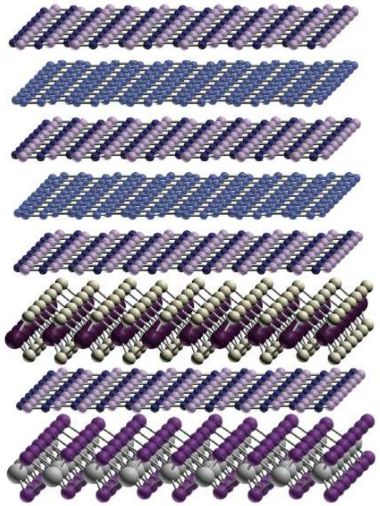
MX_2 (M: Mo, W, Nb, Re, Ni, or V) (X: S, Se, or Te)



Oxides **MoO_3, V_2O_5**

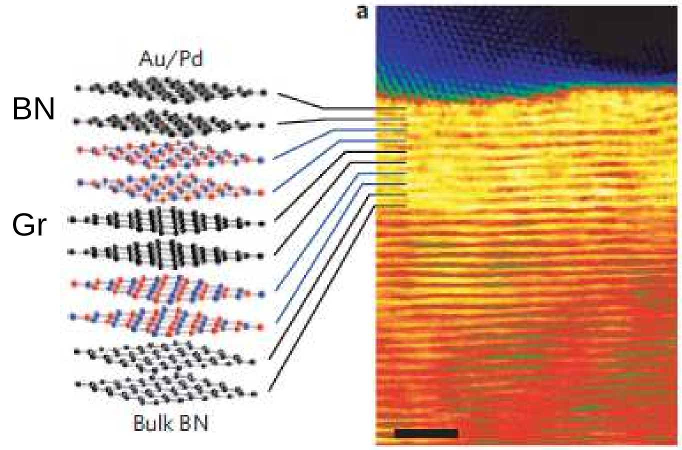
Phosphorene

2D materials



K. S. Novoselov, Rev. Mod. Phys. 83, 837 2011

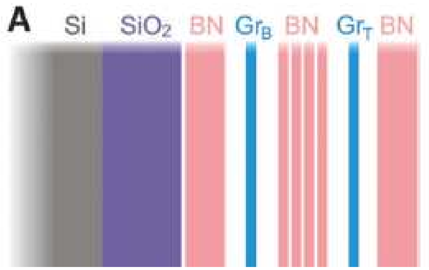
Graphene-based superlattices



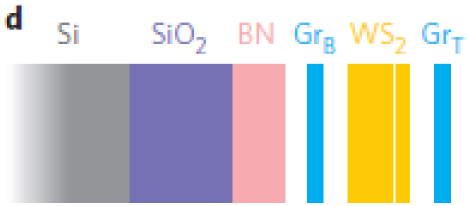
2nm

S. Haigh et al. Nat. Mat. 11 764 (2012)

Field-Effect Tunneling Transistor Based on Vertical Graphene Heterostructures

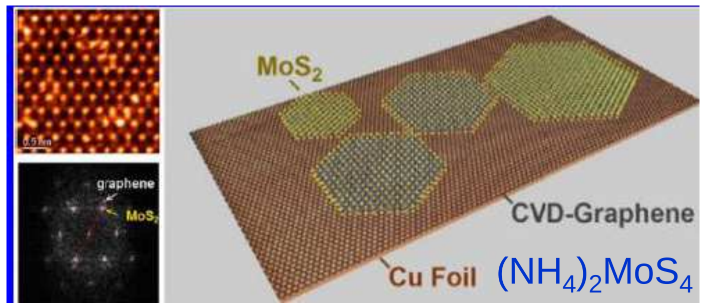


Britnell et al. Science 335, 947 (2012)



Georgiou, Nat. Nanotech. 2012

van der Waals Epitaxy of MoS_2 Layers on graphene



Shi et al. Nano Lett. 2012, 12, 2784

Conclusions

- Growth of large area high-quality, single-crystal 2D materials , required for the practical realization of 2D material-based technologies and for high-volume manufacturing, is a challenging tasks.

- With respect to graphene, 2D materials (monolayer and few-layer films) growth processes are still in their infancy, and many groups around the world are investigating ways of producing them (control of thickness, purity and point defects, such as chalcogen vacancies).

- Another crucial point in the fabrication of electronic devices is related to the electric contact between 2D materials and metals, which needs to be ohmic and have low resistance.

- Before these production processes can be used in any high-volume manufacturing environment, the growth conditions that yield high-quality films need to be stablished and optimized.

- If large-area materials growth is successful, 2D material technology could enable a new generation of **flexible electronics** for wearable and bendable systems.

Fiori et al Nat. Nanotech 2014

GRAPHENE FLAGSHIP

launched in 2013, 10 years, budget of €1 billion

142 academic and industrial research groups 23 countries

The Graphene Flagship is tasked with bringing together academic and industrial researchers
to take graphene from the realm of academic laboratories into European society, thus generating economic growth, new jobs and new opportunities.

GRAPHENE FLAGSHIP

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- WP 1: Materials
- WP2: Health and Environment
- WP3: Fundamental Science
- WP4: High Frequency Electronics
- WP 5: Optoelectronics
- WP6: Spintronics
- WP7: Sensors
- WP8: Flexible Electronics
- WP10: Nanocomposites
- WP9: Energy
- WP11: Production
- WP 12: Innovation

Thanks for your attention!