Wafer scale production of graphene: opportunities and challenges

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HVM Graphene+ 2014 Conference
Oxford, UK 15 May

www.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.

Leiden

Nijmegen

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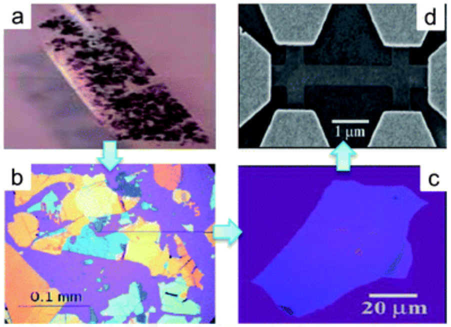
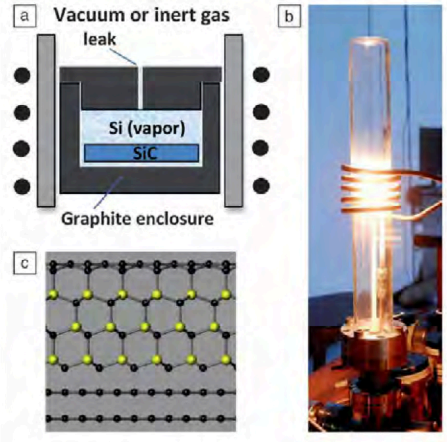
Production methods

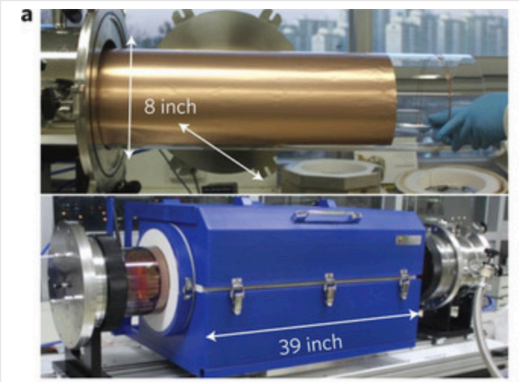
- Mechanical exfoliation

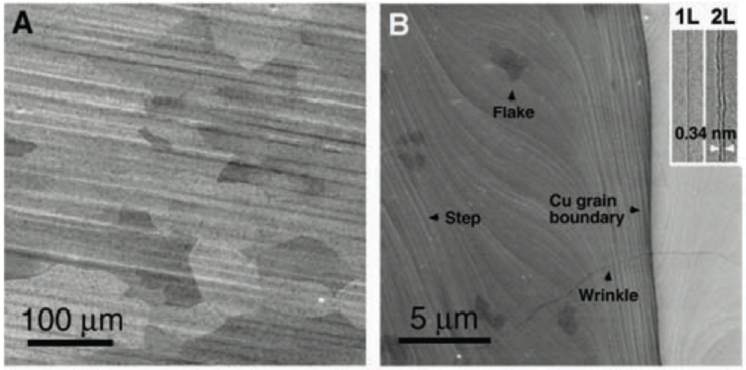


- Thermal decomposition of SiC



- CVD on transition metals





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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)

