TOWARDS ELECTROCHEMICAL DELAMINATION OF C PLANE SAPPHIRE CVD GROWN GRAPHENE

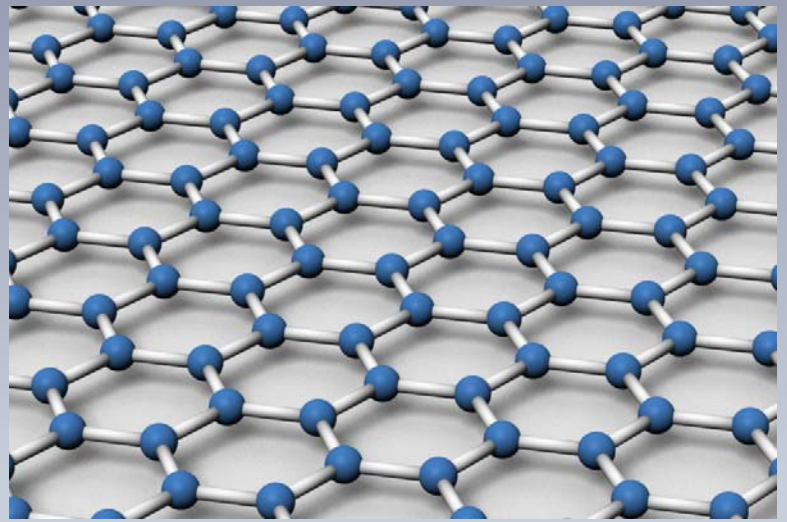
Brendan Coyne REU Summer 2016

Mentors: Lester Lampert PI: Dr. Jun Jiao
Otto Zietz
Thomas Lindner

Portland State
UNIVERSITY

GRAPHENE

- Isolated and characterized in 2004 by Andre Giem and Konstantin Novoselov later becoming subject of 2010 Nobel Prize of Physics
- 2D material consisting of a single layer of sp2 covalently bonded carbon atoms



Credit: James Hedberg http://jameshedberg.com

PROPERTIES OF GRAPHENE

- High strength and flexibility
- Electrically and thermally conductive
- Over 97% transparent
- Impermeable to most atoms

Credit: Illustration by Matt Collins

BRINGING GRAPHENE TO SCALE

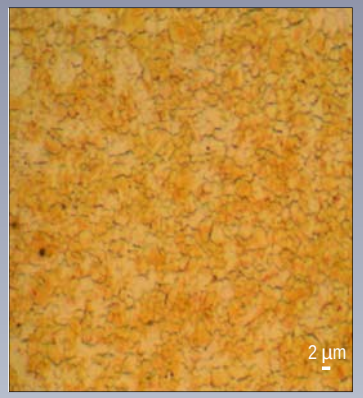
Outstanding Barriers Preventing Market Scale Graphene Applications

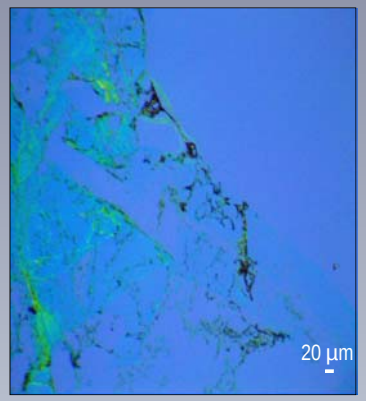
Graphene Production:

- Crystal size
- Single layer

Transfer Methods:

- Wrinkles
- Cracks
- Residues

a. 

b. 

c. 

a. Graphene on Cu coated SiO_2/Si wafer
b. Graphene wet etch transfer
c. Graphene wet etch transfer

