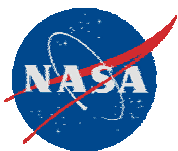


Acoustic Wave Sensors for Hydrogen and Other Gases

Faculty: Venkat R. Bhethanabotla and Babu Joseph
Students: Stefan Cular, Randy Williams, Ling Miao,
Subramanian Sankaranarayanan, Krishnan Srinivasan,
Jackie Shepard and Heather Latham
University of South Florida

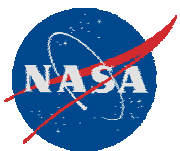
Start Date = Second quarter, 2003

Planned Completion = Fourth quarter, 2006



Research Goals and Objectives

- Develop surface acoustic wave hydrogen sensor at technology readiness level 3-5
 - Room temperature operation
 - Response and recovery times on order of seconds
 - Robust, repeatable, reproducible and inexpensive
- Realize necessary advances in
 - SAW devices
 - Nanomaterial sensing films
 - Theoretical methods to guide these two
- Apply above device and material development to other sensors
 - High frequency TSM hydrocarbon sensor
 - Hexagonal SAW sensor for hydrogen and other gas/vapor applications
 - Hexagonal SAW sensor in liquid phase applications

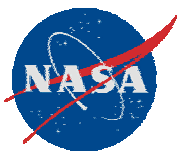


Relevance to Current State-of-the-Art

- Room temperature operation
- Faster responding and recovering
- Repeatability improvement with nanomaterial sensing layers
- Sensitivity improvement with nanomaterial sensing layers
- Selectivity improvements with hexagonal devices
- Easy adaptability to other gases and liquids with different sensing materials

Relevance to NASA

- Sensitive, selective & fast responding hydrogen (and other gas/liquid) sensors
- Robust, low power, smart sensors capable of self-correction for long-term missions



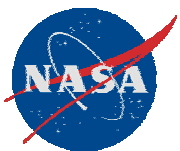
Budget, Schedule and Deliverables

Budget: Year 1: 60,000; Year 2: 100,000; Year 3: 100,000
(including 45% USF overhead)

Year 4: 150,000 (requested)

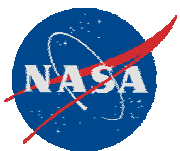
Schedule and Deliverables

ID	SAW Hydrogen Sensor	2002	2003					2004				2005				2006			
		Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	
1	SAW device design and fabrication																		
2	RF test-bed construction																		
3	Nano-Pd and alloy sensing material development and synthesis																		
4	Oscillator circuit for field device																		
5	Sensor testing in test bed and test-bed improvement																		
6	Extensive laboratory-bench testing																		
7	Packaging and field device development																		
8	Modeling studies																		
9	Proposals, presentations and papers																		



