Rapid CVD growth of millimetre-sized single-crystal graphene using a cold-wall reactor

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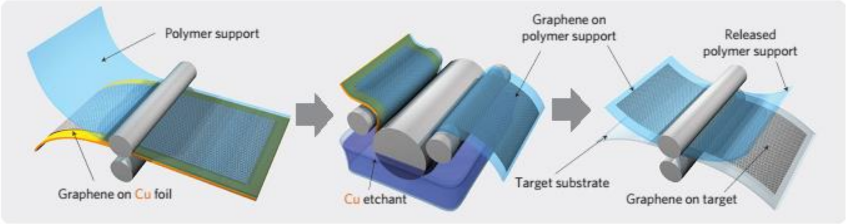
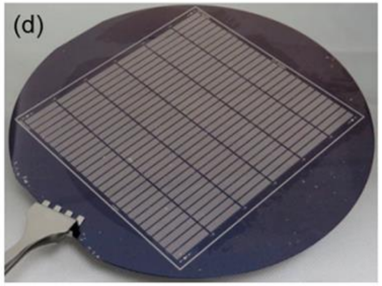
Large-scale applications of CVD graphene

Innovations for industry adoption:

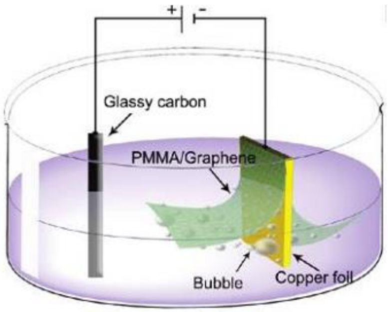
- Roll-to-roll processing allows high throughput
- CMOS integration: growth of graphene on 30-inch wafers
- Etchant-free electrochemical transfer allows re-using the substrate



Bae, S. *et al. Nat. Nanotechnol.* **5,** 1–5 (2010).

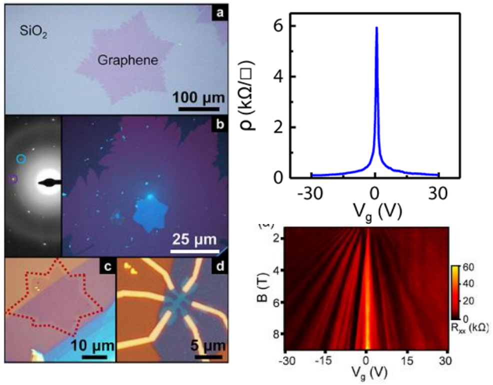


Rahimi, S. *et al.*
ACS Nano **8,** 10471–9 (2014).

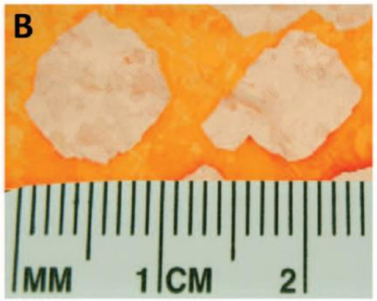


Wang, Y. *et al*
ACS Nano **5,** 9927–33 (2011).

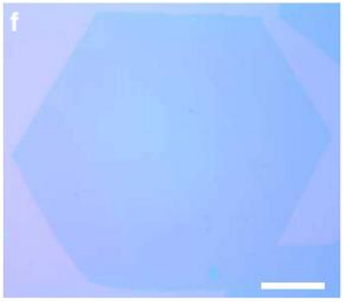
Large-crystal CVD graphene: avoiding grain boundaries



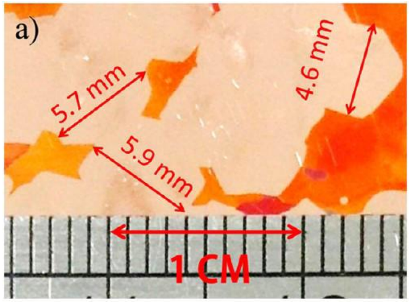
Petrone *et al.*
Nano Lett. **12,** 2751–6 (2012).



Hao *et al.*
Science **342,** 720–3 (2013)



Zhou *et al.*
Nat. Commun. **4,** 2096 (2013)



Gan, L. & Luo, Z
ACS Nano **7,** 9480–8 (2013)

- Electrical properties can be comparable to exfoliated flakes.
- Single crystals can be as large as several mm (even cm).