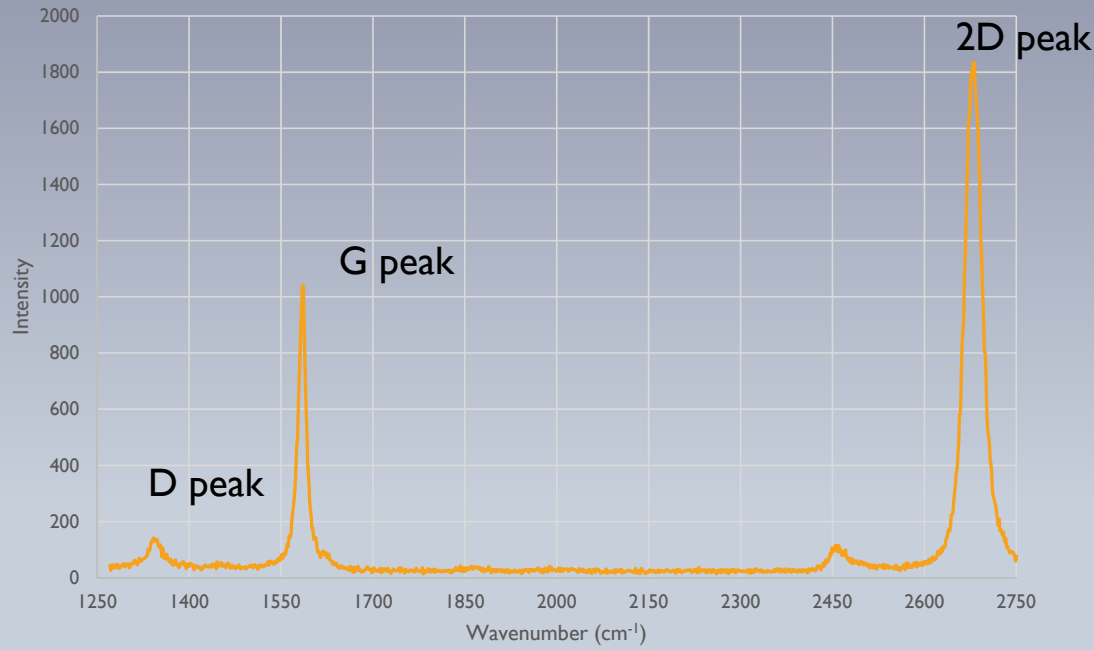
RAMAN SPECTROSCOPY AND GRAPHENE SPECTRUM

Raman Spectroscopy: a measurement of vibration due to inelastic scattering of monochromatic light, commonly used to characterize chemical makeup.

Graphene Spectrum:

- D peak (1350 cm^{-1})
- G peak (1580 cm^{-1})
- 2D peak (2690 cm^{-1})

