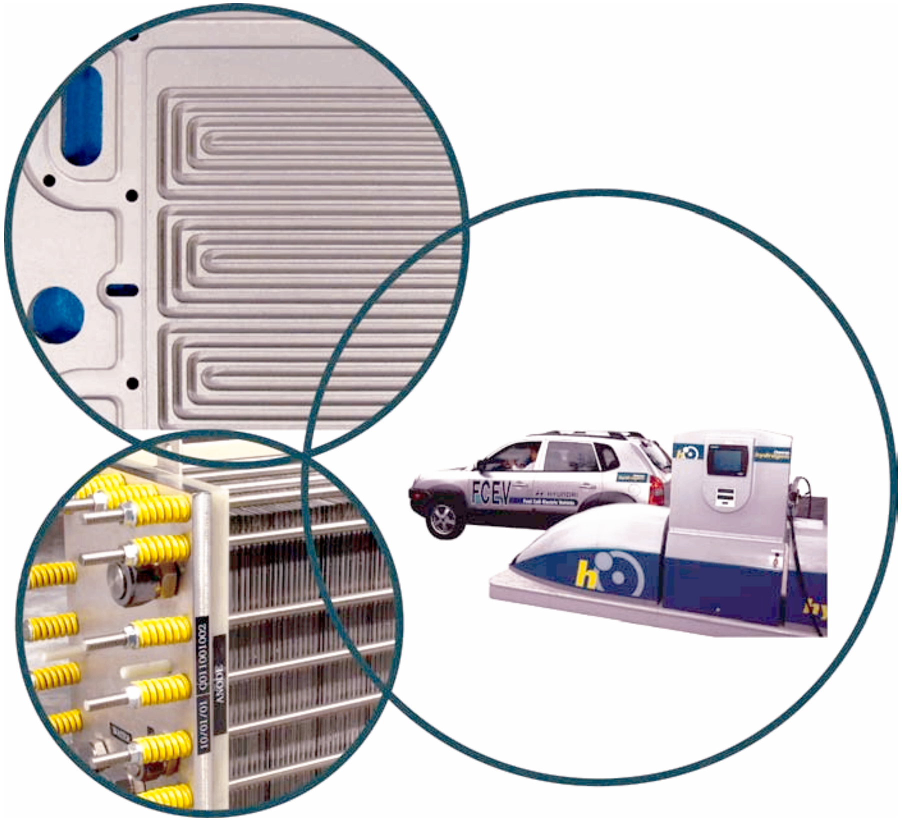
Optically Read MEMS Hydrogen Sensor



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Scott Hunter
Oak Ridge National Laboratory

Annual Merit Review
Washington, DC
June 9, 2010

Project ID #:SCS018

Overview

Timeline

- Start: Late FY 2007
- Finish: Project continuation & direction determined annually by DOE

Budget

- Project funding profile
  - FY 2007: $125k
  - FY 2008: $300k
  - FY 2009: $200k*

*Project moved to VT for 1 year

Barriers

- D. Liability Issues
- E. Variation in Standard Practice of Safety Assessments for Components and Energy Systems
- *Technical Targets on next slide*

Partners & Collaborators

- University of Tennessee
- Advanced Catalyst Systems
- Agiltron, Inc.
- United Protective Technologies

Overview

- **Technical Targets**
  - H_2 concentration measurement range: 0.1%-10%
  - Operating temperature: -30 to 80°C
  - Response time: less than one second
  - Accuracy: 5% of full scale
  - Gas environment: ambient air, 10-98% relative humidity range
  - Lifetime: 10 years
  - Interference resistant (e.g., hydrocarbons)

Relevance - Objectives

Project goal: Develop optics-based sensing technology that achieves DOE R&D targets for hydrogen safety sensors.

Month-Year	Milestones
May 2009	Milestone: Complete characterization of response time, recovery time, sensitivity and accuracy within the operating temperature range (100% complete)
Jul 2009	Milestone: Establish commercialization partnership (75% complete)
Sep 2009	Milestone: Demonstrate sensor performance and compliance with safety goals (75% complete)

Technical Highlights

FY 2009

– Functionalized Polymer-Film Microcantilever Arrays (MCA)

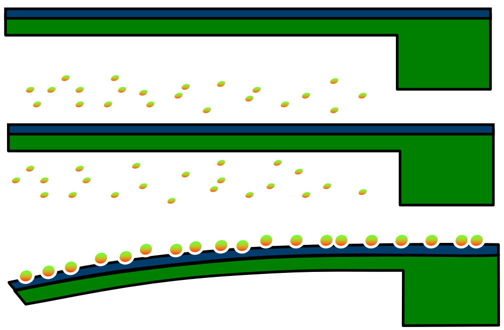
- Work performed in collaboration with University of Tennessee, Department of Chemistry
- Fabricated and tested MCA coated with composite films of select polymers
  - Cantilevers are responsive to H_2 but minimally responsive to chemical interferents
  - Reversible cantilever responses to all chemicals in air sample
  - MCA provided patterned response for each chemical; pattern recognition software enabled quantification of each chemical present in the air sample
  - Determined best performing phases with respect to ability to discriminate against CO_2, water vapor, methane
- Completed selectivity, sensitivity and regeneration analyses of the functionalized polymer-film cantilevers
- We now have a prototype MCA sensing device that provides qualitative and quantitative information on H_2 present in air sampling