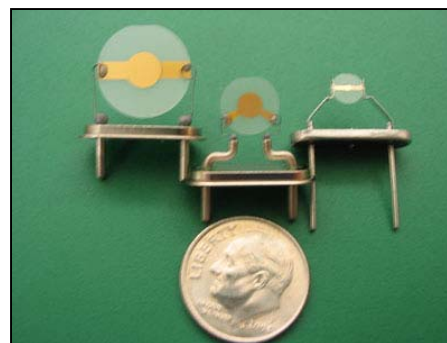
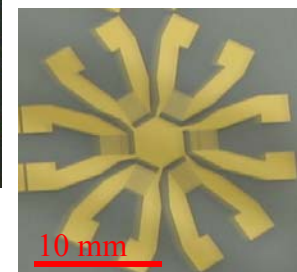
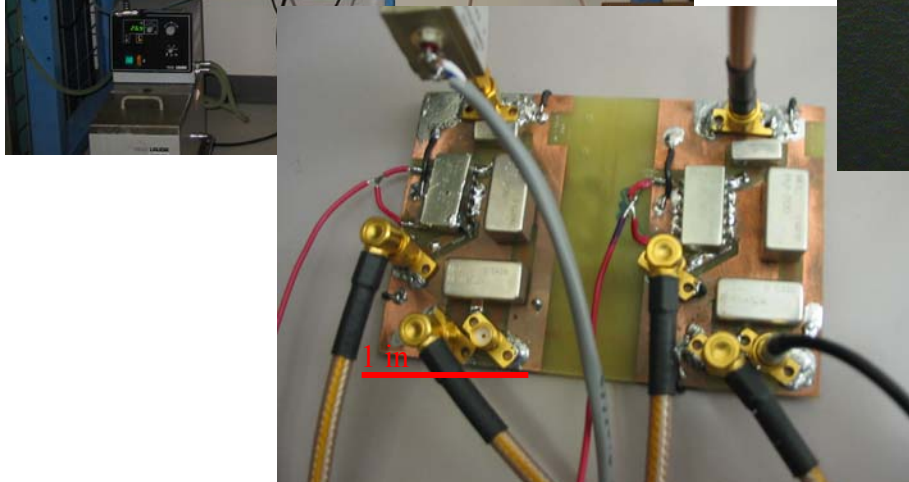
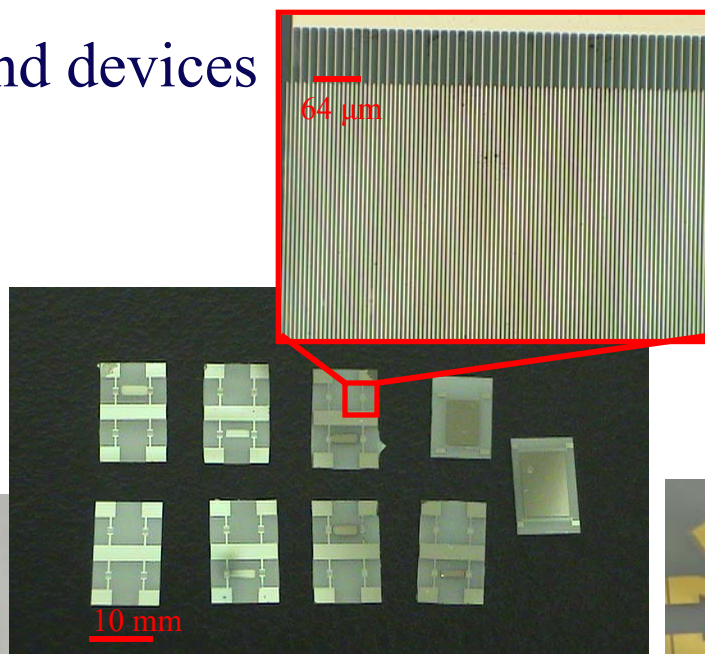
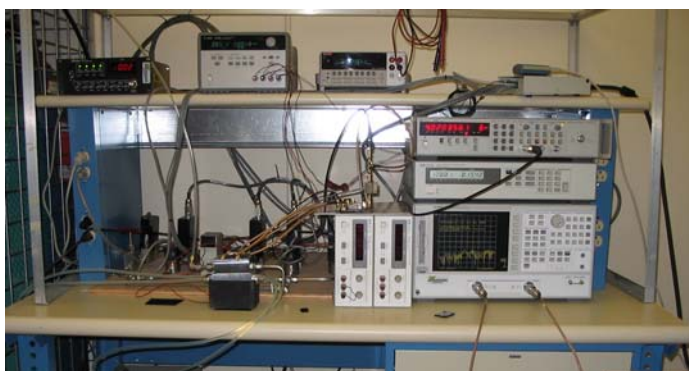
Anticipated Technology End Use

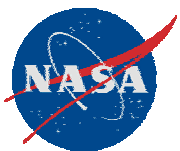
- Hydrogen sensors for leak detection in space shuttle operations
- Hydrogen sensors for leak detection in terrestrial hydrogen applications such as fuel cells, automobiles, and fueling stations
- SAW and TSM sensors in gas, vapor and liquid sensing applications, such as for leak detection, process concentration monitoring, chemical and biological agent detection, medical diagnostics and environmental monitoring



