Graphene-Based Composite Sensors for Energy Applications

Presented By
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Presentation Overview

Background

Attributes of Graphene As A Sensor Material

Research Hypothesis, Goals, & Tasks

Results

Graphene Synthesis

Device Fabrication

Electrical Characterization

Summary

Current Status

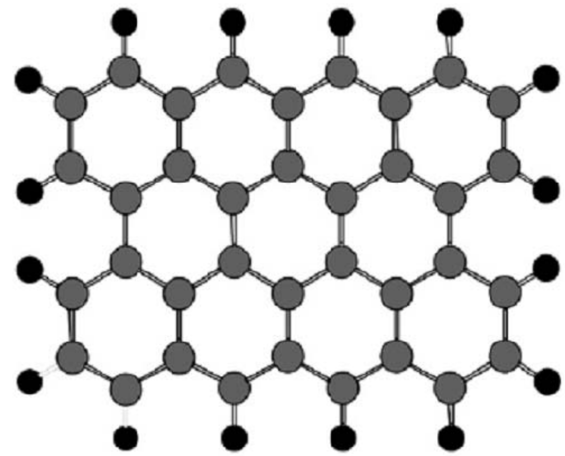
Future Directions

Graphene As A Sensor Material

Structure of graphene

- Monolayer of sp^2 bonded C-atoms
- p orbitals normal C-monolayer
- Ideally one layer but frequently multilayers

Edge View



Top View

Attributes as gas sensor material

- Charge carrier density altered by adsorption
- Low carrier density ⇒ high sensitivity
- High carrier mobility ⇒ rapid response

Graphene should provide the basis for high sensitivity, rapid response chemoresistive sensors!

Basic Question: How can target specificity be achieved?

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

Basic Hypothesis

Gas adsorption mediated by different types of nanoparticles attached to independent chemoresistive graphene sensors can yield a unique electrical response pattern for each adsorbed gas species.

Research Goals

Validate the hypothesis for graphene-nanoparticles (G-nP) composites

Demonstrate feasibility of a G-nP composite "electronic nose"

Research Tasks

Synthesis of graphene

Fabrication of G-nP composite sensors

Characterization of graphene films & sensor properties

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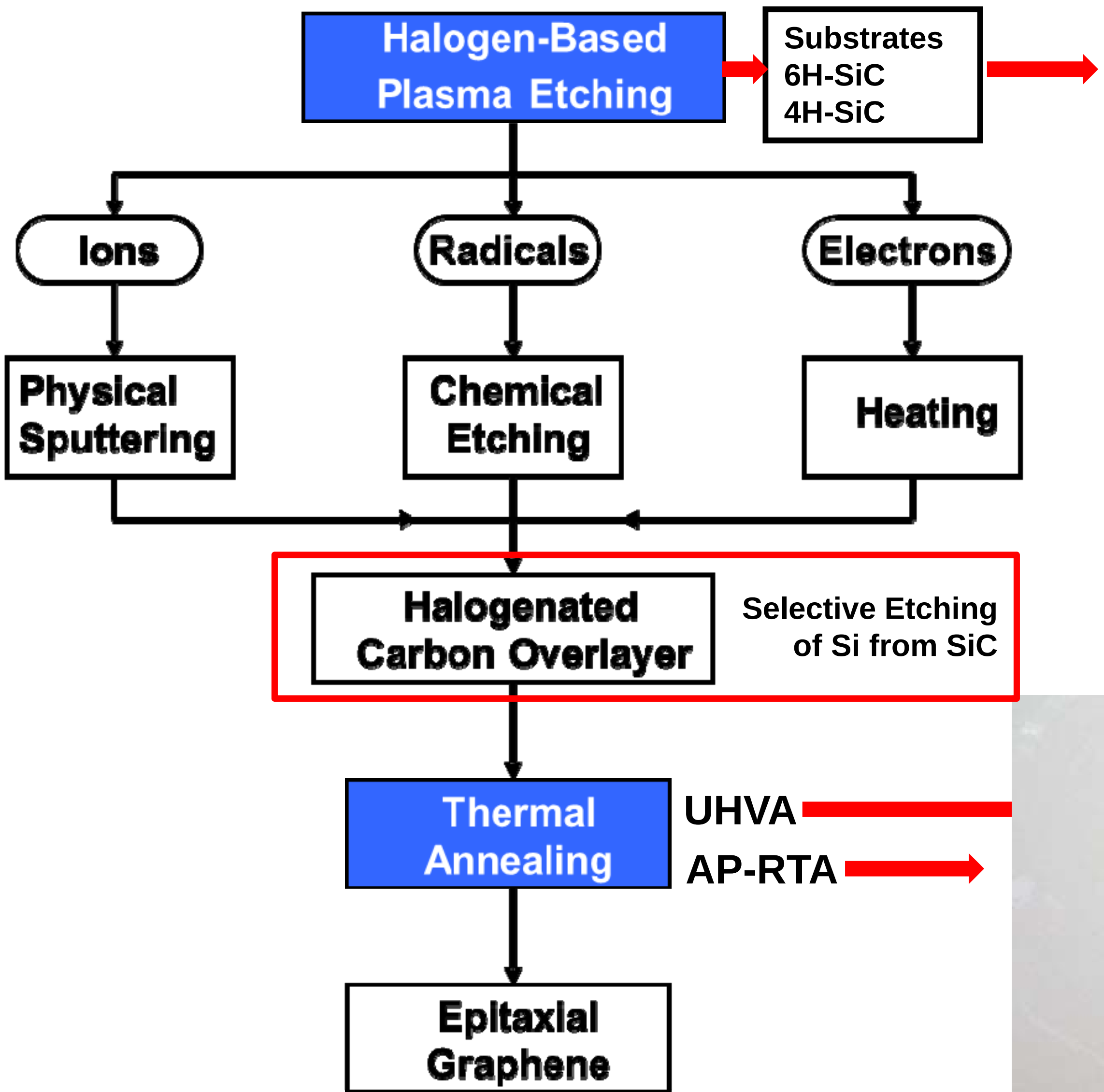
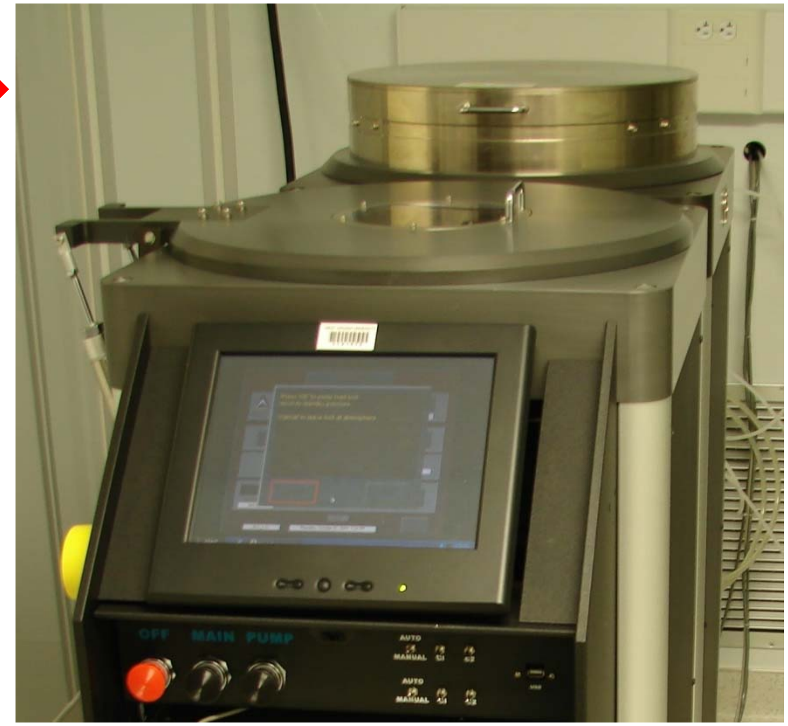
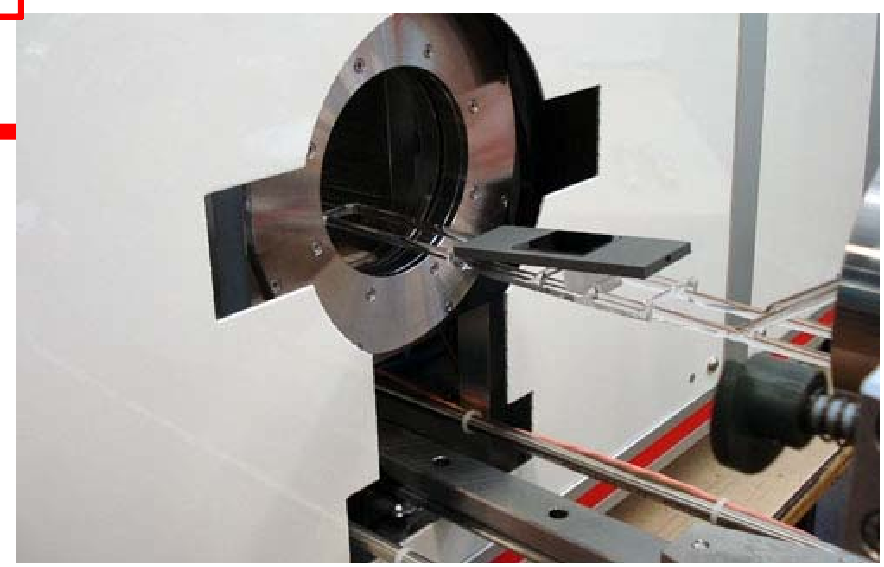
Synthesis Of G/SiC Films

