Graphene Nucleation Control: Methods for Analysis and Quality Control

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1. Image: Graphene production sequence.
   1. Precursor/Catalyst interaction
   2. Graphene Nucleation/Merging
   3. Aspects of device Manufacturing

2. This presentation enables you:
   1. Graphene Grower: Add understanding graphene nucleation based on SIMS results. One important parameter: Carbon content in/on foil!
   2. Device maker: How to design graphene domain boundary free devices: What conditions to use? Match your requirements
   3. Nucleation tuning has 2 aspects: 1.Catalyst engineering, 2. CVD conditions
   4. How this talk is structured: I start with aspects of catalyst engineering and then talk about CVD conditions
The three methods of catalyst engineering and how they effect catalyst roughness as well as graphene nucleation density.

To minimize graphene domain boundaries -> Nucleation density needs to be reduced.

Note some methods increase/reduce roughness.

In the following I will explain WHY each of these treatments has the effect shown here
The untreated Cu foil is rough due to cold rolling.
Graphene nucleates along cold rolling striations (see (a)(i-iii)).
Centre figure is a SIMS Carbon profile of untreated foil.
SIMS shows carbon contamination along rolling striations. Contamination extends 200nm deep into Cu bulk.
If Cu foil already contains carbon before growth this may lead to uneven supersaturation of carbon upon CH4 exposure and increased nucleation along these regions (see supplementary slide Carbon Supersaturation in Cu).
**Take away message:** Remove 200nm of surface layer -> Remove areas of high C conc. -> Nucleation density is reduced.
Why polishing reduces nucleation density?

**Twofold effect!** -> Remove contamination layer (as shown on previous slide) AND reduces roughness

Practical limitations. Best is chemical mechanical polishing (CMP) further improvement practically difficult to obtain

Also consider: Roughness results in wrinkling after transfer!!! See supplementary slide “Roughness induced wrinkling”
Use of oxygen reduces nucleation density by 6 orders of magnitude!!!
WHY is oxygen so effective in reducing nucleation sites????
Reason often stated in literature: Cu-Oxide is passivating active sites on Cu foil therefore reducing sites where graphene can nucleate
-> BUT!!!! The Cu –CuOx interface is unstable at higher temperatures as has been shown in many in-situ and ex situ studies already in the 70’s and 80’s!!!! There exists no Cu-CuOx interface at the temperatures where we grow graphene!

HERE: To prove Cu-Oxide is not passivating active nucleation sites and to be able to trace effect of oxygen I ONLY OXIDISE CU BACKSIDE.
Floating on H2O2 oxidises ONLY Cu backside, front side remains untreated! Floating for different times from 0s-300s as shown above yield in different CuOx thickness at backside.
Graph shows the longer I oxidse backside, the more the nucleation density is reduced!

So why is Oxygen reducing nucleation density? -> I will show in next slide
SIMS maps of annealed foils: (a) Untreated Cu foil heated in Ar to 1065\textdegree C for 30min (b) Backside oxidized foil (BO) heated in Ar (same conditions)

In (a) we still see carbon localization along rolling stations! This shows it is not atomic carbon (which would readily diffuse at these temperatures) but otherwise structured carbon (e.g. with C-C bonds) which cannot as easily diffuse in Cu foil. This excess carbon supersaturates foil and causes increased nucleation!

In contrast (b): **No carbon localisation and less carbon in total** in surface region probed!
Freq. density distribution quantifies that backside oxidation results in less areas of high carbon density i.e. redistribution and removal of carbon on top surface!

What’s the mechanism???? -> Next slide
Cu smelting is how industry turns a Cu-ore (very dirty) into pure (very clean) Cu
Smelting: Cu-ore is molten. Air (containing oxygen) is blown onto molten Cu matte ->
This oxidises unwanted impurities (e.g. S, Fe, C,...)
Cu is cleaner now, but contains a lot of oxygen
This oxygen is reduced by injecting natural gases

-> Smelting is just like our improved CVD growth on Cu -> First oxygen, then
hydrocarbon!
If copper-CuOx interface is heated Cu-Ox reduces (even in an inert atmosphere!):

CuO (cupric oxide) $\rightarrow$ Cu$_2$O (cuprous oxide)

Cu is a weak catalyst for dissociating graphitic carbon (compared to e.g. Fe, Co, Ni) therefore it does not dissociate the ingained impurities (from the cold rolling process) but these act as nucleation sites.

As CuOx is reduced (at high temp) more Oxygen becomes soluble in Cu bulk where O reacts with carbon (just like in smelting!) and impurities become mobile and can desorb!

