UNIVERSITY OF
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DEPARTMENT OF ENGINEERING

Graphene Nucleation Control: Methods for Analysis and Quality Control

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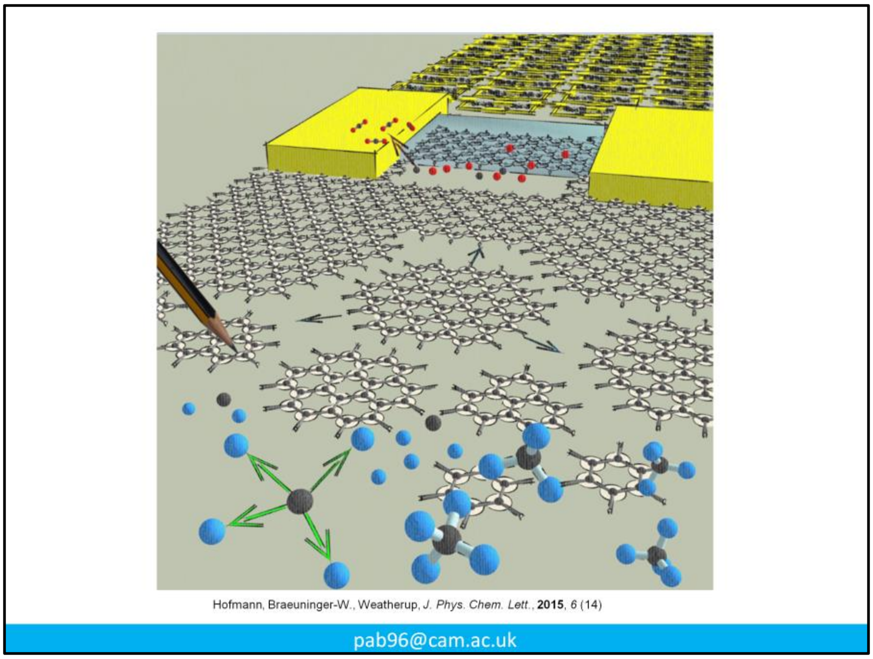

Hofmann, Braeuninger-W., Weatherup, *J. Phys. Chem. Lett.*, **2015**, *6* (14)

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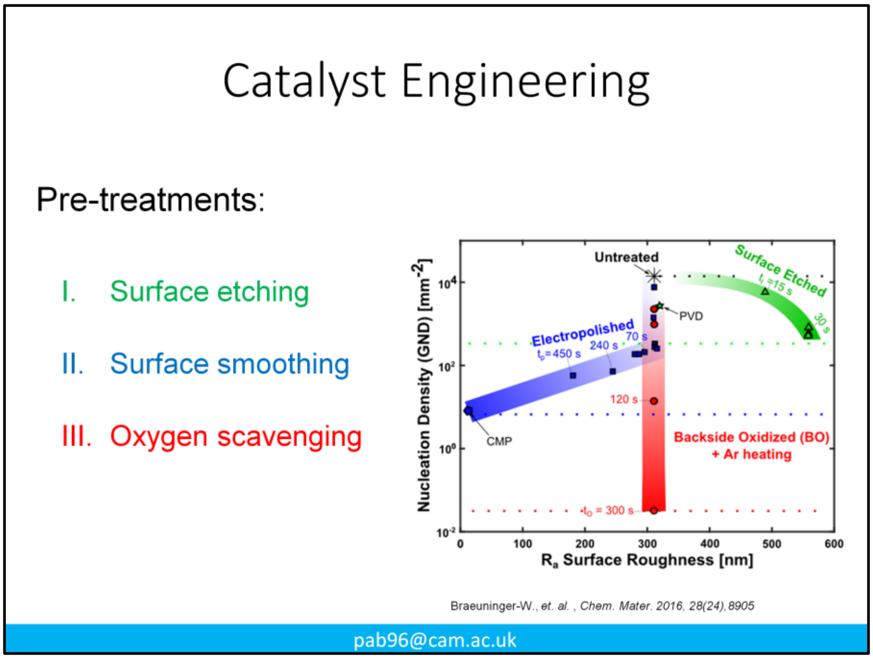
1. Image: Graphene production sequence.
    1. Precursor/Catalyst interaction
    2. Graphene Nucleation/Merging
    3. Aspects of device Manufacturing
2. **This presentation enables you:**
    1. Graphene Grower: Add understanding graphene nucleation based on SIMS results. One important parameter: Carbon 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



Catalyst Engineering

Pre-treatments:

I. Surface etching

II. Surface smoothing

III. Oxygen scavenging

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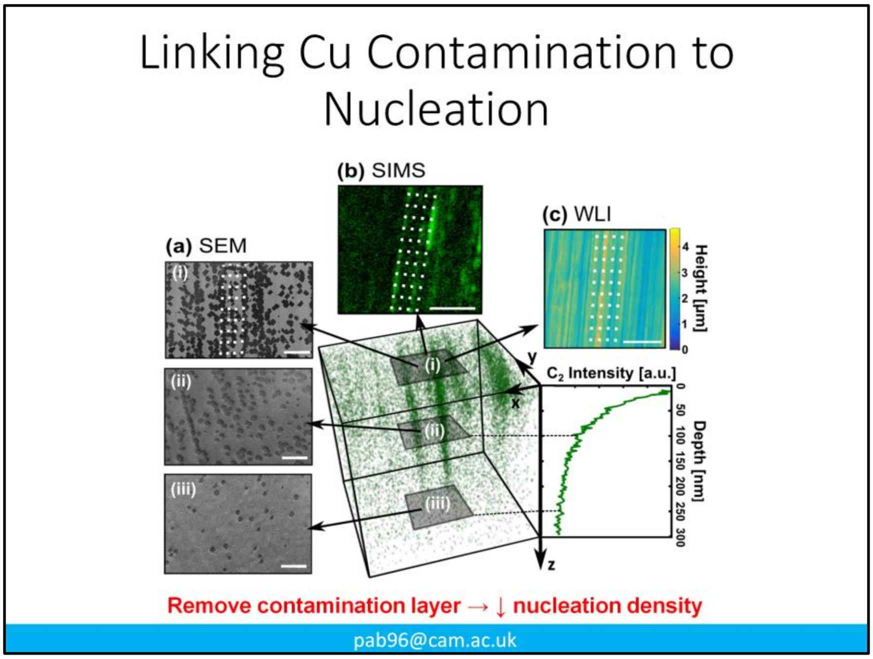
The three methods of catalyst engineering and how they effect catalyst roughness as well as graphene nucleation density.
To minimize graphene domain boundaries -> Nucleation density needs to be reduced.
Note some methods increase/reduce roughness.
In the following I will explain **WHY each of these treatments has the effect shown here**