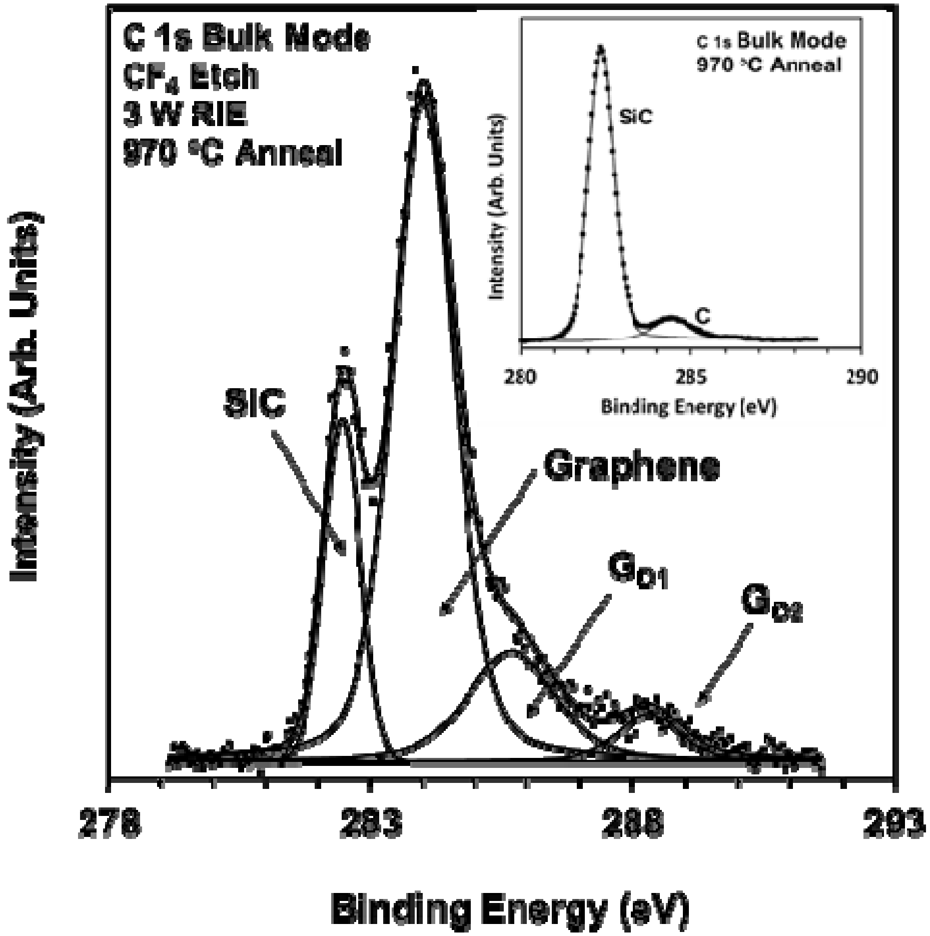


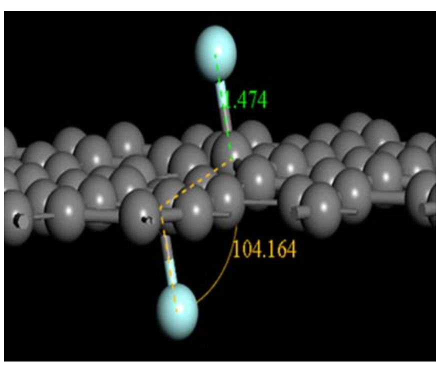


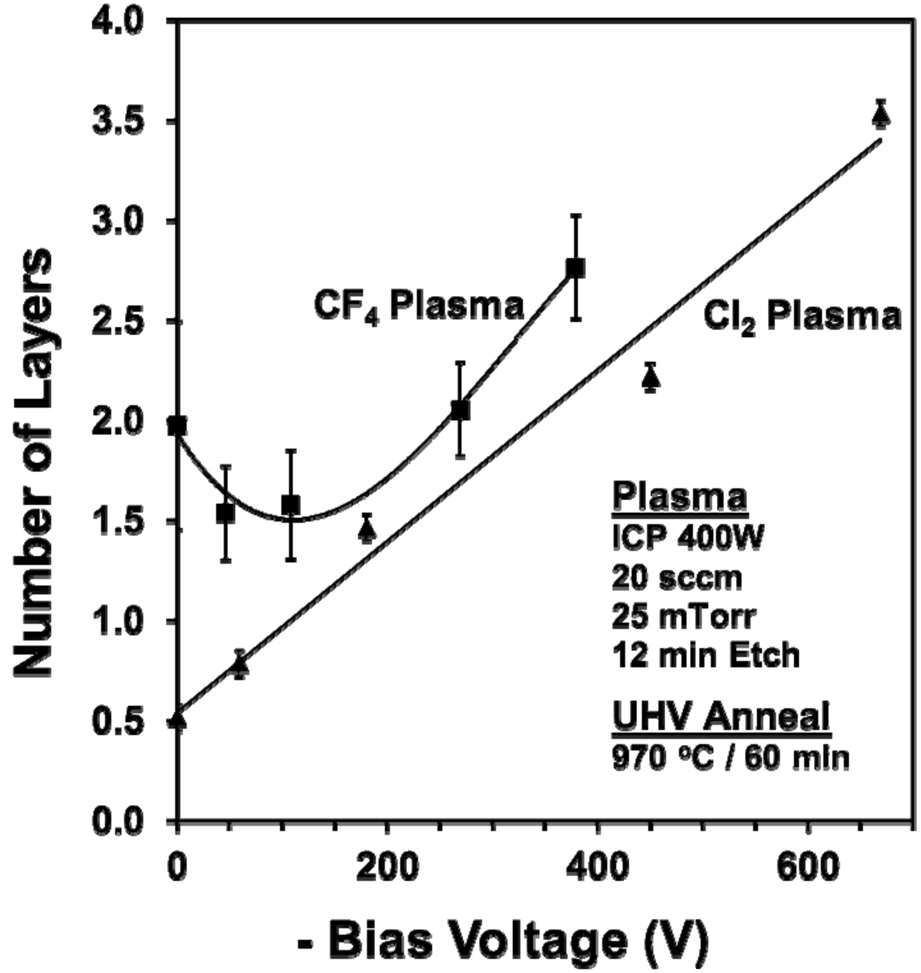


Stinespring & coworkers, *J. Vac. Sci. Technol.* 30 (2012) 030605.