Results – H₂ Sensor

RF test-bed, oscillator circuit, and devices

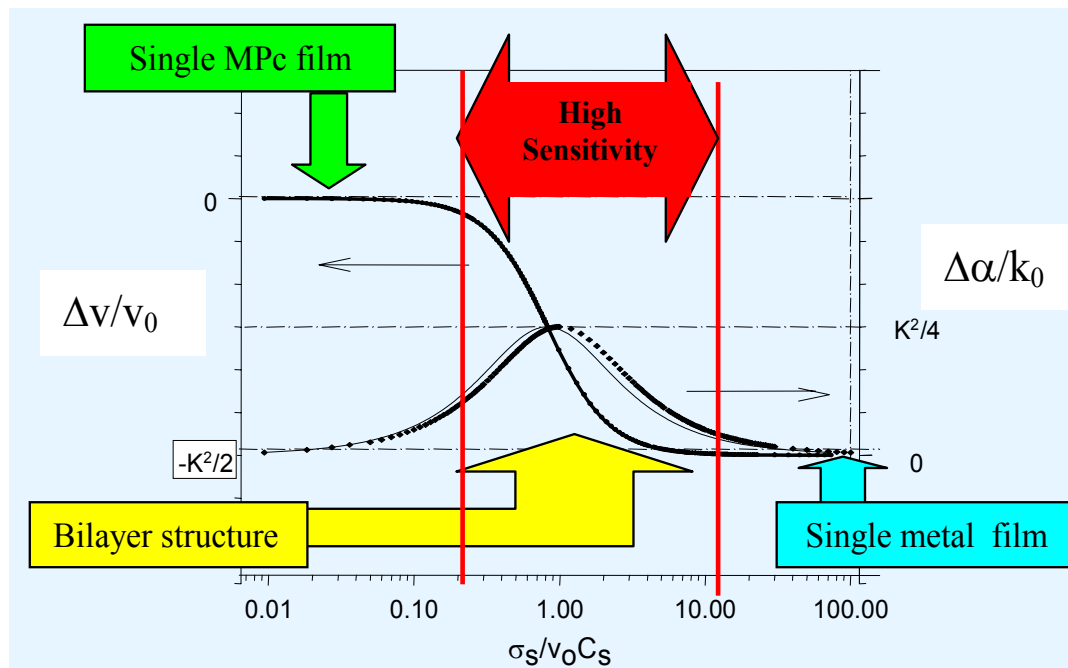


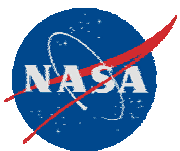


Results – H₂ Sensor

Bilayer sensing structure of metal-free phthalocyanine and nanomaterial Pd

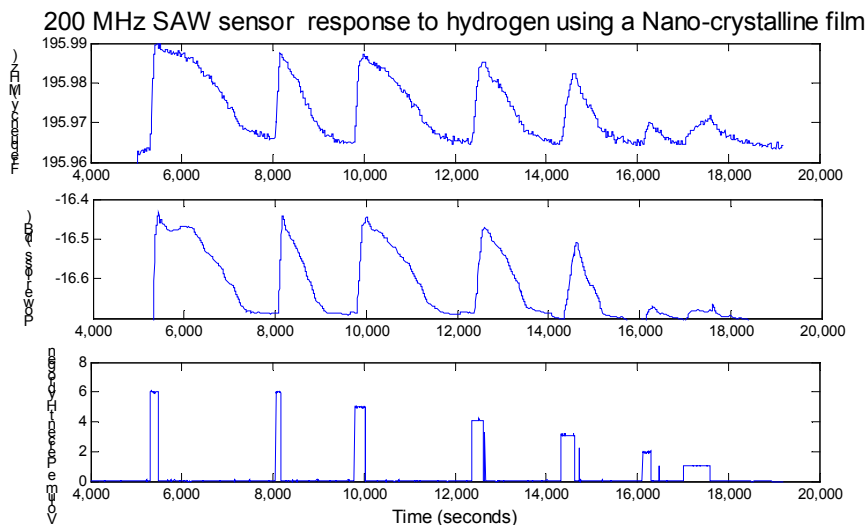
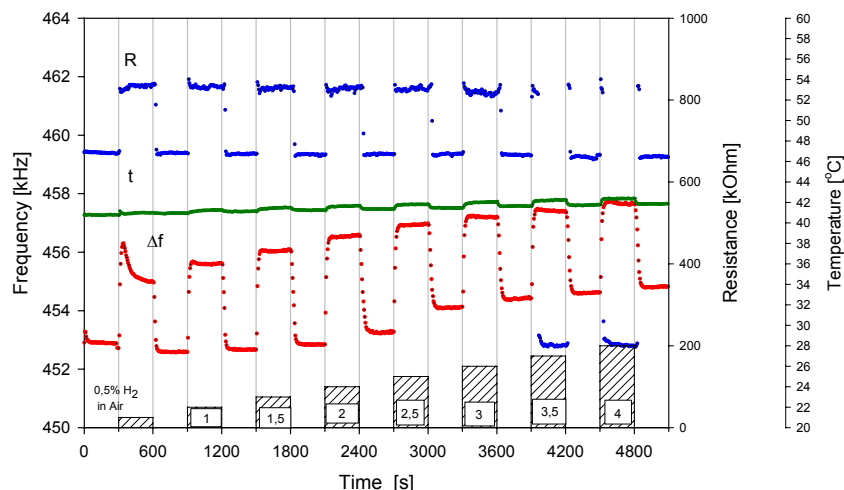
- Optimization of electro-acoustic response mechanism for larger signal by manipulating sheet conductivity