Linking Cu Contamination to Nucleation

Remove contamination layer → ↓ nucleation density

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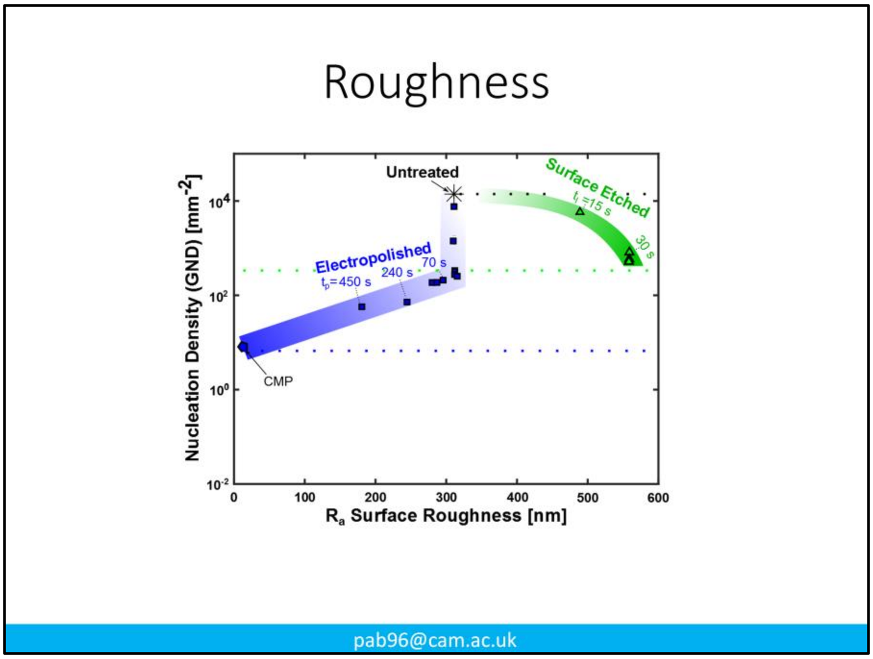
The untreated Cu foil is rough due to cold rolling
Graphene nucleates along cold rolling striations (see (a)(i-iii))
Centre figure is a SIMS Carbon profile of untreataed foil.
SIMS shows carbon contamination along rolling striations. Contamination extends 200nm deep into Cu bulk.
If Cu foil already contains 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.



Roughness

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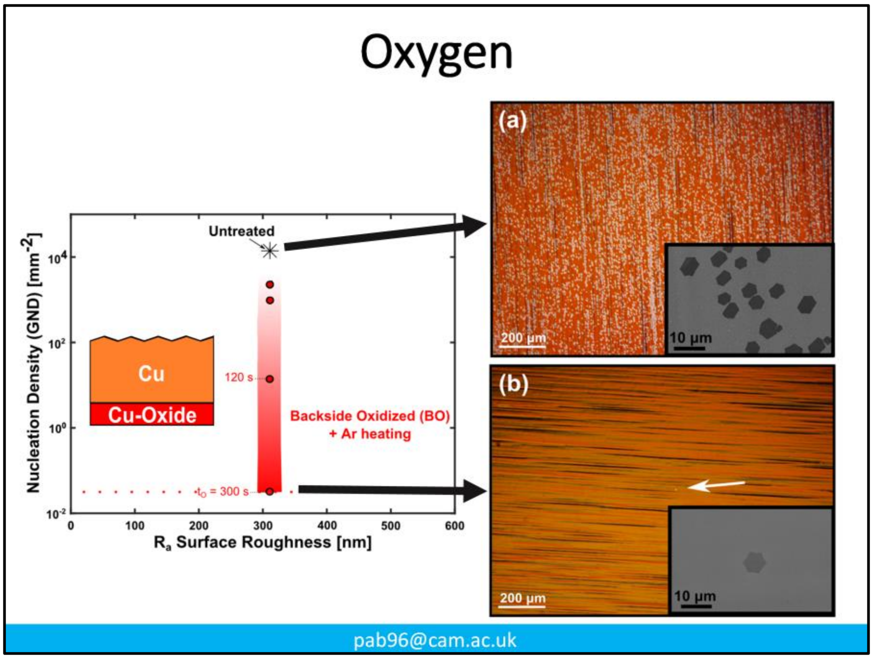
Why polishing reduces nucleation density?
Twofold effect! -> Remove contamination layer (as shown on previous slide) AND reduces roughness
Practical limitations. Best is chemical mechanical polishing (CMP) further improvement practically difficult to obtain
Also consider: Roughness results in wrinkling after transfer!!! See supplementary slide “Roughness induced wrinkling”