Technical Highlights

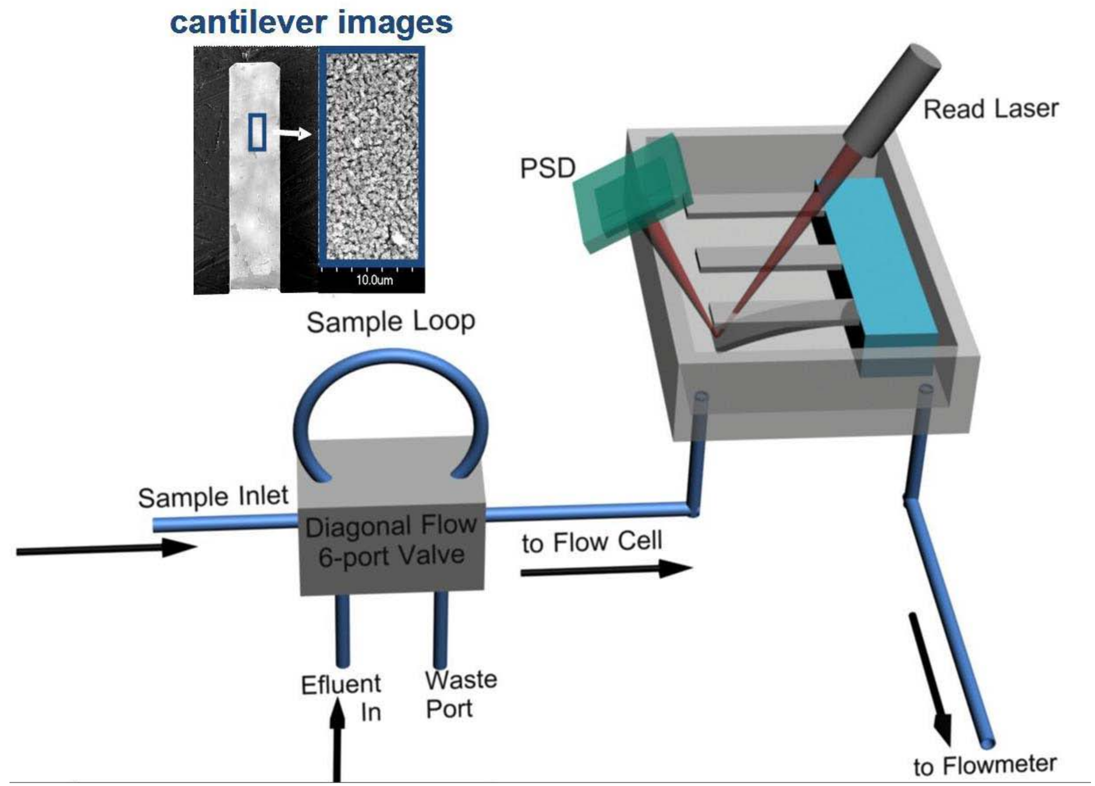
FY 2010

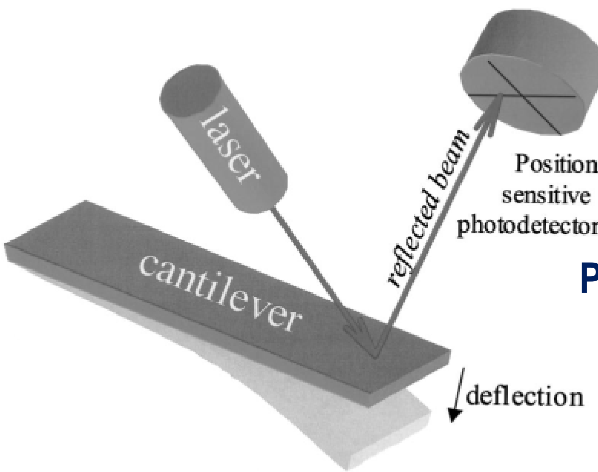
- Developed new highly porous nanoparticle palladium coated microcantilever sensor arrays
  - Developed a new wet chemical Pd film deposition technique on Ag/Cr coated cantilever sensors using a galvanic $PdCl_2$ exchange reaction
  - Large sensor surface area in comparison with film volume leads to very fast sensor response and recovery times
  - Completed selectivity, sensitivity, response and recovery time and regeneration analyses of the nanoporous Pd coated sensors – excellent response characteristics
  - Excellent stability, repeatability and life measurements have been observed during more than a year of operation
  - First field portable instrument fabricated to demonstrate operational performance of the Pd based sensors
  - Sensor commercialization partners identified and agreements in progress

Technical Approach –
Microcantilever Hydrogen Detection



Functionalized (blue layer) micro-cantilever bending in response to changes in surface stress induced by adsorption of a gas or vapor





Probe laser beam is reflected off the surface of the cantilever sensor and the amount of bending is recorded by a position sensitive photodetector (PSD).

Cantilever sensor is located within a flow cell to control sensor exposure to calibrated H_2 and potential interferent gas streams