BUT, the use of single-crystal CVD graphene in applications still not very common. Why?

- Large-crystal growth not trivial to implement due to high variability between different systems.
- Very long growth times required for mm-sized crystals.

Our CVD system: Aixtron BM Pro

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- Cold-wall reactor
- 4-inch heating stage
- Bottom + top heater

Standard growth procedure:

25 mbar

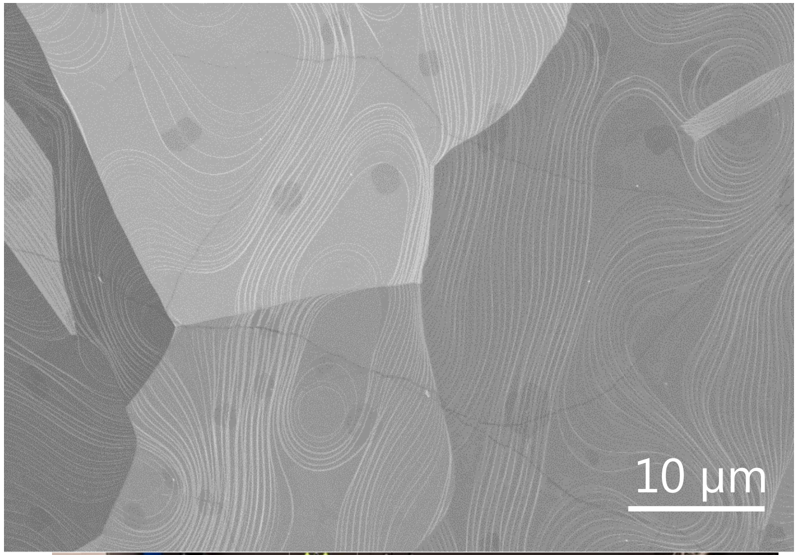
Copper annealing in hydrogen

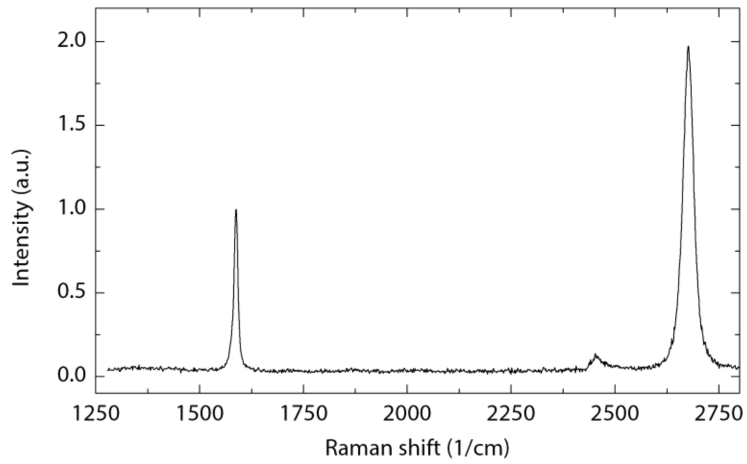
1060 °C bottom + 950 °C top

1 sccm CH_4 + 980 sccm Ar + 20 sccm H_2 (optional?)

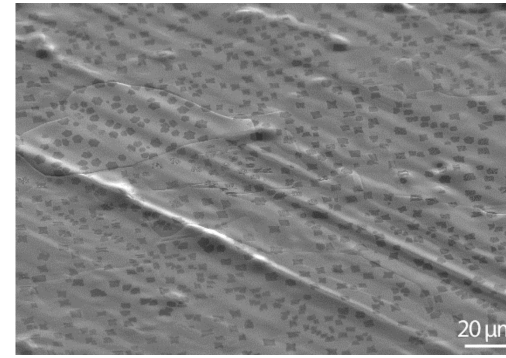
Continuous film grown in 5 minutes

Good-quality and highly repeatable growth, but polycrystalline, with grain size limited to ~10 µm.



