Wafer scale production of graphene: opportunities and challenges

Richard van Rijn

HVM Graphene Conference 5 November 2013
hvm-uk.com

Applied Nanolayers

Who are we

- Applied Nanolayers BV
  – Company building a 200 mm CVD wafer production line for graphene in The Netherlands.

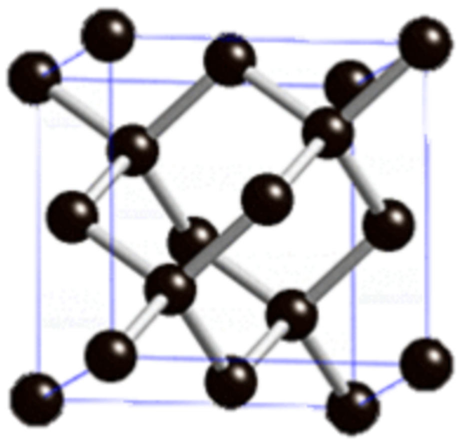
Applied Nanolayers

Outline

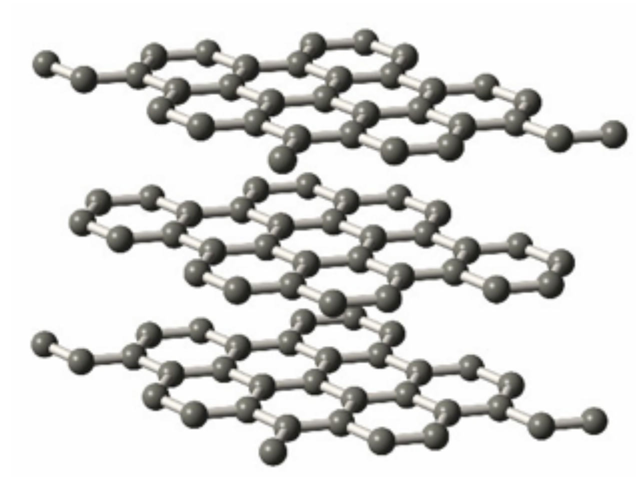
- ~~Graphene background and properties~~
- Production methods and challenges
- Transfer methods
- Quality control

ANL
Applied Nanolayers

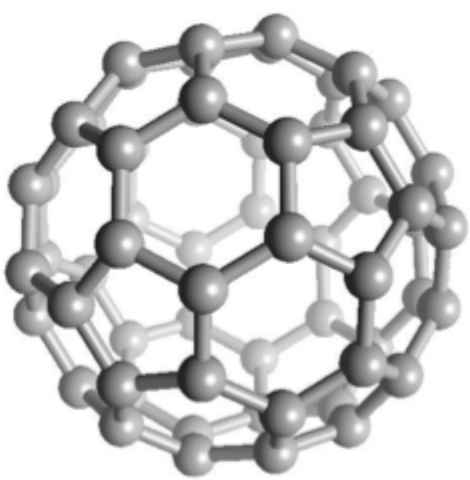
Carbon



diamond



graphite



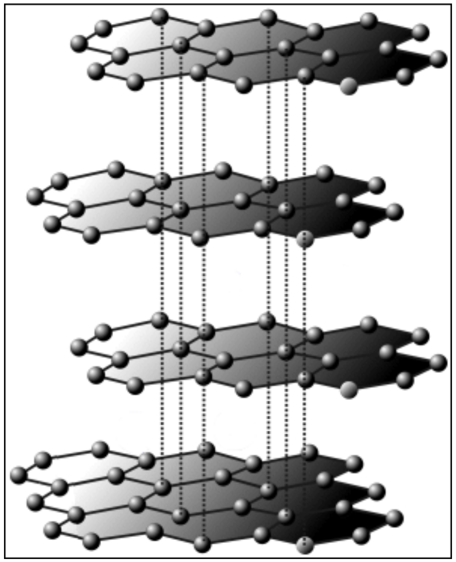
bucky balls

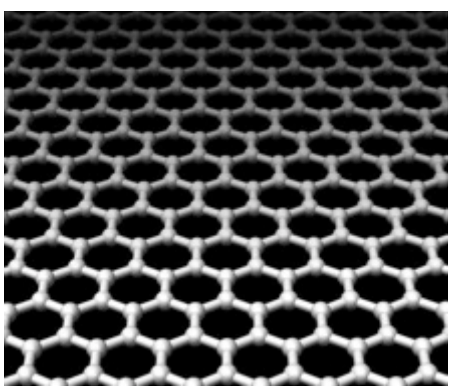
nanotubes

ANL Applied Nanolayers

Graphene

graphite





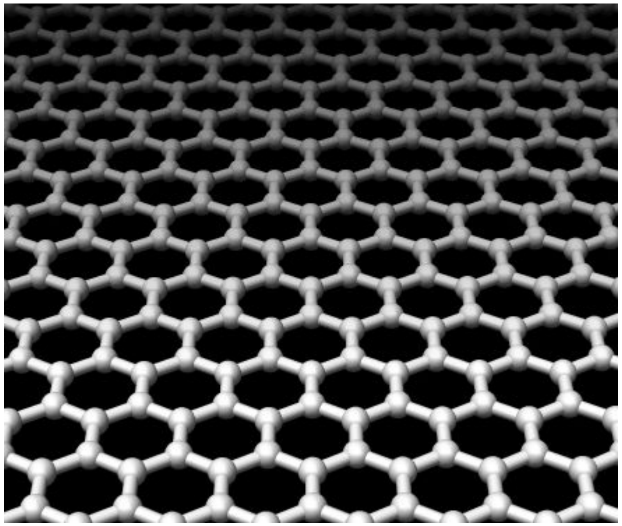
Prof. Andre Geim
Nobel Prize
Physics 2010

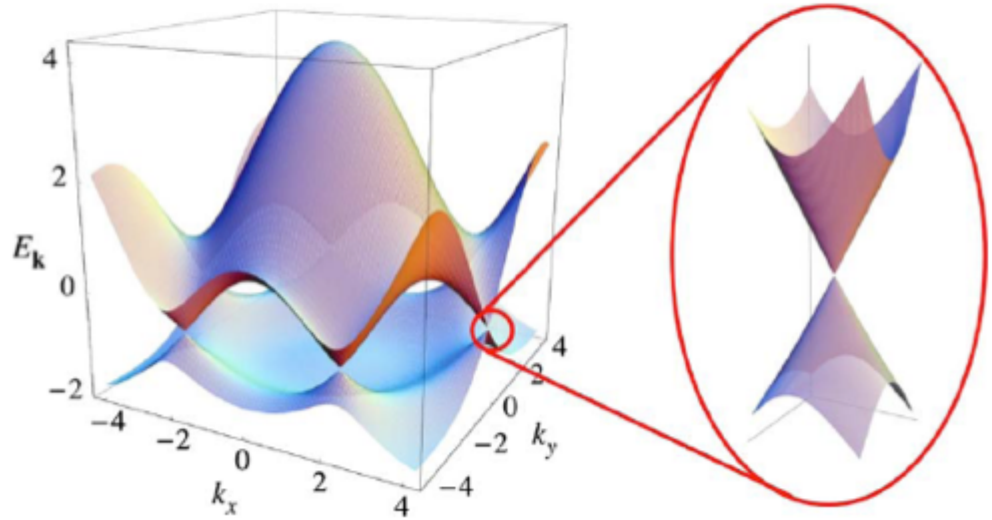
'dream material':

- Thinnest possible material!
  - first 'proposed' in 1947 (P.R. Wallace)
- Many special properties
  - first explored in 2004 (Geim et al.)