Oxygen

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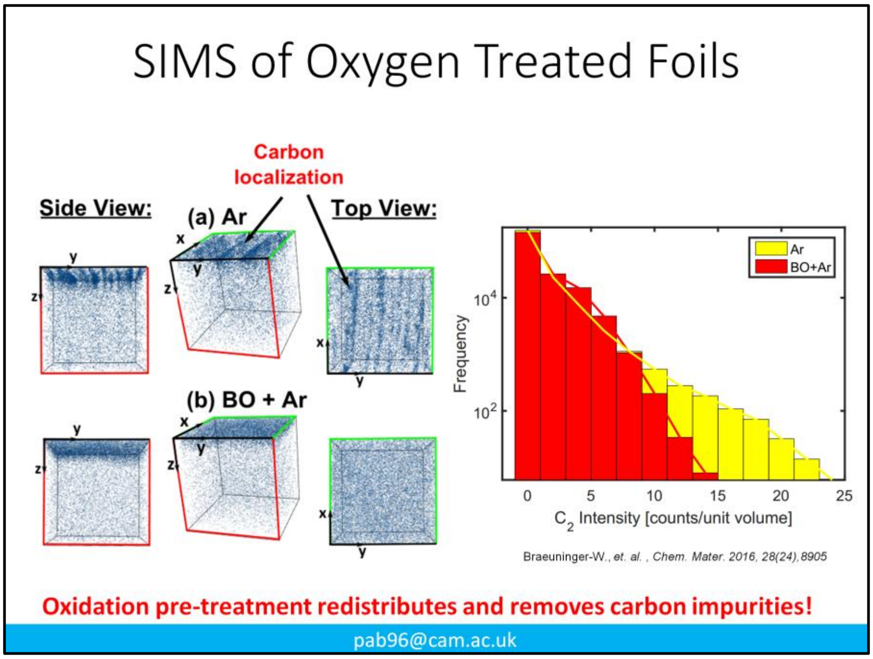
Use of oxygen reduces nucleation density by 6 orders of magnitude!!!
WHY is oxygen so effective in reducing nucleation sites????
Reason often stated in literature: Cu-Oxide is passivating active sites on Cu foil therefore reducing sites where graphene can nucleate
-> BUT!!!! **The Cu –CuOx interface 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 H_2O_2 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 of Oxygen Treated Foils

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Oxidation pre-treatment redistributes and removes carbon impurities!

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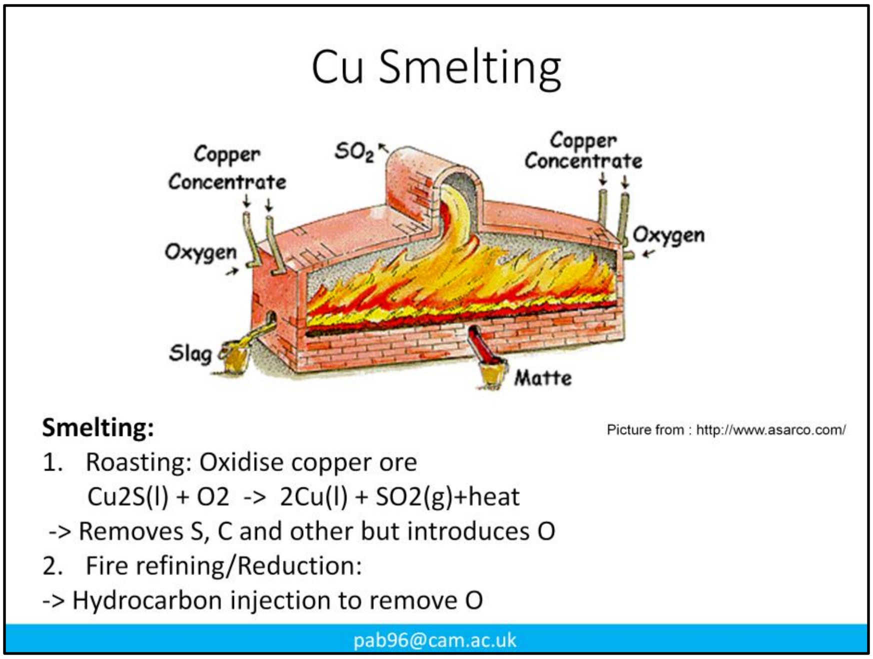
SIMS maps of annealed foils: (a) Untreated Cu foil heated in Ar to 1065degC for 30min (b) Backside oxidzed foil (BO) heated in Ar (same conditions)

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

Picture from : http://www.asarco.com/

Smelting:

