Optical Fiber Based Sensors for Future Fossil Energy Applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

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March 23, 2017

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Presentation Overview

- NETL R&IC Sensor Material and Optical Fiber Sensor Program Overview
    - Fossil Energy Needs Driving Advanced Sensors
    - Enabling Materials for Harsh Environment Sensing
    - Current Capabilities, Research Thrusts, and Partnerships
- Highlights of Recent Results and On-Going Activities
    - H_2 Sensing Materials for SOFCs
    - Stability of High Temperature Functional Sensor Layers
    - Thermal Emission Based High Temperature Sensing
    - Theoretical Investigations of High Temperature Oxide Sensor Materials
    - Enhanced Temperature Stability for Distributed Interrogation
    - Embedding of Sensors for High Temperature Applications
    - Optical Fiber Materials Research and Development
- Summary and Conclusions

Fossil Energy Needs Driving Advanced Sensors

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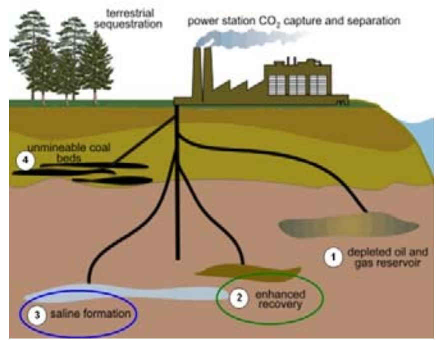
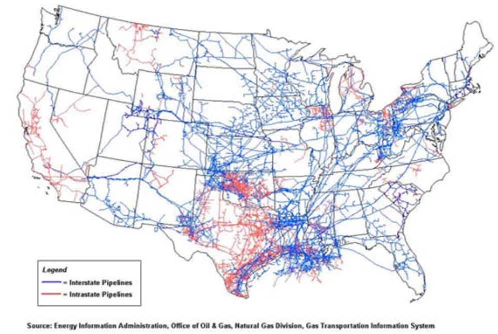
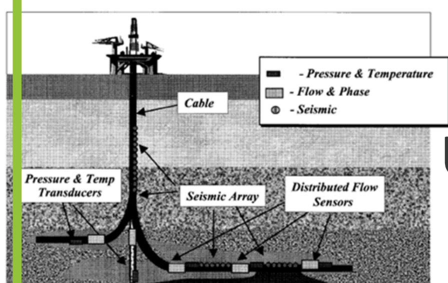
Power Generation (Combustion, Fuel Cells, Turbines, etc.)

CO_2 Sequestration



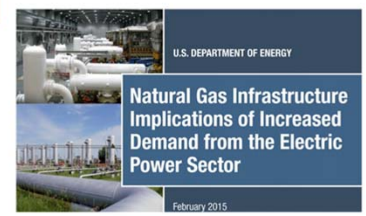
Natural Gas Infrastructure





Unconventional Oil & Gas

Properties of Methane	
Chemical Formula	CH4
Lifetime in Atmosphere	12 years
Global Warming Potential (100–year)	28–36



NETL Has Needs, On-going Funded Projects, and In-House Research Activity in Harsh Environment Sensing for a Broad Array of Applications.

Fossil Energy Needs Driving Advanced Sensors

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Short Term Focus

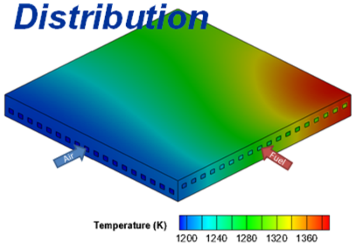
	Coal Gasifiers	Combustion Turbines	Solid Oxide Fuel Cells	Advanced Boiler Systems
Temperatures	Up to 1600°C	Up to 1300°C	Up to 900°C	Up to 1000°C
Pressures	Up to 1000psi	Pressure Ratios 30:1	Atmospheric	Atmospheric
Atmosphere(s)	Highly Reducing, Erosive, Corrosive	Oxidizing	Oxidizing and Reducing	Oxidizing
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

SOFC Temperature : 700-800°C

Anode Stream : Fuel Gas (e.g. H_2-Containing)

Cathode Stream : Air or O_2

Example : Solid Oxide Fuel Cells Internal Gas and Temperature Distribution



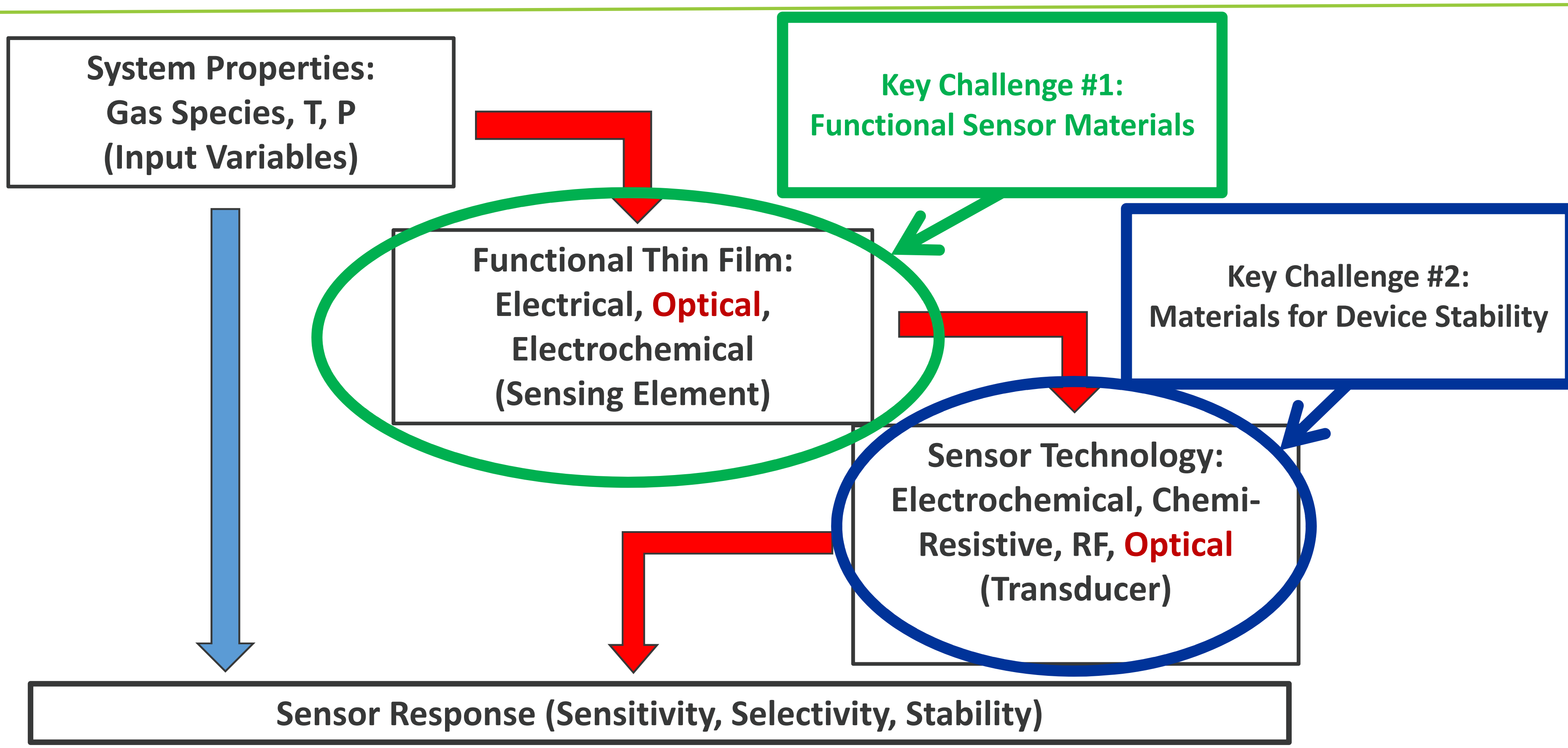
<u>Incompatible with Traditional Sensing Technologies</u>

1) Limits of High Temperature Electrical Insulation
2) Limited Access Space
3) Requires Multi-Point Sensing
4) Electrified Surfaces
5) Flammable Gas Atmospheres

Gradients in Temperature and Composition of Gas Stream Internal to an SOFC are Critical Process Parameters for Maximized Efficiency / Lifetime.

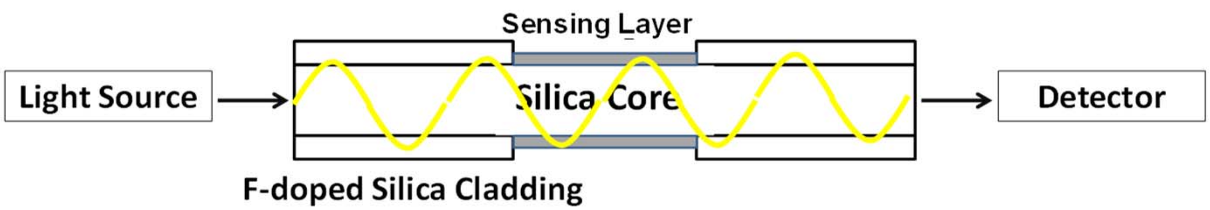
In-House Efforts Have Exploited the SOFC Technology as a Demonstration Platform for Harsh Environment Embedded Sensors in Electrified Components.

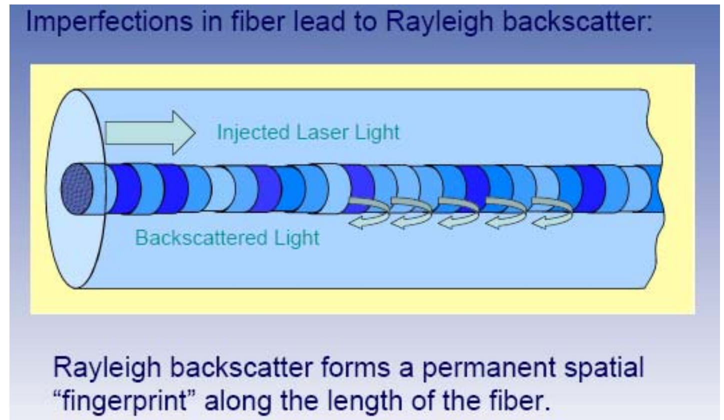
Enabling Harsh Environment Sensor Materials



Emphasis on Optical Fiber Based Sensors

e.g. Evanescent Wave Sensors





→ **Eliminate Electrical Wiring and Contacts at the Sensing Location**

→ **Tailored to Parameters of Interest Through Functional Materials**

→ **Eliminate EMI and Potential Interference with Electrical Systems**

→ **Compatibility with Broadband and Distributed Interrogation**

Optical Fiber Based Sensors are Particularly Well-Suited for Harsh Environment and Electrified System Applications.

