Optical Fiber Based Sensors for Future Fossil Energy Applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

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April 10, 2018

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- Juddha Thapa
- Ting Jia

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
  - Multi-Component Speciation Through Broadband Interrogation
  - O_2 Sensing Materials
  - SOFC Applications of Optical Fiber Sensors (Embedding and Interrogation)
  - Existing Plant Applications of Optical Fiber Sensors (Boiler Application Field Validations)
  - Theoretical Investigations of High Temperature Oxide Sensor Materials
  - Sapphire Fiber Growth and Cladding Research
  - UCR Fellow / Outreach Program on SAW Sensor Devices
- Summary and Conclusions

Fossil Energy Needs Driving Advanced Sensors

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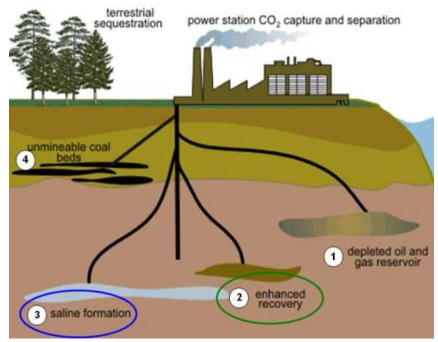
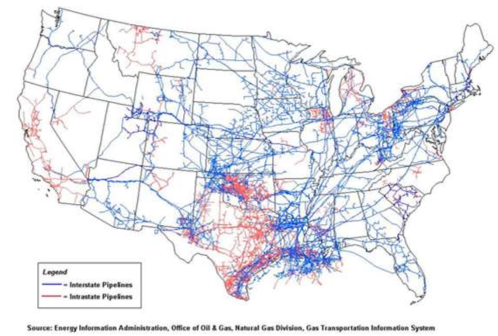
Power Generation (Combustion, Fuel Cells, Turbines, etc.)

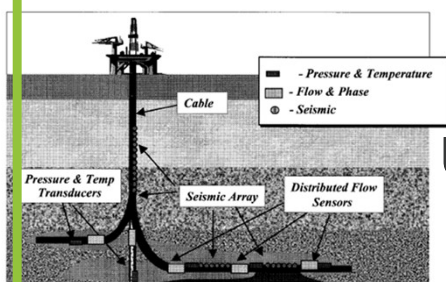
CO_2 Sequestration



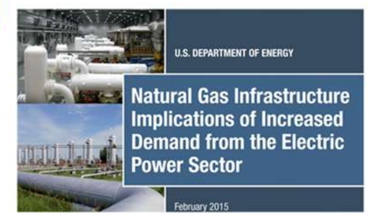
Natural Gas Infrastructure



Unconventional Oil & Gas



Properties of Methane	
Chemical Formula	CH_4
Lifetime in Atmosphere	12 years
Global Warming Potential (100-year)	28–36



Increased Visibility Through Embedded Sensor Technology Can Improve Reliability, Resiliency, and Efficiency Across the Fossil Energy Infrastructure.

Fossil Energy Needs Driving Advanced Sensors

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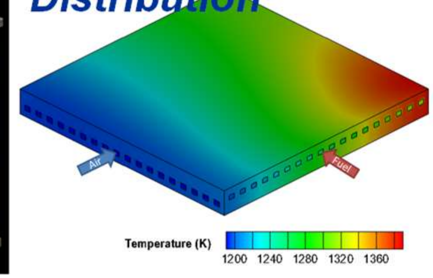
Short Term Focus