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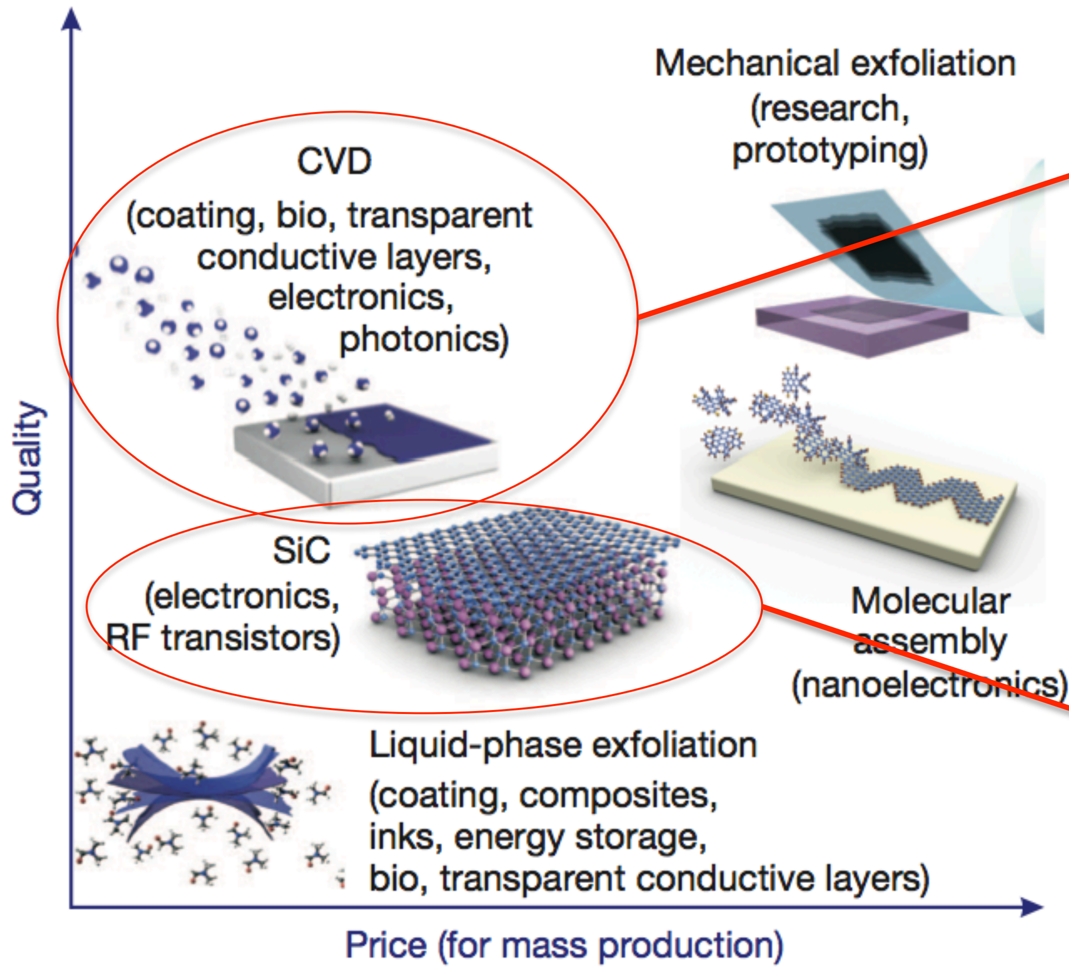
Production methods



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)

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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.