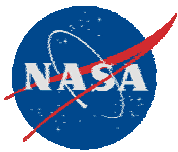




Results – H₂ Sensor

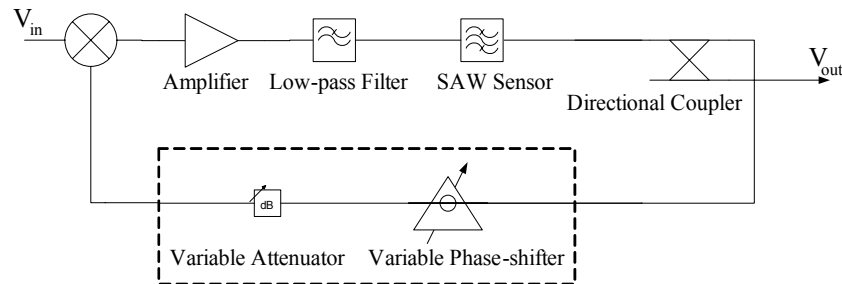
- 3 kHz shift to 3% H₂
 - 120 nm H₂Pc
 - 20 nm Pd
 - 41 °C
 - 1000 sccm
- 40 kHz shift to 4% H₂
 - 115 nm H₂Pc
 - 200 nm Pd
 - 30 °C
 - 1000 sccm
 - In air



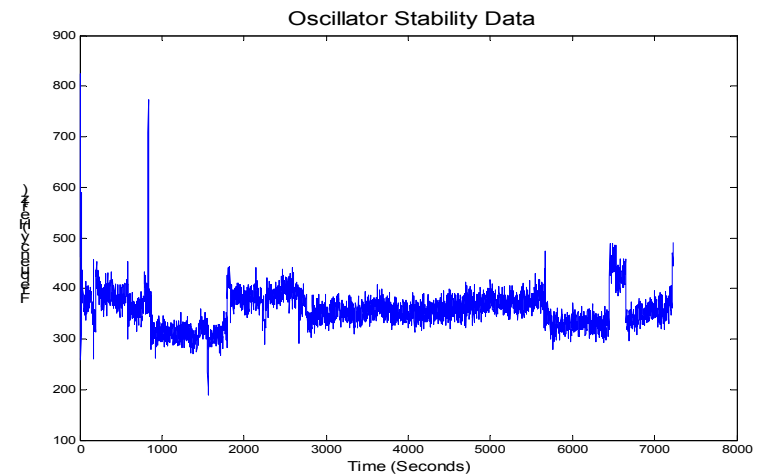
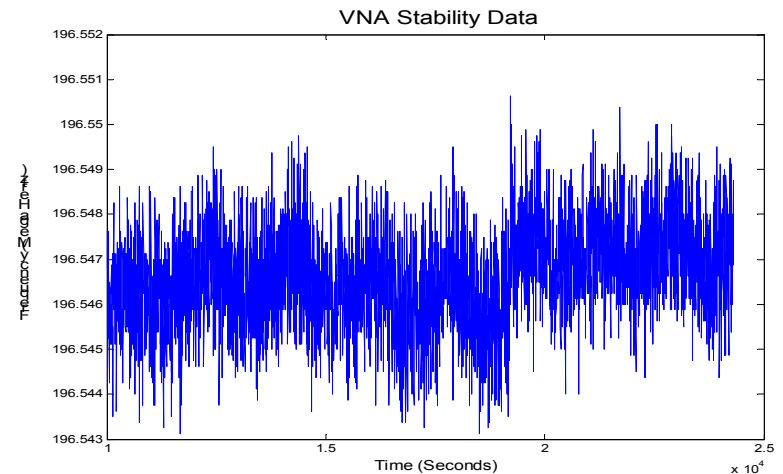