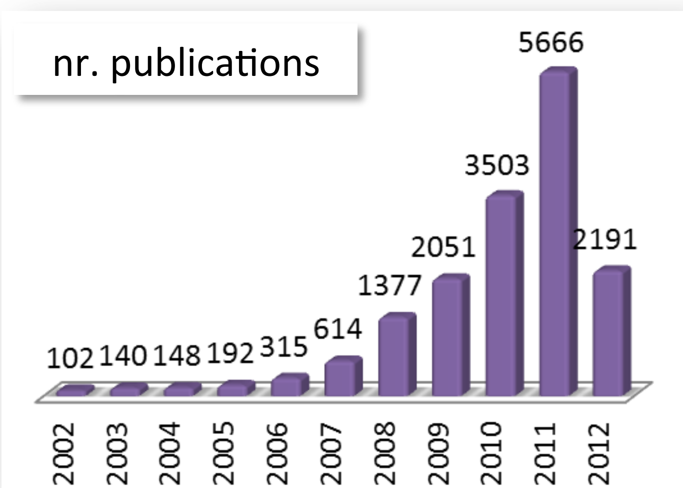
Applied **Nanolayers**

Graphene trivia





Castro Neto, Guinea, Peres, Novoselov, Geim, *Rev.Mod.Phys.* **81**, 109 (2009)

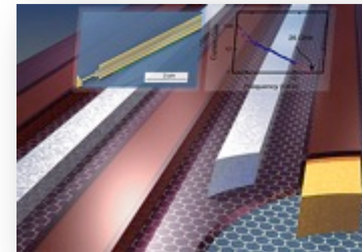


- Electrons behave as 'massless Dirac fermions': $E = \hbar v_F \sqrt{k_x^2 + k_y^2}$
- High electron (and hole) mobility
- Promising for future (flexible) electronics

Applied Nanolayers

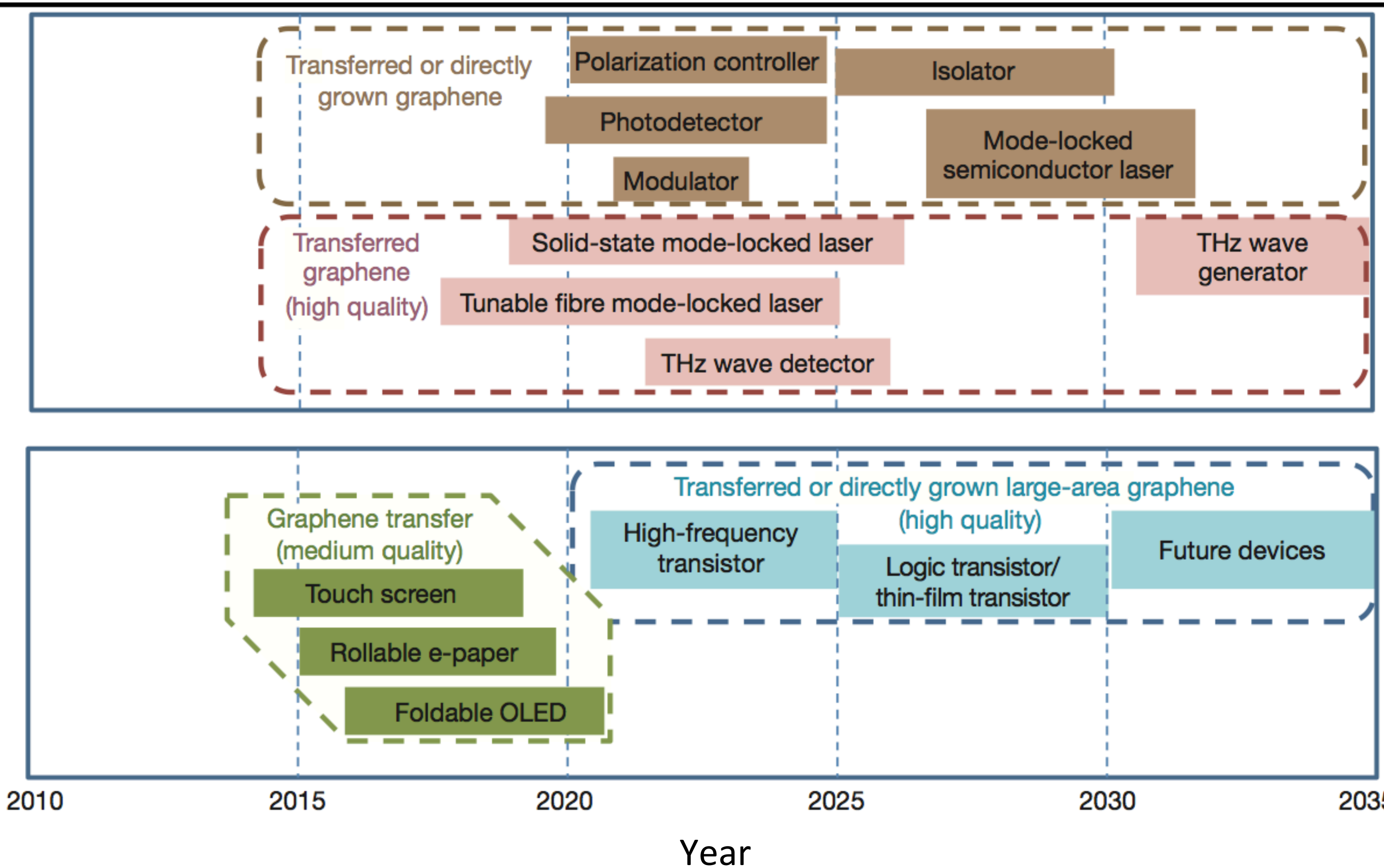
Properties

- Special properties and applications:
  - High electron (hole) mobility
    200,000 $cm^2V^{-1}s^{-1}$: future chip technology addition to/(replacement of silicon?); 100 GHz transistor, 10 GHz mixer (IBM); low spin-orbit interaction (spintronics?)
  - Strong and flexible
    1 TPa: (200 x steel): flexible electronics, MEMS resonators, sensors, membranes, coatings, enforcing material in composites, graphene 'paper'
  - High thermal conductivity
    5000 $Wm^{-1}K^{-1}$: heat sink for electronic circuits
  - Optical properties
    graphene-based laser; 2.3% absorption of white light through single graphene layer; transparent conductor: replacement of indium-tin-oxide (touch screens)
  - Chemically inert
    protective coating: anti-corrosive, anti-adhesive, anti-friction/wear; impermeable
  - Efficient in charge storage
    'ultra-capacitor': replacement of lithium batteries
  - Efficient in hydrogen storage
    energy storage medium
  - Bio-compatible
    bio-sensors, bio-compatible coatings, anti-bacterial