Recent Activity Focused on Wireless Sensors

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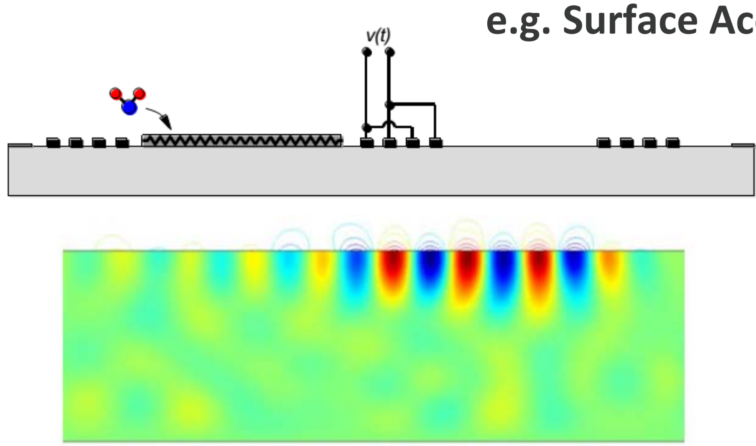
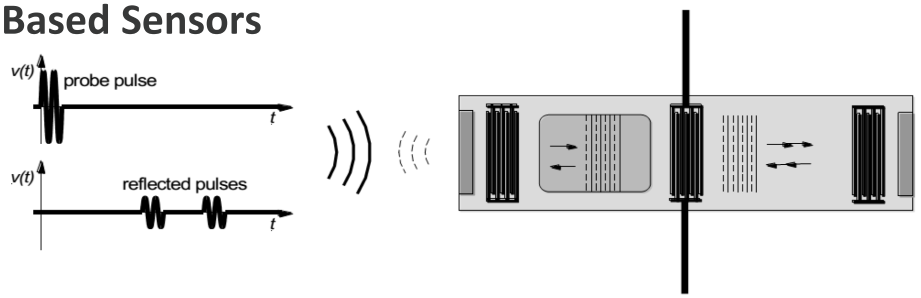
e.g. Surface Acoustic Wave Based Sensors

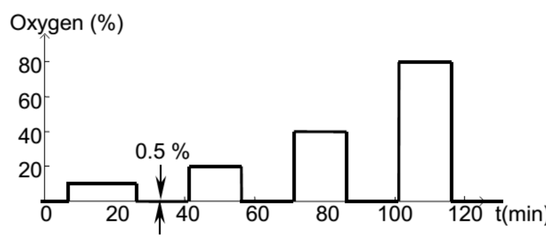


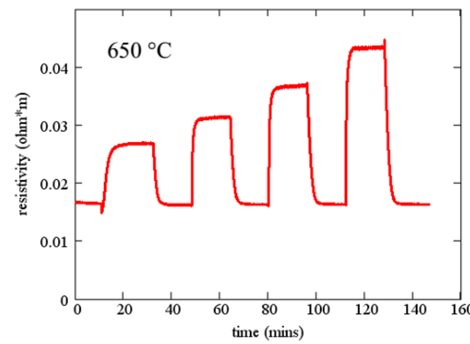


Surface Acoustic Wave Devices for Harsh Environment Wireless Sensing

David W. Greve [1,2,*], Tao-Lun Chin [1,2], Peng Zheng [1,2], Paul Ohodnicki [1], John Baltrus [1] and Irving J. Oppenheim [1,3]

Sensors **2013**, *13*, 6910-6935; doi:10.3390/s130606910



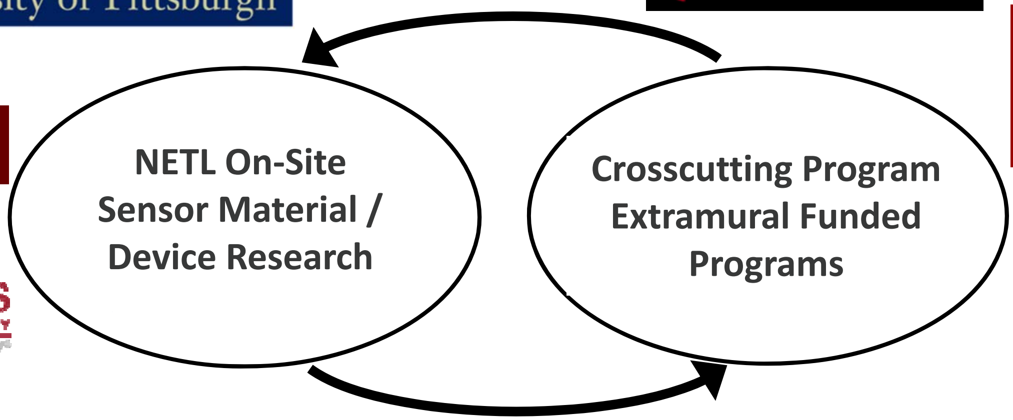


More Recent Activity Has Been Initiated on Surface Acoustic Wave Based Sensors Compatible with Wireless Interrogation.

Collaborative Interactions with Universities

Numerous Joint Publications (U. Pitt, U. Albany, OSU, U. Conn. VA Tech, Stevens)

Several Joint Patent Applications (U. Pitt., Stevens, OSU)



The NETL Research & Innovation Center Seeks Opportunities to Engage with Partners Funded Through the Crosscutting Program to Promote the Goals and Missions of NETL.

Collaborative Interactions with Universities

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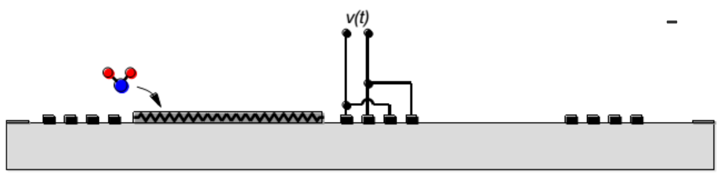
Promoting Development of High Temperature Wireless Sensor Technology

e.g. Surface Acoustic Wave Based Sensors



<u>NETL Research & Innovation Center</u>

- New Project Activity on Sensing Layers
- Collaborating on Materials for Device Stability
- Seeking Opportunities to Support UCR Projects
  - Characterization Support
  - Access to Unique NETL Facilities

Dr. Robert Fryer, ORISE Researcher

1865 THE UNIVERSITY OF MAINE

UCONN UNIVERSITY OF CONNECTICUT

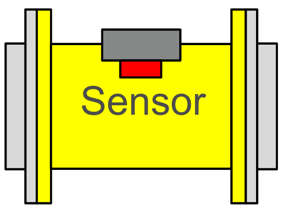
More Recently, The Crosscutting Program University Outreach Program Has Begun to Initiate Formalized Collaborations Between the NETL Research & Innovation Center and Partners.

Collaborative Interactions with Industry

Highly Selective and Stable Multivariable Gas Sensors for Enhanced Robustness and Reliability of SOFC Operation

(1) Potyrailo et al. *Nat. Photonics* **2007**, *1*, 123-128
(2) Potyrailo et al. *Chem. Rev.* **2011**, *111*, 7315–7354
(3) Carpenter et al. *Anal. Chem.* **2012**, *84*, 5025-5034
(4) Potyrailo et al. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15567–15572
(5) Potyrailo et al. *Nat. Commun.* **2015**, *6*, 7959
(6) Potyrailo *Chem. Rev.* **2016**,*116*, 11877−11923

Performer: GE Global Research
Award Number: DE-FE0027918
Partners: SUNY Polytechnic Institute, GE–Fuel Cells LLC
Project Duration: 10/01/2016-03/31/2018



Program objective

To achieve selectivity and stability of gas sensing by implementing a new generation of gas sensors, such as multivariable sensors [1-6].

Phase 1 focus

To develop new sensing materials, perform lab tests for sensitivity and stability, field validate developed sensors on a SOFC system.

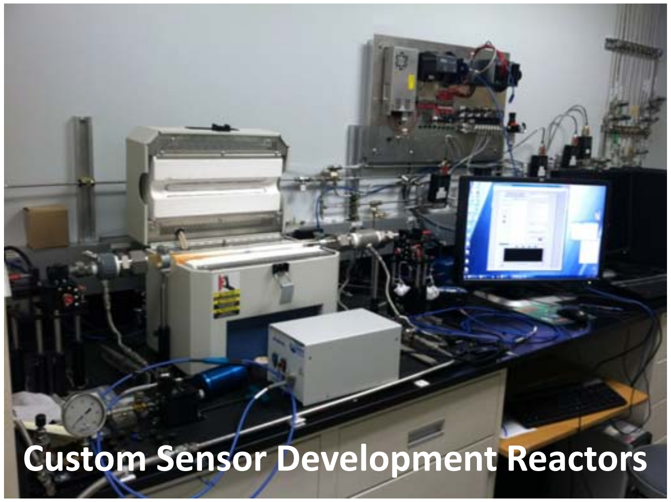
Phase 1 will advance fundamental understanding of multivariable gas sensing at high temperatures for cost-effective and stable SOFC sensors. Generated data will allow development of recommendations for Phase 2 deliverables.

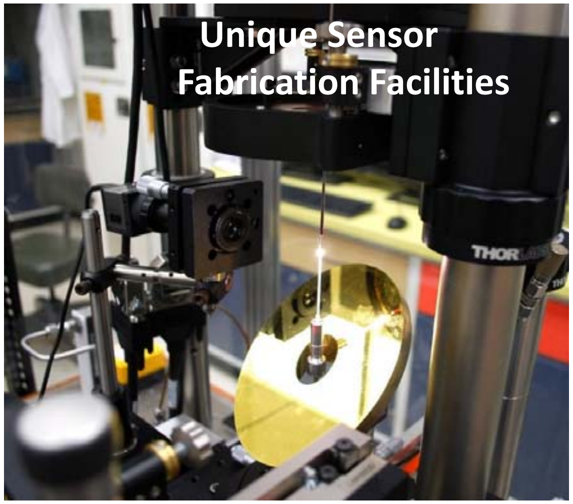
Project Benefits

Developed sensor approach will become a robust tool for any SOFC system, directly affecting system robustness and reliability as well as optimizing operation.

More Recently the Team Has Identified Opportunities for Industrial Partnerships and Collaborations to Promote Technology Development and Deployment.

Unique Facilities of the Project Team





Laser Heated Pedestal Growth System for Fabricating Single Crystal Fibers

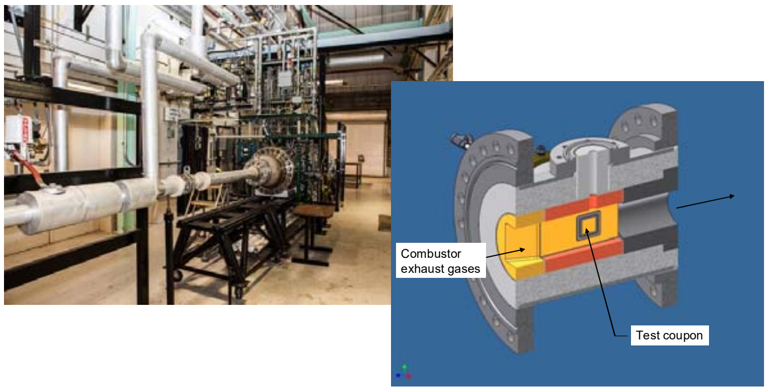
Custom Sensor Development Reactors Simulate:
→ Power Generation and Combustion Systems
→ Subsurface / Geological Environments
→ Pressurized Gas and Oil-Based Systems

Commercial and Custom Optical Interrogator Systems for Optical Fiber Sensors

NETL On-Site Research Has Developed Capabilities for Sensor Material and Optical Fiber Sensor Device Development and Optimization for Harsh Environment Applications.