1. Roasting: Oxidise copper ore
   Cu2S(l) + O2 -> 2Cu(l) + SO2(g)+heat

-> Removes S, C and other but introduces O

2. Fire refining/Reduction:

-> Hydrocarbon injection to remove O

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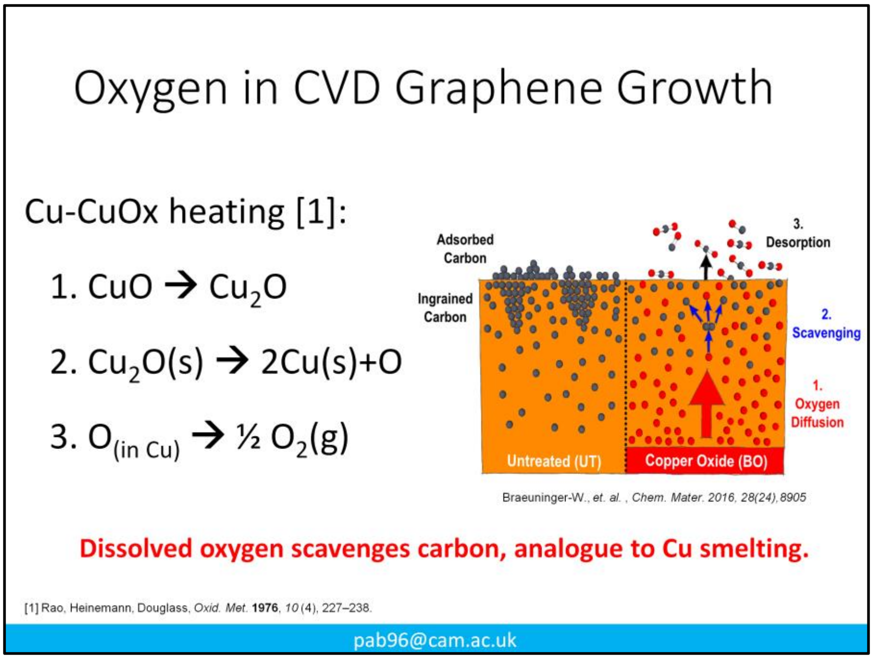
Cu smelting is how industry turns a Cu-ore (very dirty) into pure (very clean) Cu
Smelting: Cu-ore is molten. Air (containing oxygen) is blown onto molten Cu matte ->
This oxidises unwanted impurities (e.g. S, Fe, C,…)
Cu is cleaner now, but contains a lot of oxygen
This oxygen is reduced by injecting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

-> Smelting is just like our improved CVD growth on Cu -> First oxygen, then hydrocarbon!



Oxygen in CVD Graphene Growth

Cu-CuOx heating [1]:

1. $CuO \rightarrow Cu_2O$
2. $Cu_2O(s) \rightarrow 2Cu(s)+O$
3. $O_{(\text{in Cu})} \rightarrow \frac{1}{2} O_2(g)$

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Dissolved oxygen scavenges carbon, analogue to Cu smelting.

[1] Rao, Heinemann, Douglass, *Oxid. Met.* **1976**, *10* (4), 227–238.

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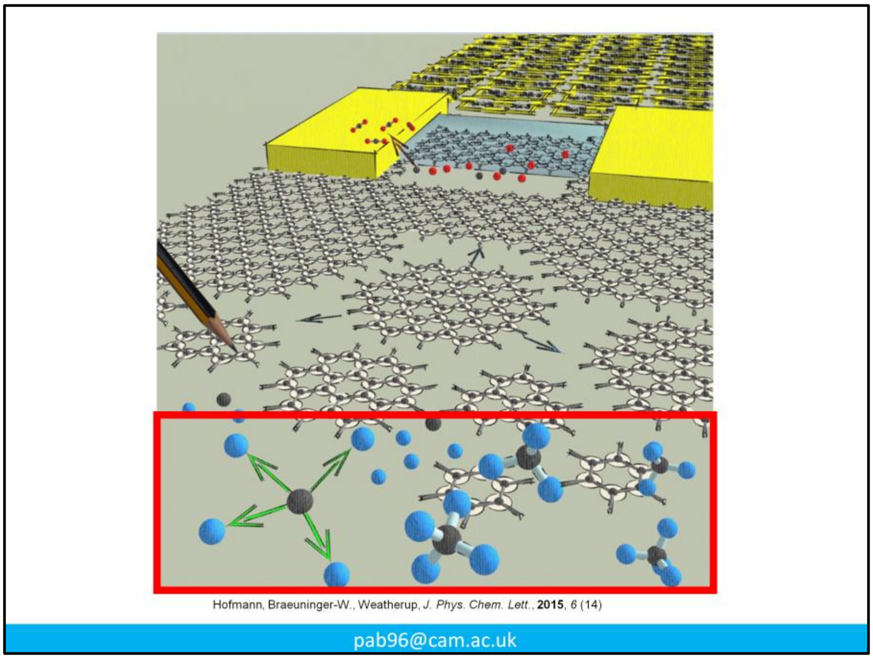
If copper-CuOx interface is heated Cu-Ox reduces (even in an inert atmosphere!):
CuO (cupric oxide) → Cu_2O (cuprous oxide)
Cu is a weak catalyst for dissociating graphitic carbon (compared to e.g. Fe, Co, Ni) therefore it does not dissociate the ingrained impurities (from the cold rolling process) but 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!



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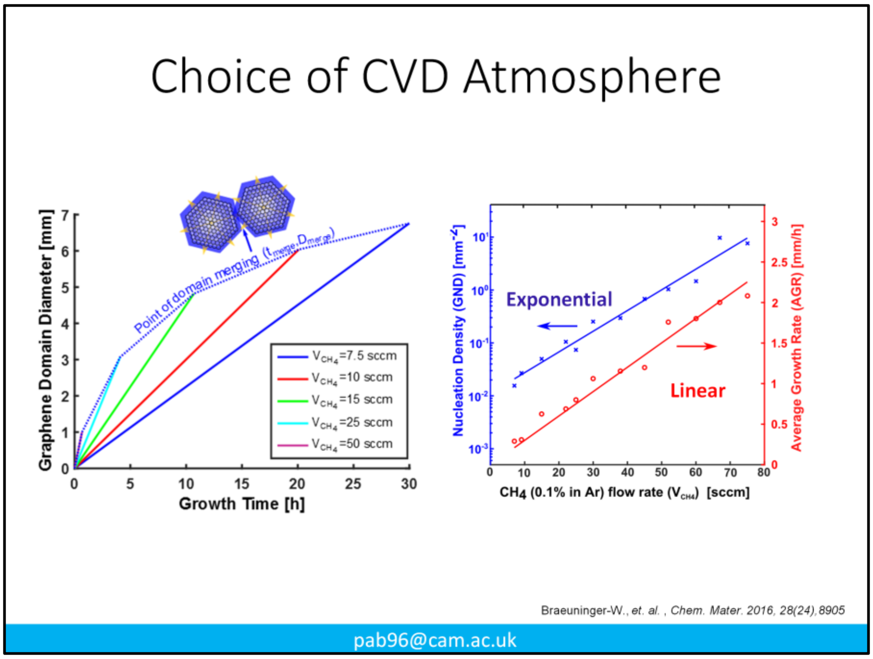
1. So far just talked about catalyst engineering. Now let’s talk about how to **tune** the **CVD growth atmosphere for optimal results!**