I.e. Oxygen scavenges the impurities!
1. So far just talked about catalyst engineering. Now let’s talk about how to **tune** the **CVD growth atmosphere for optimal results**!
Graphene growth rate as a function of methane partial pressure -> Linear relationship!
Nucleation density as a function of methane partial pressure -> Exponential relationship!
-> Combining these into one graph yields Max Domain Size vs growth time graph
So, growing a few mm sized graphene domains can be done in a few hours BUT centimetre sized domains takes several days!
E.g. 4mm domains takes about 8h.... Note merging them into continuous film takes even longer!
BTW Cu pockets are not necessary rather tune growth atmosphere properly in your reactor!

How big of graphene domains should we grow? -> The answer is it depends on your device needs! See next slide:
What’s the probability of a domain boundary intersecting with your device area? Scaling from graphene domain size 3mm to graphene domain size 6mm only yield a reduction in domain boundary intersection from 0.8% to 0.3% but the price to pay is 15h more growth time!!!
(For derivation of this formula and more details see supplementary information of Braeuninger-W., et. al., Chem. Mater. 2016, 28(24), 8905 or supplementary slide “Intersection Probability”)
Summary:
Most important catalyst engineering parameter: Carbon in/on Cu foil! Remove it and nucleation density will drop! Most effective for this is Oxygen!
(Note Oxygen not only removes carbon inside the Cu foil but also carbon adsorbed on the Cu foil i.e. in-situ cleaning see supplementary slide “Extrinsic and Extrinsic Carbon”)
CVD atmosphere tuning: Trade-off between large domains and growth time
Device making: What domain intersection probability can you afford? Use formula to work out fastest growth time to match your requirement!
If you have any questions please get in contact with me directly via pab96@cam.ac.uk. I’m very interested in your opinion and look forward to discussing with you!
Supplementary Slides
Carbon Supersaturation in Cu

- Carbon supersaturation required for graphene growth even in Cu!
- After growth more carbon in the surface region.

Supersaturated regions = nucleation sites

Brauernger-W., et al., Chem. Mater. 2016, 28(24), 6905

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Extrinsic and Extrinsic Carbon

Contamination is not only intrinsic to Cu foil but also adsorbed C

Brauninger W. et al., Chem. Mater. 2016, 28, 241 0005

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CVD Growth Process

Braunsinger-W, et. al., Chem. Mater. 2016, 28(24), 8805

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Roughness before/after annealing

Braeuninger-W., et al., Chem. Mater. 2016, 28(24), 8905

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Roughness induced wrinkling

Brauninger-W., et. al., Chem. Mater. 2016, 28(24), 6905

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Electropolishing (2.7V, 10.3M $\text{H}_3\text{PO}_4$)

$$d_p = \frac{J \times t_p \times M}{4 \times e \times N_A \times \rho}$$

Braunsteger-W., et. al., Chem. Mater. 2018, 28(24), 8605
Backside Oxide

![Graph showing Relative O\(^{+}\) Intensity vs Depth (nm) with two curves: UT and BO\(_{\text{back}}\)]

Braunstingel-W., el. al., Chem. Mater. 2016, 28(24): 6855

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SIMS O\textsuperscript{-} depth profiles

![Graph showing SIMS O\textsuperscript{-} depth profiles with various depth profiles for different conditions.

Braakmeer-W., et al., Chem. Mater. 2018, 28(24), 8905

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C and C\(_2\) carbon depth profiles

(a) Relative C intensity [a.u.]
(b) Relative C\(_2\) intensity [a.u.]

Brauninger-W. et al., Chem. Mater. 2016, 28(24), 8905

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C$_2$O and CNO depth profiles

(a)

Relative C$_2$O Intensity [a.u.]

Depth [nm]

(b)

Relative CNO Intensity [a.u.]

Depth [nm]

Brauninger-W., et al., Chem. Mater. 2016, 28(24) 8905

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Intersection Probability

\[ A_{\text{Segment}} = \frac{1}{4} L_D D_G - \frac{1}{4\sqrt{3}} L_D^2 \]

\[ A_{\text{Intersection}} = 12 \cdot A_{\text{Segment}} \]

\[ A_{\text{UnitCell}} = \frac{3\sqrt{3}}{4} D_G^2 \]

\[ P = \frac{A_{\text{Intersection}}}{A_{\text{UnitCell}}} = 4 \left( \frac{1}{\sqrt{3} \alpha} - \frac{1}{3\alpha^2} \right) \]

Brauninger-W., et al., Chem. Mater. 2016, 28(24), 8905

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