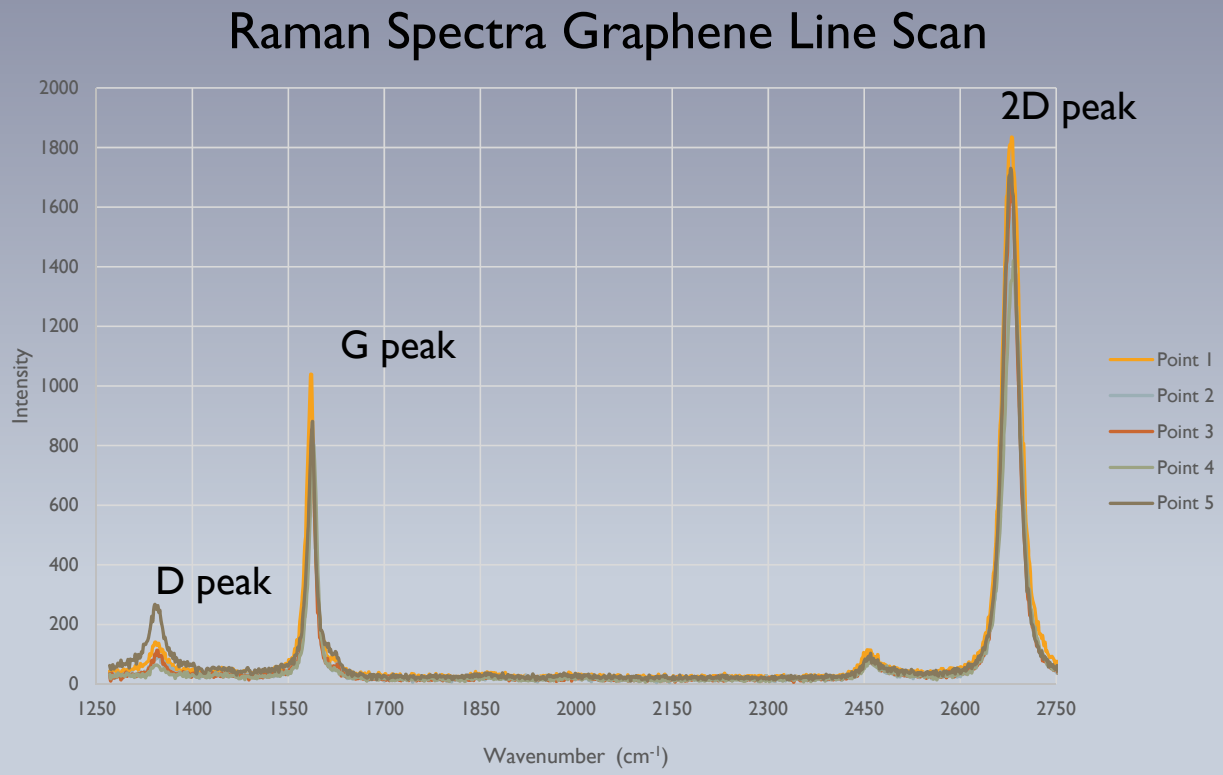
Graphene Raman Spectra



RAMAN AND EVALUATING GRAPHENE QUALITY

Indicators of graphene quality

- Spectra uniformity over multiple points
- Low D:G ratio ($I_{D/G}$) indicates level of disorder
- 2D:G ratio ≥ 1.25 indicates monolayer
- $FWHM_{2D}$ < 30 cm^{-1} indicates uniformity of sample point



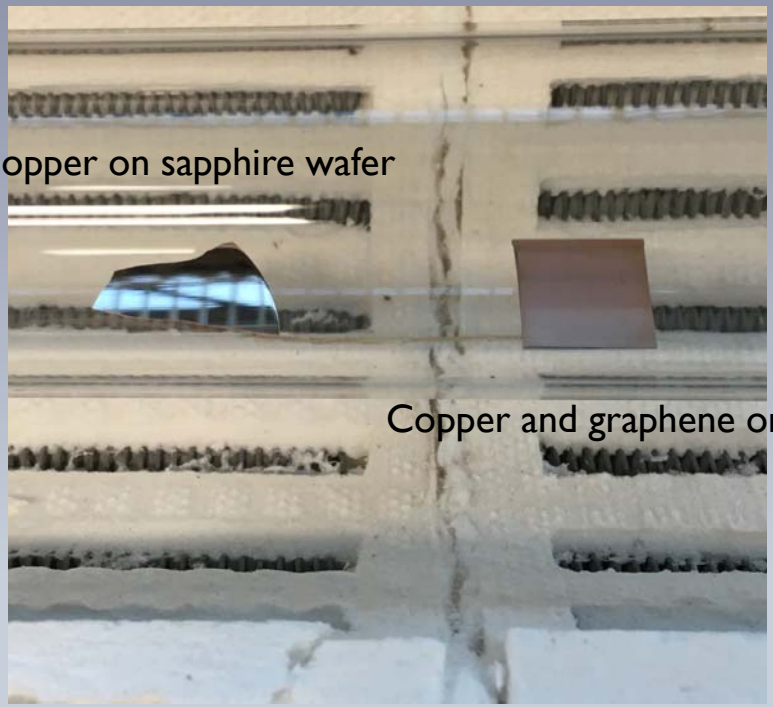
IMPROVING QUALITY AND TRANSFER METHODS

C plane sapphire wafers:

- Increased copper crystal size
- Better copper wafer adhesion

Less volatile transfer:

- Minimize impact of transfer



Copper on sapphire wafer

Copper and graphene on SiO_2/Si wafer

Samples in oxygen rich furnace

THEORY OF TRANSFER

- Induce sufficient oxidation of copper substrate under graphene.

$$4\ Cu\ (s) + O_2\ (g) = 2\ Cu_2O\ (s)$$

- Apply appropriate electric potential to electrolytic cell to reduce oxidized copper between graphene and the wafer.