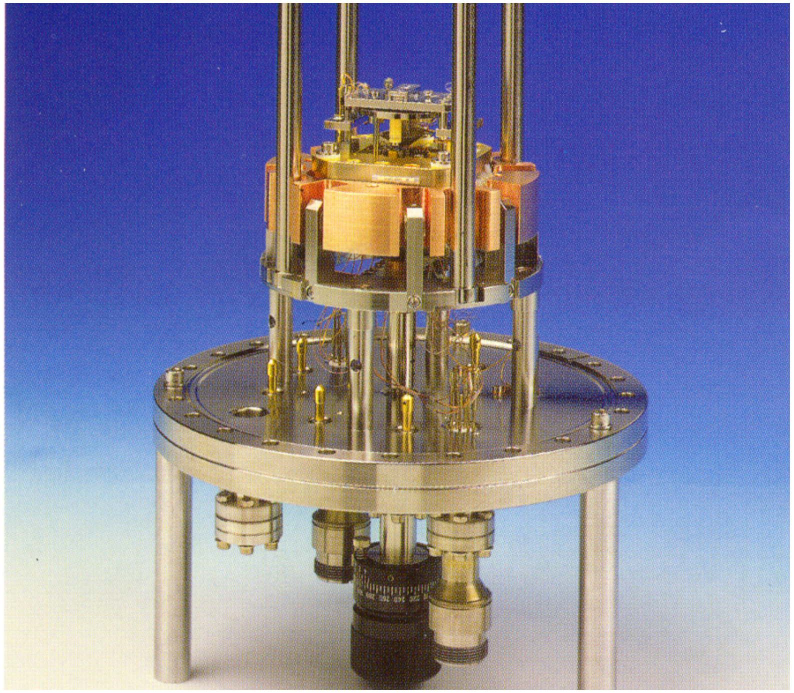
Live STM studies of graphene growth

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

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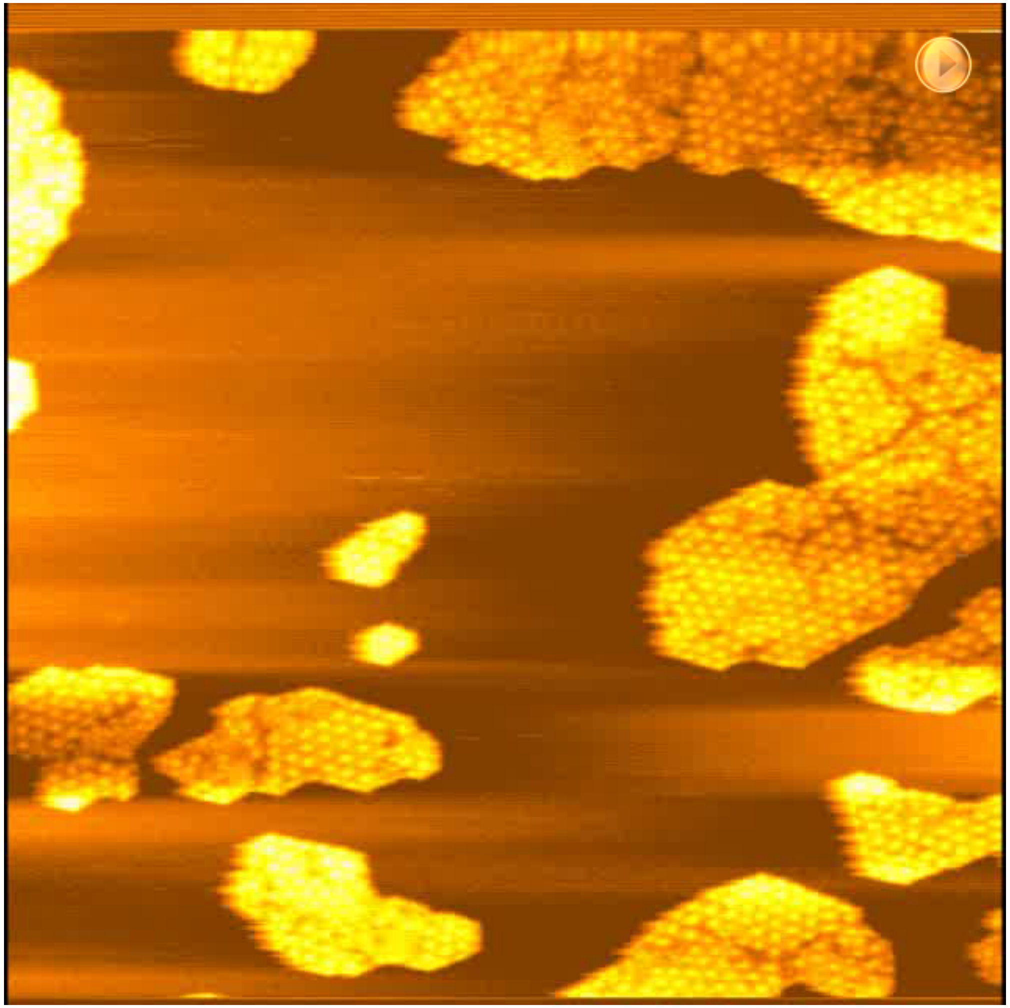
Graphene growth on rhodium

