Graphene-Based Composite Sensors for Energy Applications

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Overview Of Presentation

Background

Graphene As A Sensor Material

Hypothesis, Goals, & Research Issues

Status of Key Research Areas

Graphene Synthesis & Post Synthesis Surface Modification

Nanoparticle Nucleation and Growth

Sensor Fabrication & Electrical Characterization

Test Unit & Gas Response

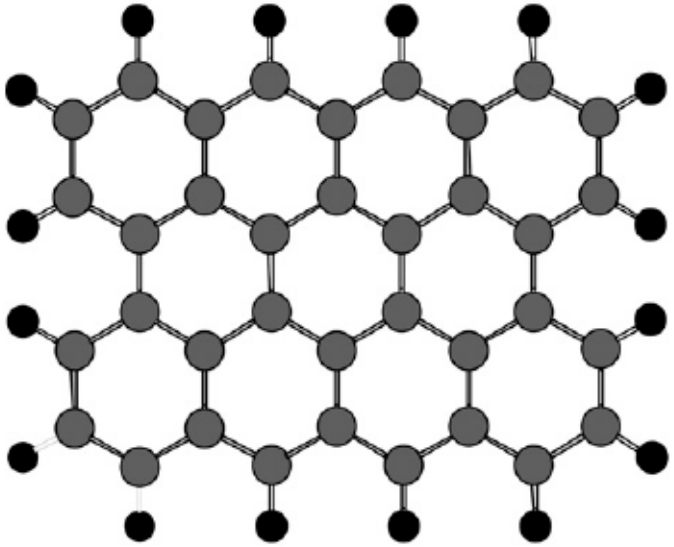
Summary of Key Results

Acknowledgements

Graphene As A Sensor Material

Structure of graphene

- Flat monolayer of sp^2 bonded C-atoms
- p orbitals normal C-monolayer
- May include multilayer films



Top View

Edge View

As a gas sensor material

- High charge carrier mobility
- Low charge carrier density
- Adsorbed molecules alter carrier density
- Chemoresistive graphene gas sensors have a rapid response and high sensitivity

Basic Question: How can target specificity be achieved?

Fundamental scientific issue addressed in this research → **Basic Hypothesis of this Research**

Hypothesis

Gas adsorption mediated by different types of nanoparticles attached to independent graphene chemoresistive sensors can yield an electrical response pattern specific to each adspecies.

Research Goals

Validate the hypothesis and use graphene-nanoparticle composites to develop a high sensitivity, rapid response electronic nose capable of operating over a wide range of conditions including high temperature energy applications

Research Issues

Synthesis of graphene & graphene-nanoparticle composites

Characterization of electrical properties

Sensor fabrication & testing

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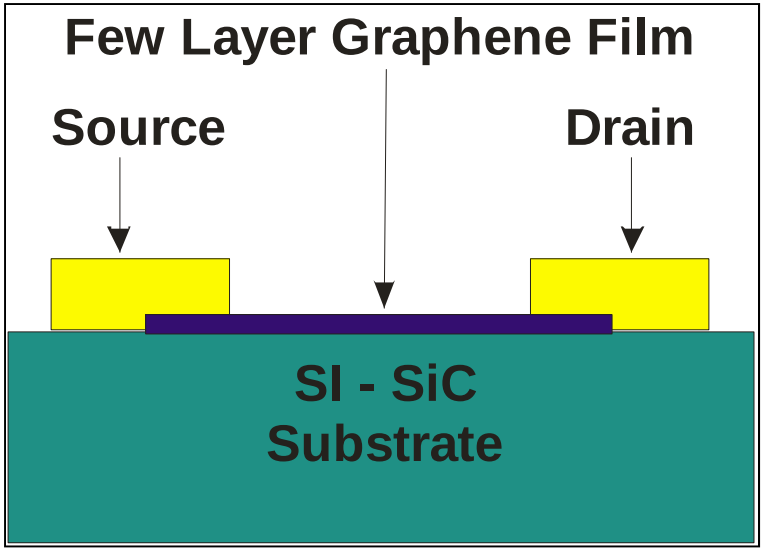
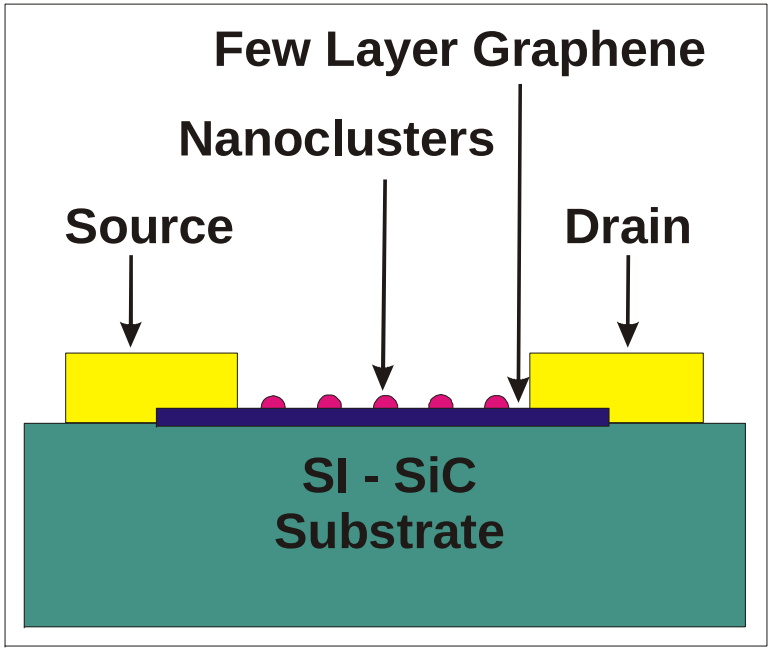
Roadmap - Basic Sensor Design



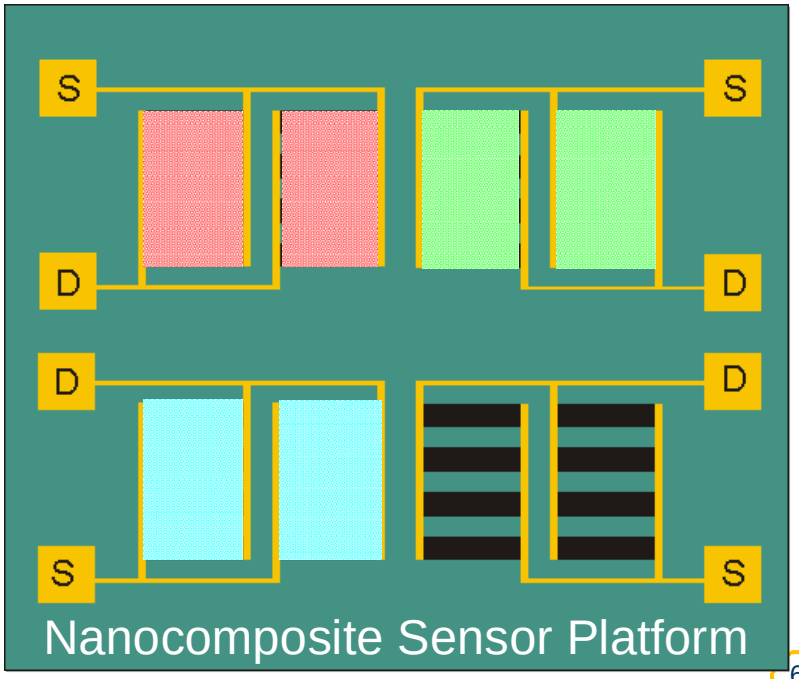


Graphene synthesis

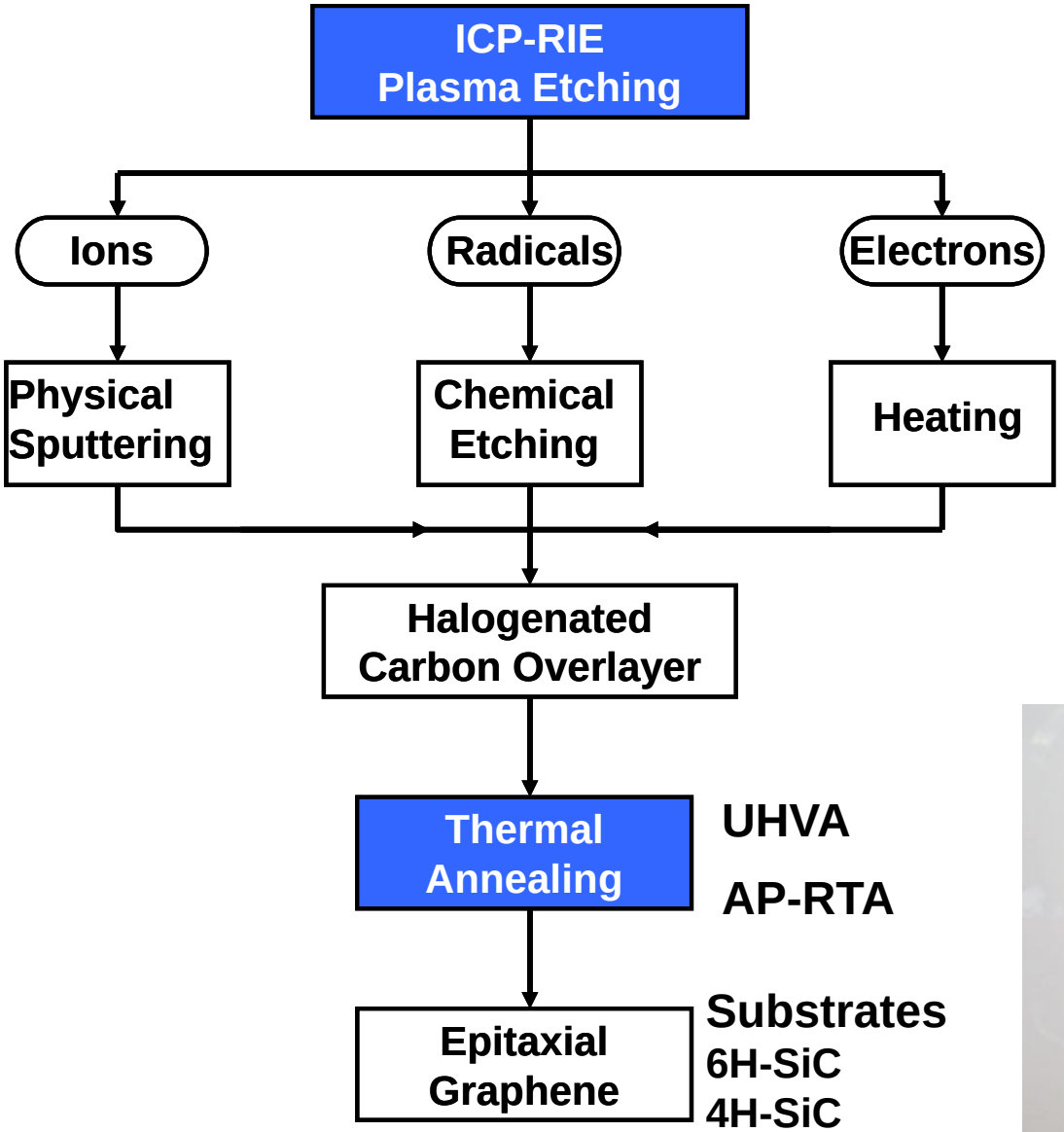
Post synthesis surface modification
- Control defect levels
- Modify electrical properties
- Provide nucleation sites for nanoparticles