Applied Nanolayers

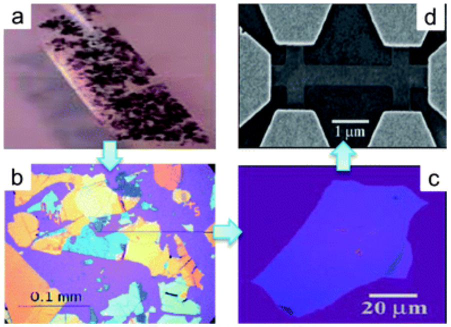
Applications



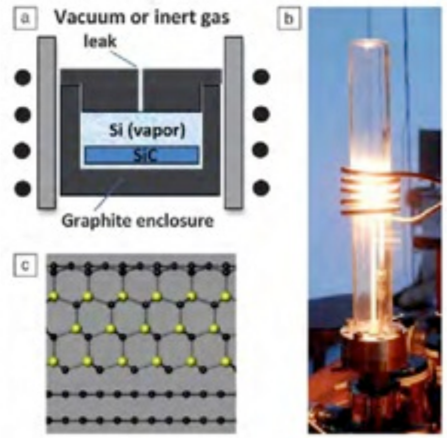
Novoselov et al. *A roadmap for graphene*, Nature **490** (2012)

Production methods

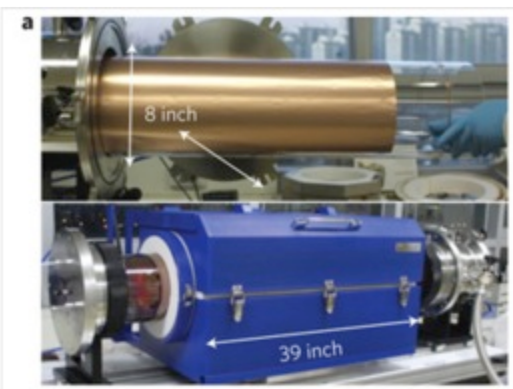
- Mechanical exfoliation

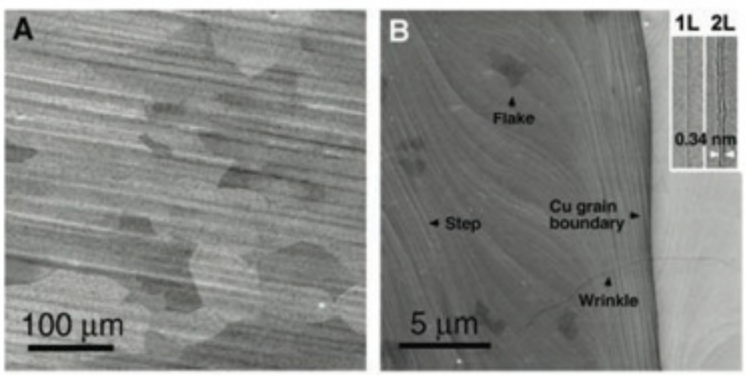


- Thermal decomposition of SiC



- CVD on transition metals





ANL
Applied Nanolayers

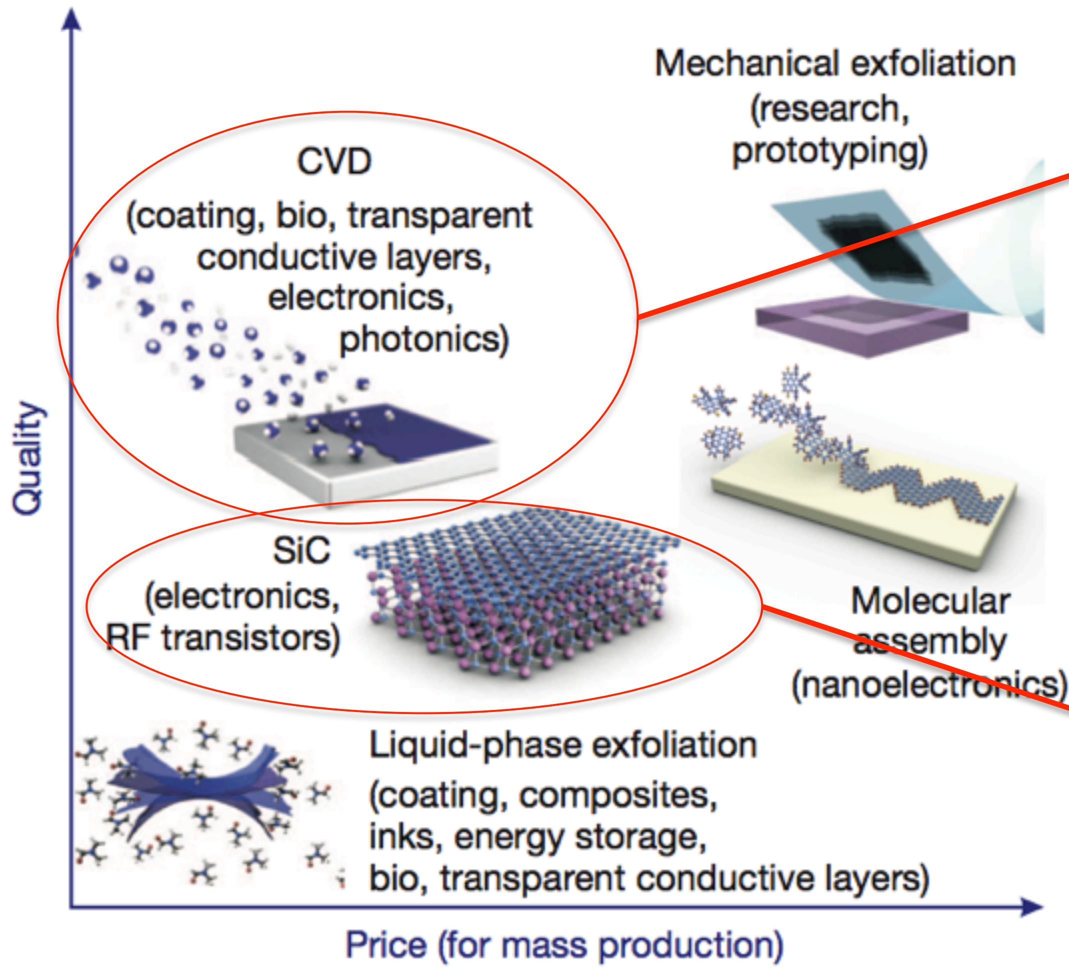
Productions methods

Method	Crystallite size (μm)	Sample size (mm)	Mobility (ambient) ($cm^2 V^{-1} s^{-1}$)	Applications
Mechanical exfoliation	> 1000	> 1	> $2{\cdot}10^5$	Research
Chemical exfoliation	≤ 0.1	Infinite as overlapping flakes	100	Coating, paint/ink, composites, transparent conductive layers, energy storage, bioapplications
Chemical exfoliation via graphene oxide	~ 100	Infinite as overlapping flakes	1	Coating, paint/ink, composites, transparent conductive layers, energy storage, bioapplications
CVD	1000	~ 1000	10000	Photonics, nanoelectronics, transparent conductive layers, sensors, bioapplications
SiC	50	100	10000	High frequency transistors and other electronic devices

Novoselov et al. *A roadmap for graphene*, Nature **490** (2012)

Applied Nanolayers

Production methods



Growth on metal and subsequent cold transfer to desired substrate

Grown and used on SiC

Novoselov et al. *A roadmap for graphene*, Nature **490** (2012)

CVD graphene

- Growth on metals:
  - Single crystals
  - Foils
  - Epitaxial layers

- Metals:
  - Cu (cheap, low carbon solubility, SLG)
  - Ni (cheap, high carbon solubility, MLG)
  - Rh, Ru, Pt, Au, Ir, etc. (expensive)

- Methods
  - Thermal CVD
  - PE CVD
  - Carbon segregation

Graphene as a platform

- 2D materials used with graphene:
  - h-BN (insulator)
  - MoS2 (semiconductor)
  - Many more…
- CVD production of h-BN layers is possible.
- h-BN and graphene can be grown or transferred on top of each other.
- Hybrid h-BN/graphene layers can also be synthesized.