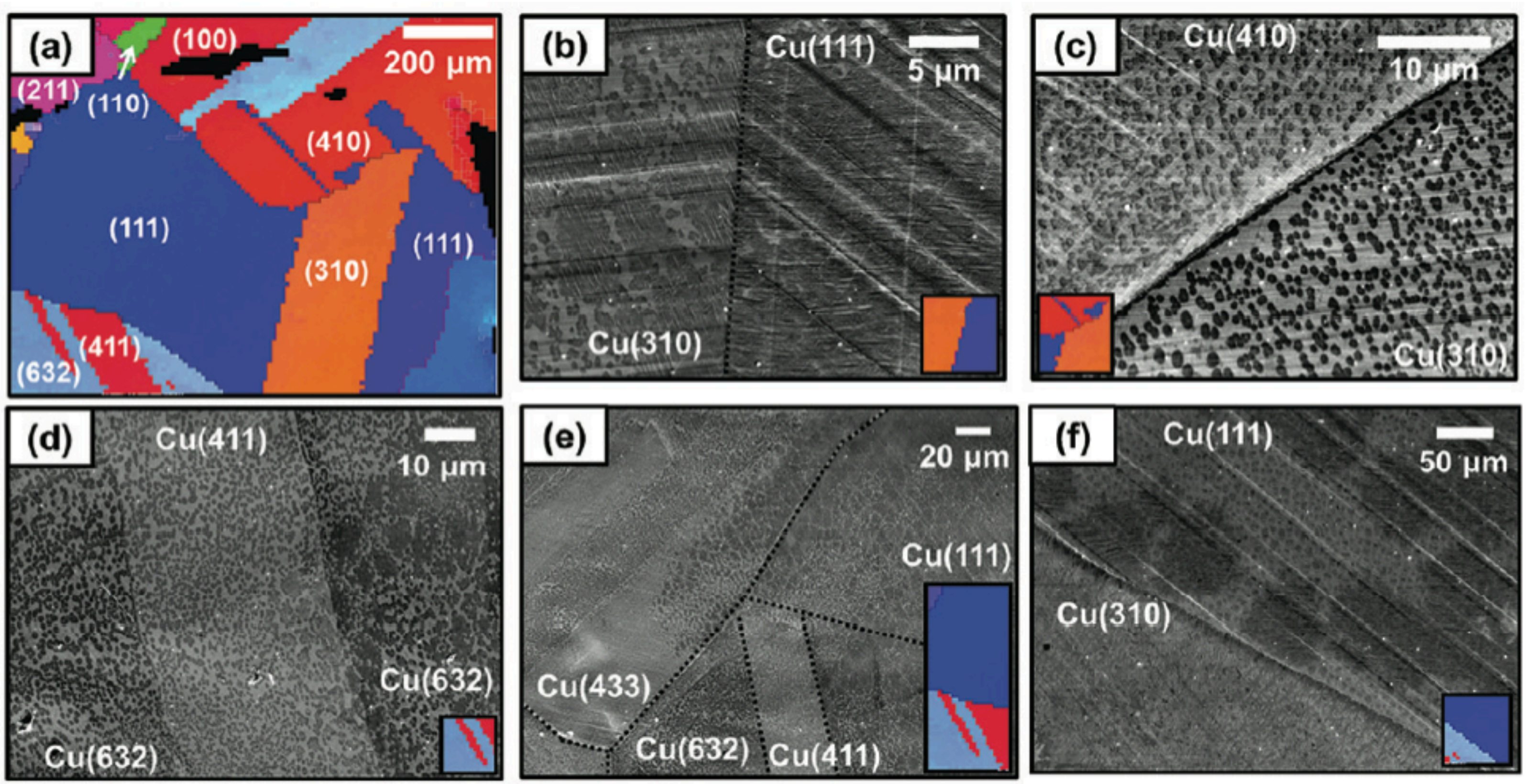
Start: Rh(111) seeded with graphene at RT by C_2H_4

Movie: further C_2H_4 exposure at 975 K at 3×10^{-9} ~1×10^{-8} mbar



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

Substrate orientation: or the problem with foil



Cu(111) gives highest quality graphene

Wood et al. Nano Letters (2011)

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Crystalline Substrate Orientation