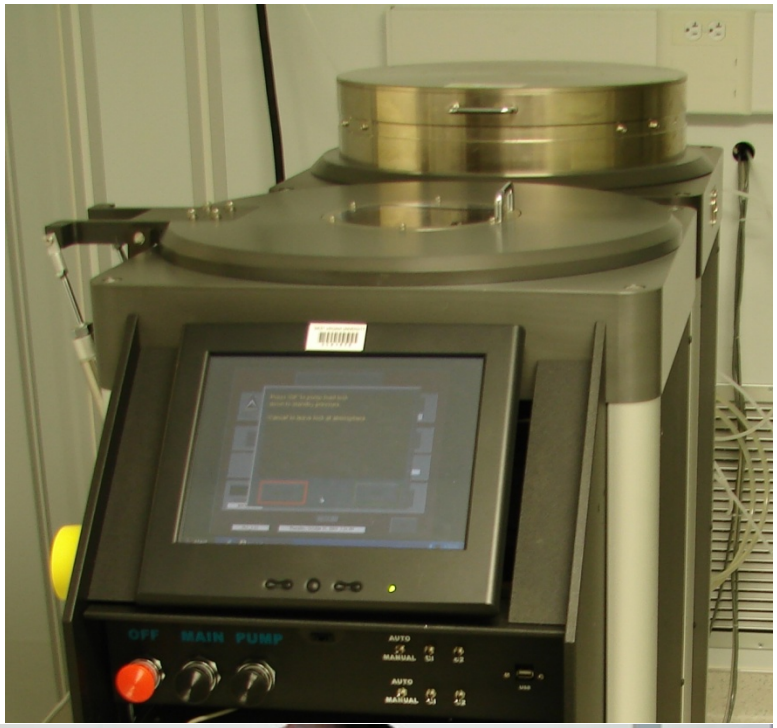
Nucleation & growth of nanoparticles

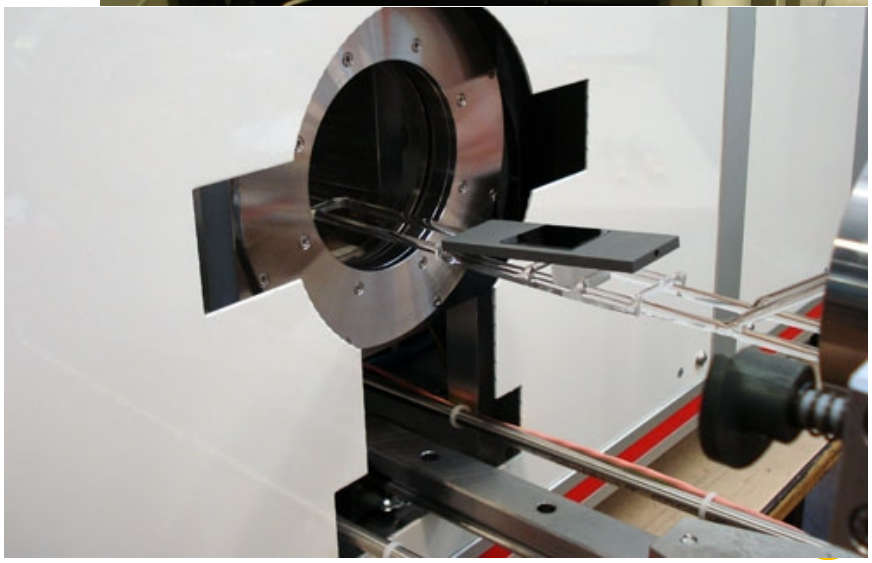
Sensor fab, electrical characterization, & sensor testing



