# Epitaxy of GaAs on transferred CVD graphene

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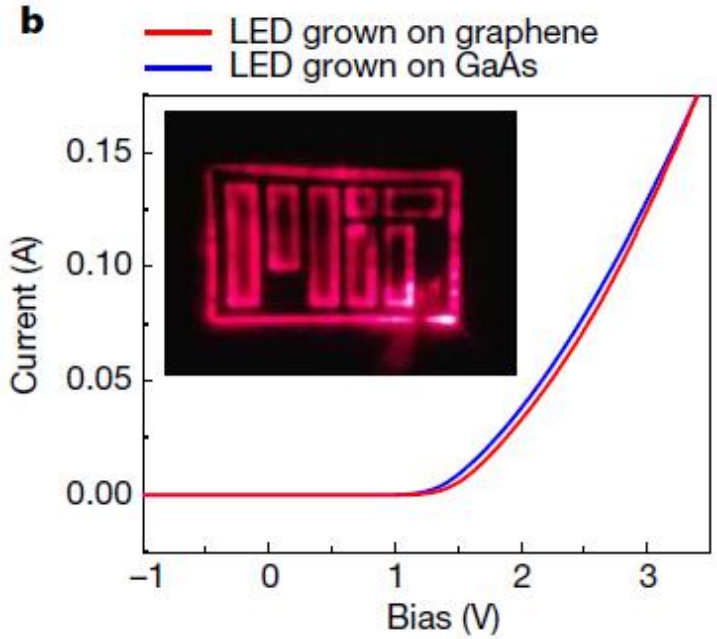
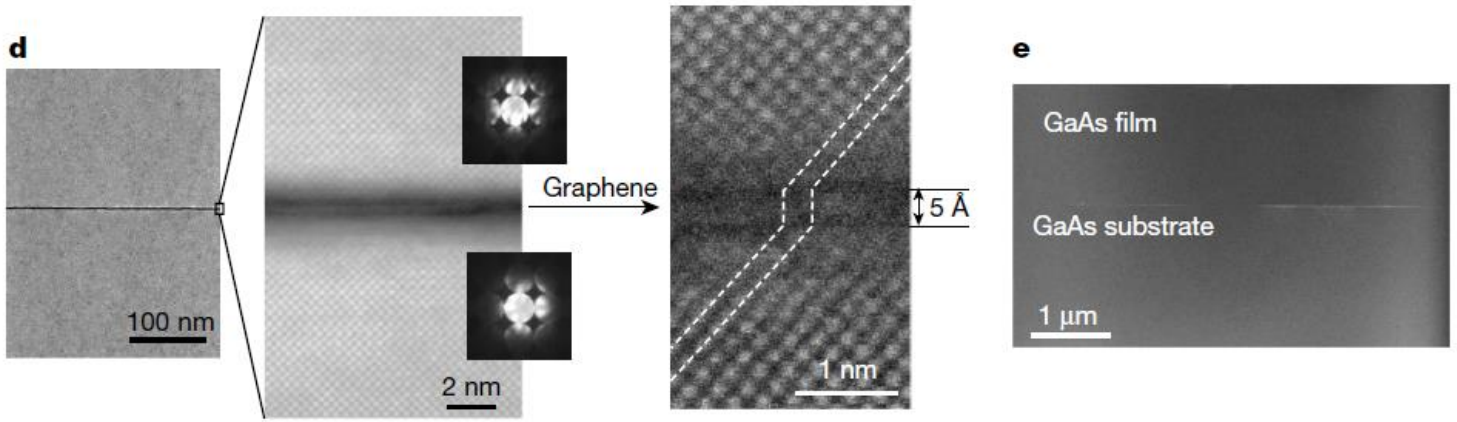
Stanford University

# Motivation: Remote epitaxy through graphene

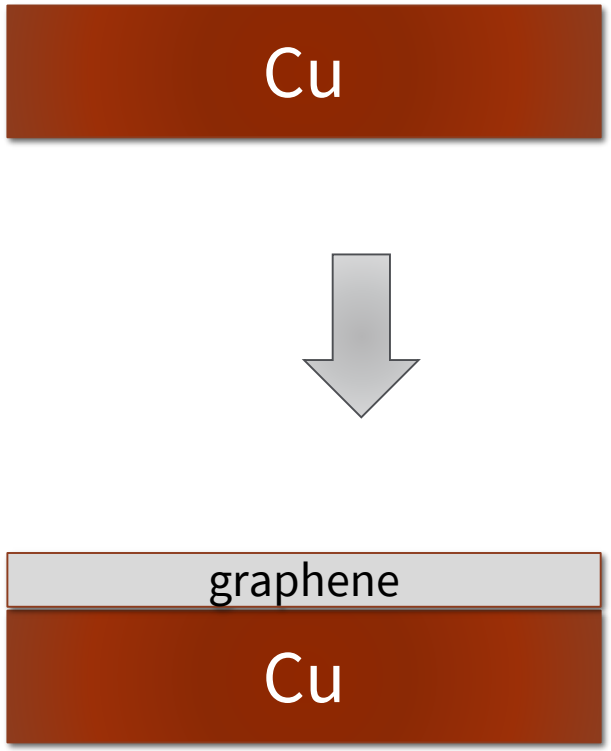
- On surfaces with no dangling bonds, weak van der Waals interactions make it possible to epitaxially grow materials with a large lattice constant mismatch
- Recently, Kim *et al* have shown that epilayer can align to substrate *underneath* graphene, allowing single-crystal growth registered to the substrate
- Epilayer can still be easily released
- Reuse of substrates is possible: potential to reduce cost of high-quality thin films of many materials



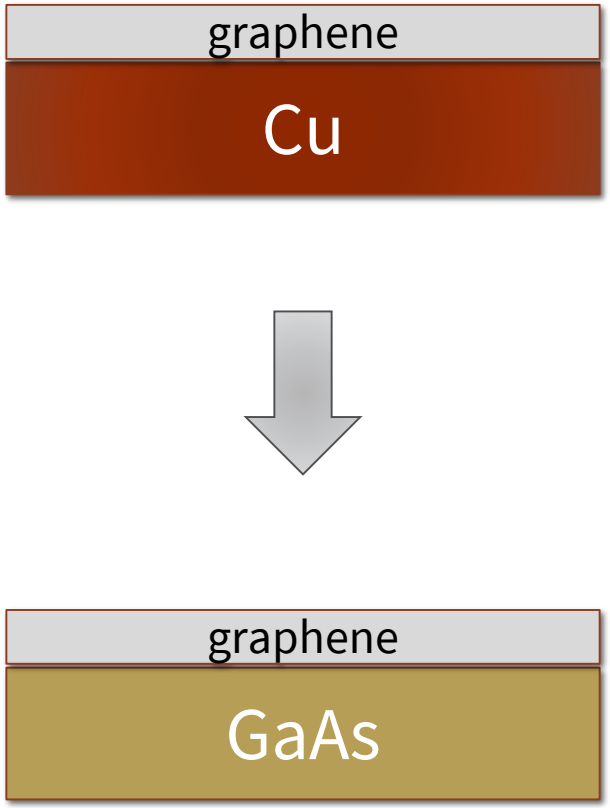




Y. Kim *et al*, *Nature* **544**, 340 (2017)

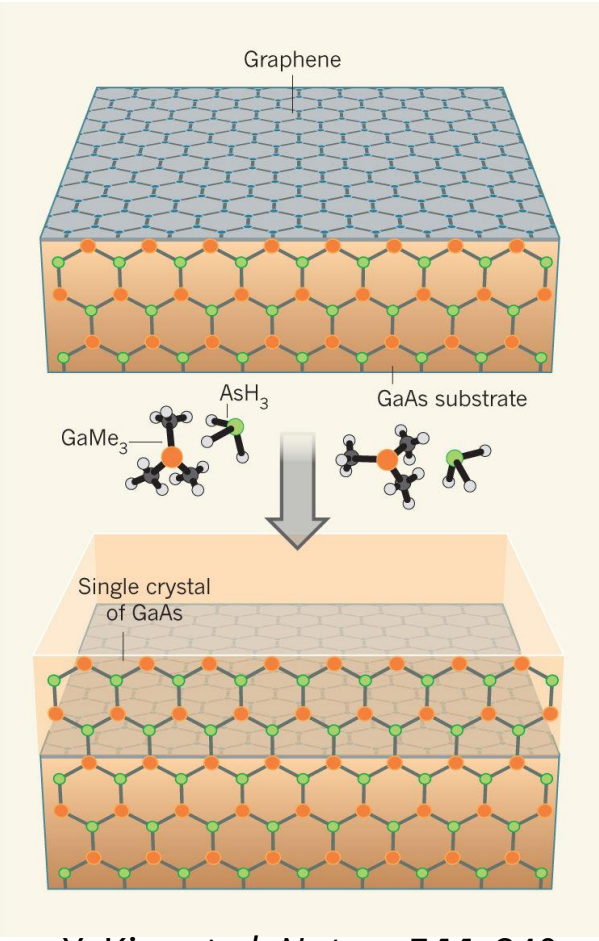
## CVD graphene




## Transfer Process




## MOCVD GaAs



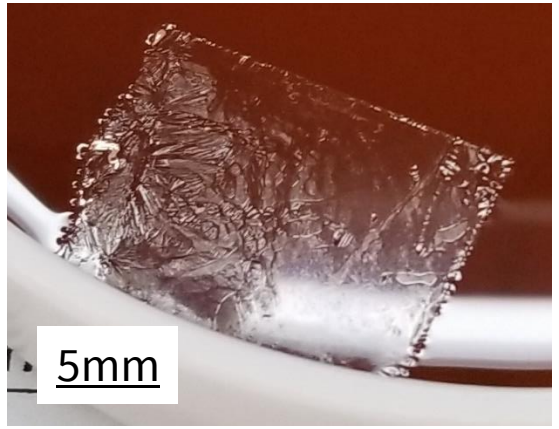

Y. Kim *et al*, *Nature* **544**, 340 (2017)

# CVD graphene

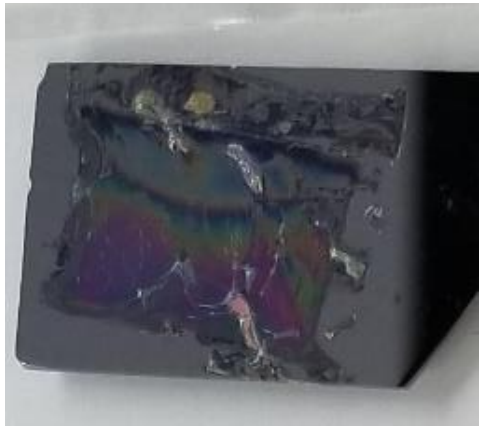

- Cut Cu foil big but no more than 4 x 4 inches.
  - Small foils would fly.
- Acetic acid treatment of copper foil before growth
  - 1 hour
  - To improve copper surface roughness.
- Aixtron Black Magic (standard recipe)
  - Flow $H_2$, Ar, $CH_4$
  - P=10 mbar
  - Temperature = 1050C.