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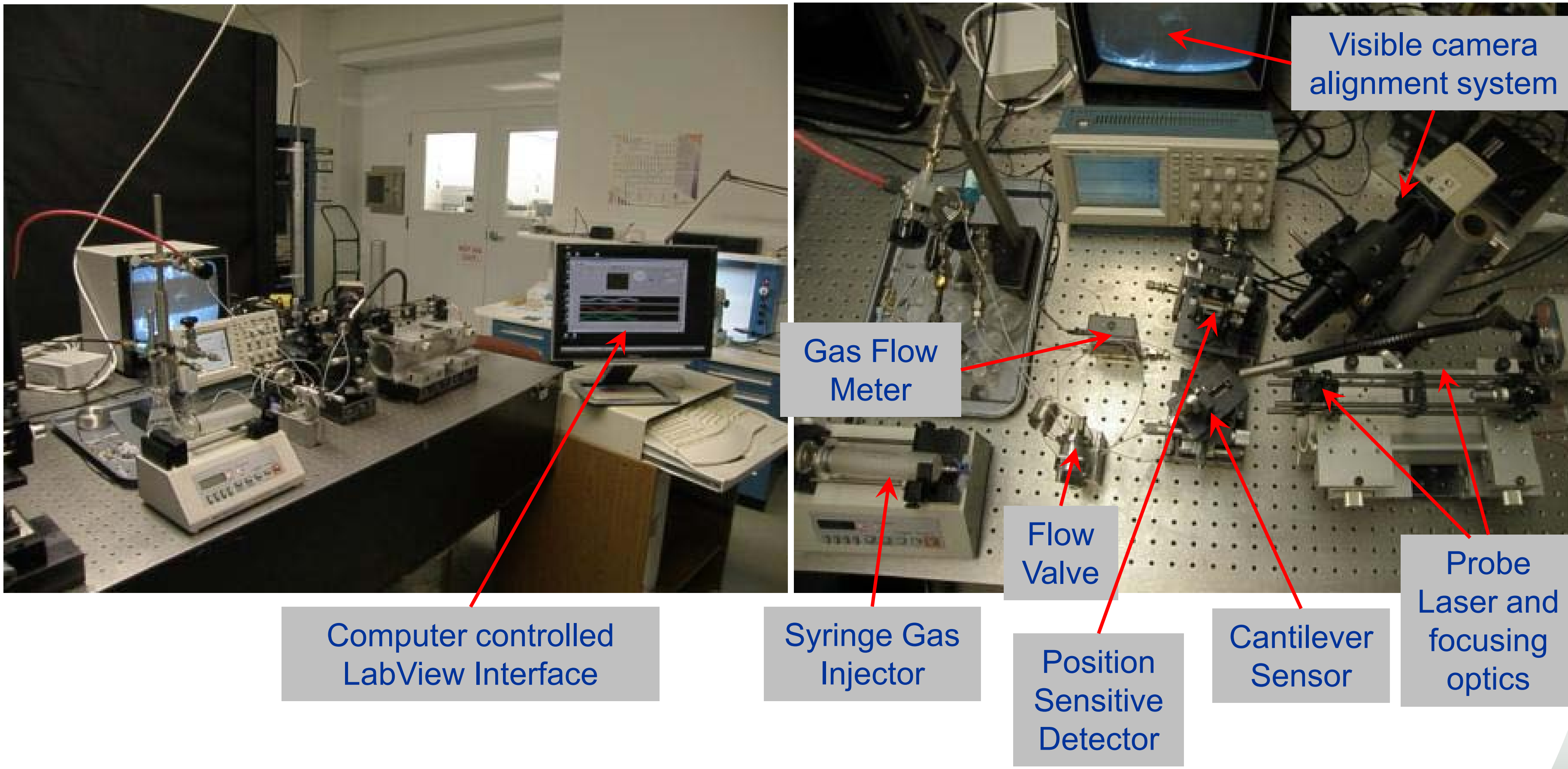
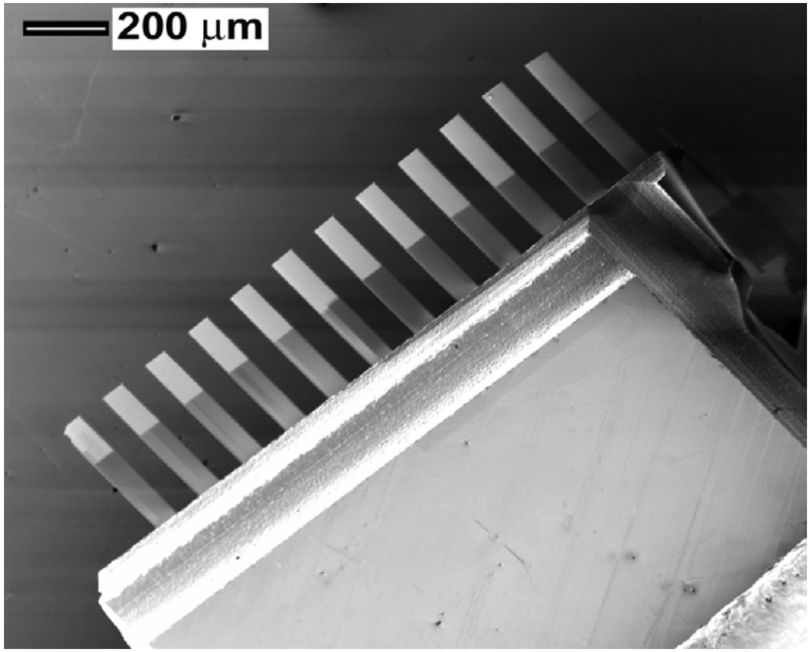
Testing Hydrogen Sensors –

Microcantilever sensor lab bench system



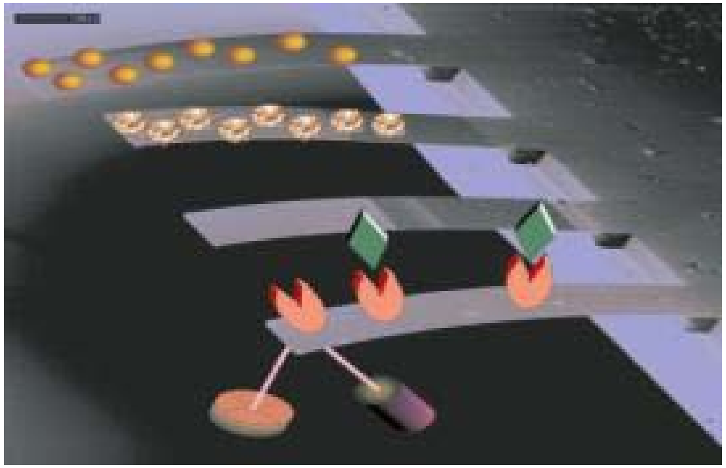
Lab bench setup for the H_2 sensitivity and potential interferent measurements

Sensor Material Development -
Functionalized multi-cantilever arrays



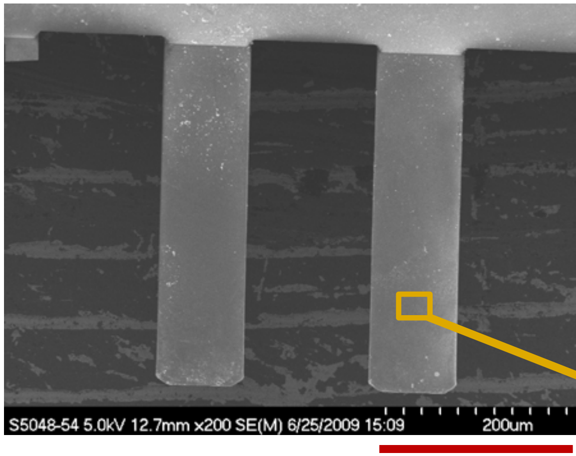
We use commercially available microcantilever arrays which are differentially functionalized with materials that potentially interact with H_2 to produce a bending response