	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

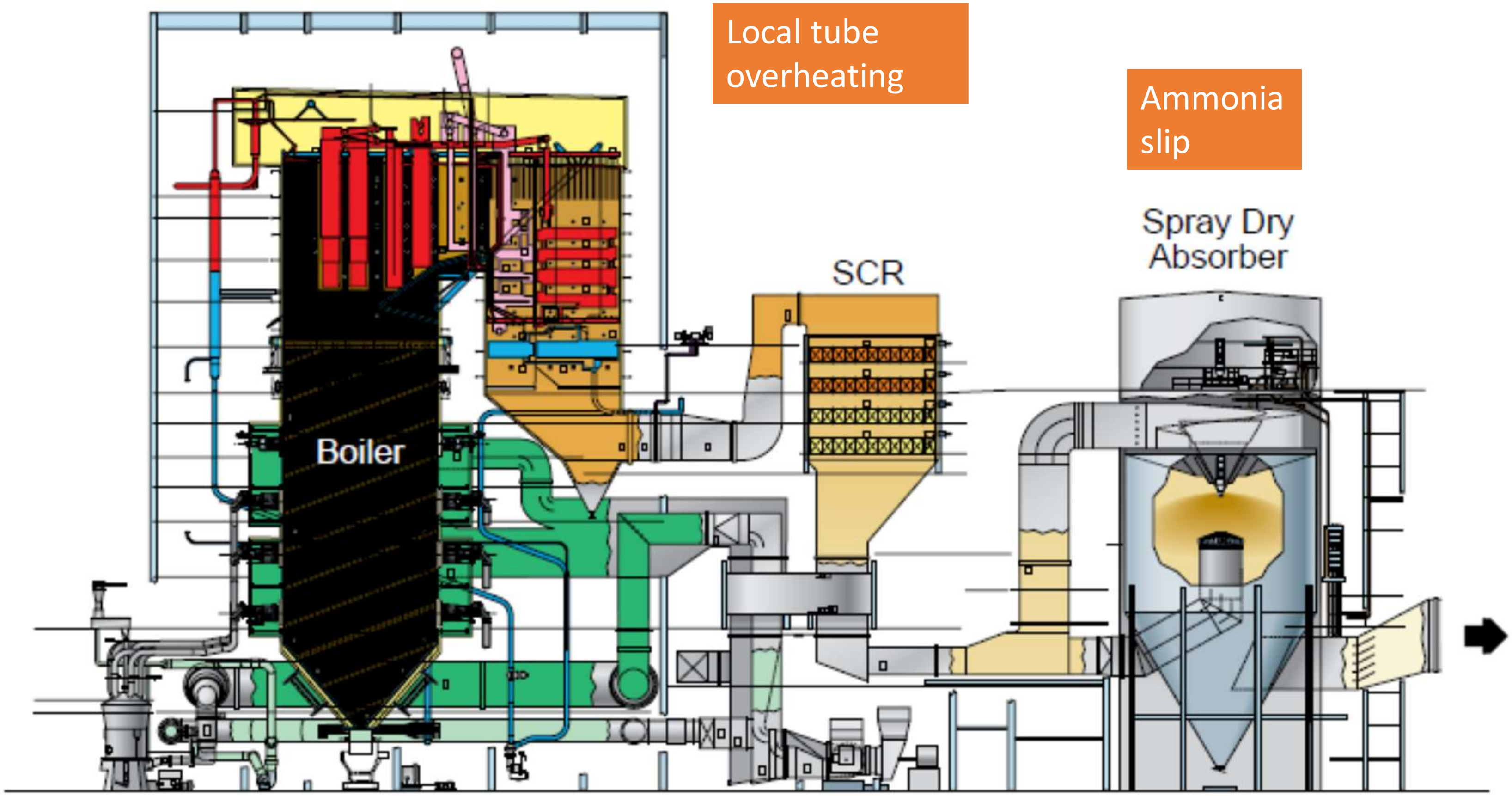


Incompatible with Traditional Sensing Technologies

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

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

Challenges in Existing Coal Fired Power Plants



Local tube overheating

Ammonia slip

Combustion control and air in-leakage

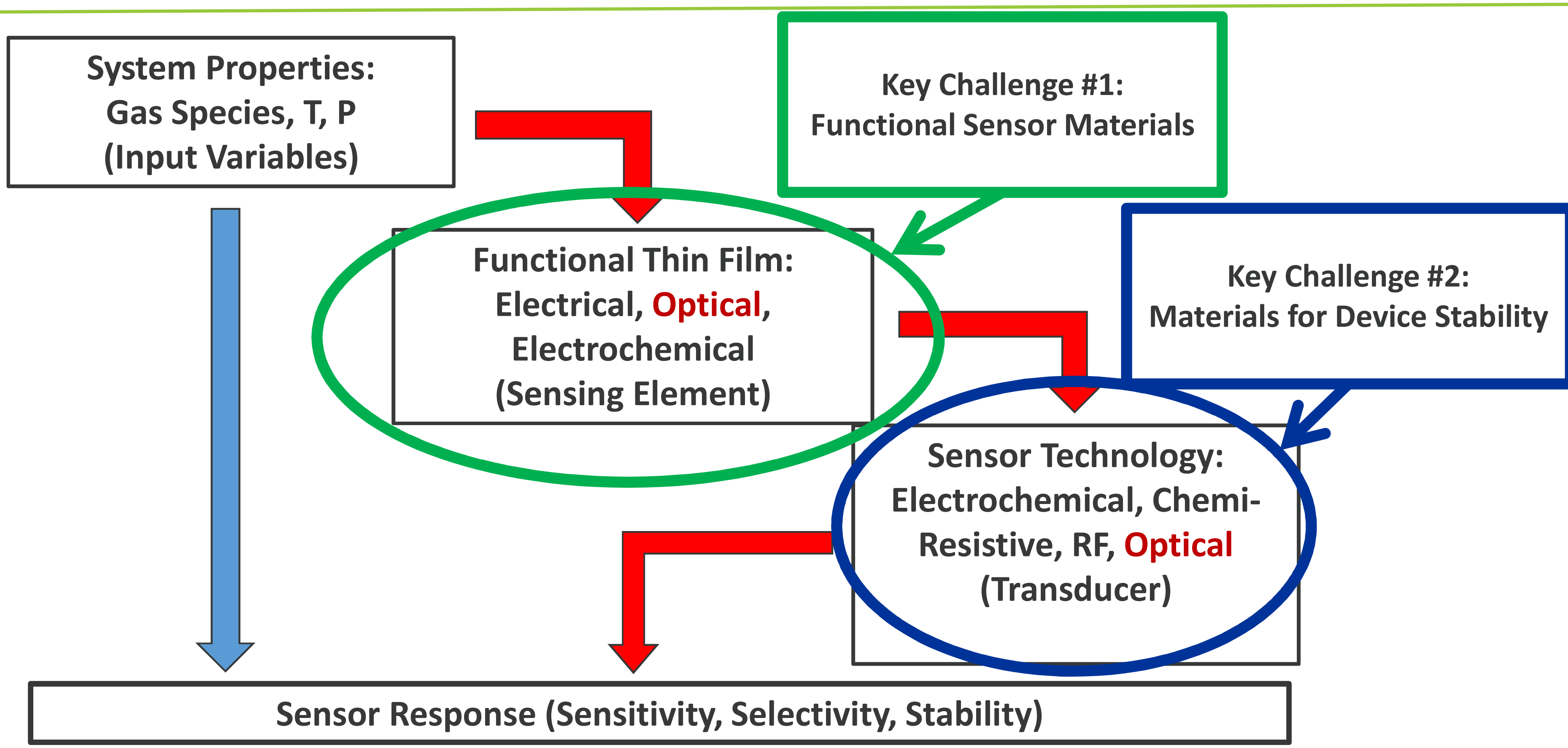
Mill performance

Water / WW chemistry

Controls optimization

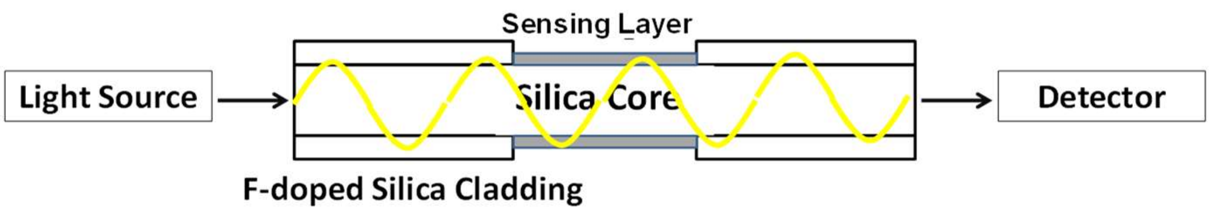
Cross-section of John W. Turk Jr. USC Plant. Courtesy of Babcock & Wilcox.

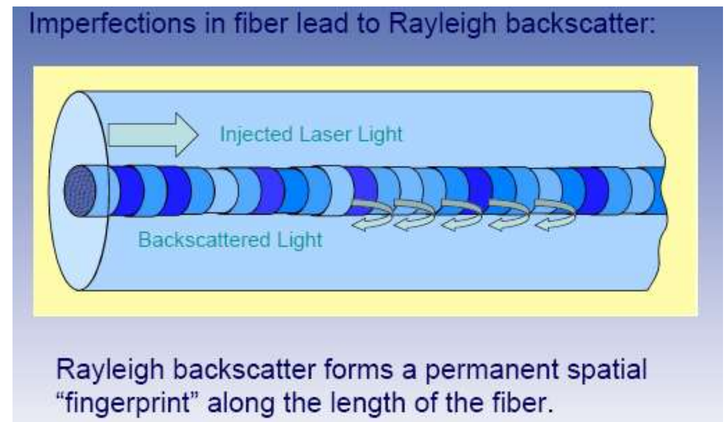
Enabling Harsh Environment Sensor Materials



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**

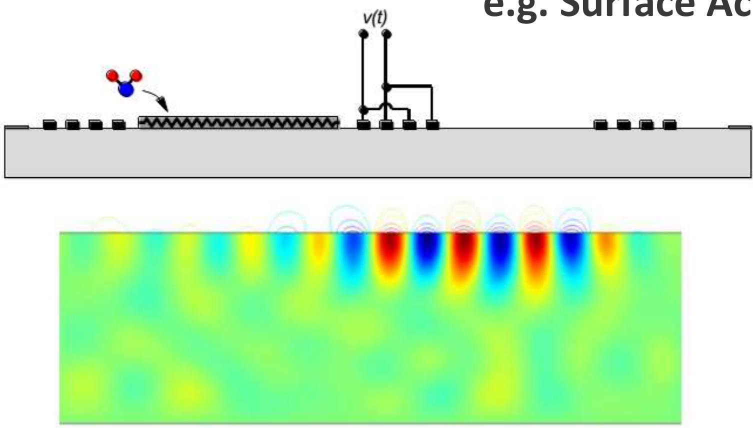
→ **Eliminate EMI and Potential Interference with Electrical Systems**

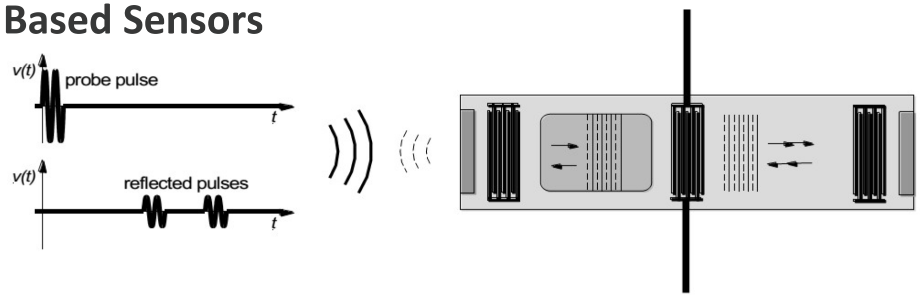
→ **Compatibility with Broadband and Distributed Interrogation**

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

Recent Activity Focused on Wireless Sensors

e.g. Surface Acoustic Wave Based Sensors

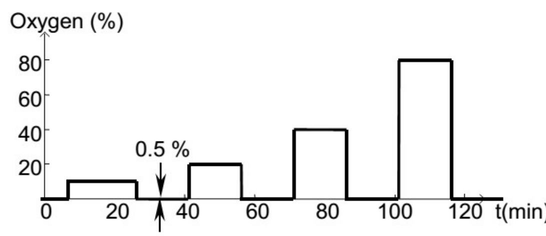


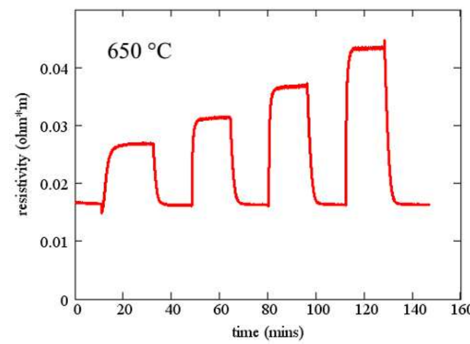


Surface Acoustic Wave Devices for Harsh Environment Wireless Sensing

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

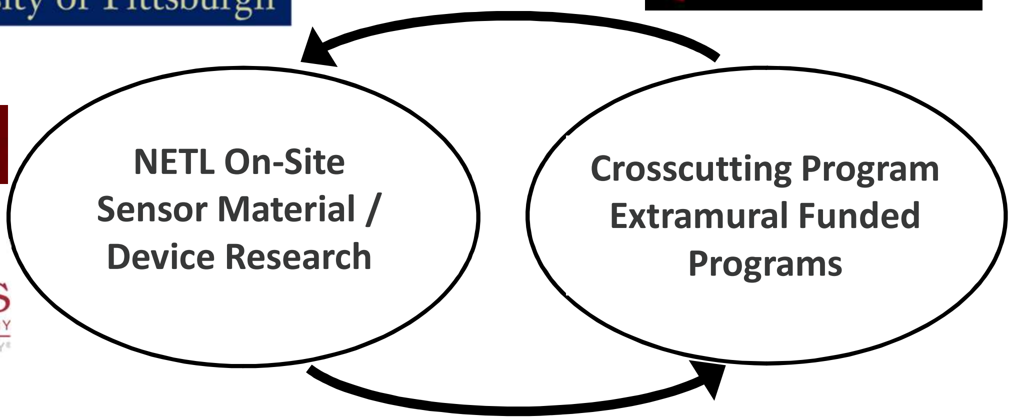




More Recent Activity Has Been Initiated on Surface Acoustic Wave Based Sensors Compatible with Wireless Interrogation.