Surface Chemistry of UHVA G/SiC Films



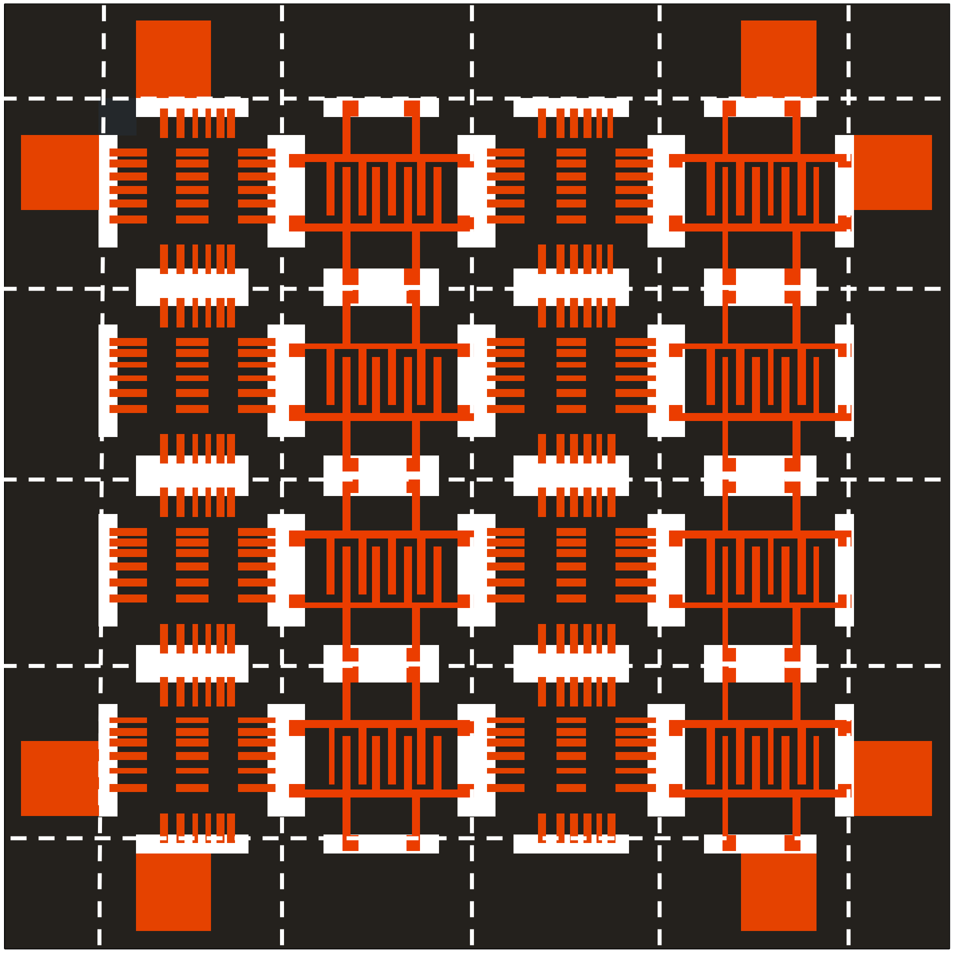




Raghavan, Denig, Nelson, Chaudhari, & Stinespring, *Carbon*, 99 (2016) 212-221.

Duan, Stinespring, & Chorpening, *Chemistry Open*, 4 (2015) 642-650.

Device Fabrication



- Grow uniform graphene film on 1 cm x 1 cm SiC substrate
- Use shadow mask & oxygen ICP-RIE to remove graphene & form SiO_x strips while protecting 2 mm x 2 mm graphene regions
- Use shadow mask and e-beam evaporation to produce Au/Ti device patterns
- Use wafering saw to produce 2.5 mm x 2.5 mm die for testing

- Two different device patterns formed
  TLM pattern – used for measuring electrical properties
  Sensor pattern – used for sensor testing and characterization