# Graphene transfer: initial attempts

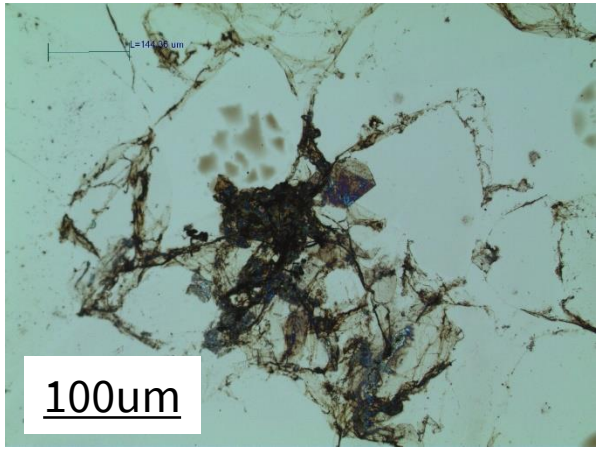
- Cut foil
- **Spin PMMA** (no scaffold), bake on hotplate
- Remove backside graphene with **O2 plasma etch**
- **Copper etch**: 8 hours
- Transfer to DI **water bath** (x2)
- Clean with **SC2**
- DI **water bath** (x2)
- Clean with **SC1**
- DI water bath (x2)
- Transfer to **GaAs** after oxide is stripped with 37% HCl
- **Bake** on hotplate
- Remove PMMA with **acetone**



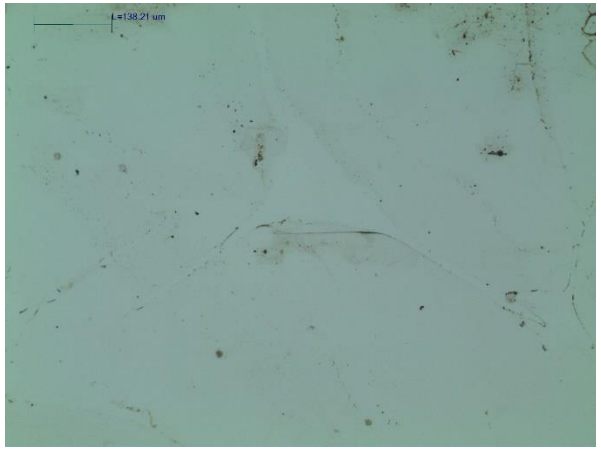

PMMA/graphene on $FeCl_3$



PMMA/graphene on GaAs




Worst place on sample



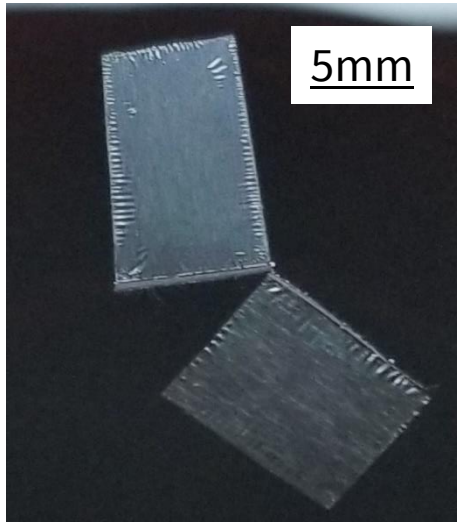
Best place on sample: ~300*500 $um^2$

OM image: graphene on GaAs

# Graphene transfer: optimized for coverage

- Cut foil
  - Use sharp scissors
- Tape foil to PET, spin PMMA, bake using oven
  - Use green scotch tape
  - Hotplate heating is nonuniform and can cause tears
- **Copper etch**: 1 hour
  - This time is sufficient
- Transfer to DI **water bath** (x2)
  - Last bath is overnight
- Clean with **SC2**
- DI **water bath** (x2)
- Transfer to **GaAs** after oxide is stripped with 3% HCl
  - If the acid is too strong substrate will be damaged
- **Bake** on hotplate
- Remove PMMA with **acetone**

*it is not necessary to remove backside graphene
*SC1 is particularly violent – remove from process

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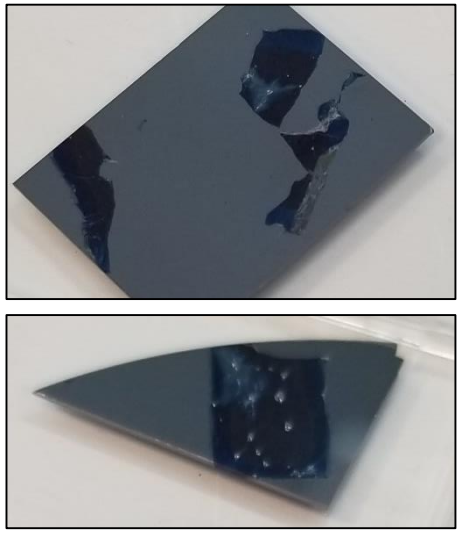
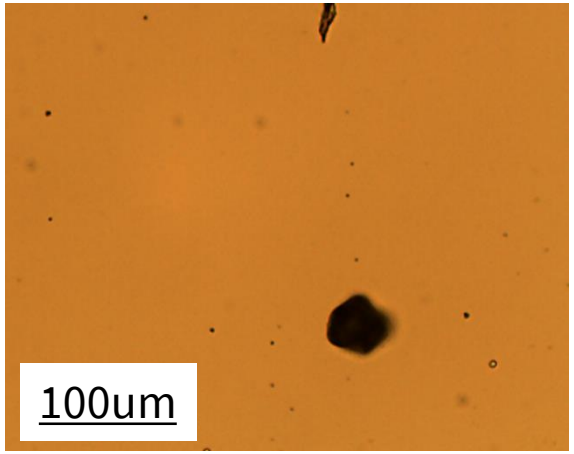
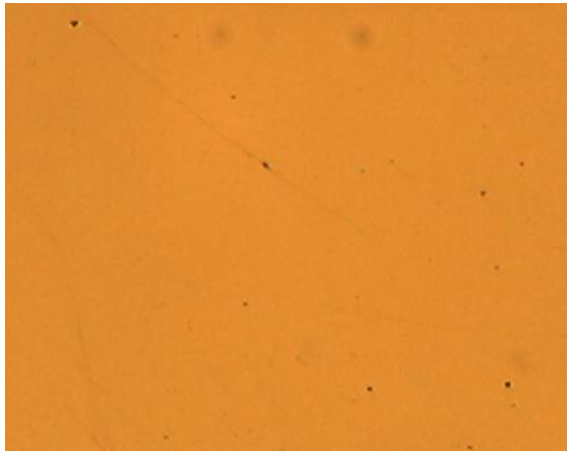


PMMA/graphene on GaAs




Worst place on sample



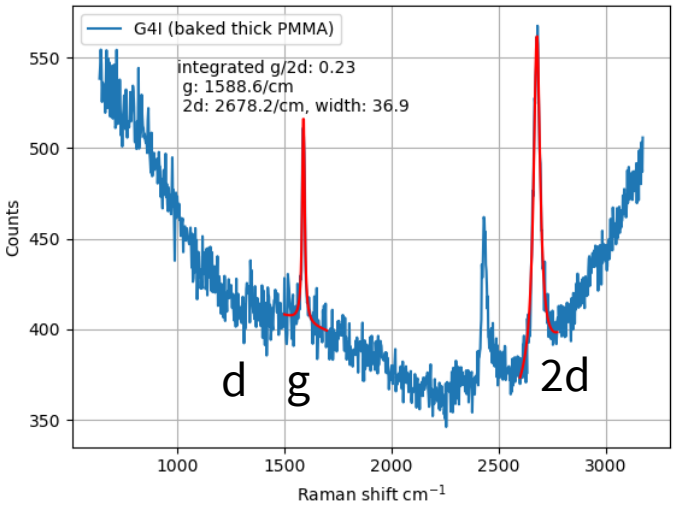
Best place on sample

OM image: graphene on GaAs

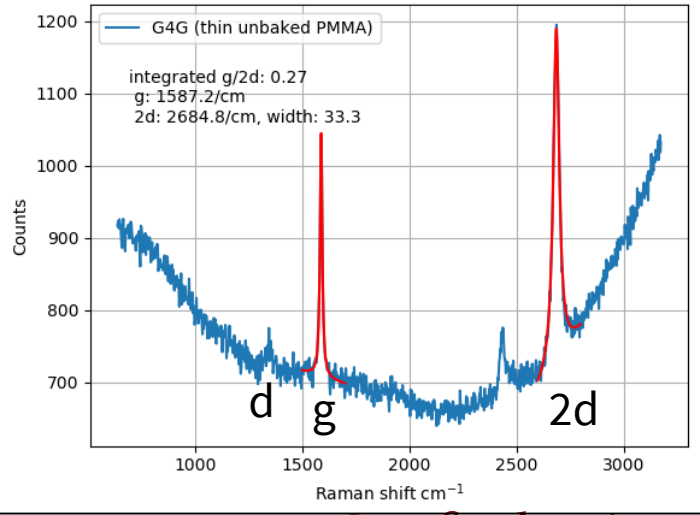
# Transfer process characterization

- We investigated **PMMA thickness** (200nm vs 50nm) and **PMMA baking vs. drying**
- **Defectivity:** All samples have acceptable defectivity
  - Unbaked PMMA must be dried overnight
- **Tears and coverage** difficult to evaluate on GaAs because there is no oxide spacer for visibility
  - Thin PMMA may give better results but we have not confirmed this
  - We did not investigate further because it is not the limiting factor for MOCVD growth