Collaborative Interactions with Universities

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



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

Unique Facilities of the Project Team

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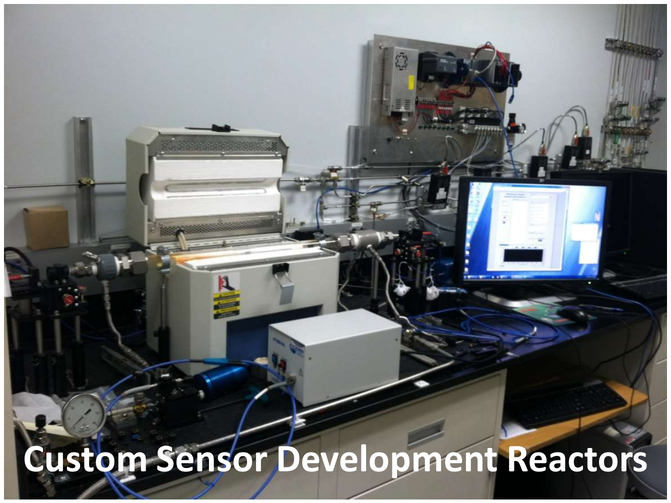


Laser Heated Pedestal Growth System for Fabricating Single Crystal Fibers

Custom Sensor Development Reactors Simulate:

→ Power Generation and Combustion Systems

→ Subsurface / Geological Environments

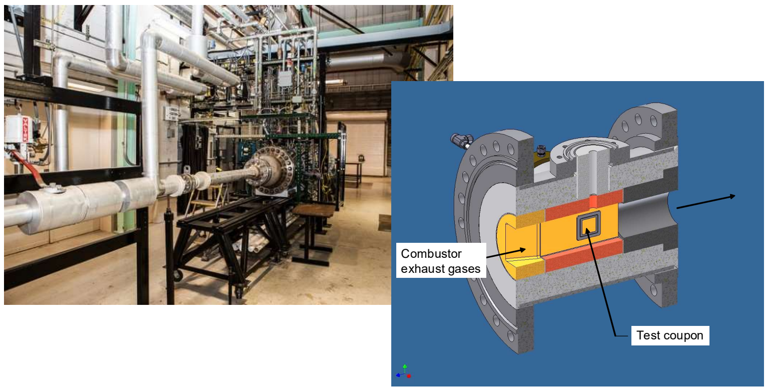
→ Pressurized Gas and Oil-Based Systems

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.

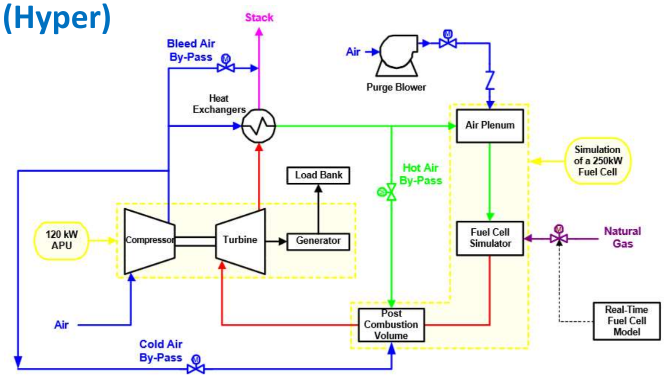
Unique Facilities Available at NETL

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)

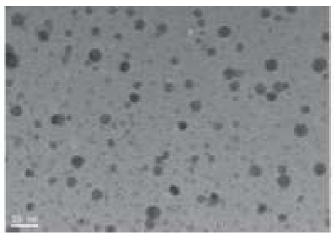


- A 300kW solid oxide fuel cell gas turbine (SOFC-GT) power plant simulator
- 120 kW Garrett Series 85 APU with single-shaft turbine, 2-stage radial compressor, and gear driven generator
- 100+ process variables measured including rotational speed (1,200Hz; 40,500 rpm), air/fuel flow, temperature (turbine: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

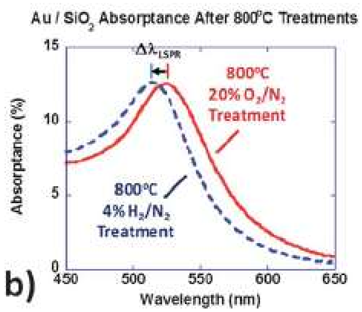
Pilot Scale Facilities Exist at NETL for Demonstrations of Prototype Sensor Concepts Under Application Relevant Conditions (Turbine, Combustion, SOFC).

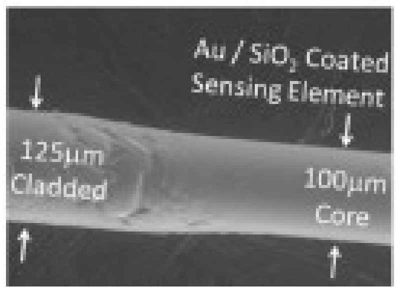
Functional Thin Films for High Temperature Sensing

Au-Nanoparticle Incorporated Oxides

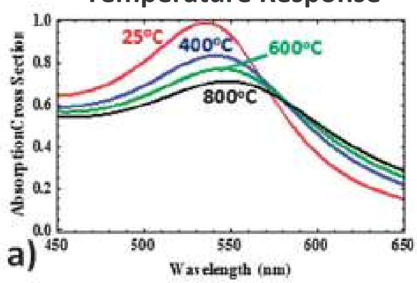


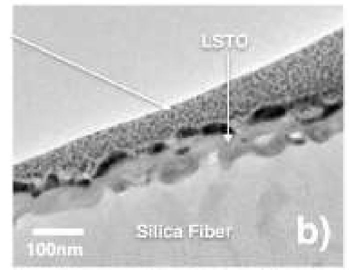
Gas Stream Response

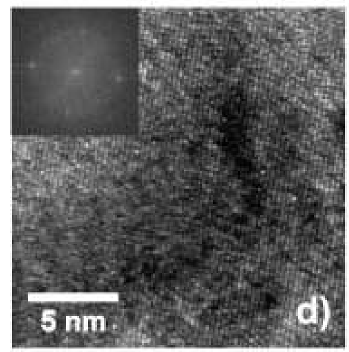




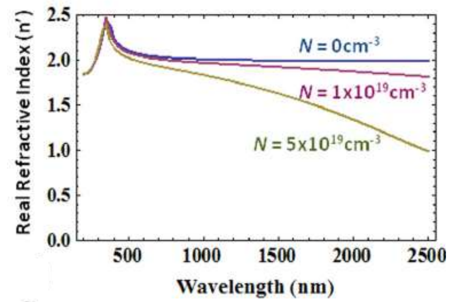
Temperature Response

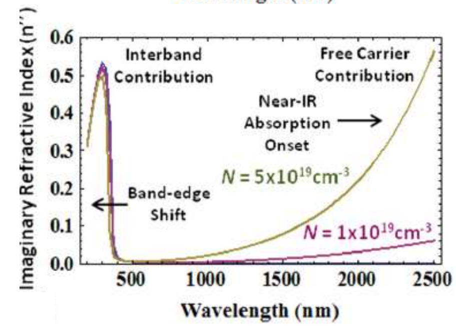






High Electronic Conductivity Oxides





Au-Nanoparticle / Oxide and High Electronic Conductivity Oxide Based H_2 Sensing Materials Leveraging the Fiber Optic Sensing Platform for SOFC Relevant Applications (~700-800°C).