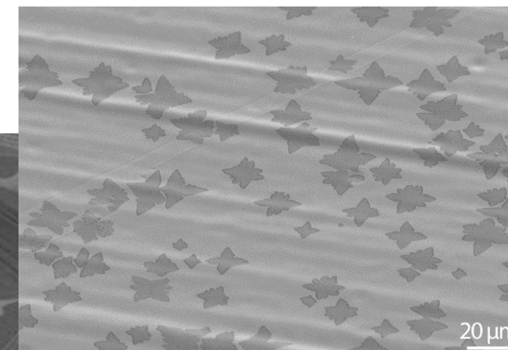


Reducing the nucleation density



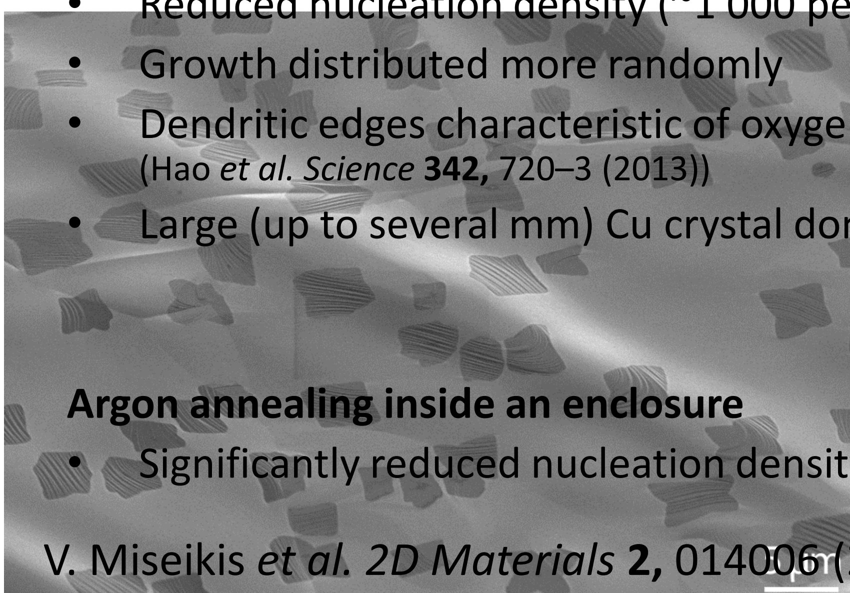
Hydrogen annealing

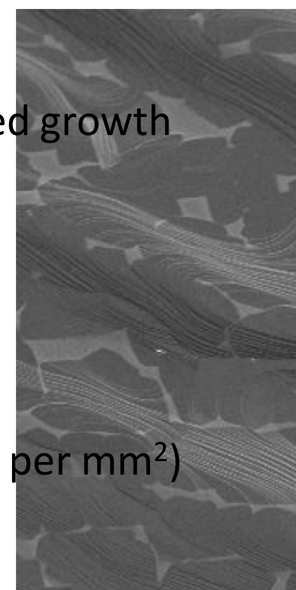
- High nucleation density (~10 000 per mm^2)
- Growth along the copper foil rolling grooves
- Compact edges

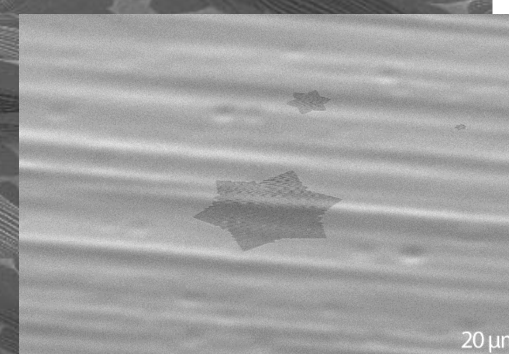


Argon annealing

- Reduced nucleation density (~1 000 per mm^2)
- Growth distributed more randomly
- Dendritic edges characteristic of oxygen-assisted growth (Hao *et al. Science* **342,** 720–3 (2013))
- Large (up to several mm) Cu crystal domains







Argon annealing inside an enclosure

- Significantly reduced nucleation density (~5-10 per mm^2)