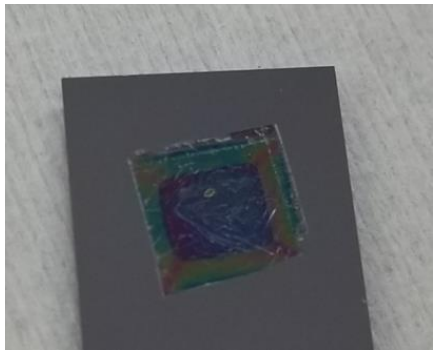
**Thick, baked PMMA**




**Thin, unbaked PMMA**

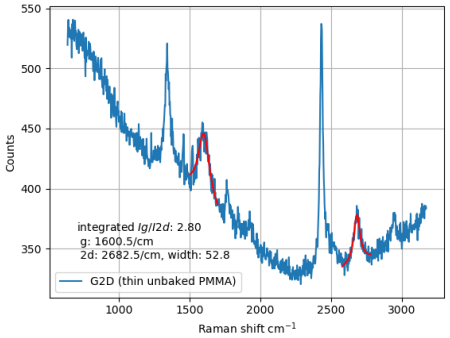



**Thick, baked PMMA**



**Thin, baked PMMA**

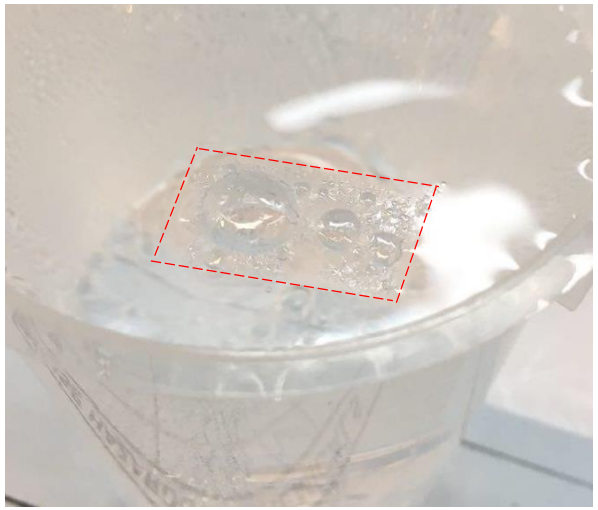
**Thin, unbaked PMMA**
**Insufficient drying time**



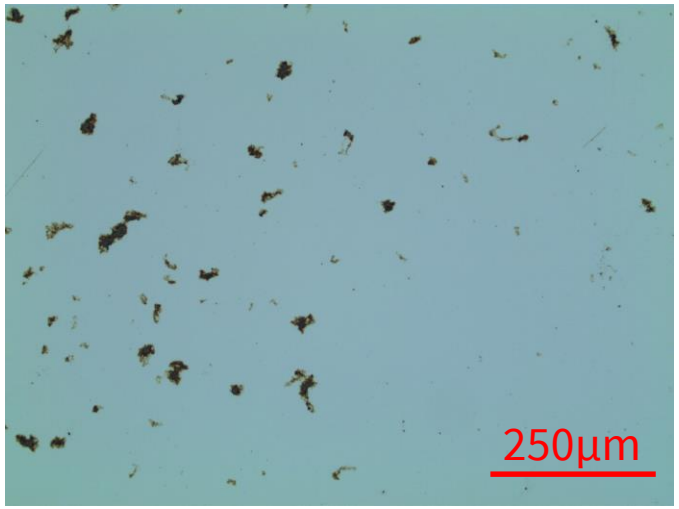
# Graphene transfer: problems

- We ordered a new batch of copper etchant
- Etchant from the new batch caused residue not removed by SC2 cleaning
  - Fortunately there was more expired copper etchant in the storage room
- SC2 can bubble violently

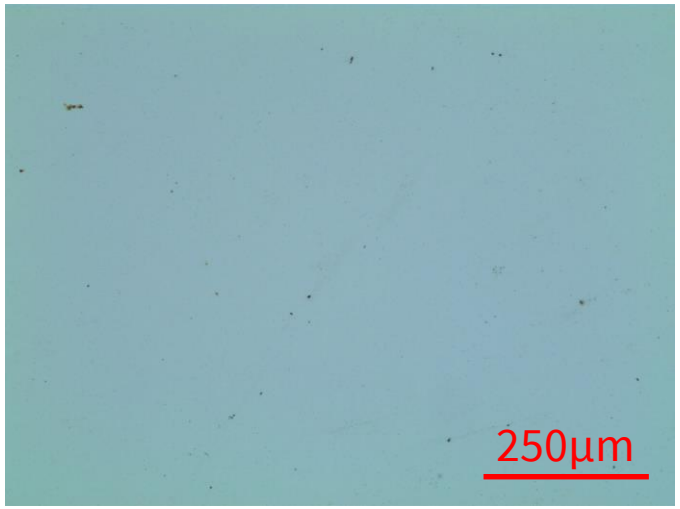
**Graphene/PMMA on SC2**



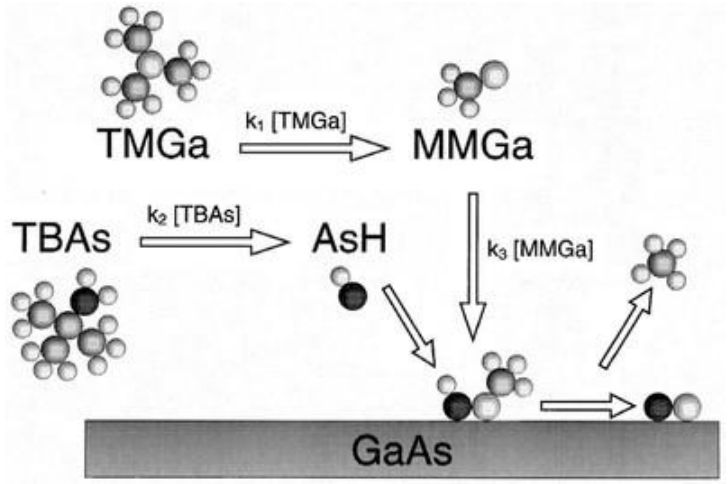
**New copper etchant**




**Old copper etchant (identical transfer)**



# MOCVD GaAs




Aixtron 200 III-V MOCVD system

Parameters:

- Growth time
- Growth temperature
- Flow rate
- V-III ratio

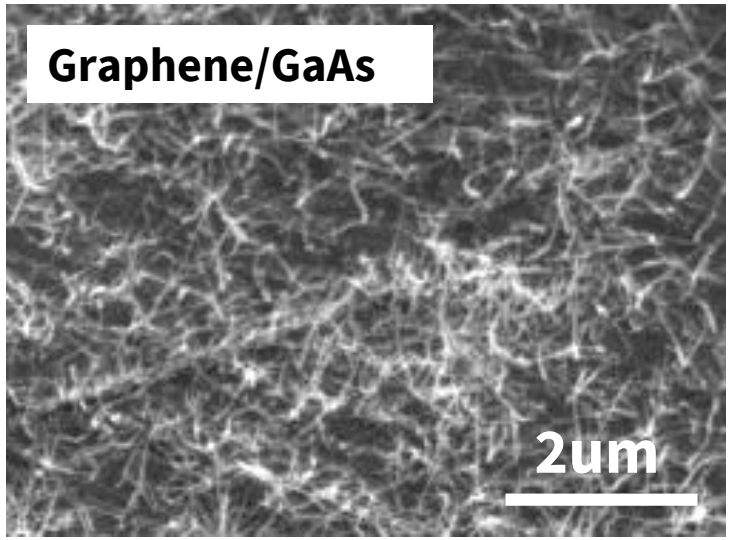
Growth rate:

- ~30nm/min @650C
- ~2nm/min @450C

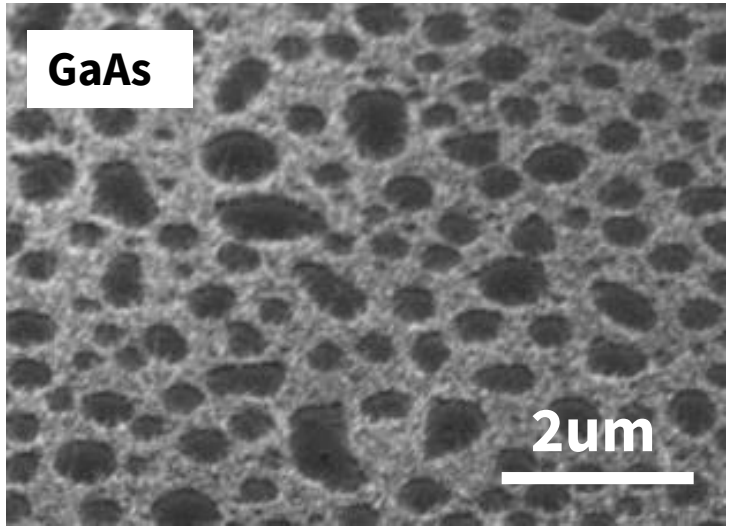
Goal:

- Nucleate for 100nm with good density
- Growth for 1.5um for planarization

# Nanowires in Nucleation Step




G4AB

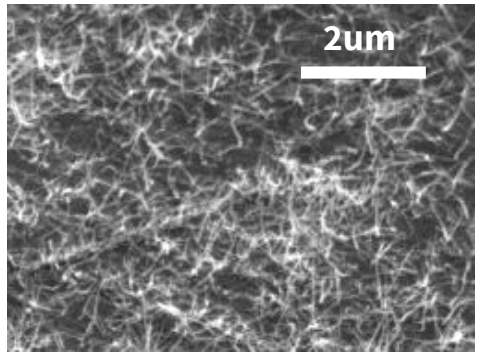



G4AB

- **Crystallinity**
  - Nano wires prefer (111)
  - Our wafer is (100), which might explains the randomness of nano wires.
- **1. Flow rate**
  - Low V/III ratio encourages nano wires.
  - Change to high V/III ratio.
- **2. Temperature**
  - Nano wires decompose in high T.
  - Increase T and suppress nano wires.
- **3. Metal particle**
  - Metal encourages nano wires.
  - Make it more clean.

# Get rid of nanowires

G4AB

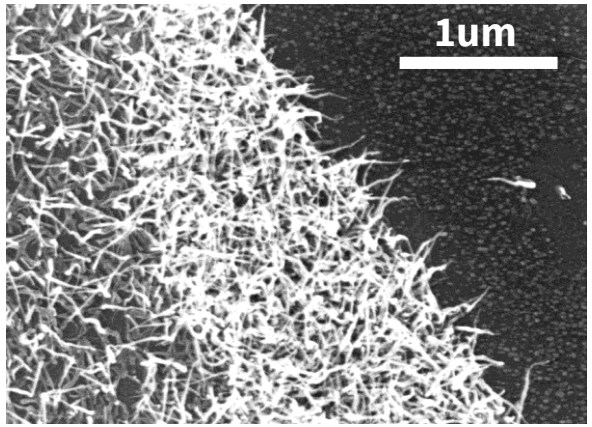



Temp = 450C
As/Ga = 10/1

## 1. High Flow Ratio

Temp = 450C
As/Ga = 15/1

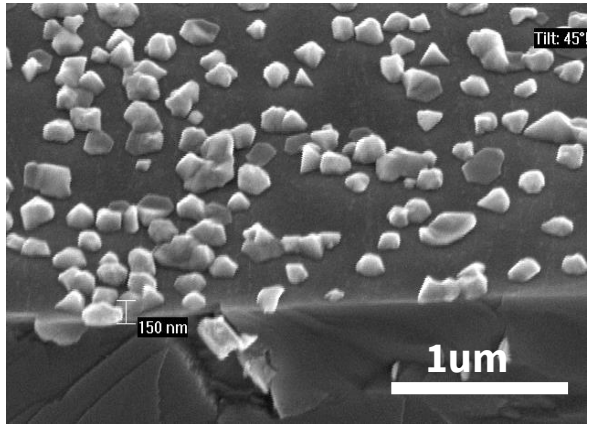
G6H




- Nano wire density is similar, or even worse.
- The paper we follow used MBE As and Ga flux. Their result might not be applied directly.

## 2. High Temperature

Temp = 500C
As/Ga = 10/1



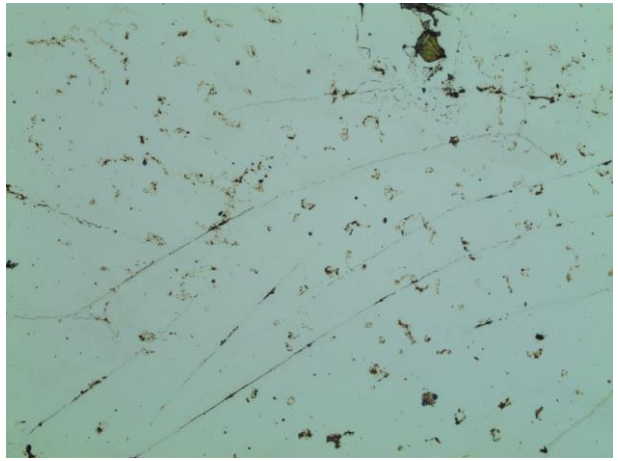

G4K

- Nano wires did go away.
- Nucleation density did not increase with longer time.
- Nucleation has irregular shapes.