Functional Thin Films for High Temperature Sensing

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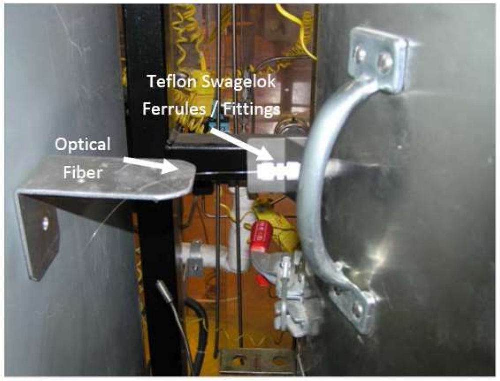
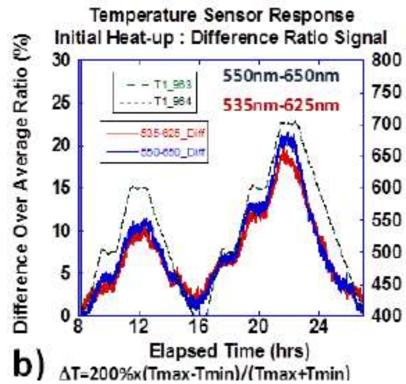
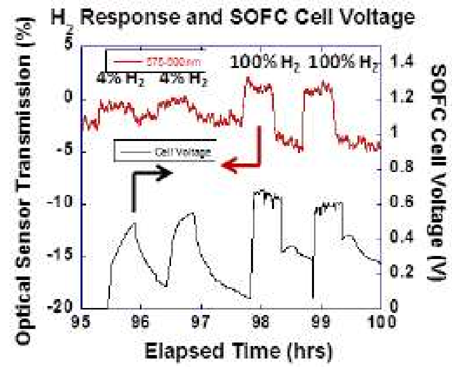
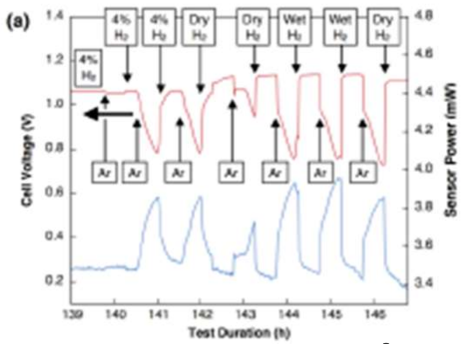


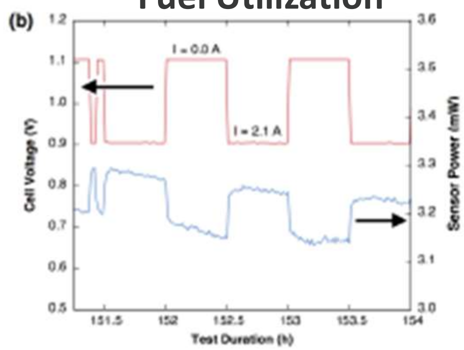




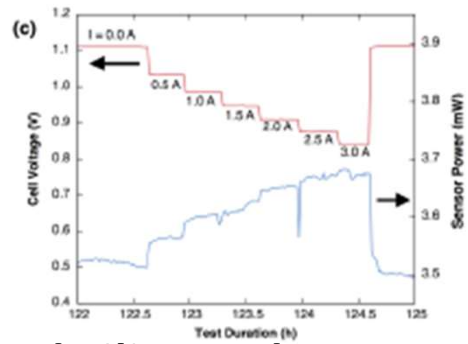
Fuel Gas Stream Variations



Fuel Utilization

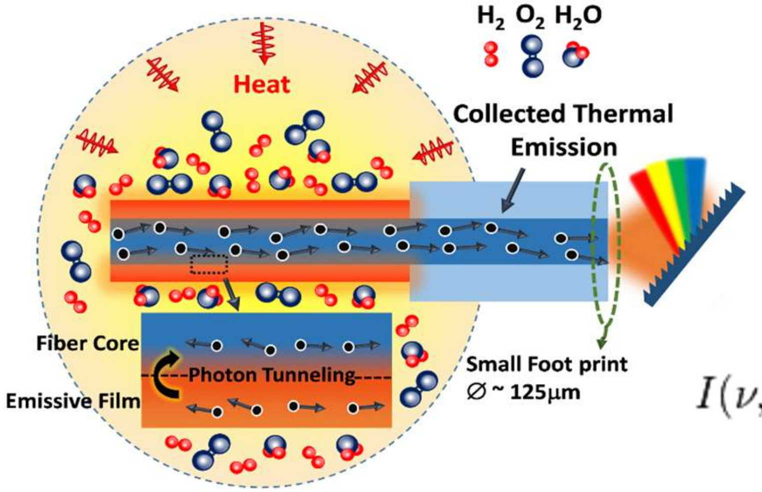


Fuel Utilization



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

New Paradigm : Thermal Emission Based Sensing



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

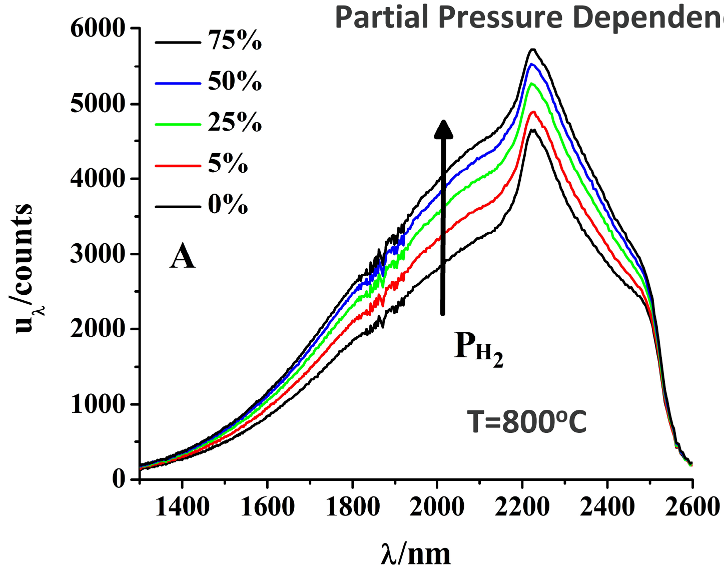
Planck's Law of Blackbody Radiation

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

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

Absorptivity Emissivity

Thermal Emission H_2 Partial Pressure Dependence



Thermal Emissivity-Based Chemical Spectroscopy through Evanescent Tunneling

Zsolt L. Poole and Paul R. Ohodnicki*

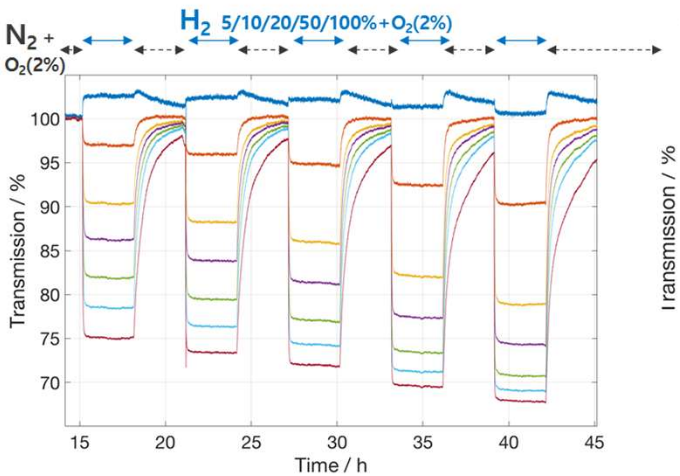
Adv. Mater. **2016**, *28*, 3111–3114

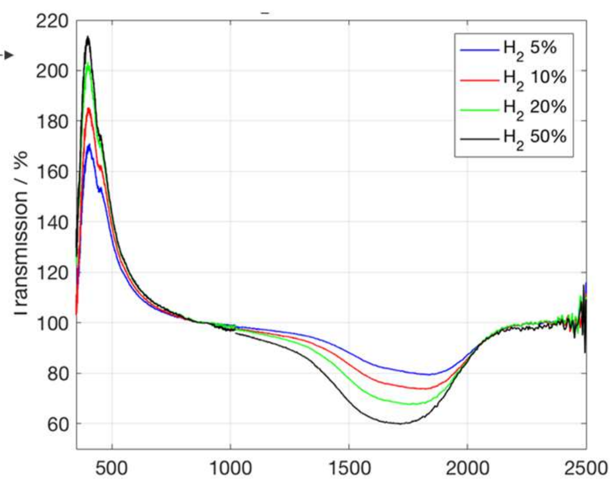
We Have Recently Discovered that Direct Thermal Emission Monitoring of the Functional Sensor Layer as Well as Characteristic Absorption of the Silica Fiber Can Be Used for Sensing.