Synthesis Of G/SiC Films

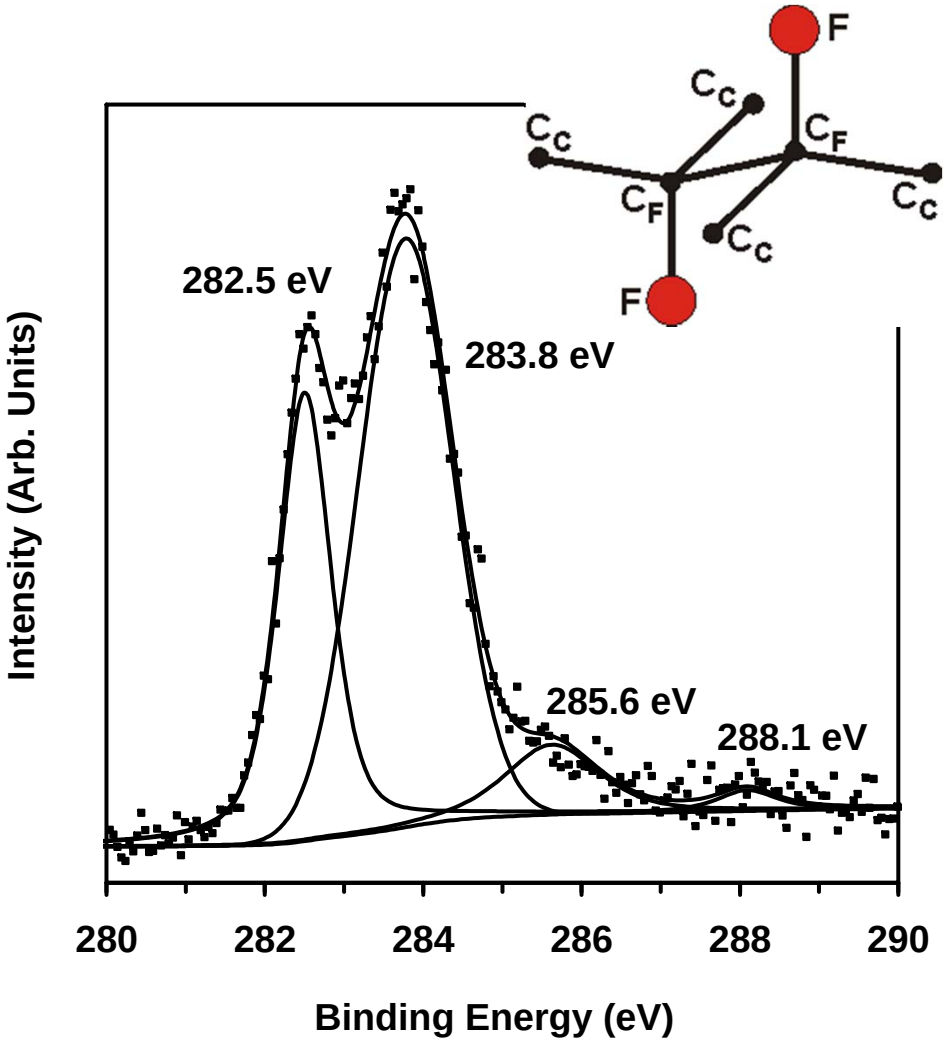


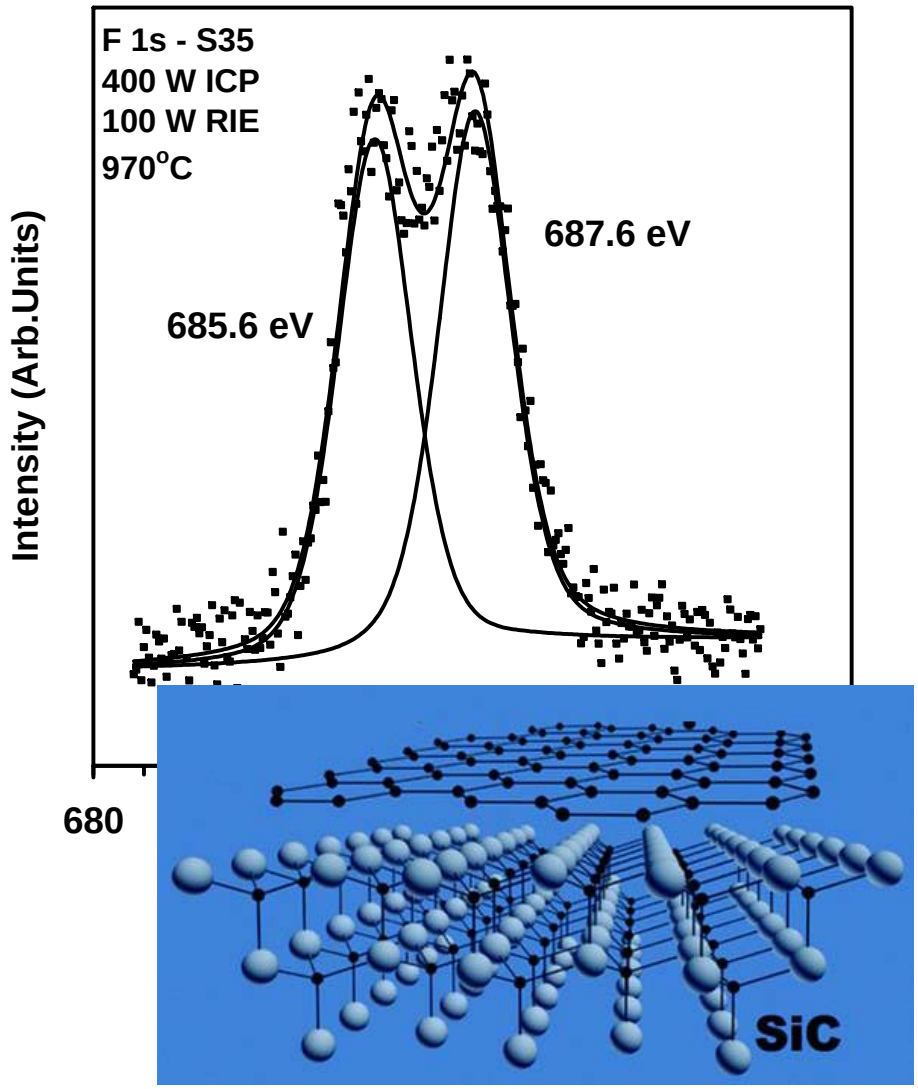




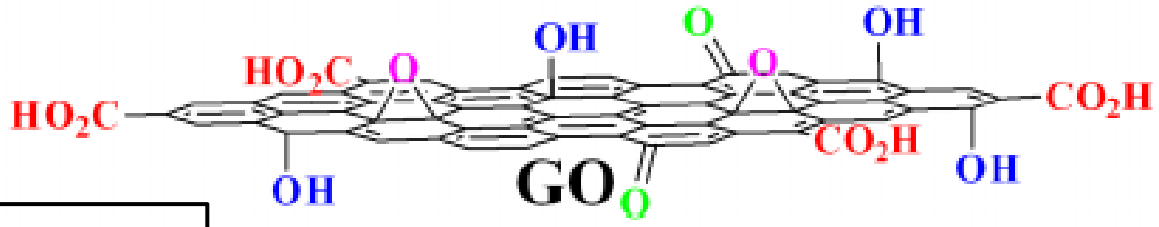
Stinespring & coworkers, J. Vac. Sci. Technol. 30 (2012) 030605-5.

