Controlling the size, number of layers and planarity of CVD graphene single-crystals

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Outline

1. Chemical vapor deposition: fundamentals and challenges
2. Control of the structural quality
3. Control of the number of layers
4. Cu substrate surface roughness considerations
5. Conclusions

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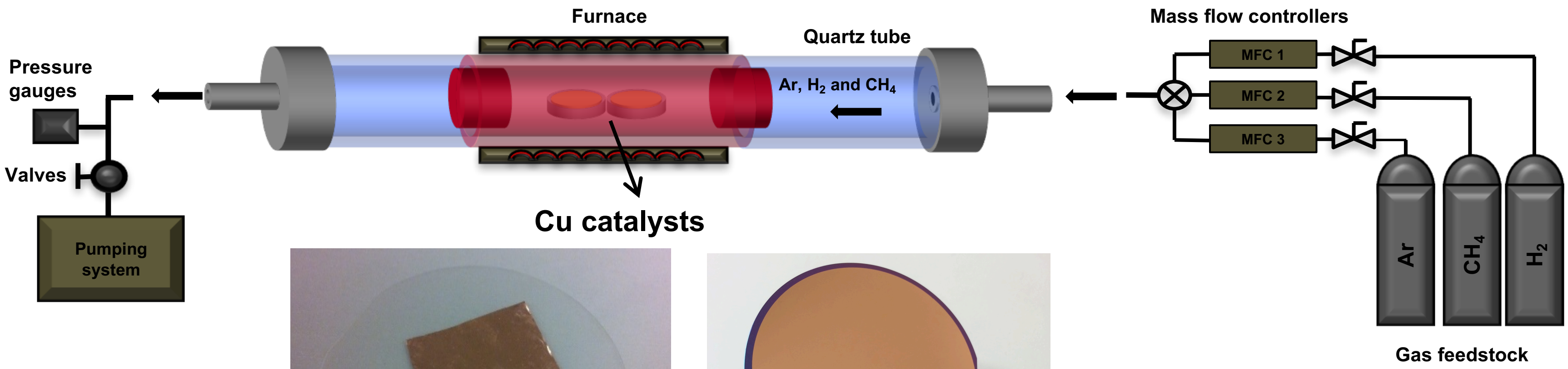
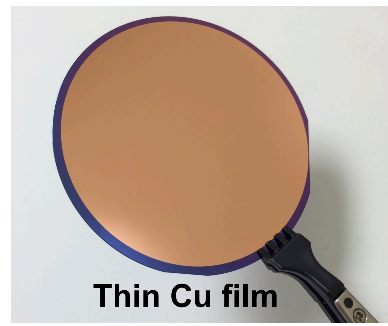
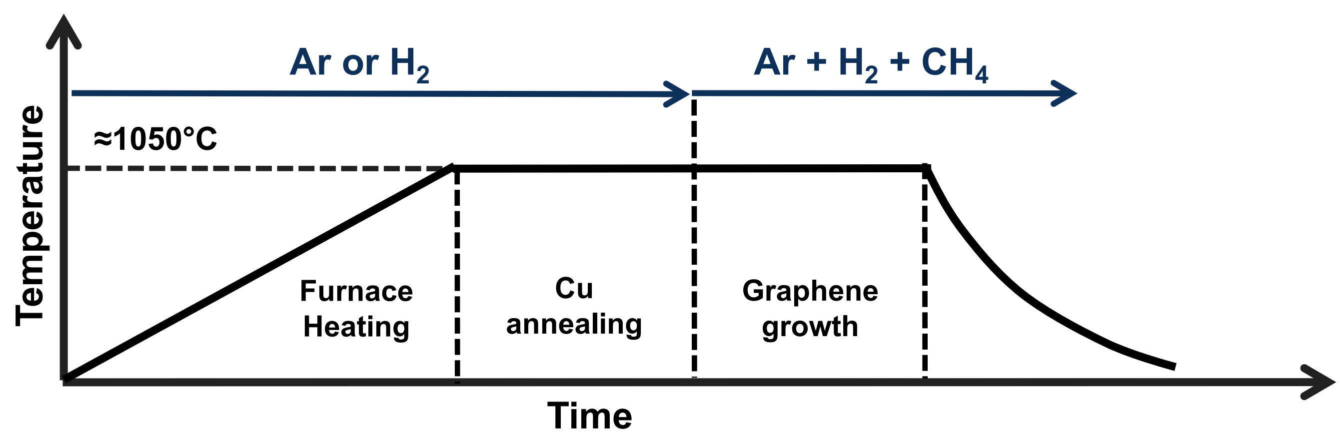
Chemical vapor deposition of graphene

Hot-wall CVD furnace



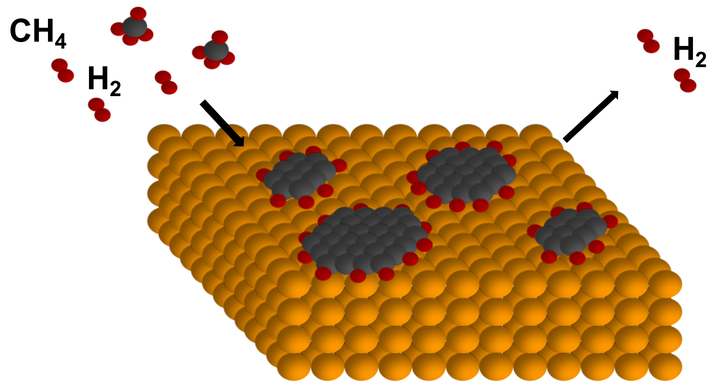


CVD protocol: temperature and gas flow profile



Working principle & challenges

Nucleation, growth & coalescence of graphene domains/single crystals



Main challenges

1. High structural quality
2. Control over the number of layers
3. Physical integrity
4. Planar aspect

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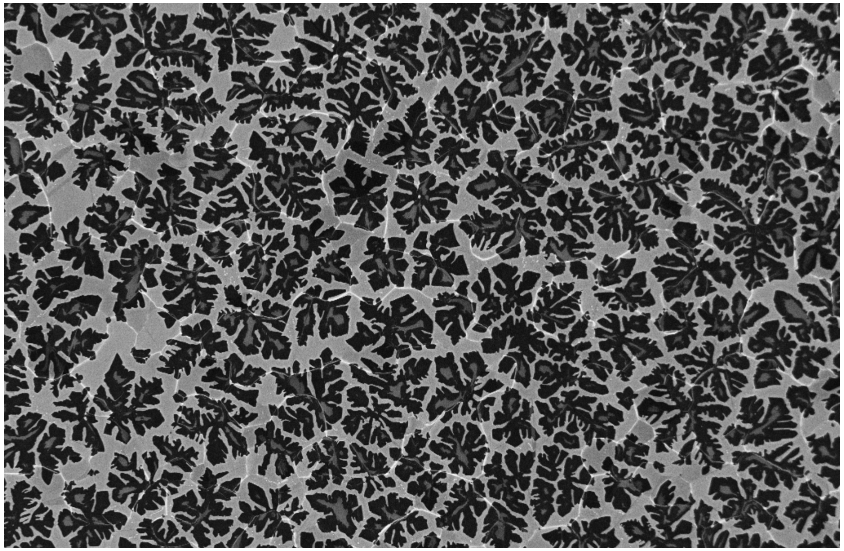
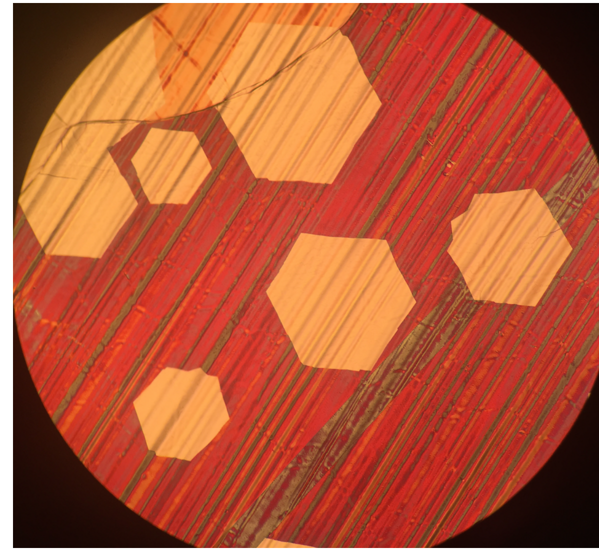
Structural quality of graphene

