Graphene production at industrial scale

GENERAL GRAPHENE
10239 Cogdill Road, Knoxville, TN 37932
info@generalgraphene.com

Abstract

Graphene is a two-dimensional (**2D**) allotrope of carbon; effectively a planar and atomically thin sheet of graphite. In this 2D form, graphene exhibits remarkable thermal and electrical properties with an unprecedented surface-to-volume ratio enhancing sensitivity. *As expected, the industrial production, transfer and handling of 2D graphene is challenging*. Here, challenges unique to the industrial scale production of graphene are presented: the scientific/technical solutions were guided by maximizing graphene material quality under the constraint of minimized cost.

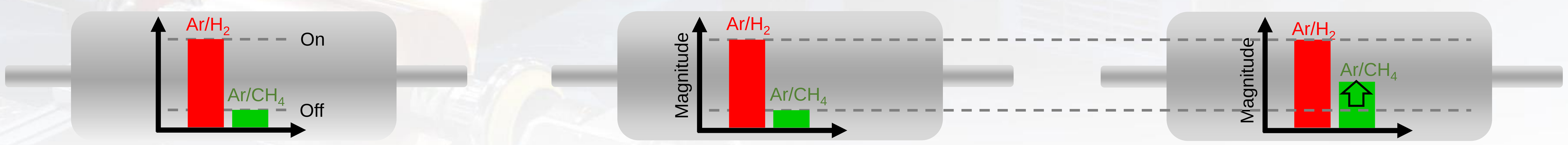
Introduction & Method

Pristine, atomically thin graphene is produced using ***a**tmospheric pressure* **C**hemical **V**apor **D**eposition (**CVD**) on copper (**Cu**) foil substrates. Industrial, cost-effective throughput requires a *continuous* growth process. Fortunately, the roll–to–roll continuous method of production is compatible with Cu foil substrate required for monolayer graphene growth. At General Graphene, we have adapted CVD to the roll-to-roll method. In doing so, the advantage of working with well defined gas concentrations, in a fixed volume, is lost, which is a key strength afforded by CVD in quartz tubes (*see below*).

Time–controlled method: Quartz tube (*static substrate*, *low throughput*)

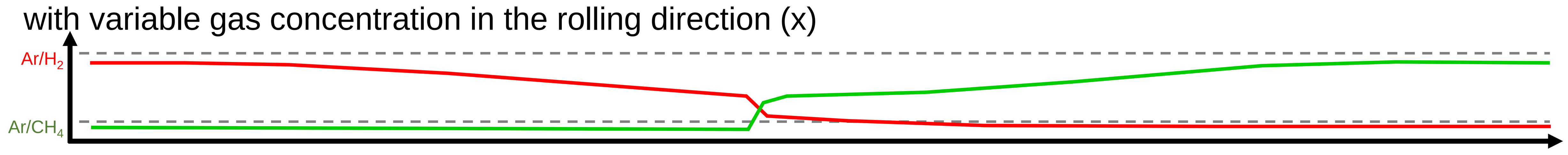
Graphene growth occurs in two basic stages; (1) Cu foil annealing then (2) graphene growth. Fixed volumes of precursor gases, e.g., Ar, H_2 and CH_4, flow at constant concentration for a fixed time, then exchanged.

t_0: Cu foil annealing — t_{1a}: graphene growth (initial) — t_{1b}: graphene growth (final)