## 3. Reducing contamination

# Cleaner I: Longer Cu Etching Time

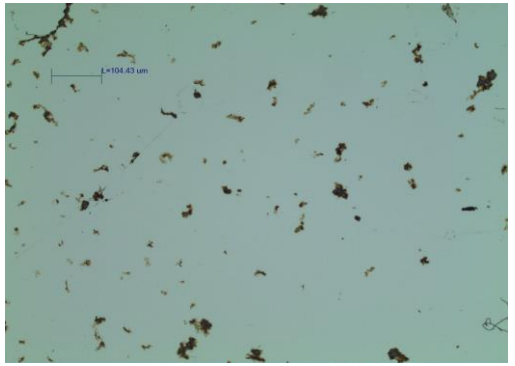
**1hr Cu Etching**

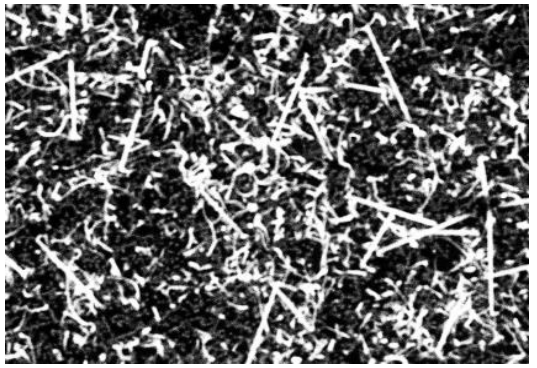


G4A

OM image:
Graphene on GaAs

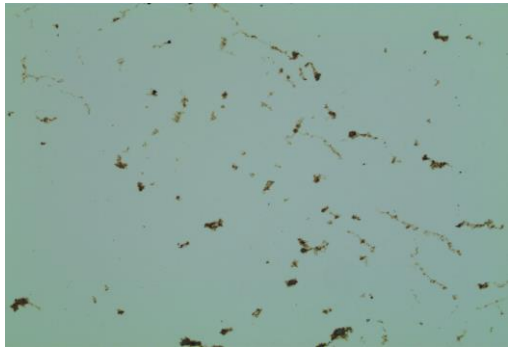
**2hr**

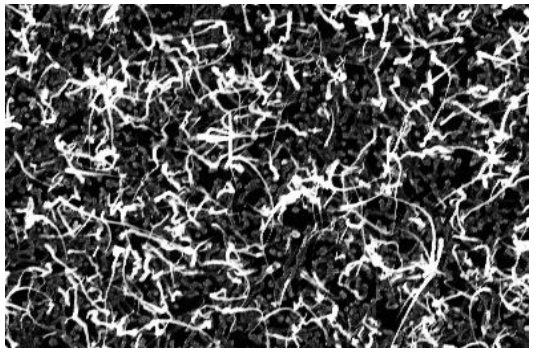




G6B

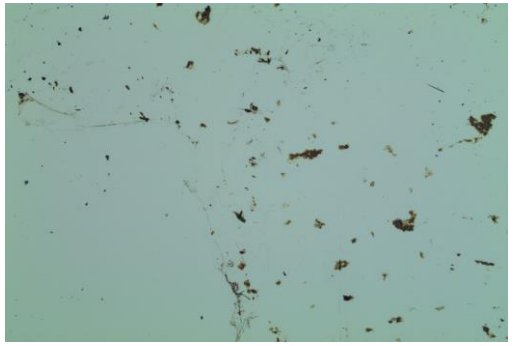
**4hr**

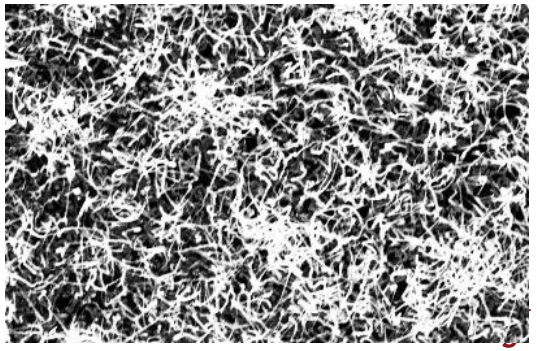




G6C

**12hr**



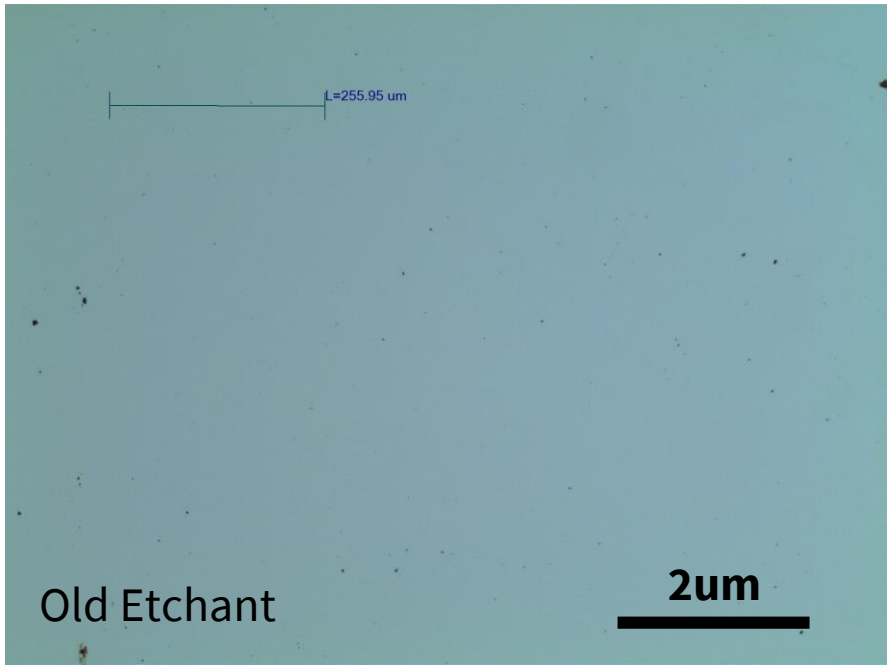


G6E

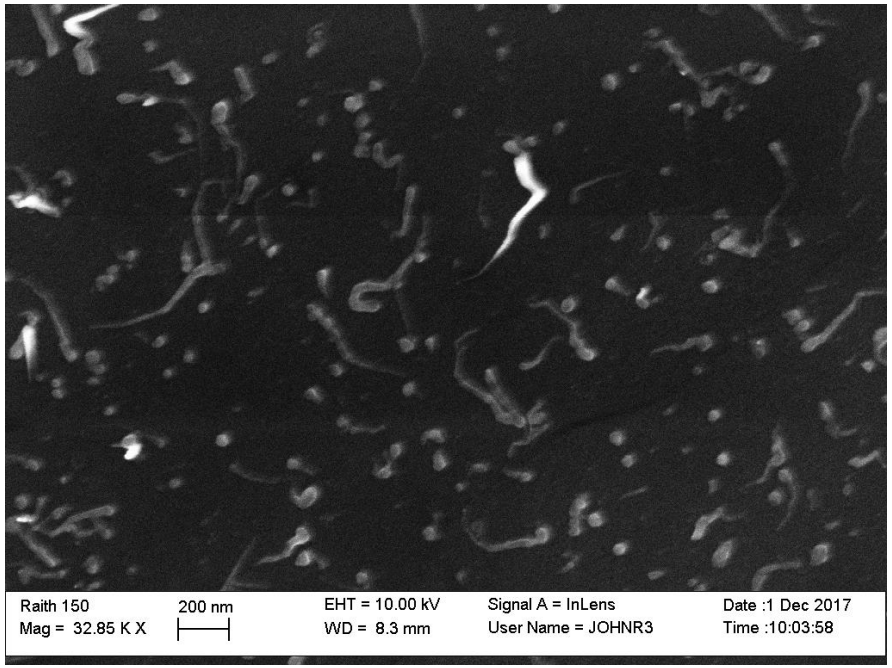
- Marginal Improvement ☹

# Cleaner II: Old (Expired) Etchant is the Best Etchant

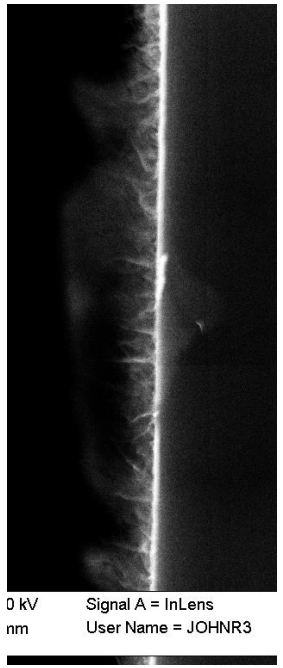
G6G




G6G

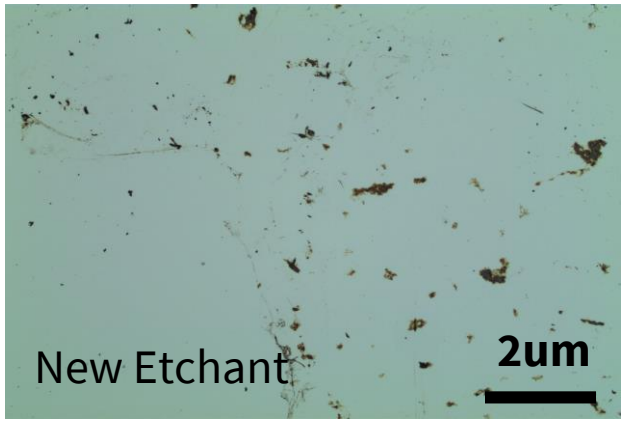



G6G




Compare to:

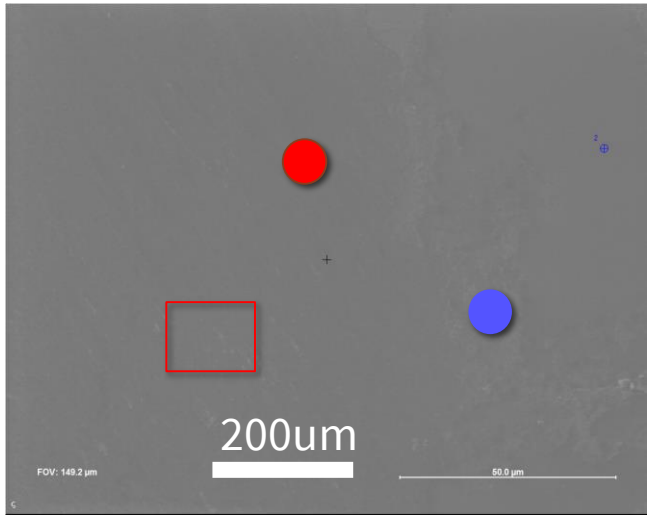
G6E



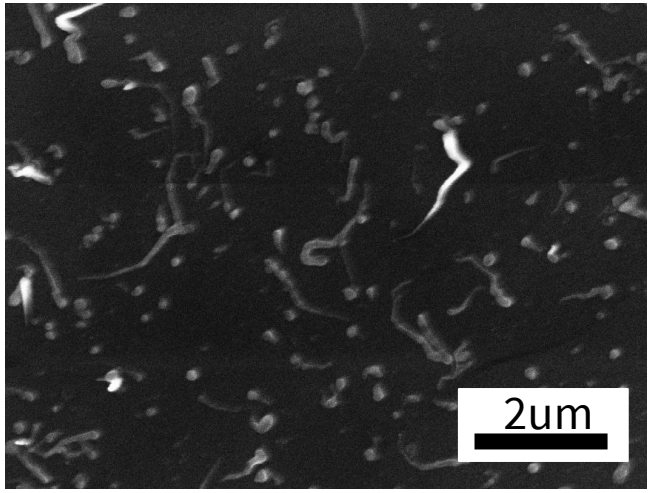

- New etchant creates metallic like residuals.
- 100% reproducibility.
- Quality is better with old, expired etchant
- Even with old etchant, we still had nano wire.

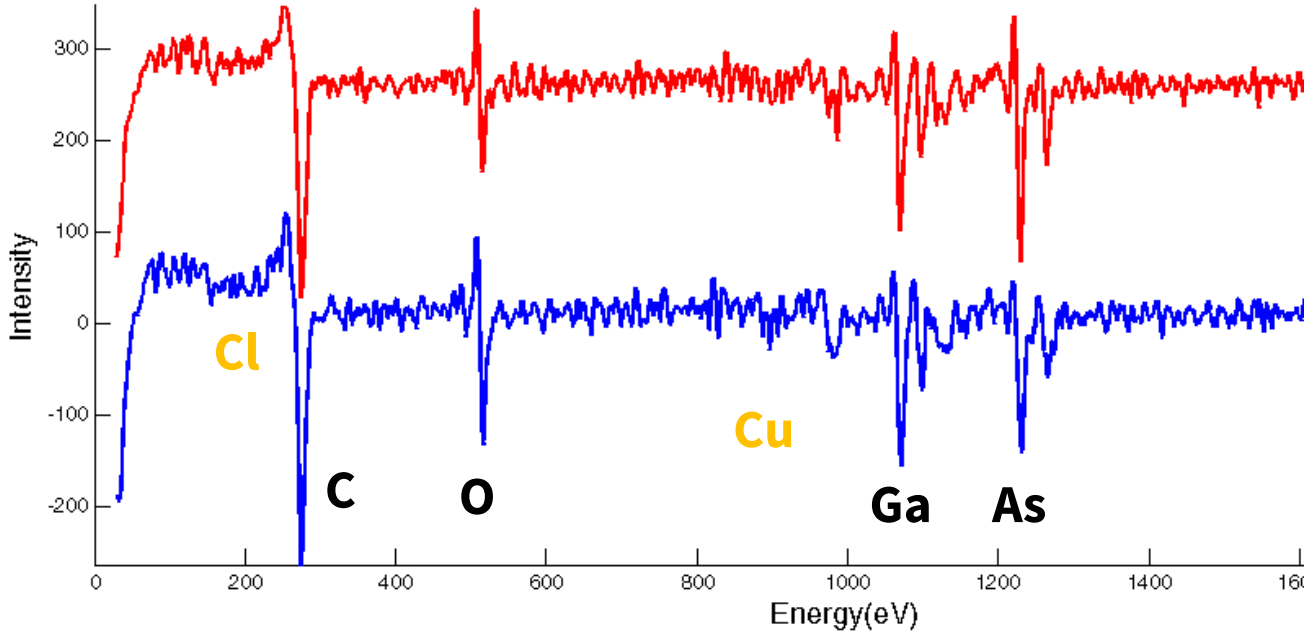
# Auger Spectrum of Contamination

G6G




G6G



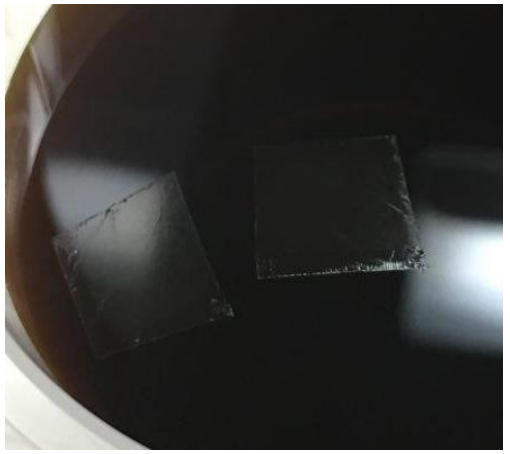




- A hint of Cu and Cl.
- Probably came from the copper etching step.
- Add more DI water bath !!

