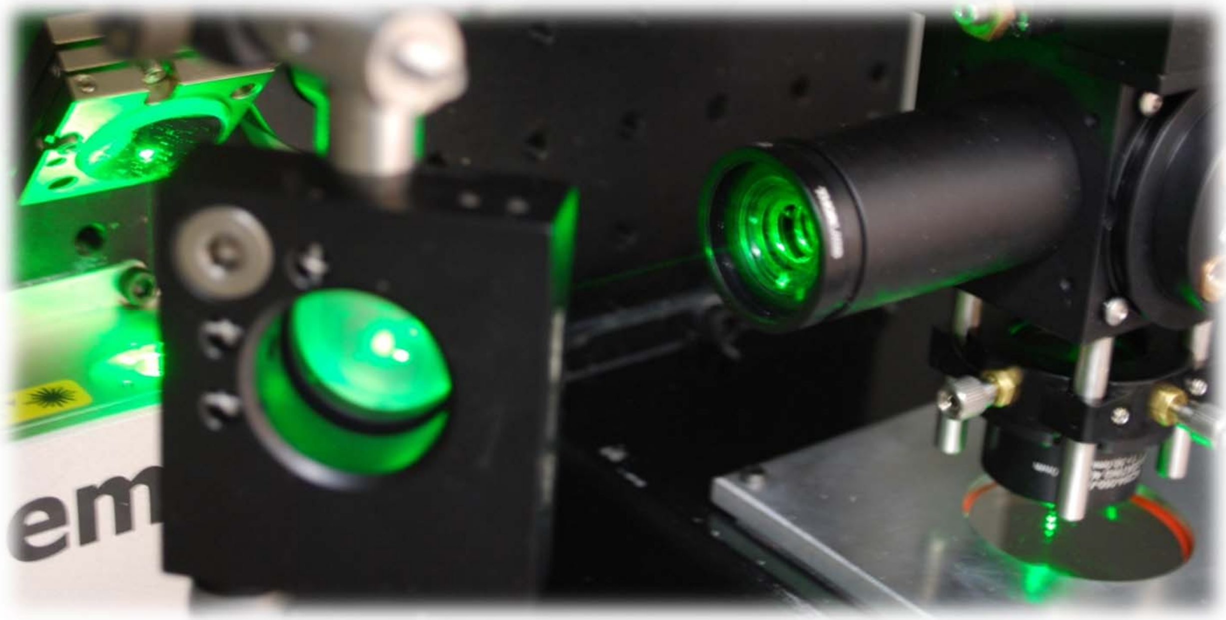
NATIONAL ENERGY TECHNOLOGY LABORATORY



Optical Thin Films for High Temperature Sensing in Advanced Fossil Energy Applications

Presenter: Benjamin Chorpening

Project PI: Paul R. Ohodnicki, Jr.

Project Team: Thomas Brown, Congjun Wang, John Baltrus, Michael Buric, Andrew Schultz, Gordon Holcomb, and Joseph Tylczak

U.S. DEPARTMENT OF ENERGY

Crosscutting Research Review, Pittsburgh, PA, May 21,2014

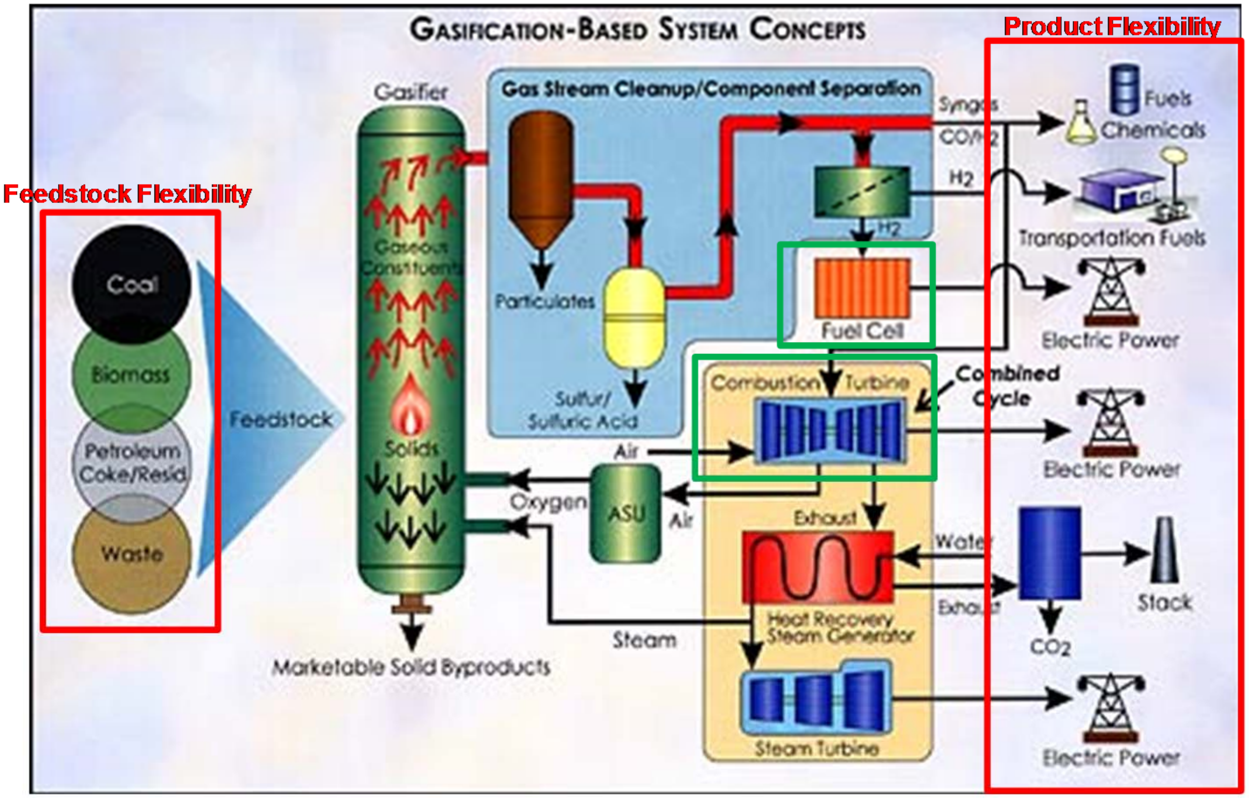
Overview of Presentation

- Motivation and Background
- Project Overview
- Recent Research and Development Effort Updates
- Summary and Conclusions

Motivation and Background

Advanced Fossil-Based Power Generation

Advanced
Fossil-Based
Power Generation
Involves High
Temperature
Gas Streams
(Coal or Natural Gas)



http://www.fossil.energy.gov/programs/powersystems/gasification/howgasificationworks.html

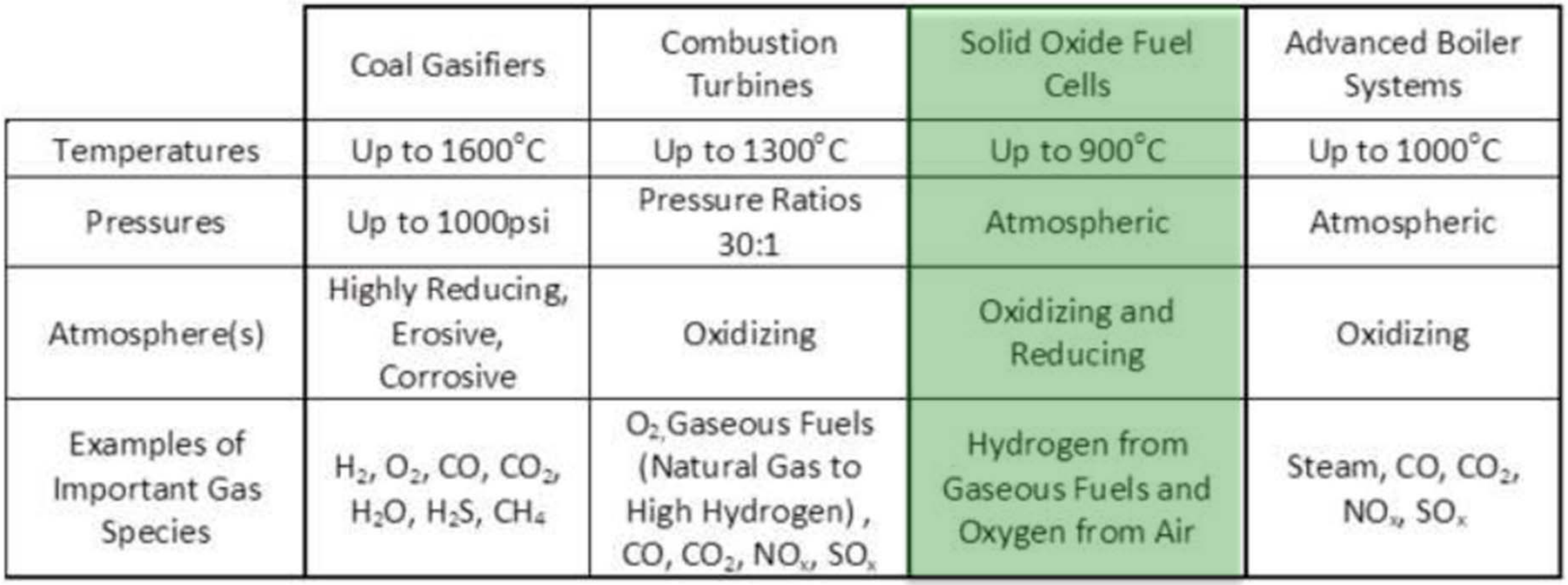
Fossil-Fuel Based Power Plants of the Future are Highly Complex Making Sensors and Controls of Crucial Importance.

Advanced Sensors and Controls Can Also Significantly Impact the Existing Fleet of Utility-Scale Fossil Plants.

Advanced Fossil-Based Power Generation

Table of Relevant Harsh Environments in Advanced Fossil Energy Technologies

Short Term Focus



	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
Examples of Important Gas Species	H_2, O_2, CO, CO_2, H_2O, H_2S, CH_4	O_2, Gaseous Fuels (Natural Gas to High Hydrogen) , CO, CO_2, NO_x, SO_x	Hydrogen from Gaseous Fuels and Oxygen from Air	Steam, CO, CO_2, NO_x, SO_x

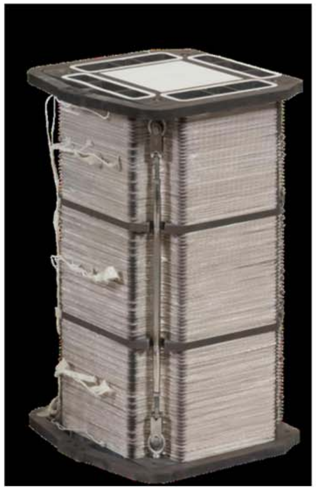
A Wide Range of Gas Species are Relevant.

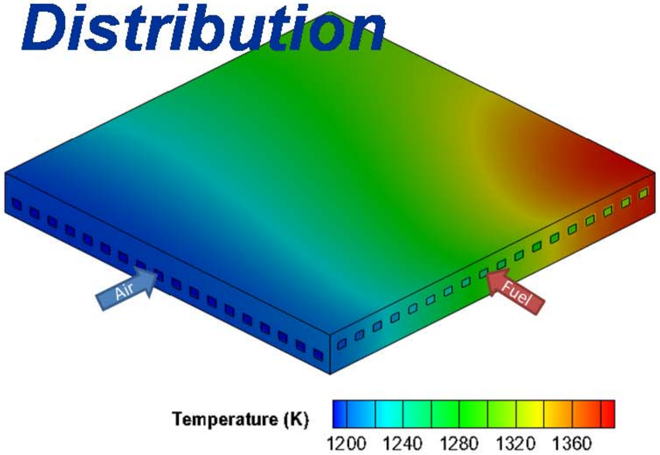
Embedded Sensors Must Operate in Extreme Conditions (T, P, corrosive).

Similar Needs Exist in a Wide Range of Other Industries (Aerospace, Aviation, Manufacturing, etc.).