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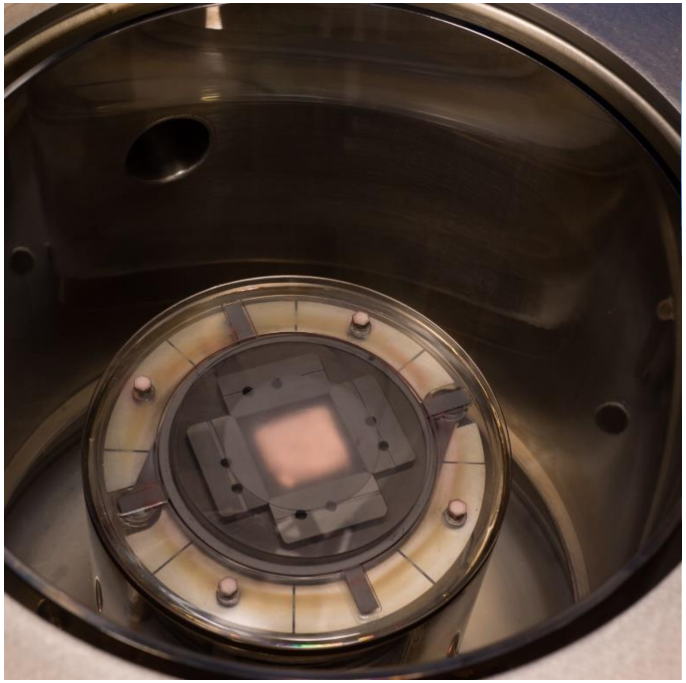
Sample enclosure

- 6 mm-thick graphite spacers placed directly on the bottom heater
- Sample and the spacers covered with a quartz disk
- Limits gas flux and creates more equilibrium conditions (10 cm^3 vs 21 litres)
- Reduces the deposition of evaporated copper in the main chamber



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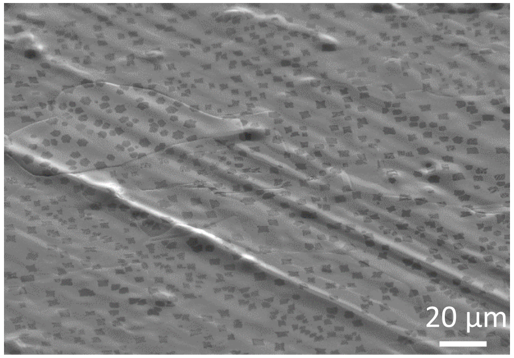

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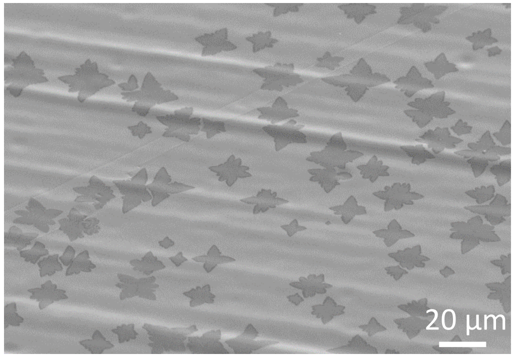

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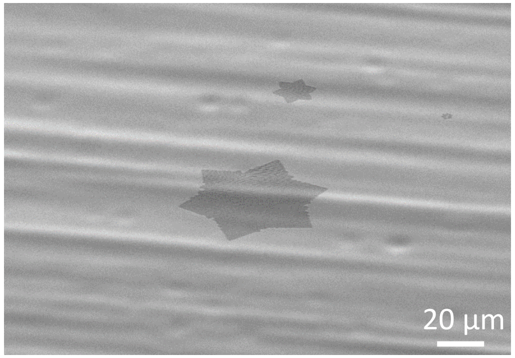

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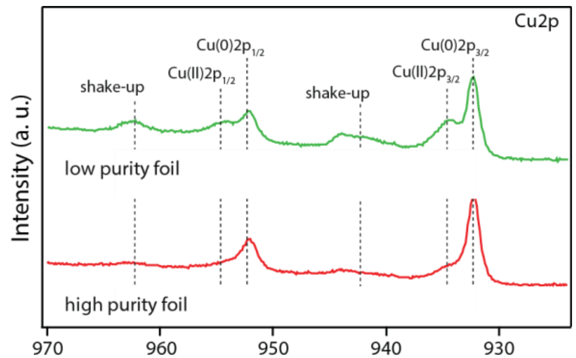
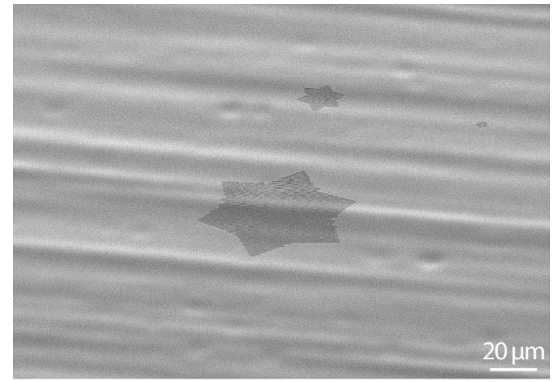
The effect of oxygen content in copper