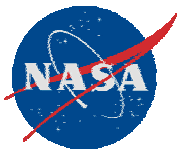
Results – H₂ Sensor

Oscillator circuit for field device and improved stability for dual delay-line



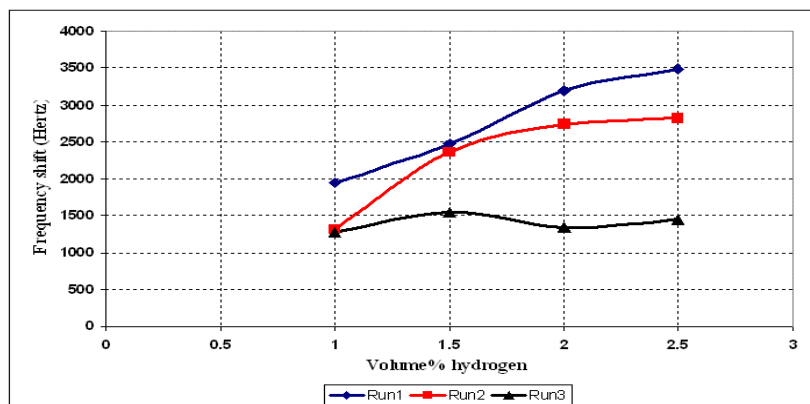
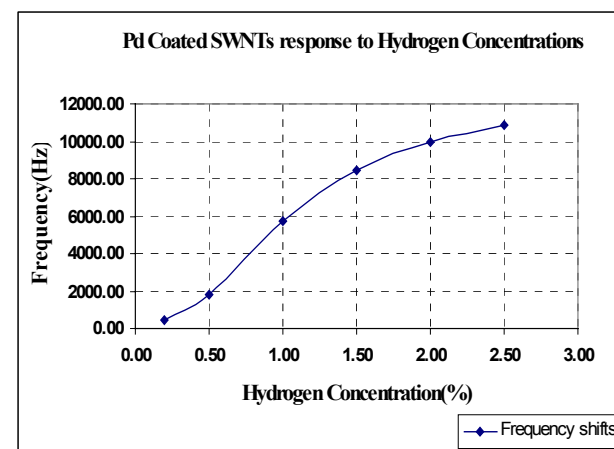
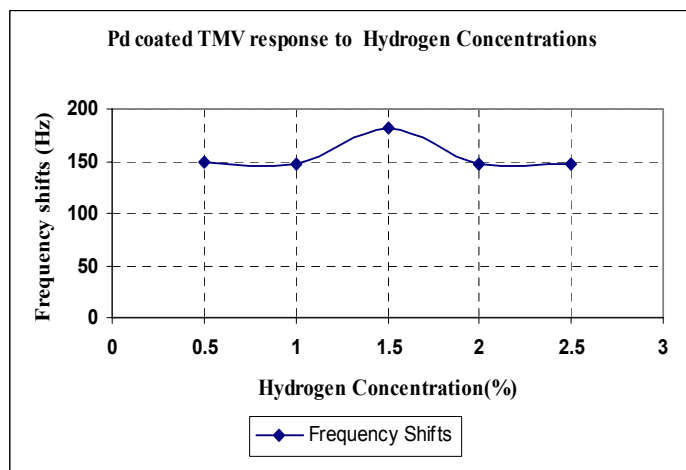
- 5 kHz Noise on test system at beginning
- 40 Hz noise through optimization



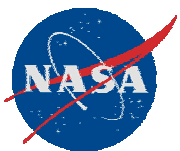


Results – H₂ Sensor

Comparison – Pd-TMV, Pd-SWNT, and Pd film – 315 MHz resonator with SiO₂ layer

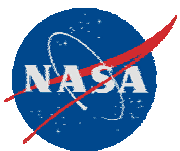


- Frequency shifts independent of concentration for Pd-TMV
- Large, concentration dependant shifts for Pd-SWNT
- Film degradation for pure Pd



Summary - Hydrogen Sensor Development

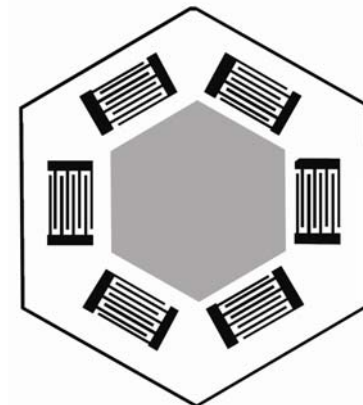
- Optimized bilayer films show huge electro-acoustic response
- Nanomaterial sensing layers show promise at improving response
- Pd-SWNT layers show the most promise with 3x response resolution compared to pure Pd films in mass loading experiments
- Nanomaterial films show much better robustness
- Pd-TMV response is an unexplained increase of frequency