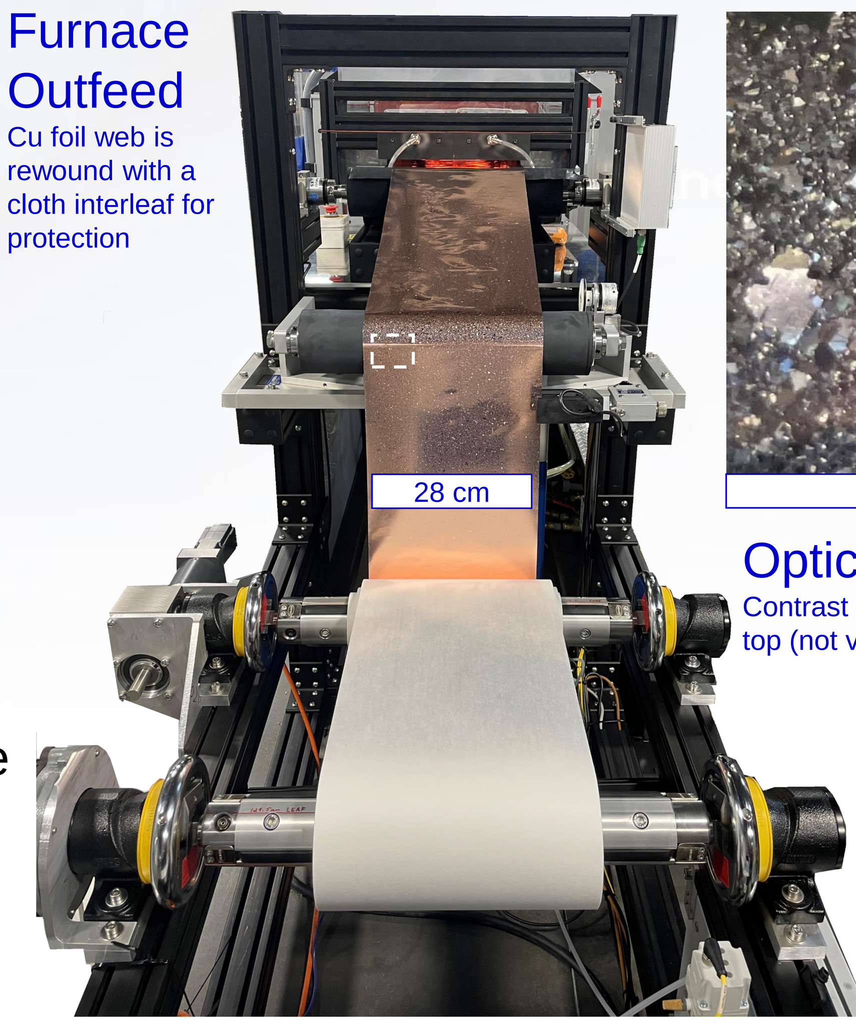


Position-controlled method: Furnace duct (*moving substrate*, *high throughput*)

Graphene growth occurs using the same annealing + growth process but the substrate moves through a furnace with variable gas concentration in the rolling direction (x)

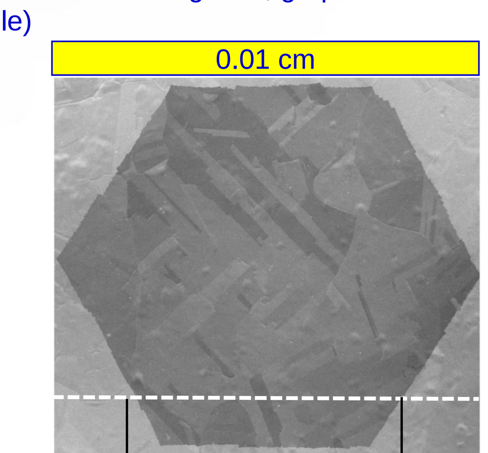


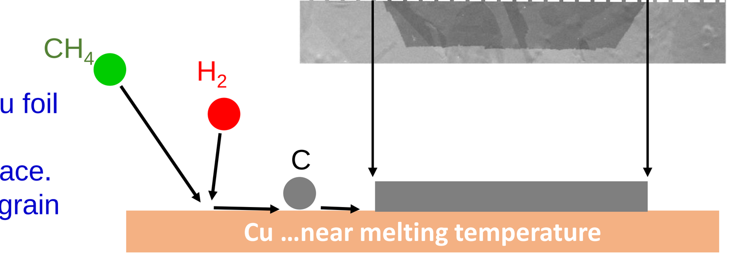
x_0: Cu foil annealing (initial) ← x_1: graphene growth → (final)



Furnace Outfeed
Cu foil web is rewound with a cloth interleaf for protection

Optical image
Contrast from individual Cu grains, graphene on top (not visible)