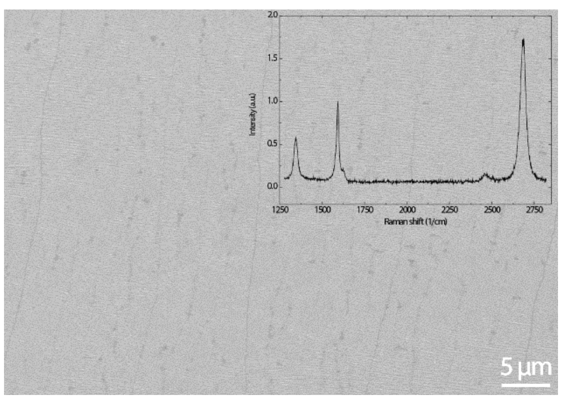


Growth with Ar annealing



Low purity foil (99.8%) / high oxygen content

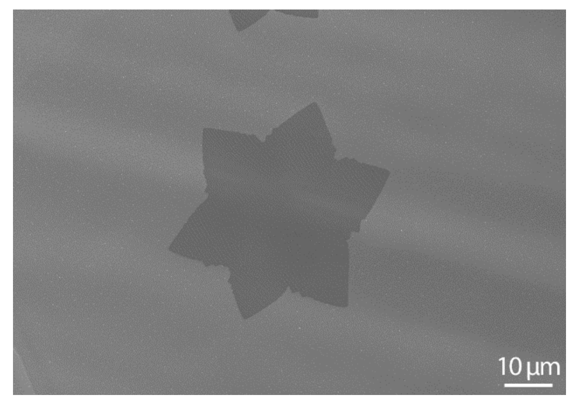
Growth with Ar annealing



High purity foil (99.98%) / low oxygen content

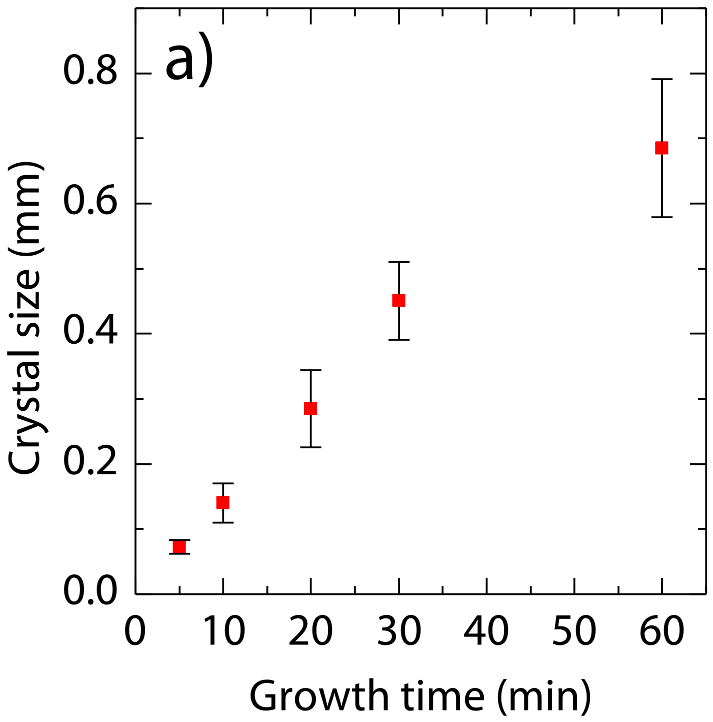
2 min @ 180 °C

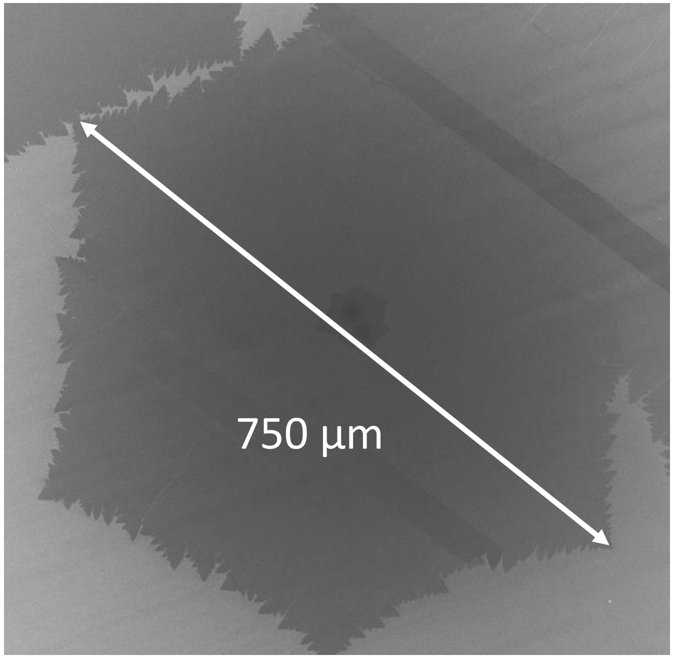