ANL Applied Nanolayers

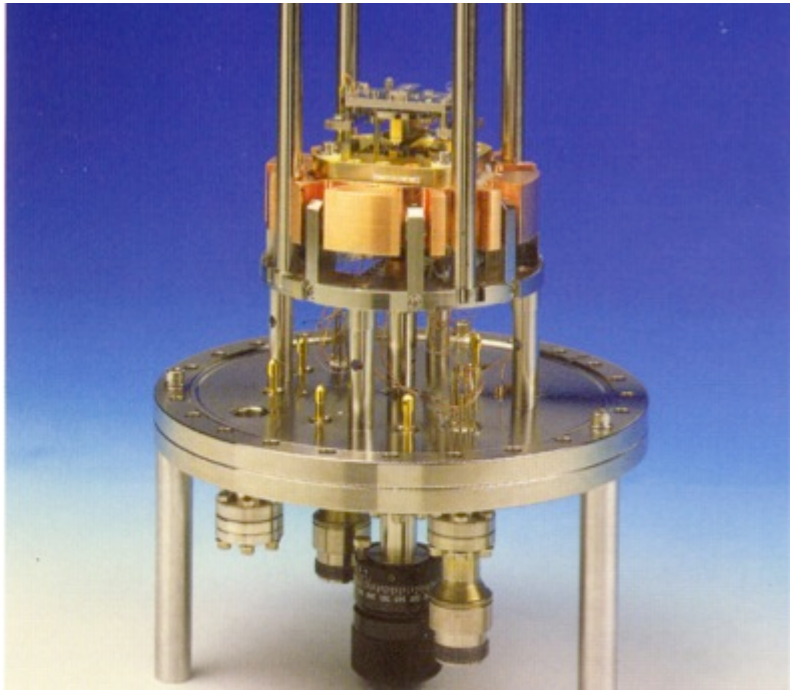
Live STM studies of graphene growth

High speed

- Speed: ***video-STM***
  0.01 – 25 frames/s
  (256x256 pixels) x2

Variable temperature

- Range: *- 50 K – 1300 K*
- Sweep: *- full T-range:*
  same area in sight' over 300 K
- 'Secret':- *finite-element analysis*



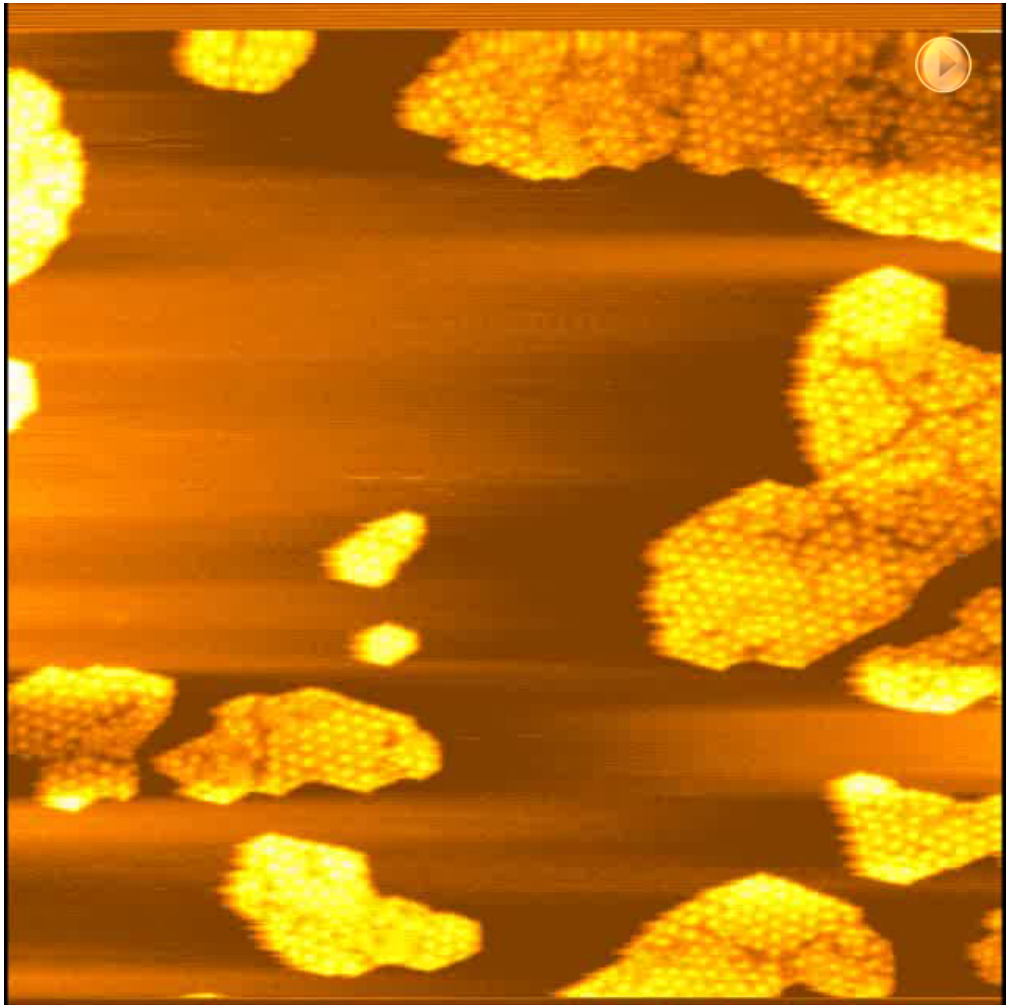
Hoogeman *et al.*, Rev.Sci.Instrum. **69** (1998) 2072
M.J. Rost *et al.*, Rev.Sci.Instrum. **76** (2005) 053710

