Growth of Spatially-Arranged Millimeter-Size Single-Crystal Graphene on Thin Cu Film

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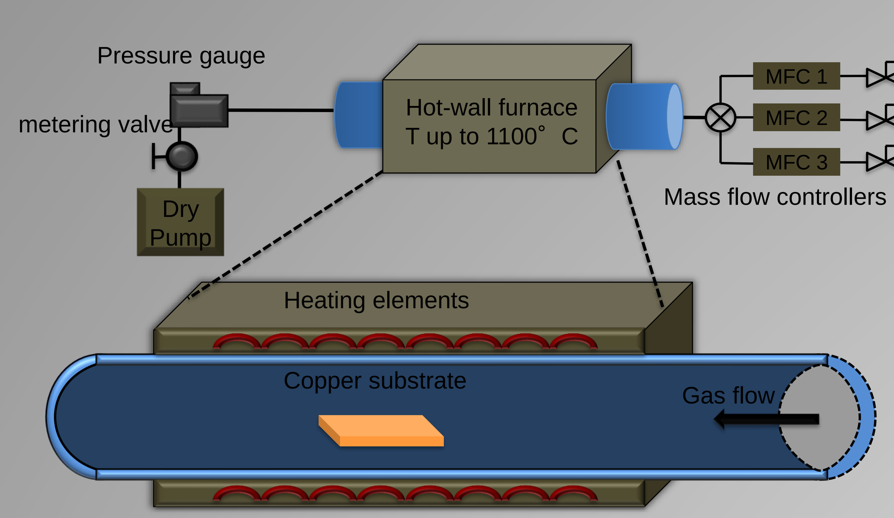
Chemical vapor deposition (CVD) of graphene on Cu catalyst is the most promising technique to produce large-area single-layer graphene films [1]. Unfortunately, CVD graphene is polycrystalline and structural defects arising from graphene grain boundaries (GGBs) are known to reduce drastically its excellent electrical and mechanical properties [2]. The best strategy to reduce the density of GGBs consists in drastically reducing graphene nucleation sites as well as controlling their positions so that they are able to expand and become large-area graphene defect-free domains eventually [3, 4]. In this research, we focus on using a reversible passivation layer made of CuO_x to localize graphene domains on the catalytic surface. Localizing graphene nucleation sites would allow us to predict the location of GGBs and align graphene devices on defect-free single-crystal domains.