Choice of CVD Atmosphere

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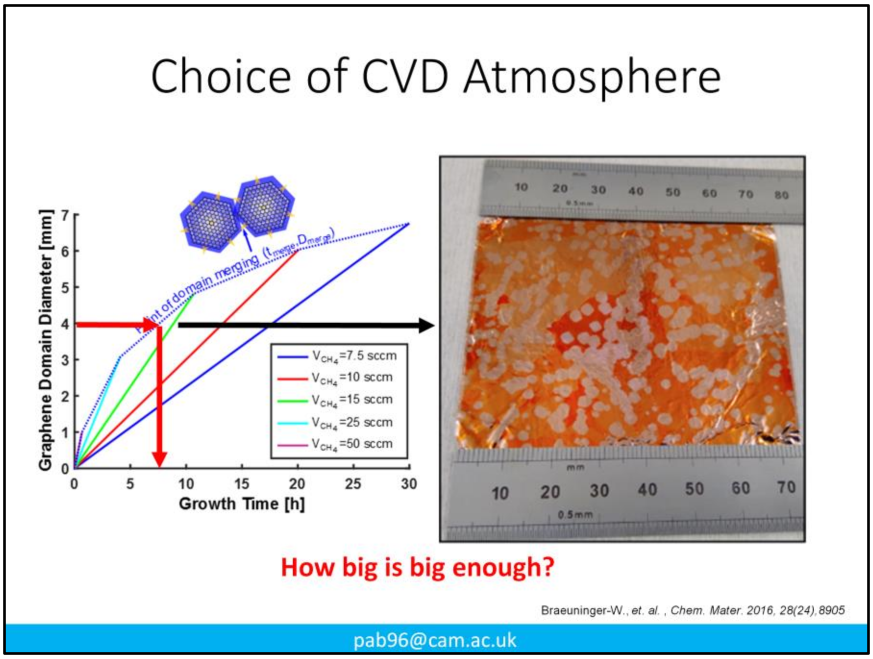
Graphene growth rate as a function of methane partial pressure -> Linear relationship!
Nucleation density as a function of methane partial pressure -> Exponential relationship!
-> Combining these into one graph yields Max Domain Size vs growth time graph



Choice of CVD Atmosphere

How big is big enough?

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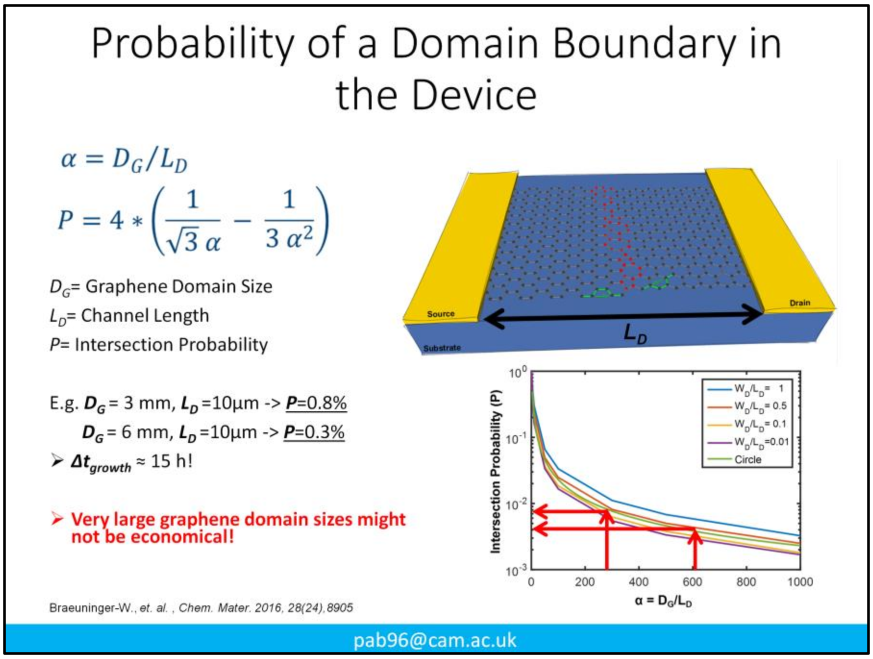
So, growing a few mm sized graphene domains can be done in a few hours BUT centimetre sized domains takes several days!
E.g. 4mm domains takes about 8h…. Note merging them into continuous film takes even longer!
BTW Cu pockets are not necessary rather tune growth atmosphere properly in your reactor!

How big of graphene domains should we grow? -> The answer is it depends on your device needs! See next slide:



Probability of a Domain Boundary in the Device

$$\alpha = D_G/L_D$$

$$P = 4 * \left(\frac{1}{\sqrt{3}\,\alpha} - \frac{1}{3\,\alpha^2}\right)$$

D_G= Graphene Domain Size
L_D= Channel Length
P= Intersection Probability

E.g. $\boldsymbol{D_G}$ = 3 mm, $\boldsymbol{L_D}$ =10µm -> **P=0.8%**
$\boldsymbol{D_G}$ = 6 mm, $\boldsymbol{L_D}$ =10µm -> **P=0.3%**

- ➢ $\boldsymbol{\Delta t_{growth}}$ ≈ 15 h!