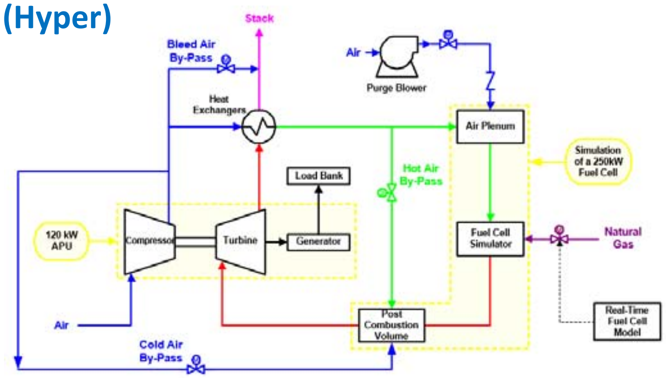
Unique Facilities Available at NETL

High-Pressure Combustion Facility (Aerothermal Rig)



- Simulates hot gas path of a turbine
- Natural gas or hydrogen fuel
- Capable of 2 lb/s air flow @ 10atm
- Temperature: up to 1300°C
- Optically-accessible combustor and test sections

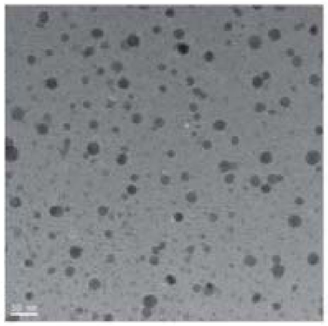
Hybrid Performance Facility (Hyper)



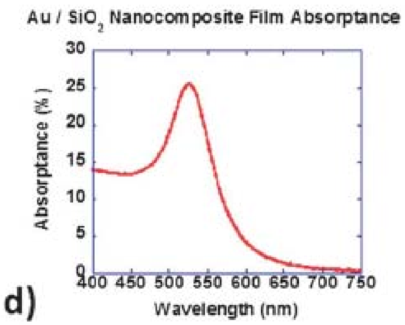
- A 300kW solid oxide fuel cell gas turbine (SOFC-GT) power plant simulator
- 120 kW Garrett Series 85 APU with single-shaft turbine, 2-stage radial compressor, and gear driven generator
- 100+ process variables measured including rotational speed (1,200Hz; 40,500 rpm), air/fuel flow, temperature (turbine: 637°C; SOFC: 1133°C), pressure (up to 260kPa), etc.

Pilot Scale Facilities Exist at NETL for Demonstrations of Prototype Sensor Concepts Under Application Relevant Conditions (Turbine, Combusion, SOFC).

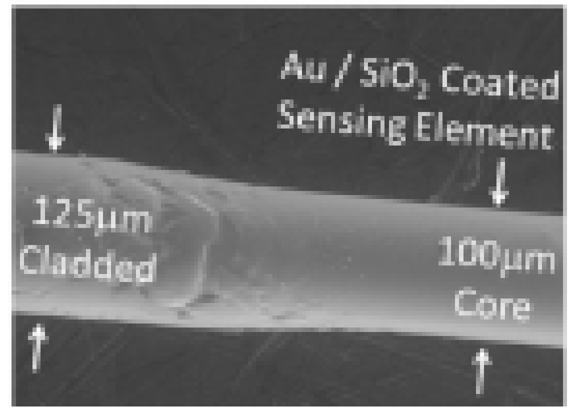
Functional Thin Films for High Temp Sensing



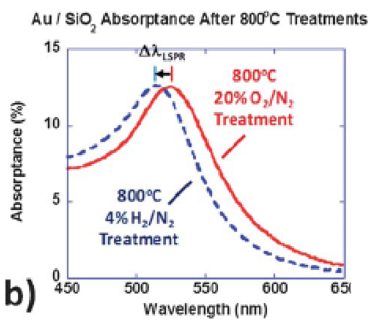
c)



d)

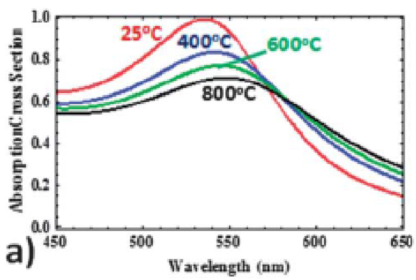


Gas Stream Response

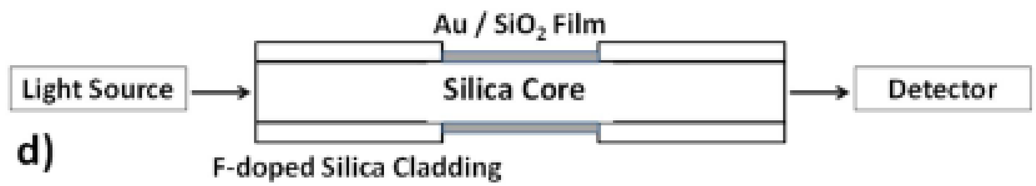


b)

Temperature Response



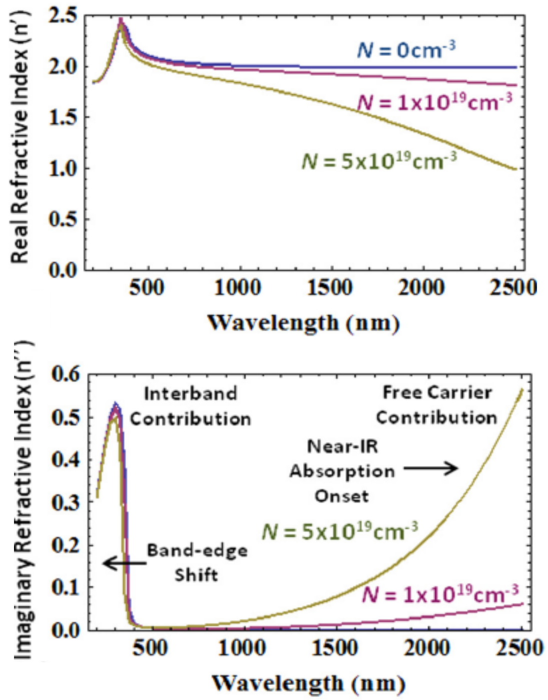
a)

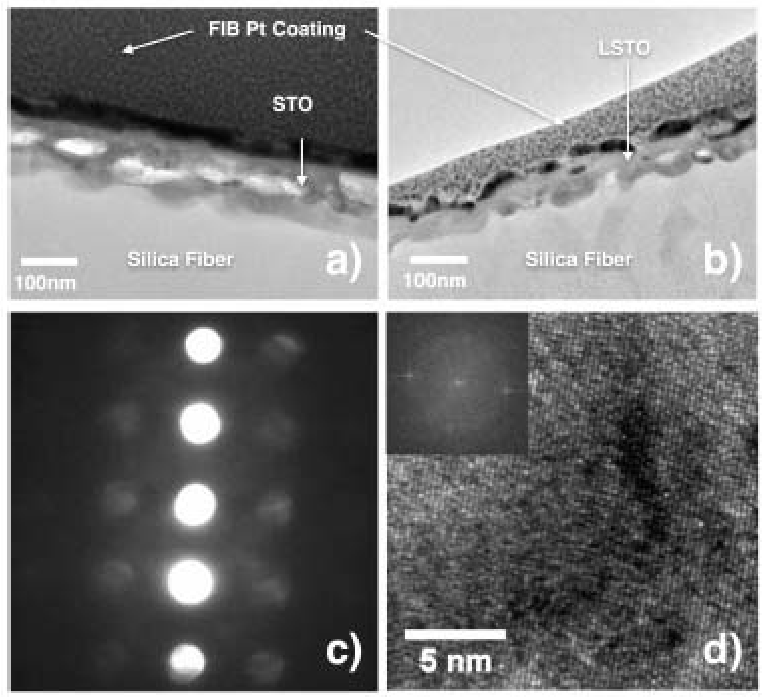


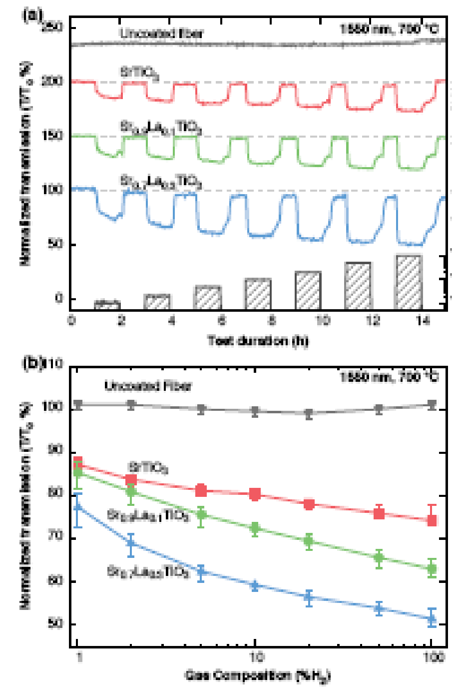
d)

Au-Nanoparticle Incorporated Oxide Thin Films for Multi-Parameter Gas Sensing By Leveraging the Fiber Optic Sensing Platform for SOFC Relevant Applications (~700-800°C).

Functional Thin Films for High Temp Sensing







High Electronic Conductivity "Plasmonic" Oxides Have Been Demonstrated to Show Great Promise for High Temperature Optical Sensing, e.g. La-doped $SrTiO_3$.

