



Bimetallic Alloys for Surface Modification of Metal- Insulator-Semiconductor (MIS) Gas Sensors

Steve Marshall

Robert Bastasz

J. William Medlin

University of Colorado

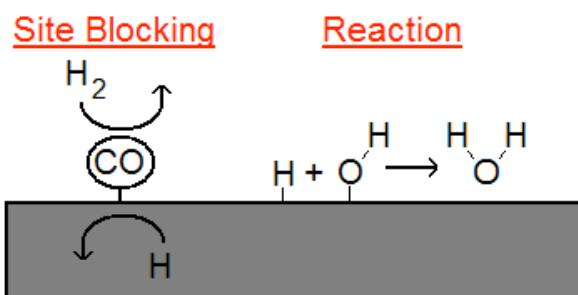
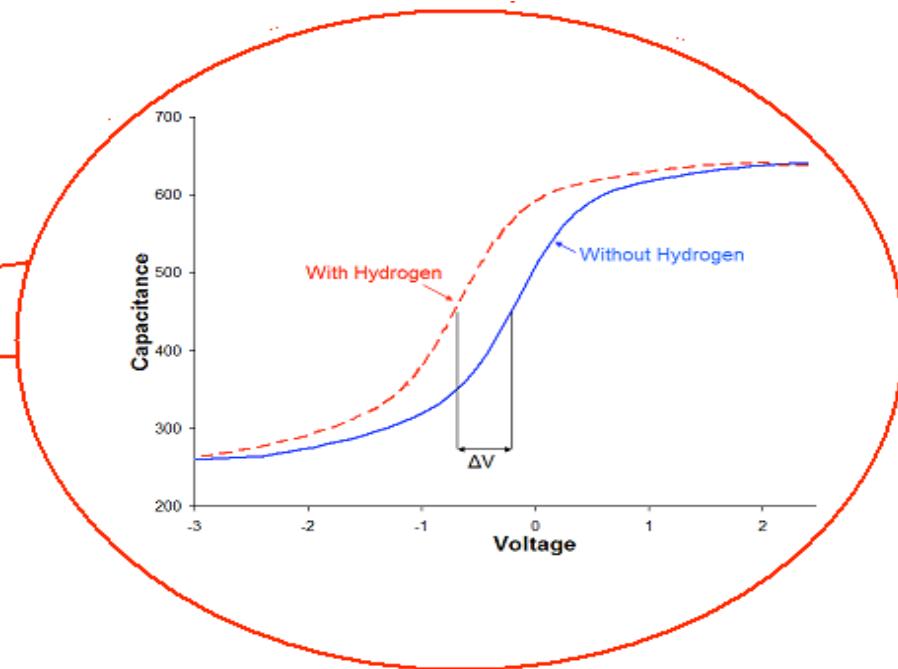
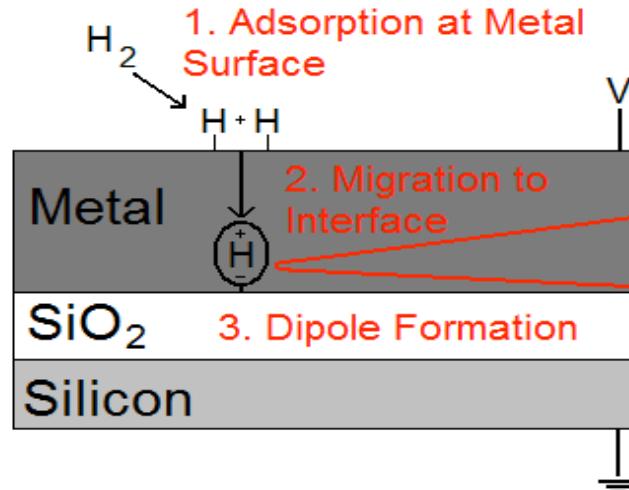
Department of Chemical Engineering

Sandia National Labs

Micro and Interfacial Sciences



MIS Sensors are Highly Sensitive Hydrogen Detectors



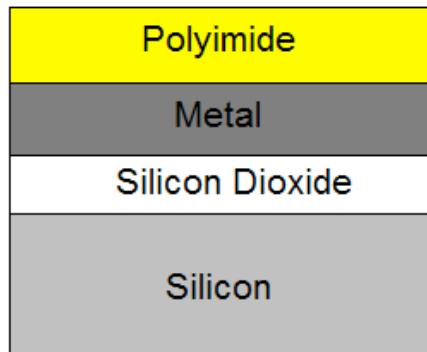
- MIS Sensors are sensitive to hydrogen for over 10 decades of hydrogen pressure¹
- Numerous applications include gas sensing in transformers, fuel cells, and hydrogen plasmas
- However, limited selectivity has stalled industrial implementation