Emerging Trends : Multivariate Optical Based Sensing

Sn-Doped In_2O_3

Intermediate Temperature Sensing

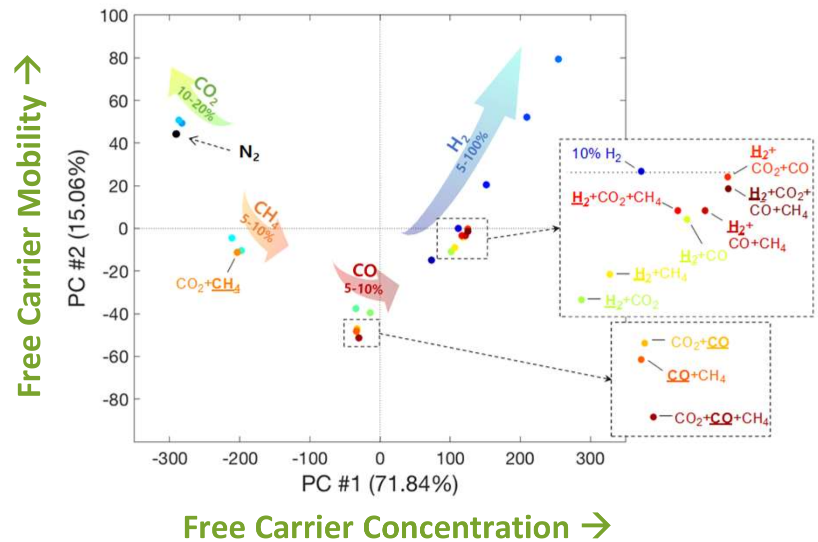




T = 350°C, Proof of Principle Study

Multi-variate Analysis

Complex Gas Phase Chemistries

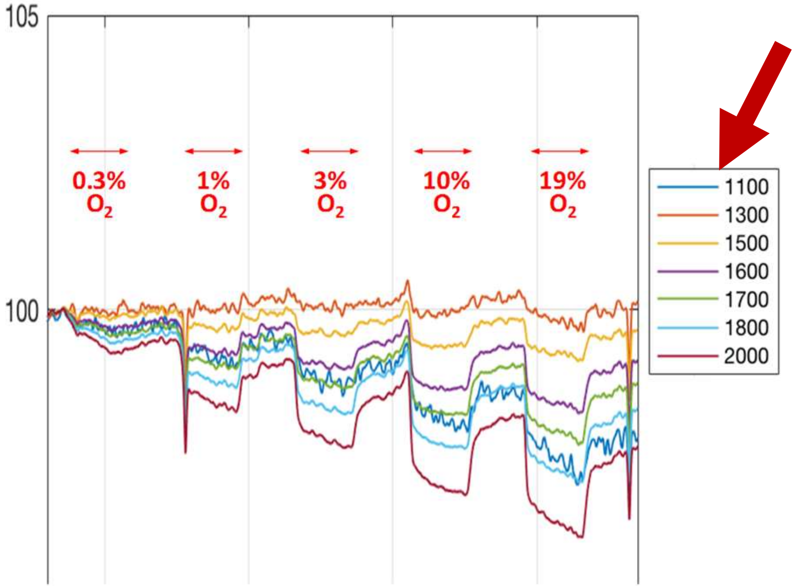


A Primary Advantage of Optical Based Sensors Lies in the Capability for Multi-Variate Analysis of Broadband Wavelength Signals Which is an Emerging Trend Being Explored.

Functional Thin Films for High Temperature Sensing

$(La_{1-x}Sr_x)MnO_3$

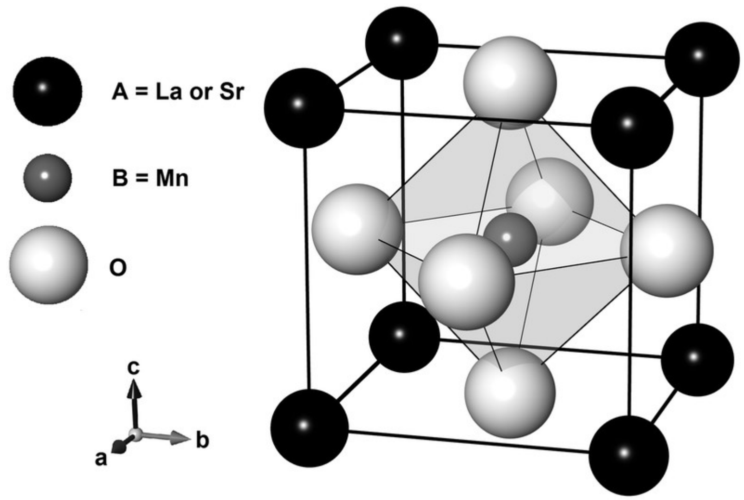
High Temperature O_2 Sensing



Near-IR Wavelength Range

Perovskite Oxides

Correlated Electronic Properties



More Recent Work is Targeting LSM and Related Perovskite Oxides for High Temperature O_2-Sensing. Responses are Consistent with p-Type Electronic Conductivity of Oxides.

Computational Methods Applied to Sensor Materials

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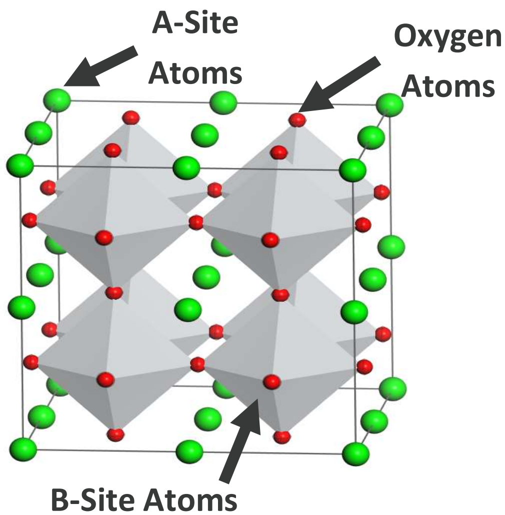
Perovskite Type : ABO_3

Examples: STO, LSTO, LSM, LSC, LSCF, etc.



DFT Based Modeling of Electronic Band Structure

→ T = 0K → **Optical, Magnetic, and Electronic Transport Properties**

↓

Phonon Band Structure Calculation

→ Finite T → **"Time Averaged" Electronic Band Structure** → Finite T → **Optical, Magnetic, and Electronic Transport Properties**

↓ Finite T

Thermodynamic Properties (ΔS, ΔH, ΔG, C_p)

We are Developing and Applying Computational Methodologies and Techniques with a Goal of Obtaining High Temperature Functional Properties from First Principles.

Computational Methods Applied to Sensor Materials

Temperature effect on electronic structure:

- electron-phonon interaction

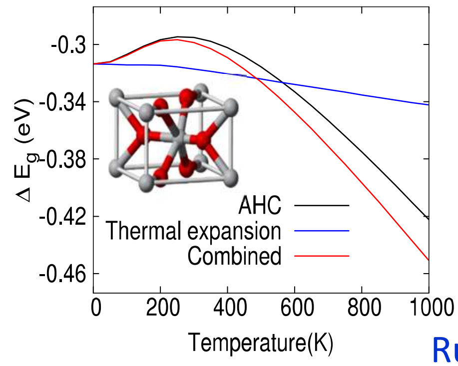
$$\epsilon_{\mathbf{k}n}(T) - \epsilon_{\mathbf{k}n}(\mathbf{0}) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},\nu} \frac{a^{(2)}_{\mathbf{q}\nu;\mathbf{q}\nu}}{\omega_{\mathbf{q}\nu}} \left[\frac{1}{2} + n_{\mathrm{B}}(\omega_{\mathbf{q}\nu}, T)\right] + \cdots$$

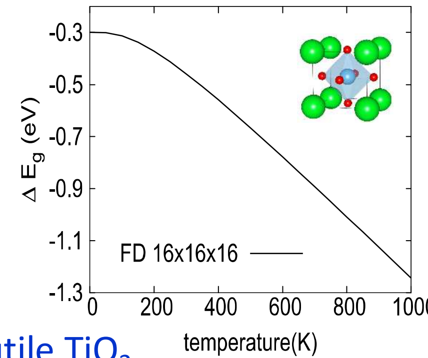
  - Allen-Heine-Cardona (AHC) theory
  - Finite displacement method (FD)
- Lattice thermal expansion
  - Quasiharmonic approximation

$$F(\mathbf{a}) = E_{T=0}(\mathbf{a}) + \frac{1}{2}\sum_{\mathbf{q},\lambda} \hbar\omega_{\mathbf{q},\lambda} + k_B T \sum_{\mathbf{q},\lambda} \ln\left[1 - \exp\left(-\frac{\hbar\omega_{\mathbf{q},\lambda}}{k_B T}\right)\right]$$

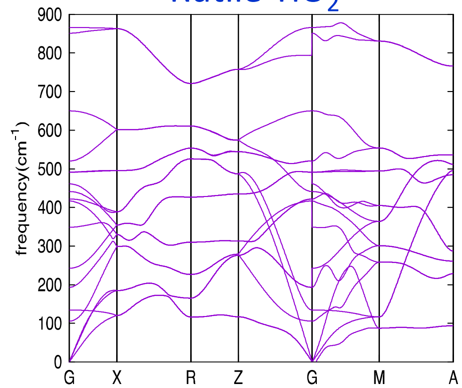
DFT Energy | Phonons

- Electron-phonon interaction is the major contribution.