Functional Thin Films for High Temp Sensing

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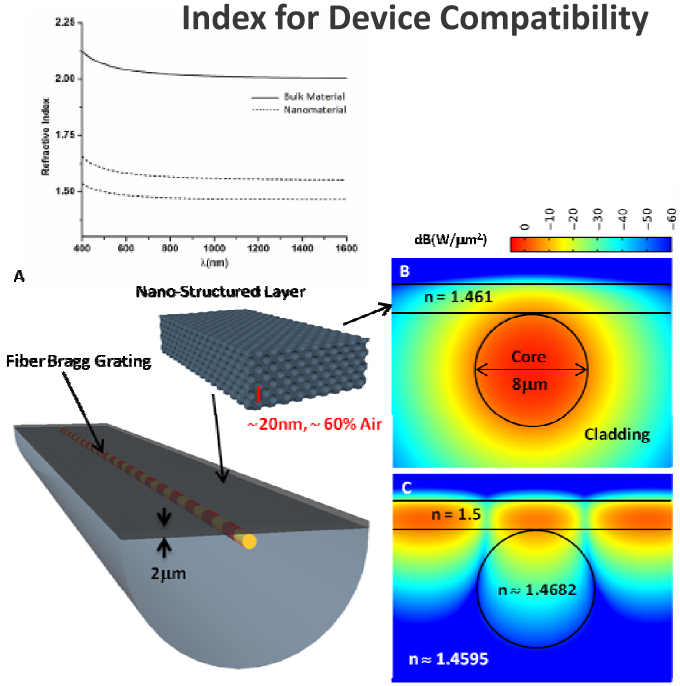
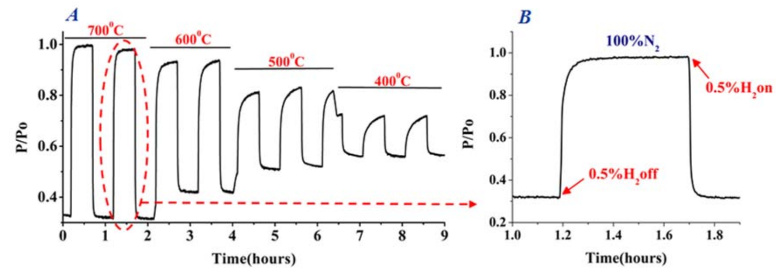
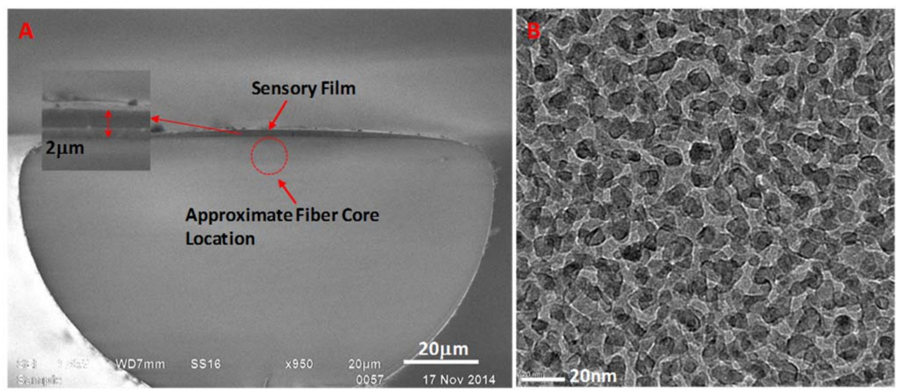
Nanostructuring to Tailor Refractive Index for Device Compatibility



University of Pittsburgh





Engineered Porosity of the Functional Oxide Based Sensing Layers Has Been Explored and Demonstrated in Collaboration with Prof. Kevin Chen at University of Pittsburgh.

Functional Thin Films for High Temp Sensing

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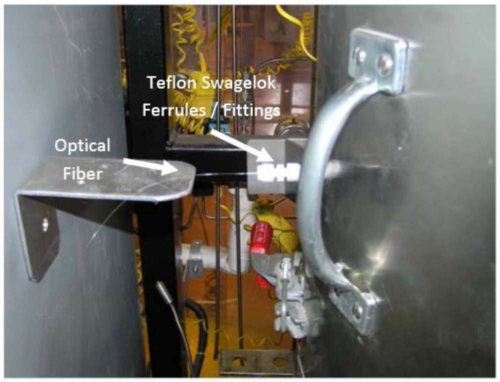
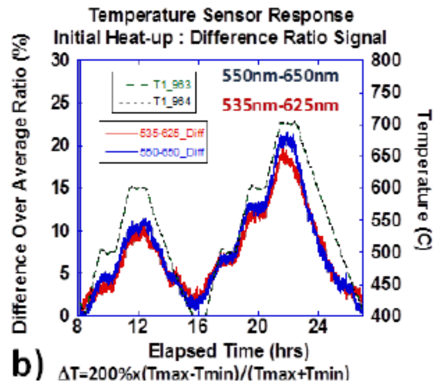
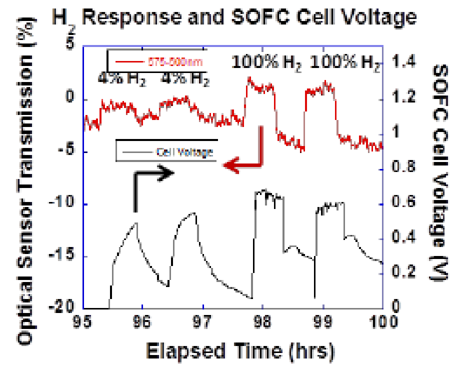
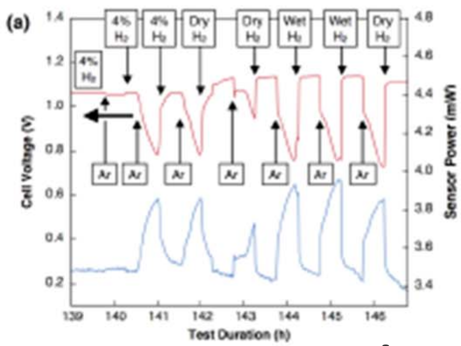


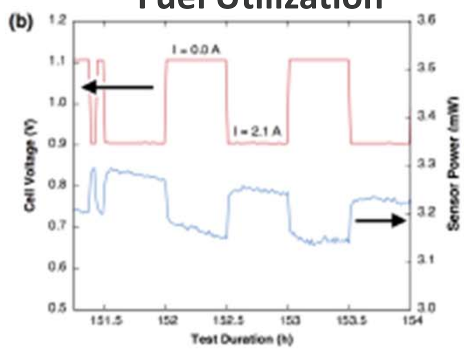




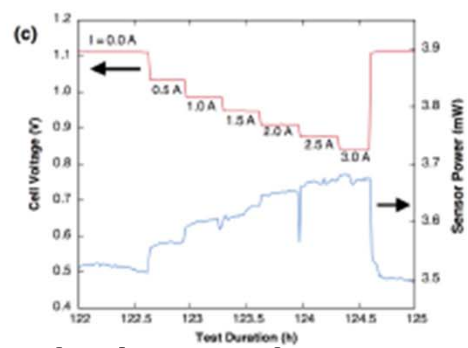
Fuel Gas Stream Variations



Fuel Utilization



Fuel Utilization



Proof of Concept Demonstrations for Both Au-Incorporated Silica and La-Doped $SrTiO_3$ Based Functional Sensor Layer Enabled Optical Fiber Sensors.

Functional Thin Films for High Temp Sensing

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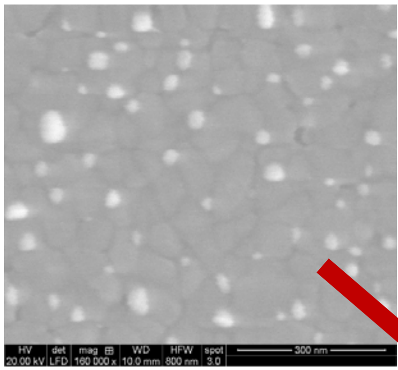
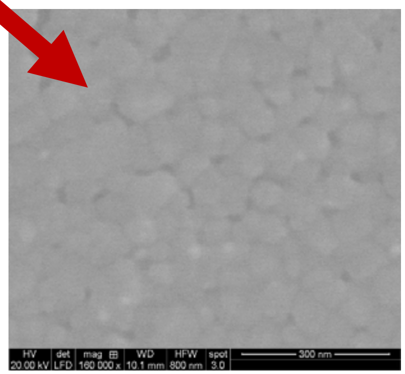


Au / TiO_2

Pre-Exposure

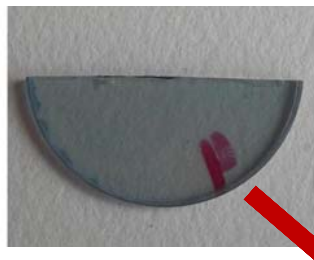
800°C

29% H_2/N_2



Au / TiO_2

Pre-Exposure

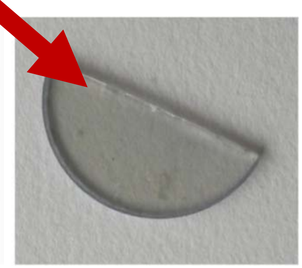


700°C

29% H_2/N_2

800°C

1% H_2/N_2

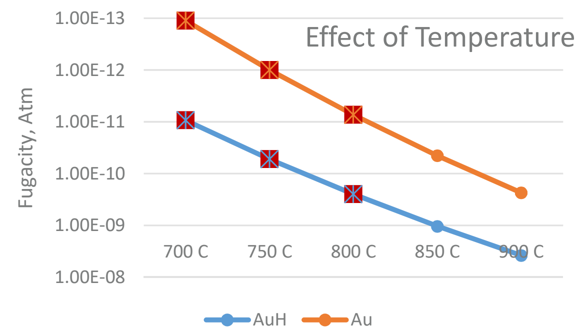


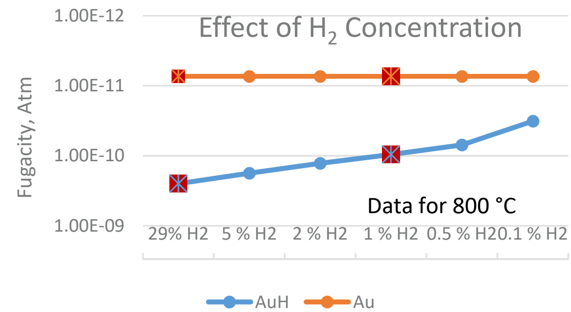
800°C

29% H_2/N_2

$$Au(s) \rightleftarrows Au(g)$$

$$Au(s) + \tfrac{1}{2} H_2(g) \rightleftarrows AuH(g)$$



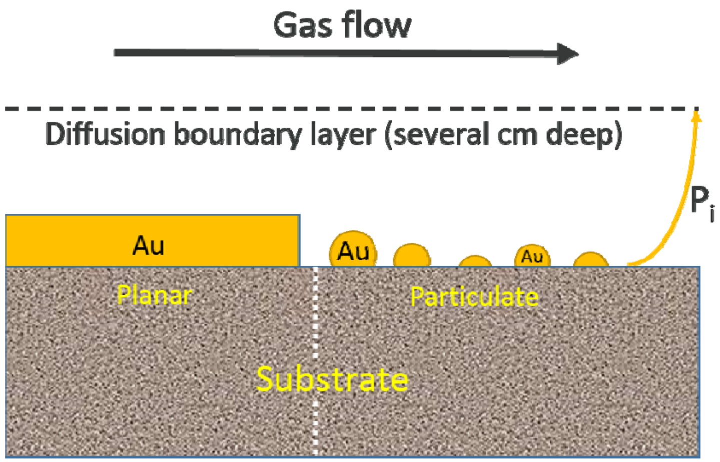


High Temperature, Longer Term Stability Experiments Have Highlighted the Importance of Reactive Evaporation of Noble Metal Nanoparticle and Thin Film Sensing Layers.