Electron image
A single graphene grain viewed looking down on Cu foil (dark hexagon). The lower contrast (greyish) background is the texture of the underlying Cu surface. The symmetry of the grain edge indicates a single grain of commonly oriented carbon atoms

Results

Single layer graphene is produced by CVD using following parameter ranges

Recipe

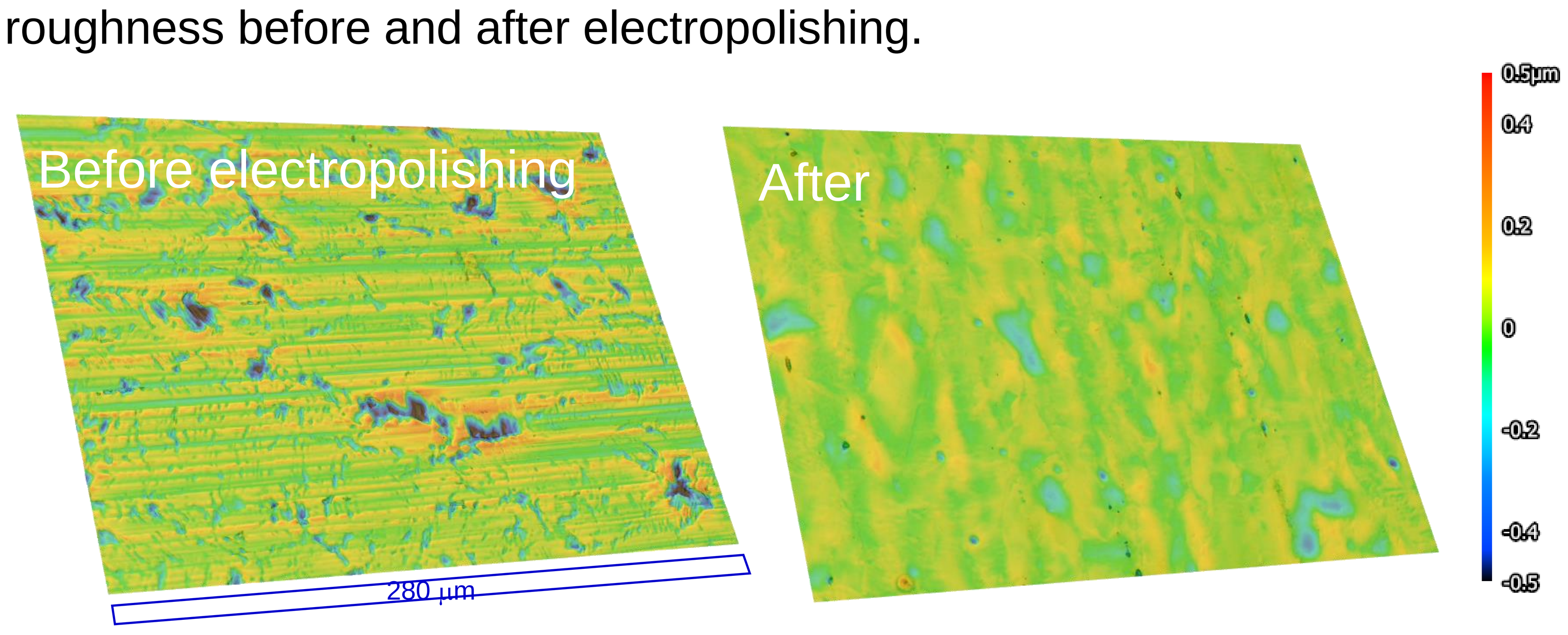
- Cu foil substrate (20 – 70 μm)
- 2%H_2/Ar @ 10^1–10^2 [L/min]
- 1000 ppm CH_4/Ar @ 10^1 – 10^2 [L/min]
- T ≥ 10^3 [C]
- t = 600 [cm] / 20 [cm/min] = 30 [min] …where 720 [cm] is the furnace CVD length

Additional Growth Recipe Features

- Methane (CH_4) concentration must increase, or must be sufficient, to overcome the reduction in exposed catalytic Cu surface area as the graphene layer approaches full coverage
- Hydrogen (H_2) serves a dual role of promoting CH_4 dehydrogenation while also chemically reducing any copper oxides at the surface, i.e., Cu_2O and/or CuO

Results *…before CVD*

As received Cu foil substrate must be electropolished to reduce the surface roughness as excessive roughness degrades graphene quality leading to a defective monolayer. Scanning laser profilometry is used to assess the Cu foil roughness before and after electropolishing.