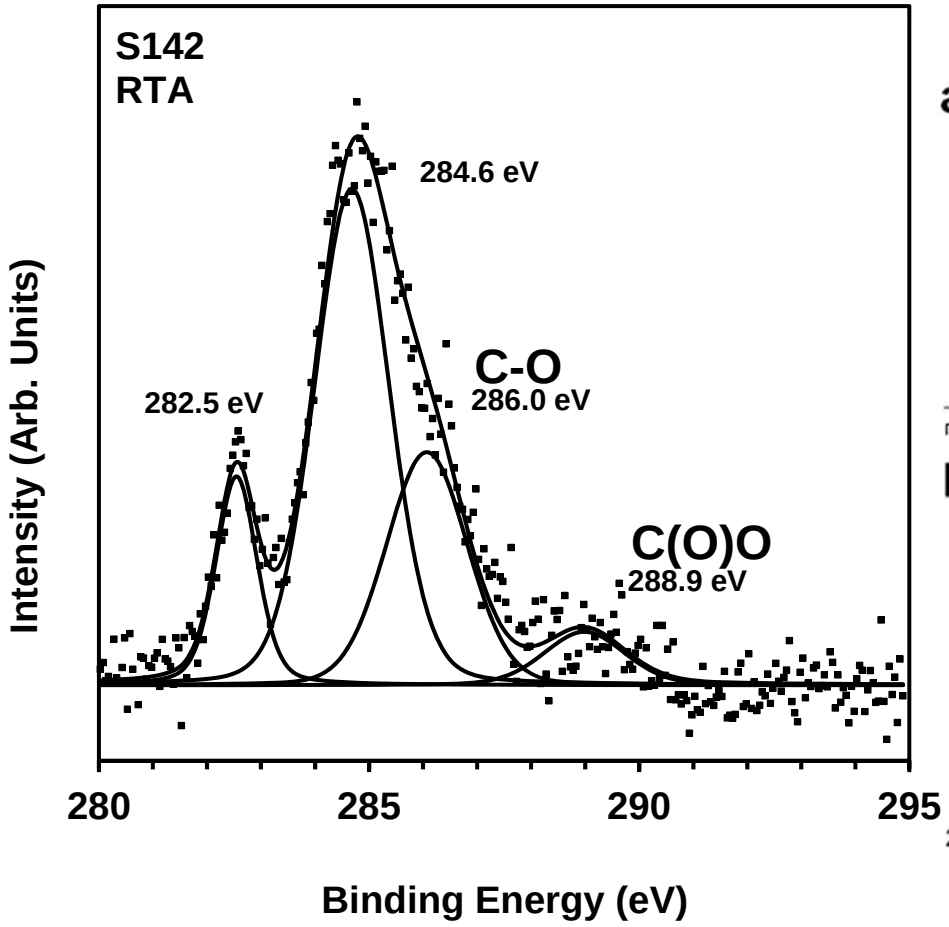
UHVA G/SiC Films

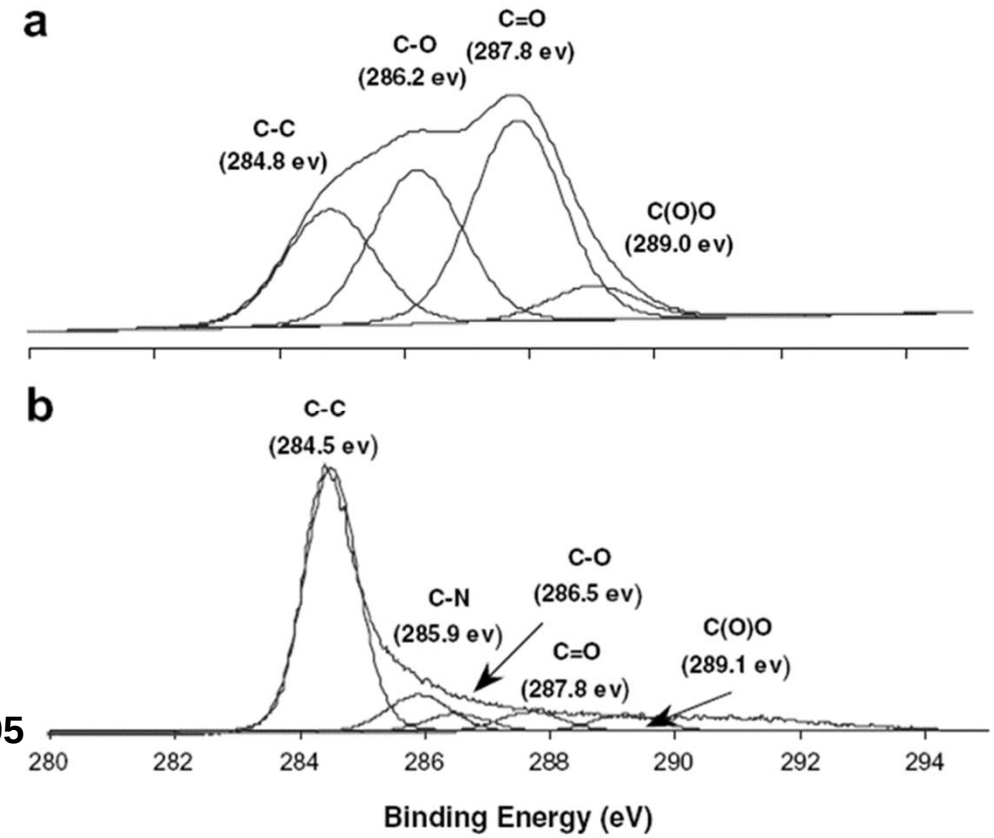




AP-RTA G/SiC Films



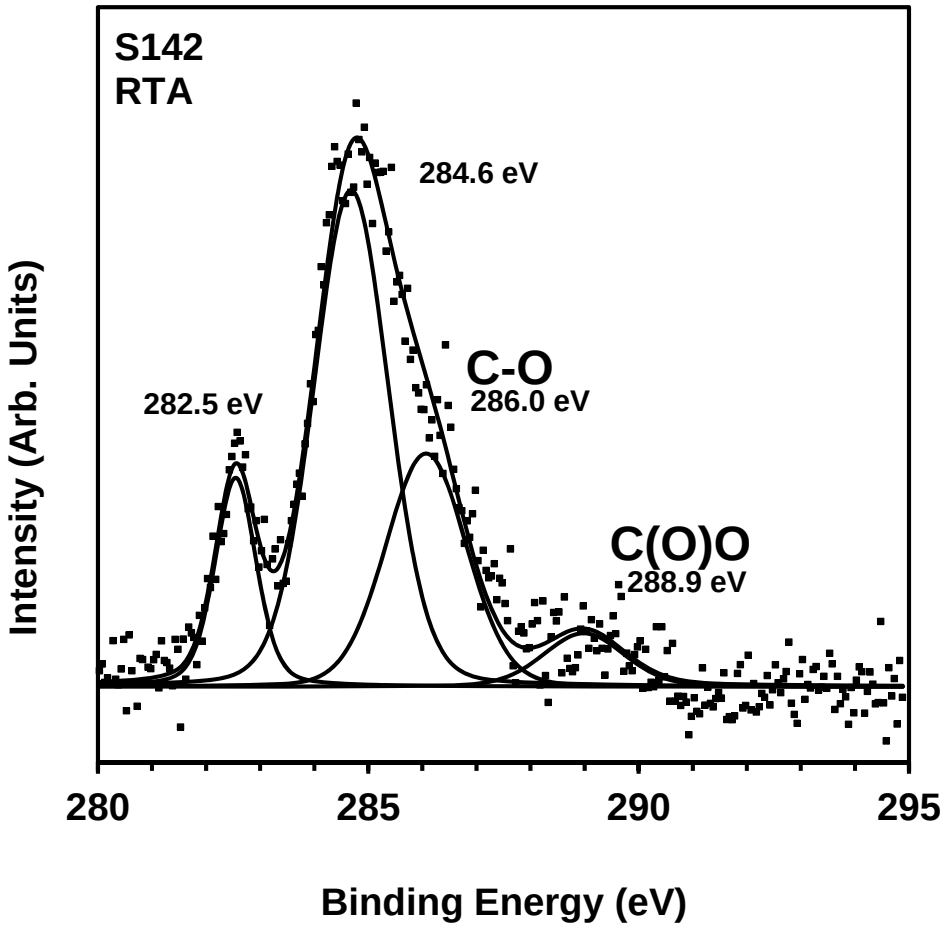


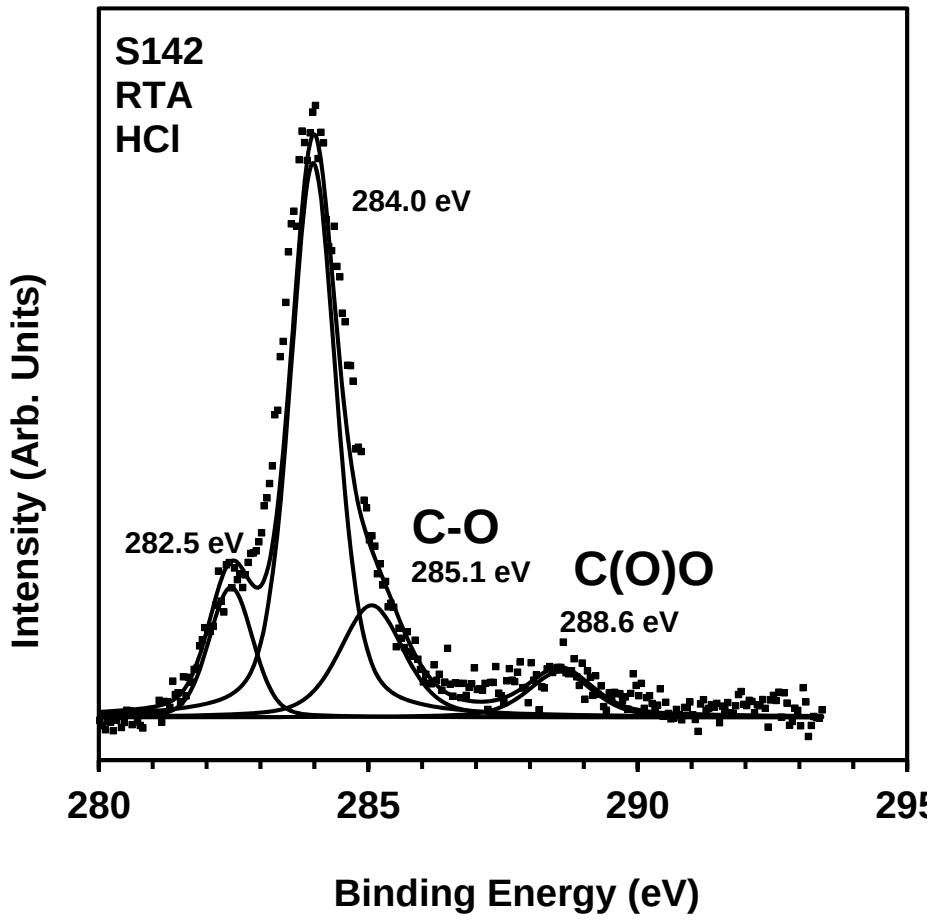


a) Graphene oxide and b) hydrazine reduced GO

Stankovich et al., Carbon 45(2007)1558-1565.

Post Synthesis Surface Modification





- Enhancement and narrowing of the C-C peak / reduction of Si-C
- Reduction of the C-O defects / relatively no change in edge defects
- The ability to control the surface defects is useful since they influence electrical properties & are potential sites for particle nucleation