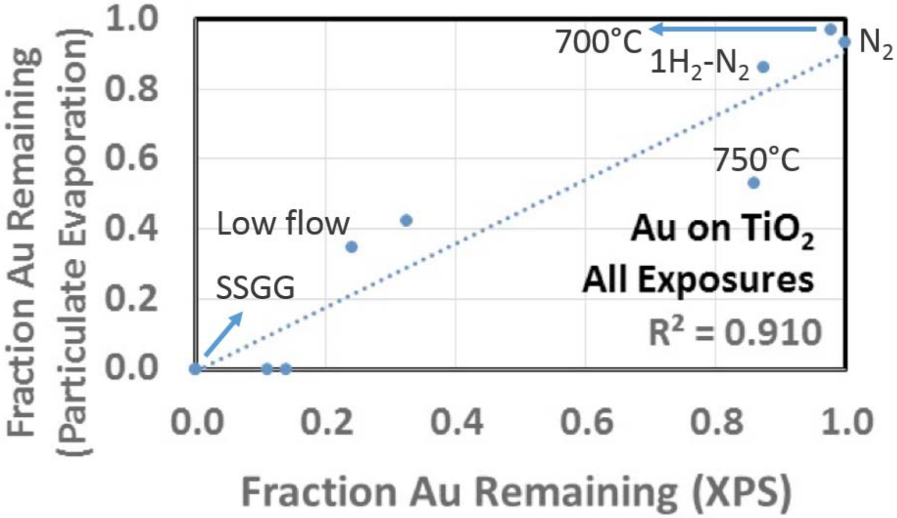
Functional Thin Films for High Temp Sensing

Estimates of Total Mass Loss Based on Gas Phase Diffusion Models

J. P. Baltrus, G. R. Holcomb, J. H. Tylczak, and P. R. Ohodnicki, Journal of the Electrochemical Society 164 (4), B159-B167.



$$Au(s) + \frac{1}{2} H_2(g) \rightleftarrows AuH(g)$$



Accounting for Nanoparticulate Microstructure Allowed for Improved Agreement with Experimental Results

Quantitative Model Develoment Has Initiated to Understand Factors Impacting Stability of Various High Temperature Metals Including Microstructure / Gas Phase Chemistry.

New Paradigm : Thermal Emission Based Sensing

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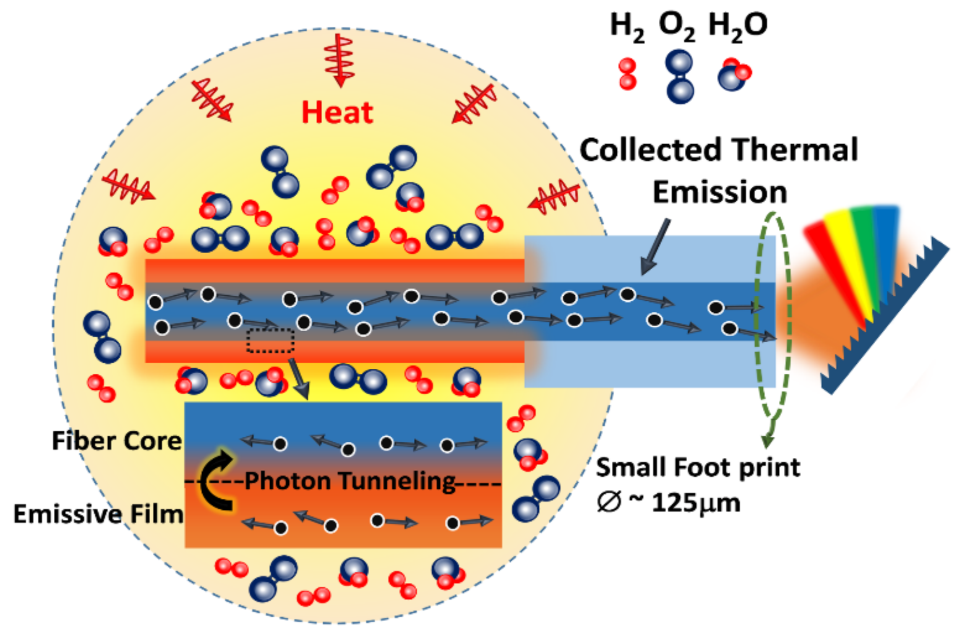


Thermal Emissivity-Based Chemical Spectroscopy through Evanescent Tunneling

Zsolt L. Poole* and Paul R. Ohodnicki

Adv. Mater. **2016**, *28*, 3111–3114

Exploiting Kirchoff's Law Between Absorptivity / Emissivity

Planck's Law of Blackbody Radiation

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$\alpha_\lambda = \epsilon_\lambda$$

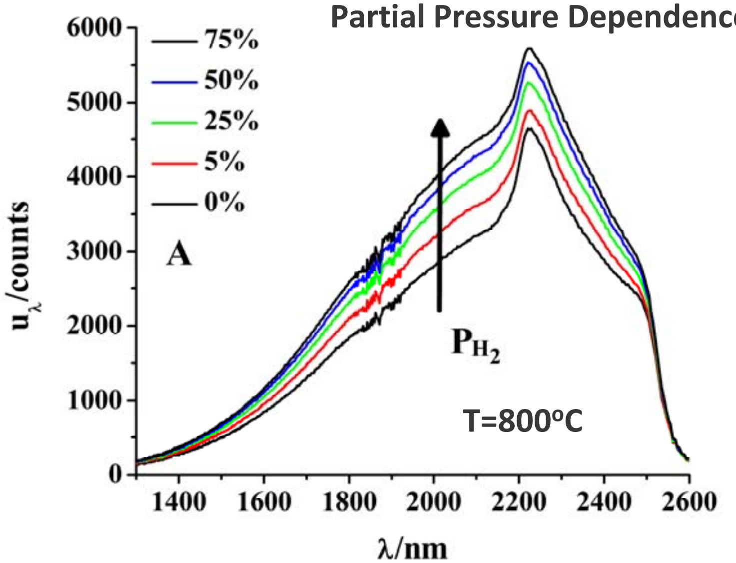
Absorptivity

Emissivity

We Have Recently Discovered that Direct Thermal Emission Monitoring of the Functional Sensor Layer as Well as Characteristic Absorption of the Silica Fiber Can Be Used for Sensing.

New Paradigm : Thermal Emission Based Sensing

Thermal Emission H_2 Partial Pressure Dependence



Thermal Emissivity-Based Chemical Spectroscopy through Evanescent Tunneling

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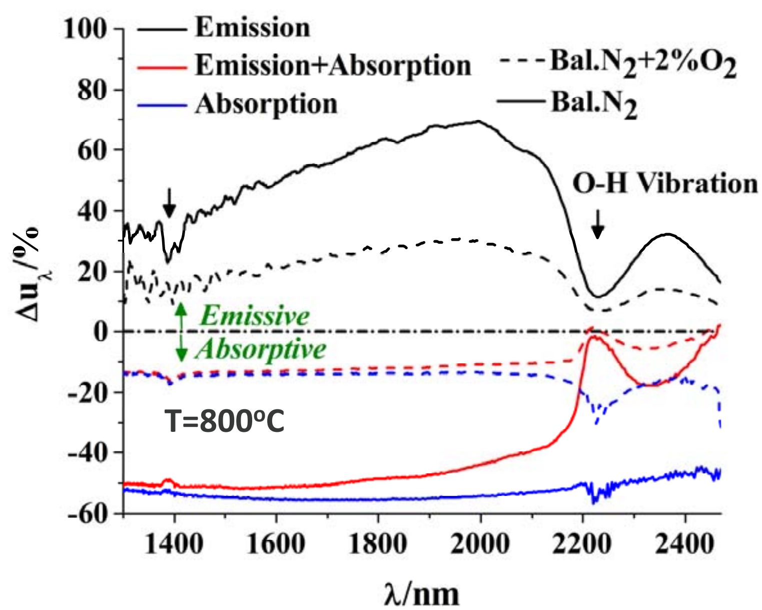
Inverted Responses for Conventional Transmission Spectroscopy and "Emission" Spectroscopy



High Electronic Conductivity Based TiO_2 Thin Films Showed Clear and Pronounced Thermal Emission Responses to H_2 Partial Pressure Which Inversely Correlated with Transmission.

Emerging Trends : Multivariate Optical Based Sensing

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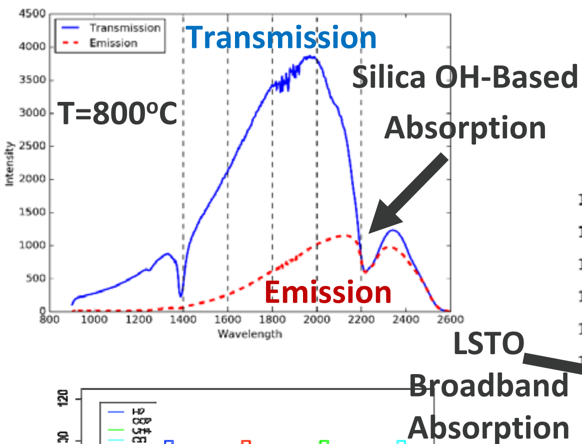
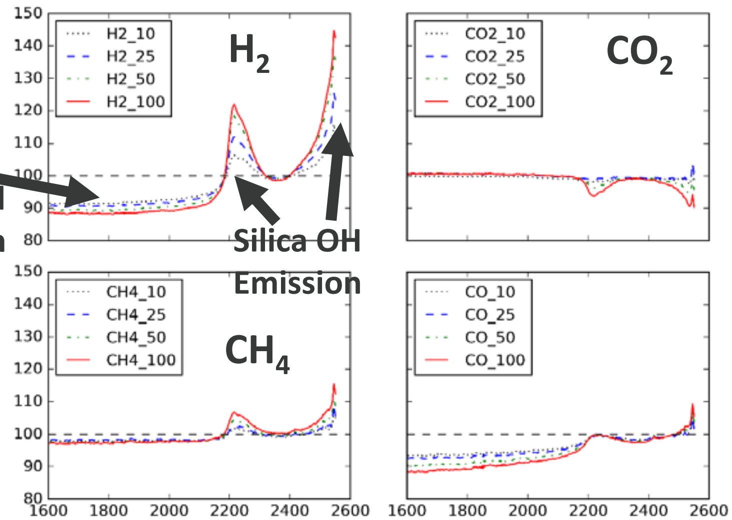
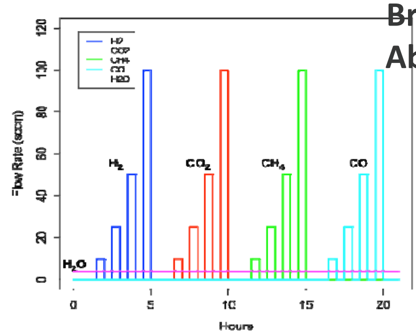


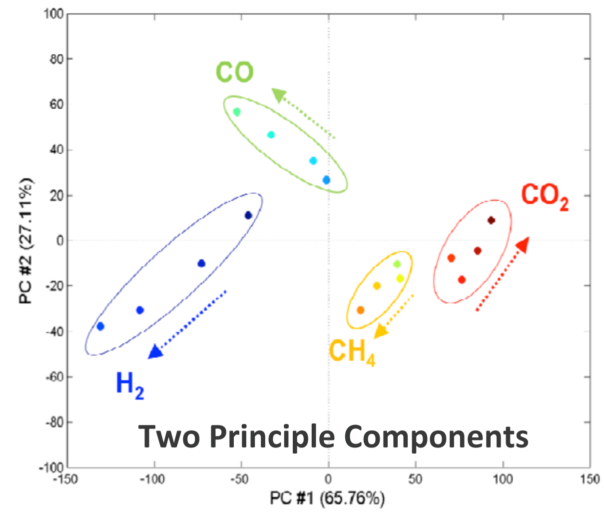
An Increased Emphasis is Being Placed on Discriminating Multi-Component Species within Complex Gas Mixtures Through Advanced Multi-Variate Techniques

Spectra for Different Gas Species





Principle Component Analyses



A Primary Advantage of Optical Based Sensors Lies in the Capability for Multi-Variate Analysis of Broadband Wavelength Signals Which is an Emerging Trend in the Community.