ANL Applied Nanolayers

Graphene growth on rhodium

Start: Rh(111) seeded with graphene at RT by C_2H_4

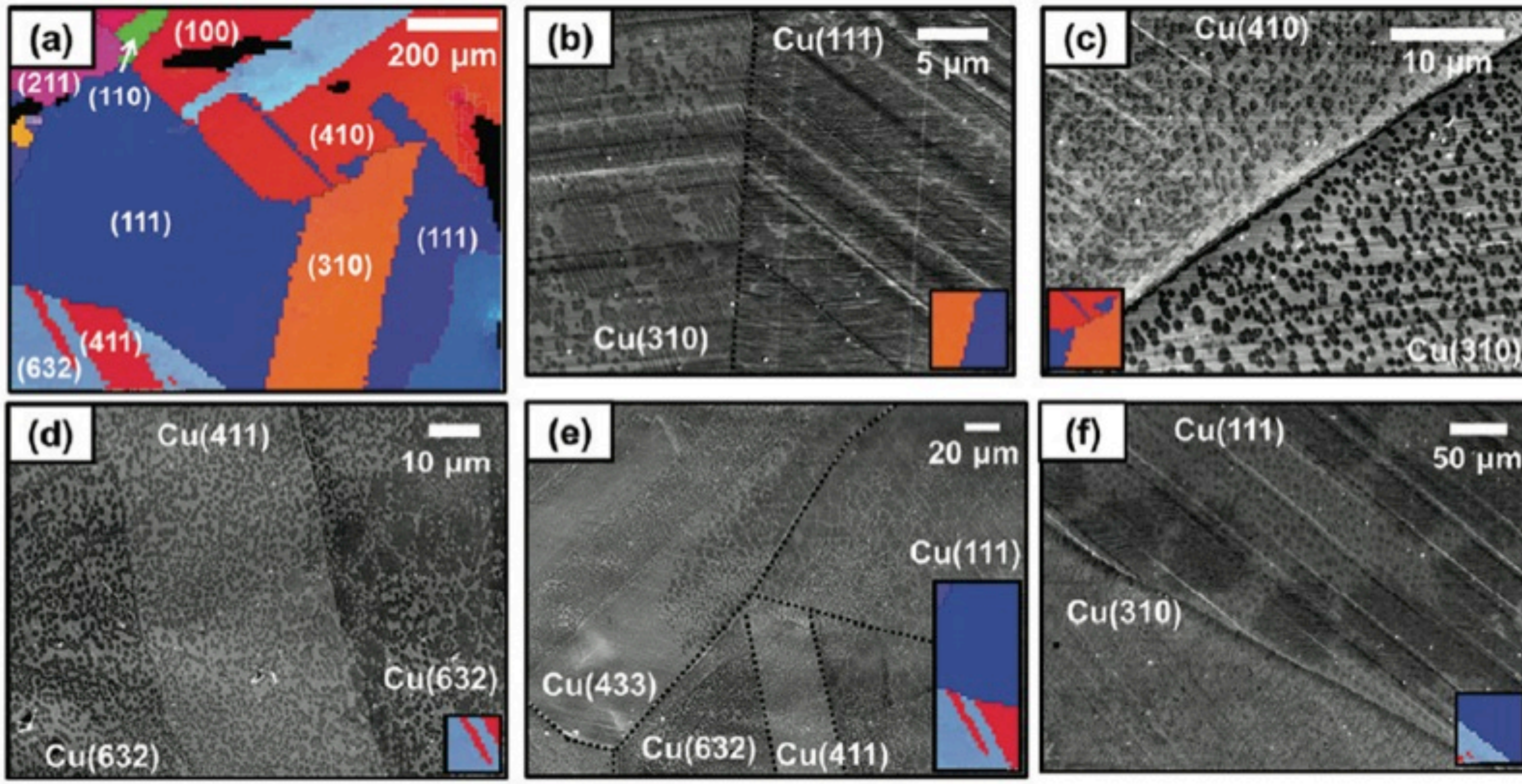
Movie: further C_2H_4 exposure at 975 K at $3X10^{-9}$ ~1 $X10^{-8}$ mbar



Real time: 76mins
170 X 170nm^2
I = 50 pA
V = -1.84 V

Applied Nanolayers

Substrate orientation: or the problem with foil



Cu(111) gives highest quality graphene

Wood et al. Nano Letters (2011)

ANL Applied Nanolayers

Crystalline Substrate Orientation

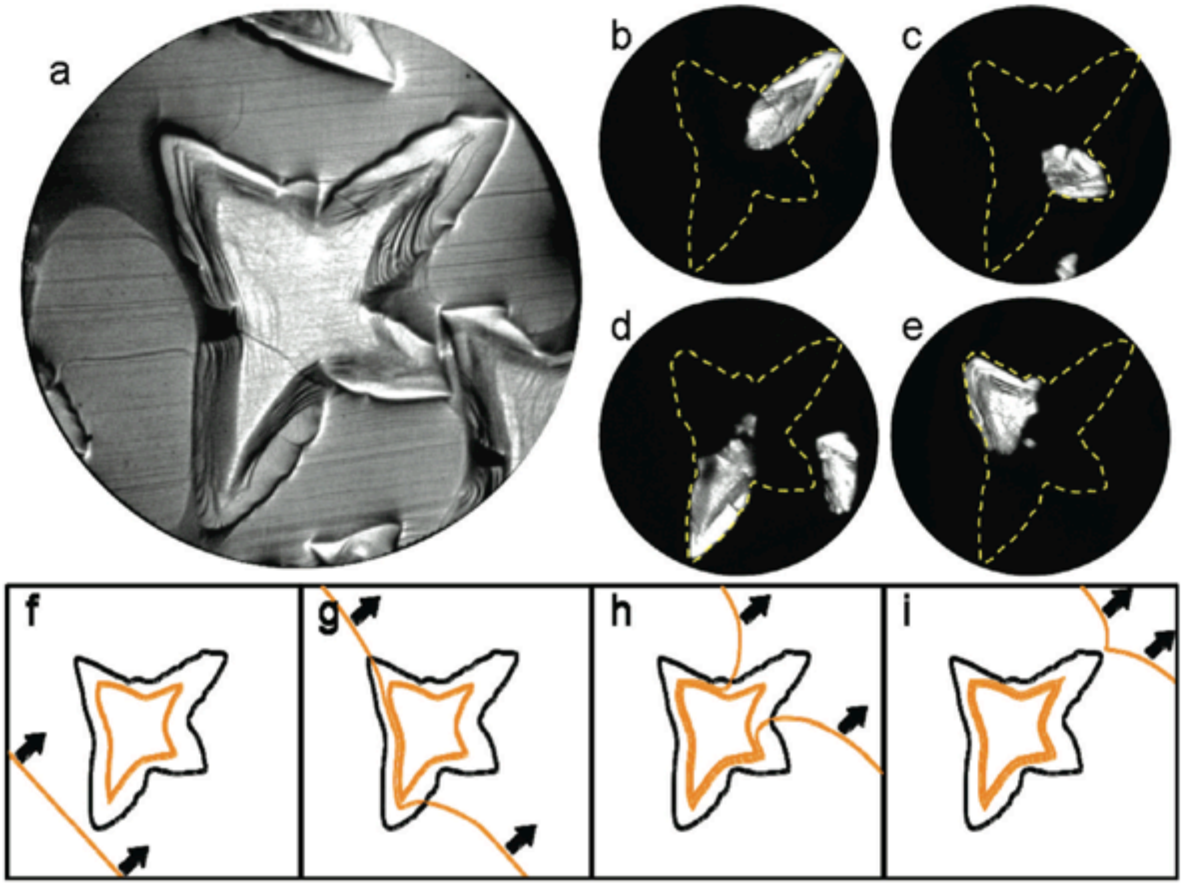


FIGURE 3. Bright (a) and dark field (b−e) LEEM images of a large graphene island on Cu(100) showing the spatial distribution of rotational variants. The graphene (01) direction is rotated by (b) 28°, (c) 2°, (d) 8°, and (e) 42°, relative to Cu(001) (FOV = 20 μm, yellow dashes are the approximate island boundary). Cu step edge accumulation during growth results in a Cu hillock beneath the graphene island, as can be seen in (a). The hillock formation process is illustrated in (f−i).