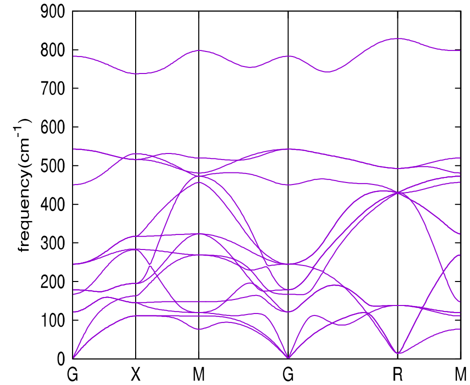




Rutile TiO_2



Cubic STO



Example #1: Temperature Dependent Bandgap of TiO_2 and $SrTiO_3$.

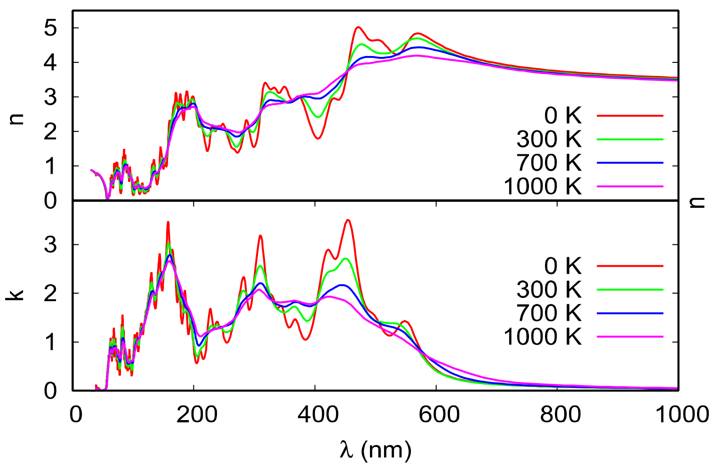
Computational Methods Applied to Sensor Materials

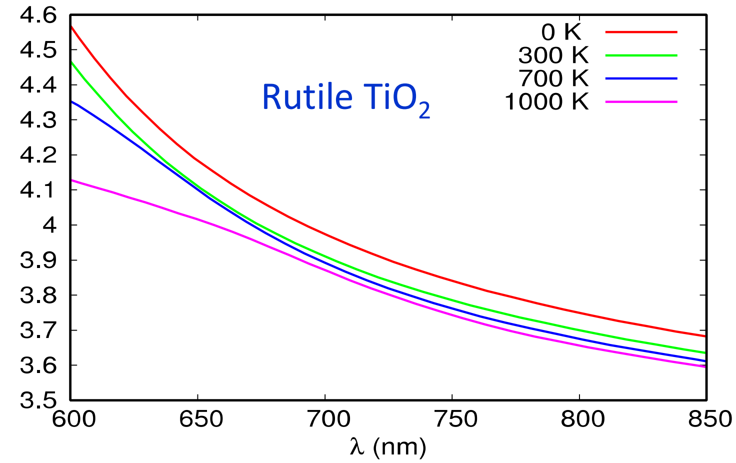
- Current DFT theory to calculate the dielectric constants does not include electron-phonon coupling.
- We propose a statistical method based on atomic displacements.

$$\mathbf{u}_n = \sum_{\mathbf{q},i} \mathbf{u}_{n,\mathbf{q}i} = \sqrt{\frac{\hbar}{m_n}} \sum_{\mathbf{q},i} \frac{\hat{n}_{\mathbf{q}i} e^{i(\mathbf{q}\cdot\mathbf{R}_n + \phi_{\mathbf{q}i})}}{\sqrt{(e^{\hbar\omega_{\mathbf{q}i}/k_B T} - 1)\omega_{\mathbf{q}i}}}$$

1. Generate a set of configurations according to the phonon dispersion.
2. A random phase is added to each phonon modes.
3. Calculate the dielectric constants for each configuration.
4. Configurational average.

- Curves of optical properties get smoothed as temperature increases.



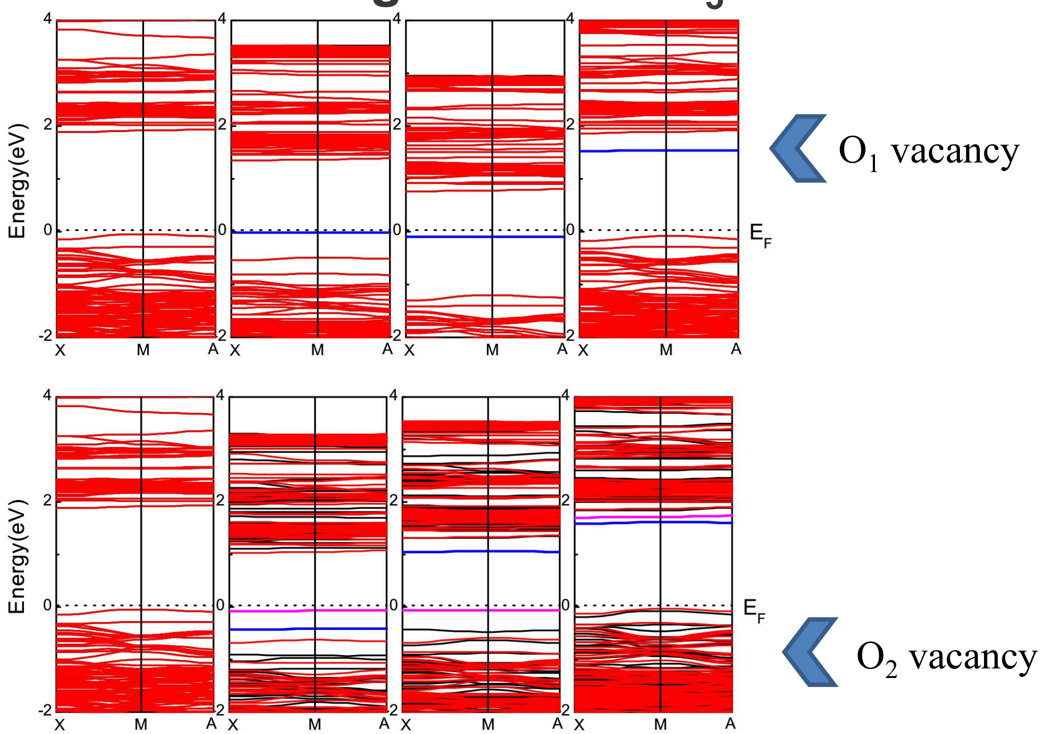


- Y.-N. Wu, W. A. Saidi, P. Ohodnicki, B. Chorpening, Y. Duan, "*Temperature effect on electronic structure and optical properties of rutile TiO_2*", **Physical Review B** (2018) to be submitted.

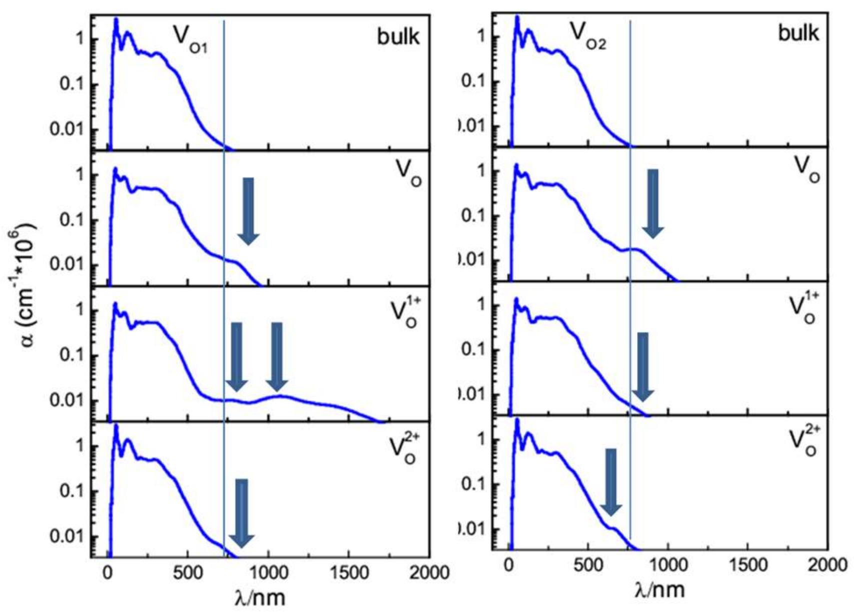
Example #2: Finite Temperature Extrapolation of Optical Constants for TiO_2.