Growth with Ar annealing



Thermally oxidised high purity foil

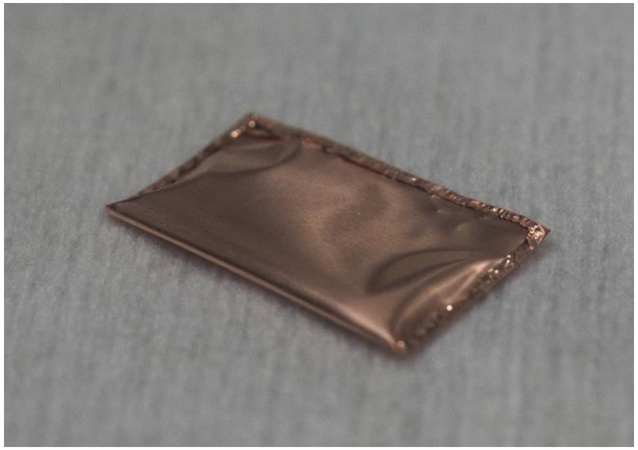
Flat foil: graphene crystals approaching 1 mm

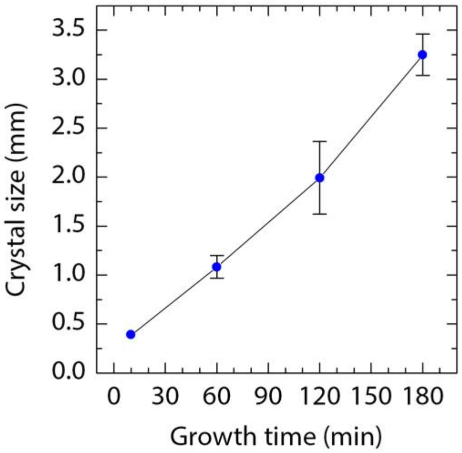


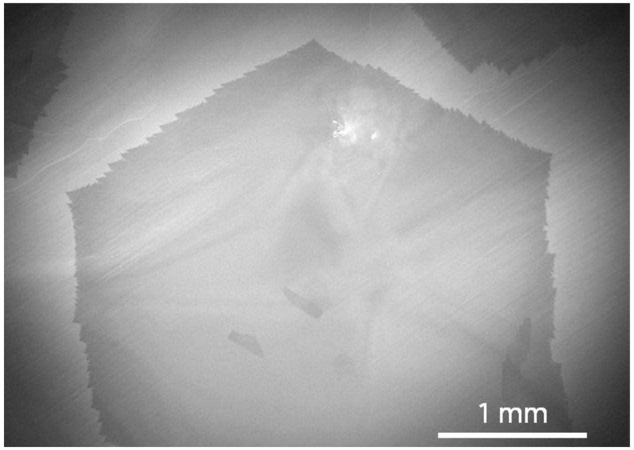


- Growth rate linear ~15 µm/min
- Up to 750 µm crystals grown before they start merging