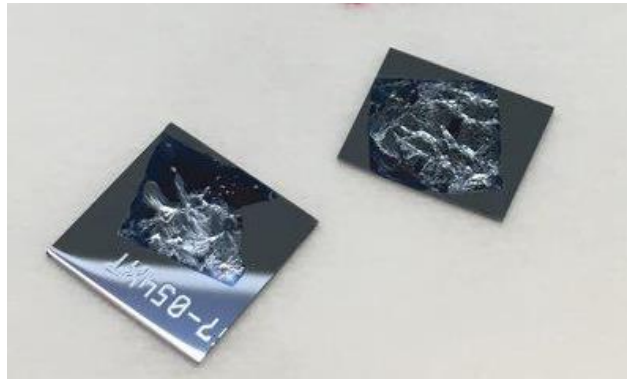
- Thanks Ricardo for Auger!

# Graphene transfer: optimized for cleanliness

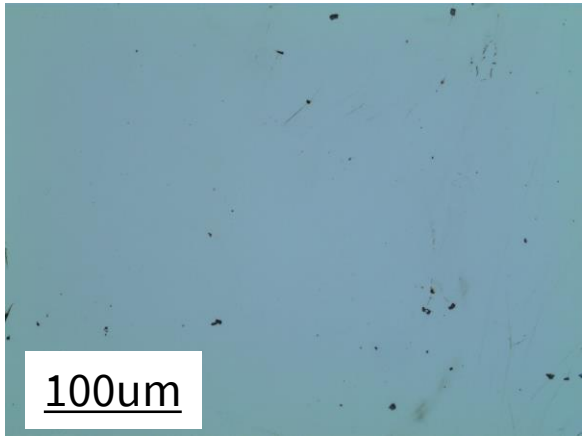
- Cut foil
- Tape foil to PET, spin PMMA, bake using oven
- **Copper etch**: 1 hour using **expired etchant**
- Transfer to DI **water bath** (x4-5)
  - Only 2 hours for last bath, not overnight (time constraints)
- Clean with **SC2** (15-30 minutes)
  - Longer times appear to be better
- DI **water bath** (x4-5)
- Transfer to **GaAs** after oxide is stripped with 3% HCl
- **Bake** on hotplate
- Remove PMMA with **acetone**



PMMA/graphene on $FeCl_3$



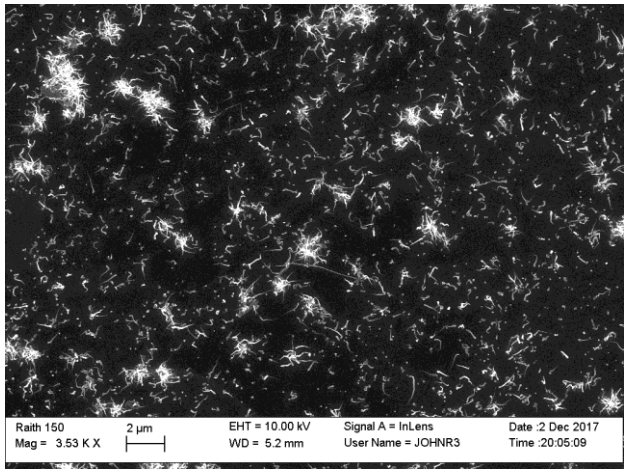
PMMA/graphene on GaAs
(SC2 was very violent)



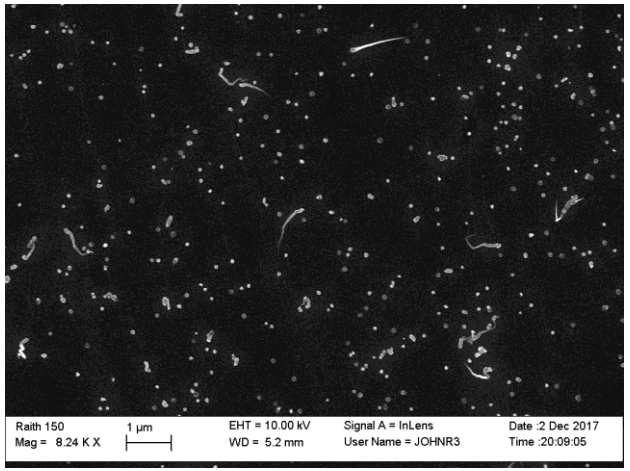

Worst place on sample
OM image: graphene on GaAs

Best place on sample

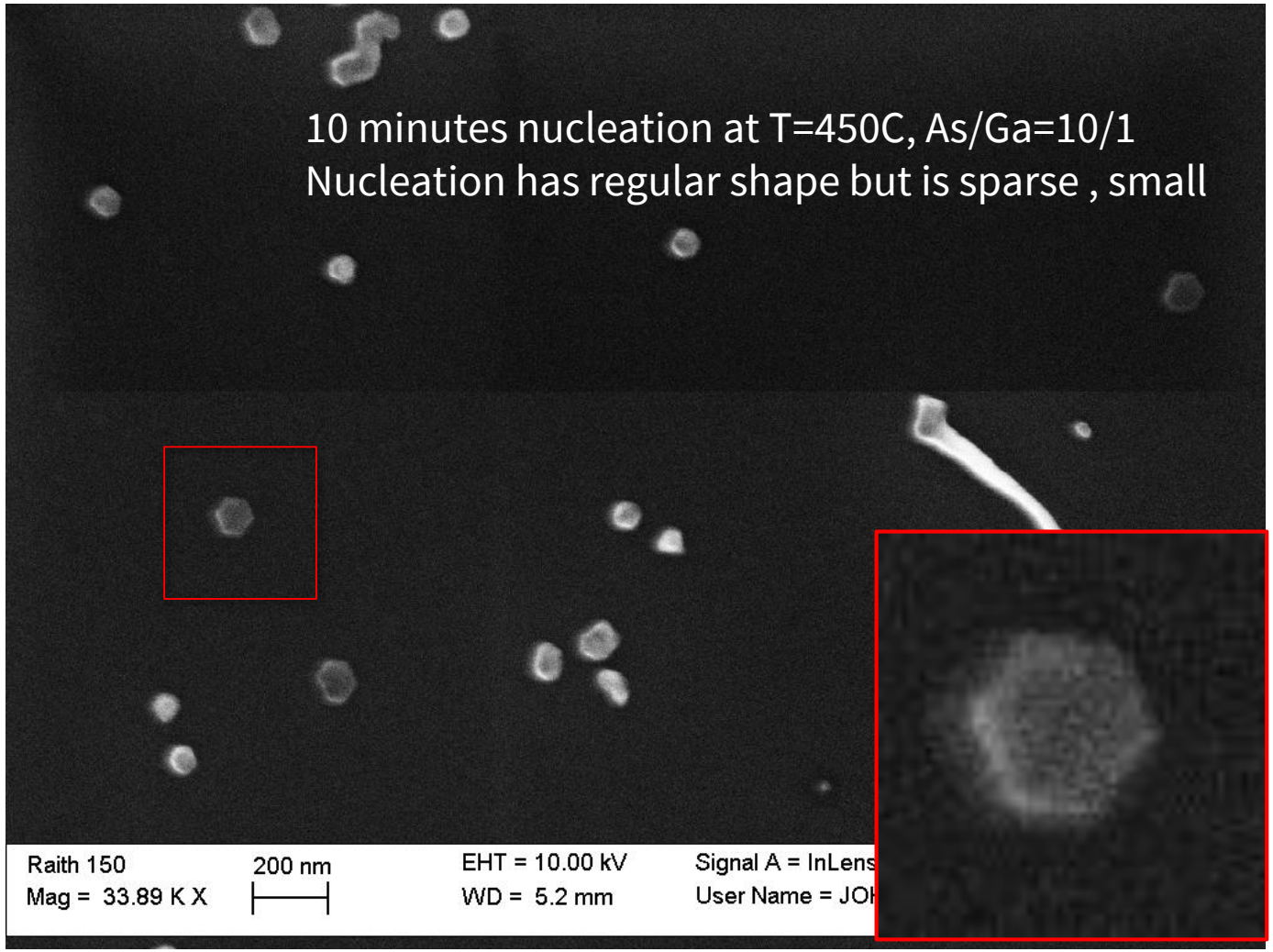
# Cleaner III: Double the DI water cleaning steps