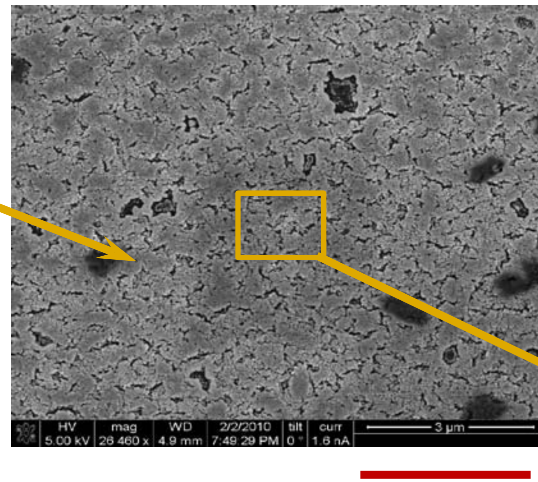
Schematic of cantilevers coated with different thin films to invoke an array of response to H_2 and potential interferents

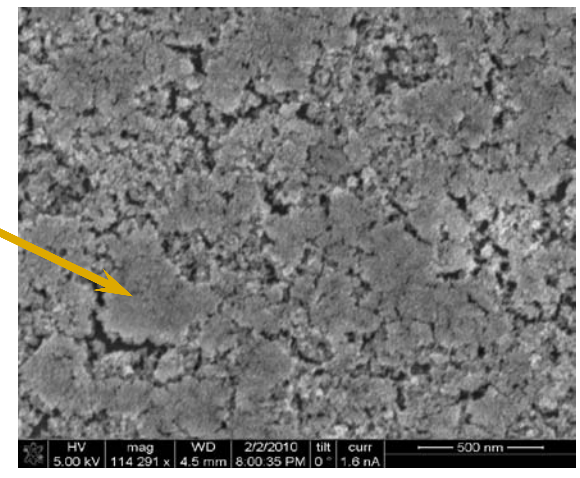


Sensor Material Development - Nanostructured Palladium Surface Coatings

Microcantilever sensor coated with an H_2 sensing nanostructured Pd thin film



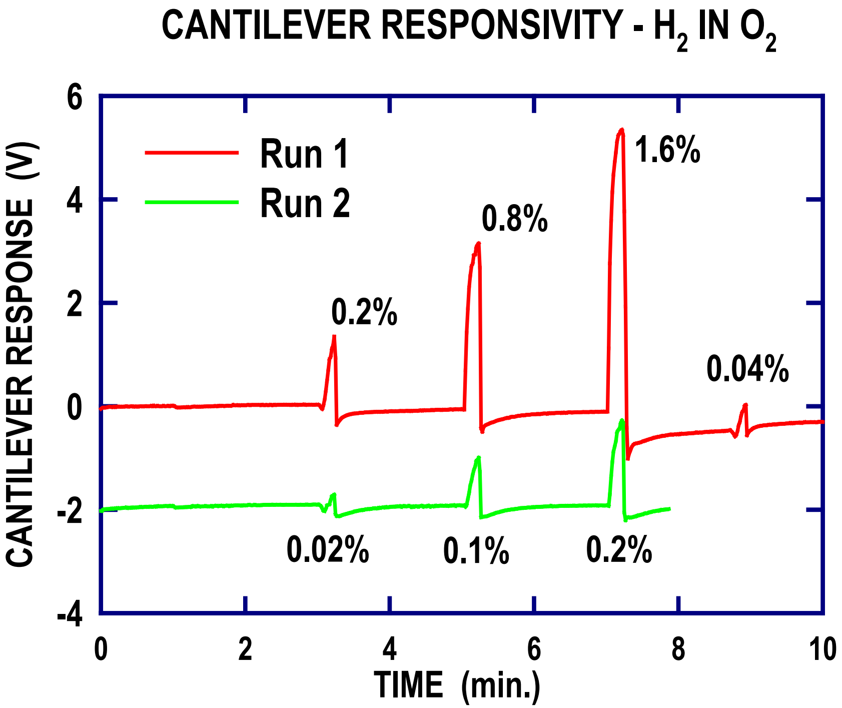


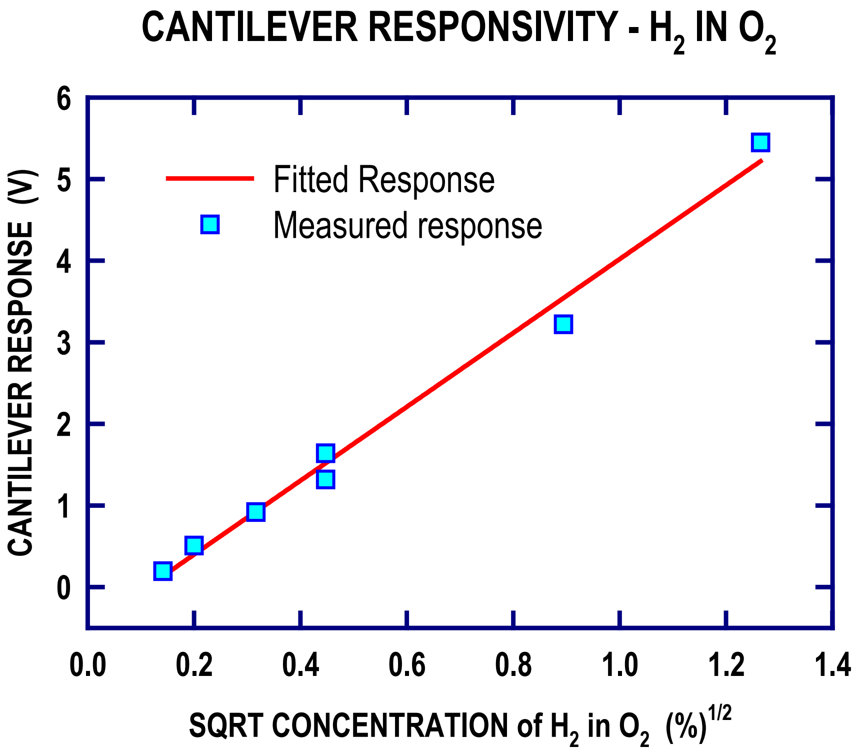


- Wet chemical galvanic $PdCl_2$ exchange reaction with thin silver/chromium sputtered film leads to very nanoporous textured Pd metal surfaces
- Conjectured to lead to fast response and recovery times