Advanced Fossil-Based Power Generation

Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution





Temperature : 700-800°C
Anode Stream : Fuel Gas (e.g. H_2-Containing)
Cathode Stream : Air or O_2

Spatial Distribution in Temperature and Fuel Gas Composition

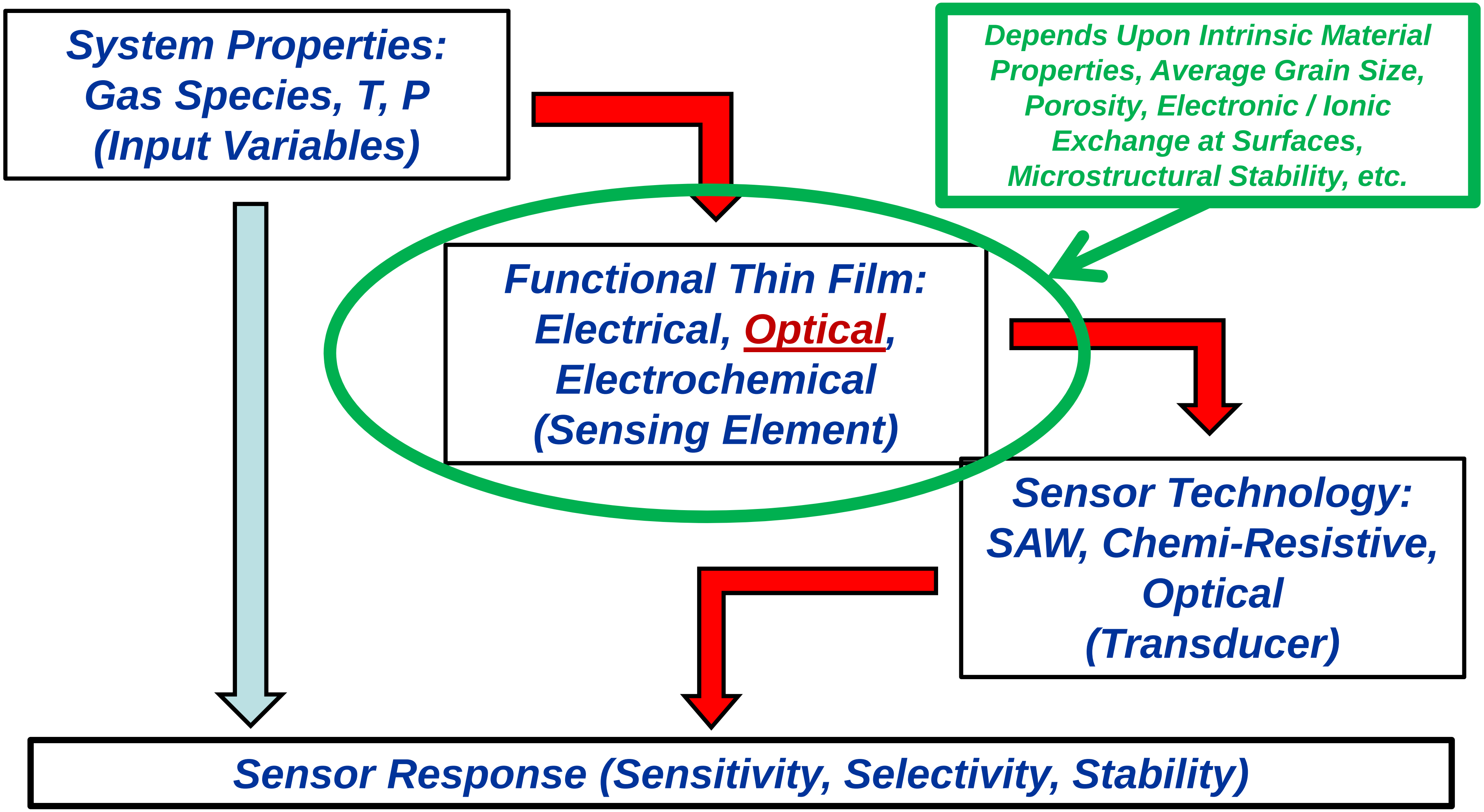
Incompatible with Traditional Sensing Technologies

1) At Limits of High Temperature Electrical Insulation
2) Limited Access Space
3) Only Single-Point, Single-Parameter Sensing

Stable Sensors Capable of Embedding in Harsh Environments Would Enable Unprecedented Access to New Process Information.

Project Overview

Thin Film Functional Sensor Layers in Harsh Environment Sensing Applications



System Properties:
Gas Species, T, P
(Input Variables)

Depends Upon Intrinsic Material Properties, Average Grain Size, Porosity, Electronic / Ionic Exchange at Surfaces, Microstructural Stability, etc.

Functional Thin Film:
Electrical, Optical, Electrochemical
(Sensing Element)

Sensor Technology:
SAW, Chemi-Resistive, Optical
(Transducer)

Sensor Response (Sensitivity, Selectivity, Stability)

Example: Pd-Thin Films for H_2-Sensing Applications

Fiber Optic Sensor for Hydrogen Concentrations near the Explosive Limit

Michael A. Butler*

Sandia National Laboratories, Albuquerque, New Mexico 87185

J. Electrochem. Soc., Vol. 138, No. 9, September 1991

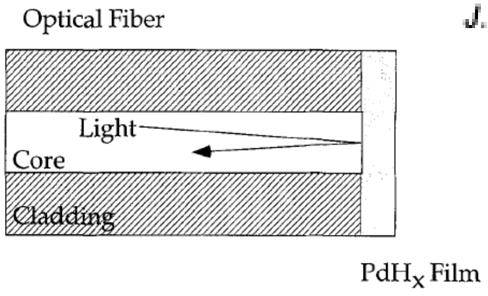


Fig. 1. Representation of the micromirror hydrogen sensor. The fiber is 125 μm in diameter with a 50 μm core. The palladium film is deposited by evaporation and is typically 10-20 nm thick.

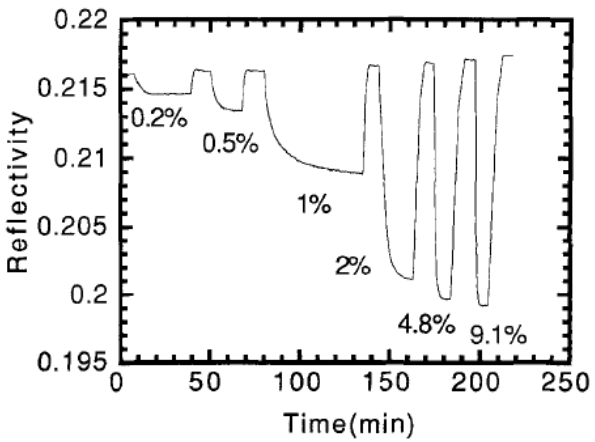


Fig. 2. Response of the micromirror hydrogen sensor to varying concentrations of H_2 in N_2. Between exposures to hydrogen, the sensor is exposed to air. This palladium film is 10 nm thick and the measurements were made at room temperature.

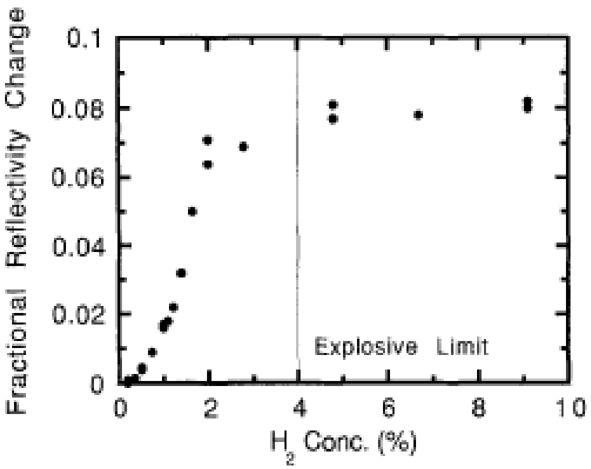


Fig. 3. Magnitude of the response of the micromirror hydrogen sensor at room temperature to varying concentrations of hydrogen in air. Note that the hydrogen actually produces a decrease in reflectivity as shown in Fig. 2. The absolute reflectivity of this film is about 22%. The vertical line indicates the lower explosive limit.

1.5 Pages Long,

> 84 Citations!

A Sensor for Leak Detection of H_2 in Potentially Explosive Conditions was Proposed by End-coating an Optical Fiber with a Pd Thin Film by Butler in 1991.

Motivation for Looking at Optical Materials

Chemi-resistive materials : the fundamentals are understood

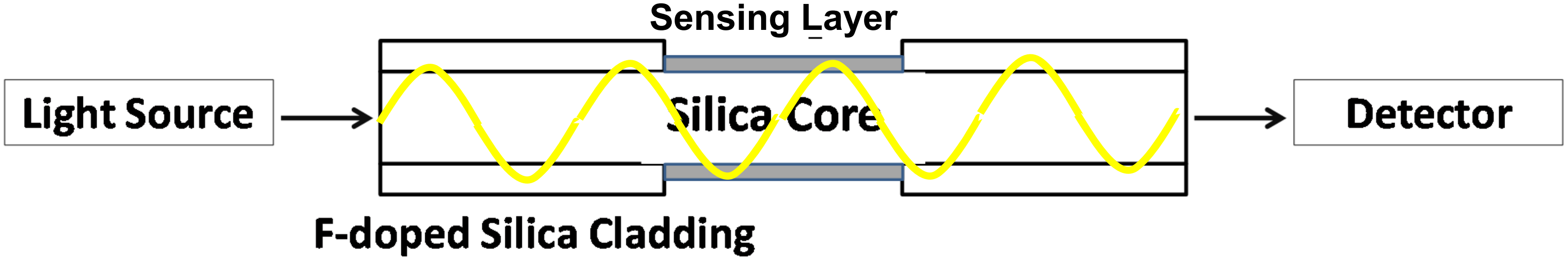
- G. Korotcenkov (2007). Materials Science and Engineering: B **139(1): 1-23**
- Gas Species Interact with Adsorbed Surface Species or Alter Defect Chemistry Changing:

  (1) Free Charge Carrier Concentration, (2) Mobility of Free Carriers

Optical materials : fundamentals are poorly understood

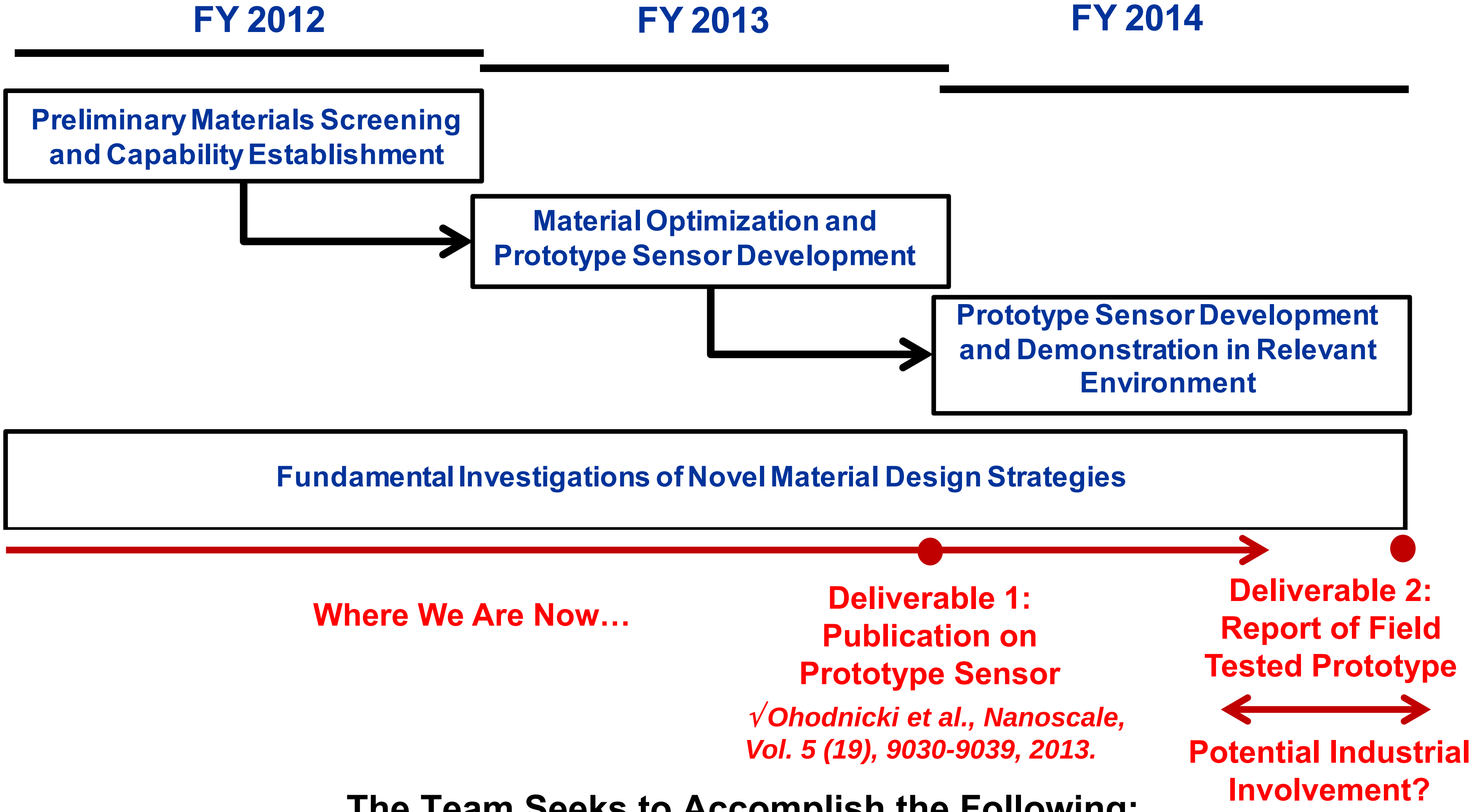
- How Do Refractive Index and Optical Absorption Depend Upon Defect Chemistry or Concentration of Adsorbed Species?
- How Can Materials with Useful Responses Be Optimally Integrated into Optical Sensing Devices?

e.g. Evanescent Wave Sensors



Silica-Based Fibers are Stable up to Temperatures Approaching 900°C

Functional Sensor Material Project Timeline



FY 2012

FY 2013

FY 2014

Preliminary Materials Screening and Capability Establishment

Material Optimization and Prototype Sensor Development

Prototype Sensor Development and Demonstration in Relevant Environment

Fundamental Investigations of Novel Material Design Strategies

Where We Are Now…

Deliverable 1:
Publication on
Prototype Sensor

√*Ohodnicki et al., Nanoscale, Vol. 5 (19), 9030-9039, 2013.*

Deliverable 2:
Report of Field
Tested Prototype

Potential Industrial
Involvement?

The Team Seeks to Accomplish the Following:

1) **Identify Novel Sensor Material Approaches / Generate IP for Potential Commercialization**
2) **Increase TRL of One Approach Through Prototype Demonstration**
3) **Deliver High Quality Technical Publications and Presentations**

Advanced Functional Sensor Material Project Team Regional University Partnerships

University of Pittsburgh

Sensor Interrogation Methodologies

Supporting Sensor Material R&D

NETL

Office of Research and Development

VirginiaTech
Invent the Future®

Sensor Device Platform Stability

Project Leadership / Coordination

Sensor Material R&D

Sensor Packaging and Prototype Development

The Project Team is an Interdisciplinary Team Centered within the Office of Research and Development with Strategic University Collaborations to Accelerate and Enhance the Project Outputs.