Nanoparticle Nucleation & Growth on Graphene

Nanoparticles deposited on graphene from solution

Hypothesis is that particles will nucleate and grow on surface defects

Initial studies performed using Ag and Au nanoparticles

- Ag forms an oxide, Au does not
- Both easily detected using SEM / XPS / AFM

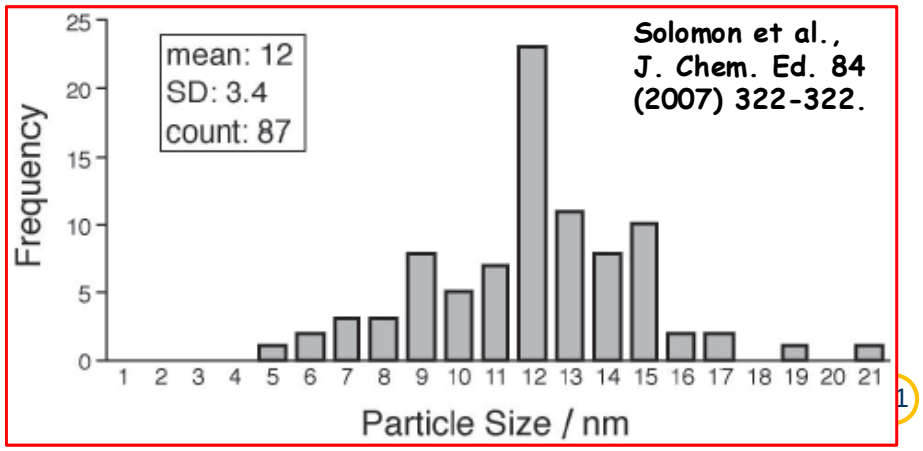
Simple Reaction Mechanisms

$$AgNO_3 + NaBH_4 > Ag + \tfrac{1}{2} H_2 + \tfrac{1}{2} B_2H_6 + NaNO_3$$

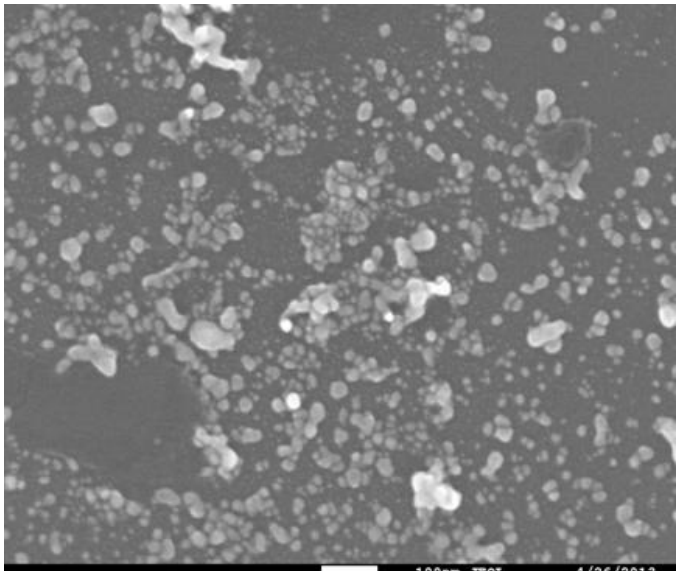
Simple Reaction Sequence

Sample immersed in 10mM $AgNO_3/H_2O$

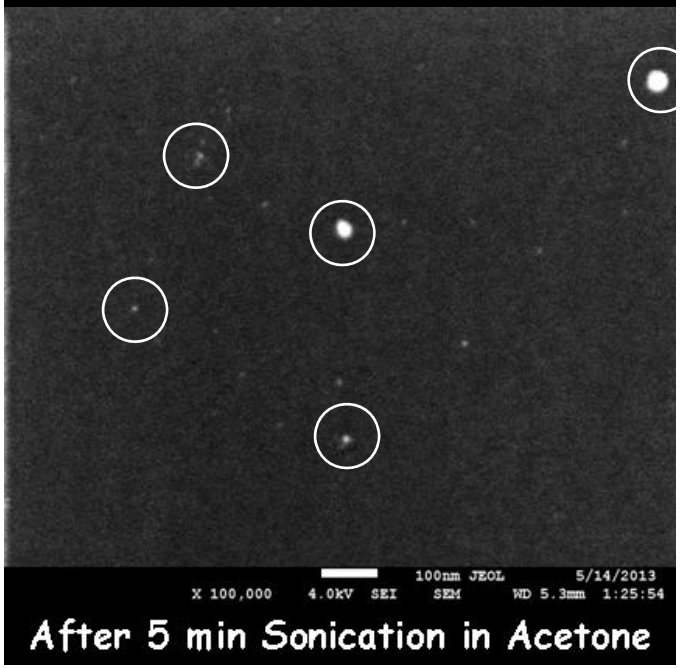
25mM $NaBH_4/H_2O$ & incubated 12 hours



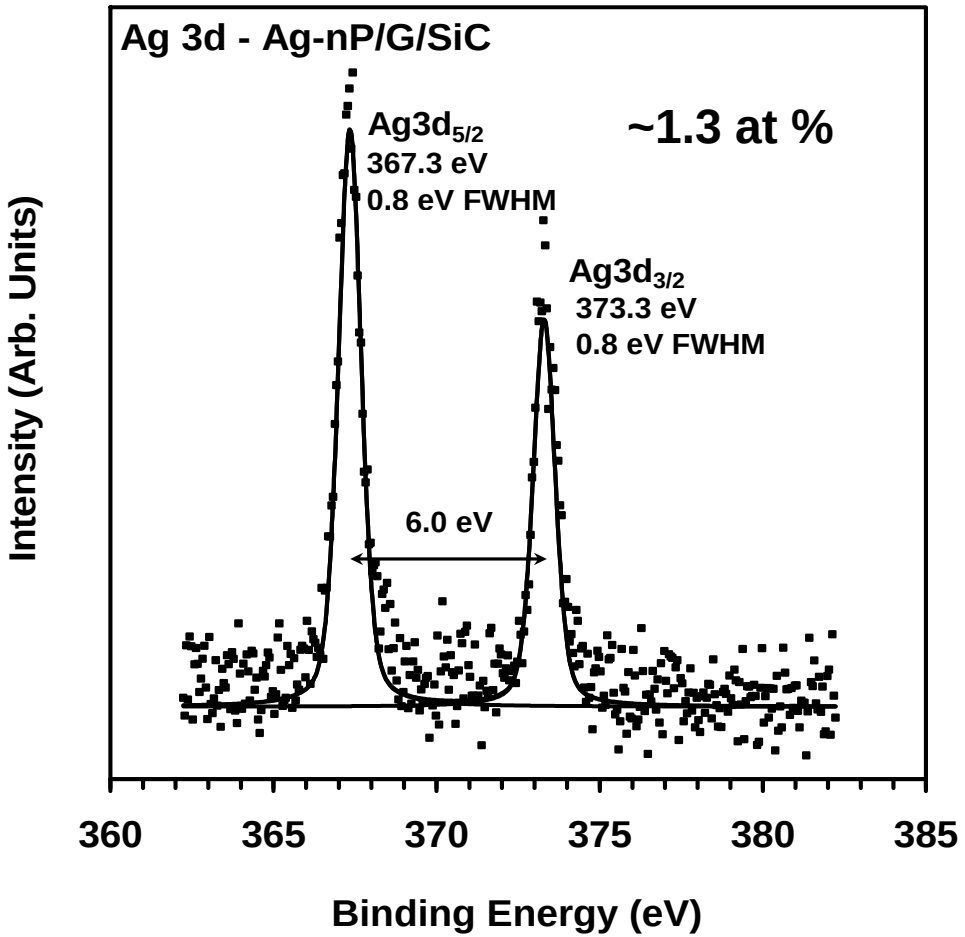
Ag Nanoparticle Nucleation & Growth



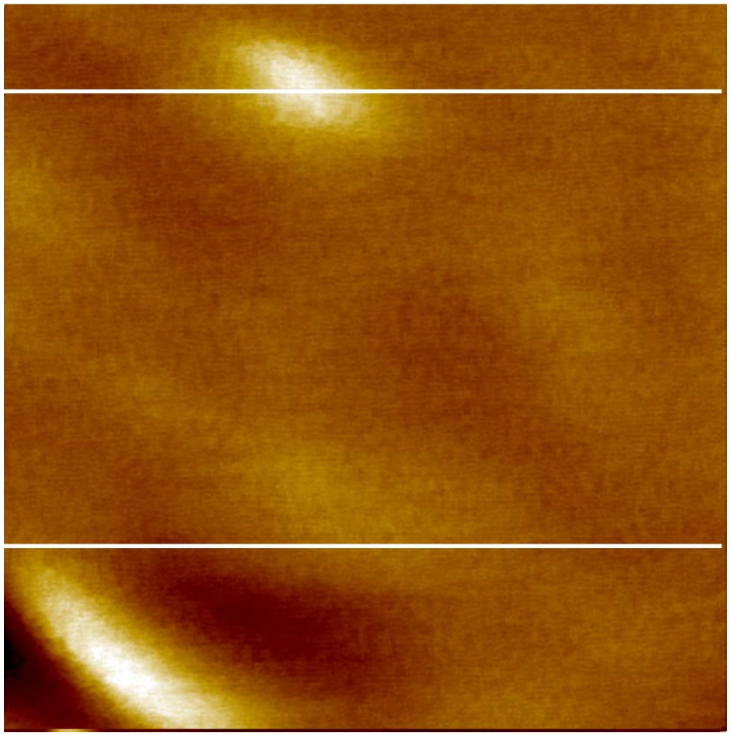
After Nucleation and Growth

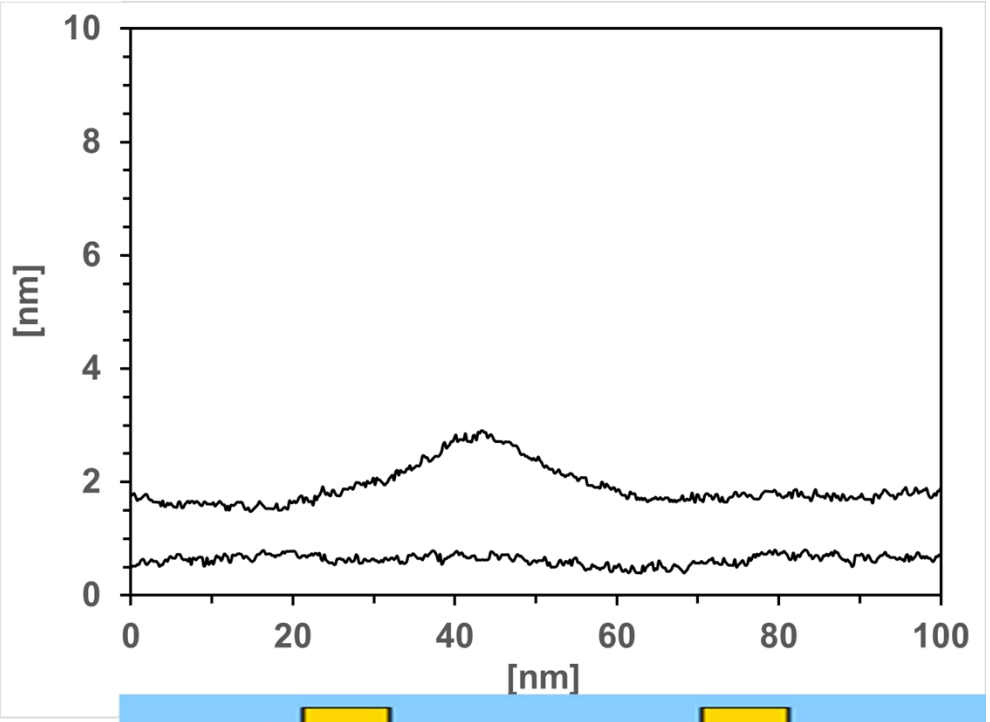


After 5 min Sonication in Acetone



Au Nanoparticle Nucleation & Growth

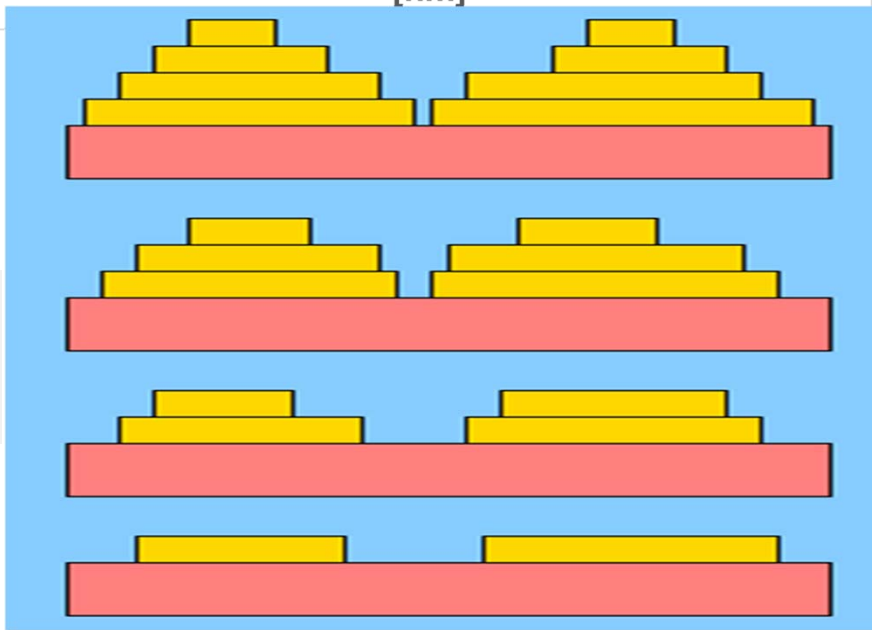




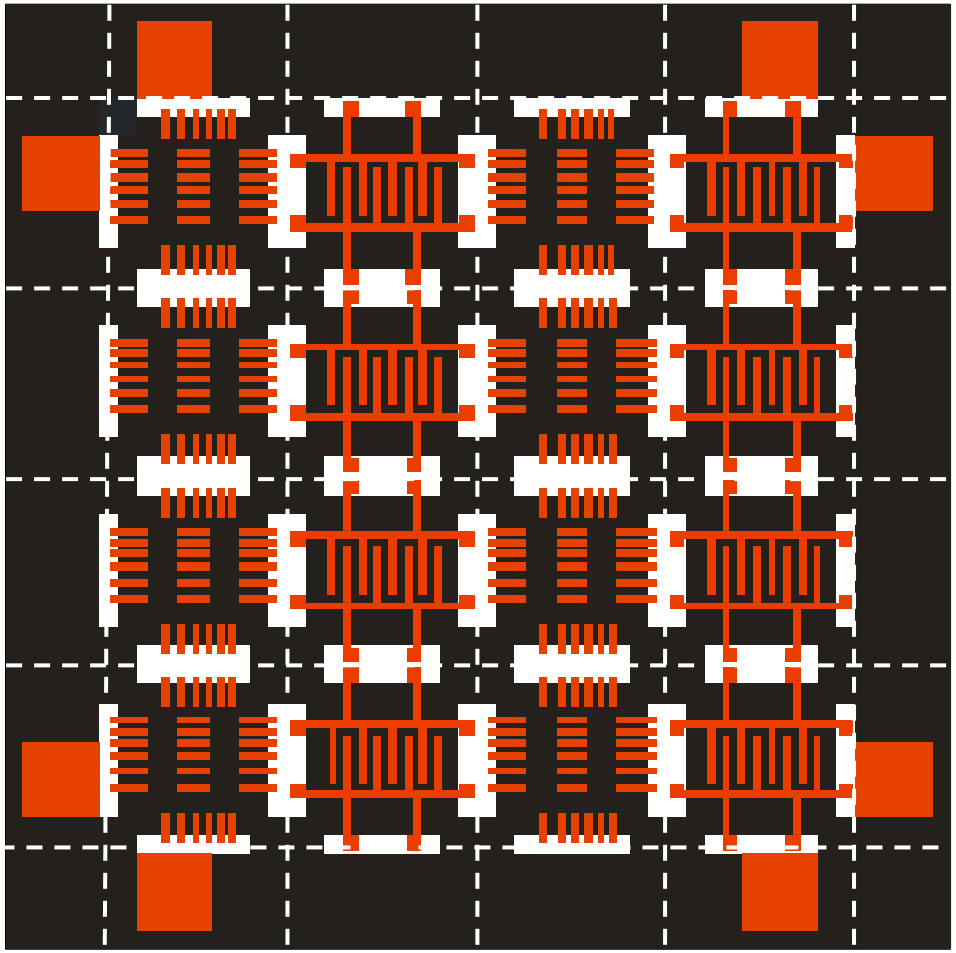
Particle Dimensions
Diameter: 25 nm – 150 nm
Height: 0.5 nm – 5 nm

- Ultrasonically removed particles are spheroidal
- Associated with homogeneous nucleation & deposition from solution

- Attached particles are pyramidal