Technical Accomplishments –

Low threshold and wide dynamic range response



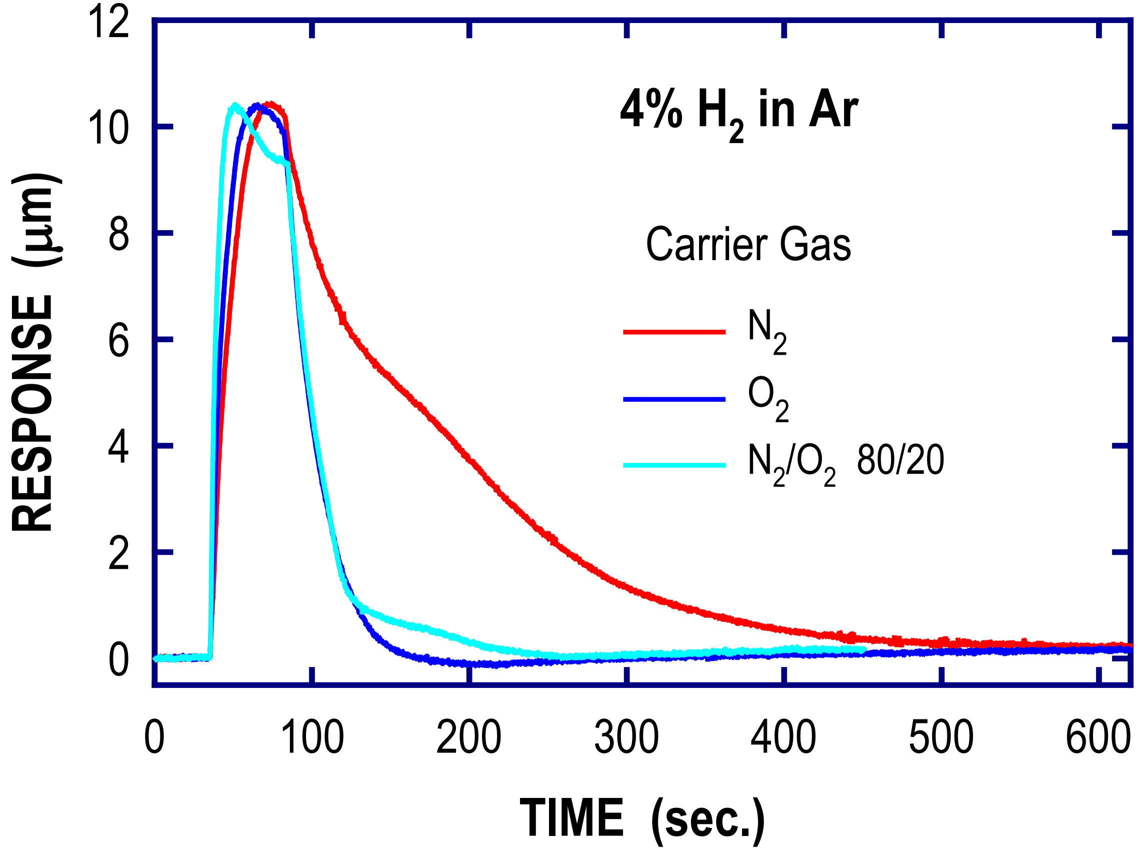


Representative sensitivity measurements using Pd/Ag coated microcantilever H_2 sensors.

- **Detection threshold – 0.01% H_2**
- **Dynamic range – > 3 orders of magnitude**

Technical Accomplishments –
Fast sensor response and recovery

Fast Response (< 3 sec) and recovery (< 10sec) in simulated air



Sensor response to a 4% H_2/Ar gas mixture after the microcantilever had been passivated by flowing the various carrier gases through the flow cell

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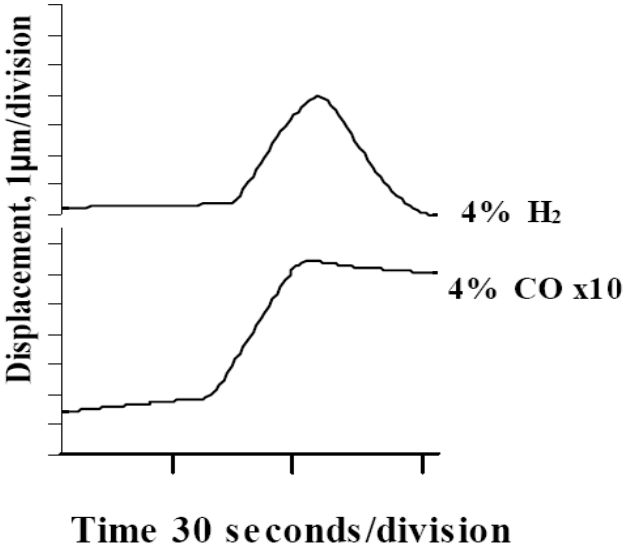
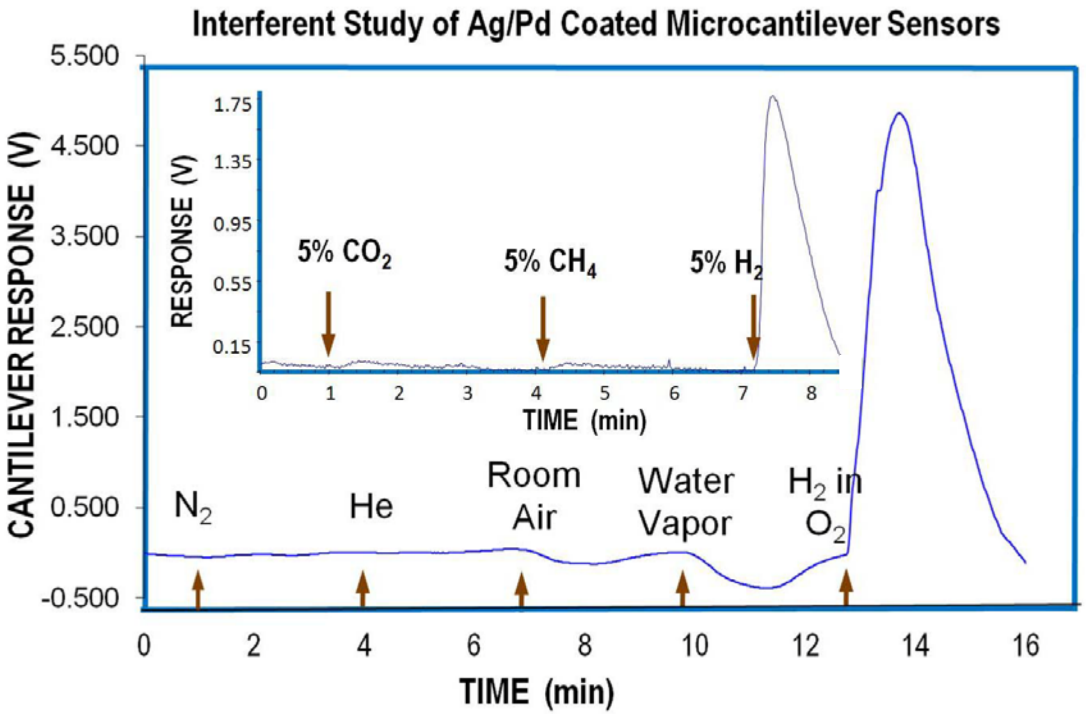
Technical Accomplishments –
Excellent specificity to common impurities and carrier gases