Challenge: controlling the shape, size and orientation of domains

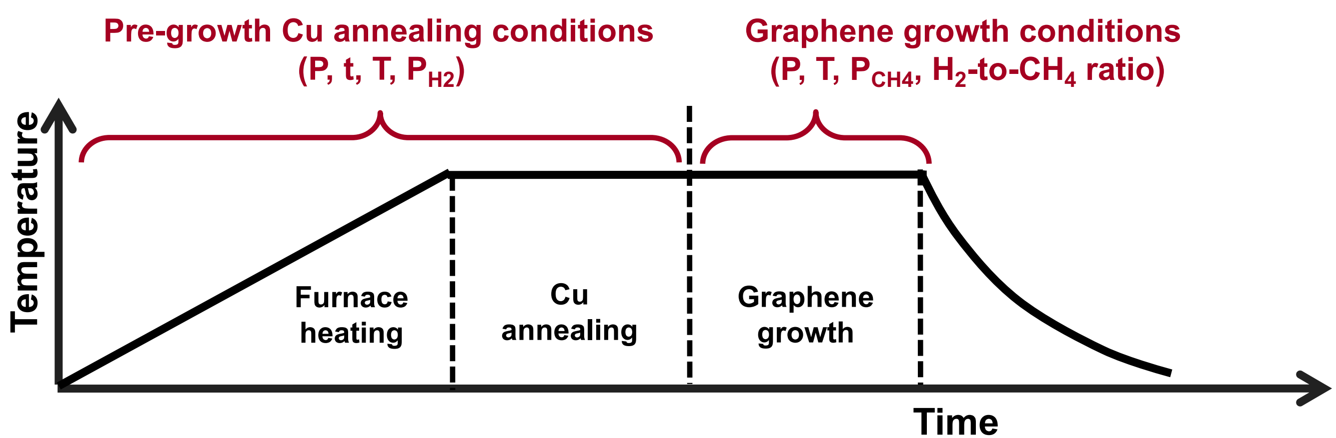


50 µm



1000 µm

Key parameters:

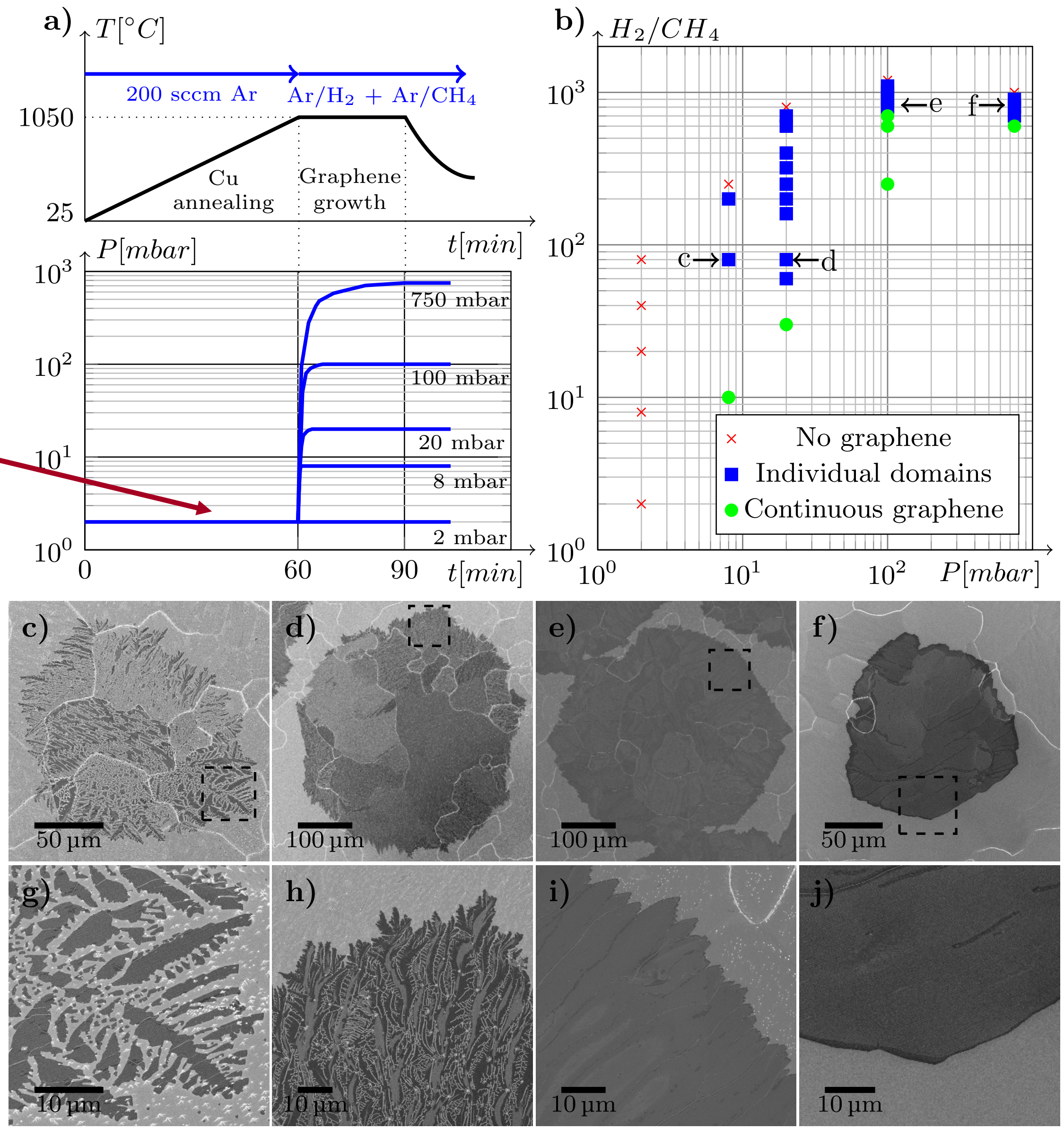


Structural quality: Graphene growth conditions

Systematic study on thin Cu films

Pressure-controlled CVD

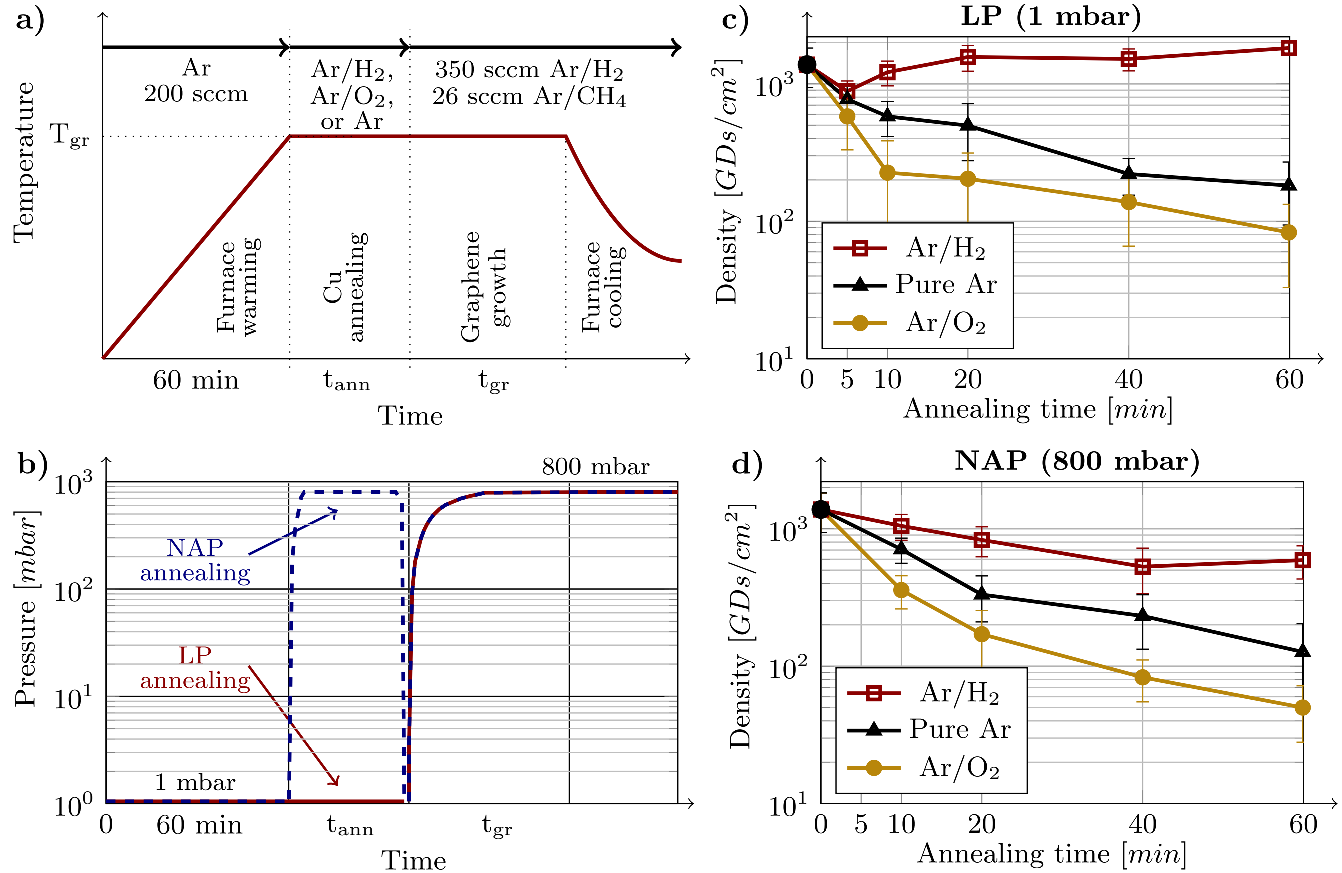
Identical Cu annealing conditions



[B. Huet & J.-P. Raskin, Chemistry of Materials, 2017]

Structural quality: Cu annealing conditions

Systematic study: Cu foil in-situ thermal treatment



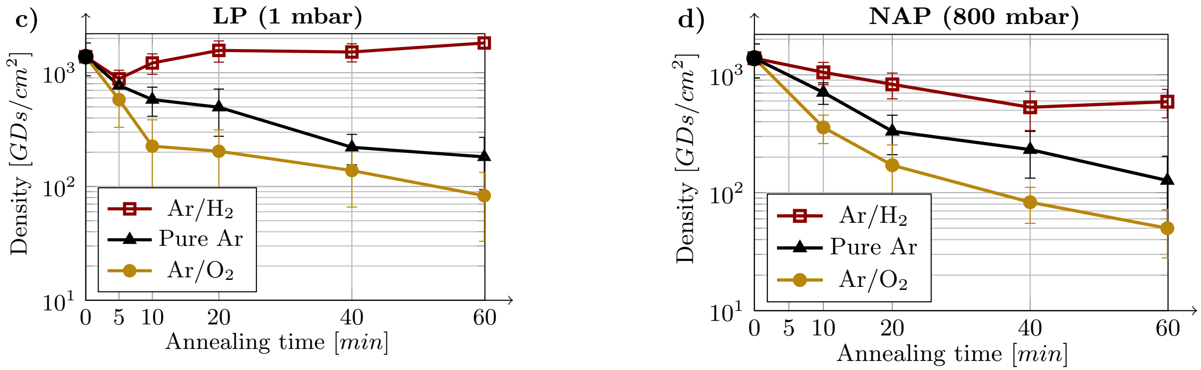
[B. Huet & J.-P. Raskin ,Carbon, 2018]

Factors determining the density of nuclei:

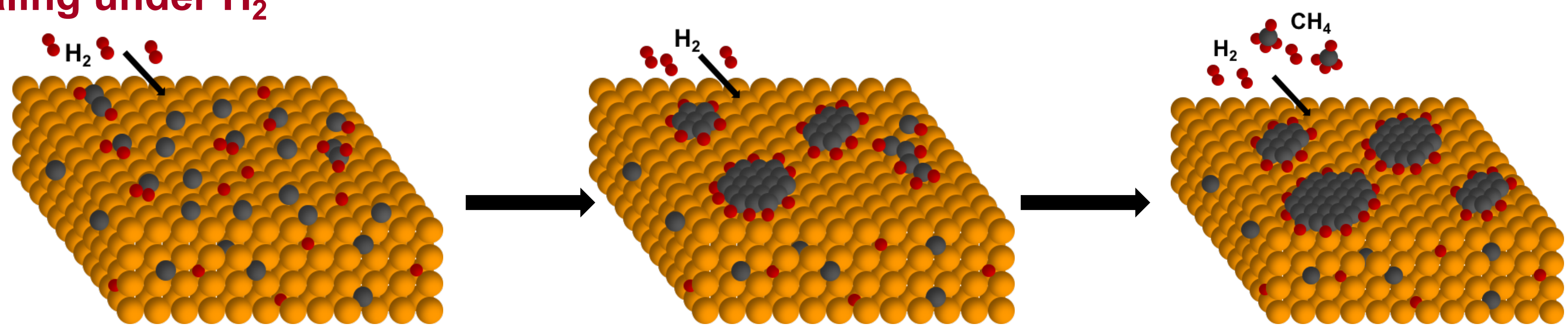
1. Cu oxide layer=passivation?
2. Passivation of active sites?
3. Surface smoothing?
4. Restructuration of Cu surface?
5. Reduction of carbon content in Cu?

Structural quality: Cu annealing conditions

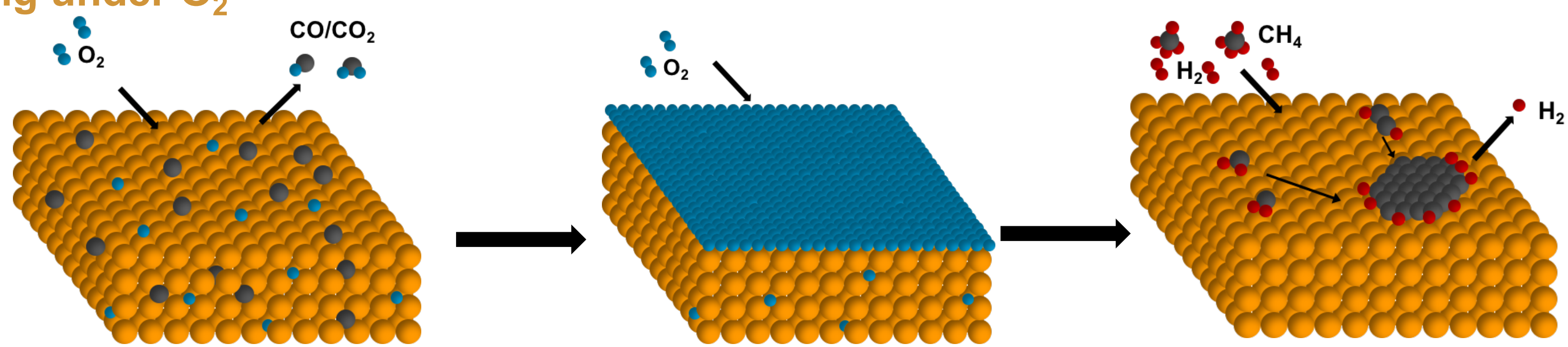
Major mechanism: Cu substrate decarburization