- Suggests heterogeneous nucleation with Volmer-Webber growth

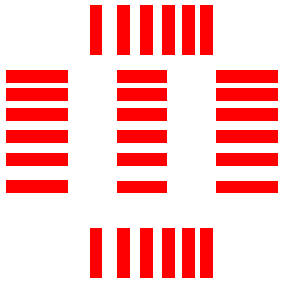


Device Fabrication

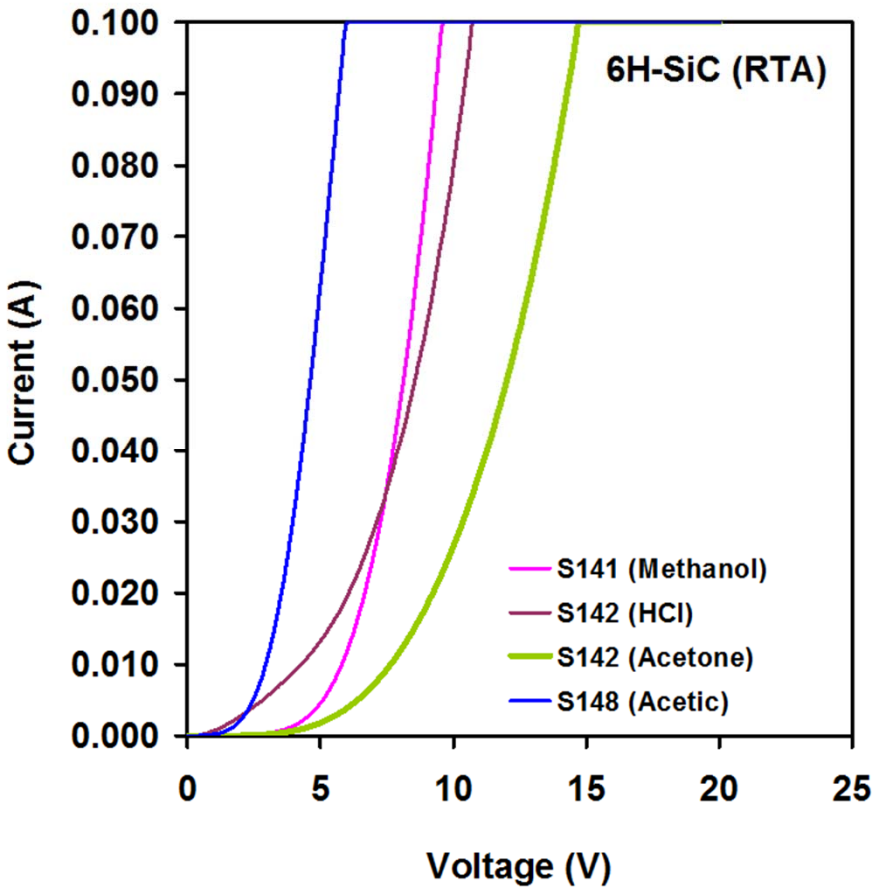


- Deposit uniform G/SiC film on 1 cm x 1 cm substrate
- Use shadow mask #1 & oxygen plasma to remove graphene & form SiO_x strips while protecting 2 mm x 2 mm graphene regions
- Use shadow mask #2 and e-beam evaporation to produce Au/Ti device patterns (TLM & sensor)
- Use wafering saw to produce 2.5 mm x 2.5 mm die for testing
- TLM pattern - electrical properties
  Sensor pattern – sensor testing

G/6H-SiC Electrical Characterization

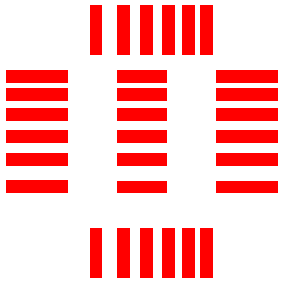


- Select contact array
- Measure I-V characteristic for each contact pair in array
- Determine the resistance for each contact pair



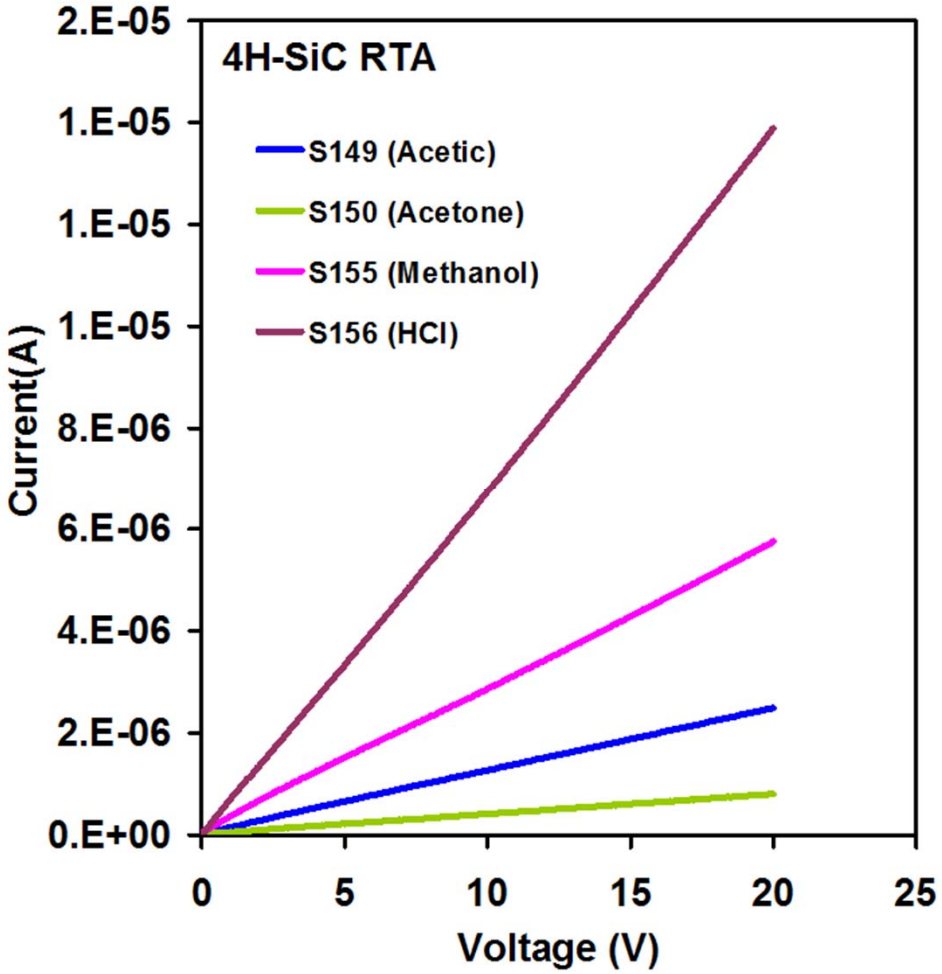
- Using standard TLM analysis, plots of resistance versus aspect ratio yield the contact resistance and film resistance
- Analysis of I-V data using Richardson-Dushman equation yields the carrier density and Schottky barrier height
- Resistance and carrier density of G/6H-SiC comparable to exfoliated graphene
- Unlike normal graphene, fluorine & oxygen defects open band gap
- Surface modified G/6H-SiC films retain Schottky behavior