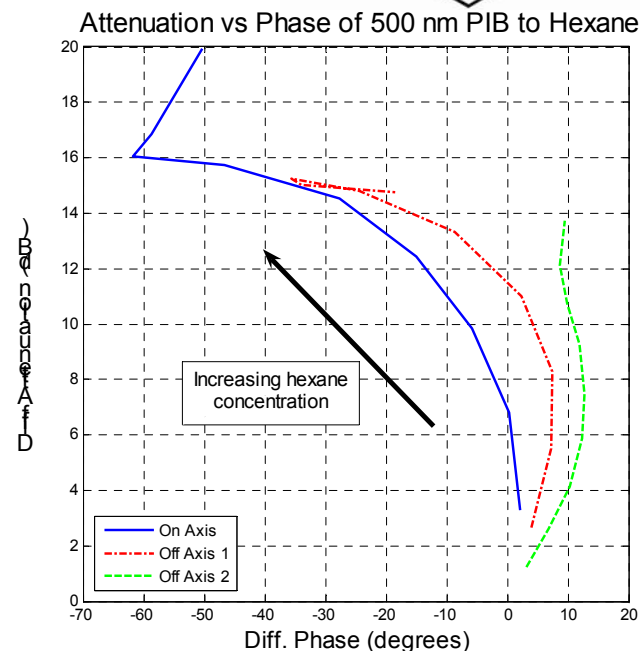
Results – Other sensors Hexagonal SAW Device

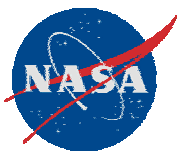
- Results indicate unique and signature-type responses to adsorbed vapors in PIB films

- Our Hexagonal SAWs permit multi-parameter extraction without the need for sequential measurements



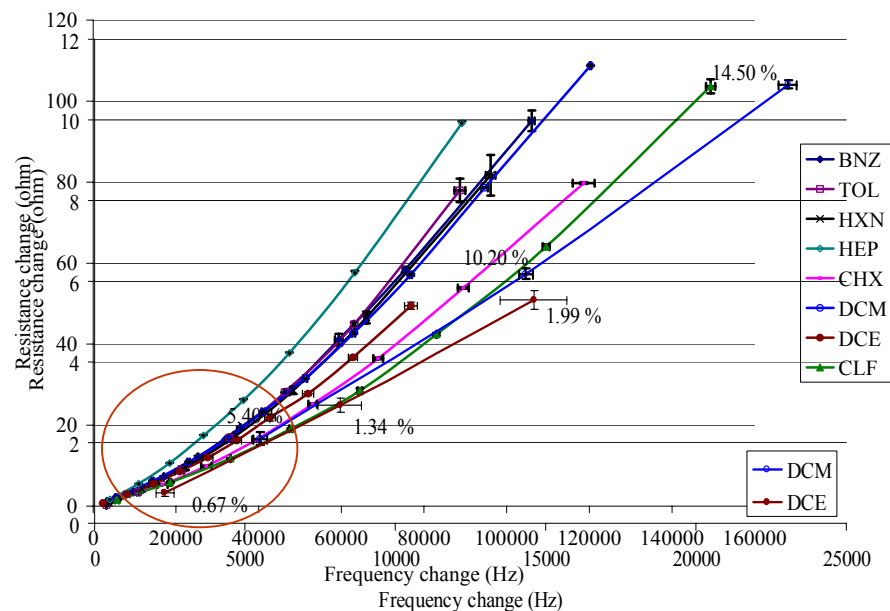
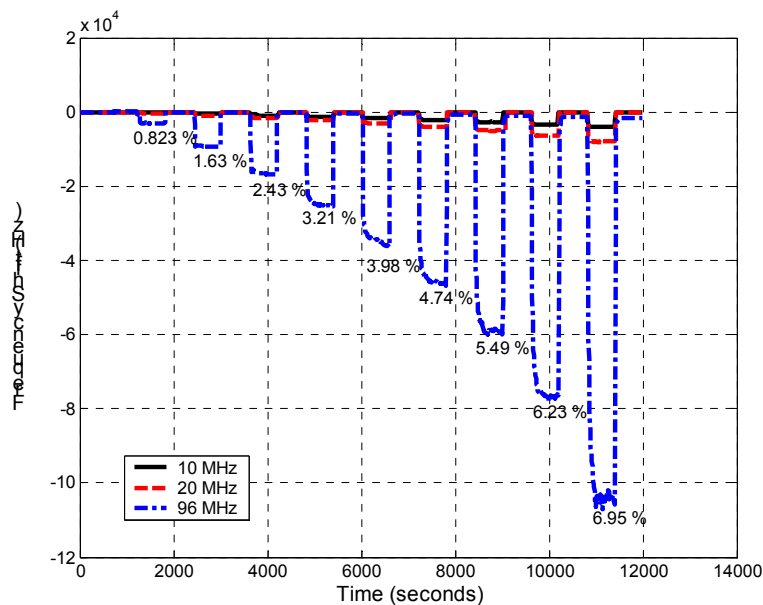
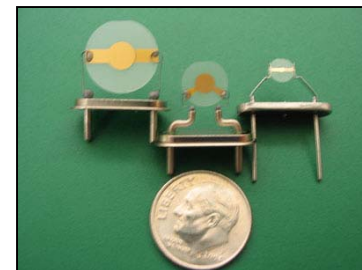
Hexane	
ppm	Volume %
14,280.1	1.4
28,158.1	2.8
41,650.8	4.2
54,773.9	5.5
67,542.5	6.8
79,970.7	8.0
92,072.0	9.2
103,859.0	10.4
115,344.0	11.5
126,538.3	12.7