Nanostructured Pd coated cantilever shows negligible response to most potential interferents





Differences in temporal response and signal magnitude allow discrimination between more significant interfering species

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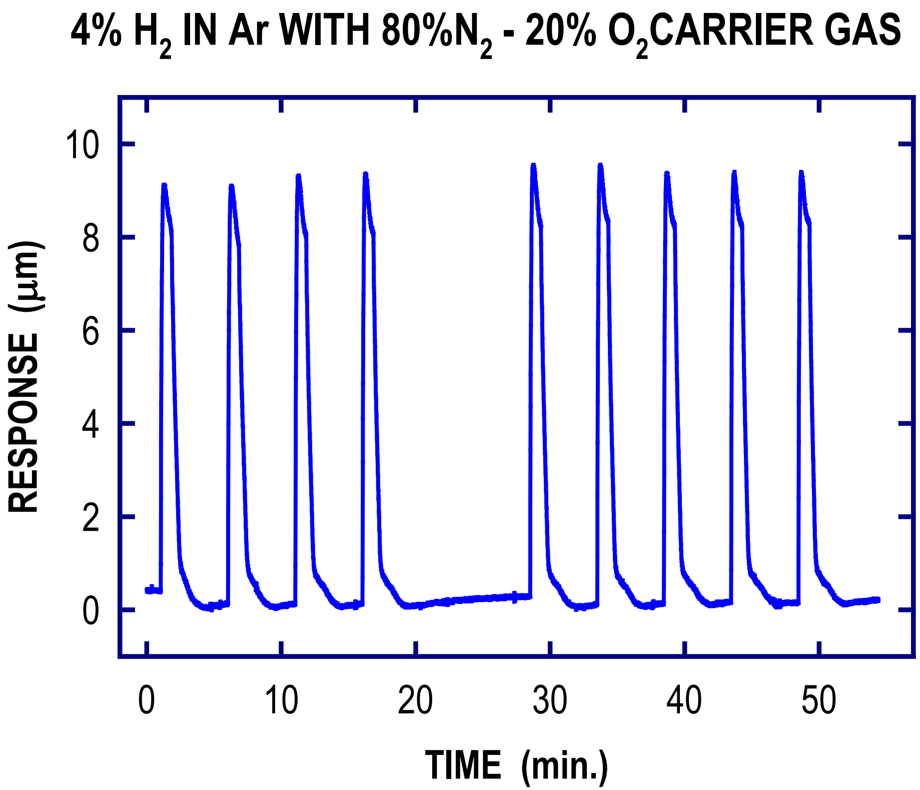
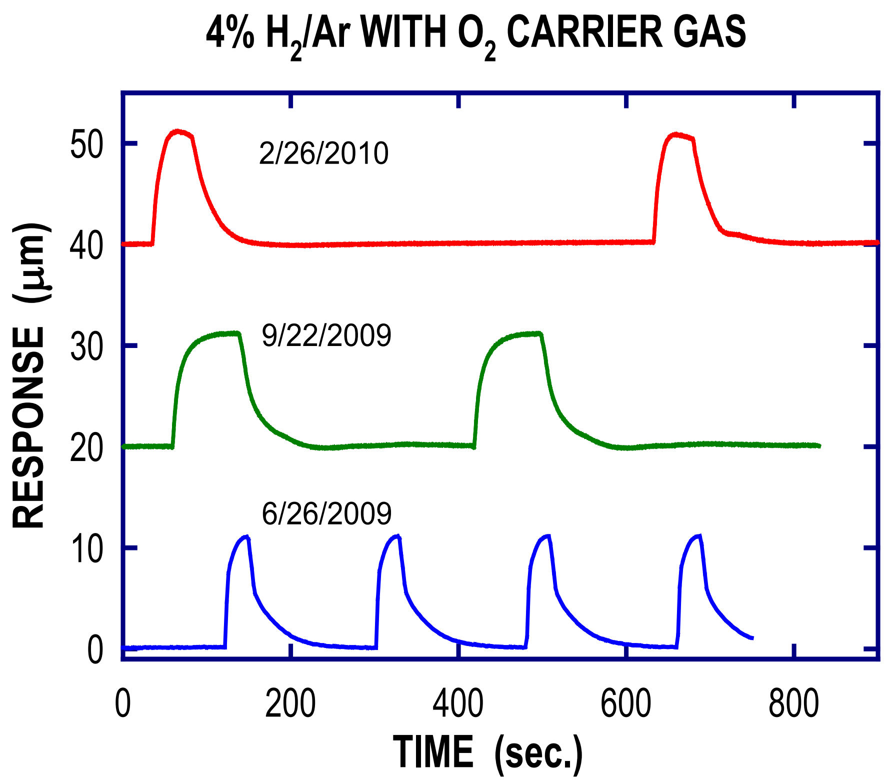
Technical Accomplishments –
Sensor accuracy, repeatability and lifetime



High sample-to-sample repeatability of the sensor bending response in a simulated H_2/ air environment



Single microcantilever response to a 4% H_2 /Ar-O_2 mixture over an 8 month period