Laser scanning profilometry
A surface roughness range of 1 um was required to encapsulate all Cu foil surface roughness spanning an area of 280 μm x 210 μm while, after roll-to-roll electropolishing in 85 wt% H_3PO_4, the roughness range to encapsulate all surface roughness, over the same area, was reduced to 500 nm, a value acceptable for subsequent annealing

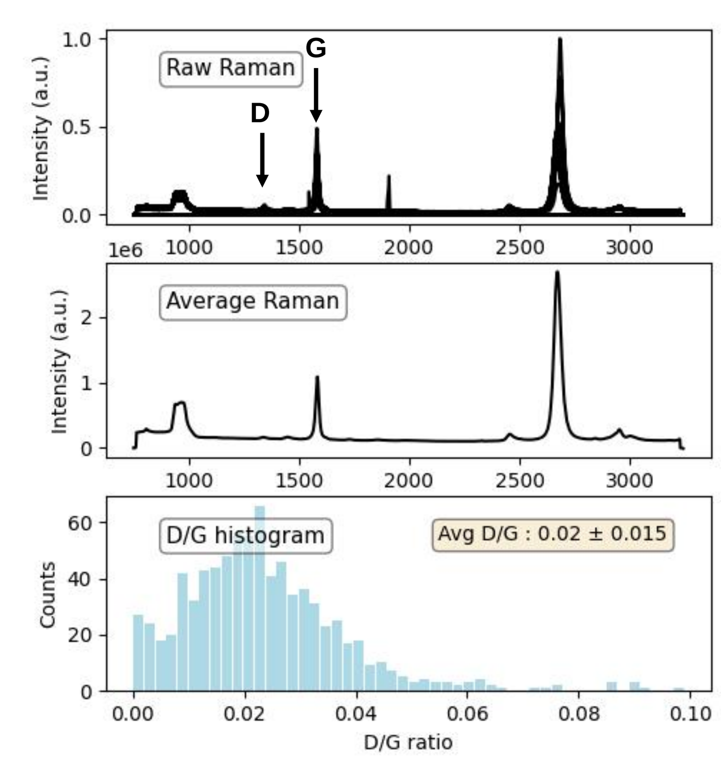
Results *…after CVD*

Raman microscopy is an invaluable, nondestructive tool for quantification of graphene nanostructure providing information on the defect density as well as excessive CVD growth where multiple layers of graphene may deposit

Raman microscopy
(top) A single Raman spectra; x–axis is Raman shift Δν [cm^{-1}]

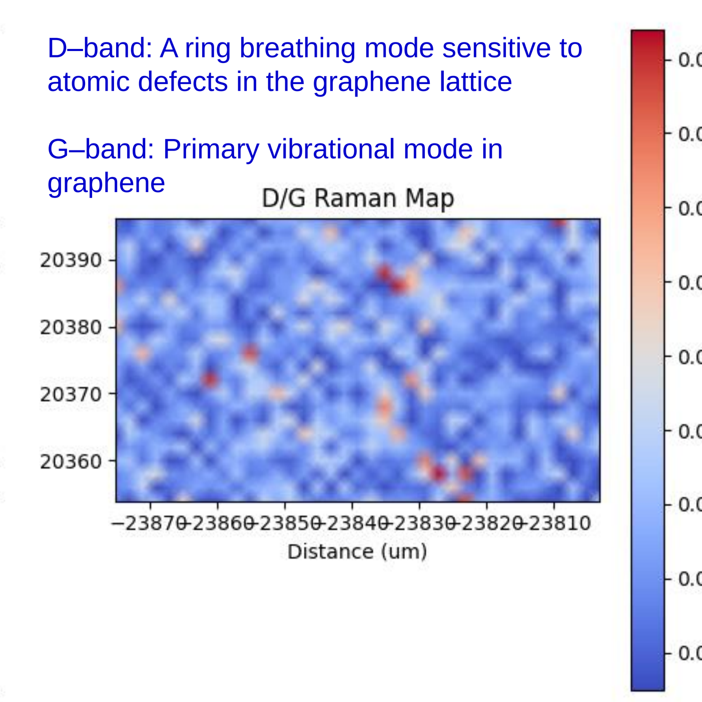
(middle) Spectra averaging over multiple laser exposures, acquired at macroscopic spacings, are required for a statistically meaningful characterization of roll sized samples; x–axis is Raman shift Δν [cm^{-1}]