Collaborative Interactions with the Project Team

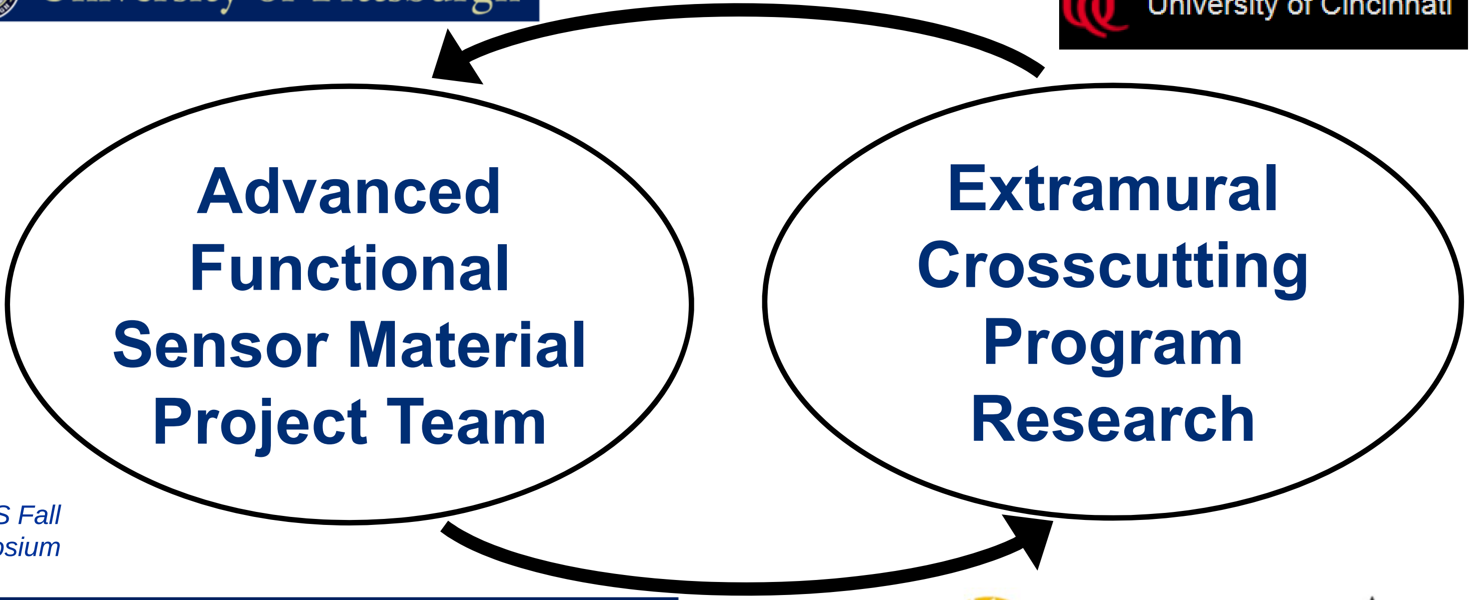
2 – Joint Peer-reviewed Publications (U. Pitt, U. Albany)

1 – Joint Patent Application (U. Pitt.)

1 - Additional Joint Publication Currently in Preparation (U. Conn.)

University of Pittsburgh

University of Cincinnati



Advanced Functional Sensor Material Project Team

Extramural Crosscutting Program Research

Upcoming MRS Fall Meeting symposium

UCONN UNIVERSITY OF CONNECTICUT

UNIVERSITY AT ALBANY
State University of New York

The Team Also Seeks to Establish New Collaborations with Other NETL-Funded Projects and Others to Help Promote the Mission of the Laboratory and the Crosscutting Research Program.

Unique Capabilities / Facilities of the Project Team

In-Situ Characterization Tools

- High Temp. X-ray Diffraction
  - Temperatures up to 1300ºC
  - Gases Including H_2, O_2, N_2, CO
- High Temperature Scanning Electron Microscopy
  - ~ 0.5 torr of H_2O(g) or Air
  - Temperatures up to 900ºC
- X-ray Photoelectron Spectroscopy with a Reaction Chamber
  - Temperatures up to 1300ºC
  - Gases Including H_2, O_2, N_2, CO

In-Situ Property / Device Measurements

- Ambient Pressure Reactors:
  - H_2, O_2, N_2, CO, CO_2, CH_4
  - Temperatures up to 900ºC
  - Full System Automation
- Elevated Pressure Reactor:
  - H_2, O_2, N_2, CO, CO_2, CH_4
  - Temperatures up to 900ºC
  - Pressures up to 900psi
- Film Resistivity
- Film Transmittance (~300-2500nm)
- Film Reflectance (~300-2500nm)

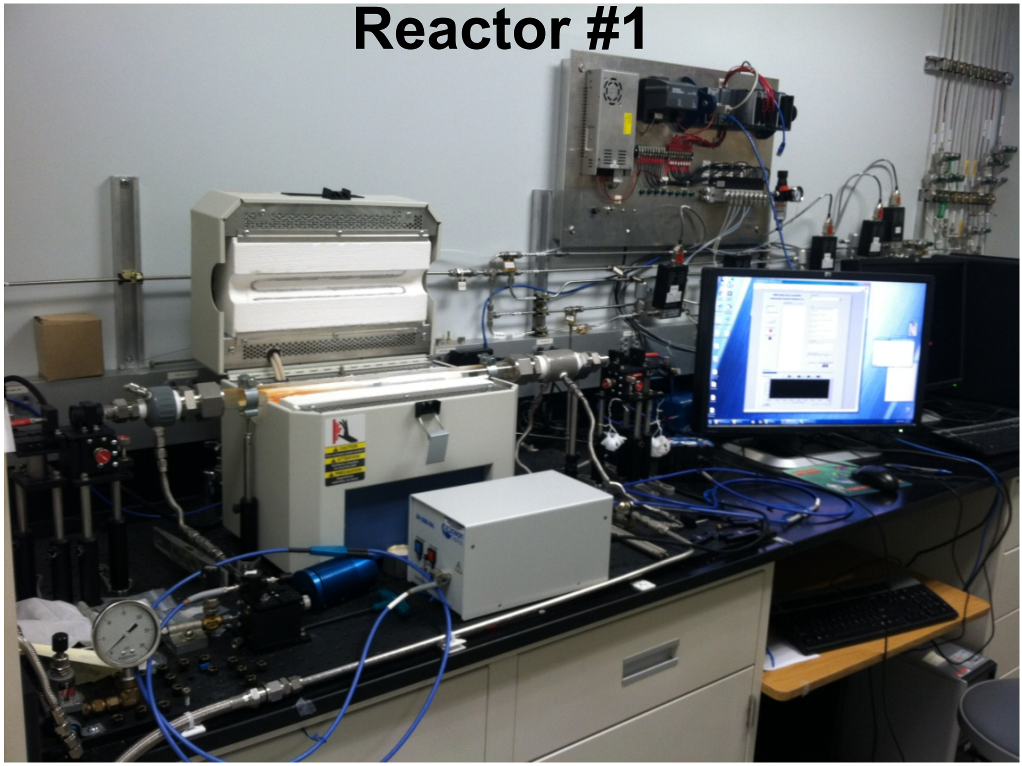
The Team Also Has Access to Microscopy, Nanofabrication, and Deposition Capabilities through Carnegie Mellon University.

A Well Equipped Set of Unique Facilities Can Be Leveraged in Collaborations with Extramurally Funded Research Efforts or Others.

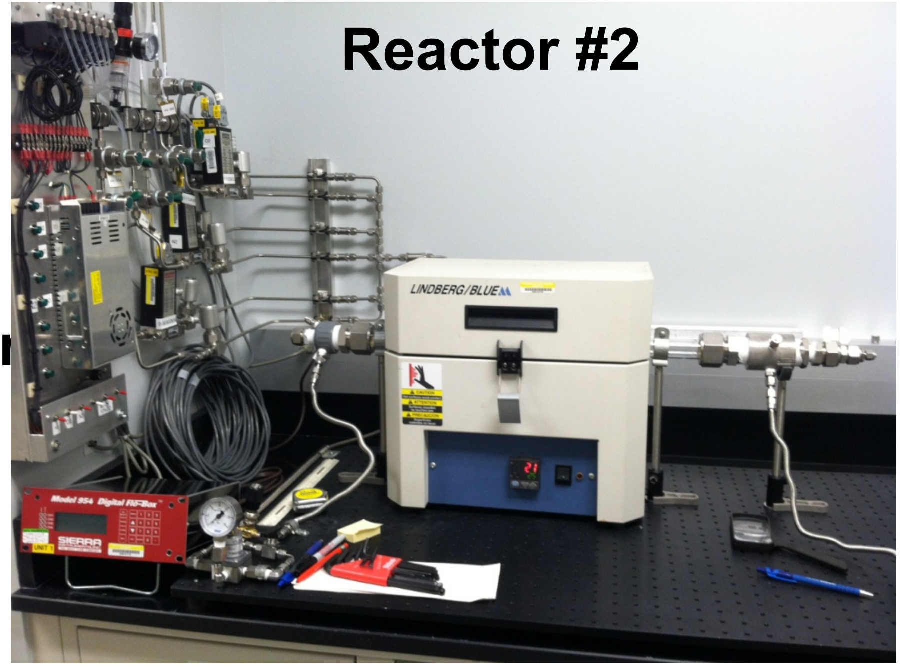
In-Situ Characterization Facilities

Thomas Brown

Temperatures up to 1000°C
Mixtures of H_2, N_2, O_2, CO, CO_2
Currently Atmospheric Pressure



Reactor #1



Reactor #2

Unique Capabilities for Fully Automated Characterization of Electrical and Optical Properties of Thin Films and Sensors at High Temperatures in Various Gas Mixtures Have Been Established

Publications, Patents, and Partnership Opportunity

Peer-Reviewed Publications Published / Accepted

- P. R. Ohodnicki, Future of Instrumentation International Workshop (FIIW), 2012, 1-4
- M. P. Buric, P. R. Ohodnicki, J. Duy, SPIE Nanoscience & Engineering, 84630D-84630D-14, 2012
- P. R. Ohodnicki, T. D. Brown, M. P. Buric, J. P. Baltrus, B. Chorpening, SPIE Nanoscience & Engineering, 845608-845608-12, 2012
- PR Ohodnicki, S Natesakhawat, JP Baltrus, B Howard, TD Brown, Thin Solid Films, 520 (19), 6243-6249 (2012)
- PR Ohodnicki, C Wang, S Natesakhawat, JP Baltrus, TD Brown, Journal of Applied Physics 111 (6), 064320-064320-11, (2012)
- P. R. Ohodnicki et al., Nanoscale, Vol. 5 (19), 9030-9039, 2013.
- P. R. Ohodnicki et al, Thin Solid Films, Vol. 539 (31) 327-336 (2013).
- M. Buric, P. Ohodnicki, and B. Chorpening, Proc. SPIE 8816, Nanoengineering: Fabrication, Properties, Optics, and Devices X, 88160N, 2013 (doi: 10.1117/12.2024167)
- P. R. Ohodnicki, T. Brown, Nanomaterials and Energy, Vol. 3 (2) 40-46 (2014).
- P. R. Ohodnicki et al., Sensors and Actuators B, Accepted and in Press, 2014.

Three Patents Awarded and Several Applications Submitted

Dr. Paul R. Ohodnicki, Jr.

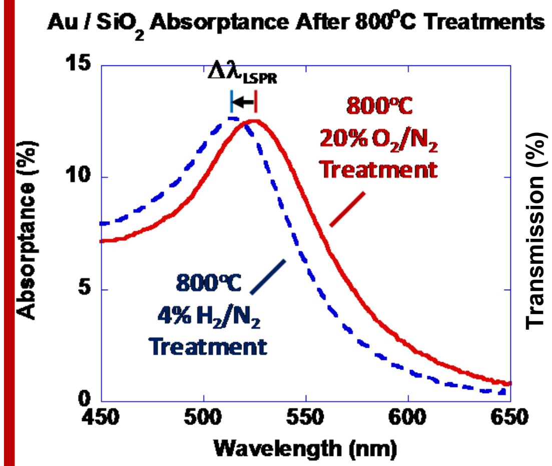
paul.ohodnicki@netl.doe.gov

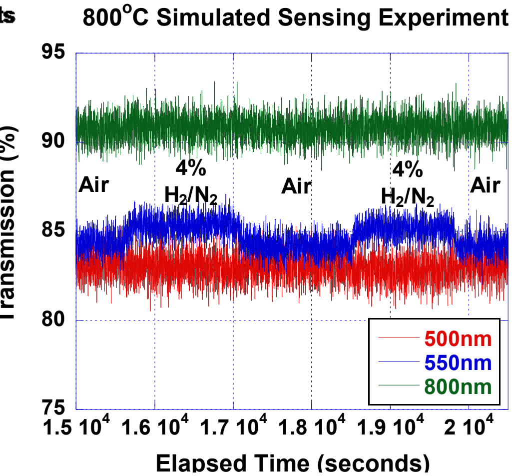
412-386-7389

Partnership Opportunity Notice:

http://www.netl.doe.gov/business/crada/pdfs/13-443223.pdf

Primary Sensing Material Design Strategies





Design Strategy #1: Plasmonic Au Nanoparticle Incorporated Oxides

"Catalytically Active Oxides"
Au / TiO_2, Au / YSZ, etc.