Cu(100) gives four different graphene domains in one graphene island

Wofford et al. Nano Letters 2010

Applied Nanolayers

Grain boundary

Grains and grain boundaries in single-layer graphene atomic patchwork quilts

Pinshane Y. Huang[1]*, Carlos S. Ruiz-Vargas[1]*, Arend M. van der Zande[2]*, William S. Whitney[2], Mark P. Levendorf[3], Joshua W. Kevek[4], Shivank Garg[3], Jonathan S. Alden[1], Caleb J. Hustedt[5], Ye Zhu[1], Jiwoong Park[3,6], Paul L. McEuen[2,6] & David A. Muller[1,6]

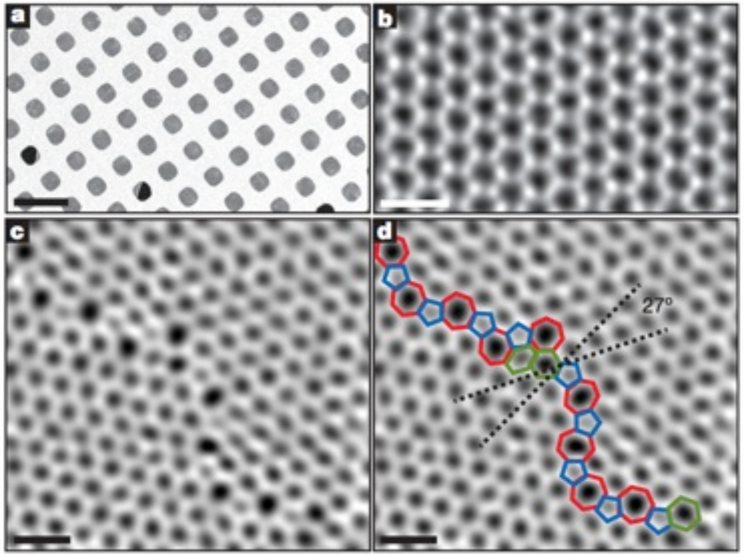


Figure 1 | Atomic-resolution ADF-STEM images of graphene crystals. **a**, Scanning electron microscope image of graphene transferred onto a TEM grid with over 90% coverage using novel, high-yield methods. Scale bar, 5 µm. **b**, ADF-STEM image showing the defect-free hexagonal lattice inside a graphene grain. **c**, Two grains (bottom left, top right) intersect with a 27° relative rotation. An aperiodic line of defects stitches the two grains together. **d**, The image from **c** with the pentagons (blue), heptagons (red) and distorted hexagons (green) of the grain boundary outlined. **b–d** were low-pass-filtered to remove noise; scale bars, 5 Å.

20 JANUARY 2011 | VOL 469 | NATURE | 389

Applied Nanolayers

Grain boundary

Tailoring Electrical Transport Across Grain Boundaries in Polycrystalline Graphene

Adam W. Tsen,[1] Lola Brown,[2] Mark P. Levendorf,[2] Fereshte Ghahari,[3] Pinshane Y. Huang,[1] Robin W. Havener,[1] Carlos S. Ruiz-Vargas,[1] David A. Muller,[1,4] Philip Kim,[3] Jiwoong Park[2,4]*

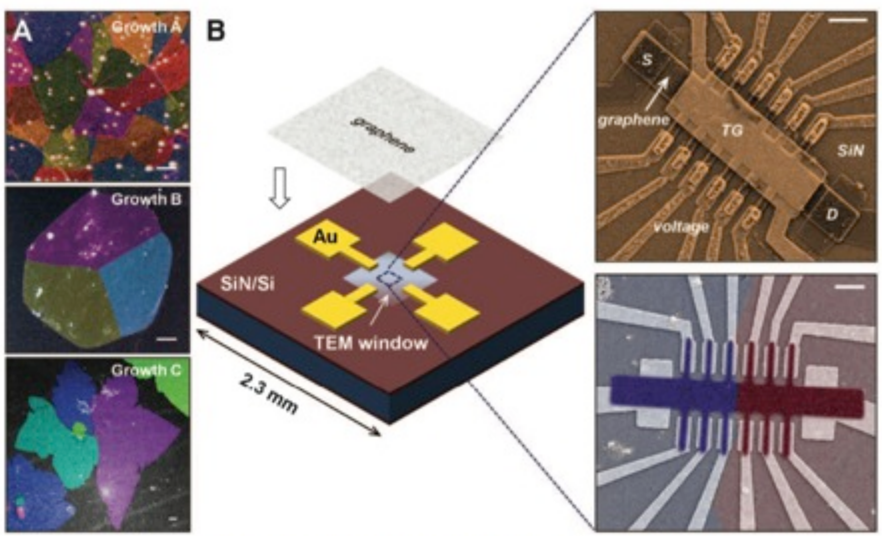
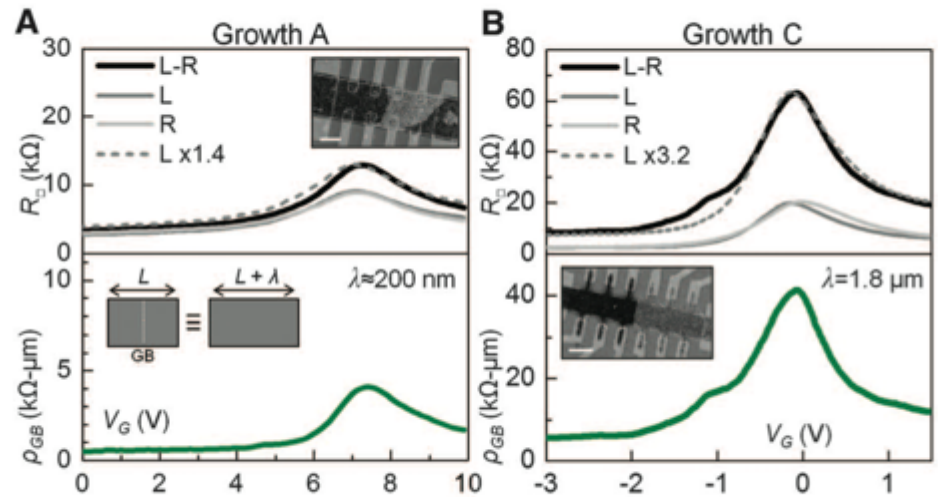


Fig. 1. (**A**) Composite false-color DF-TEM images of CVD graphene produced using three different growth conditions—A, B, and C—yielding average domain size *D* of 1, 10, and 50 μm, respectively, in continuous films. (**B**) (Left) Schematic of specially fabricated TEM chip compatible with electron-beam lithography and electrical measurements. (Top right) SEM image of top-gated, graphene Hall bar device. (Bottom right) Overlaid SEM and DF-TEM images showing device crossing a single GB of two domains from growth C. Scale bars, 1 μm.