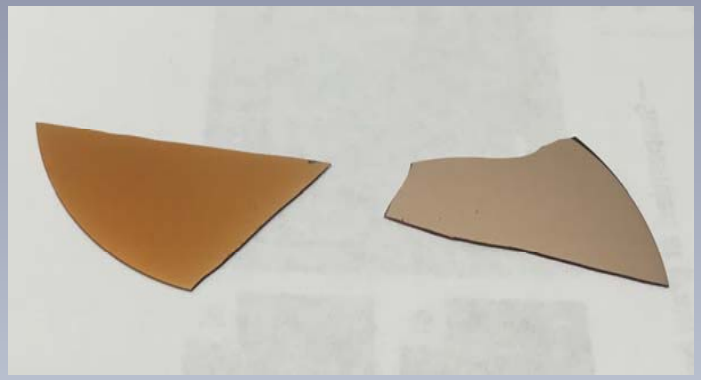
$$2\ Cu_2O\ (s) + H_2O\ (l) + 2\ e^- = 2\ Cu\ (s) + OH^-\ (aq)$$

$$2\ H_3O^+\ (aq) + 2\ e^- = H_2\ (g) + 2\ H_2O\ (l)$$

- Slowly immerse wafer in electrolytic cell and use the buoyancy of graphene coating (polymethyl methacrylate "PMMA") to pull graphene from the wafer.

OXIDATION OF COPPER OPTICAL EVALUATION

a.



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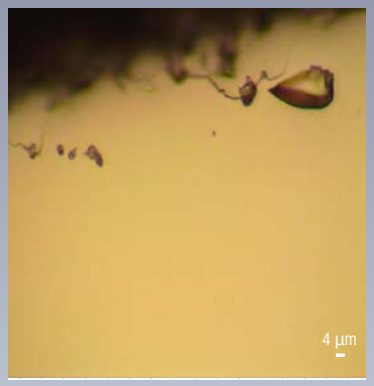

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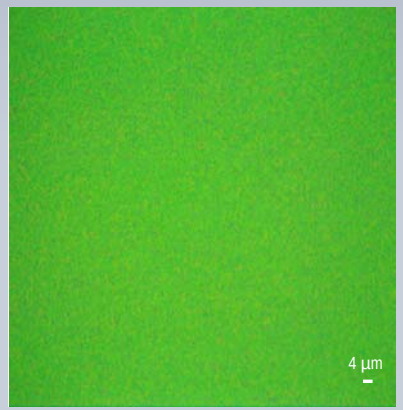

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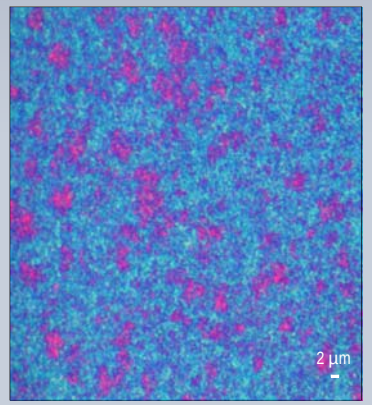
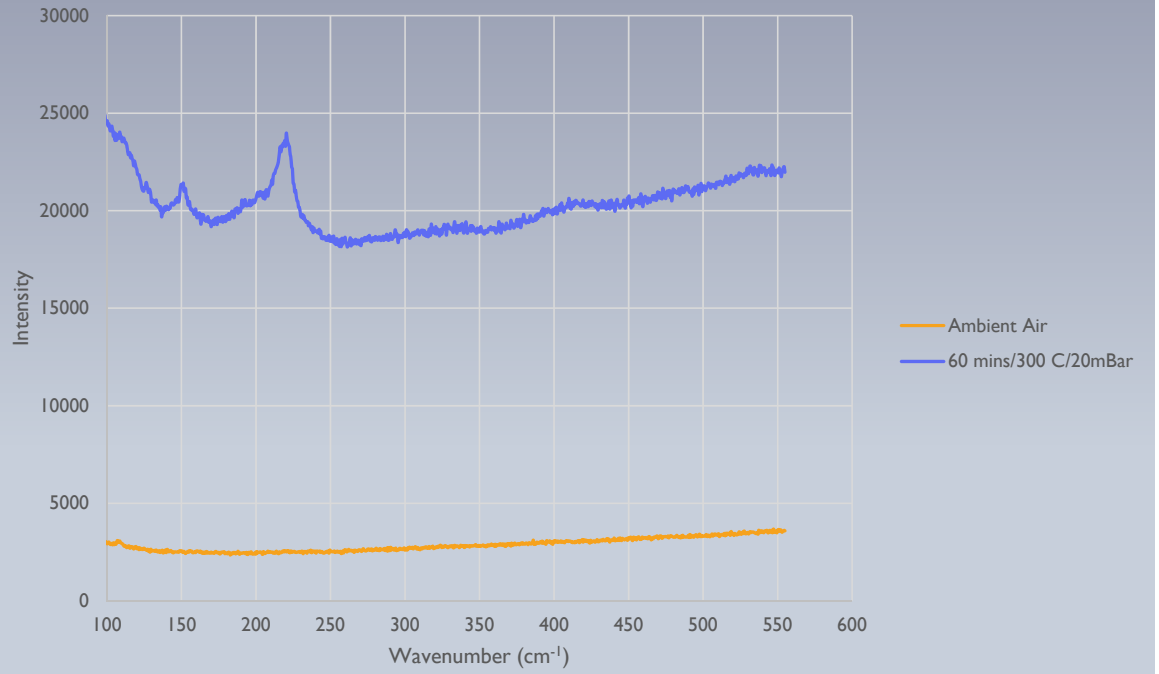