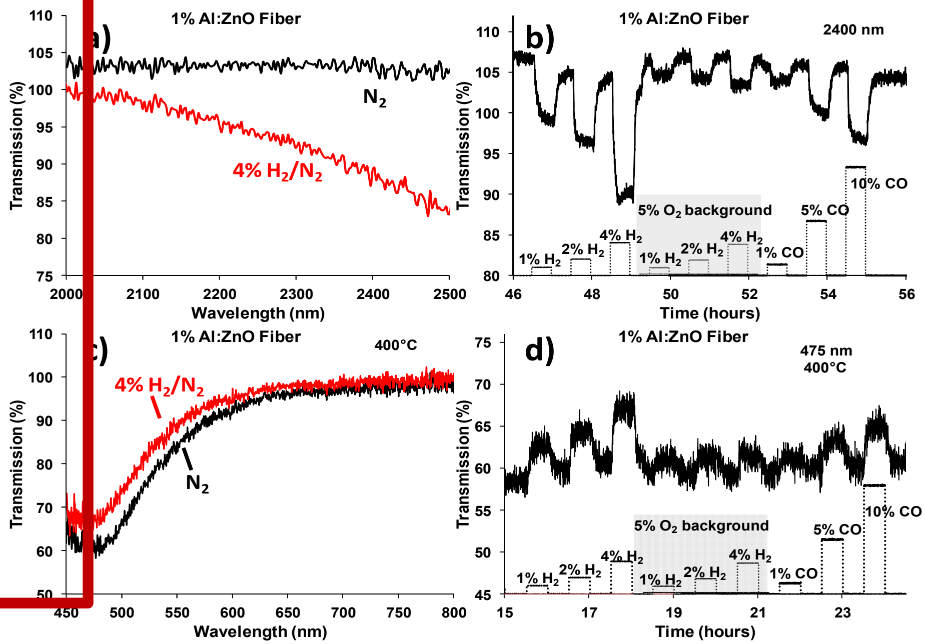
"Inert Oxides"
Au / SiO_2, Au / ZrO_2, etc.

Emphasis of Today's Presentation

Design Strategy #2: Transparent Conducting Metal Oxides

Al-Doped ZnO

Others…?



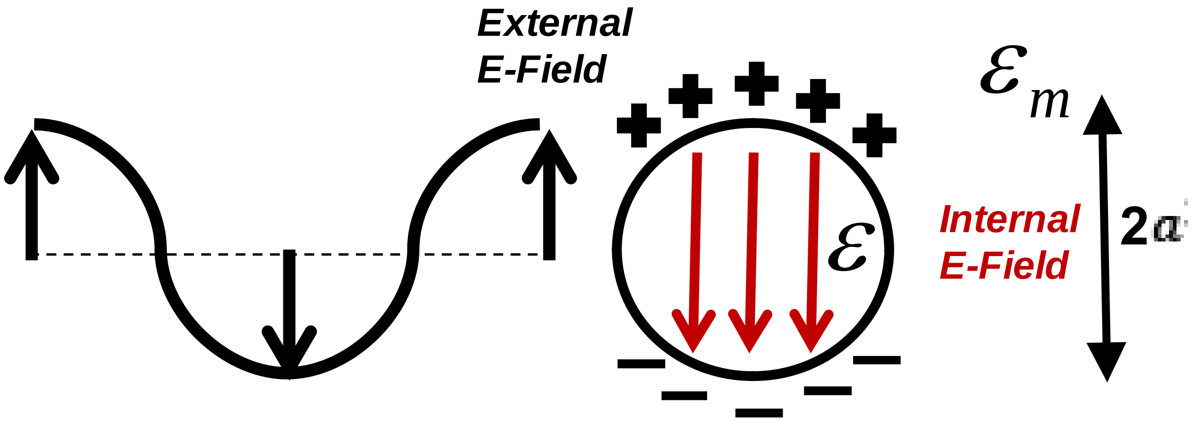
Crosscutting Research Review, Pittsburgh, PA, May 21,2014

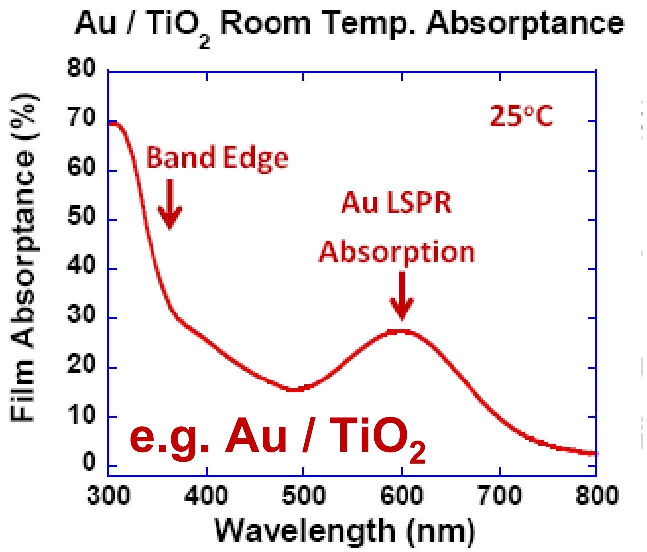
Recent R&D Updates :
Combined Gas and Temperature Optical Sensing Using Au-Nanoparticle Based Plasmonic Oxides

Based largely on an accepted manuscript in press in Sensors and Actuators B

Surface Plasmon Resonance Based Sensing

Localized Surface Plasmon Resonance (LSPR) in Noble Metal Nanoparticles is Associated with the Free Electrons





$$\left(Q_{Abs} = \frac{4\pi^2 a^3 \sqrt{\epsilon_m}}{2\lambda} Im\left[\frac{\epsilon_{Au}-\epsilon_m}{\epsilon_{Au}+2\epsilon_m}\right]\right)$$

A Peak in Absorption Occurs if:

Re[ε]□-2 ε_m

Froelich Condition

Surface Charges Create an Internal Field that Acts as a Restoring Force on Displaced Charge Carriers Resulting in an Oscillation with an Associated Resonance.

High Temperature Gas Sensing Using Au-Nanoparticle Incorporated Oxides

Au / TiO_2

Gold Nanoparticle-Doped TiO_2 Semiconductor Thin Films: Gas Sensing Properties**

By *Dario Buso, Michael Post, Carlo Cantalini, Paul Mulvaney,* and *Alessandro Martucci**

Adv. Funct. Mater. 2008, 18, 3843–3849

Au / WO_3

Optical hydrogen sensitivity of noble metal–tungsten oxide composite films prepared by sputtering deposition

Masanori Ando[a,*], Rupert Chabicovsky[b], Masatake Haruta[a]

Sensors and Actuators B 76 (2001) 13–17

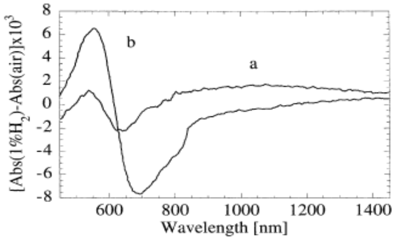


Fig. 8. Difference spectra obtained by subtracting the absorption spectra of the Au–WO_3 composite film in fresh air from those in air containing 1 vol.% H_2 at temperatures of: (a) 200°C; (b) 250°C.

Au / YSZ

Plasmonic Based Kinetic Analysis of Hydrogen Reactions within Au–YSZ Nanocomposites

Nicholas A. Joy, Charles M. Settens, Richard J. Matyi, and Michael A. Carpenter*

dx.doi.org/10.1021/jp11228h | *J. Phys. Chem. C* XXXX, XXX, 000–000

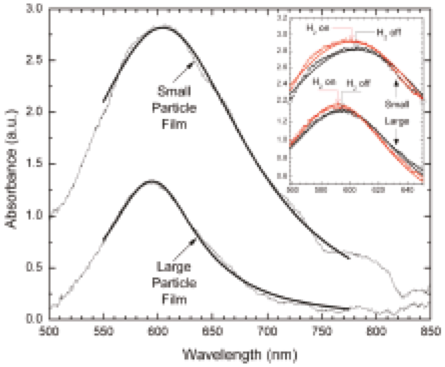
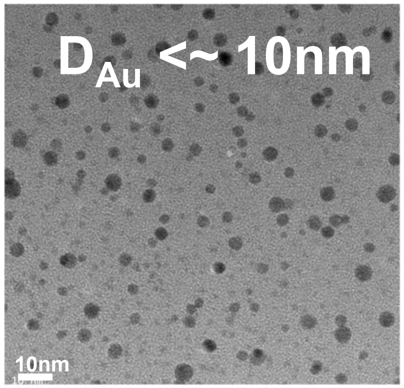
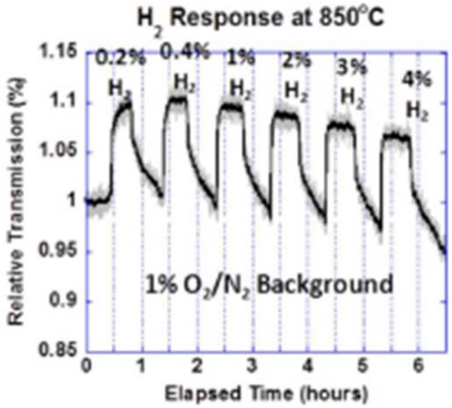


Figure 2. Example of the LSPR absorption spectra acquired during the experiment and the corresponding Lorentzian fits. The inset illustrates the ~3–5 nm peak shift upon gas exchange.

Au Nanoparticles in SiO_2





"Catalytically Active Oxides"

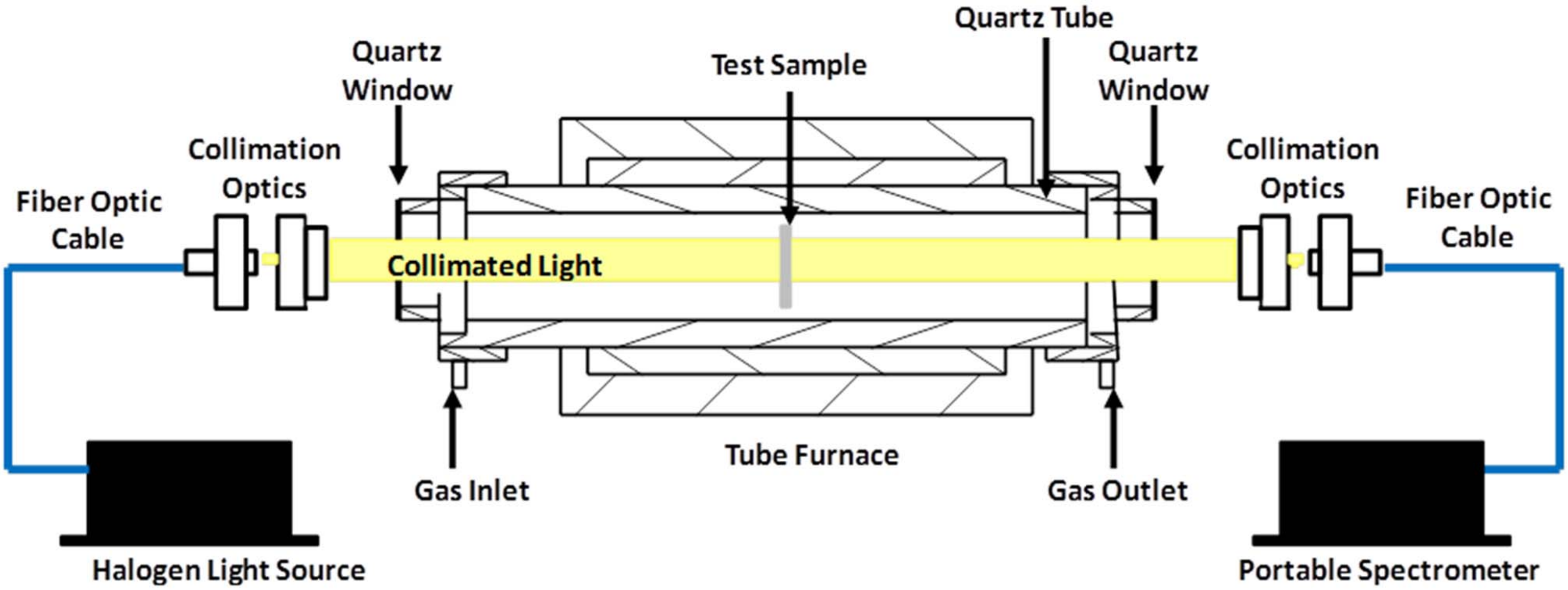
Examples: Au / NiO, Au / Co_3O_4, Au / YSZ, Au / TiO_2, Au / ZnO, Others

"Inert Oxides"

Examples: Au / SiO_2, Au / ZrO_2, Au / Al_2O_3

In-Situ Optical Measurements on Film Samples

Simple Schematic

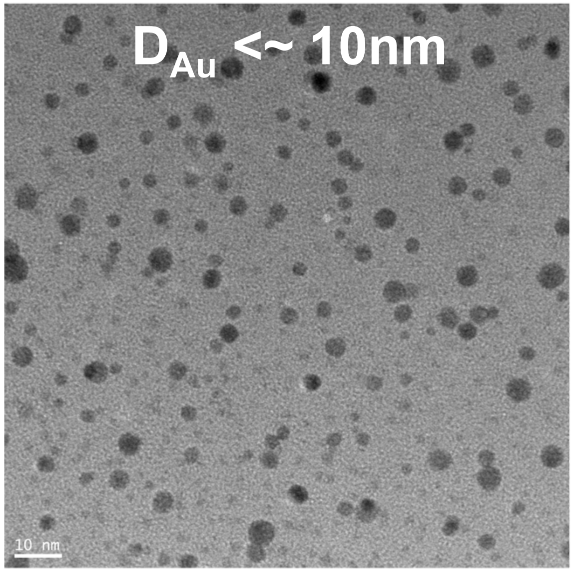


We Have Designed and Built a System that Allows us to Monitor Optical Transmission of Film Samples at Elevated Temperatures.

High Temperature Stable Systems: Au Incorporated "Inert" Oxides

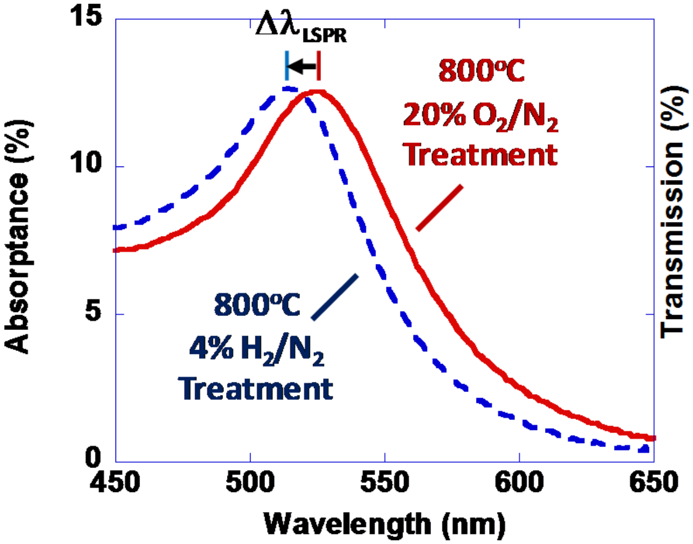
US 8,411,275 B1, P. R. Ohodnicki and T. D. Brown, 2013.