Annealing under H_2

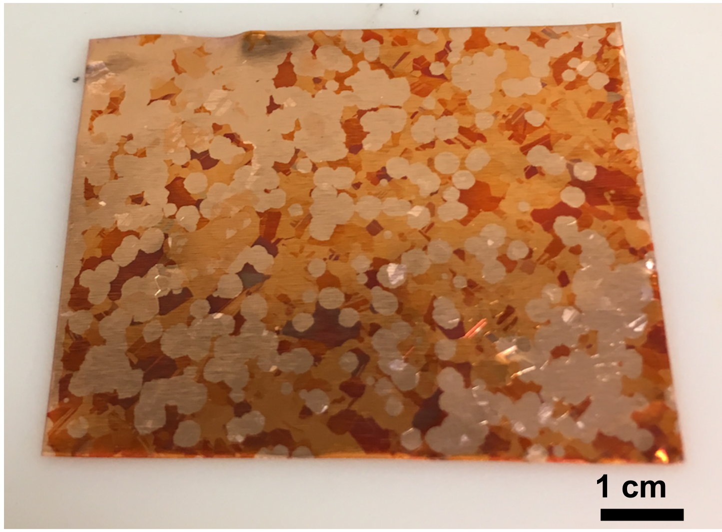


Annealing under O_2



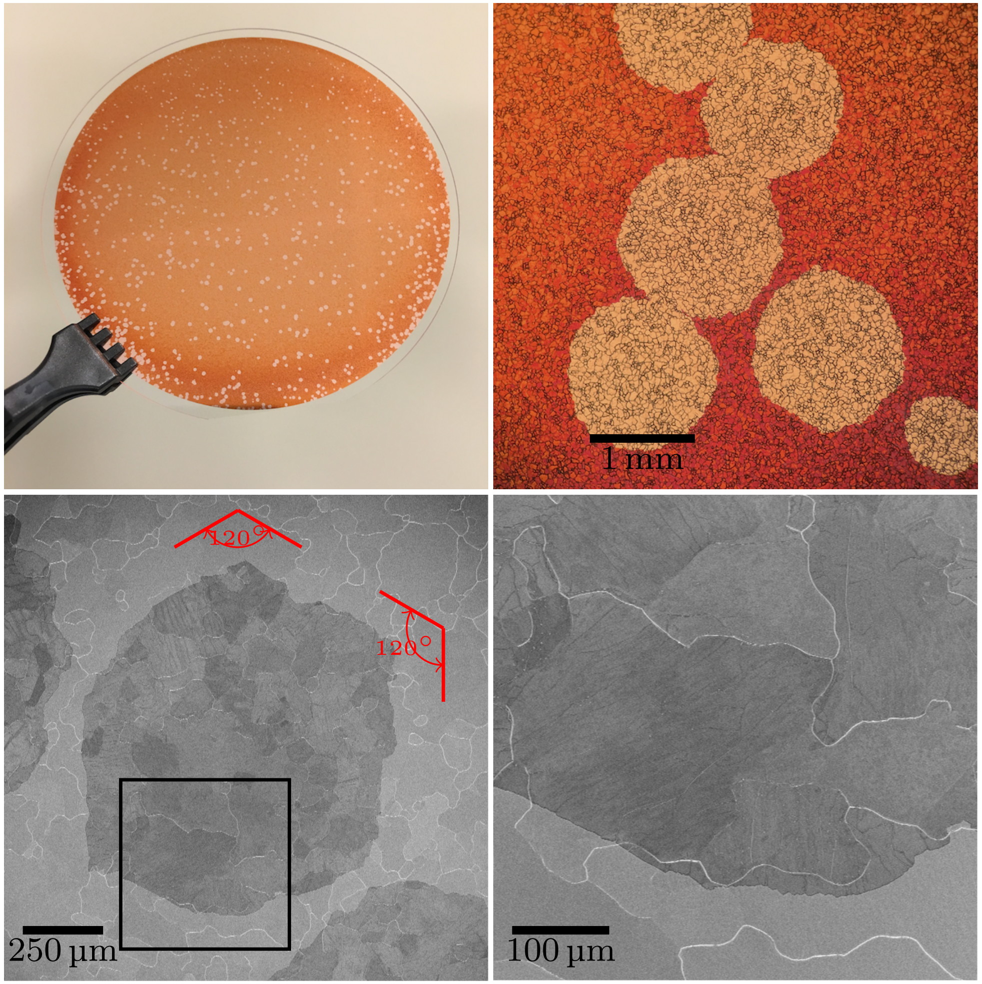
Structural quality: mm-size domains

Cu foils



[B. Huet & J.-P. Raskin ,Carbon, 2018]

Thin Cu films



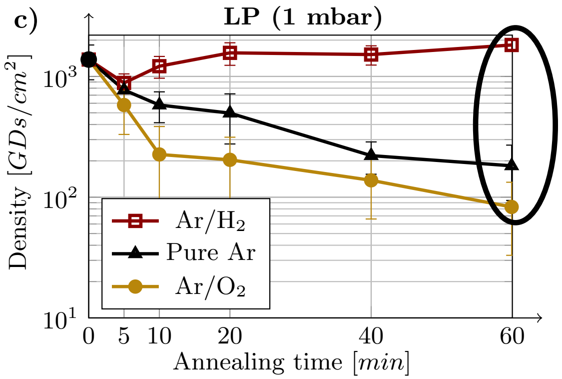
[B. Huet & J.-P. Raskin, Chemistry of Materials, 2017]

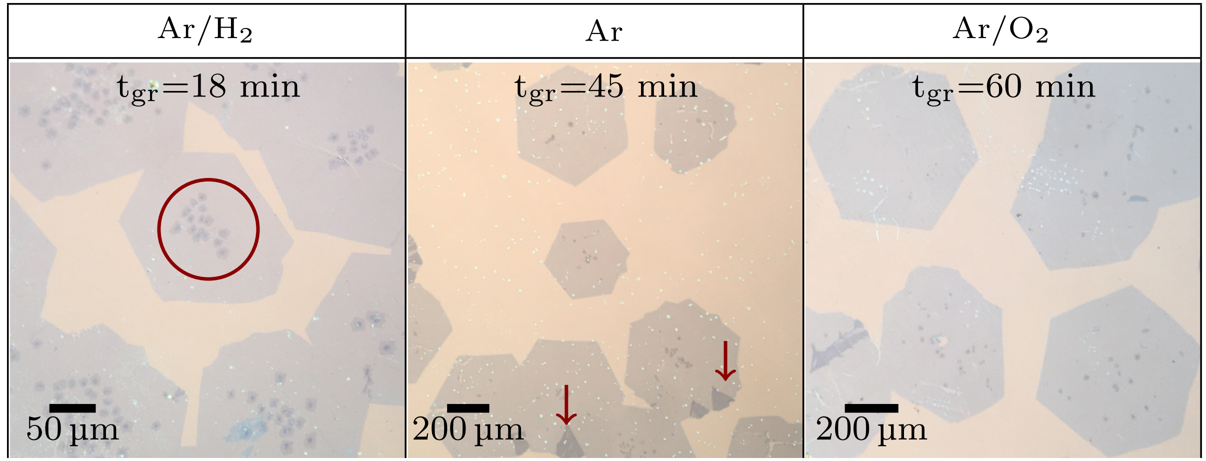
Outline

Number of layers

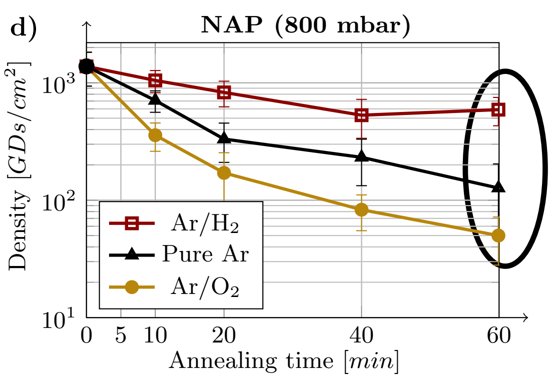
Cu foil in-situ thermal treatments: transferred graphene