G/4H-SiC Electrical Characterization



- Both UHVA and RTA G/4H-SiC have low conductivity

- Surface modified G/4H-SiC exhibits Ohmic behavior



Summary

- Electrical properties of native and surface modified G/SiC quite diverse

- Raise interesting questions concerning the underlying physics

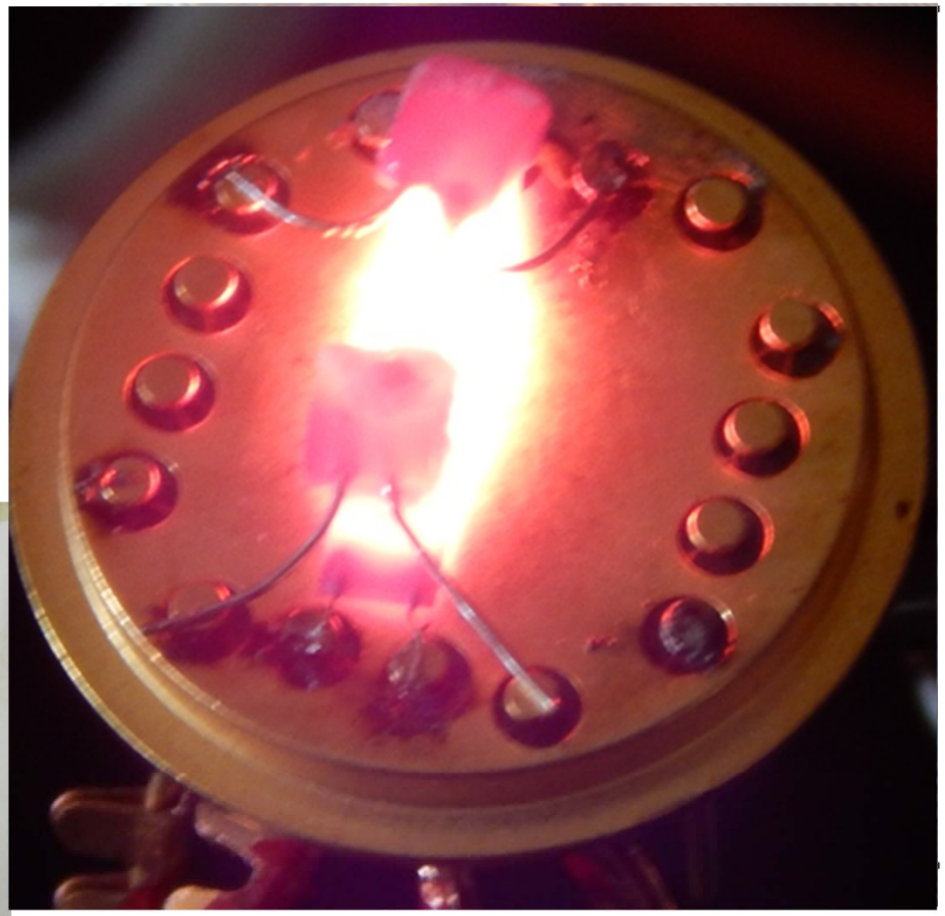
- Electrical properties well suited for next phase of sensor development

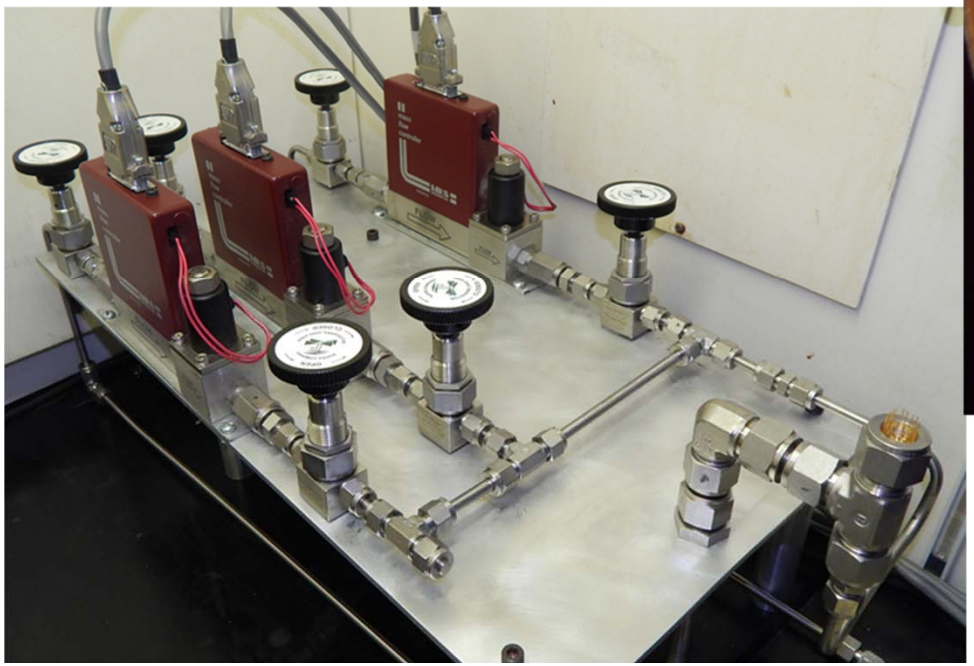
Sensor Platform and Test Unit

- Sensor mounted on TO header with microheater and RTD for control of temperature (≤500 °C)

- Useful for both electrical property measurements & sensor development

16 Pin Transistor Outline Header





- Sensor platform incorporated into test unit for characterizing response to target species

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Task Schedule

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Graphene Synthesis & Post Synthesis Surface Modification

Nanoparticle Nucleation and Growth

Sensor Fabrication & Electrical Characterization

Test Unit & Gas Response

Summary of Key Results

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Synthesis & Post Synthesis Surface Modification

Graphene synthesis processes in hand

- One, two, and three layer G/SiC reproducibly and routinely produced
- UHVA and RTA defect structures characterized
- Continue to optimize the process

Surface modification of continued interest

- Surface modification alters defect distribution
- Influences the electrical properties
- May be useful in controlling the areal density of nucleation sites

Nanoparticle Nucleation and Growth

Ag & Au nanoparticles deposited using solution chemistry

- Evidence for both homogeneously and heterogeneously nucleated particles
- Brief ultrasonic treatment removes weakly attached particles
- Pyramidal 0.5 – 5 nm high x 25 – 150 nn diameter particles remain
- Suggest Volmer-Webber nucleation and growth mode
- Studies in progress to establish role of defect sites & determine growth kinetics

Studies of Pt, TiO_2, and ZnO nucleation & growth next in line

Sensor Fabrication & Electrical Characterization

Sensor fabrication process in hand

- Lithography free process developed for sensor & TLM structures
- Continue to optimize process

Electrical characterization and testing in progress

- Native & surface modified G/SiC films exhibit diverse electrical properties
- Raise highly interesting physics questions for further study

Key Observation: The native & modified G/SiC well suited for the sensor development and testing efforts now in progress

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University Coal Research Program