Formation of G-nP Composites

Solution based nucleation and growth chemistries

Au, Ag, Pt, Ir nanoparticles studied to date

Typical Reaction Chemistry

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

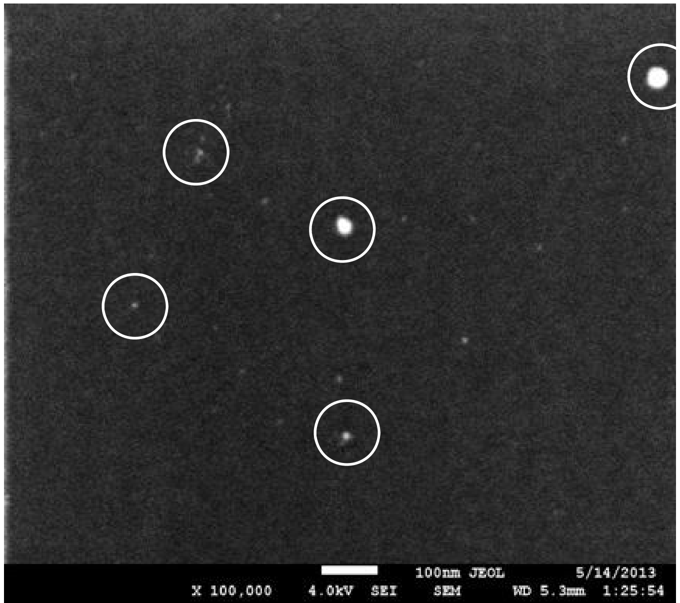
Preparation Sequence

Immerse graphene in ~10mM $AgNO_3/H_2O$

Add reducing agent ~25mM $NaBH_4/H_2O$

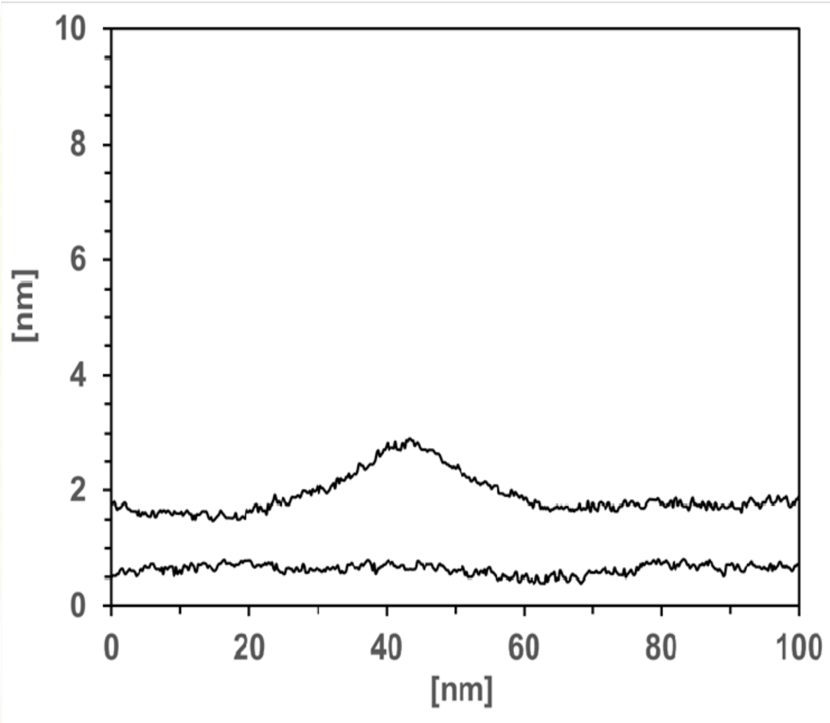
Incubate mixture at room temperature

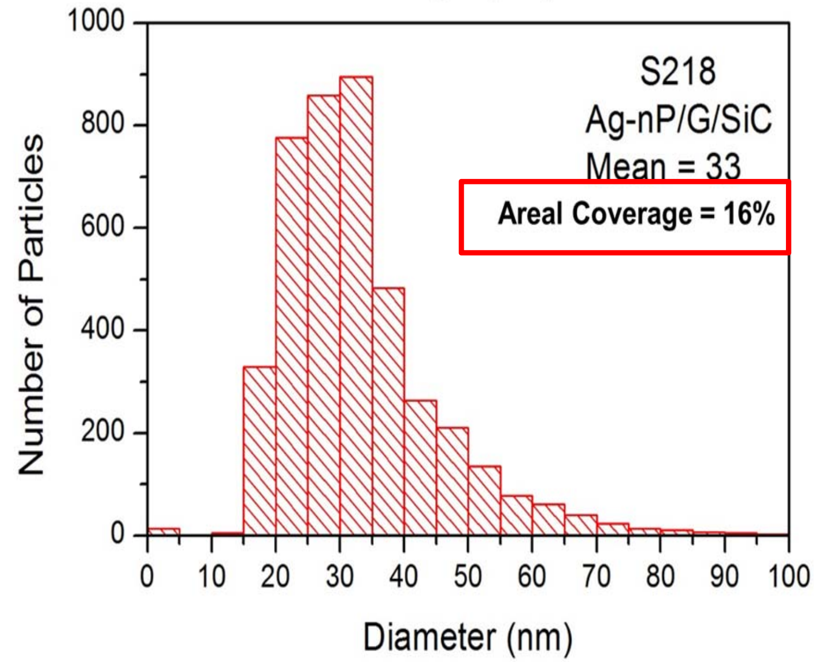
Remove & water wash



After washing

Nanoparticle Nucleation & Growth





- Particles removed by water wash are spheroidal and associated with nucleation in the solution

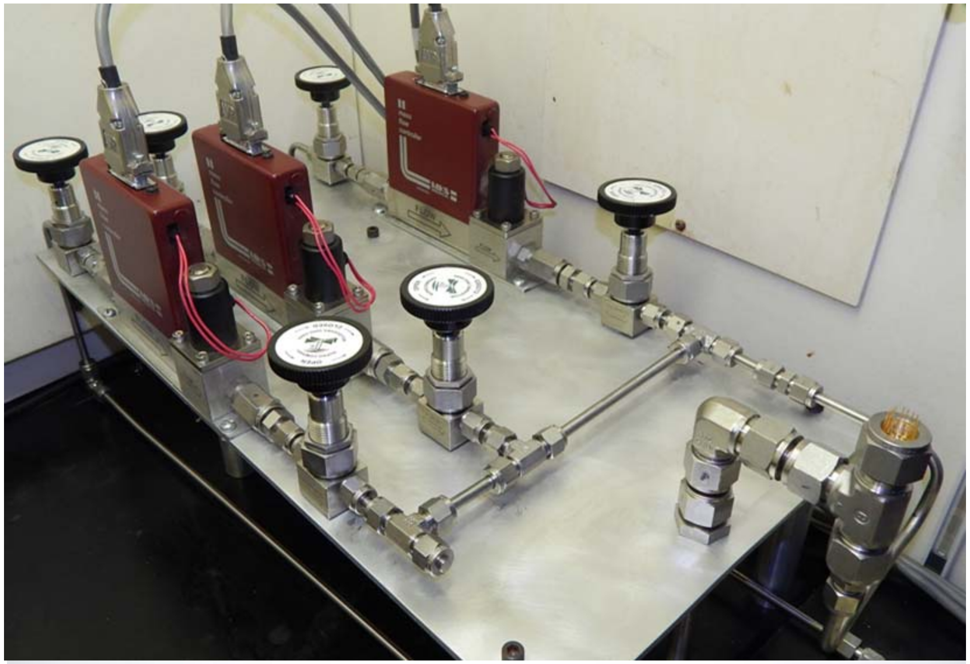
- Attached nanoparticles are pyramidal and associated with heterogeneous nucleation on the surface

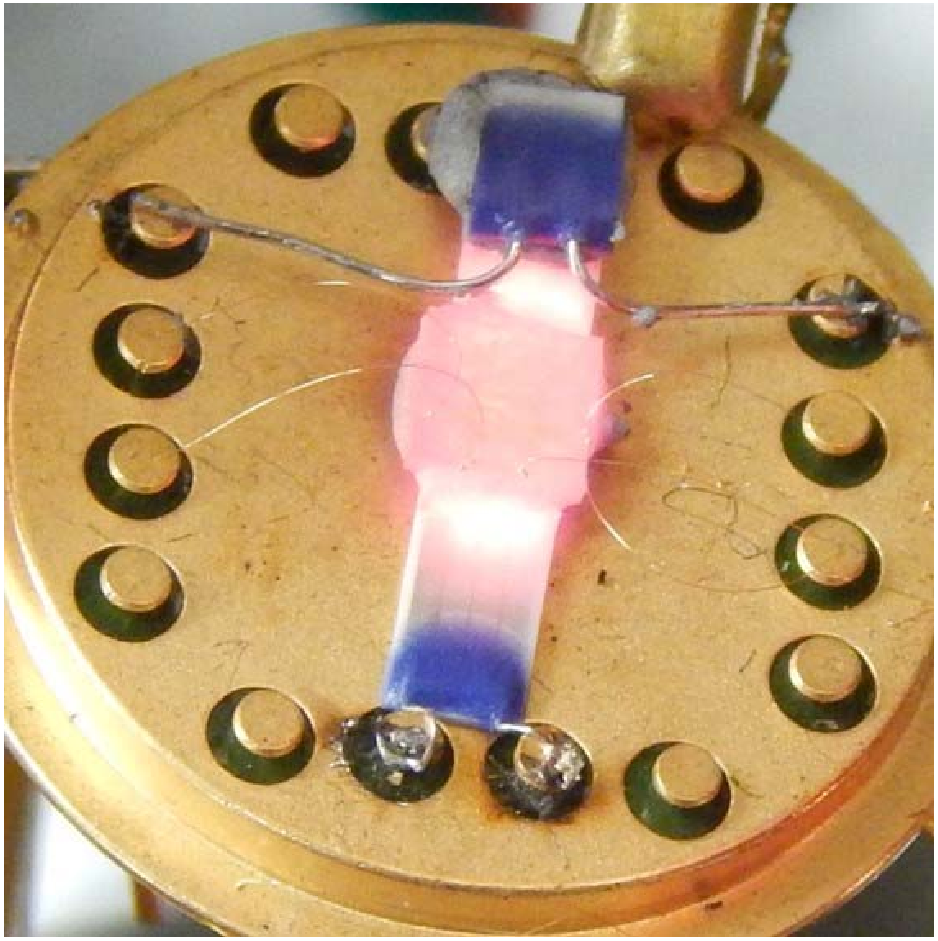
- Shape suggests Volmer-Webber growth

Key Result

Nanoparticle coverage sufficient to modify adsorption characteristics without introducing new conduction channels