Growth method determines grain boundary resistivity

Applied Nanolayers

Graphene growth challenges

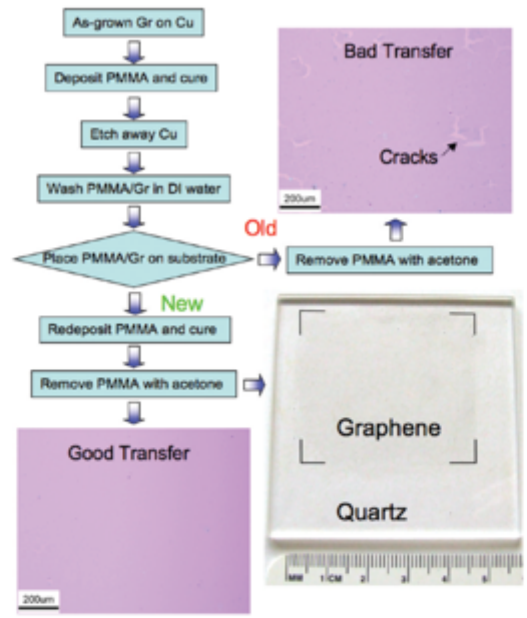
- Control number of layers precisely
- Separate nucleation and growth
- Control domain size
- Control substrate/graphene morphology
- Control Chemical doping

Applied Nanolayers

Transfer methods

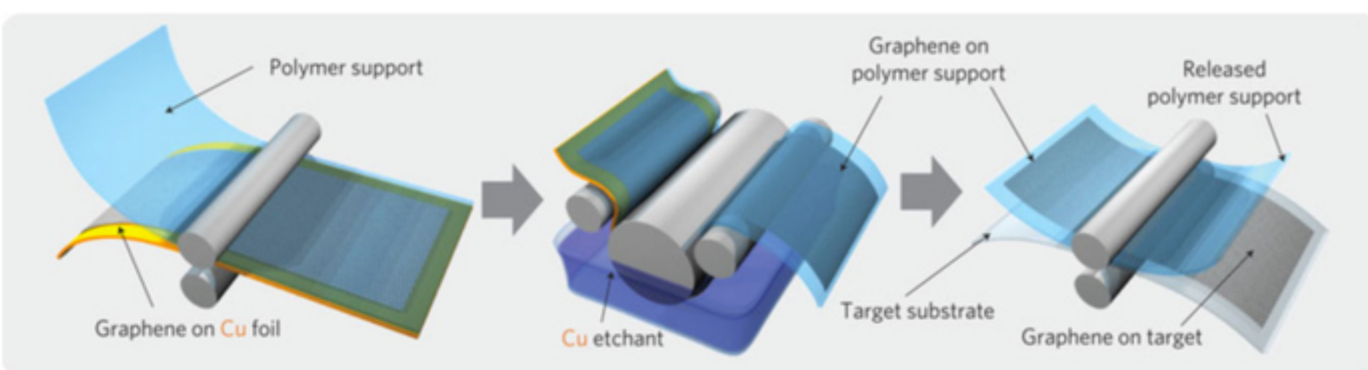
- PMMA assisted wet transfer

  Li et al, Nano Letters **9** (2009)



- Thermal release tape

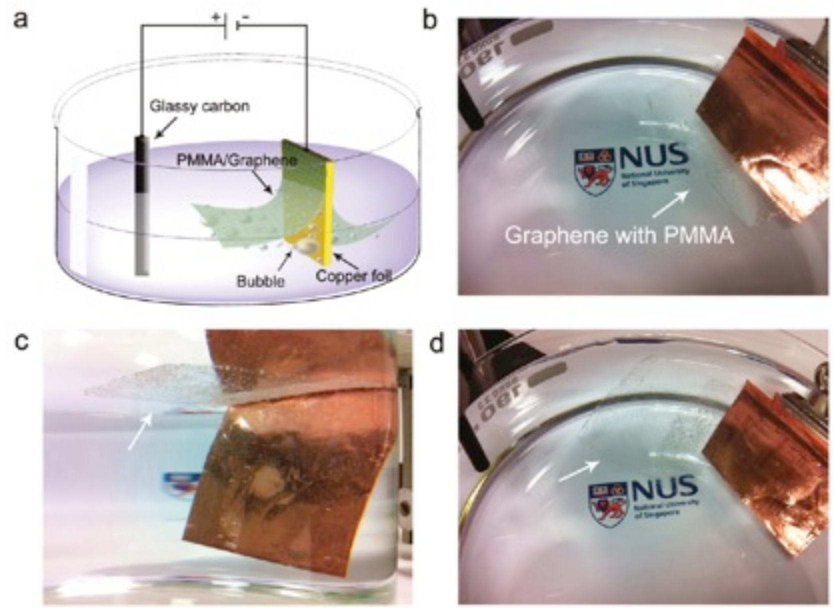
  Bae et al, Nature Nanotechnology **5** (2010)



Applied Nanolayers

Transfer methods

- Electrochemical delamination
  - No etching of (copper) substrate. H_2 used to delaminate PMMA/G film
  - Substrate re-use possible with this method