Computational Methods Applied to Sensor Materials

Antiferromagnetic $LaFeO_3$



Visible and Near-IR Optical Signatures of Oxygen Vacancies



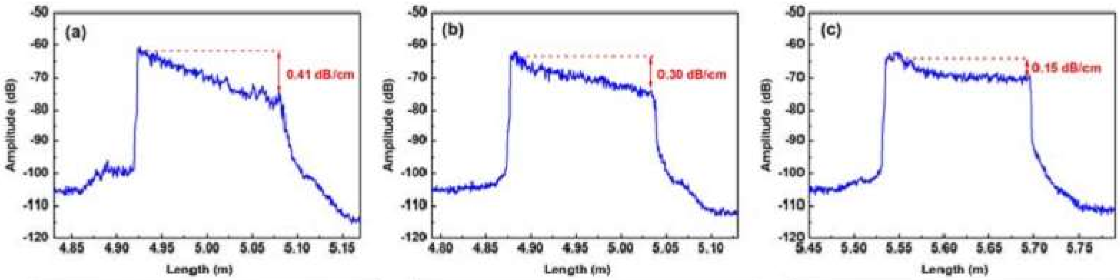
Example #3: Optical Properties of Complex Perovskites and Defect Chemistry.

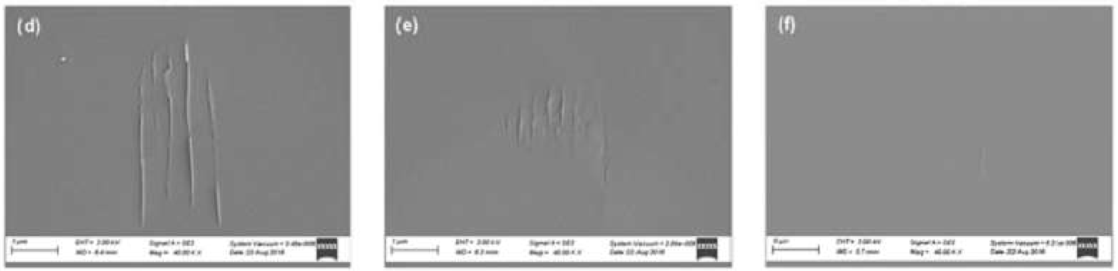
High Temperature Distributed Sensing in Silica Fibers

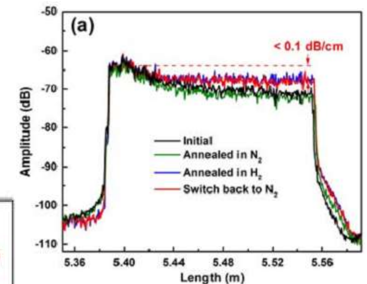
NATIONAL ENERGY TECHNOLOGY LABORATORY

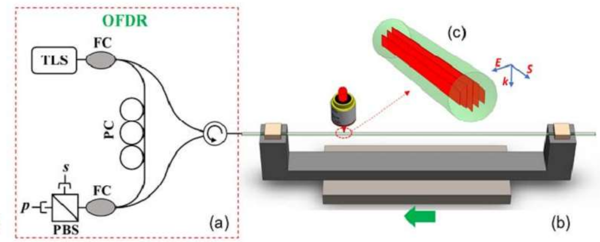
University of Pittsburgh

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

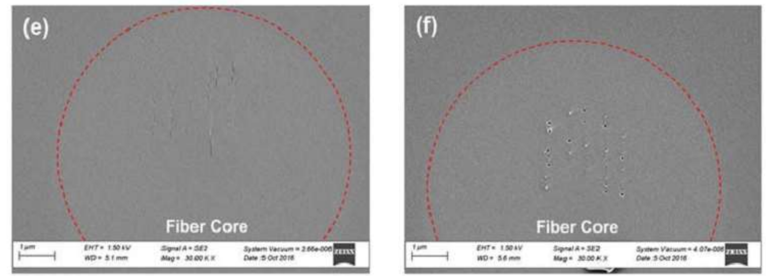








Elevated Temperature H_2 Exposure Results in Irreversible Morphological Changes to Aligned Spherical Voids

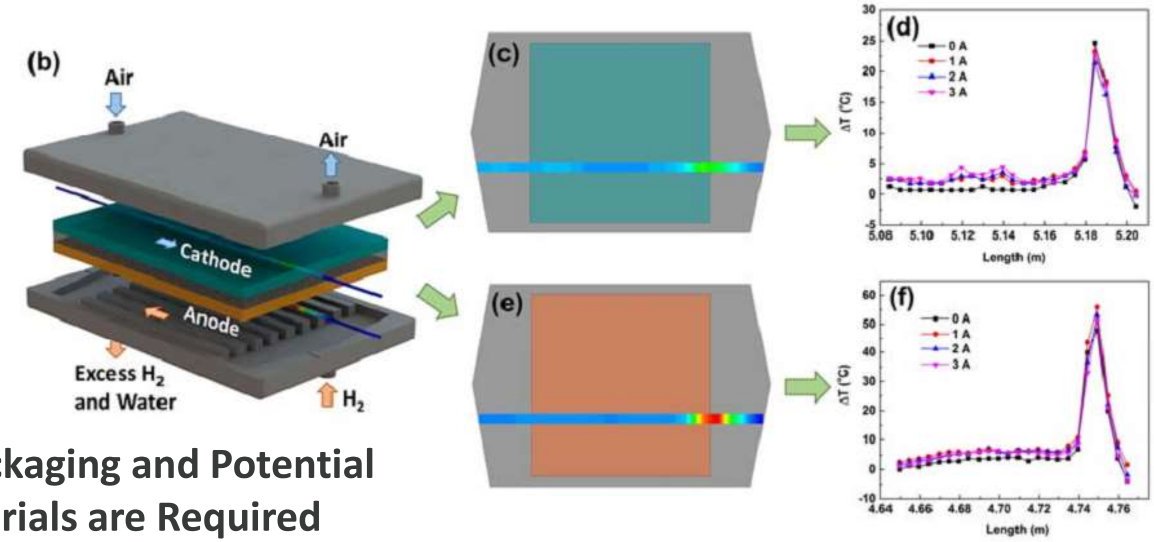


Enhanced Temperature and H_2 Stability of OFDR Rayleigh Based Interrogation of Optical Fibers Associated with Engineered Voids Within the Silica Network.

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 and Elevated Temperatures Relative to Cell Operating Temperature.



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

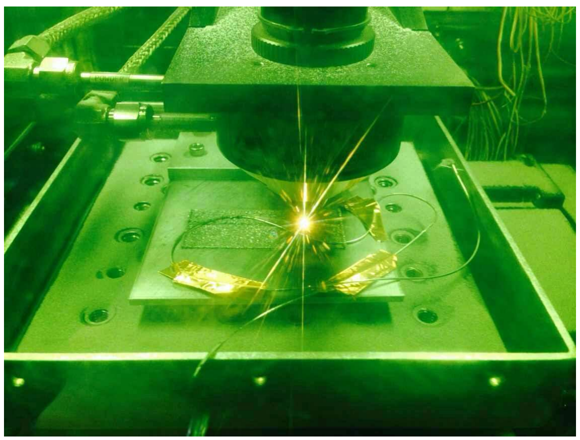
Enhanced Backscattering Processing Methodologies Have Enabled Successful Temperature Profile Measurements Throughout an Operational SOFC Anode and Cathode Stream.

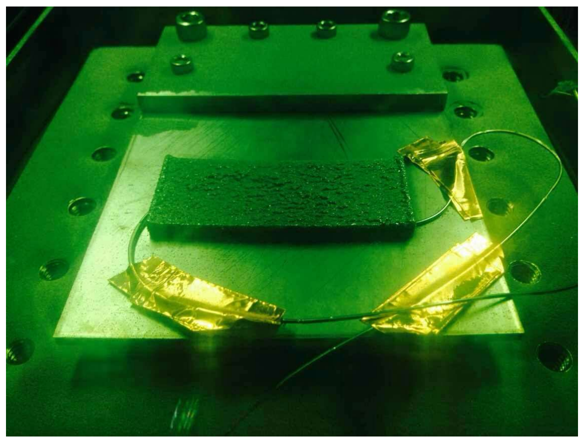
Additive Manufacturing Embedding of Silica Fibers