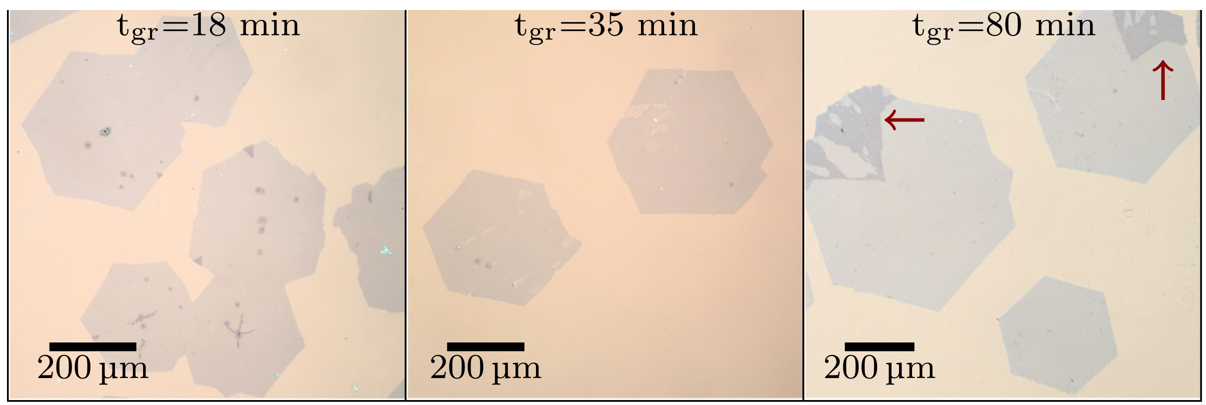
c)





d)

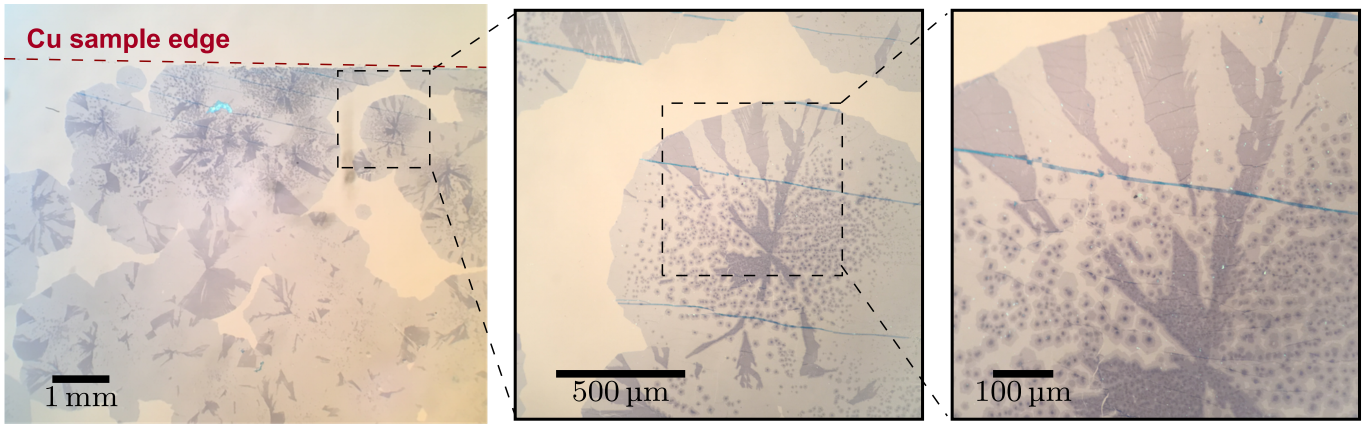


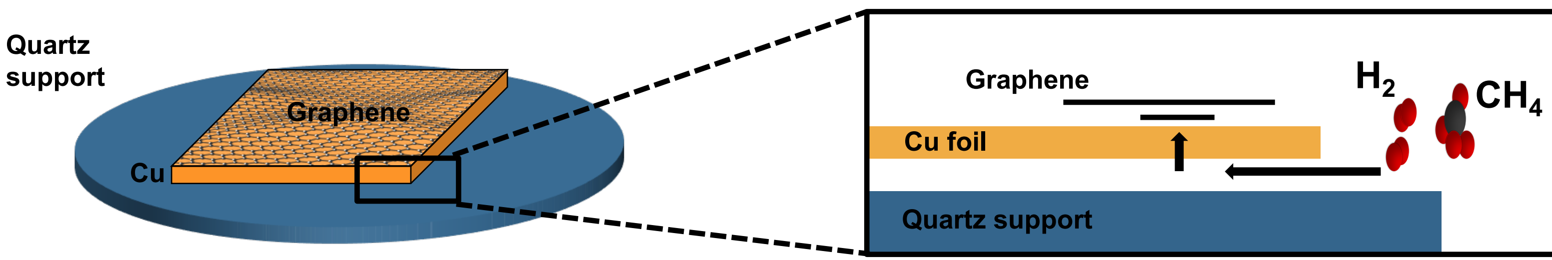


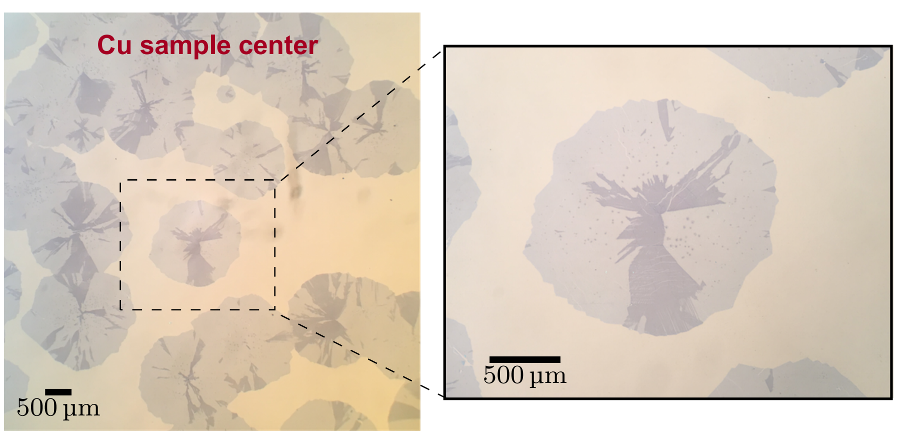
[B. Huet & J.-P. Raskin ,Carbon, 2018]