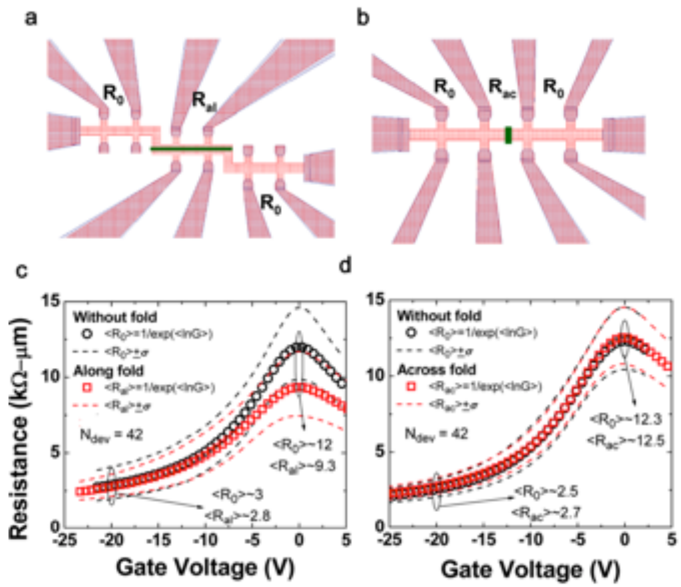


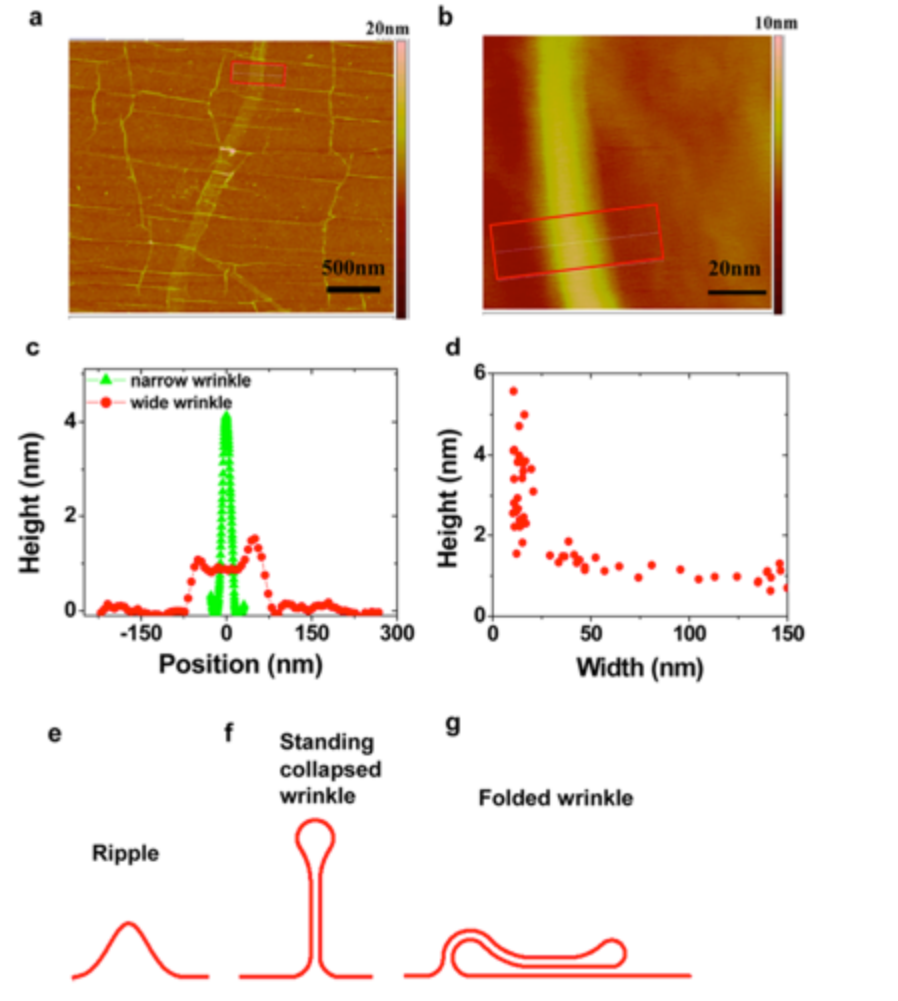
Wang et al, ACS Nano **5** (2011)

Applied Nanolayers

Transfer challenges

- Scalability/cost
- Chemical damage
- Mechanical damage
  - Holes, tears, wrinkles





Zhu et al , Nano Lett, **12** (2012)

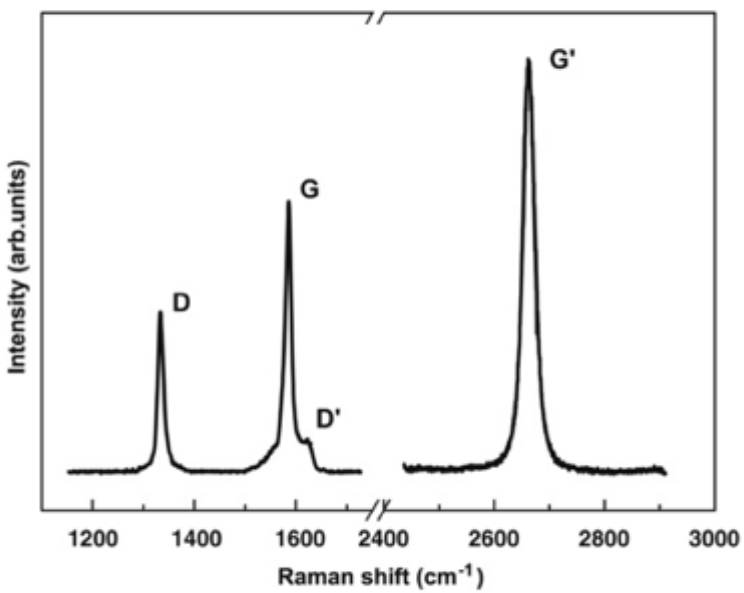
ANL Applied Nanolayers

Quality control

- Graphene quality can relate to different properties:
  - Mobility, sheet resistance, grain size, roughness, defect density
  - Uniformity of different properties:
    - Doping
    - Layer number
    - Grain size
    - Structural defects
    - Morphology
  - Many more…
- 'Low quality' and 'high quality' are meaningless without a relation to the aspects of quality they refer to (and which aspects of quality are important for specific applications)

Raman spectrocopy for quality control

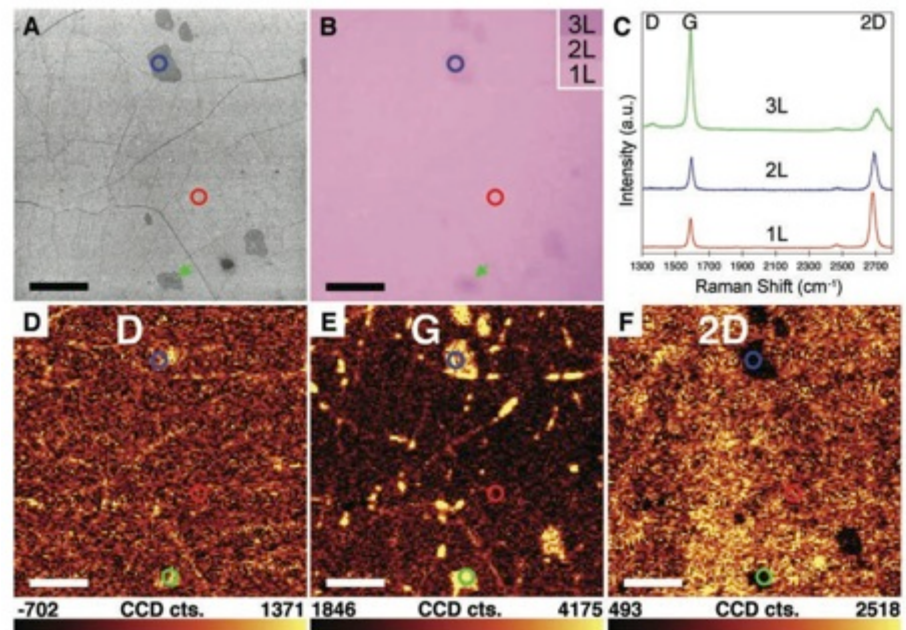
L.M. Malard et al. / Physics Reports 473 (2009) 51–87



Local properties taken from Raman spectrum relating to peak shapes, widths, heights and positions of the indicated peaks.

- Number of layers
- Presence of Raman active defects
- Average distance between defects
- Doping

Mapping with micro-Raman



Li et al, Science **324** (2009)

Applied Nanolayers

Barriers to industrialization

- Quality control of material
- Integration into manufacturing
- Security of supply
- Material cost
- Short term application
- Control over / tuning of different properties

Applied Nanolayers

Closing

- Graphene comes in more than one form.
- Many ways of producing and transferring. These will be specific to certain applications.
- For graphene to be relevant a robust quality analysis chain through manufacturing must guarantee product is always the same!
- ANL is focused on building this chain and starting up a 200 mm production facility in the Netherlands.

- Contact details: r.van.rijn@appliednanolayers.com

ANL Applied Nanolayers