1. Johansson et al. *J Appl Phys.* **84**, 1998, 44.

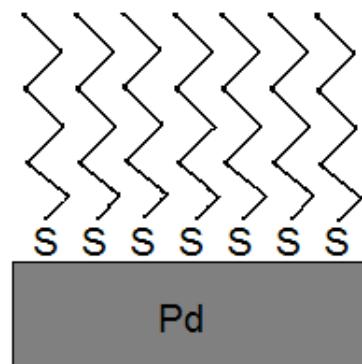


Coating Strategies for MIS Sensors

Polyimide Membranes



- Polyimide membranes exclude effects from hydrocarbons and carbon monoxide
- Effect is primarily diffusion based¹



Self-Assembled Monolayers

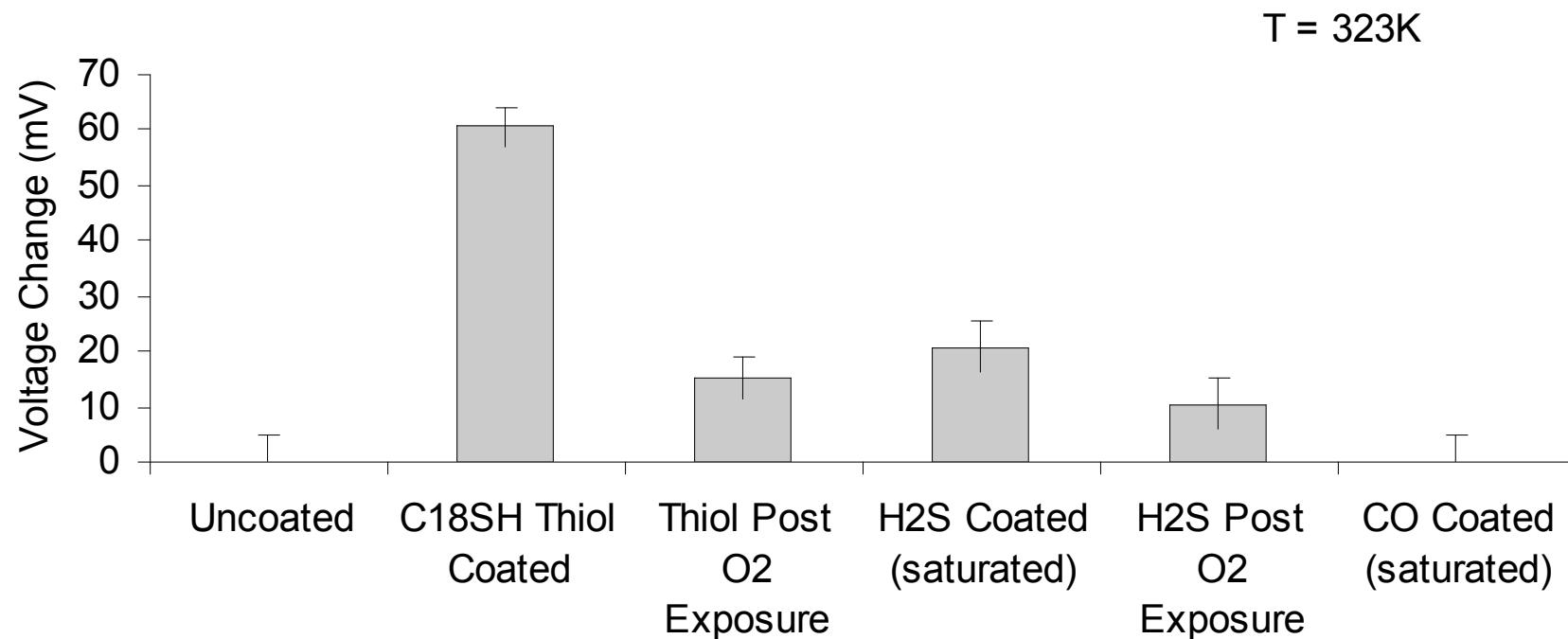
- C_nSH thiols form self-assembled monolayers (SAMs) on metal surfaces
- SAMs' tail group can serve as a platform for additional chemistry