Background: CVD of graphene

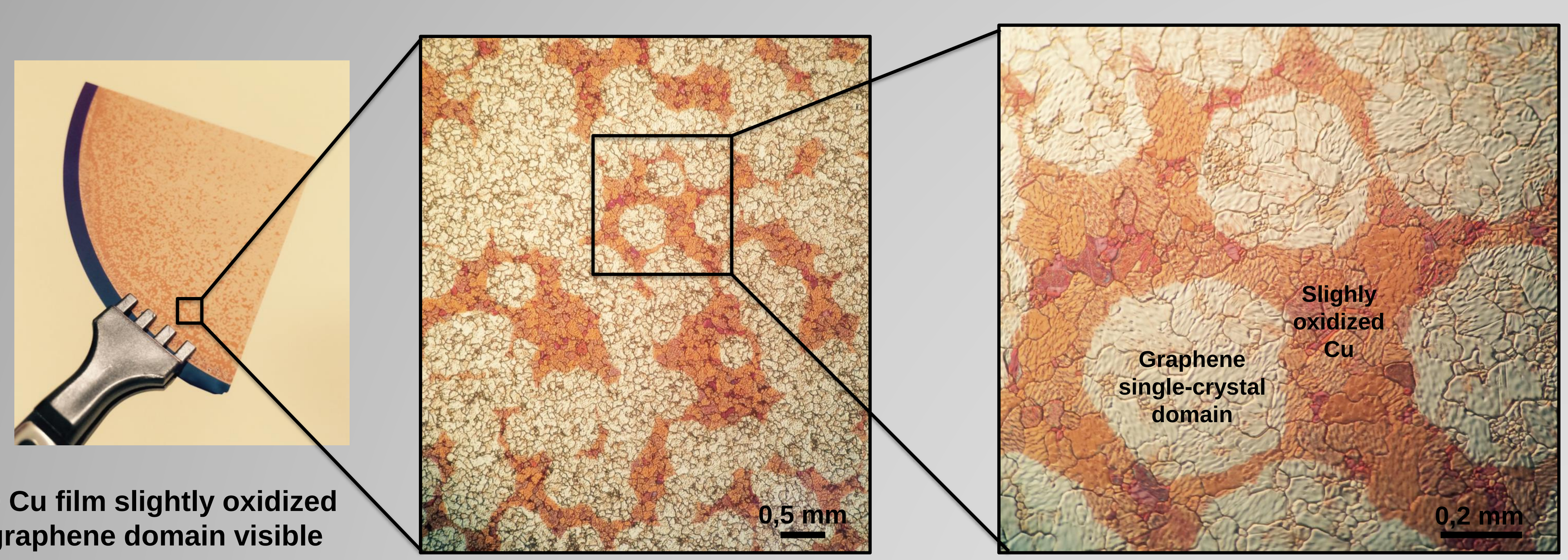
Experimental set-up



Catalytic substrate

3 inch-Si wafer thermally oxidized and coated with a thin Cu film.

Convenient technique for high yield production.



Post CVD Cu film slightly oxidized to make graphene domain visible

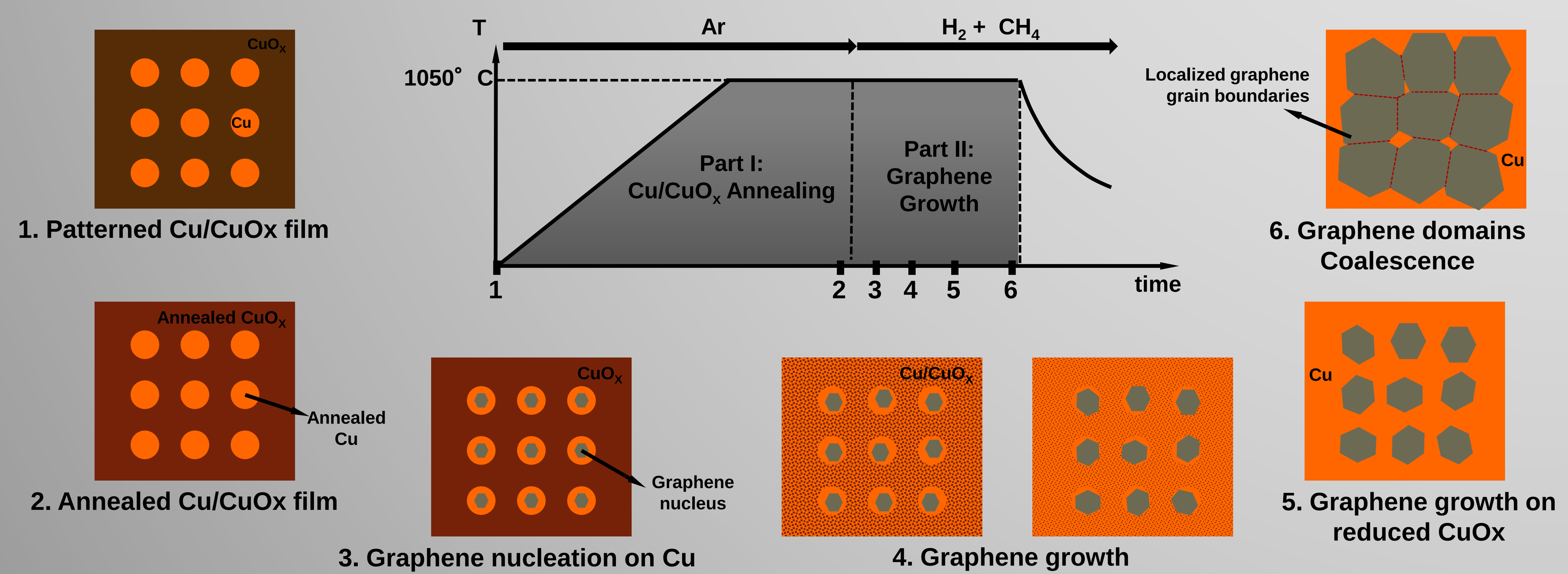
Motivations

- Chemical vapor depostion of graphene on Cu is the most promising technique to obtain large-area single-layer graphene.
- Millimeter-size single-crystal domains can be obtained with optimized CVD parameters including temperature, pressure & H_2-to-CH_4 ratio.
- The random distribution of domains is particularly troublesome for industrial fabrication of high performance graphene applications.
- Controlling the location of graphene nucleation sites would make the alignment for device fabrication process possible and efficient.