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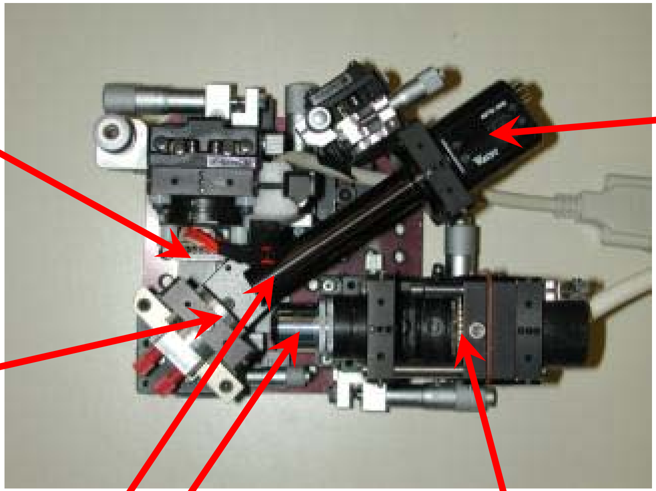
Technical Accomplishments –
First Field portable instrument

Position sensitive detector

Imaging camera used for optical alignment



Cantilever sensor array

Focusing optics

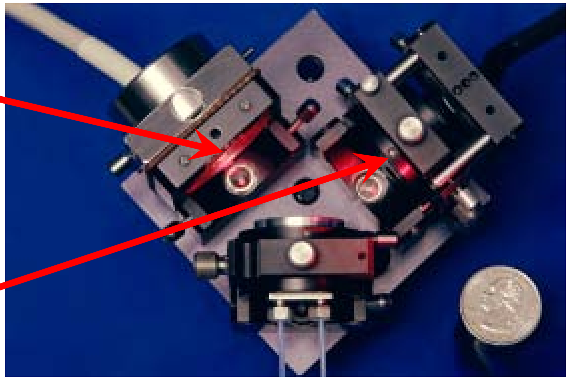
Laser array

First field portable prototype sensor hardware incorporating the same features as the benchtop apparatus but on a much reduced scale. This unit is operated by a standard laptop computer.

The unit is fabricated on a 4” optical breadboard

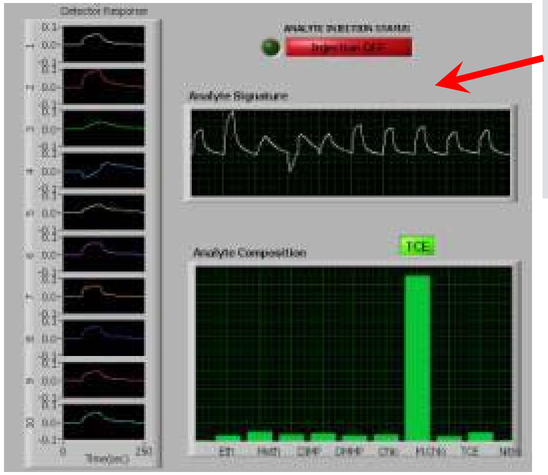
Technical Accomplishments –
Advanced field portable instrument

VCSEL Laser Array

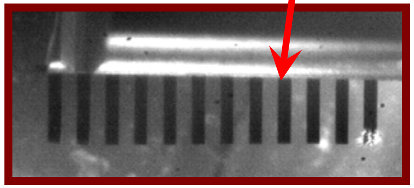


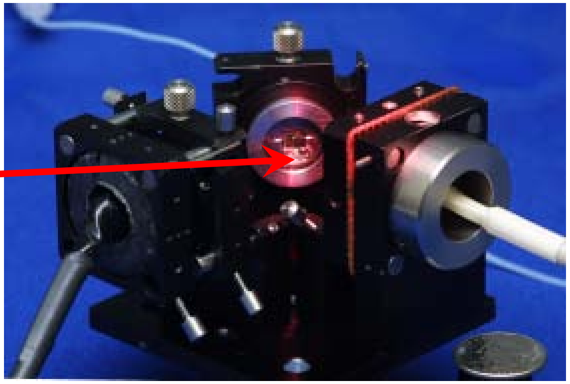
Position Sensitive Detector

LabView interface control and data display



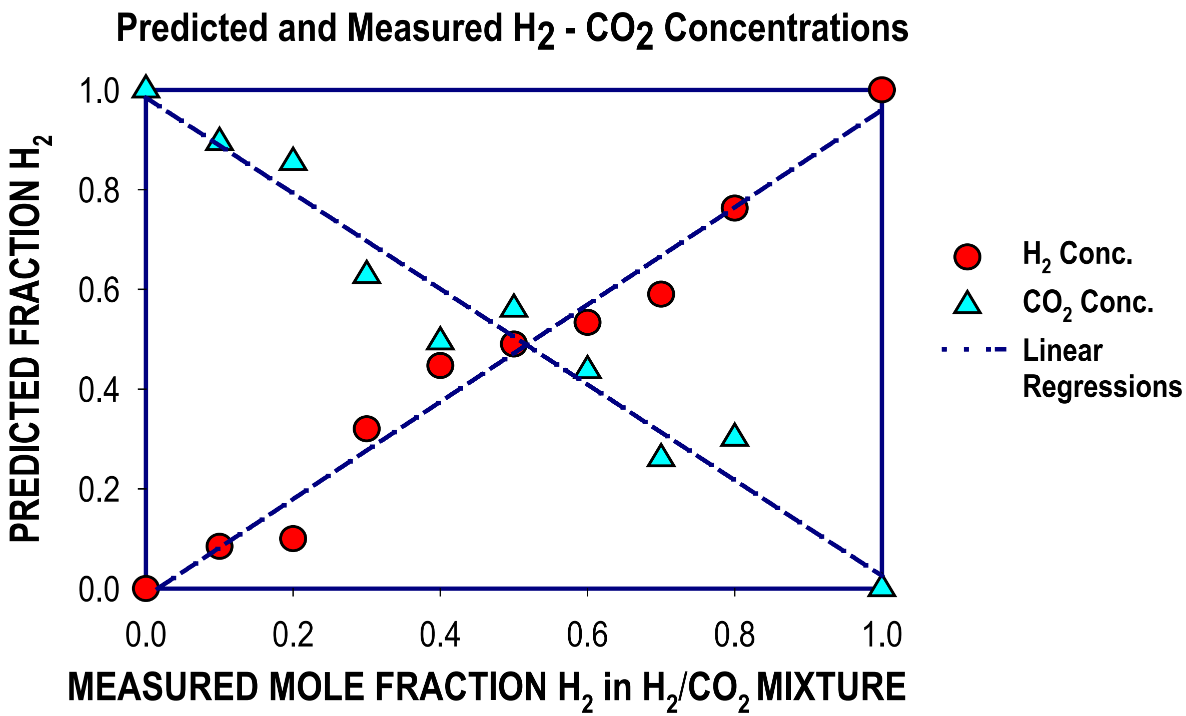
Cantilever Array





Coated arrays of cantilever sensors have been used in arrays and combined with pattern recognition algorithms to obtain quantitative estimates for H_2 and various potential interferents for enhanced selectivity

