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


Rahimi, S. et al.

Wang, Y. et al
Large-crystal CVD graphene: avoiding grain boundaries

- 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

- 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 mm²)
• Growth along the copper foil rolling grooves
• Compact edges

Argon annealing

• Reduced nucleation density (~1 000 per mm²)
• 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 mm²)

V. Miseikis et al. 2D Materials 2, 014006 (2015)
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
Reducing the nucleation density

Hydrogen annealing
- High nucleation density (~10,000 per mm²)
- Growth along the copper foil rolling grooves
- Compact edges

Argon annealing
- Reduced nucleation density (~1,000 per mm²)
- Growth distributed more randomly
- Large (up to several mm) Cu crystal domains

Argon annealing inside an enclosure
- Significantly reduced nucleation density (~5-10 per mm²)

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Vaidotas Mišeikis | Graphene 2015, Bilbao
The effect of oxygen content in copper

Thermally oxidised high purity foil 2 min @ 180 °C

Low purity foil (99.8%) / high oxygen content

Growth with Ar annealing

High purity foil (99.98%) / low oxygen content

Growth with Ar annealing

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

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
- $I(2D) / I(G) \sim 3$
- FWHM (2D) $\sim 29 \text{ cm}^{-1}$
- 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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Further information:
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