Main idea

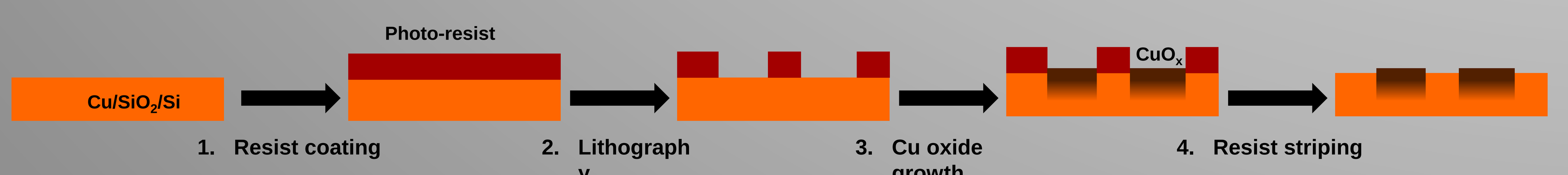
- A Cu oxide (CuO_x) passivation layer is used to prevent graphene nucleation in certain areas.
- CuO_x gradually vanishes during graphene growth stage upon reducing atmosphere required for graphene growth.
- Graphene growth can expand beyond patterned Cu areas and form a continuous film with localized grain boundaries.

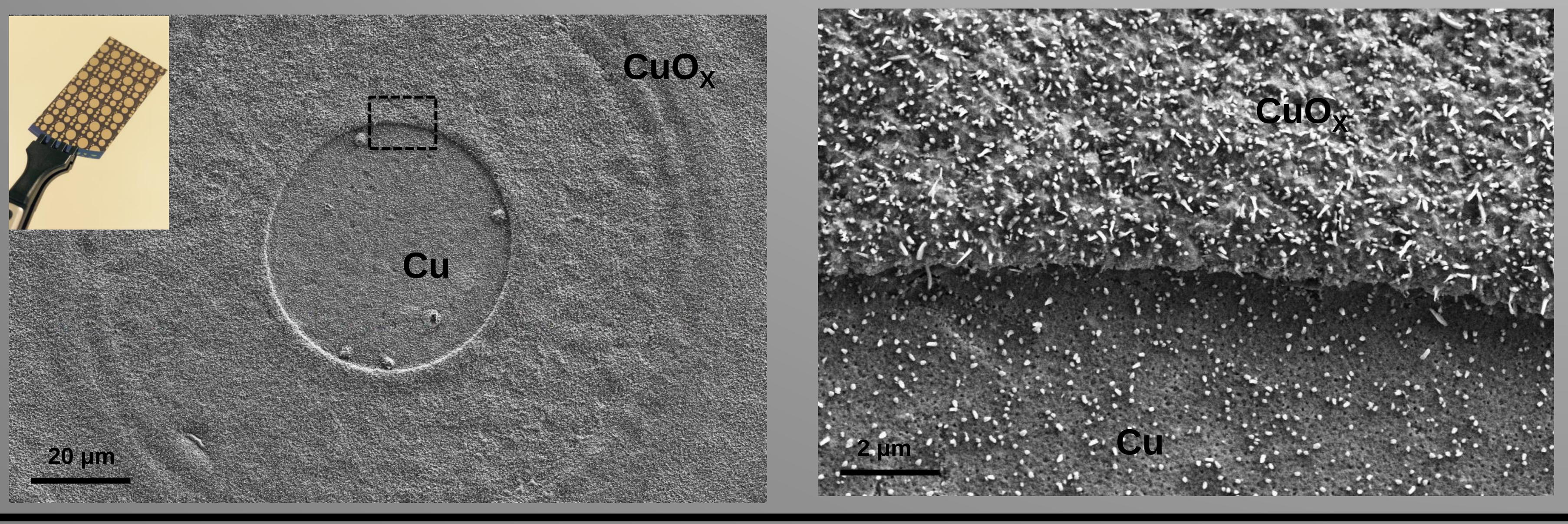
Schematic illustration of catalytic surface evolution during CVD process