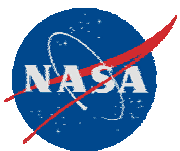




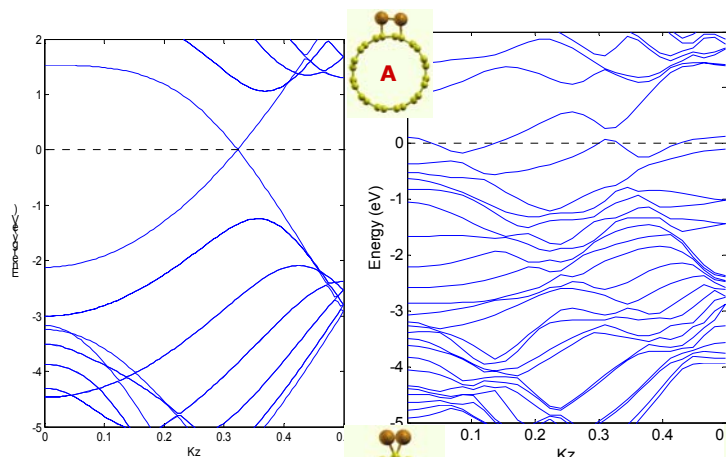
Results – Other sensors High Sensitivity 100 MHz TSM Sensor

- TSM sensor responses show promise of an improved commercial hydrocarbon sensor
- Viable environmental detectors and process monitors possible



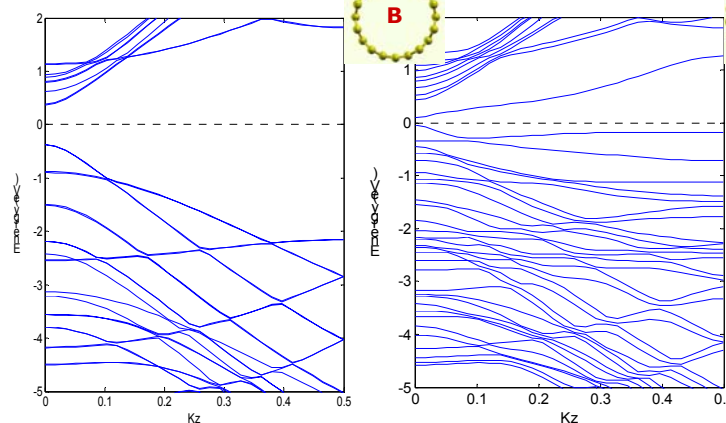


Results – Modeling Pd chains on SWNTs-Band Structure



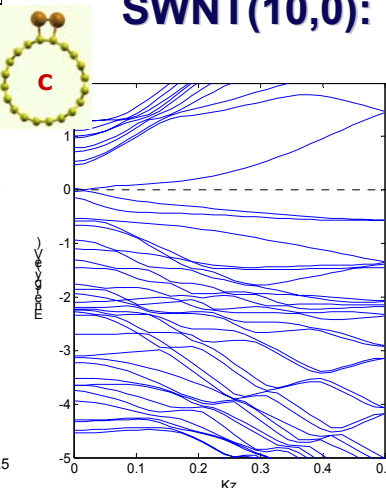
Pd narrow angled chain functionalized SWNT(6,6):

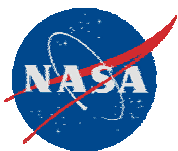
- New bands are created
- Original bands are strongly perturbed
- Metallic nature is not affected



Pd wide angled chain functionalized SWNT(10,0):