Unit #1 Film and Sensor Testing

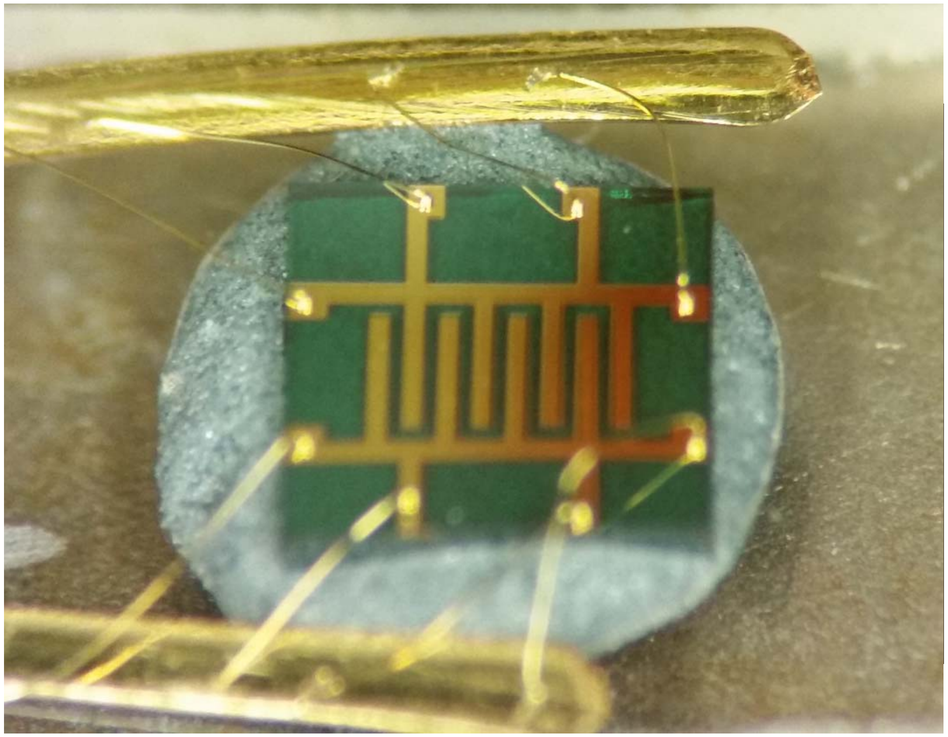




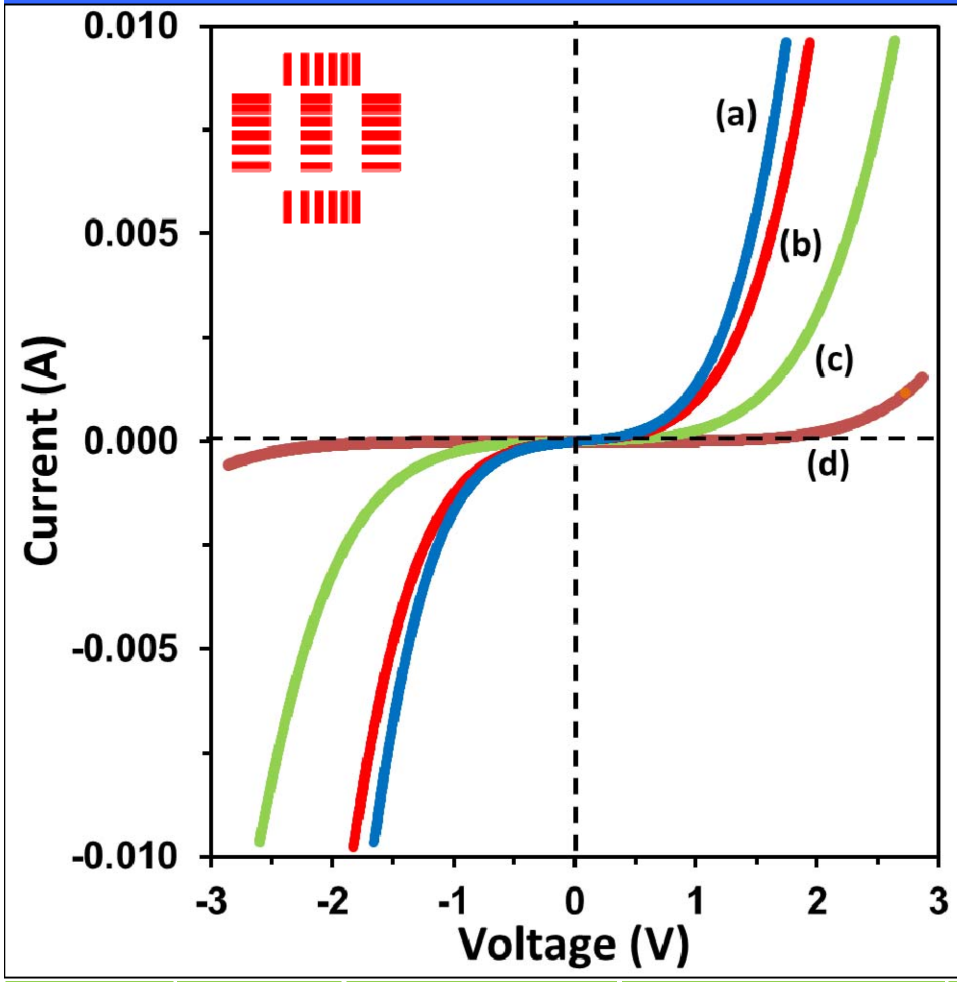
Sensor mounted 16 pin transistor outline header with microheater & RTD for temperature control & readout (Temperatures ≤800 °C)

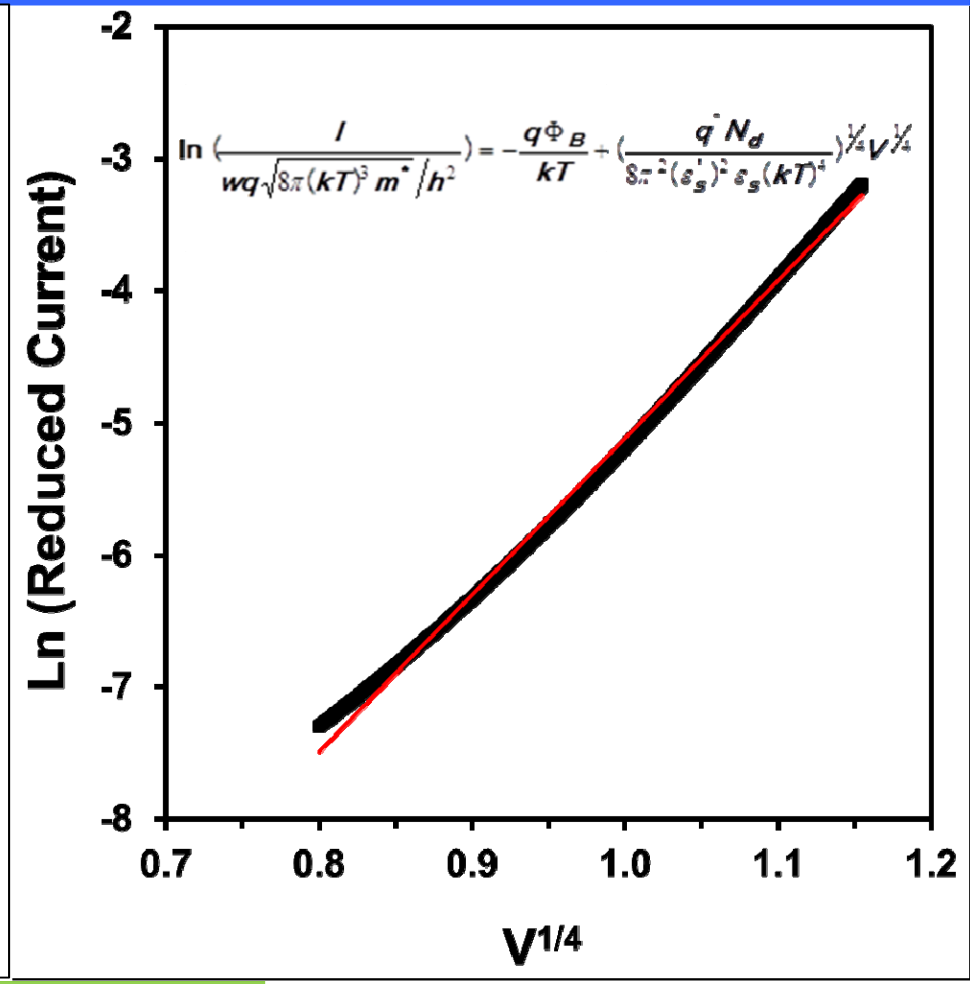
Unit #2 Film and Sensor Testing

- Large thermally stable test bed
- Temperatures to 1000°C+
- Possible to mount & test multiple sensors at the same time