- ➢ **Very large graphene domain sizes might not be economical!**

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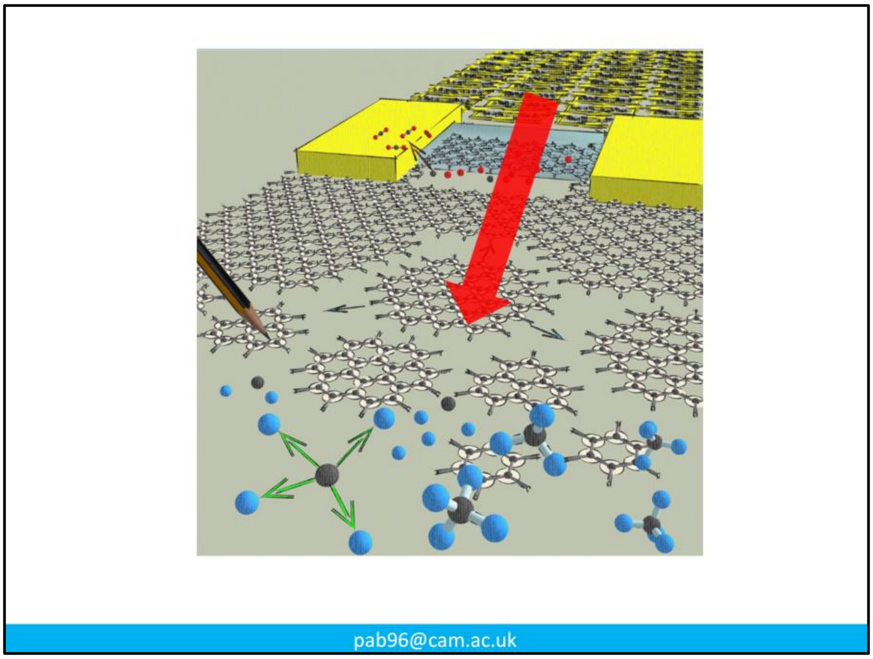
What’s the probability of a domain boundary intersecting with your device area? Scaling from graphene domain size 3mm to graphene domain size 6mm only yield a reduction in domain boundary intersection from 0.8% to 0.3% but the price to pay is 15h more growth time!!!
(For derivation of this formula and more details see supplementary information of Braeuninger-W., et. al. , Chem. Mater. 2016, 28(24),8905 or supplemntary slide ” Intersection Probability”)



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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!

Thank You!

the HOFMANN group
at the University of Cambridge

NPL
National Physical Laboratory

European Research Council
erc

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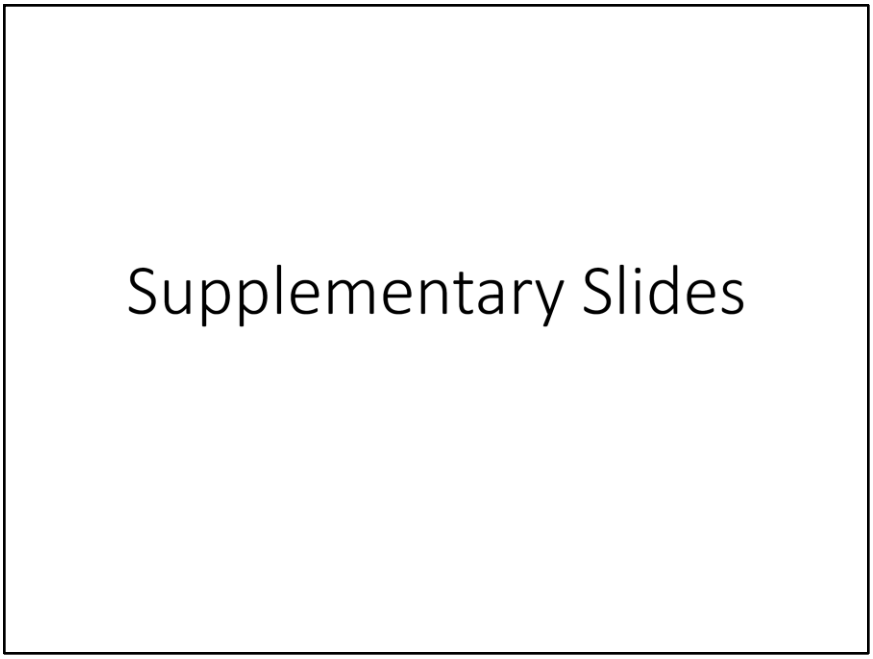
If you have any questions please get in contact with me directly via pab96@cam.ac.uk. I’m very interested in your opinion and look forward to discussing with you!

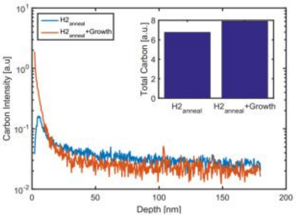


Supplementary Slides

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



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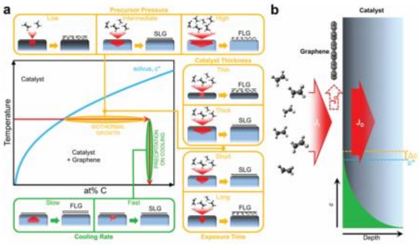

Cabrero-Vilatela, Weatherup, Braeuninger-W., Caneva,Hofmann, Nanoscale, 2016, 8, 2149