Results – Cantilever array measurements and neural network give accurate estimates for H_2 and CO_2



Experiment to demonstrate the ability of an artificial neural network (ANN) algorithm to predict component mixtures of multiple species

- Two component mixture comprised of varying concentrations of H_2 and CO_2
- Experiments were performed using arrays of silicon microcantilevers coated successively with nanostructured metal coatings.
- The graph shows the ability of the ANN to accurately predict the relative concentration of the two components

Collaborations

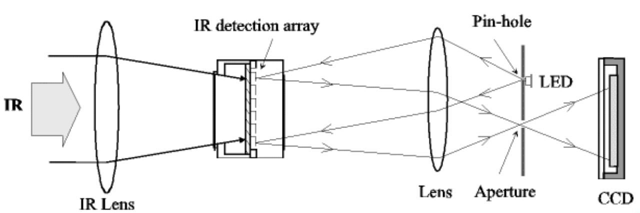
Partners:

- University of Tennessee - Improved H_2 sensor response
  - Faster response/recovery times – now around 3-10 sec – reduce to ~ 1 sec
  - Improved specificity – reduced water vapor response
  - Further studies of potential interferents – CO, EtOH, CH_4, other hydrocarbons
  - Multi-component mixture studies
- IP and patent filings – techniques, methods, coatings, applications
- Agiltron - Commercialization partnership agreements finalized

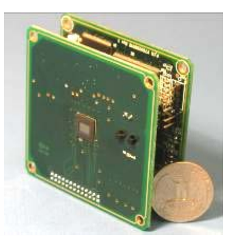
Technology Transfer:

- Agiltron collaboration
  - Tech transfer to commercialization partner for preproduction prototype development
  - Manage preproduction instrument fabrication at commercialization partner facilities

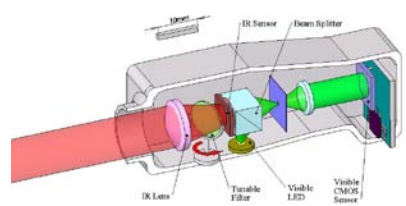
Agiltron's existing low cost microcantilever based infrared camera optical readout circuitry can easily be modified to interrogate an array of microcantilever chemical sensors

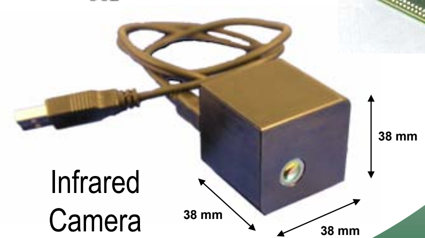


Readout Electronics



Microcantilever based infrared camera operation





Infrared Camera

Future Work

FY 2010

- **Improved H_2 sensor response**
  - Faster response/recovery times – now around 3-10 sec – reduce to ~ 1 sec
  - Improved specificity – reduced water vapor response
  - Further studies of potential interferents – CO, EtOH, CH_4, other hydrocarbons
  - Multi-component mixture studies
- **IP and patent filings – techniques, methods, coatings, applications**
- **Commercialization partnership agreements finalized**

FY 2011

- **Finish fabrication and preliminary testing of field portable instrument**
- **Implement commercialization plan with commercial partner**
  - Tech transfer to commercialization partner for preproduction prototype development
  - Manage preproduction instrument fabrication at commercialization partner facilities
- **Test pre-commercialization prototype testing at NREL Hydrogen Sensor Laboratory**
  - Short-term repeatability test
  - H_2 mixtures in air
  - Temperature and Relative Humidity
  - Response and recovery kinetics
  - Linearity/dynamic range test
  - Atmospheric pressure sensitivity
  - Long term stability
  - Interferent testing

Summary Table – Measured Performance

Present microcantilever based H_2 sensors meet all but the most stringent requirements for automotive applications

	Performance Requirement*	Measured Performance
Sensitivity Range	< 0.1% to > 4%	0.01 – 4%
Survivability Limit	100%	Linear response to 100% H_2
Response Time	Automotive: < 3 sec Stationary: < 30 sec	~ 3-5 sec
Recovery Time	Automotive: < 3 sec Stationary: < 30 sec	~ 10-20 sec
Temperature Range	Automotive: -40^{0}C to +125^{0}C Stationary: -20^{0}C to +50^{0}C	Yes
Pressure Range	Automotive: 62-107 kPa Stationary: 80-110 kPa	Yes
Ambient Relative Humidity Range	Automotive: 0 – 95% Stationary: 20 – 80%	0-100%
Interferent Resistance	No false positive responses	Excellent
Power Consumption	< 1 Watt	0.5-1 Watt
Lifetime	Automotive: 6,000 hr Stationary: > 5 years	Demonstrated > 9 months
Accuracy and Repeatability	Automotive: 5-10% Stationary: 10%	> +/- 5%

* L. Boon-Brett et al., "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," *Int. J. Hydrogen Energy*, **35**, 373-384 (2010).

Project Summary

Relevance:

Commercialize optical technology that achieves DOE R&D targets for hydrogen safety sensors

Approach:

Develop and characterize an optically based, cost effective hydrogen sensor that can be used in distributed hydrogen leak sensing applications

Technical Accomplishments and Progress:

Demonstrated that optically read microcantilever based sensors meet all the H_2 sensor performance and life operating requirements

Technology Transfer/Collaboration:

Active partnership with the University of Tennessee. New partnerships with Agiltron, Advanced Catalyst Systems and UPT – publications, patents, preproduction prototype development.

Proposed Future Research and Development:

Improved H_2 sensor response and interferent selectivity. Portable preproduction instrumentation development for competitive benchmarking at NREL.