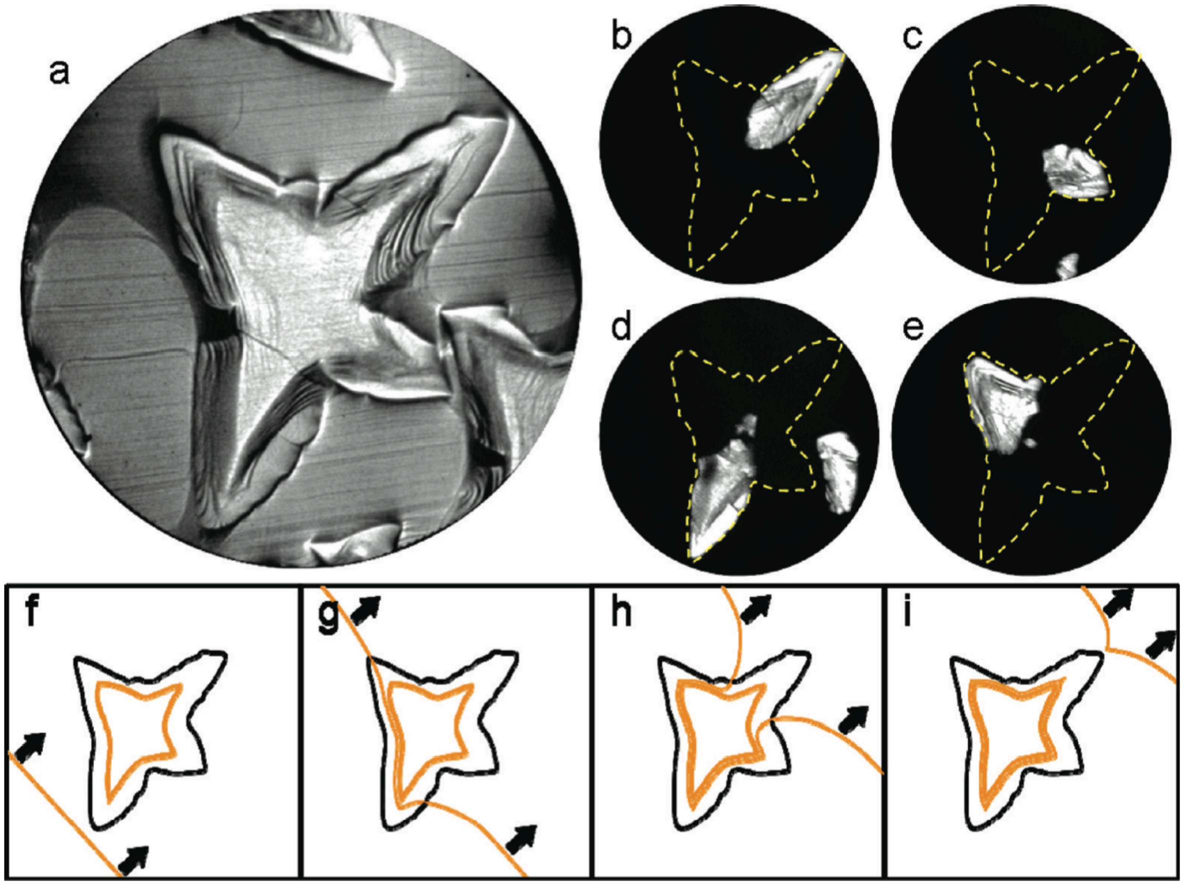

FIGURE 3. Bright (a) and dark field (b−e) LEEM images of a large graphene island on Cu(100) showing the spatial distribution of rotational variants. The graphene (01) direction is rotated by (b) 28°, (c) 2°, (d) 8°, and (e) 42°, relative to Cu(001) (FOV = 20 μm, yellow dashes are the approximate island 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

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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]

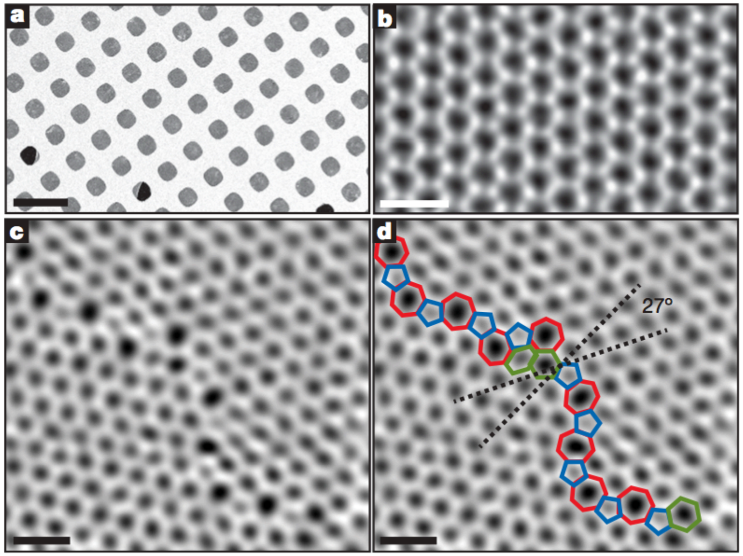

Figure 1 | Atomic-resolution ADF-STEM images of graphene crystals. **a**, Scanning electron microscope image of graphene transferred onto a TEM grid with over 90% coverage using novel, high-yield methods. Scale bar, 5 μm. **b**, ADF-STEM image showing the defect-free hexagonal lattice inside a graphene 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