1. Li et al. *Sens Act B. 115, 2006*, 86.



Self-Assembled Monolayers Functionalize MIS Sensors

**Voltage Change on Addition of 400ppm Acetylene with
H₂ Background**

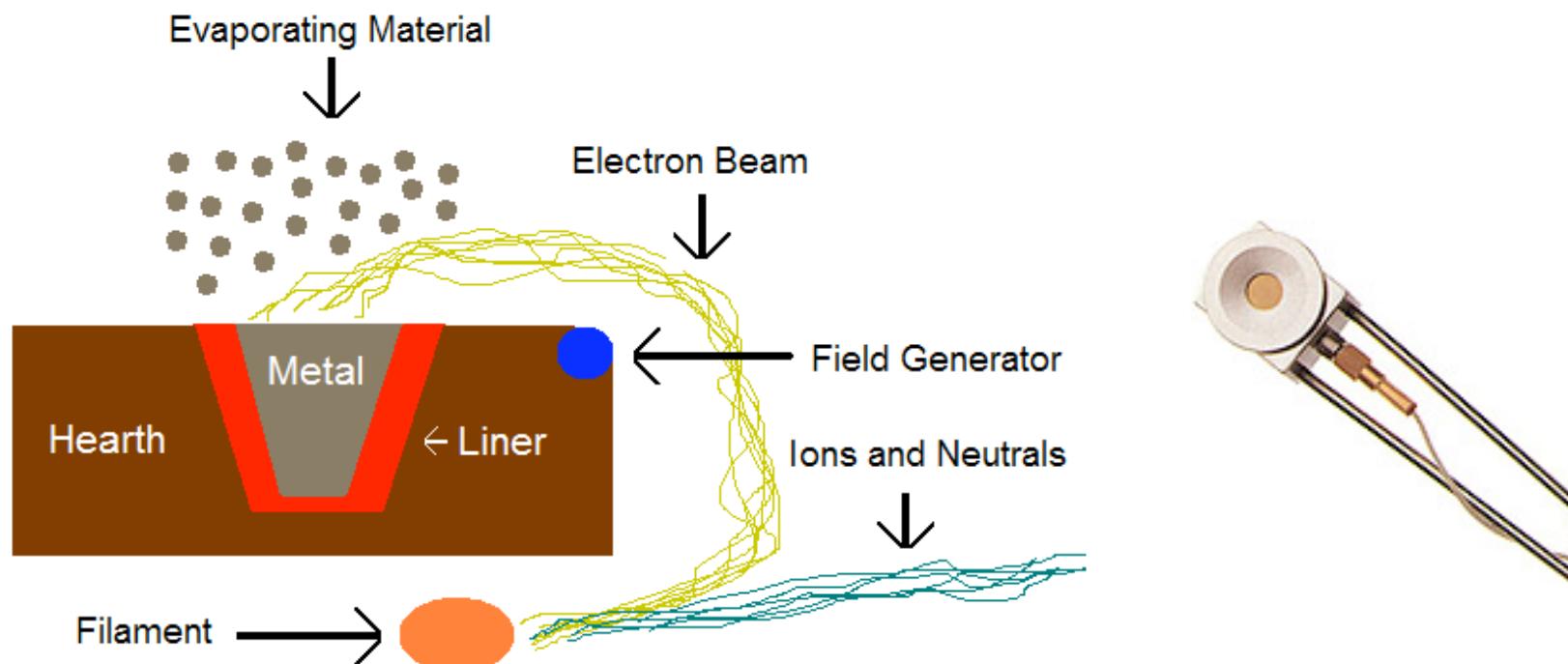


Preventing Oxidation May Lead to a Robust Acetylene Detector
→ Bimetallic Alloys



Bimetallic Alloys Allow for Sensors With Unique Properties

- Alloys can incorporate individual properties of both metals or create new electronic structures
- Deposited through electron beam evaporation





Recent Work Allows Rational Alloy Selection

Pd / Ag

- Silver is used as a promoter for industrial acetylene hydrogenation¹
- SAMs deposited on silver resist oxidation better than palladium²

Pd / Au

- Low weight percent gold alloys show heightened response to catalytic activities with sulfur⁵

1. Khan et al. *Cat. Let.* **108**, **2006**, 159.

2. Love et al. *J. Am. Chem Soc.* **125**, **2003**, 2597.

3. Kulprathipanja et al. *J Mem Sci.* **254**, **2005**, 49.

4. Ruban et al. *Phys Rev B.* **59**, **1999**, 15990.

5. Venezia et al. *J Catalysis.* **215**, **2003**, 317.

6. Medlin et al. *J Phys Chem B.* **107**, **2003**, 217.

Pd / Cu

- Palladium-copper alloys resist restructuring under sulfur³
- SAMs deposited on copper resist oxidation better than palladium²
- Copper alloys very well with palladium⁴