Electrical Characterization of Graphene Films



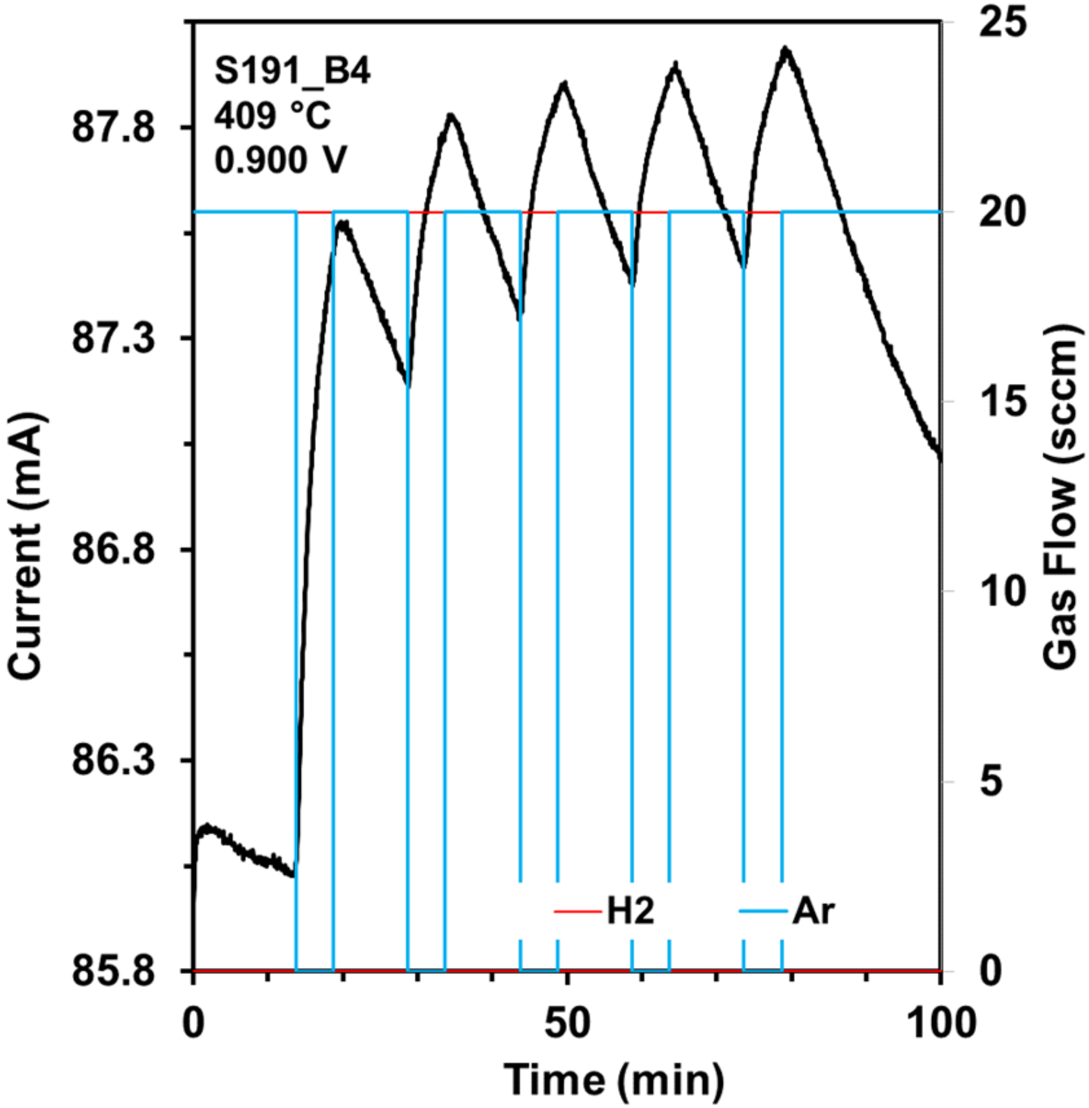


# layers	Φ_b eV	N_d $10^{14}cm^{-2}$	ρ 10^{-6}ohm-cm	μ $cm^2/V\ s$
1	0.52	2.01	1.61	665.3
2	0.51	3.26	0.19	377.5
3	0.56	5.75	0.08	176.5

Graphene produced by mechanical exfoliation

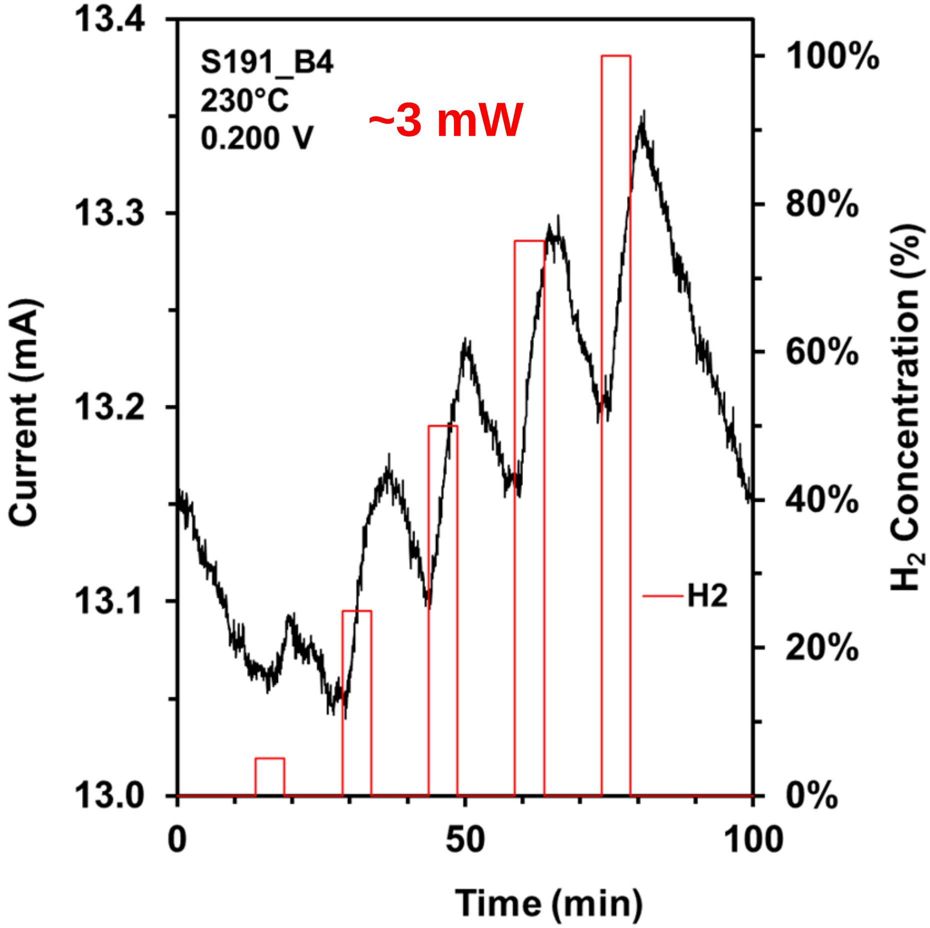
Reduced graphene oxide by chemical exfoliation