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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]*

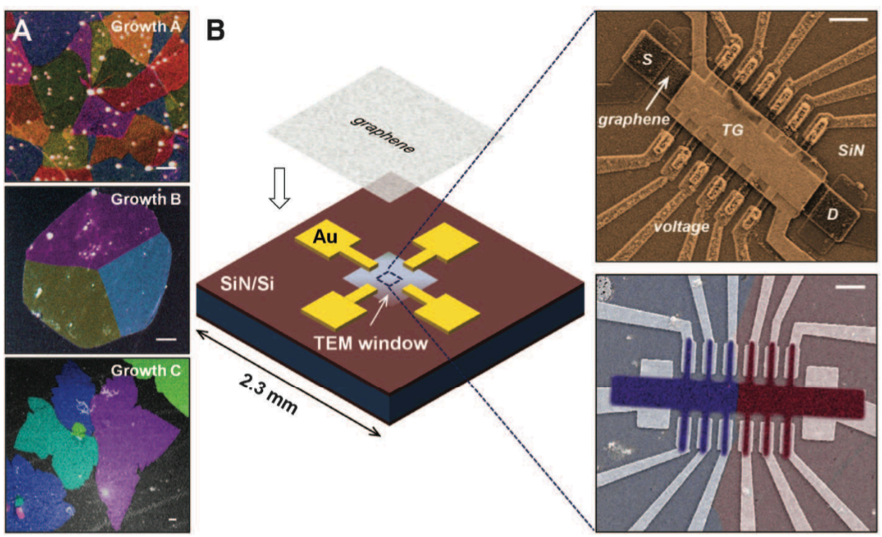
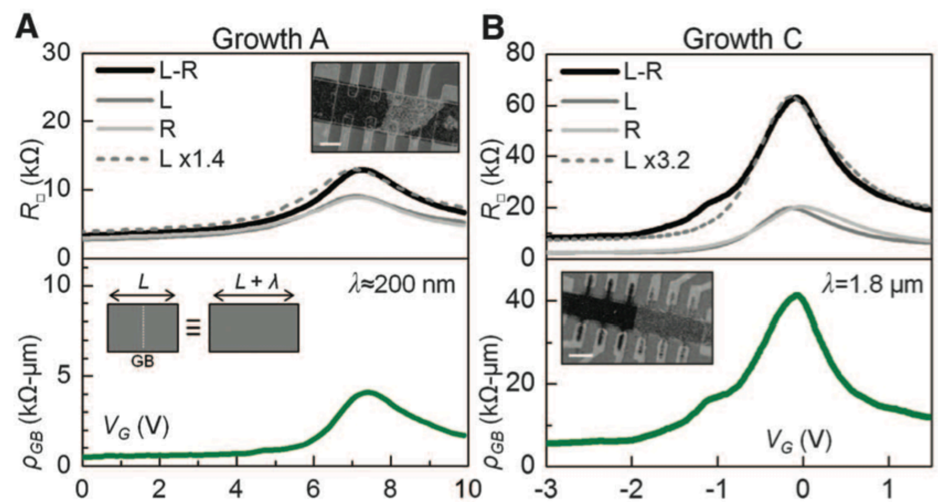


Fig. 1. (**A**) Composite false-color DF-TEM images of CVD graphene produced using three different growth conditions—A, B, and C—yielding average domain size *D* of 1, 10, and 50 μm, respectively, in continuous films. (**B**) (Left) Schematic of specially fabricated TEM chip compatible with electron-beam 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.