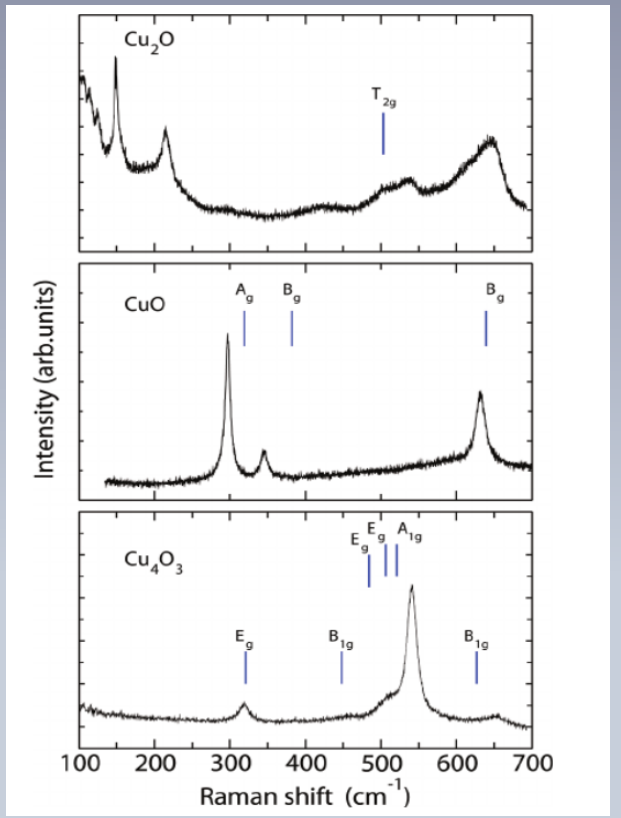
a. 20 mins/200 ˚C/20 mBar vs ambient air
b. Ambient air exposed
c. 20 mins/200 ˚C/20 mBar
d. 60 mins/300 ˚C/20 mBar

All samples on sapphire wafers

OXIDATION OF COPPER RAMAN EVALUATION

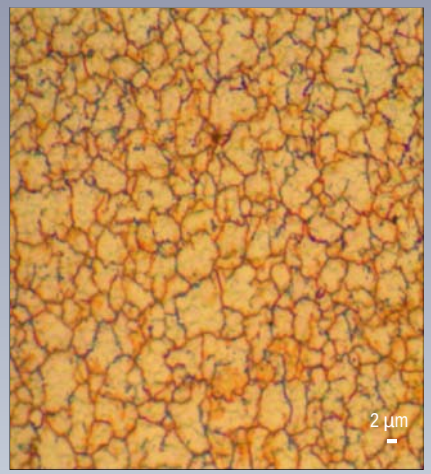
Raman Spectra of Copper Exposed to Oxygen