Computational Methods Applied to Sensor Materials

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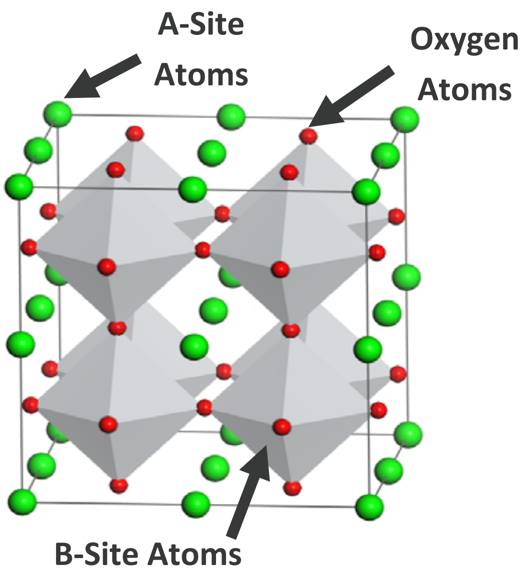
Perovskite Type : ABO_3

Example: $SrTiO_3$, La-doped $SrTiO_3$



DFT Based Modeling of Electronic Ground State

Dielectric Constants → **Optical Constants**

Lattice Phonon Dispersion → **Thermodynamic Properties**

Direct Summation Over Empty States

$$\varepsilon^{(2)}_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2w_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \times \langle u_{c\mathbf{k}+\mathbf{e}_\alpha \mathbf{q}} | u_{v\mathbf{k}} \rangle \langle u_{c\mathbf{k}+\mathbf{e}_\beta \mathbf{q}} | u_{v\mathbf{k}} \rangle^*$$

Kramers-Kronig Relationship

$$\varepsilon^{(1)}_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon^{(2)}_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega'$$

Supplement Ground State with Phonon Free Energy Contributions

$$\Delta\mu^0(T) \approx \Delta E^{DFT} + E_{ZP} + F^{PH}(T)$$

$$F_{harm}(T) = rk_B T \int_0^\infty g(\omega) \ln[\, 2\sinh(\frac{\hbar\omega}{2k_B T})]d\omega$$

We are Developing Computational Methodologies and Techniques That Enable Prediction and Explanation of Functional Properties from First Principles at High Temperature.

Computational Methods Applied to Sensor Materials

NATIONAL ENERGY TECHNOLOGY LABORATORY

DFT+PBE+GGA+U

U(Ti(3d))=7.5

The calculated band-gap:

2.17 eV (indirect)

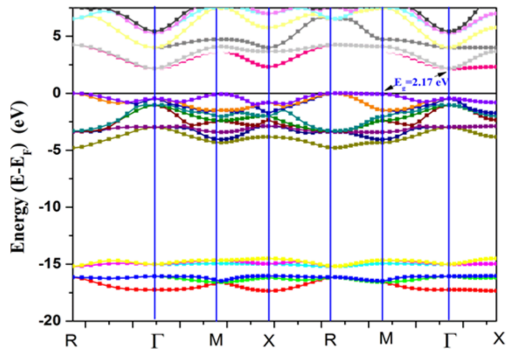
3.03 eV (direct)

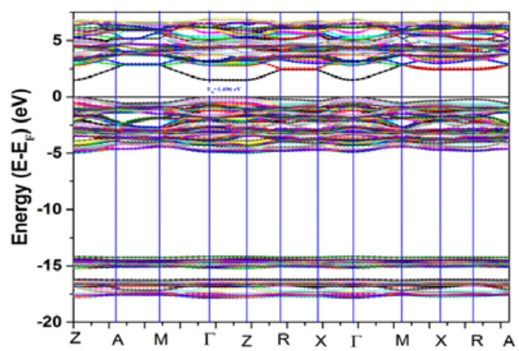
Adjusted U-Parameter for Greatest Consistency with Experiment

La – Doping Adds an Electron to the Conduction Band

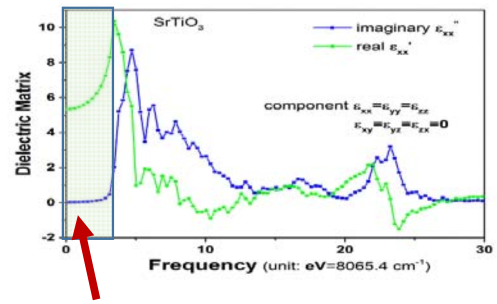
Impacts to Effective Dielectric Constants Can Be Simulated

Electronic Band Structure

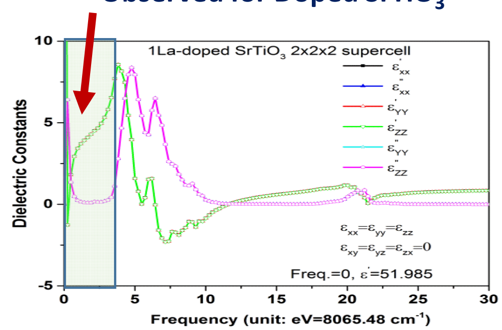




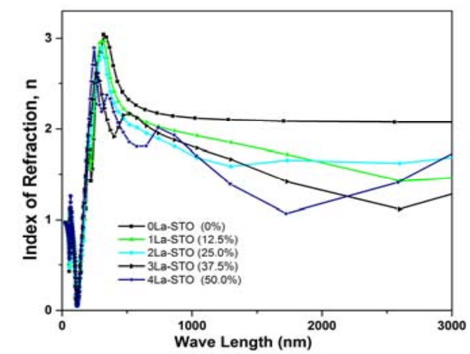
Dielectric Constants

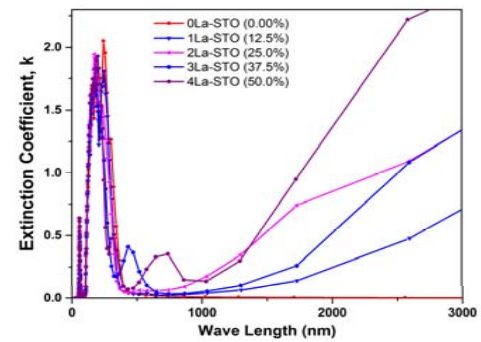


Free Electron Based "Drude" Features Observed for Doped $SrTiO_3$



Optical Constant Trends with Doping



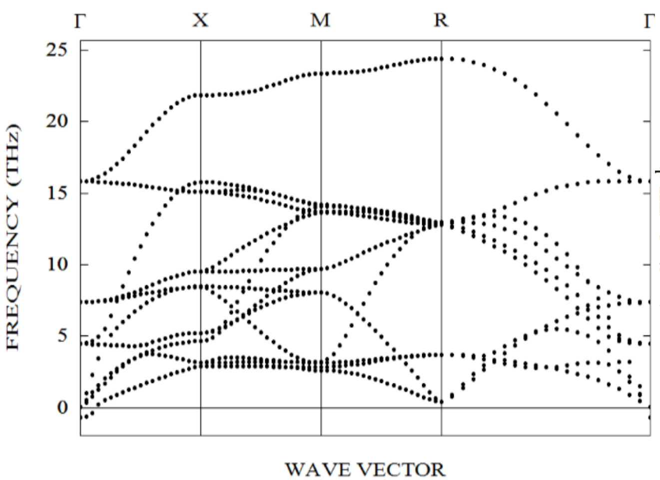


The Connection Between Electronic Band Structure and Optical Constants is Being Investigated for SrTiO3, La-Doped SrTiO3 and Other Materials Systems Under Investigation.

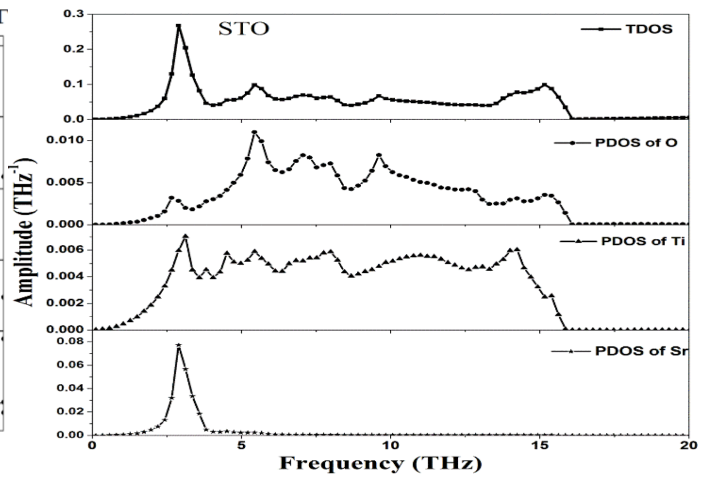
Computational Methods Applied to Sensor Materials

NATIONAL ENERGY TECHNOLOGY LABORATORY

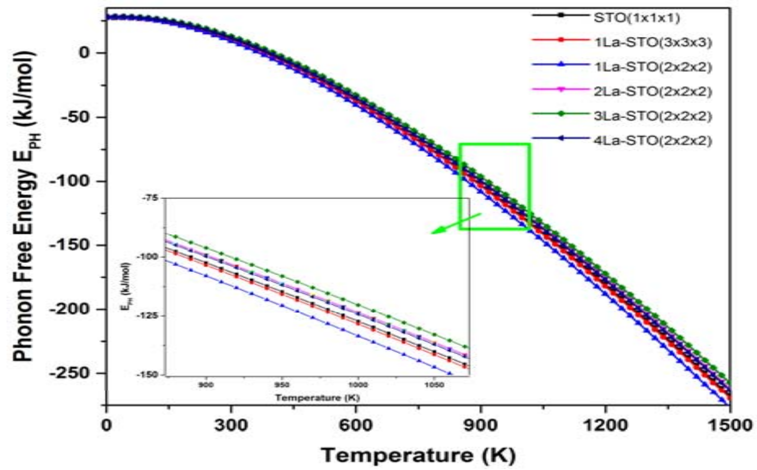
Phonon Band Structure Calculations



Phonon Density of States Calculations



Thermodynamic Free Energy Terms at Finite Temperatures Including Entropy



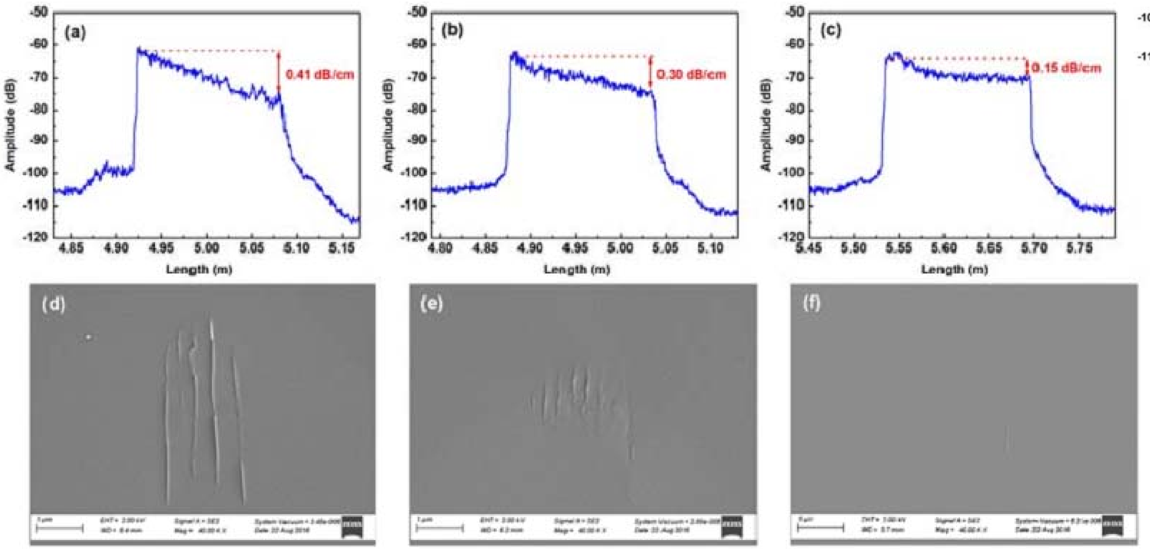
Initial Finite Temperature Calculations are Focused on Phonon Band Structure and Density of States Calculations for Thermodynamic Property Predictions.