(bottom) The D band to G band, integrated intensity ratio is a measure of nanostructure quality – an excessive quantity of defect exists for D/G > 0.1. The histogram shows a statistical snapshot of a 10^2 cm^2 foil area.



D–band: A ring breathing mode sensitive to atomic defects in the graphene lattice

G–band: Primary vibrational mode in graphene



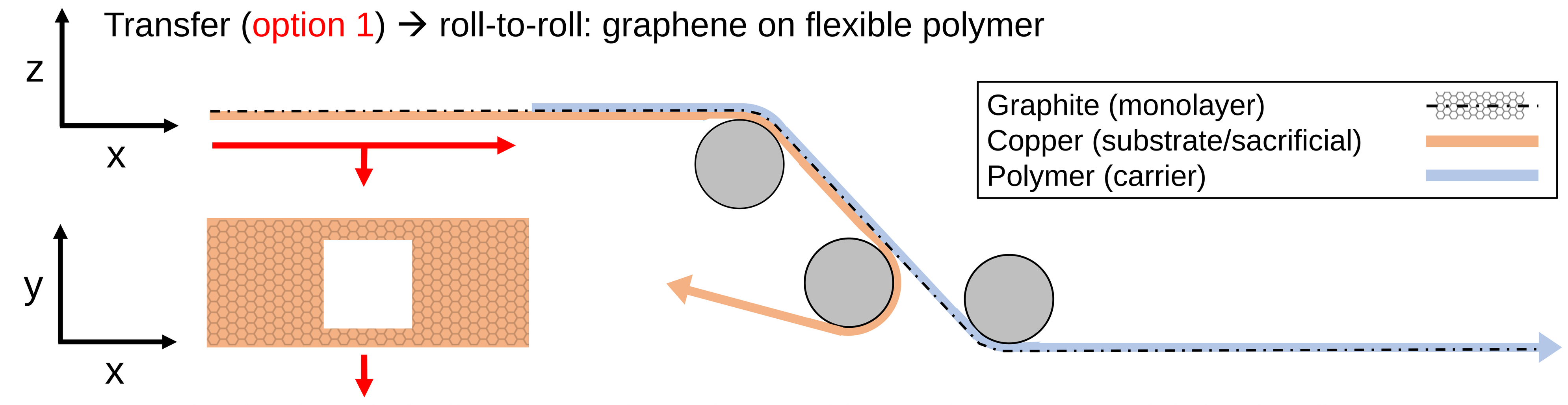
Final Graphene Transfer

The process flow as summarized above is amenable to multiple pathways of graphene transfer. Graphene "transfer" consists of;

1. Application of a polymeric support to the exposed surface of graphene
   - Poly (methyl methacrylate) (PMMA) [spin coating[2], spray coating[1,2]]
   - Polyethylene terephthalate/ethylene vinyl acetate (PET/EVA) [film lamination[1,2]]
2. Original substrate removal
   - Wet etching[1,2]
   - Oxidative[1,2]
   - Electrochemical[1,2]
3. Transfer to new substrate[2]
   - Polymer dissolution/cleaning

([1,2]) red numbers refers to pathway options shown at the right

Transfer (option 1) → roll-to-roll: graphene on flexible polymer



Transfer (option 2) → die cut: graphene inserted into IC/sensor nanofabrication flow