Au Nanoparticles in SiO_2

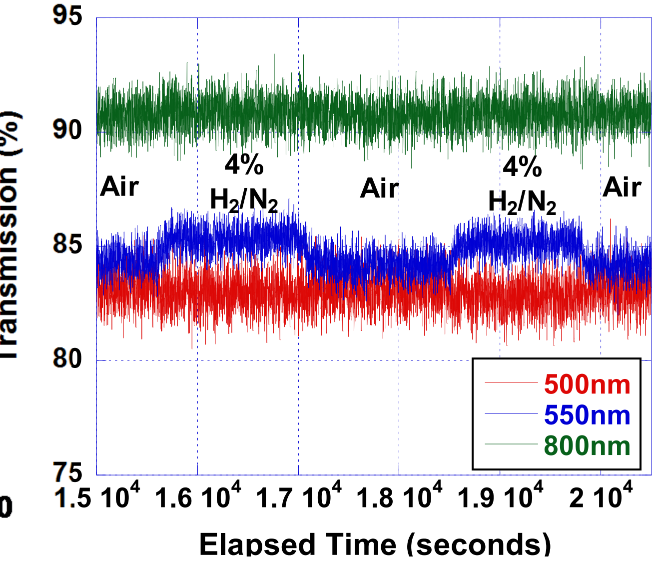


Gas Response

Au / SiO_2 Absorptance After 800°C Treatments



800°C Simulated Sensing Experiment



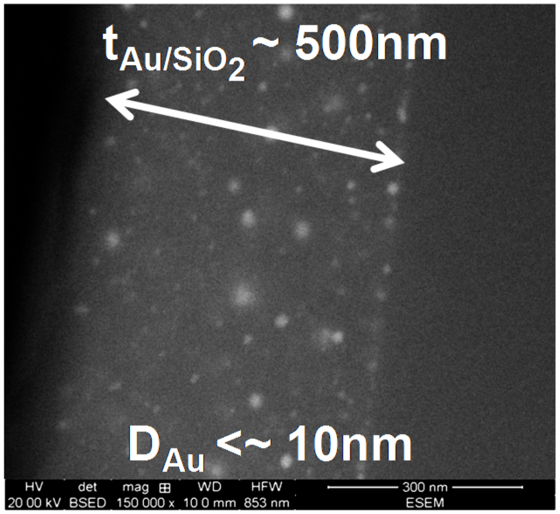
Despite a Low Electronic and Ionic Conductivity of SiO_2, Significant Responses to H_2 Have Been Observed For Au / SiO_2 Films Resulting in an LSPR Absorption Peak Shift to Shorter λ.

SiO_2 and Related Systems are Expected to Exhibit Improved Temperature Stability as Compared to Other More Active Oxides (TiO_2, WO_3, etc).

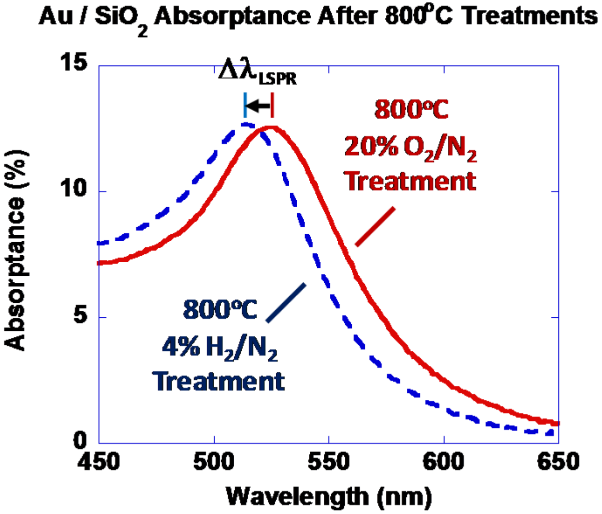
What is the LSPR Gas Sensing Mechanism?

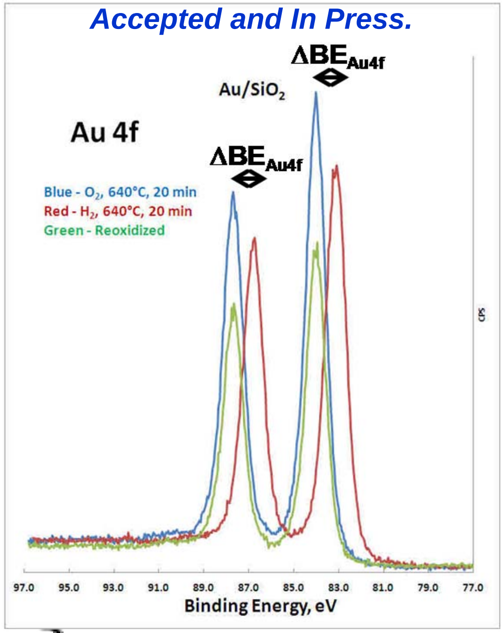
J. Baltrus et al., Applied Surface Science, Accepted and In Press.

Film Cross-Section



Gas Response





Binding Energy Shifts Suggest Charge Transfer

Absorption Cross Section of Au Nanoparticles

$$\left(Q_{Abs} = \frac{4\pi^2 a^3 \sqrt{\epsilon_m}}{2\lambda} Im\left[\frac{\epsilon_{Au}-\epsilon_m}{\epsilon_{Au}+2\epsilon_m}\right]\right)$$

Matrix Phase Dielectric Constant

NiO, WO$_3$

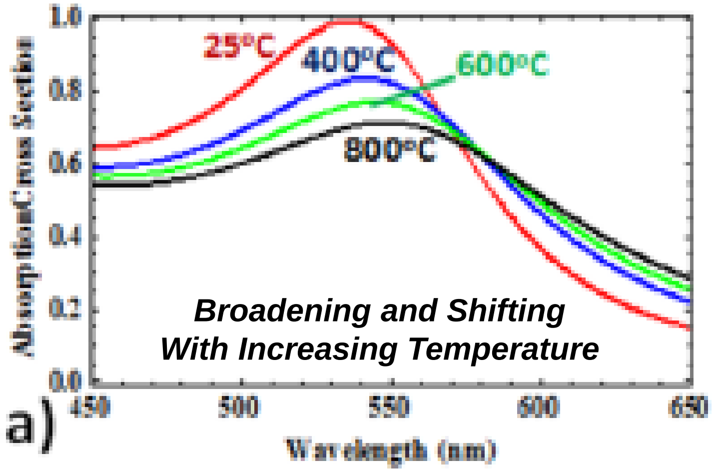
$$\varepsilon_{Au} = \varepsilon_{Au}(N,\Gamma)$$

TiO$_2$, SiO$_2$, YSZ *Free Carrier Density in Au*

Damping Frequency of Free Carriers in Au

Three Primary Parameters Can Change in Response to Changes in Environmental Conditions for Potential Use in Sensing Applications.

Theoretical Origin of Au LSPR Temp. Dependence

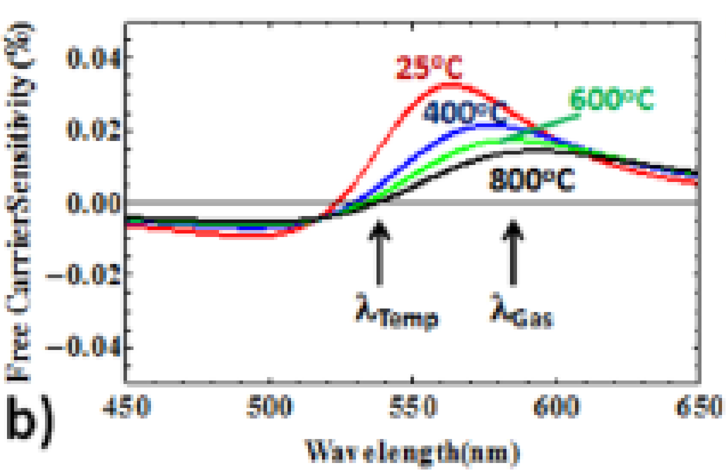


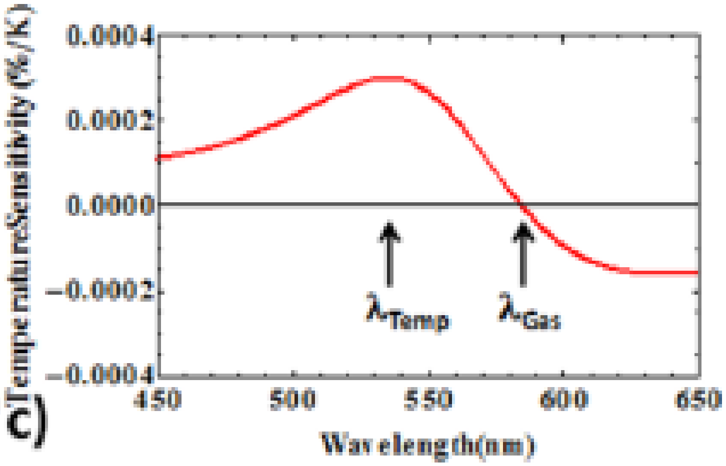
Theoretically Simulated Temperature Dependence of Au LSPR in SiO_2.

$\Gamma = \Gamma(\rho_{Au})$, $\Gamma\uparrow$ as $T\uparrow$ ← **Resistivity**

$\varepsilon_m = \varepsilon_m(T)$ ← **Refractive Index**

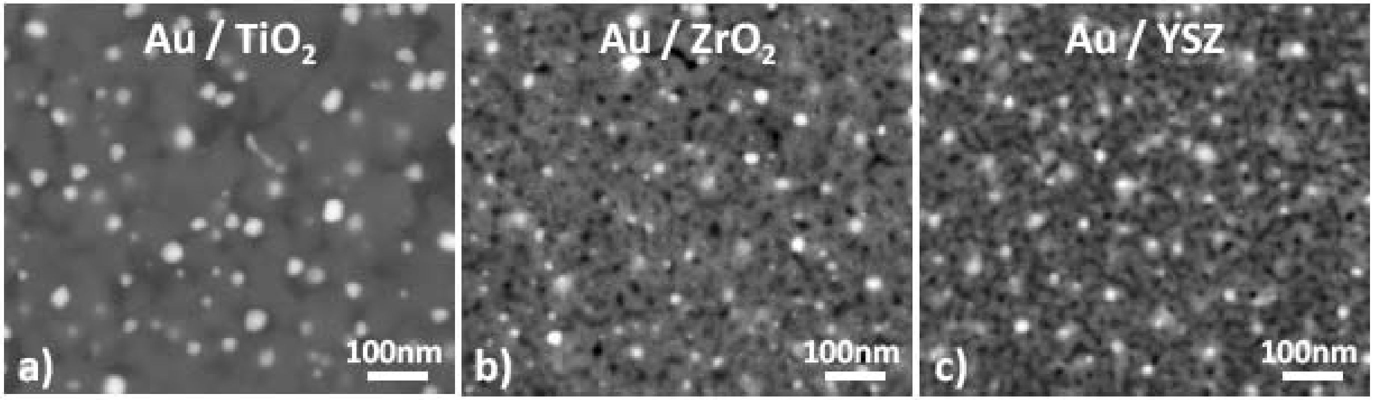
$N = N(V_{Au})$, $N\downarrow$ as $T\uparrow$ ← **Thermal Expansion**

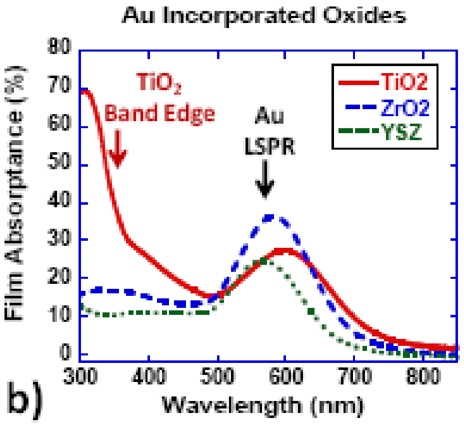


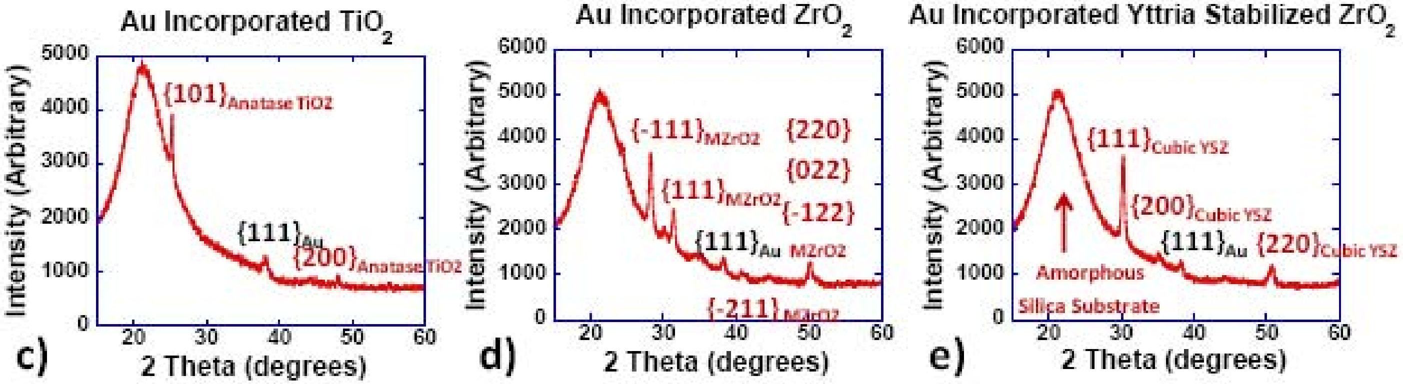


Wavelength Dependences of the Sensitivity to Changes in Chemical Composition and Temperature of a High Temperature Gas Stream are Different.