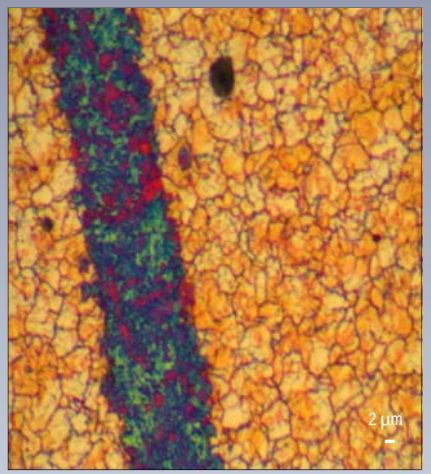


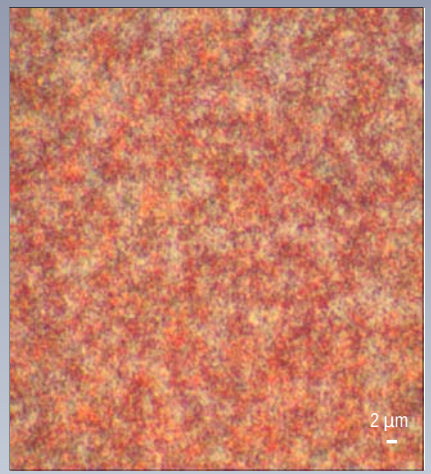


Credit: Debbichi et al. The Journal of Physical Chemistry May 2012

OXIDATION OF COPPER UNDER GRAPHENE OPTICAL EVALUATION

a. 

b. 

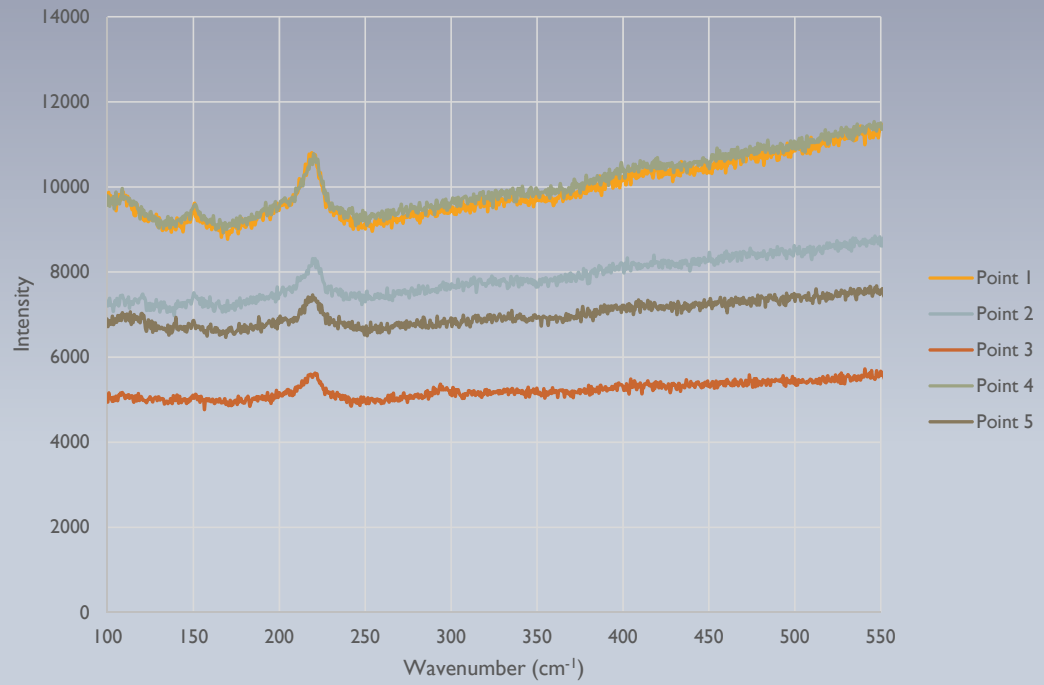
c. 