Growth using copper "pocket"







- Nucleation significantly lower than 1 crystal per mm^2
- Growth of up to 3.5 mm single-crystals in 3 hours

- PMMA transfer can be challenging due to foil deformation

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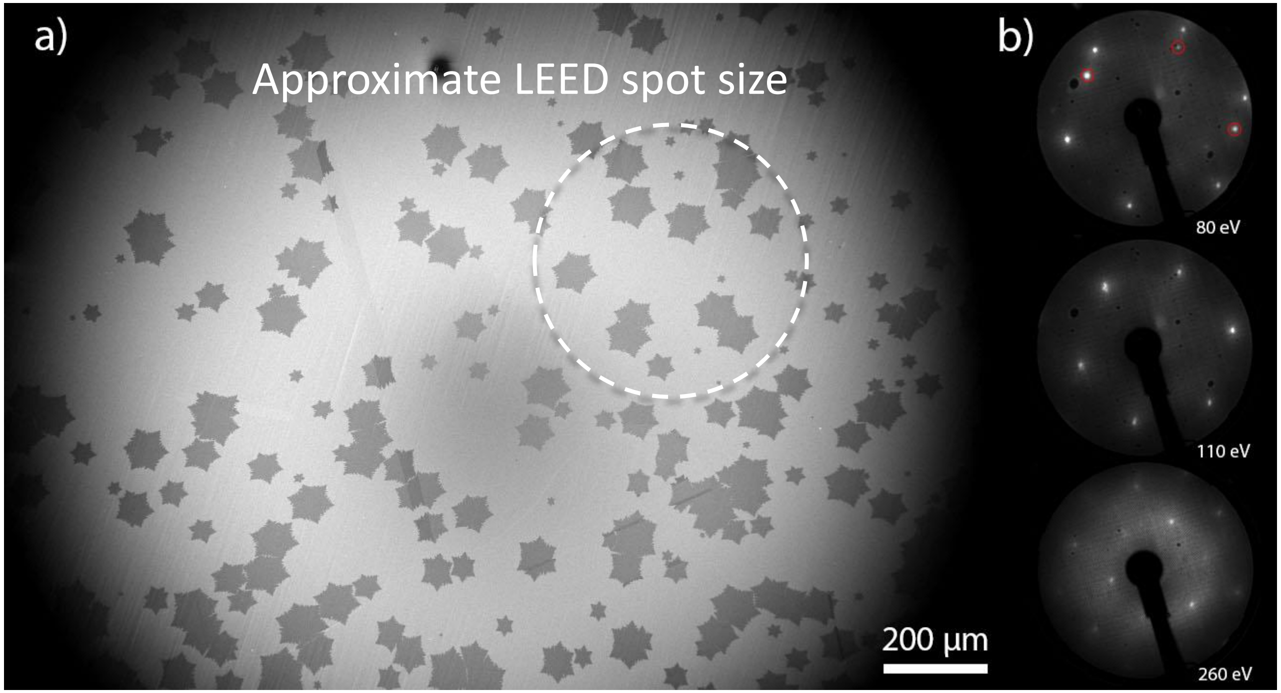
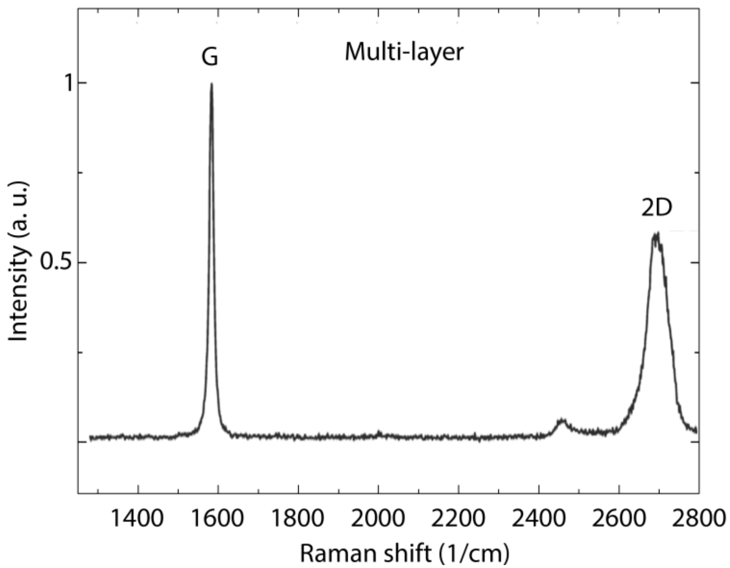
Rotationally aligned growth