Examples of Au-Incorporated Oxides





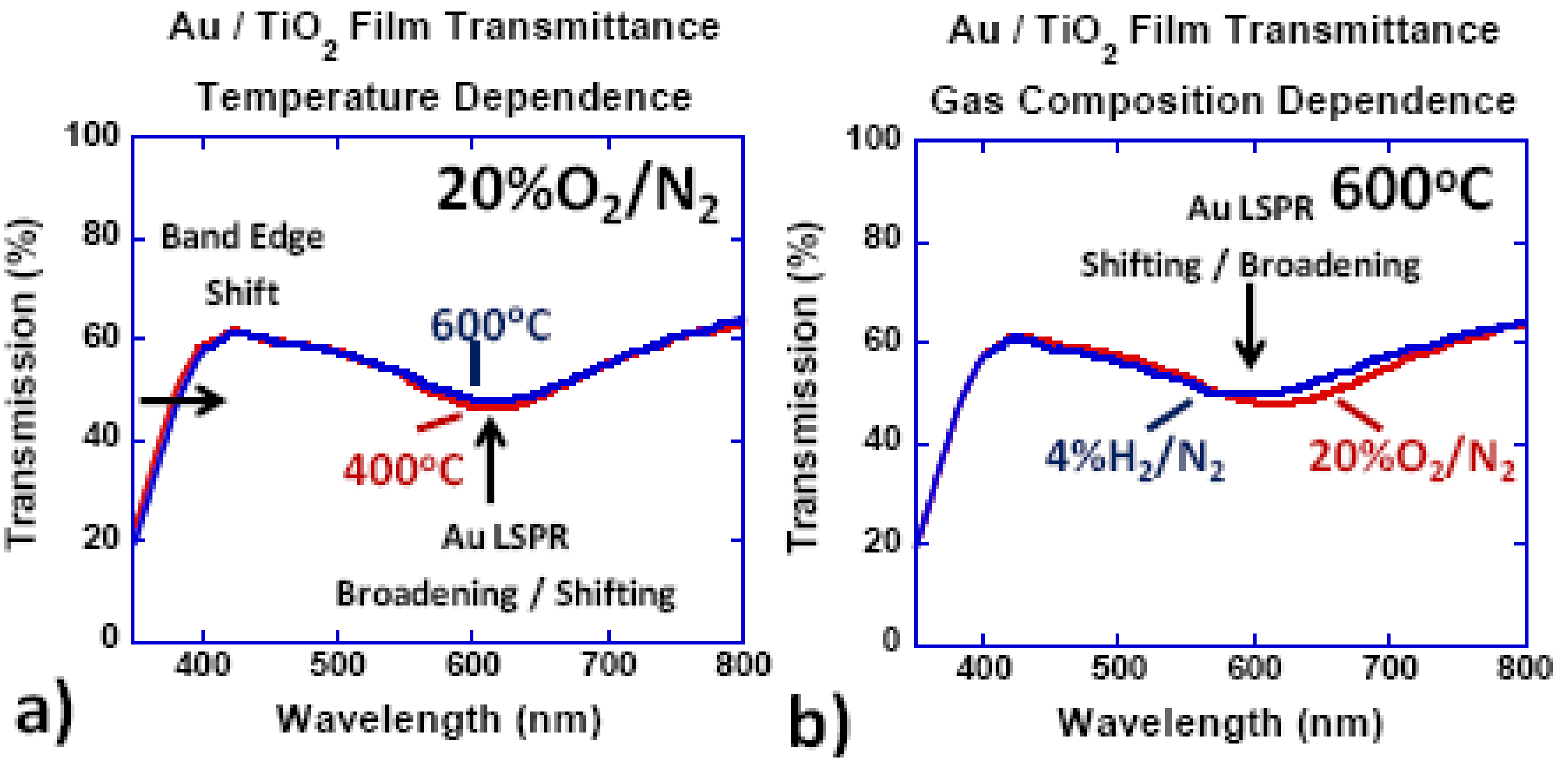


Base Metal Oxides

Summary	TiO_2	ZrO_2	YSZ
λ_{Min} (nm)	1089	1323	933
Thickness (nm)	121	176	132
n @ λ_{Min}	2.254	1.876	1.770

A Series of Different Au-Nanoparticle Incorporated Oxides were Prepared Using Standard Wet-Chemistry Based Sol-Gel Recipes.

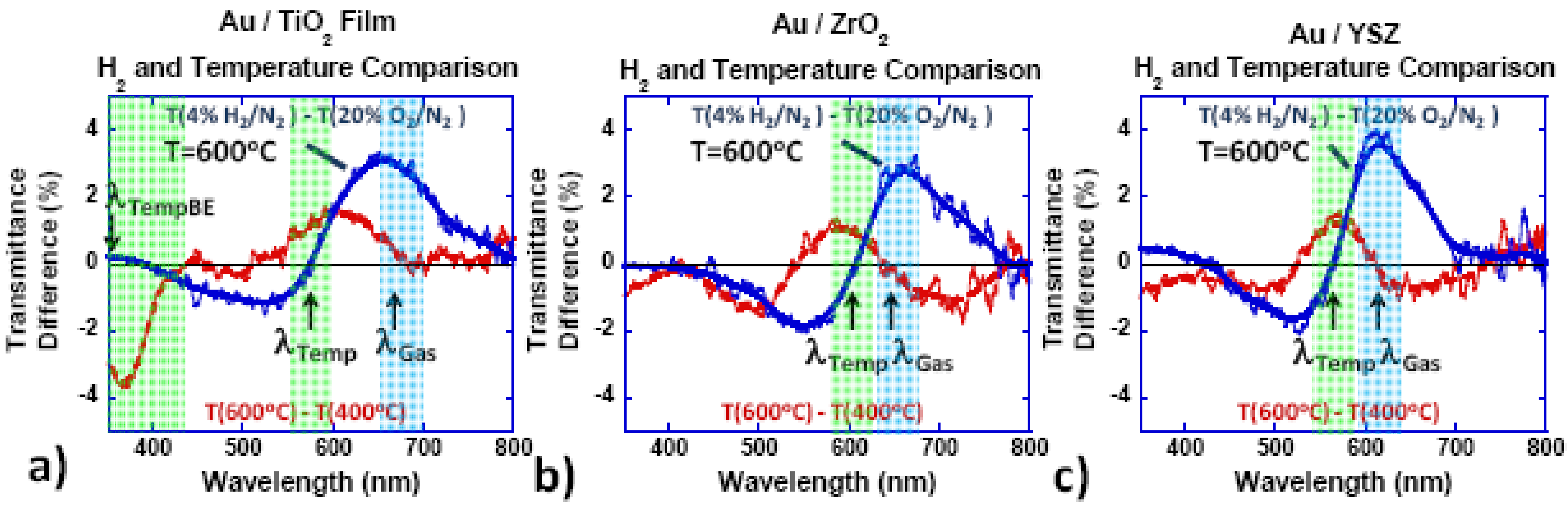
Optical Spectrum Dependence on Gas Stream Temperature and Composition



Transmittance Spectra of Synthesized Films are Sensitive to Both the Temperature and the Gas Stream Composition.

The Wavelength Dependences for Each Response are Unique.

Wavelength Dependent Responses



By Interrogation in Different Wavelength Ranges, One Expects to Identify Responses that are Preferentially Sensitive to Chemical Composition or Temperature of a Gas Stream.

For Oxides with a Well-Resolved Band-Edge in the Wavelength Range of Interest, Band-Edge Monitoring Can Also Be Exploited.

Optical Temperature Sensing Using Oxides

"Optical temperature sensor based on ZnO thin film's temperature dependent optical properties", S. Chengua et al., Review of Scientific Instruments, 82, 084901 (2011).

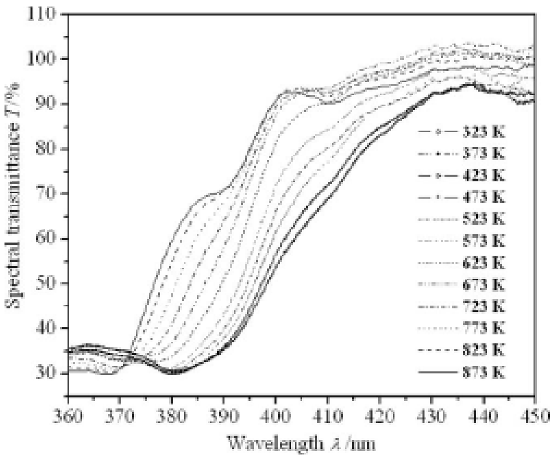


FIG. 3. Spectral transmittance under different experimental temperatures.

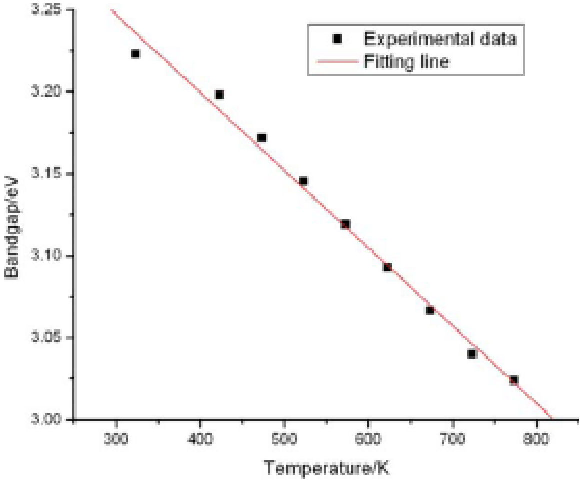


FIG. 4. (Color online) Experimental data and fitted line.

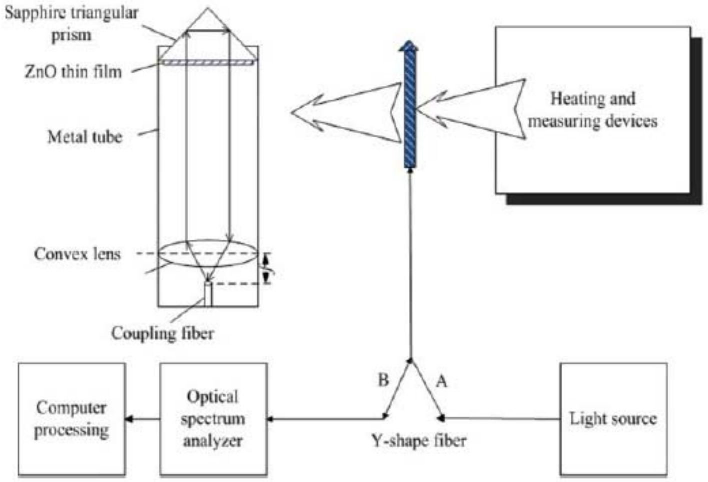


FIG. 2. (Color online) Schematic diagram of fiber temperature sensor system.

$$E_g = E_0 - \alpha T^2/(T + \beta)$$ ***Varshni, Physica 34, 149 (1967)***

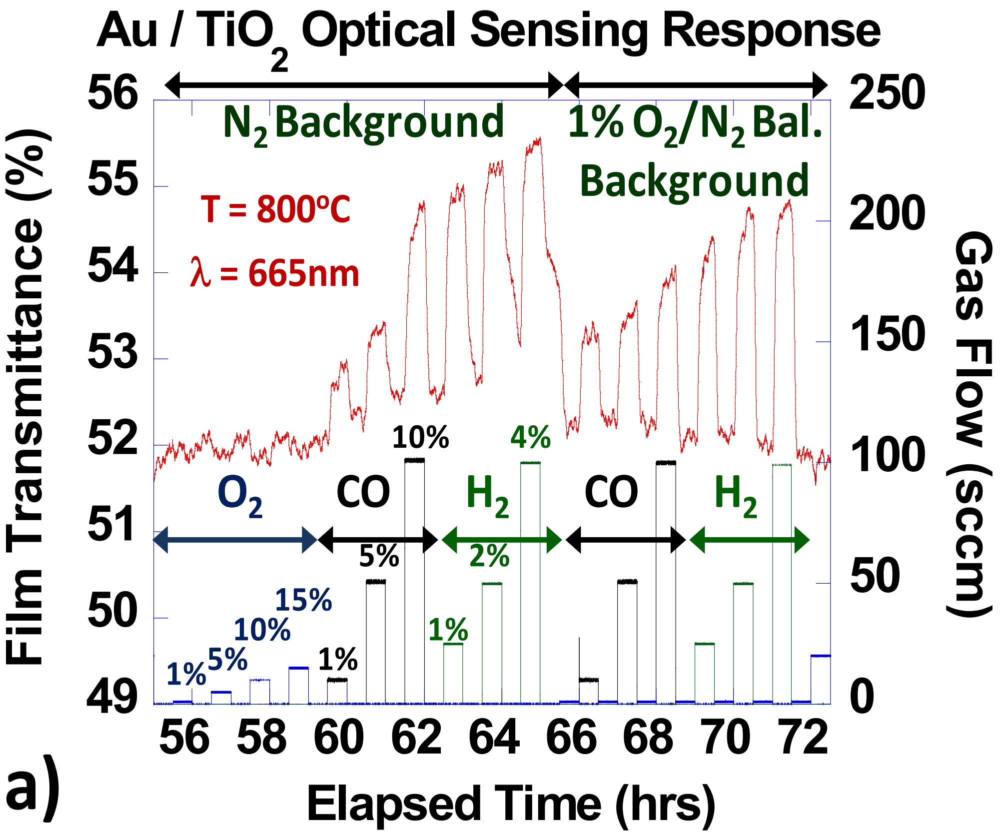
Metal Oxides Such as ZnO Have Been Proposed for Use as Temperature Sensors By Monitoring the Film Transmission in the Vicinity of the Band-Edge.