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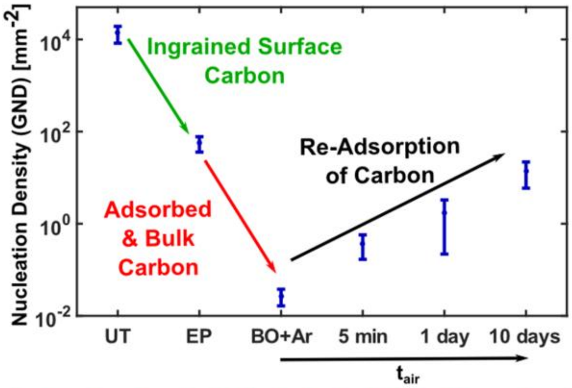
Extrinsic and Extrinsic Carbon



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

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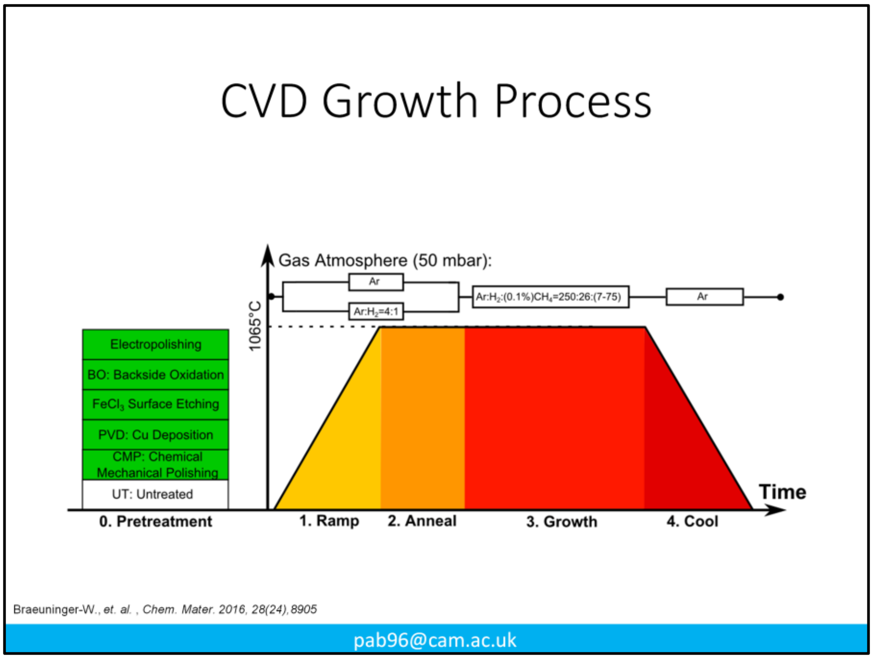

CVD Growth Process

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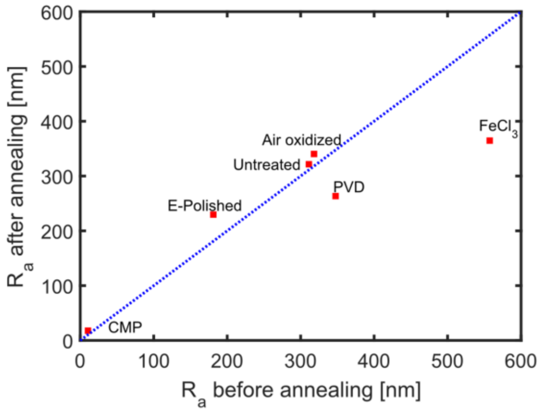
Roughness before/after annealing



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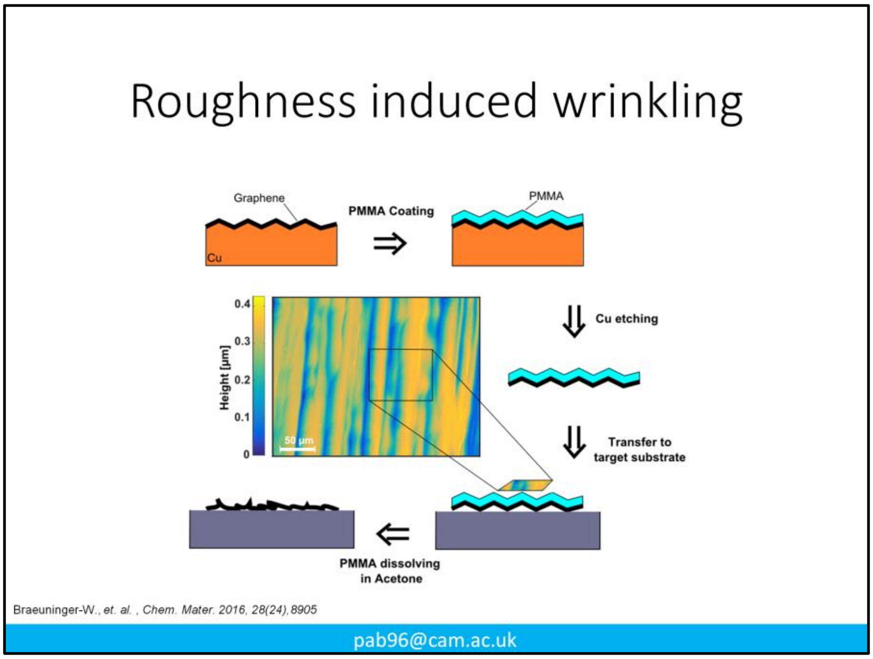