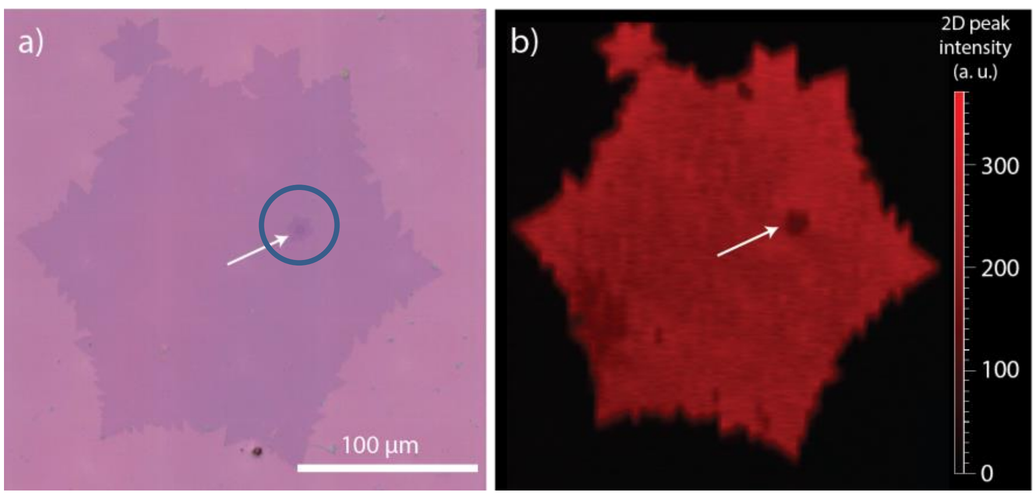


- Separate graphene crystals formed on a single Cu crystal domain have the same orientation.
- Visible with SEM, confirmed with LEED.

Raman spectroscopy

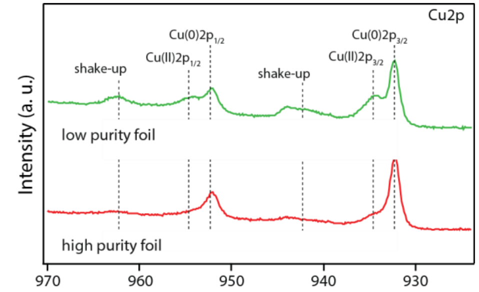
- No D-peak indicates high crystal quality
- I (2D) / I (G) ~ 3
- FWHM (2D) ~ 29 cm^{-1}
- Homogeneous Raman signature over the whole transferred crystal

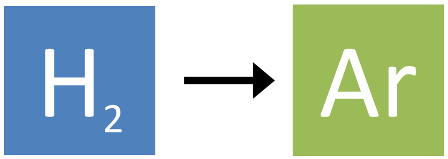


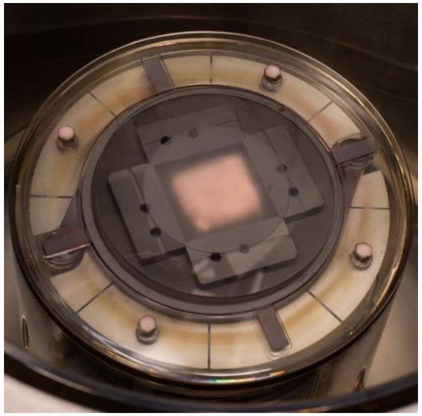


Conclusions

- Key factors for the growth of mm-scale graphene single crystals
  - Cu substrate chemistry (primarily, oxygen content)
  - annealing conditions (argon instead of hydrogen)
  - use of enclosure (external enclosure and/or copper “pocket”)
- High quality of synthesised graphene
- The growth is fast, allows routine production of mm-scale graphene crystals for applications.







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Ken Teo, Nalin Rupesinghe, Paul Greenwood

Thank you for your attention!

Further information:

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