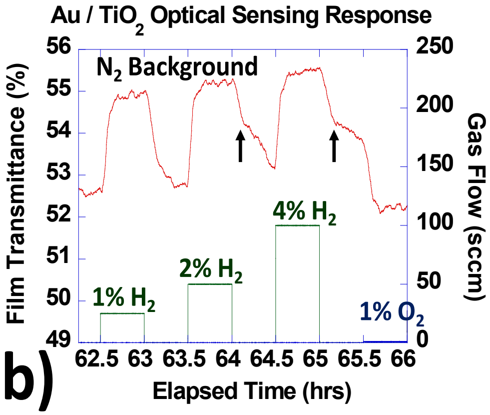
Temperature Dependent Bandgap Arises Due to Two Primary Factors:

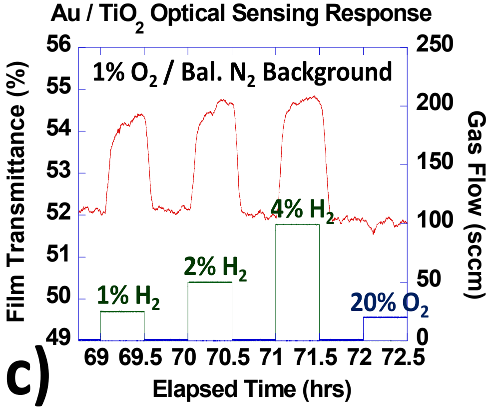
1) **Dilatation of the Lattice (Accounts for a Fraction, Linear at High T.)**
2) **Temperature Dependent Electron- Lattice Interaction (Major Effect)**

Gas Sensing at Wavelengths Near λ_{Gas}

INSERT REFERENCES HERE.



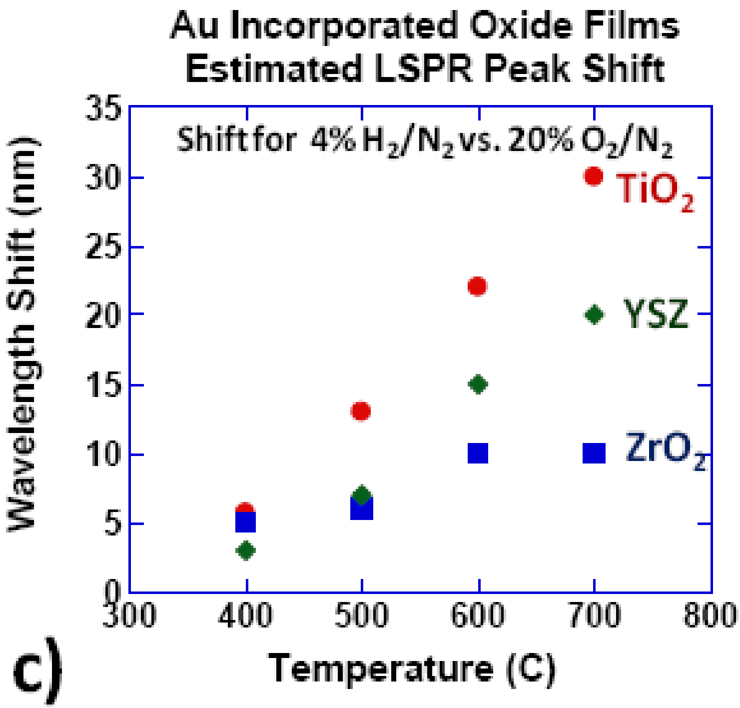


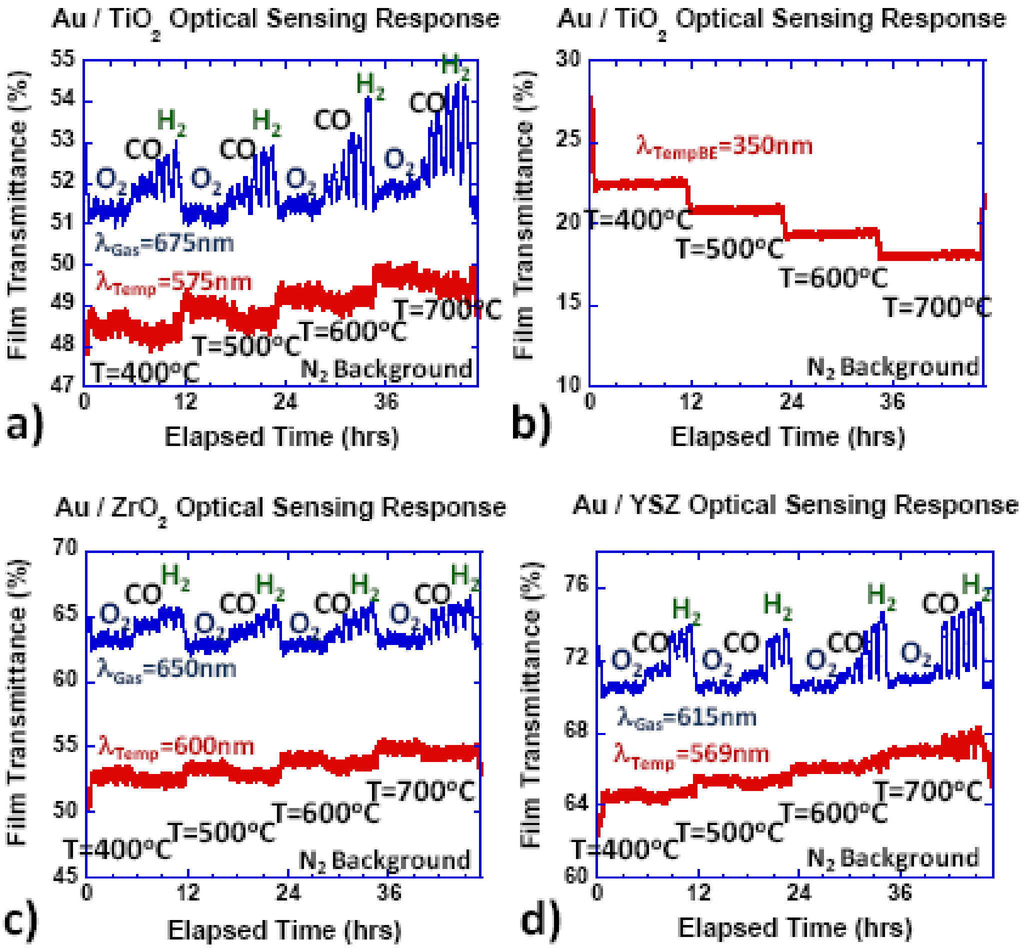


Gas Sensing Responses are Observed at a Wavelength Near the Peak Sensitivity.

Recovery Kinetics after Exposure to a H_2-Containing Atmosphere are Strongly Dependent Upon the Presence of O_2.

Combined Gas and Temperature Sensing

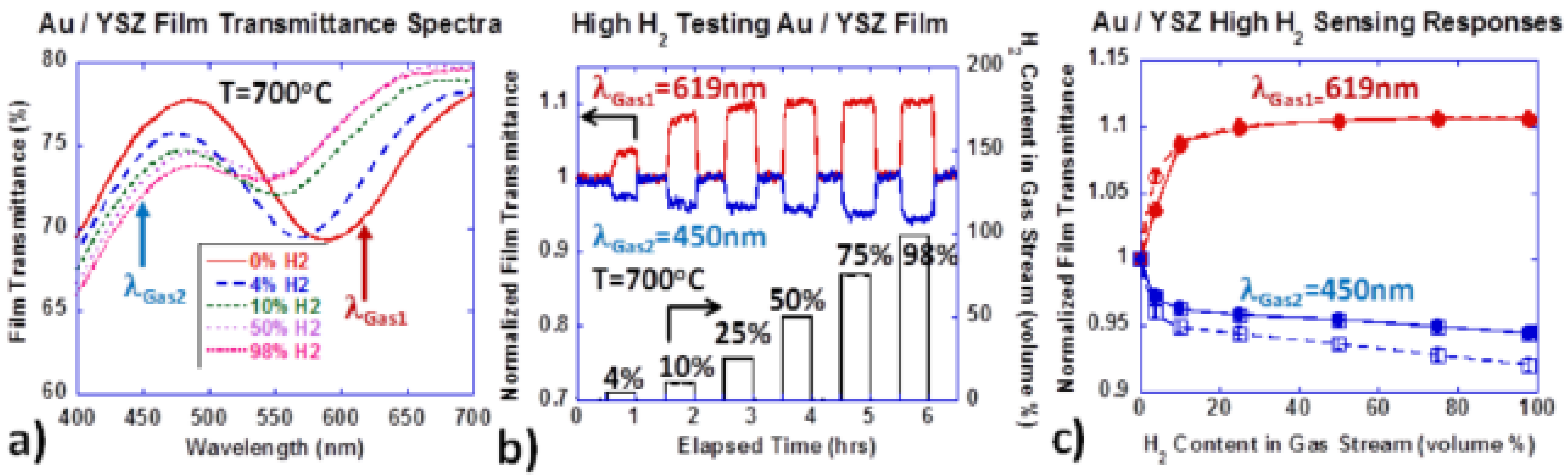




Through Careful Wavelength Selection, One Can Achieve Enhanced Relative Sensitivity to Gas Stream Composition or Temperature.

Band-Edge Interrogation Is Particularly Effective for Temperature Sensing.

Gas Sensing Responses in High H_2 Concentrations

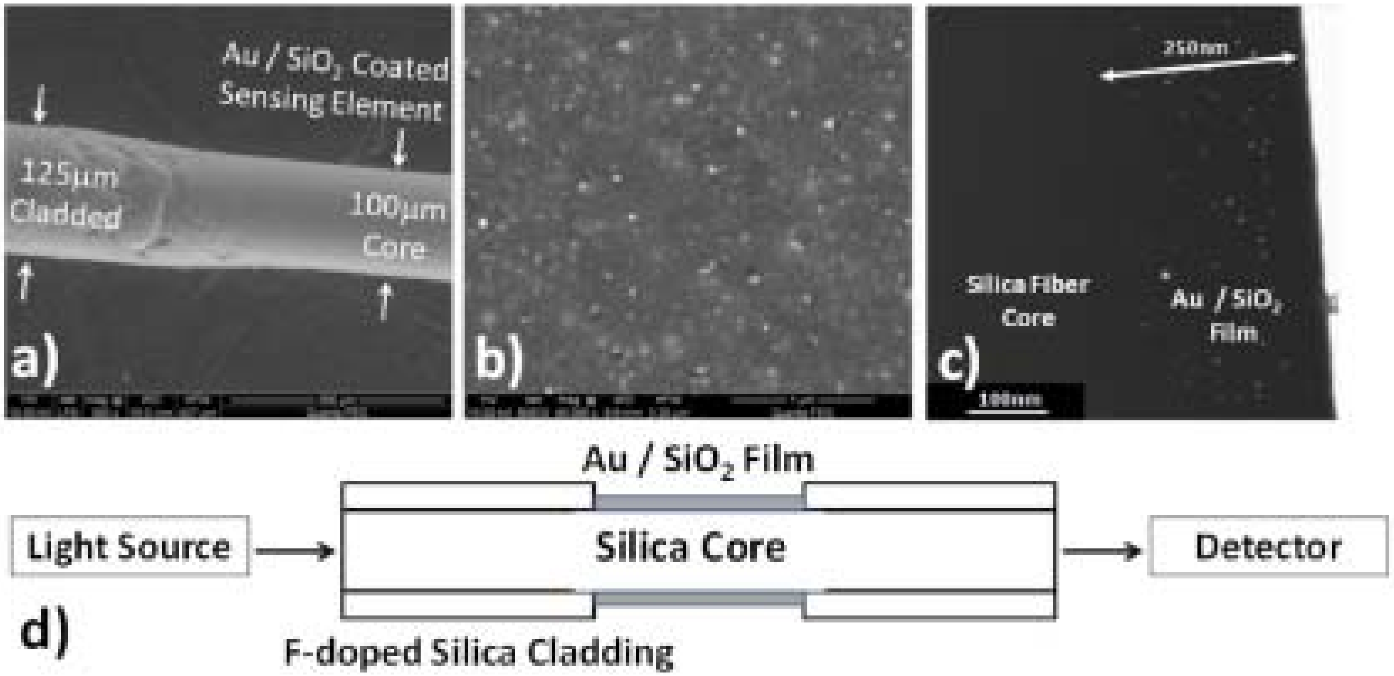


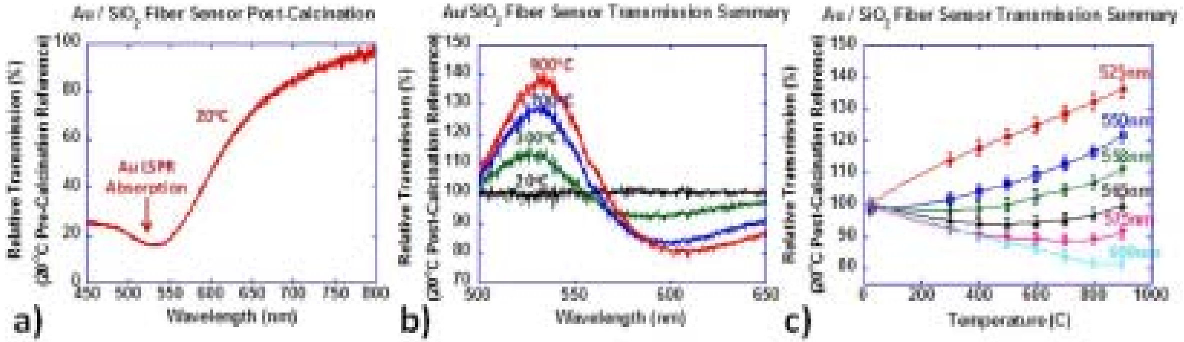
In All Three Material Systems Investigated, Saturation Effects are Observed for High H_2 Concentration Gas Streams at Interrogation Wavelengths Greater than the LSPR Absorption Peak Wavelength.