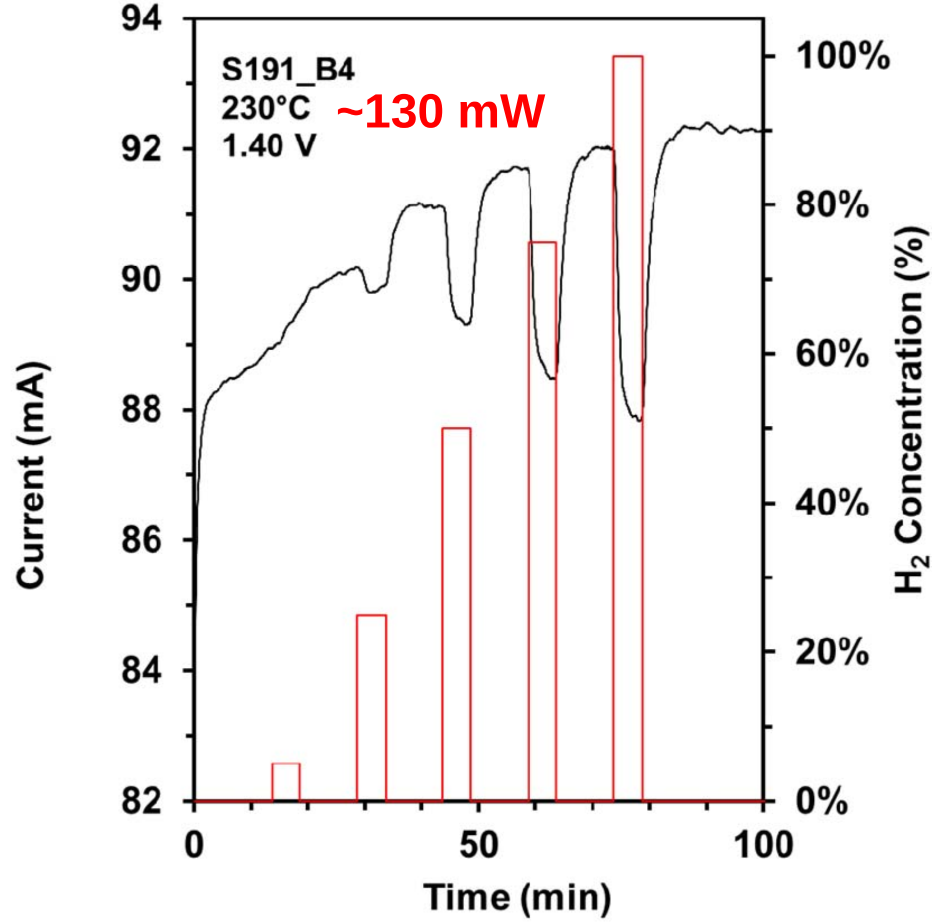
Characterization Graphene Sensors



- Effects of temperature
- Effects of composition
- Response to different gases
  - H_2 – Ar response
  - CO – Ar response
  - H_2 – CO response
- Pulse test
  - Rapid response
  - Slower decay

Chemical & Thermal Response Regimes

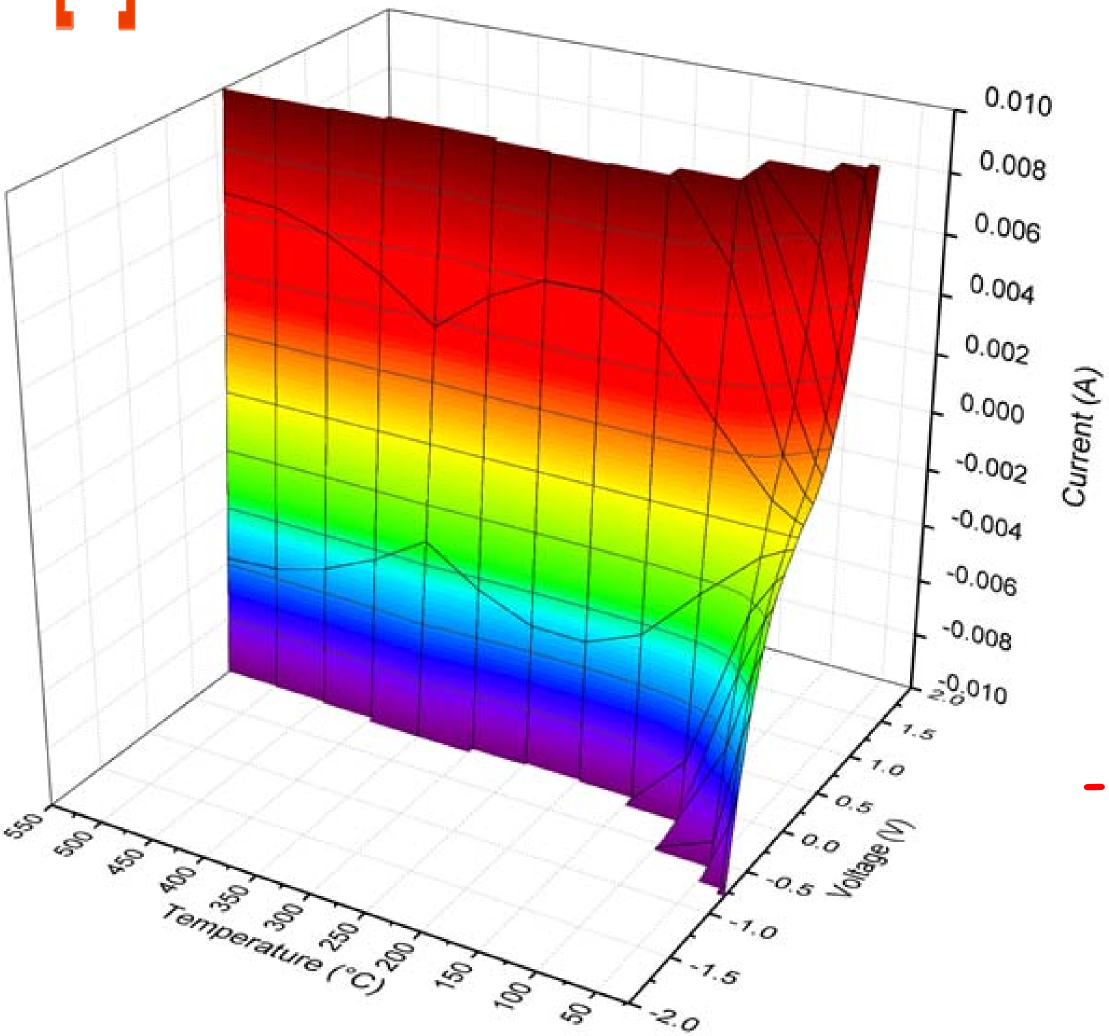




Switch between chemical and thermal response regimes by controlling operational power level

Possibility of measuring both composition & flow characteristics using same sensor

Characterization of G-nP Composite Sensors



- Fundamental differences in adsorption characteristics

- Significant differences in IV characteristics

  Graphene

  Ag n-P composite

-Key Result

Differences in electrical characteristics and gas response provide a basis for electronic nose development