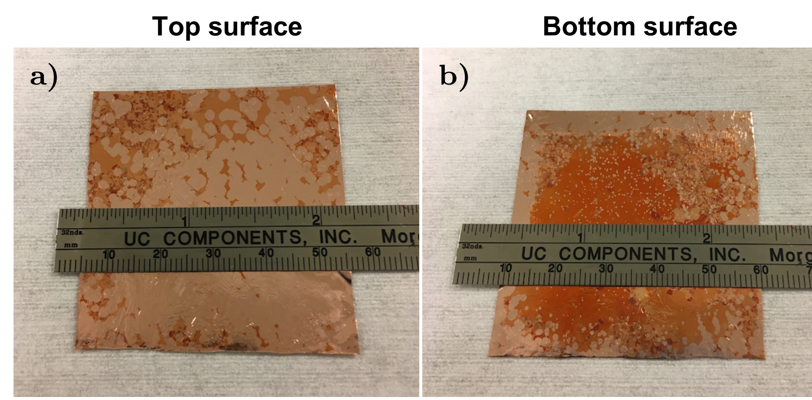
Number of layers

Compact multi-layer regions





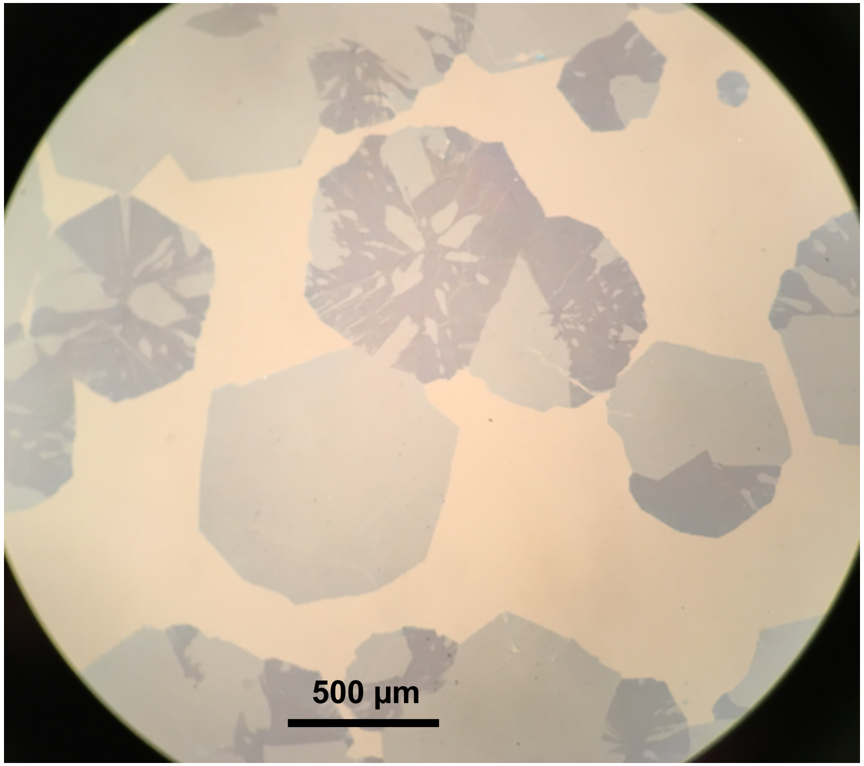


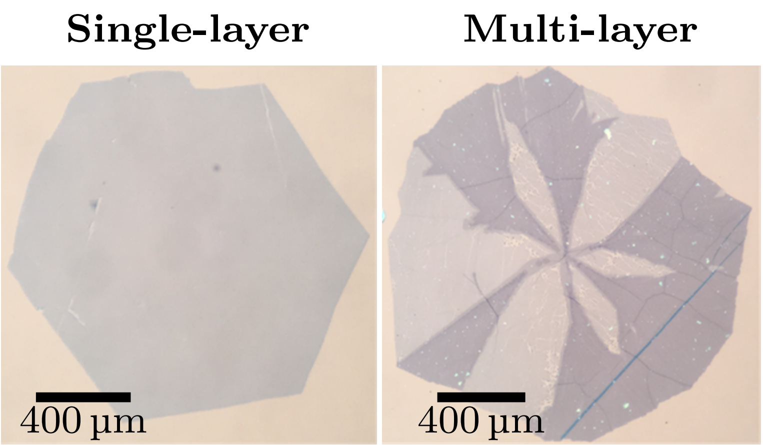


[B. Huet & J.-P. Raskin ,Carbon, 2018]

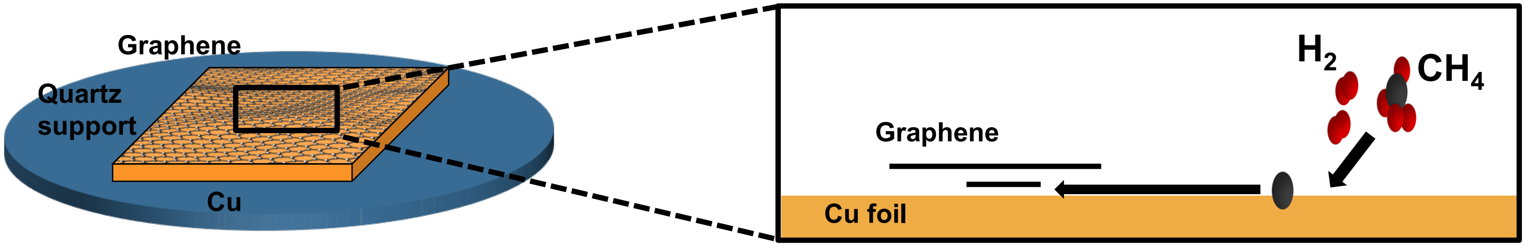
Number of layers

Branch-like multi-layer regions





[B. Huet & J.-P. Raskin ,Carbon, 2018]



⇒ Random occurrence
⇒ Only observed when annealed in Ar or Ar/O_2 atmosphere
⇒ Probably a surface-diffusion controlled and first layer graphene-assisted phenomenon

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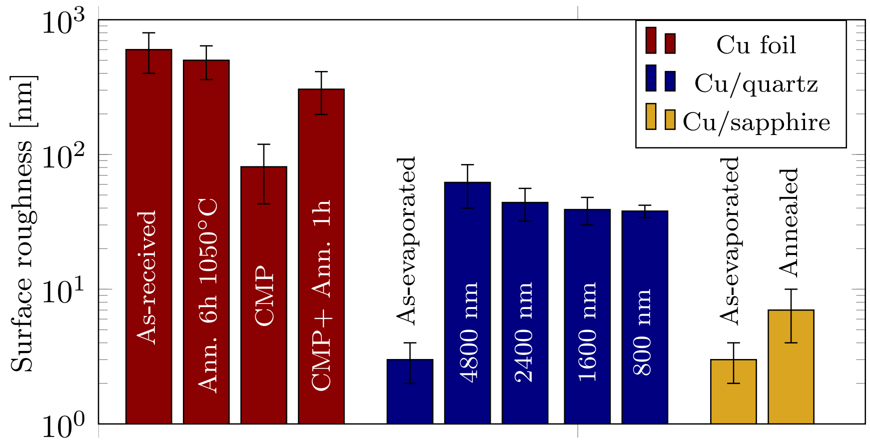
Planarity: Cu foils vs. Cu films

Comparison Cu foils: polished vs. unpolished

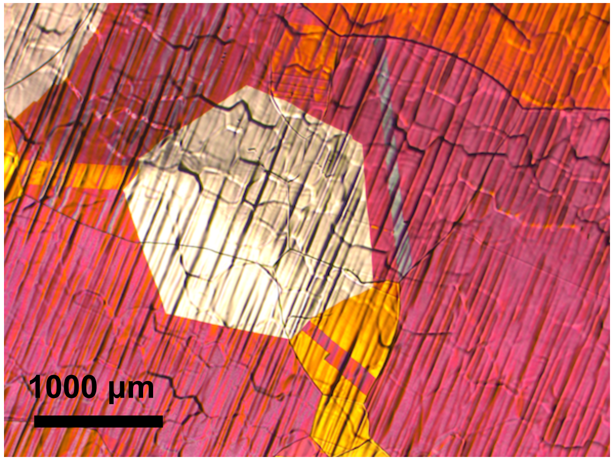


[B. Huet & J.-P. Raskin, to be submitted]

