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

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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)

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**

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.).

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**Table of Relevant Harsh Environments in Advanced Fossil Energy Technologies**

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<td>Examples of Important Gas Species</td>
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<td>Hydrogen from Gaseous Fuels and Oxygen from Air</td>
<td>(\text{Steam, CO, CO}_2, \text{NO}_x, \text{SO}_x)</td>
</tr>
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</table>
Advanced Fossil-Based Power Generation

Example: Solid Oxide Fuel Cells

Internal Gas and Temperature Distribution

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

Temperature: 700-800°C
Anode Stream: Fuel Gas (e.g. H₂-Containing)
Cathode Stream: Air or O₂

Project Overview
Thin Film Functional Sensor Layers in Harsh Environment Sensing Applications

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

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

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

Sensor Response (Sensitivity, Selectivity, Stability)

Depends Upon Intrinsic Material Properties, Average Grain Size, Porosity, Electronic / Ionic Exchange at Surfaces, Microstructural Stability, etc.
Example: Pd-Thin Films for H₂-Sensing Applications

Fiber Optic Sensor for Hydrogen Concentrations near the Explosive Limit

Michael A. Butler
Sandia National Laboratories, Albuquerque, New Mexico 87185


1.5 Pages Long, > 84 Citations!

A Sensor for Leak Detection of H₂ in Potentially Explosive Conditions was Proposed by End-coating an Optical Fiber with a Pd Thin Film by Butler in 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 H₂ in N₂. 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.
Motivation for Looking at Optical Materials

Chemiresistive materials: the fundamentals are understood
- 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?

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

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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

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.

Project Leadership / Coordination
Sensor Material R&D
Sensor Packaging and Prototype Development

Sensor Interrogation Methodologies
Supporting Sensor Material R&D

Sensor Device Platform Stability
Collaborative Interactions with the Project Team

2 – Joint Peer-reviewed Publications (U. Pitt, U. Albany)
1 - Additional Joint Publication Currently in Preparation (U. Conn.)

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.

Advanced Functional Sensor Material Project Team

Extramural Crosscutting Program Research

Upcoming MRS Fall Meeting symposium
Unique Capabilities / Facilities of the Project Team

In-Situ Characterization Tools
- High Temp. X-ray Diffraction
  - Temperatures up to 1300°C
  - Gases Including H₂, O₂, N₂, CO
- High Temperature Scanning Electron Microscopy
  - ~ 0.5 torr of H₂O(g) or Air
  - Temperatures up to 900°C
- X-ray Photoelectron Spectroscopy with a Reaction Chamber
  - Temperatures up to 1300°C
  - Gases Including H₂, O₂, N₂, CO

In-Situ Property / Device Measurements
- Ambient Pressure Reactors:
  - H₂, O₂, N₂, CO, CO₂, CH₄
  - Temperatures up to 900°C
  - Full System Automation
- Elevated Pressure Reactor:
  - H₂, O₂, N₂, CO, CO₂, CH₄
  - Temperatures up to 900°C
  - 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.
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
- P. R. Ohodnicki et al., Sensors and Actuators B, Accepted and in Press, 2014.

Three Patents Awarded and Several Applications Submitted

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Partnership Opportunity Notice:


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Primary Sensing Material Design Strategies

Design Strategy #1: Plasmonic Au Nanoparticle Incorporated Oxides
“Catalytically Active Oxides”
Au / TiO₂, Au / YSZ, etc.

“Inert Oxides”
Au / SiO₂, Au / ZrO₂, etc.

Design Strategy #2: Transparent Conducting Metal Oxides
Al-Doped ZnO
Others…?

Emphasis of Today’s Presentation
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

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

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

A Peak in Absorption Occurs if:

\[
\text{Re}[\varepsilon] - 2\varepsilon_m
\]

Froelich Condition

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High Temperature Gas Sensing Using Au-Nanoparticle Incorporated Oxides

Au / TiO₂

Gold Nanoparticle-Doped TiO₂ Semiconductor Thin Films: Gas Sensing Properties

By Dario Buon, Michel Post, Carlo Cantalini, Paul Mulvaney, and Alessandro Martucci


Au / YSZ

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

Nicholas A. Joy, Charles M. Setten, Richard J. Matyjasik, and Michael A. Carpick

Au Nanoparticles in SiO₂

Dₐu <~ 10nm

“Catalytically Active Oxides”

Examples: Au / NiO, Au / Co₃O₄, Au / YSZ, Au / TiO₂, Au / ZnO, Others

“Inert Oxides”

Examples: Au / SiO₂, Au / ZrO₂, Au / Al₂O₃

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In-Situ Optical Measurements on Film Samples

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

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High Temperature Stable Systems: Au Incorporated “Inert” Oxides

Despite a Low Electronic and Ionic Conductivity of SiO₂, Significant Responses to H₂ Have Been Observed For Au / SiO₂ Films Resulting in an LSPR Absorption Peak Shift to Shorter λ.

SiO₂ and Related Systems are Expected to Exhibit Improved Temperature Stability as Compared to Other More Active Oxides (TiO₂, WO₃, etc.).
What is the LSPR Gas Sensing Mechanism?

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

Absorption Cross Section of Au Nanoparticles

$$Q_{Abs} = \frac{4\pi^2 a^3 \sqrt{\varepsilon_m}}{2\lambda} \text{Im} \left[ \frac{\varepsilon_{Au} - \varepsilon_m}{\varepsilon_{Au} + 2\varepsilon_m} \right]$$

Matrix Phase Dielectric Constant

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

Free Carrier Density in Au

Damping Frequency of Free Carriers in Au

TiO₂, SiO₂, YSZ

Binding Energy Shifts Suggest Charge Transfer

NiO, WO₃

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

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Theoretical Origin of Au LSPR Temp. Dependence

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

Theoretically Simulated Temperature Dependence of Au LSPR in SiO₂:

\[ \Gamma = \Gamma(\rho_{Au}), \Gamma \uparrow \text{ as } T \uparrow \]

- Resistivity
- Refractive Index
- Thermal Expansion

\[ \varepsilon_m = \varepsilon_m(T) \]

\[ N = N(V_{Au}), N \downarrow \text{ as } T \uparrow \]
Examples of Au-Incorporated Oxides

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.
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).

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)

\[ E_g = E_0 - \alpha T^2 / (T + \beta) \]

Varshni, Physica 34, 149 (1967)
Gas Sensing Responses are Observed at a Wavelength Near the Peak Sensitivity.

Recovery Kinetics after Exposure to a H₂-Containing Atmosphere are Strongly Dependent Upon the Presence of O₂.
Combined Gas and Temperature Sensing

Gas Sensing Responses in High H₂ Concentrations

In All Three Material Systems Investigated, Saturation Effects are Observed for High H₂ 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 H₂ Sensing.
Fabricated Fiber Sensor Results


Fabricated Sensor Elements Based upon the Au / SiO₂ System and the Temperature Dependent Optical Transmission

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

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

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Realistic Fuel Gas Stream Composition

Estimated Contaminated Anode Stream Composition:
34.0%H₂, 23.6%CO, 22.2%H₂O, 17.0%CO₂, 3.2%N₂, 0.026%CH₄, 29ppm H₂S
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.
Some Material Instability was Observed, Au-Nanoparticles Tended to Stabilize Base Oxide Microstructure... But Au Mass Loss was Observed

→ Au-Nanoparticle Coarsening and Mass Loss

→ Anatase to Rutile Transformation (Particularly for Base TiO₂)
Kinetic Stabilization of Anatase Phase

Au-Nanoparticles Tend to Inhibit the Anatase $\rightarrow$ 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!
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