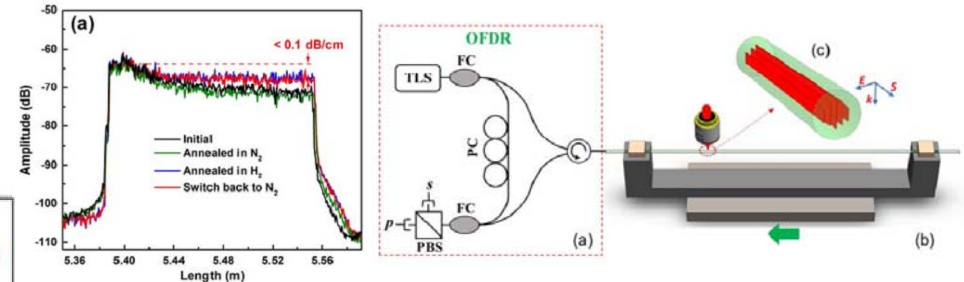
High Temperature Distributed Sensing in Silica Fibers

NATIONAL ENERGY TECHNOLOGY LABORATORY

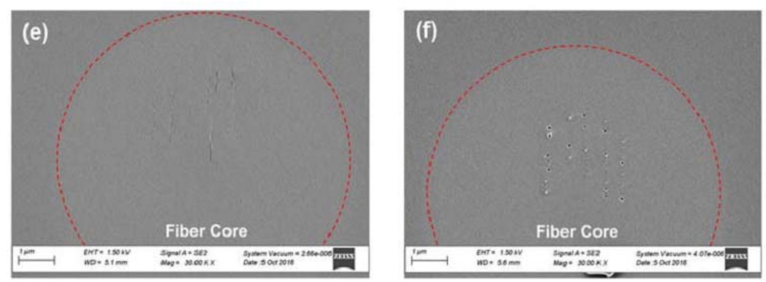
University of Pittsburgh

Different Scanning Speeds of Fiber Under → Varying Levels of Backscattering "Enhancement" Due to Nanogratings





Elevated Temperature H_2 Exposure Results in Irreversible Morphological Changes to Aligned Spherical Voids

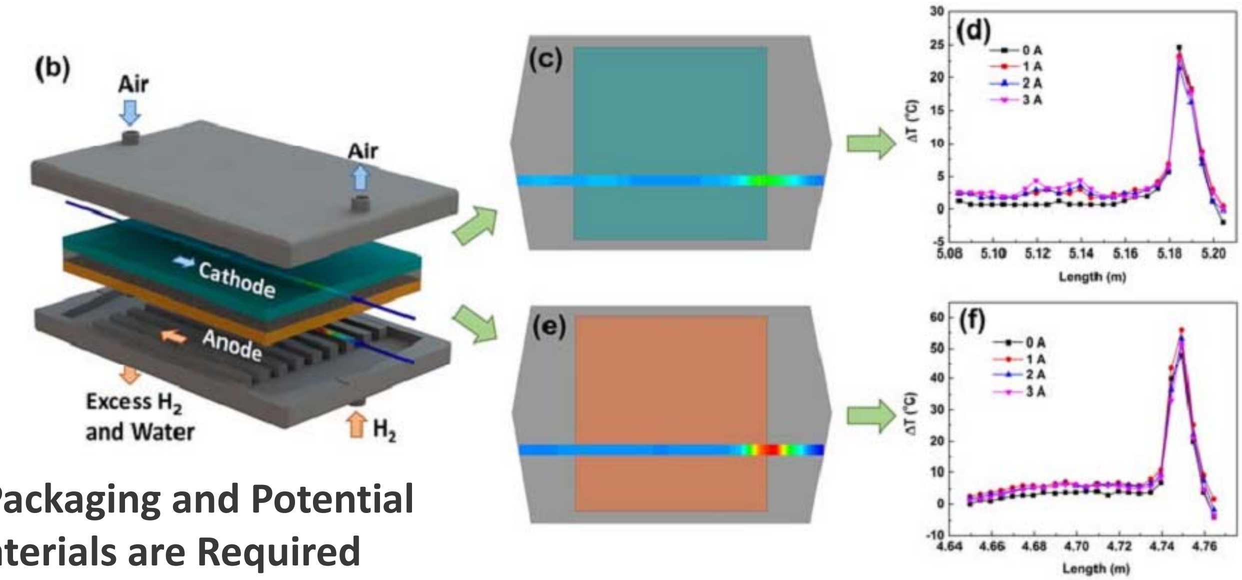


Enhanced Temperature and H_2 Stability of OFDR Rayleigh Based Interrogation of Optical Fibers Associated with Engineered Voids Within the Silica Network.

High Temperature Distributed Sensing in Silica Fibers

University of Pittsburgh

Elevated Temperatures Near the Anode Stream Inlet Due to the High Thermal Conductivity of the Fuel Gas Stream.



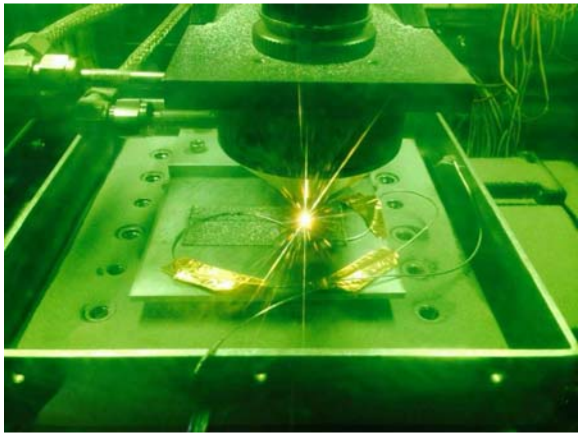
Additional Studies of Silica Fiber Sensor Packaging and Potential Exploration of Alternative Fiber Materials are Required

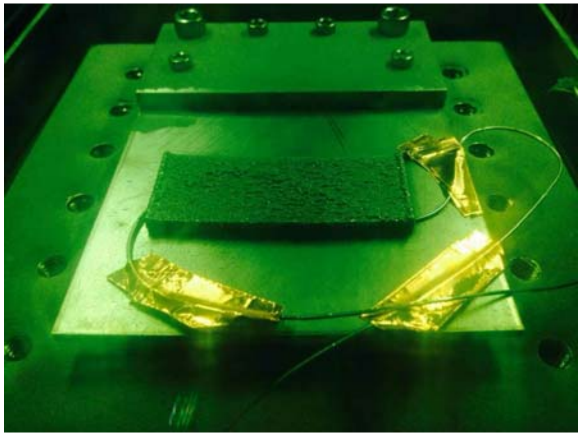
Enhanced Backscattering Processing Methodologies Have Enabled Successful Temperature Profile Measurements Throughout an Operational SOFC Anode and Cathode Stream.

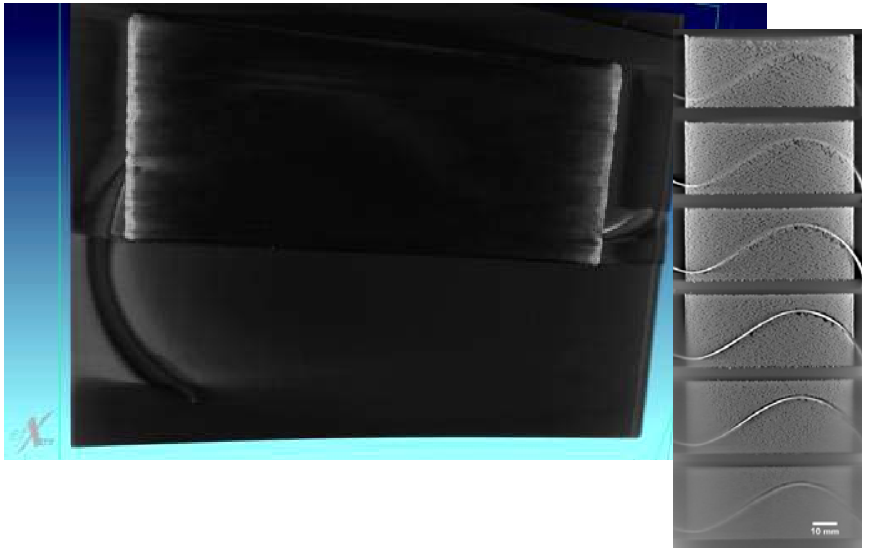
Additive Manufacturing Embedding of Silica Fibers

University of Pittsburgh

LENS Embedding Within a High Temperature Ti-Alloy Part







CT Scanning Capabilities Leveraged to Explore Structure of Embedded Sensors

Embedding of Silica Based Optical Fiber Sensors in High Temperature Metals is Being Explored Through the Exploitation of Additive Manufacturing Techniques Such as LENS.

Additive Manufacturing Embedding of Silica Fibers

University of Pittsburgh

Finite Element Simulations Being Leveraged.

Highest Principle Strain at Silica / Metal Interface.

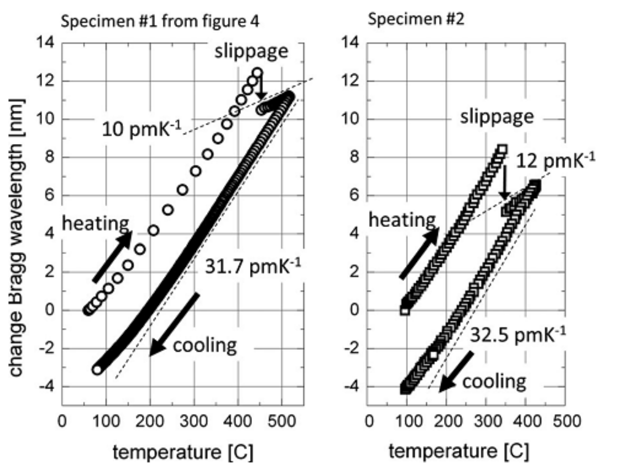


Fig. 5. Measured Bragg wavelength over temperature during temperature cycling for two samples where slippage occurred.