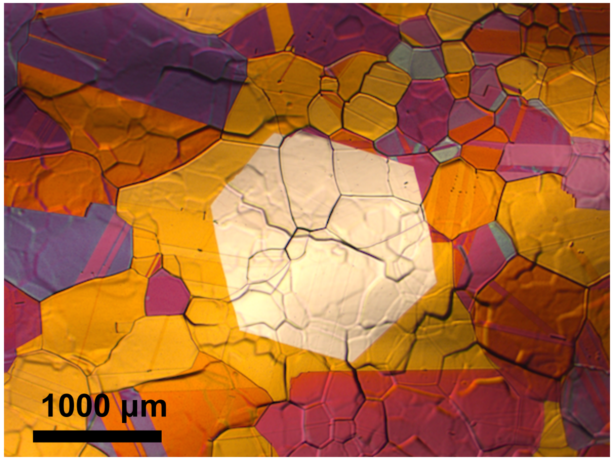
Unpolished surface

Polished surface

Unpolished surface

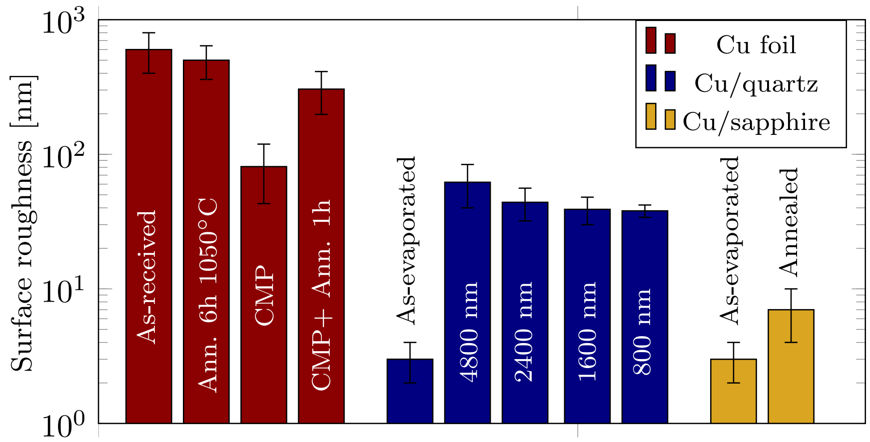


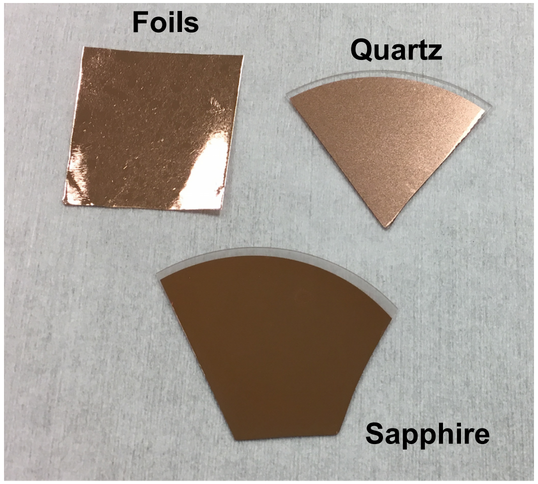
Polished surface



Planarity: Cu foils vs. Cu films

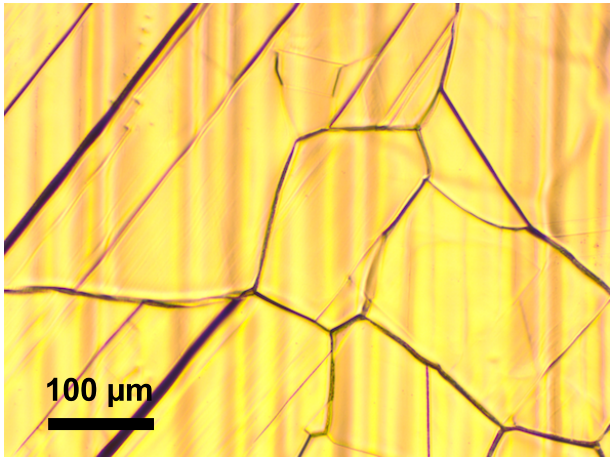
Comparison: Cu foils vs. polycrystalline Cu films



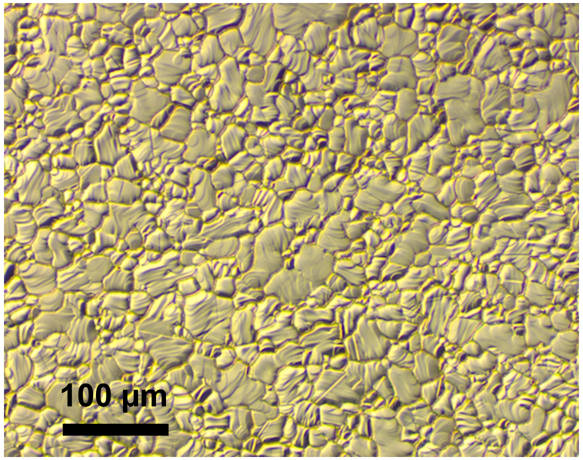


50 µm Cu foil

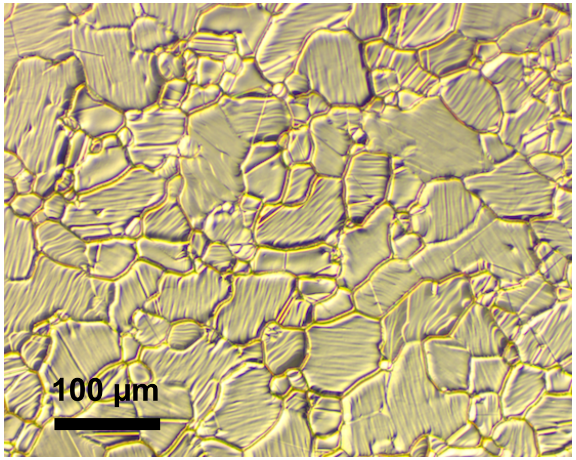
(annealed 6h 1050°C, AP)



800 nm-thick film



1600 nm-thick film



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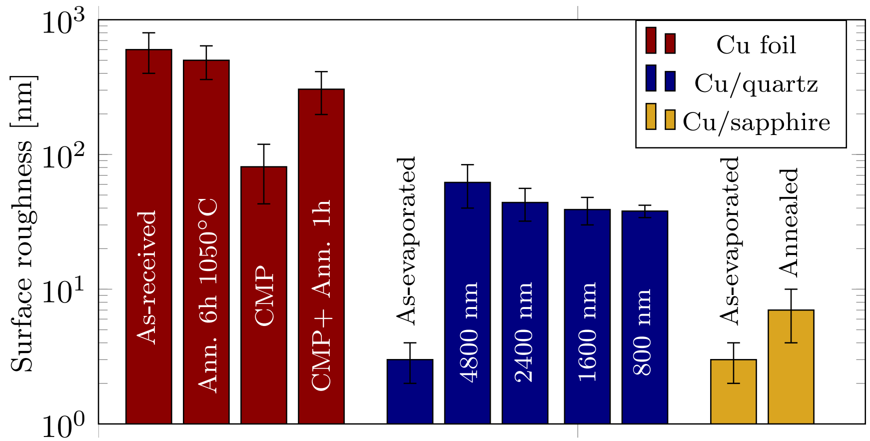
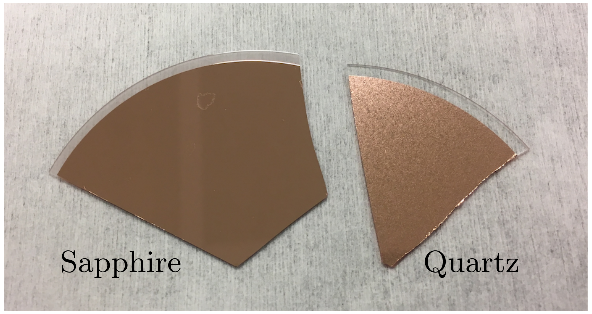
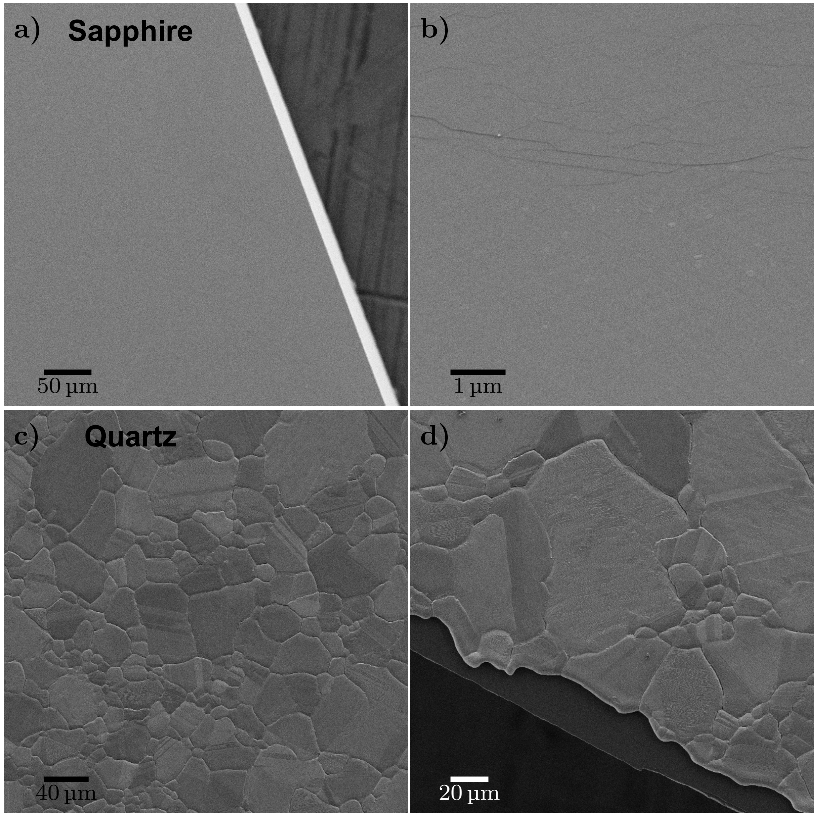
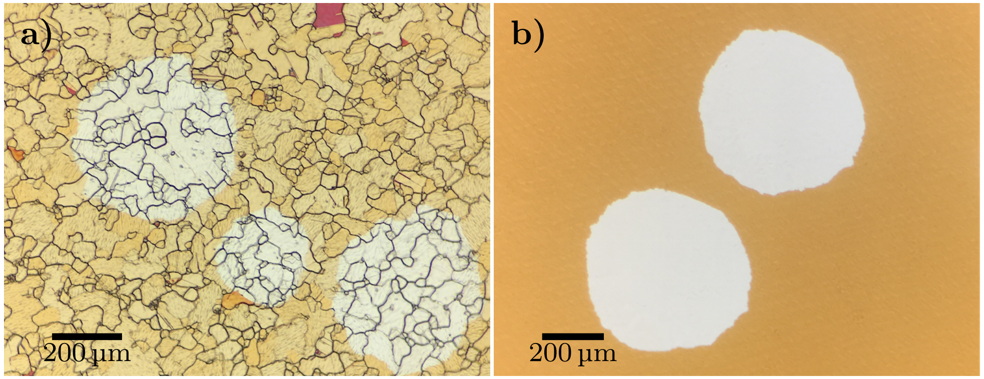
Planarity of Cu films: poly vs. epi