Roughness induced wrinkling

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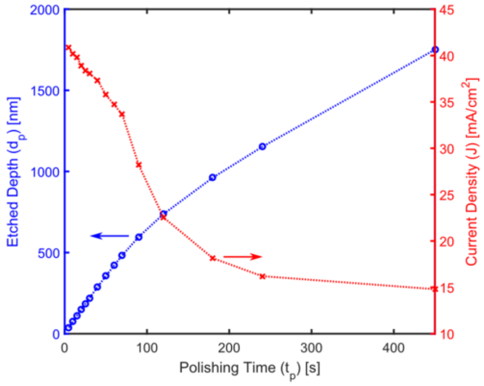
Electropolishing (2.7V, 10.3M H_3PO_4)



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

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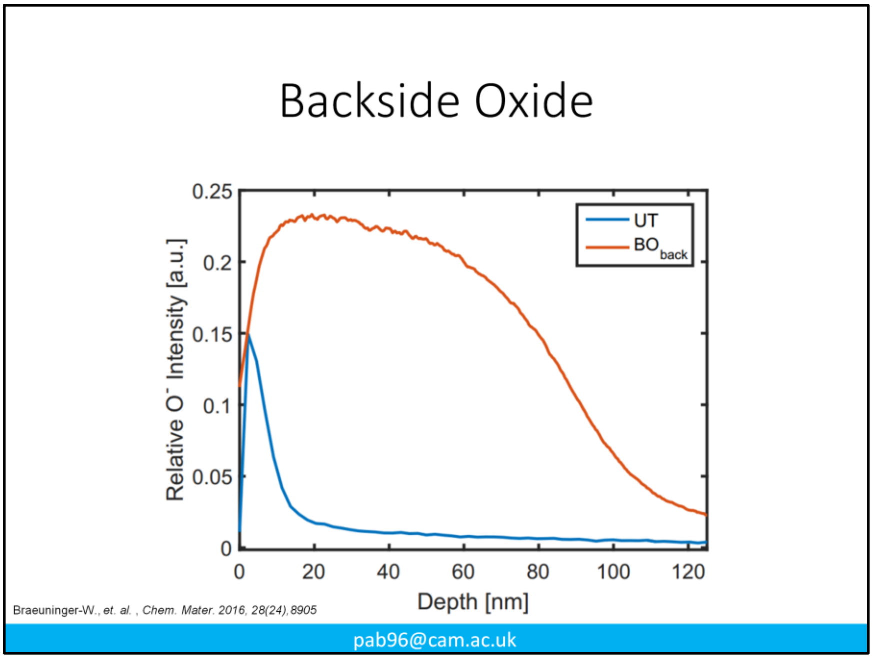

Backside Oxide

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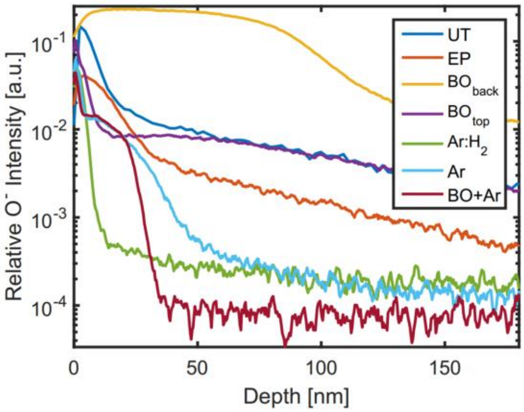
SIMS O^- depth profiles



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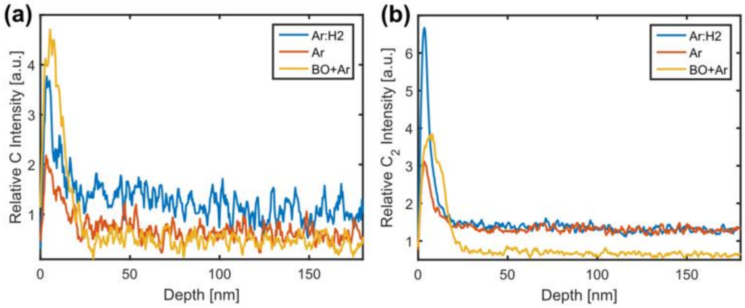
C and C_2 carbon depth profiles



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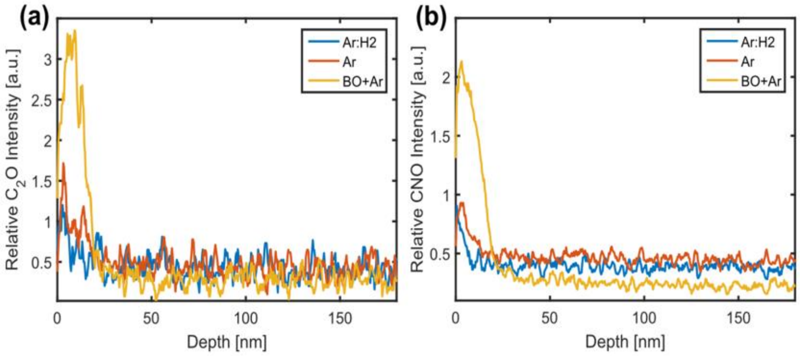
C_2O and CNO depth profiles



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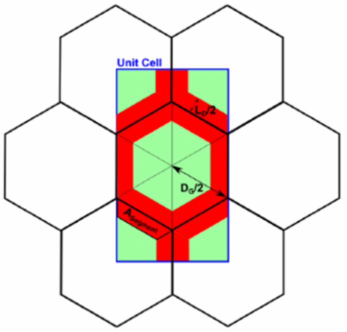
Intersection Probability



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

$$A_{Intersection} = 12 \cdot A_{Segment}$$

$$A_{UnitCell} = \frac{3\sqrt{3}}{4} D_G^2$$

$$P = \frac{A_{Intersection}}{A_{UnitCell}} = 4(\frac{1}{\sqrt{3}\alpha} - \frac{1}{3\alpha^2})$$

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