Patterned Cu/CuOx fabrication

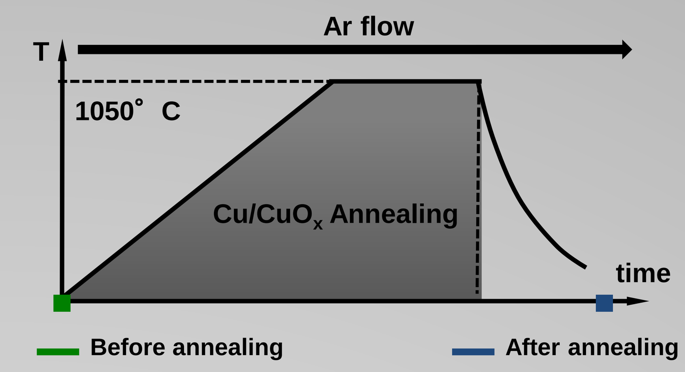
- Cu films deposited on a flat, smooth and rigid substrate can be processed by conventional micro-fabrication techniques
- A localized Cu oxide layer is obtained through lithography
- CuOx is grown in air at 300° C for an hour

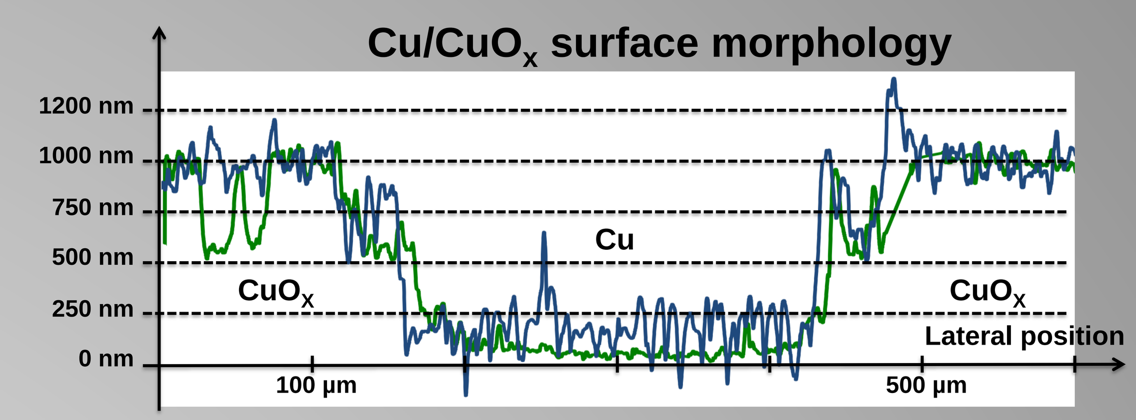


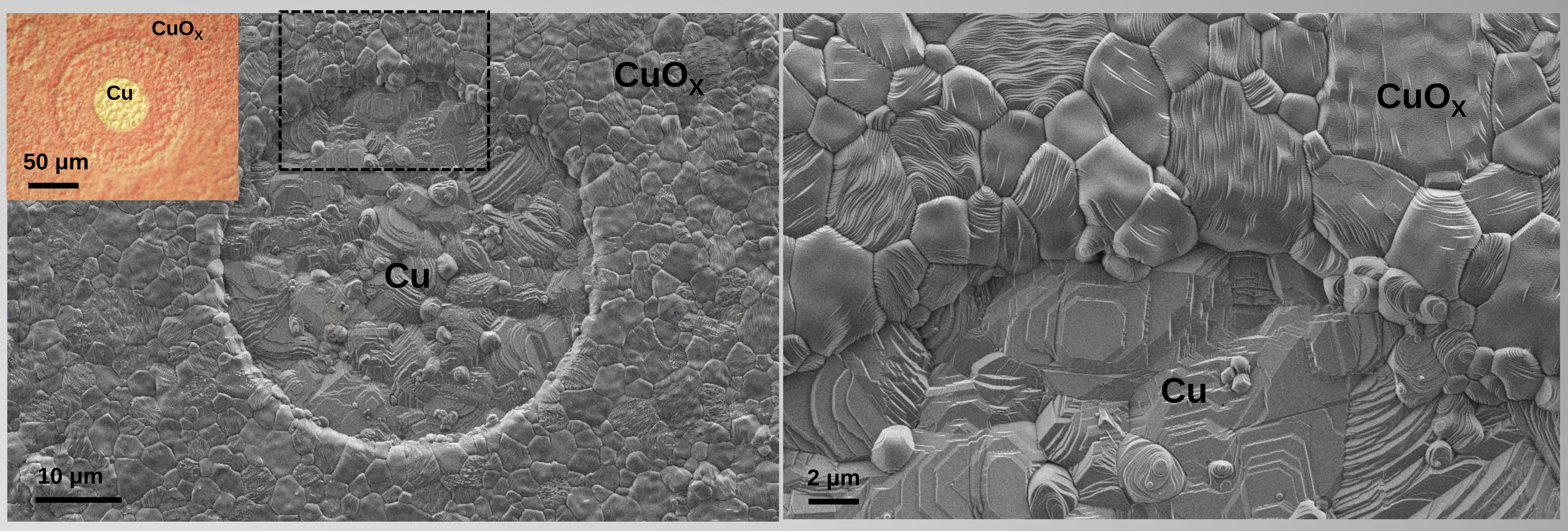


Part I: Cu/CuO_x Annealing

Observing Cu/CuO_x surface after annealing shows how looks like the catalytic surface before graphene nucleation



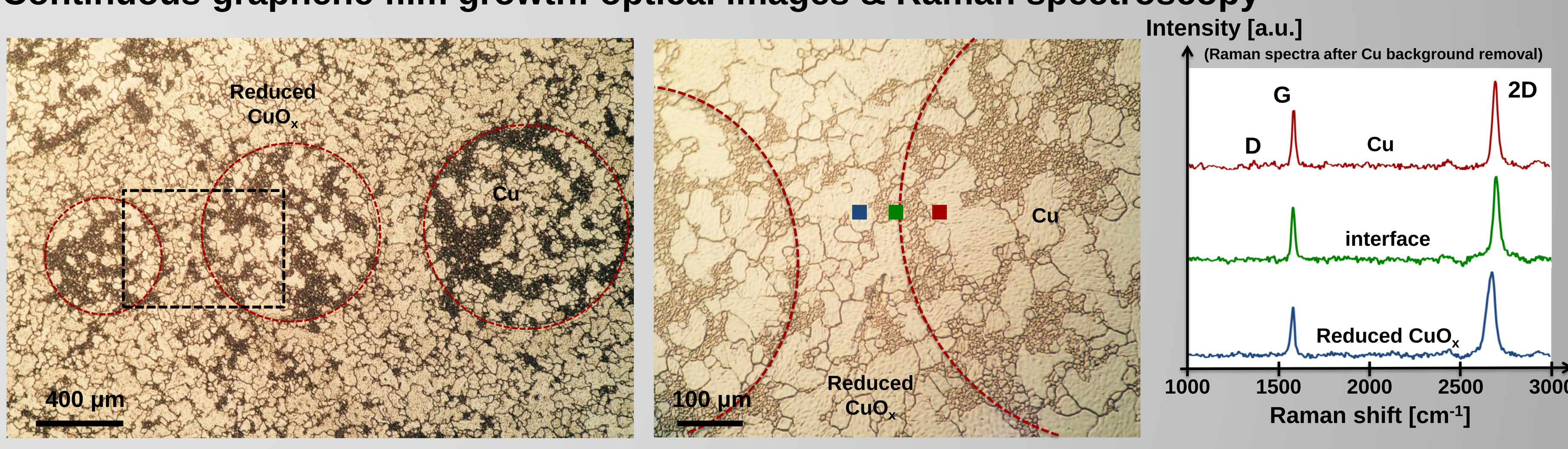