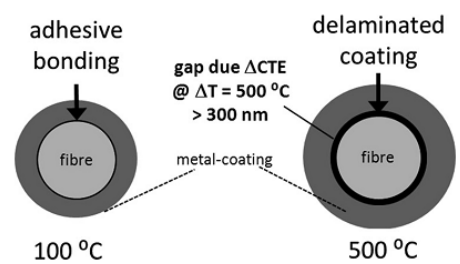


Fig. 6. Schematic visualisation of the delamination of the nickel coating from the silica fibre. Due to different CTE, estimates indicate gaps of more than 300 nm between fibre and metal coating.

Temperature and Strain Measurements With Fiber Bragg Gratings Embedded in Stainless Steel 316

Dirk Havermann, Jinesh Mathew, William N. MacPherson, Robert R. J. Maier, and Duncan P. Hand

JOURNAL OF LIGHTWAVE TECHNOLOGY, VOL. 33, NO. 12, JUNE 15, 2015

CTE

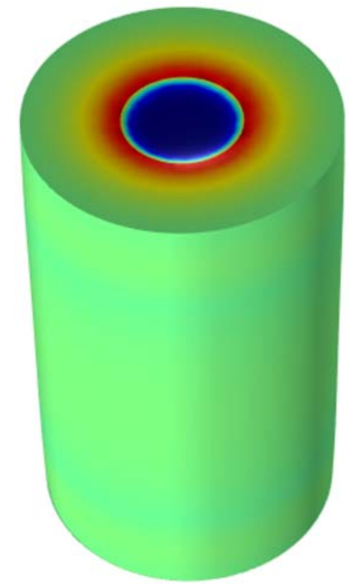
Stainless Steel 316
~$15.8 \times 10^{-6} K^{-1}$

CTE

Nickel
~$13 \times 10^{-6} K^{-1}$

CTE

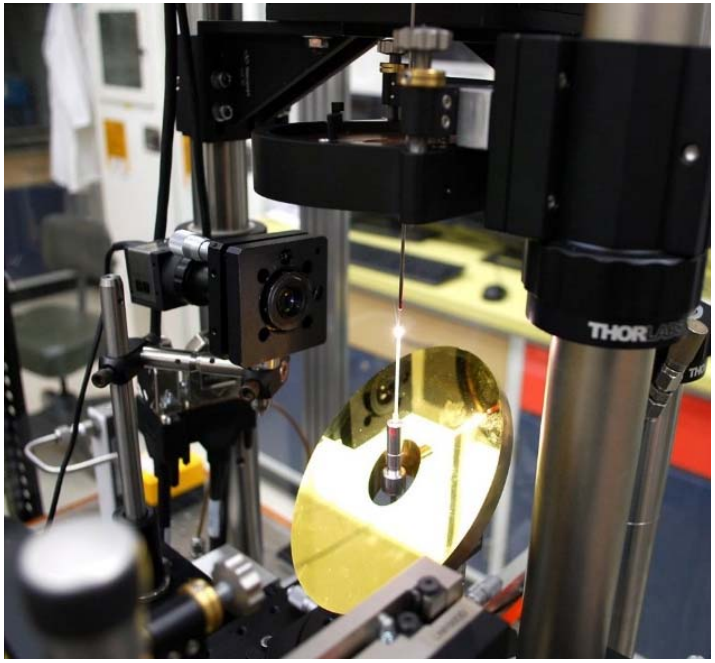
Silica
~$4.9 \times 10^{-7} K^{-1}$

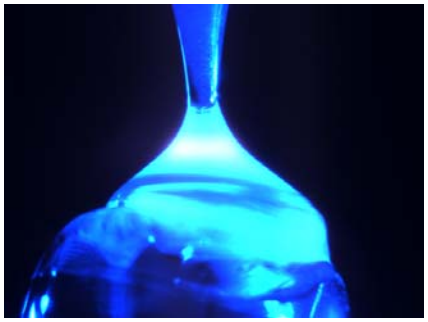


Absolute Temperature Limitations of Internal Strain (and Temperature) Monitoring Within Metals is Believed to Be Dictated By Delamination at Silica / Coating Interface.

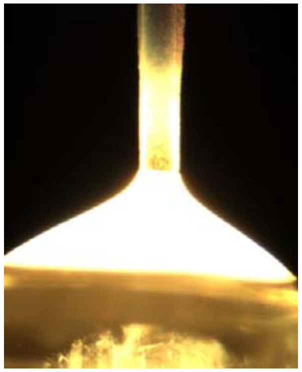
Alternative Optical Fiber Material Investigations

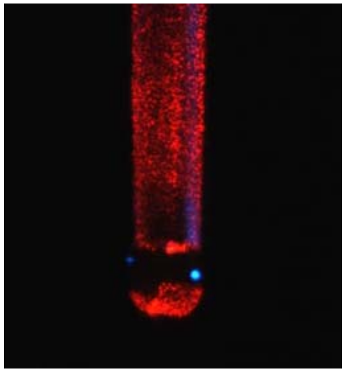
Laser Heated Pedestal Growth Processing

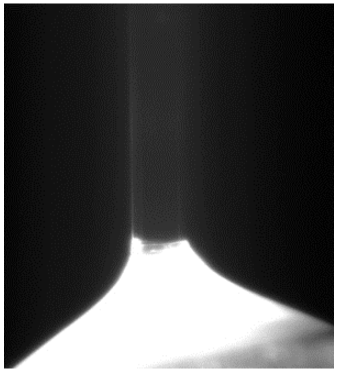




Novel Sensor Fabrication Through LHPG Process Controls







Relatively New Efforts are Focused on Fabrication of Single Crystal Sapphire Based Fiber Sensors and In-Line Processing for Sensor Functionality and Ultimately Cladding Integration.

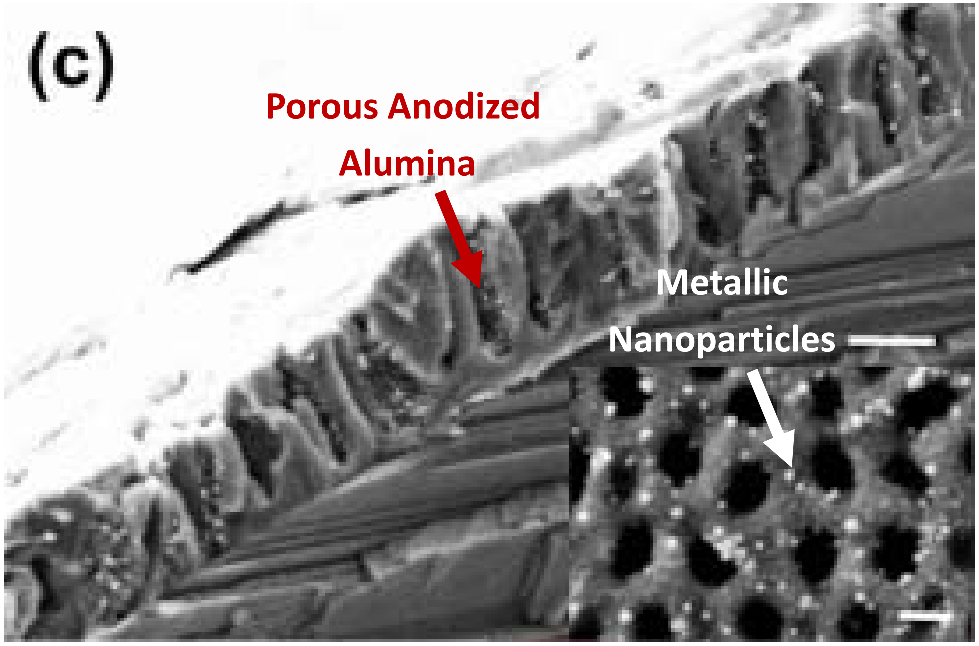
Alternative Optical Fiber Material Investigations

High Temperature Stable Sapphire Cladding Materials

A scalable pathway to nanostructured sapphire optical fiber for evanescent-field sensing and beyond

Hui Chen, Fei Tian, Jiri Kanka, and Henry Du

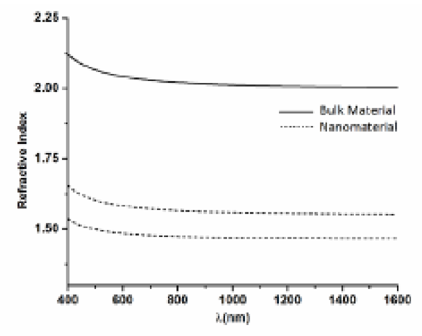
Applied Physics Letters **106**, 111102 (2015); doi: 10.1063/1.4915325

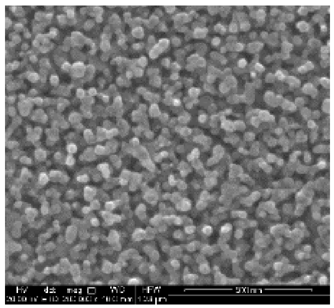


New Research Efforts Currently Being Initiated Will Target Research and Development of Cladding Layer Approaches for Sapphire Based Fibers.

Collaborations, Licensing, Partnership Opportunities

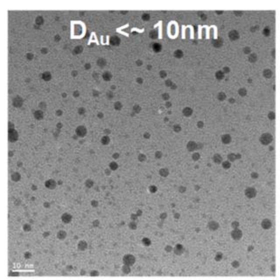
A Significant Patent Portfolio Has Been Established and is Available for Licensing By Interested Commercial Partners

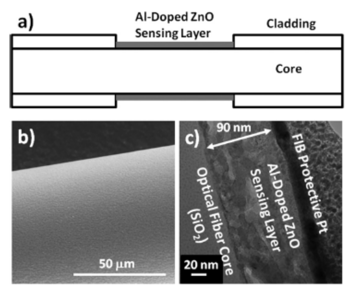




Nanostructuring to Tailor Refractive Index for Device Compatibility

Novel Classes of Sensing Materials





Novel Sensor Applications for SOFC Environments

The Team is Always Interested in Engaging in Collaborative Relationships to Promote Technology Development and Move the Technology Towards Commercialization.

Summary and Conclusions

- **NETL Has a Well Established Focus Area in Enabling Materials for Harsh Environment Sensing Applications**
- **NETL Has Excellent Capabilities for High Temperature and Harsh Environment Sensor Development**
- **Functionalized Optical Fiber Sensors Show Great Promise for a Range of Energy Related Applications**
- **NETL R&IC Has Active In-House Research In a Broad Range of Areas**
  - **Power Generation**
  - **Subsurface CO_2 Storage / Oil & Gas**
  - **Natural Gas Infrastructure**
  - **Electricity Infrastructure**
- **We are Always Interested in Collaboration Opportunities as Well as Joint Technology Development and/or Licensing of Patented Concepts**