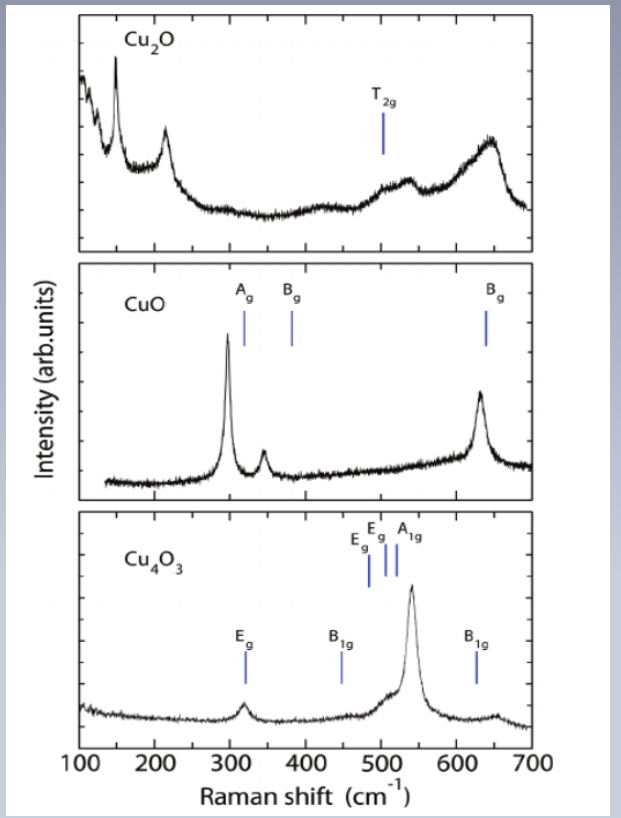
a. 60 mins/300 ˚C/20 mBar
b. 60 mins/300 ˚C/20 mBar with scratch
c. 120 mins/300 ˚C/20 mBar