- Oxidation of Cu leads to an increase of volume (by up to 70%) and creates a step edge defining the patterns.
- Annealing of Cu and CuO_x results in grain growth
- Evaporation loss of Cu and CuO_x upon annealing seems to be limited

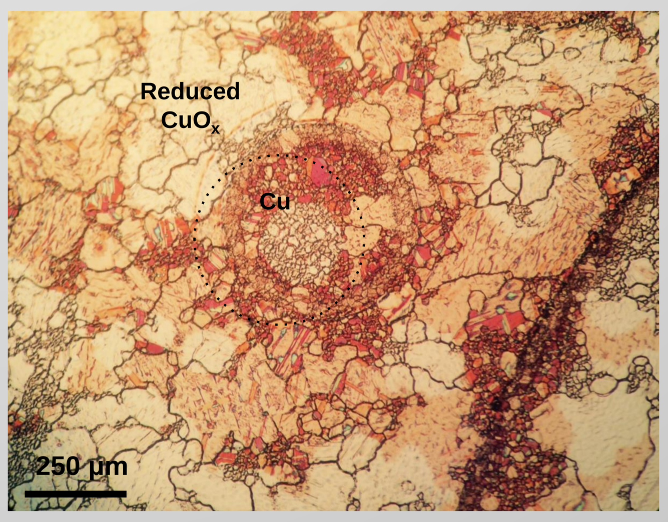
Part II: Graphene growth

Continuous graphene film growth: optical images & Raman spectroscopy



- Graphene seems to be able to grow on the whole catalytic surface.
- Raman spectra performed on the surface exibit similar features (very low I_D/I_G & $I_D/I_G \approx 2$) regardless of the copper nature (Cu or reduced CuO_x).