Short Wavelength Interrogation Below the LSPR Absorption Peak Enables Improved High Level H_2 Sensing.

Fabricated Fiber Sensor Results

P. R. Ohodnicki et al., Nanoscale, Vol. 5 (19), 9030-9039, 2013.





Fabricated Sensor Elements Based upon the Au / SiO_2 System and the Temperature Dependent Optical Transmission

Recent R&D Updates :
Realistic Contaminated Fuel Gas Stream Exposure

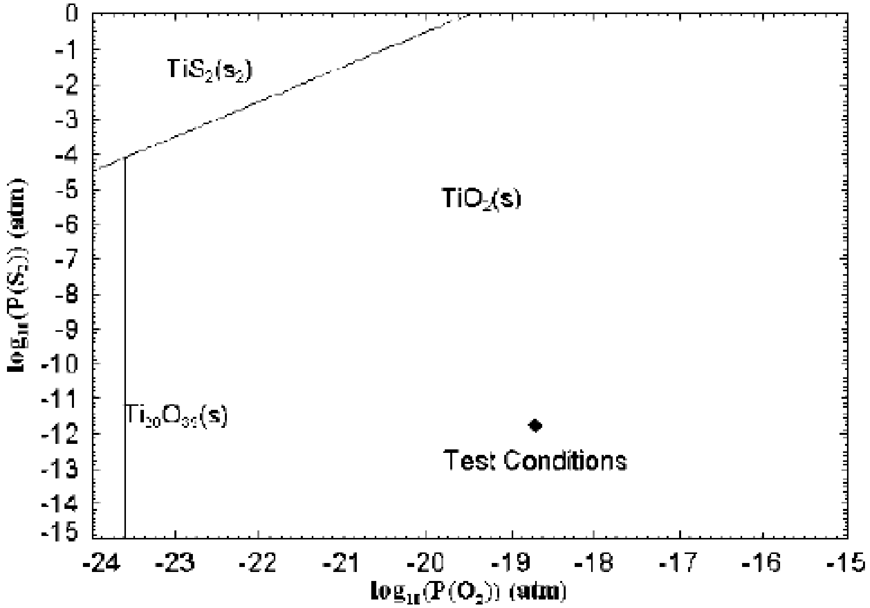
Based largely on an accepted manuscript in press in Sensors and Actuators B

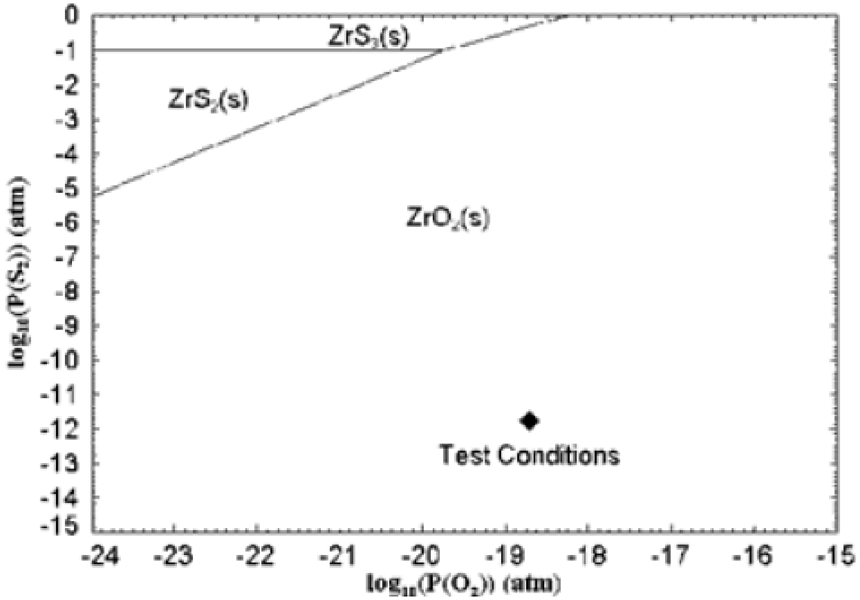
Realistic Fuel Gas Stream Composition

Estimated Contaminated Anode Stream Composition:

34.0%H_2, 23.6%CO, 22.2%H_2O, 17.0%CO_2, 3.2%N_2, 0.026%CH_4, 29ppm H_2S

Temperature = 800°C, Approximately 1 Week Exposure

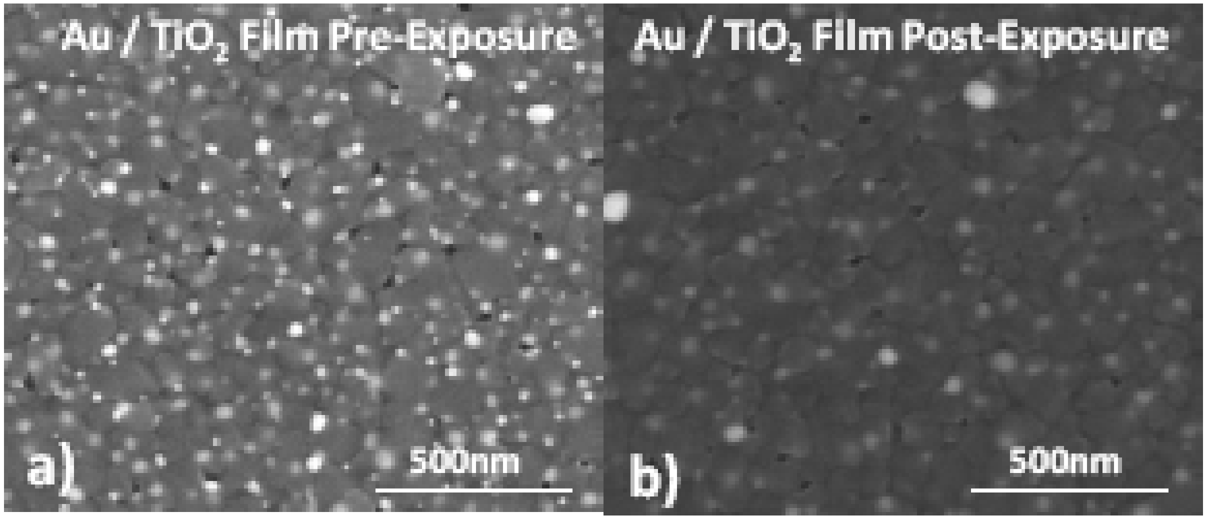


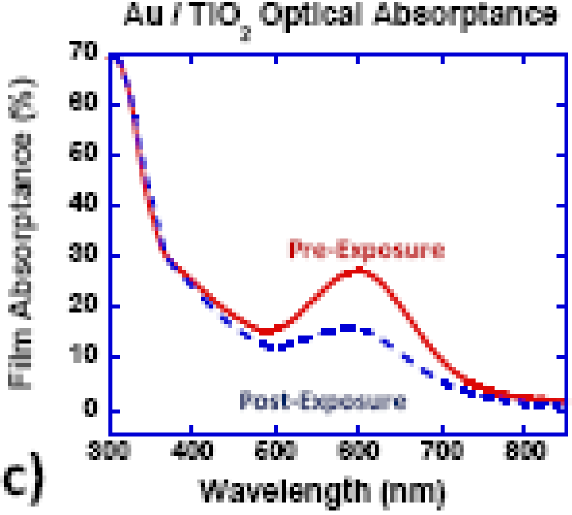


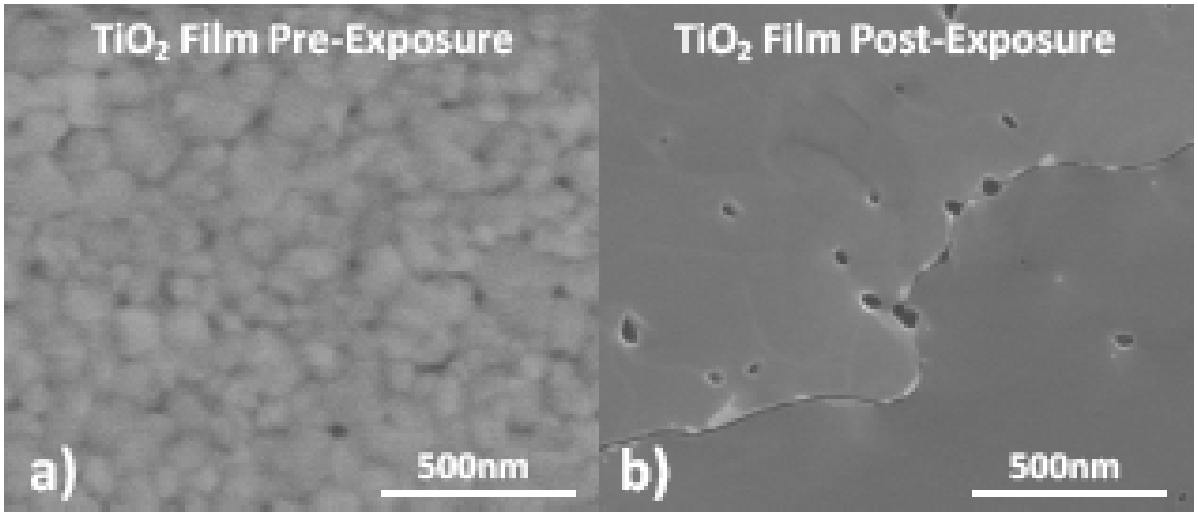
The Oxide Matrix Phases and Au are All Expected to be Stable in the Chosen Fuel Gas Stream.

All Samples were Subjected to a Realistic Fuel Gas Stream Exposure to Gain Preliminary Information About the Sensor Material Stability.

Microstructural Evolution / Instability







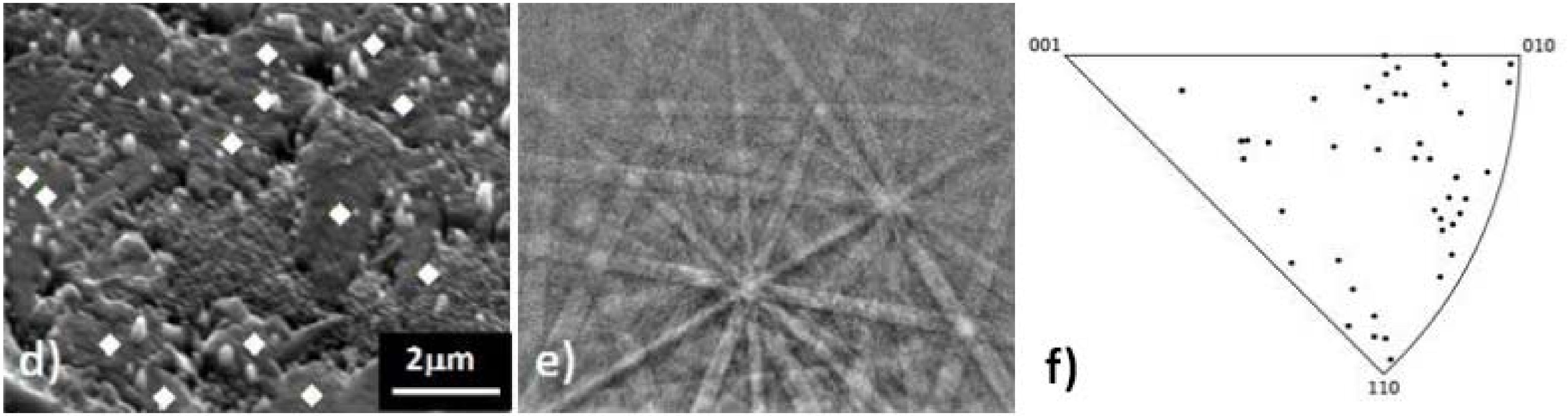
→ Au-Nanoparticle Coarsening and Mass Loss

→ Anatase to Rutile Transformation (Particularly for Base TiO_2)

Some Material Instability was Observed, Au-Nanoparticles Tended to Stabilize Base Oxide Microstructure… But Au Mass Loss was Observed

Kinetic Stabilization of Anatase Phase

Au-Nanoparticles Tend to Inhibit the Anatase → Rutile Phase Transformation, Likely Due to Grain Boundary Pinning Effects



Locally Obtained Electron Backscatter Diffraction Patterns Illustrate The Large Grains Which Form After the Exposure Step are Rutile Phase in the Au / TiO_2 Films

No Tendency for Preferred Orientation of the Large Rutile Grains Were Identified

Additional Studies are Needed of Sensor Material Stability Under Contaminated Fuel Gas Conditions Which are Underway.

Summary and Conclusions

1) The Team is Actively Working to Develop Embedded Sensors for High Temperature Fossil Applications with an Emphasis on Advanced Sensor Materials

2) The Team Welcomes Opportunities to Discuss New Collaborations and Partnerships.

3) Promising Results for Simultaneous Gas and Temperature Sensing under Application Relevant Temperatures Have Been Demonstrated in Au-Incorporated Oxides But Additional Studies of Stability in Contaminated Fuel Gas Streams are Required

4) Broadband Wavelength Interrogation Approaches May Enable Multi-Parameter Functionality of Sensors (Temperature, Gas Composition)

→ Unique Wavelength Dependences of LSPR Absorption on Temperature and Chemical Composition of a Gas Stream

→ Combined Band-edge and LSPR Sensing

Thank you for your attention!

Crosscutting Research Review, Pittsburgh, PA, May 21,2014

Acknowledgements and Disclaimer

This work was funded by the Cross-Cutting Technologies Program at NETL.