Bad Part of G6R

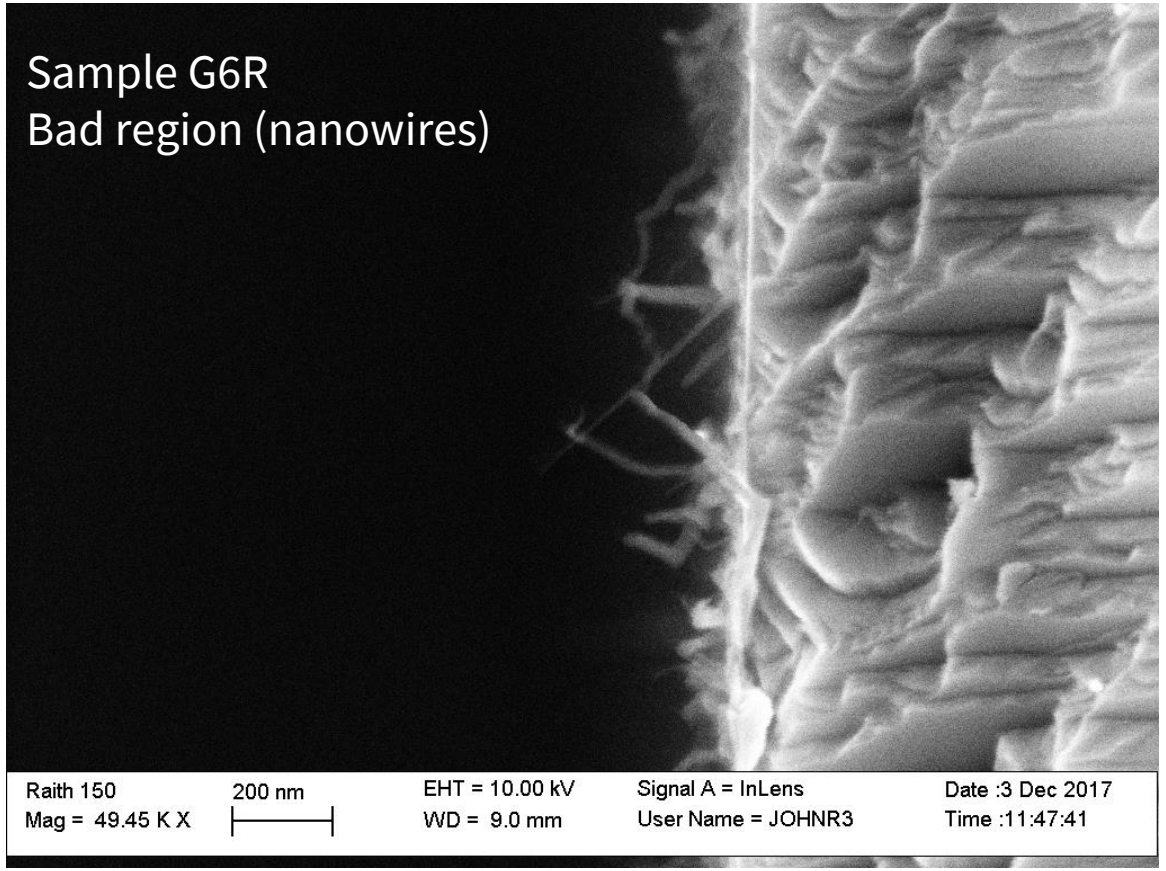


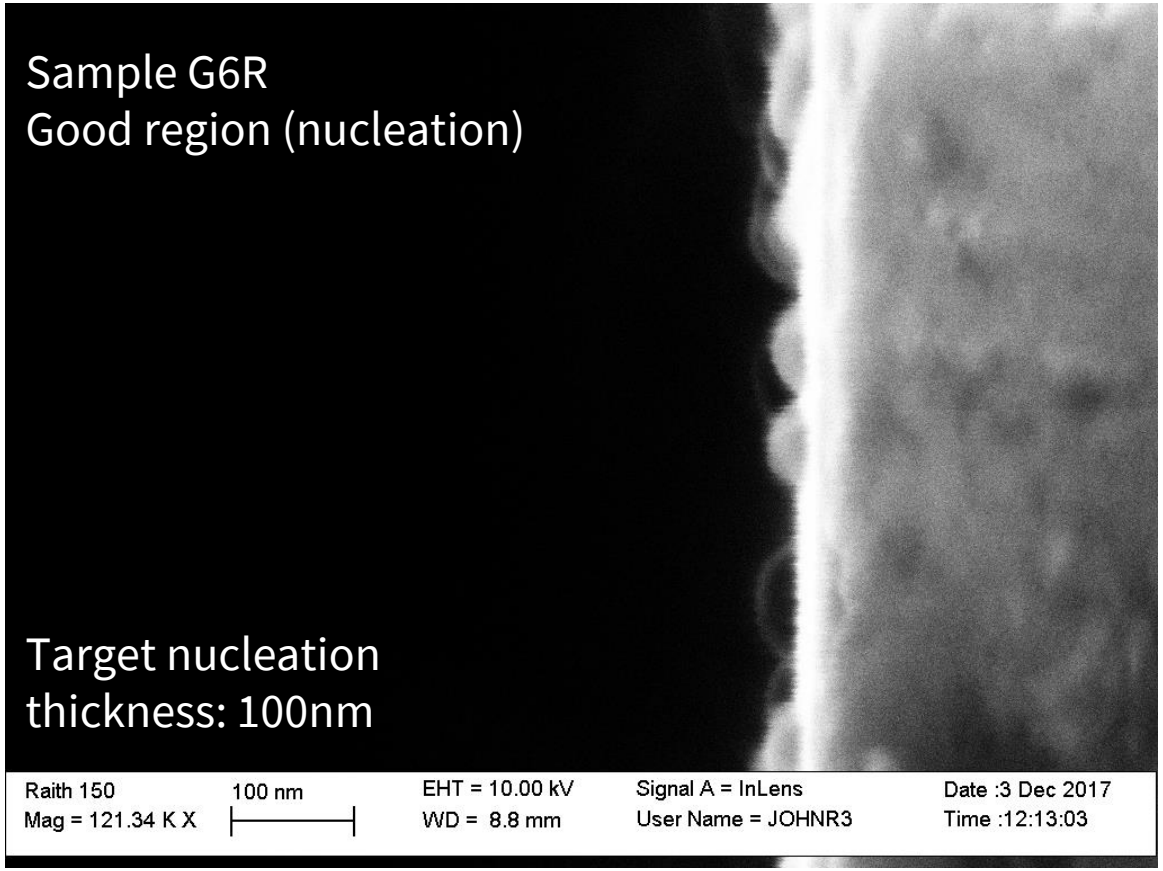

Good Part of G6R




Zoomed-in of Good Part of G6R

# Cleaner III: Double the DI water cleaning steps



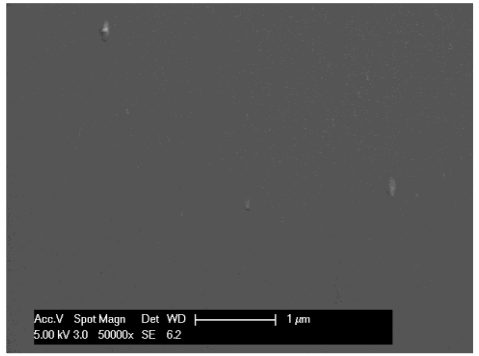



# Longer nucleation time

50-60 minutes nucleation at 450C, 10:1 TBAs:TMGa

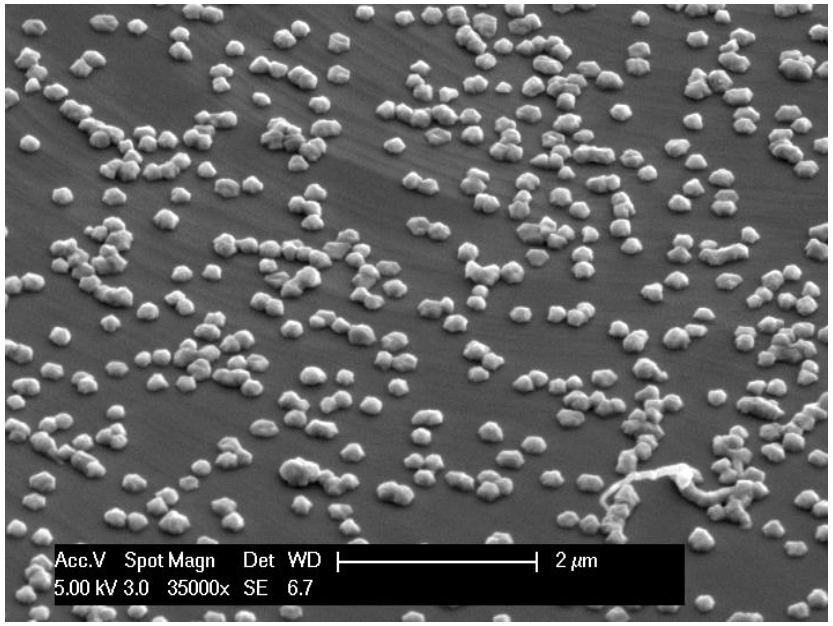
Add two more DI water baths to transfer (10 total)