Partial graphene growth: Graphene domain observation



A slight oxidation of uncovered Cu surface makes graphene domains visible

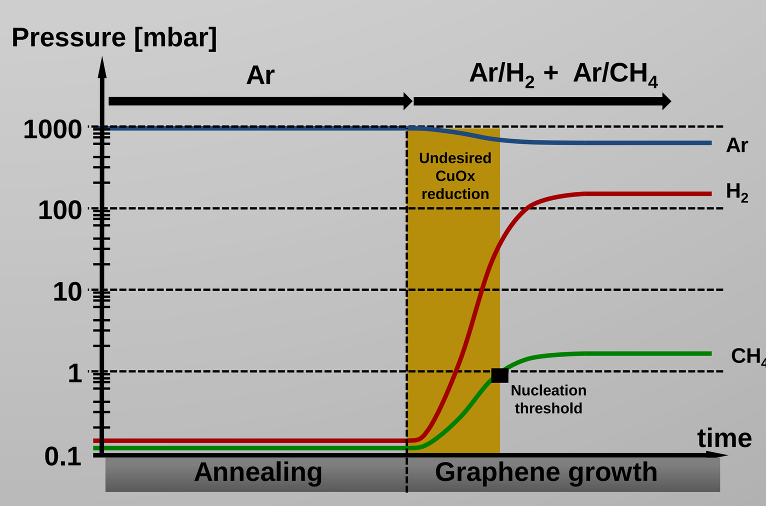
Observation:

- Graphene domain located in Cu areas as well as in reduced CuO_x areas.
- Graphene growth rate and nucleation density look similar on Cu and CuO_x.
- Graphene can grow accross the interface Cu/CuO_x
- Negligible Cu surface morphology steps is present after reduction of CuO_x

Hypothesis:

- The thick CuO_x passivation layer gets reduced before graphene nucleation

Challenge: enhancing growth selectivity on CuO_x/Cu



Facts:

- CH_4 partial pressure in the furnace must reach a certain threshold to initiate graphene nucleation.
- High temperature and H_2 partial pressure is required to obtain a low density of graphene nucleation sites.
- High temperature and H_2 partial pressure are detrimental to the lifetime of CuO_x layer.

Consequences:

- Undesired CuO_x reduction occurs in the transition regime between substrate annealing and graphene growth.

Difficulties:

- CVD parameters (such as high temperature & high H_2-to CH_4 ratio) favoring the growth of large graphene domains are detrimental to the lifetime of the CuO_x layer.

Conclusions

- Key achievement has been made on developping the process to fabricate this patterned Cu oxide layer.
- Cu oxide layer is totally reversible as no morphology steps is induced by the oxidation/reduction of copper
- The challenge lies in conserving the CuO_x layer during the early stage of graphene nucleation

Future works

- Further investigating the CVD parameters to obtain a high graphene growth selectivity between Cu and CuOx surface.
- Investigate the impact of Cu/CuO_x pattern design on graphene nucleation sites density and location

REFERENCES:
[1] **Large-Area Graphene Single Crystals Grown by Low Pressure Chemical Vapor Deposition of Methane on Copper**, Xuesong Li et al., *J. Am. Chem. Soc.*, 2011
[2] **Electronic Transport in Polycrystalline Graphene**, Oleg V. Yazyev & Steven G. Louie, *Nature Materials, 2010.*
[3] **Growth of Single Crystal Graphene Arrays by Locally Controlling Nucleation on Polycrystalline Cu Using Chemical Vapor Deposition**, Wei Wu et al., *Advanced Materials*, 2011
[4] **Control and Characterization of Individual Grains and Grain Boundaries in Graphene Grown by Chemical Vapor Deposition**, Qingkai Yu et al., *Nature materials*, 2011

2015 Material Research Society Fall Meeting & Exhibit – November 29- December 4, 2015 – Boston Massachusetts