Pd / Ni

- Tightly binds acetylene and hydrocarbons⁶
- Recent DFT studies suggests Pd/Ni alloys may improve acetylene vs ethylene hydrogenation selectivity⁷

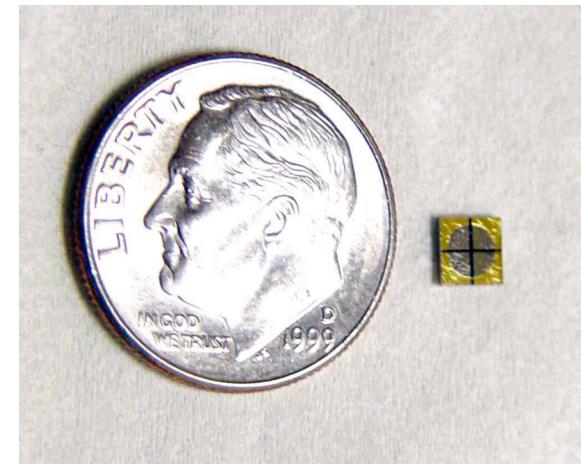
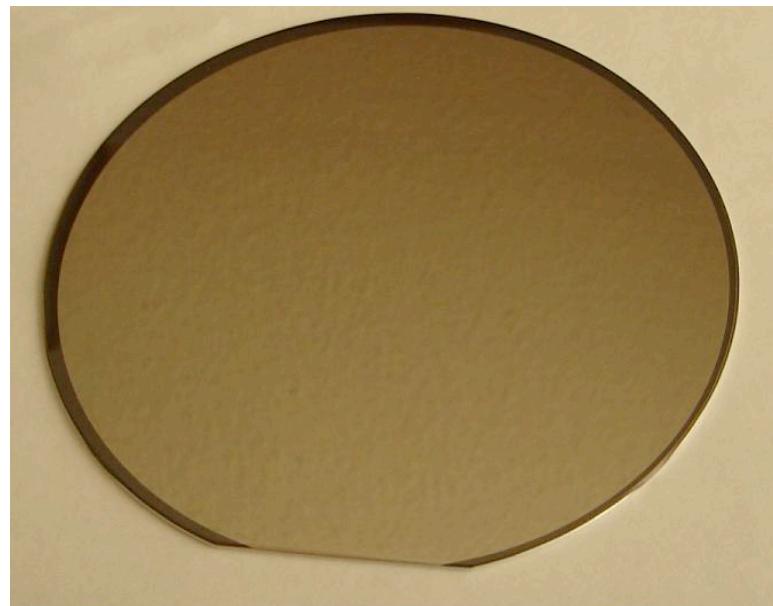
7. Goda et al. *J Phys Chem B.* **110**, **2006**, 11823.



Sensors Prepared

Wafer	Metal 1	wt %	Metal 2	wt %
1	Pd	100	-	0
2	Pd	40	Ni	60
3	Pd	60	Ni	40
4	Pd	85	Ni	15
5	Pd	95	Ni	5
6	Pd	60	Ag	40
7	Pd	85	Ag	15
8	Pd	95	Ag	5
9	Pd	60	Au	40
10	Pd	85	Au	15
11	Pd	95	Au	5
12	Pd	60	Cu	40
13	Pd	85	Cu	15
14	Pd	95	Cu	5

All sensors are 50 nm thick and have ohmic contacts placed on both the metal and silicon sides



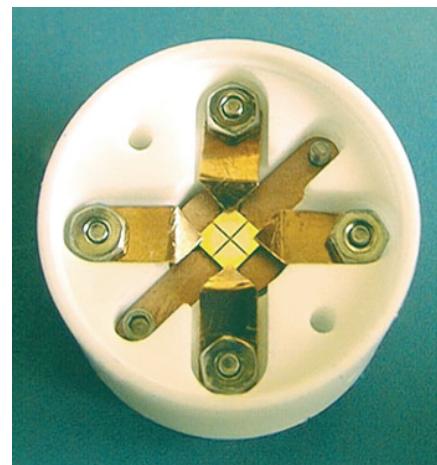


Conclusions and Ongoing Work

- Limitations in selectivity have prevented widespread implementation of MIS sensors
- Coatings and alloys may improve MIS sensor selectivity
- Sensors prepared at Sandia will be tested with a variety of techniques at the University of Colorado at Boulder

Acknowledgements:

Josh Whaley, Esther Wilcox, Kevin Donahoe, Keith Beers, Amanda Parker



QUESTIONS?



H₂S Increases Acetylene Response in MIS Sensors