**Large areas of the sample are still covered in nanowires**

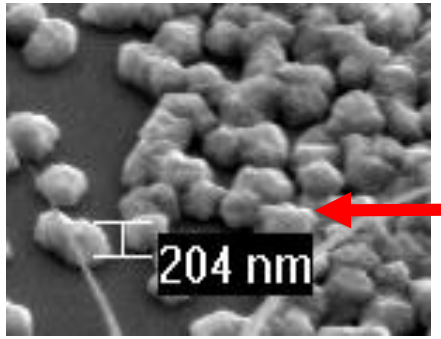



G6Y – bare GaAs region

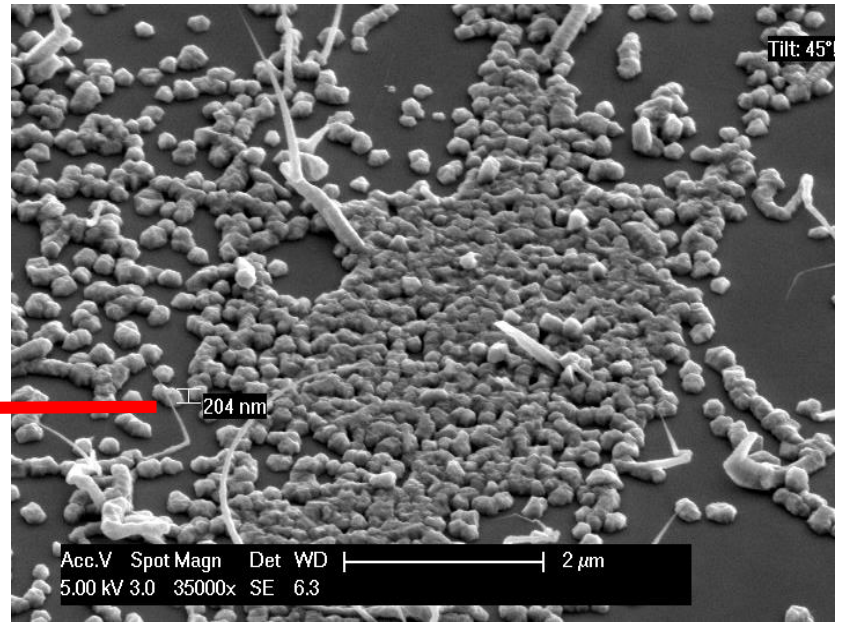
G6X




10 DI water bath + 15min SC2
Good area after nucleation




G6Y




10 DI water bath + 30min SC2
Good area after nucleation

# Attempt to grow full stack

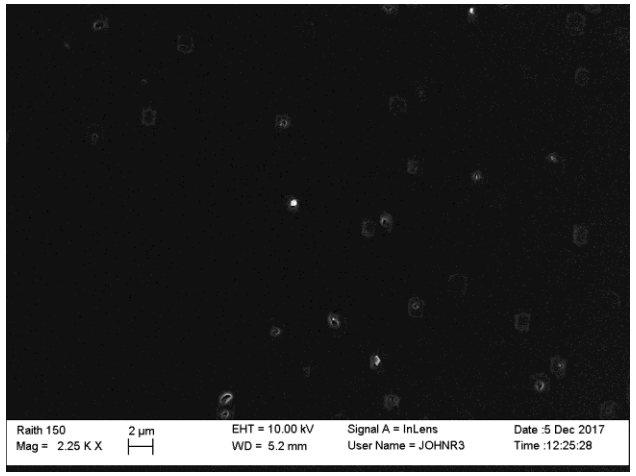
50-60 minutes nucleation at 450C

50 minutes growth at 650C (expect ~1.5μm)

10:1 TBAs:TMGa

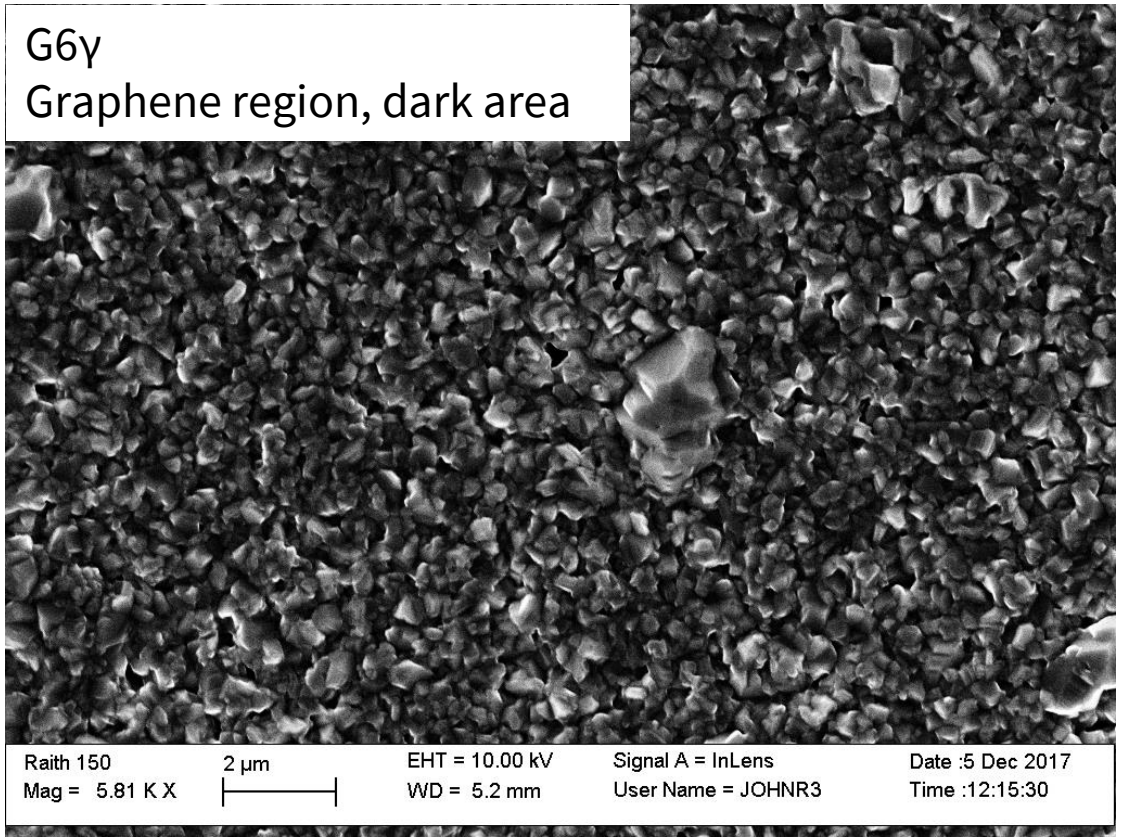
Layer does not coalesce

Graphene is covered in ‘bright’ and ‘dark’ areas

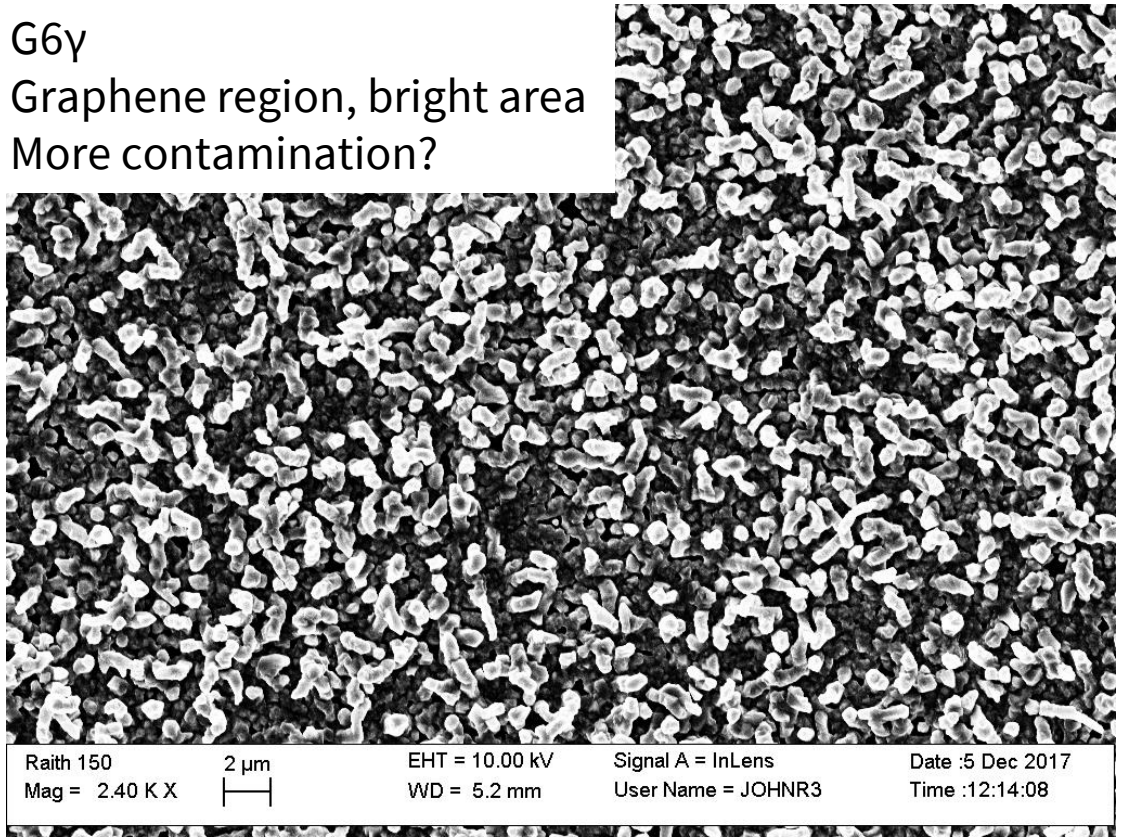



G6γ
Bare GaAs region

G6γ
Graphene region, dark area




G6γ
Graphene region, bright area
More contamination?



# Summary

- We optimized graphene transfer onto GaAs wafers for large area and for cleanliness
  - We investigated effects of PMMA thickness, baking, and SC2 cleaning
- We were able to obtain areas of good nucleation of the GaAs epilayer
- Our attempts to grow a full epilayer give rough, nonplanar films
- Contamination that causes nanowire growth is the main obstacle to nucleation and therefore film growth

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