All samples on SiO_2/Si wafers

OXIDATION OF COPPER UNDER GRAPHENE RAMAN EVALUATION

Raman Spectra Copper and Graphene Exposed to 60 mins/300 ˚C/20 mBar

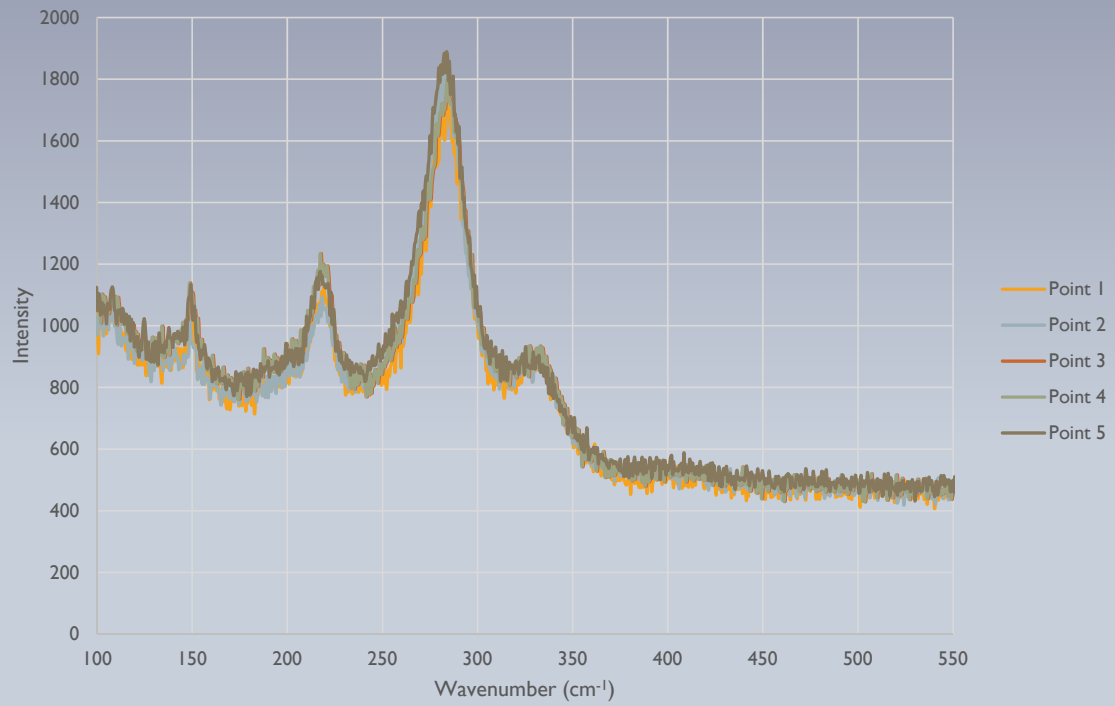


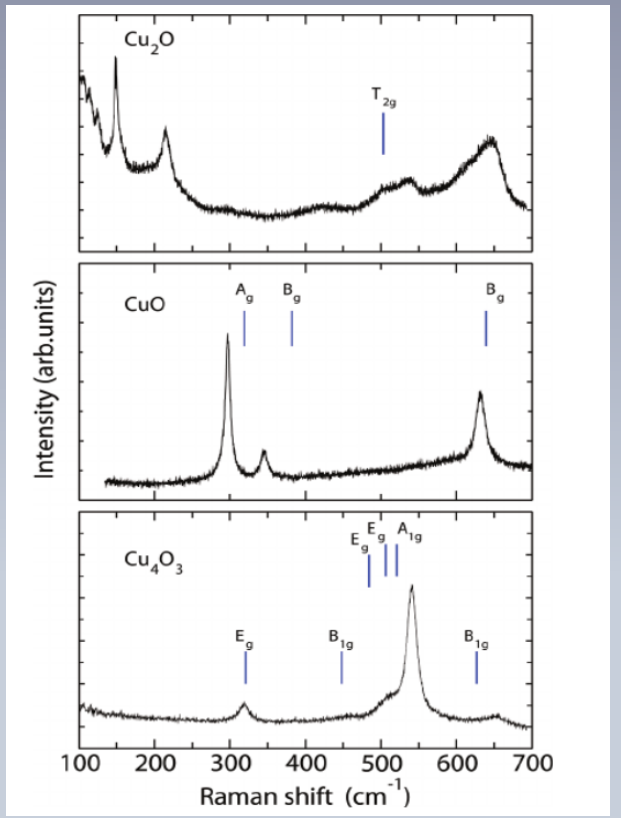


Credit: Debbichi et al. The Journal of Physical Chemistry May 2012

OXIDATION OF COPPER UNDER GRAPHENE RAMAN EVALUATION

Raman Spectra Copper and Graphene Exposed to 120 mins/300 ˚C/20 mBar





Credit: Debbichi et al. The Journal of Physical Chemistry May 2012

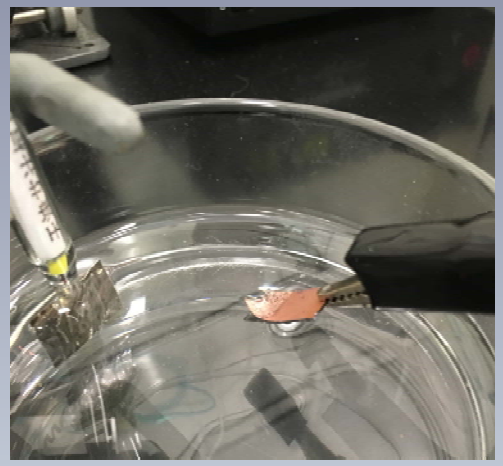
DELAMINATION TRIAL ON SIO_2/SI WAFER

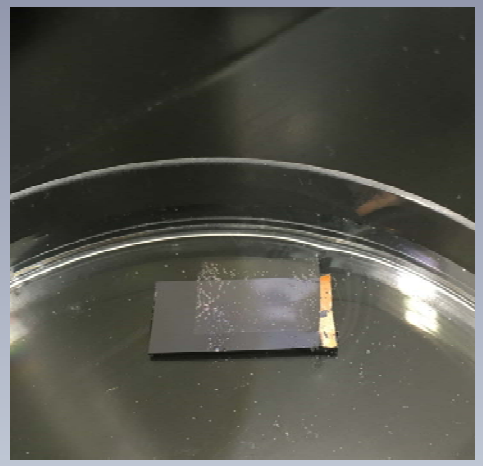
Trial Parameters:

- 2.6 volt potential
- .5 M NaCl electrolyte solution
- Approximate 45˚ angle lowered by hand as needed

Qualitative Results:

- Delamination
- Hydrogen bubbles generated
- Reaction occurred 1.5 – 4 mins
- At some edge locations graphene and copper stuck together

a. 

b. 

a. Submerging sample in electrolytic cell
b. Sample post delamination

CONTINUING RESEARCH

Next Steps:

- Raman analysis of graphene from trial delamination.
- Test "over oxidized" sample and compare transfer and determine if graphene survived oxidation.
- Determine optimal oxidation parameters for graphene grown on sapphire wafers.
- Test varying potentials to determine if delamination is possible without bubble generation.
- Consider different methods for submerging graphene.
- Compare quality of graphene via different transfer methods and electrochemical delamination at varying potentials.

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