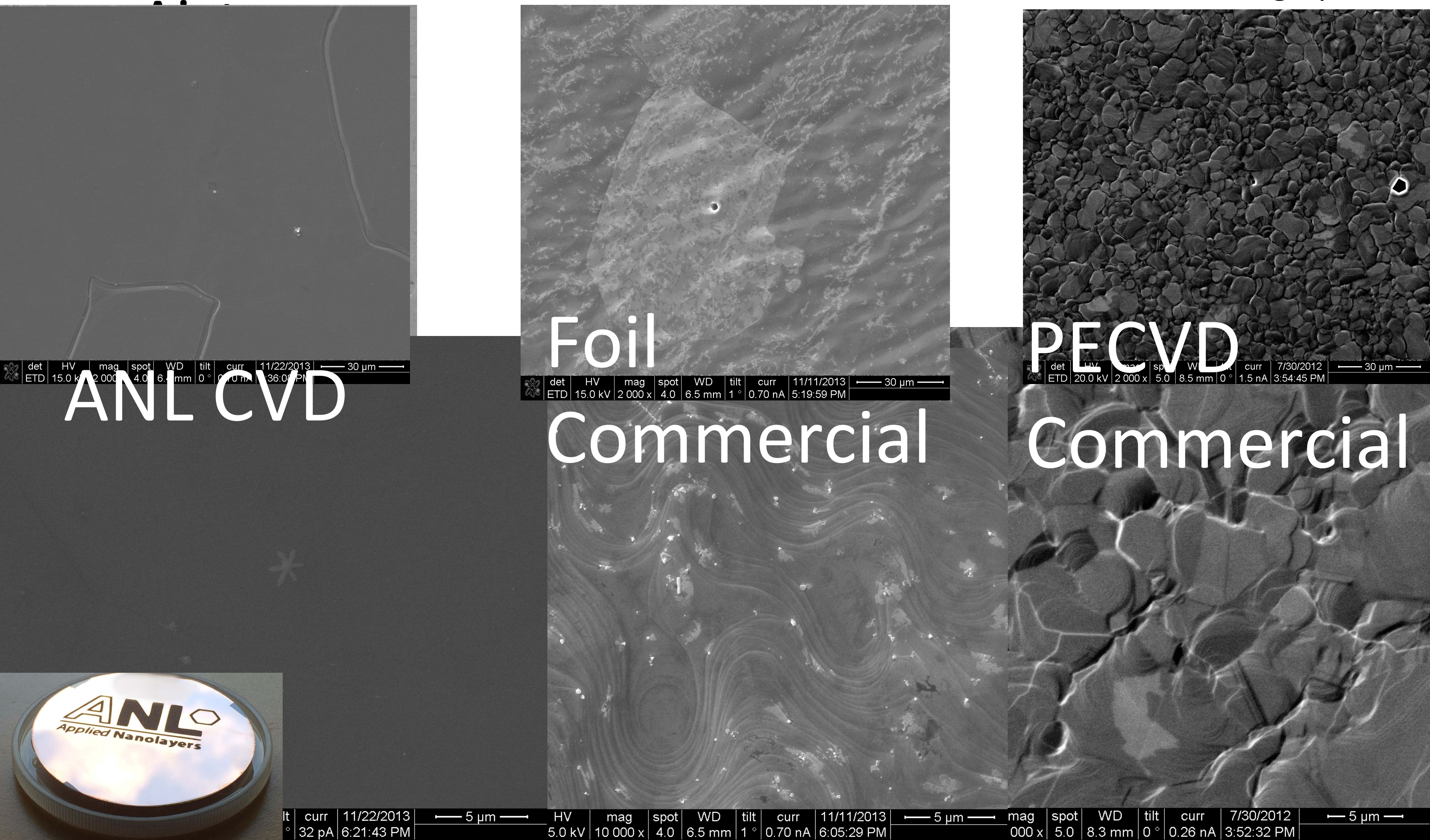
Growth method determines grain boundary resistivity

SCIENCE VOL 336 1 JUNE 2012

Pilot production comparison

2 inch sapphire wafer + Cu + LPCVD graphene

4 inch Si wafer + Cu + PECVD graphene



Closing

- Key to further graphene production improvement is the fundamental understanding of growth mechanisms.
- Establish a reliable supply chain for CVD graphene up to 200 mm substrates.
- Engineer for volume production.
- Fully automated QA toolchain.

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

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