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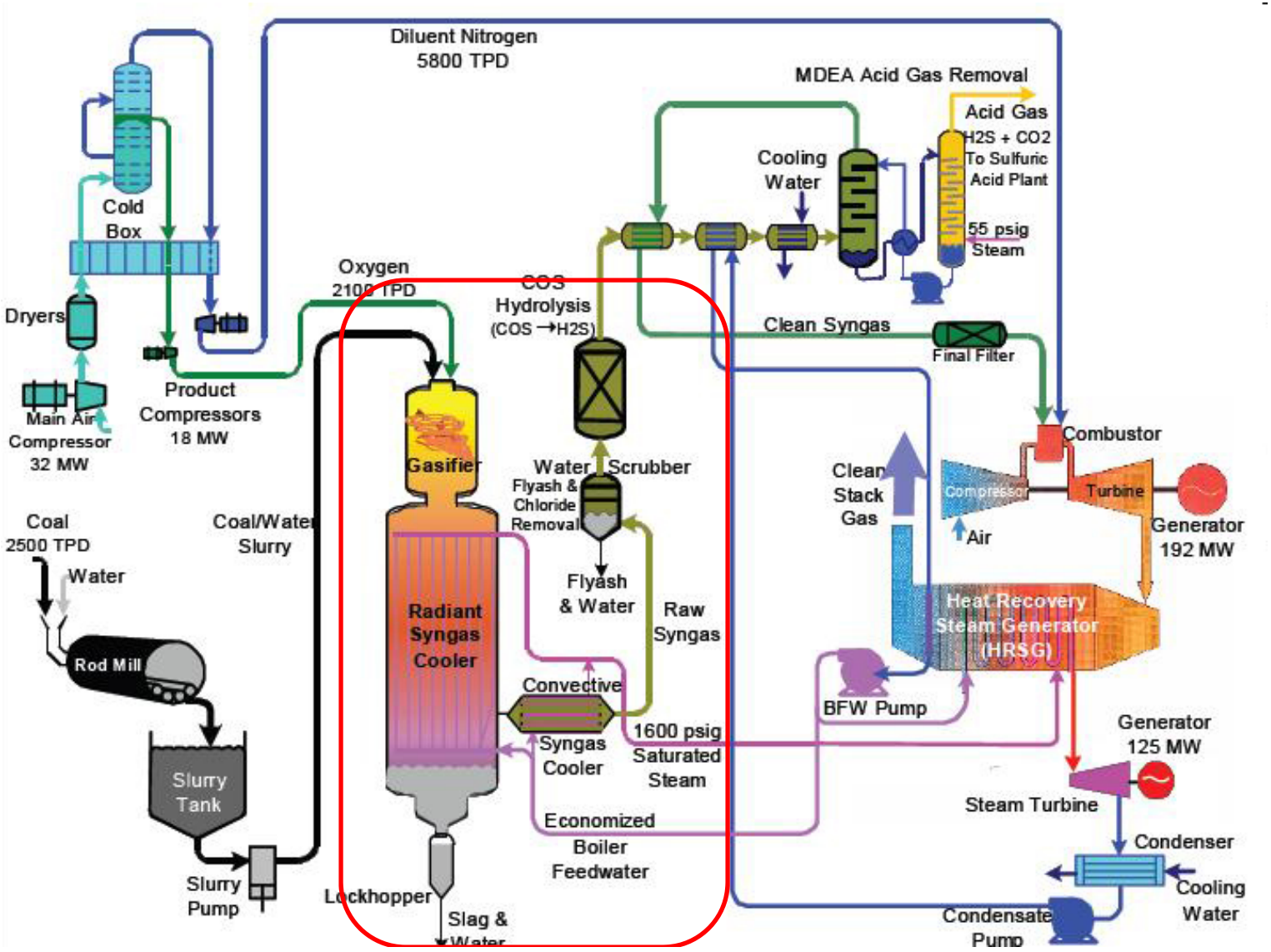
PhD Students

- Saurabh Chaudhari – Graphene synthesis & sensor fabrication
- Andrew Graves – Sensor characterization

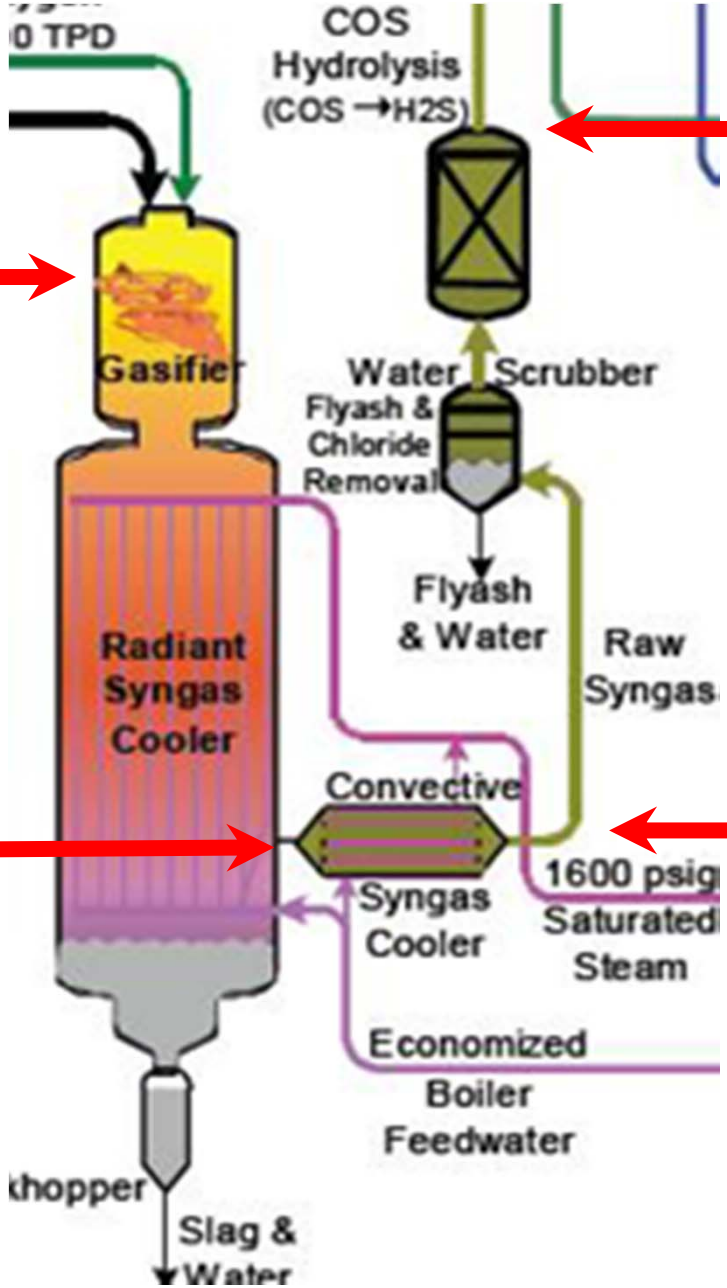
Undergrad Students

- Jason Miles - Particle nucleation and growth
- McKenzie Mills – Surface modification

Looking Ahead – Applications Environment Integrated Gasification Combined Cycle



Integrated Gasification Combined Cycle (IGCC)



2300 – 2700 °F
Very High

Requires Modified Sensor Design

1100 – 1400 °F
High

Accommodated By Ruggedized Sensor Design

350 – 400 °F

Warm

Accommodated By Current Sensor Design

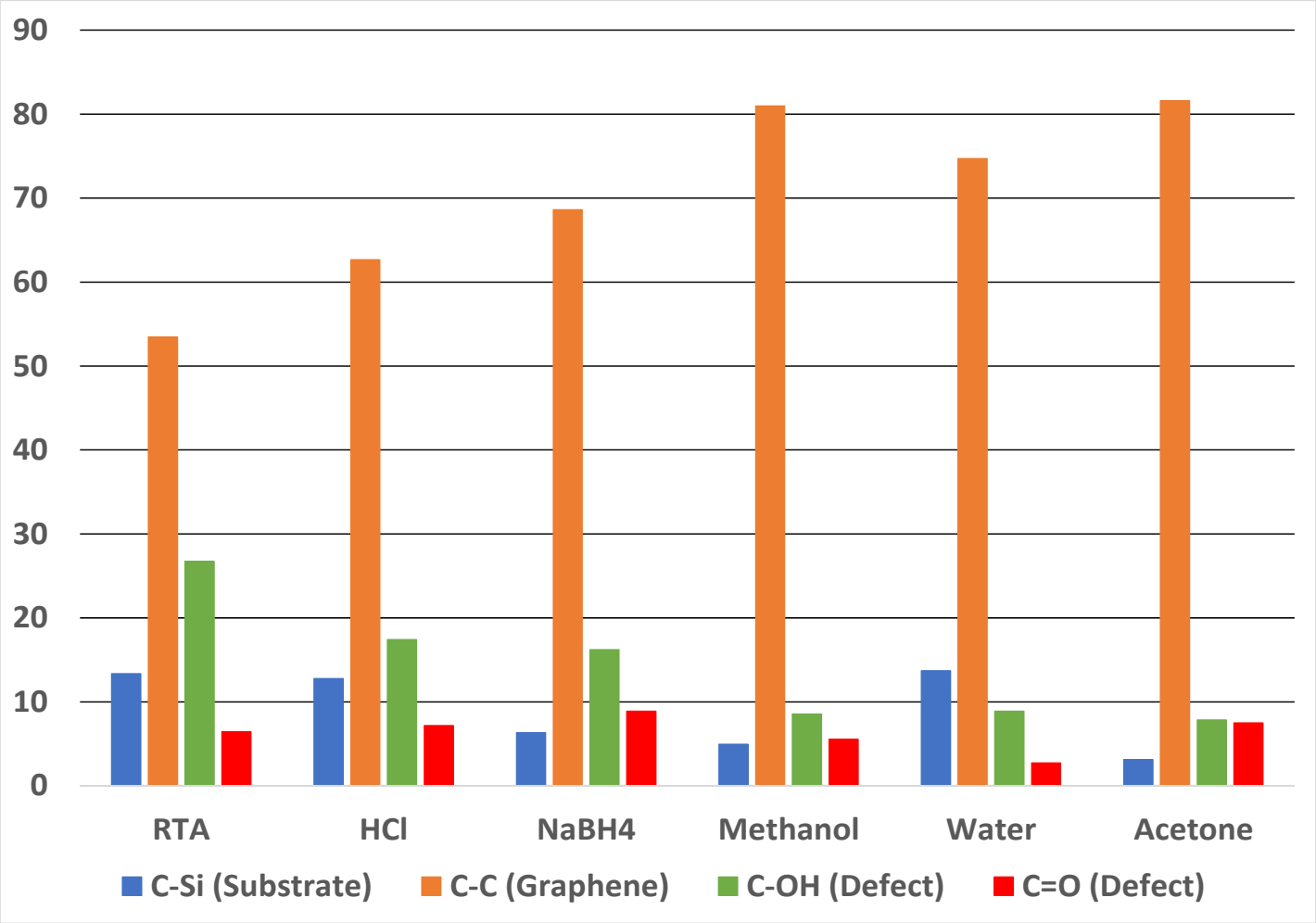
700 – 800 °F

Sensor Test Unit & Gas Response Studies

Sensor test unit operational

Temperature dependent electrical characterization and gas response measurements in progress

Post Synthesis Surface Modification



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