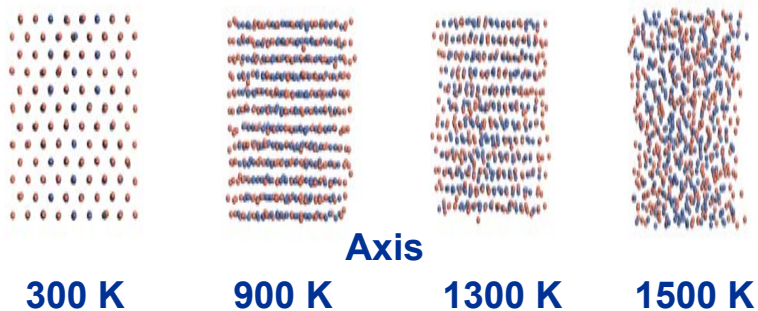
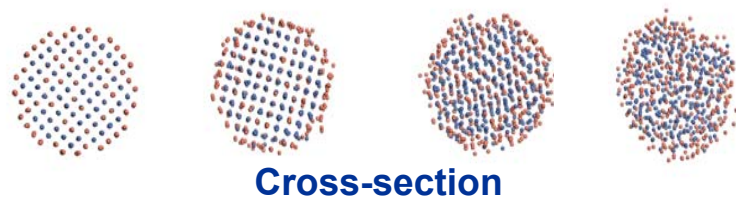
- Band gap is either significantly reduced or closed
- Semi-conducting nature is changed
- B1 site functionalization has lower symmetry





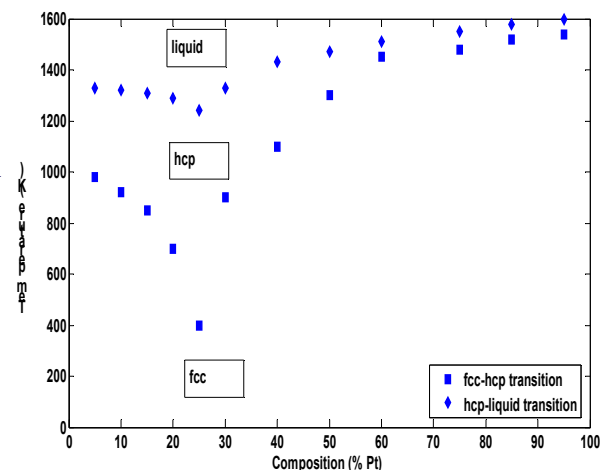
Results – Modeling Molecular Level Modeling

Phase diagrams for Pd-Pt bimetallic nanostructures

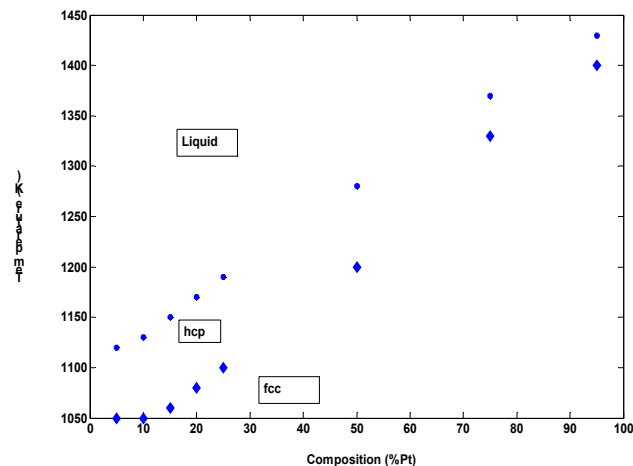


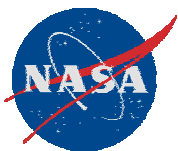
Nanowire

- Diameter ~ 2.3 nm
- Solid-Solid transition precedes final melting pt.
- Different melting mechanism.



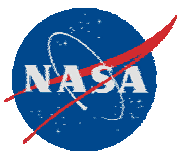
Nanocluster





Accomplishments – Collaborations, Students, Proposals and Papers

- Three Ph.D., 1 MS and 2 BS students current
- Four MS students graduated
- Four proposals written to NSF, DOE and USF
- One USF and one related NSF support obtained; One DOE support obtained on related project using DFT calculations
- One patent issued and another filed; Three company interest with one pursuing hydrogen sensor technology currently
- Collaboration with Professor Don Malocha of UCF established on wireless sensors
- Three papers accepted and one in consideration in Physical Review B, one submitted to Sensors and Actuators, and two in preparation to IEEE Sensors Journal.
- Over 30 presentations in National and international conferences (ECS, AIChE, IEEE-UFFC)
- Local industry support from Fractal Systems and Sensidyne



Future Plans

- Combine best nanomaterial investigated with best SAW device fabricated to make a prototype hydrogen sensor
- Complete high frequency TSM hydrocarbon sensor development
- Test the hexagonal SAW device fabricated in lithium niobate and lithium tantalate in vapor sensing (in particular, hydrogen sensing) and medical diagnostics (in particular, ovarian cancer detection) applications
- Continue theoretical sensor response models for these acoustic wave sensors utilizing multiple time and length scale analyses with electronic structure, molecular simulation and finite element simulation methods