Comparison Cu films: polycrystalline vs. epitaxial



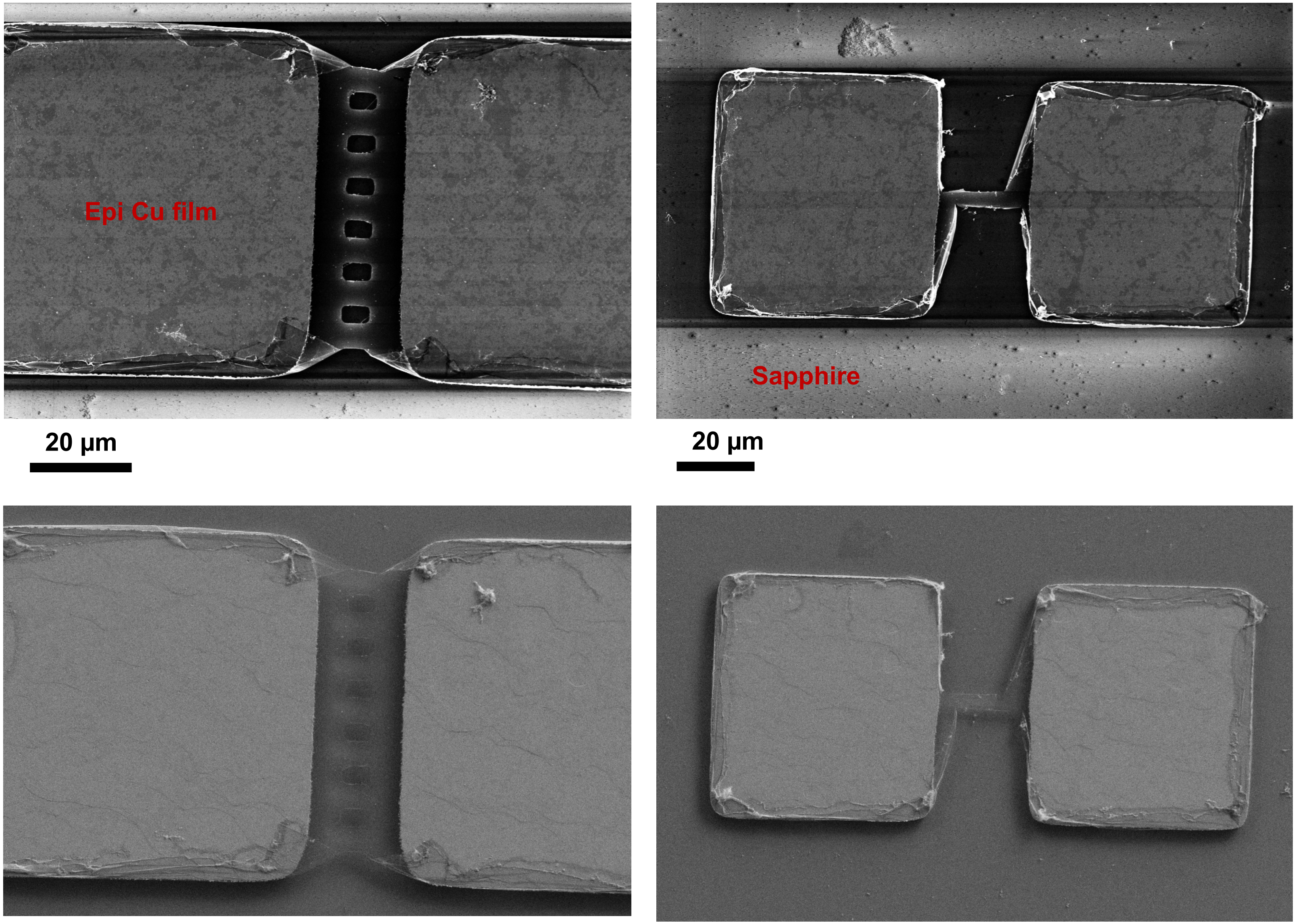






Facile and direct fabrication of on-chip structures

Using Cu film as a sacrificial layer



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Conclusions

1. High quality graphene can be produced on different Cu substrates
2. Oxygen is key to reduce the nucleation site density
3. Graphene thickness depends on the CVD protocol and the Cu configuration
4. Surface morphology of commonly used Cu foils is limited
5. Flat, smooth and rigid substrates offer new possibilities for fabrication
6. Still room for discoveries and progresses in graphene production

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Pressure-Controlled Chemical Vapor Deposition of Single-Layer Graphene with Millimeter-Size Domains on Thin Copper Film

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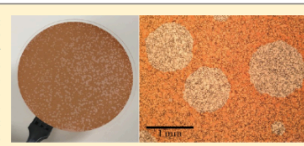
Supporting Information

ABSTRACT: In this work, single-layer graphene with compact millimeter-size domains has been obtained by chemical vapor deposition (CVD) on thin Cu film. This has been achieved by carefully adjusting the global pressure inside the CVD furnace as the graphene synthesis protocol proceeds. Global pressures in the 2−750 mbar range have been systematically investigated to determine optimal conditions for both the Cu annealing and the graphene nucleation and growth steps. It has been observed that using a high global pressure during the graphene growth is essential to grow defect-free compact domains. The low nucleation site density, required to produce large graphene domains, has been achieved by combining a high hydrogen-to-methane ratio during the graphene growth step and an in situ Cu film oxidation induced by a high pressure level of argon during the Cu annealing step. Finally, it is found that a brief evacuation of the CVD furnace from its argon atmosphere prior to the graphene growth step is a key process step to prevent the Cu film degradation. Our method provides a scalable and reproducible way to produce high quality graphene on thin Cu film which is a convenient platform for the realization of graphene-based practical applications.



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Role of Cu foil in-situ annealing in controlling the size and thickness of CVD graphene domains

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ABSTRACT

Producing graphene with minimal crystalline defects and a controllable number of layers is highly desirable for its integration in advanced technological applications. Here we show how the chemical vapor deposition (CVD) protocol can be adjusted in order to control the size, the shape and the thickness of graphene domains. More particularly, this work focuses on the correlation between the conditions employed during the Cu foil *in-situ* thermal treatment and the subsequent graphene growth. The influence of Cu pre-growth treatments has been systematically investigated by considering two different pressure regimes (1 and 800 mbar) and various gas compositions (pure Ar, Ar/H_2 and Ar/O_2 mixtures) while using identical graphene growth conditions. We show that exposing the Cu foil to oxygen, either present as residuals in the Ar feedstock or precisely dosed using the Ar/O_2 gas line, effectively contributes to reduce the catalyst carbon content prior to graphene growth and hence significantly decreases the nucleation site density. It is also found that annealing the Cu catalyst in a hydrogen-free environment favors the formation of defect-free multi-layer graphene branches that extend underneath the millimeter-size single-crystalline graphene top layer. Our results provide clear guidelines to control the formation of graphene nuclei and additional layers.

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Thank you!