GRAPHENE FOR US
International Conference
ONLINE
★ April 06-07, 2022 ★

Influence of trace oxygen species on chemical vapor deposition (CVD) graphene growth kinetics

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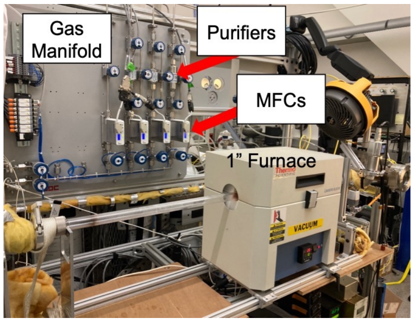
Abstract

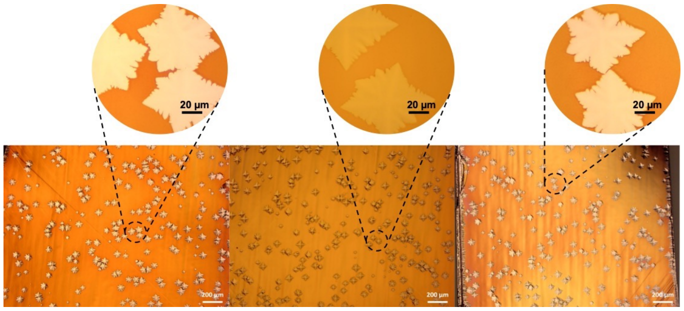
Deliberate oxidation of copper substrates prior to CVD graphene growth has proven to significantly alter the nucleation density, grain size, and defect concentration of the resulting film[1]. Here we develop a model to discuss the role of part-per-million oxygen in gas feedstocks on graphene growth kinetics. By eliminating trace oxygen in the gas feedstock and furnace atmosphere, we obtain fast, high-quality growth without the reliance of hydrogen to balance oxygen species[2]. We demonstrate the formation of a pinhole-free, continuous graphene within 1 minute due to the lack of oxygen impurities. The O_2/H_2 ratio was explored to understand the balance between grain growth and oxygen-based etching. This study sets the maximum oxygen concentration with respect to hydrogen to facilitate fast, reproducible graphene growth. Our findings highlight the competitive nature of absorbed methane intermediate species as carbon precursors and trace surface oxide as the growth inhibitor and set the limit between impurities limited growth and methane adsorption-dissociation limited growth. We assert that CVD graphene growth in standard ultra-high purity gas feedstock without downstream purification falls within the impurities limited growth regime, thus is held at the mercy of oxidizing etching reactions.

Custom low-pressure (LPCVD) system

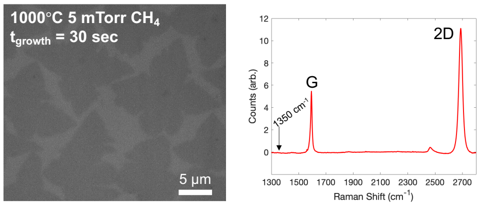
1. ULSI grade gas handling
2. O_2 removing purifiers
3. Turbo molecular pumped LPCVD
4. Load-lock to prevent system venting
5. Reproducible growth surface using electropolished copper



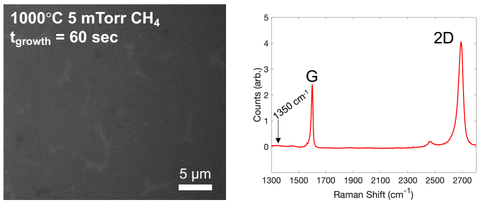
Repeated growths are identical



H_2 not required for high-quality CVD graphene

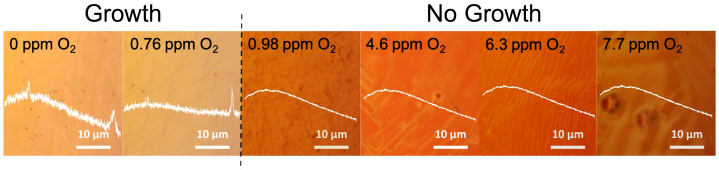


In 30 seconds, our graphene exceeds 75% coverage with no D peak present in the Raman spectra.



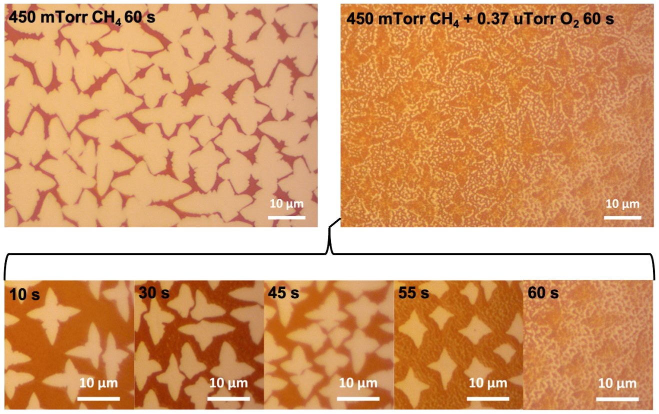
After 60 seconds, the graphene coverage approaches 90% without generating a D peak as well

ppm-level oxygen disrupts growth



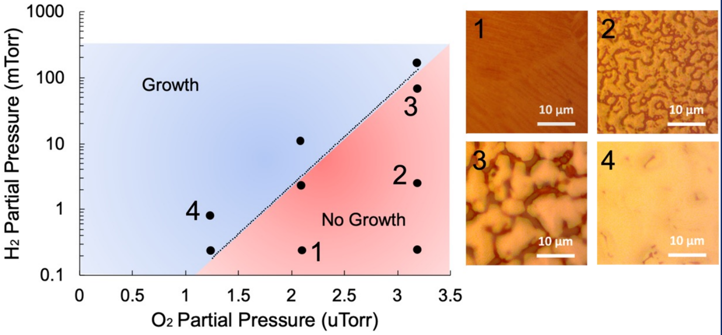
~1 ppm added O_2 enough to etch graphene → this is the typical O_2 impurity level found in most research-grade gas feedstocks!

Evolution of O_2 etching during growth



Time series demonstrates both grain edge and nucleation point etching leaving behind graphene shadows.

Growth vs. etched growth phase boundary



Linear changes in added oxygen requires exponential increases in hydrogen required to balance etching effects.

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References

[1]Choubak, Saman, et al. The Journal of Physical Chemistry C 118.37 (2014): 21532-21540.
[2]Choubak, Saman, et al. The Journal of Physical Chemistry Letters 4.7 (2013): 1100-1103.

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