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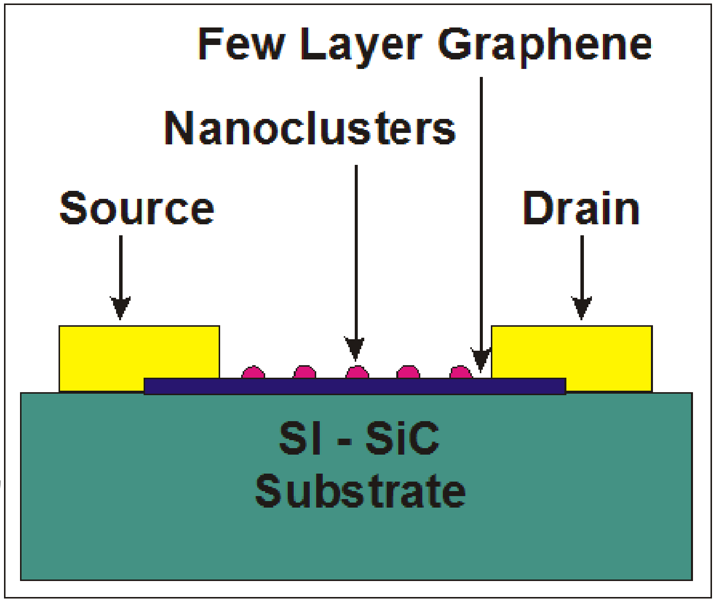

- ✓ Controllable graphene synthesis process developed
- ✓ Solution based nucleation & growth chemistries used to form G-nP composite films
- ✓ Graphene & G-nP composite sensors fabricated

Characterization and Testing

- ✓ Graphene electrical properties & gas response characterized to ~800 °C for H_2 and CO
- ✓ G-nP composite electrical properties characterized to ~600 °C
- ❑ Characterize graphene & G-nP gas response to ~1000 °C in progress
- ❑ Characterize response to additional gases

Future Directions

- Continue development of electronic nose
- Extend to liquids (electronic tongue)
- Continue optimization of graphene quality
- Explore other applications (e.g., FET)
- Continue development of theoretical understanding of the G-SiC interface and defect structures

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PhD Students

- Saurabh Chaudhari – Graphene synthesis & sensor fabrication (grad Dec 15)
- Andrew Graves – Sensor characterization

Undergrad Students

- Megan Cain – AFM Characterization / Particle nucleation and growth
- Jason Miles - Particle nucleation and growth (grad May 14)
- McKenzie Mills – Surface modification (grad May 14)

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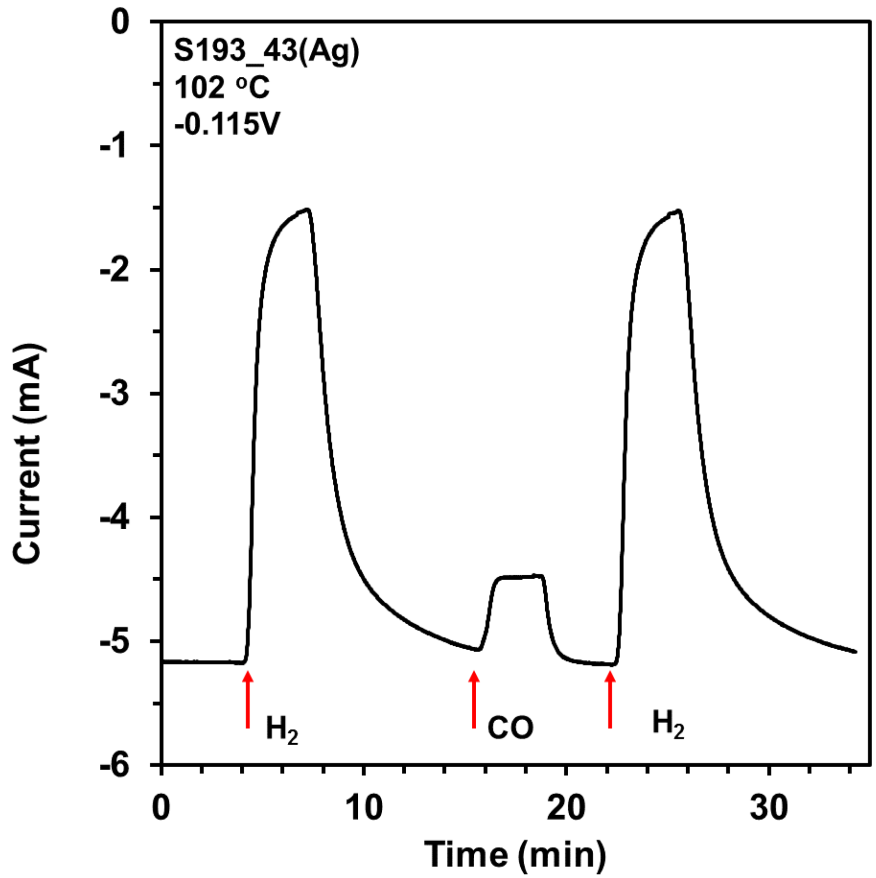
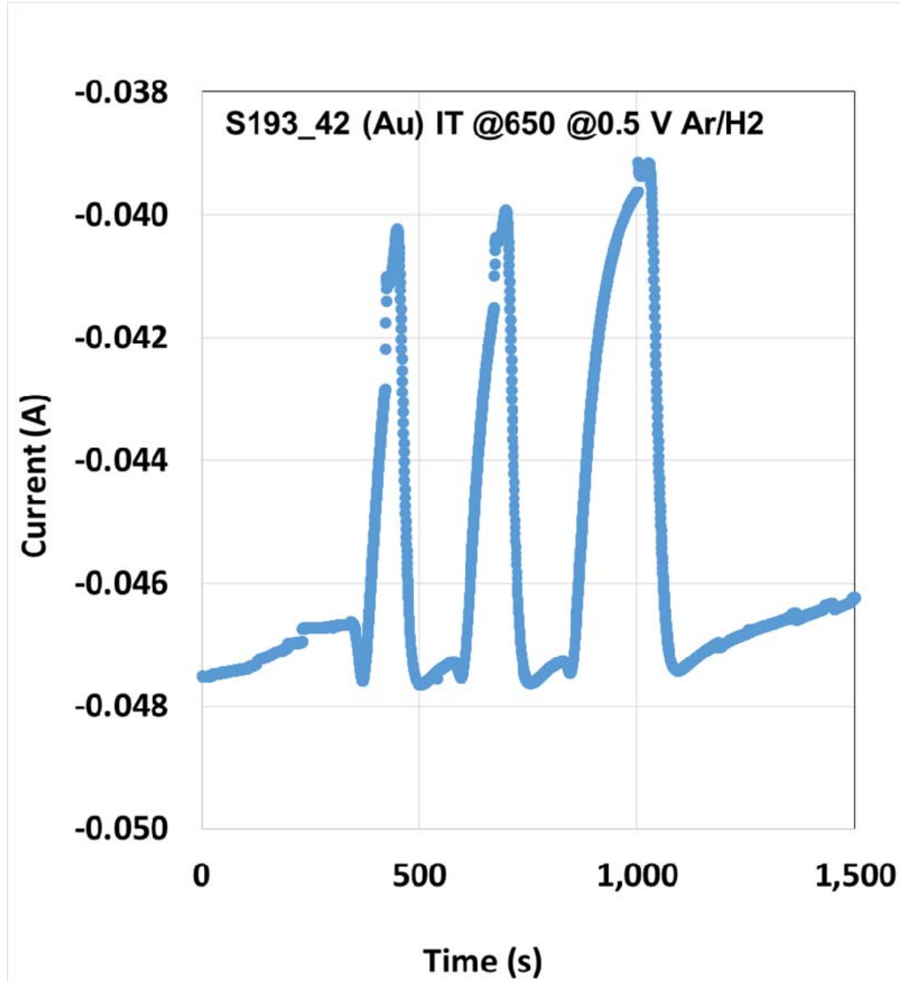
- Kolin Brown, Harley Hart, Weiqiang Ding & Trina Wafel


S193_43(Ag)
102 °C
-0.115V
Current (mA)
Time (min)
H2
CO
H2
0
-1
-2
-3
-4
-5
-6
0
10
20
30


S193_42 (Au) IT @650 @0.5 V Ar/H2
Current (A)
Time (s)
-0.038
-0.040
-0.042
-0.044
-0.046
-0.048
-0.050
0
500
1,000
1,500