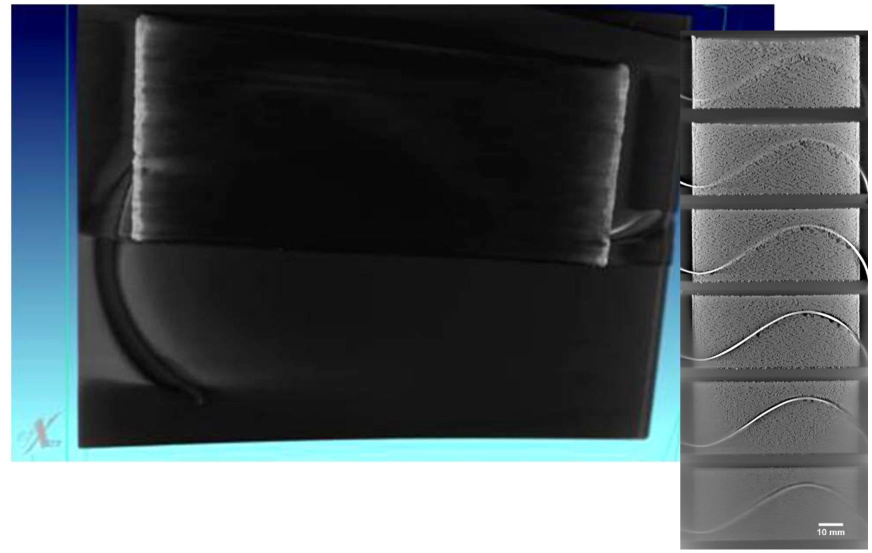
NATIONAL ENERGY TECHNOLOGY LABORATORY

University of Pittsburgh

LENS Embedding Within a High Temperature Ti-Alloy Part







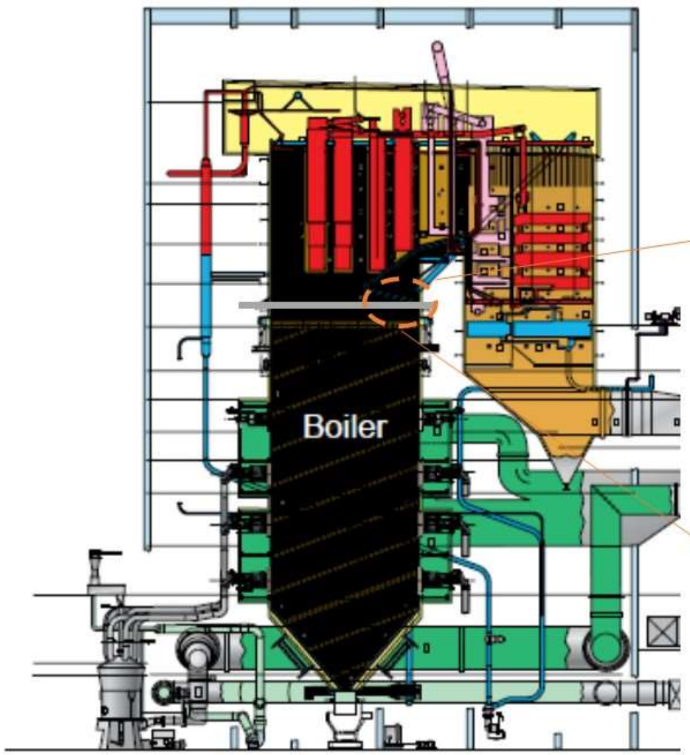
CT Scanning Capabilities Leveraged to Explore Structure of Embedded Sensors

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

Planned Field Validations: Temperatures Across the Boiler Tube Wall

NATIONAL ENERGY TECHNOLOGY LABORATORY

100+ temperatures from one optical fiber



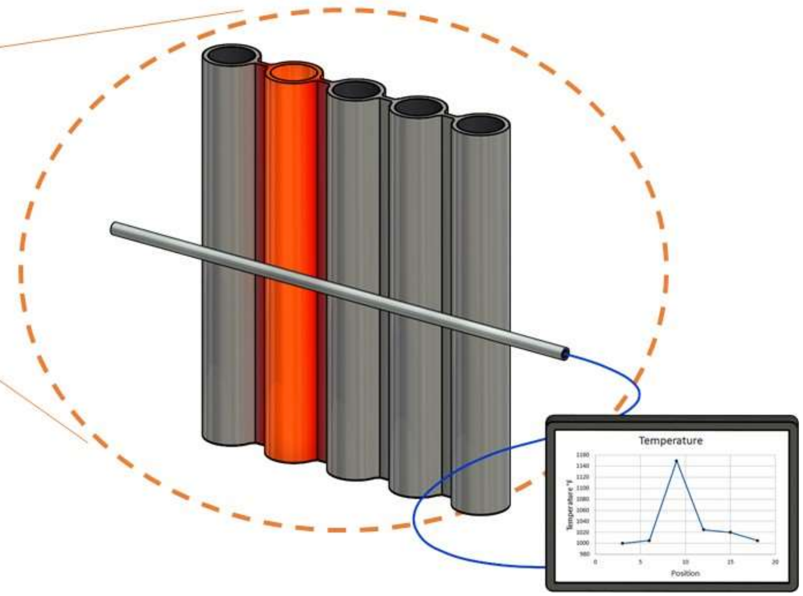
<u>Measure temperatures from every tube</u>

Expected spatial resolution 1 inch (200 ft long)

Identify local hot spots on tube wall

Outside wall for initial effort (silica fiber in air 1000°F)

Sapphire fiber later in hotter locations



- New Task
- CRADA being negotiated for test site

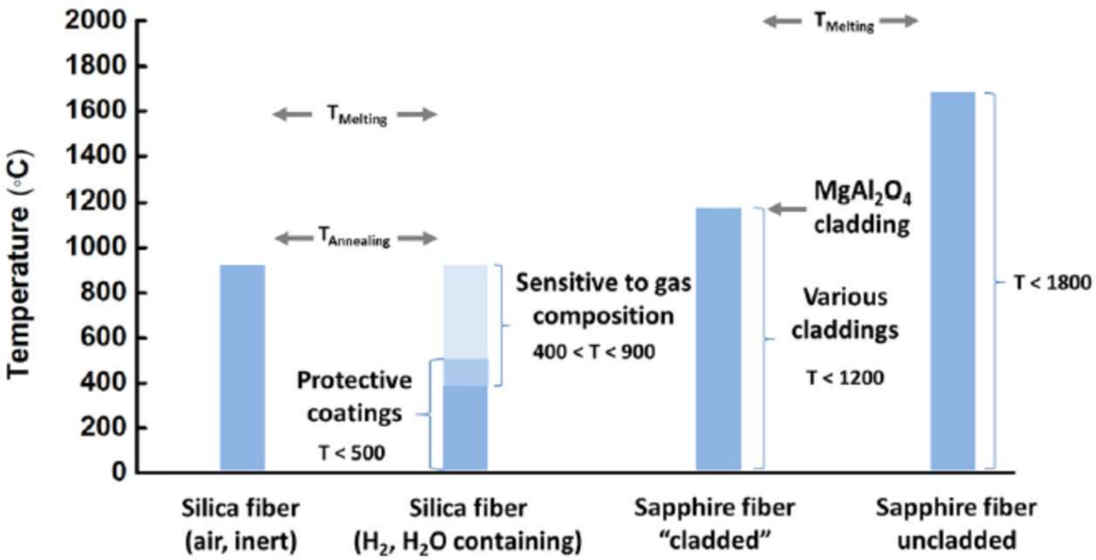
Alternative Optical Fiber Material Investigations

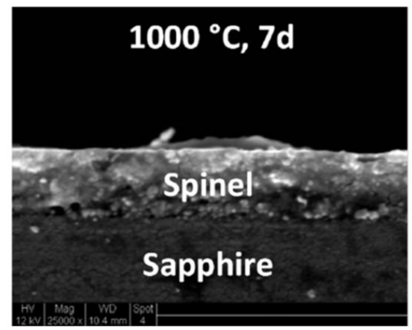
NATIONAL ENERGY TECHNOLOGY LABORATORY

Review and perspective: Sapphire optical fiber cladding development for harsh environment sensing

Hui Chen, Michael Buric, Paul R. Ohodnicki, Jinichiro Nakano, Bo Liu, and Benjamin T. Chorpening

Applied Physics Reviews **5**, 011102 (2018); doi: 10.1063/1.5010184





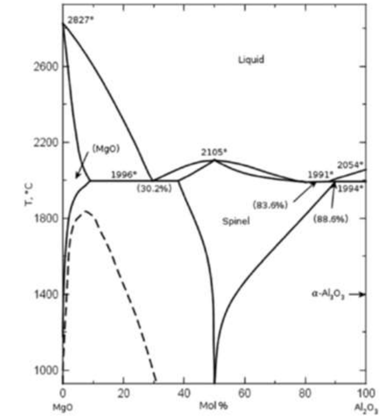
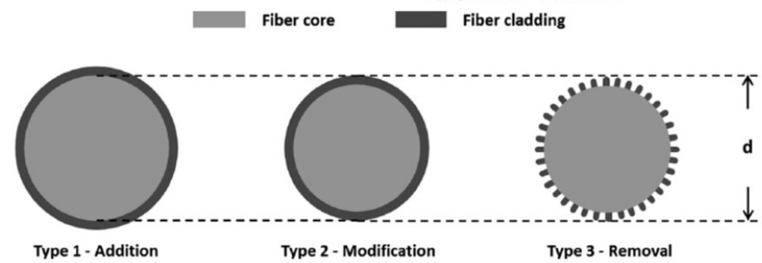


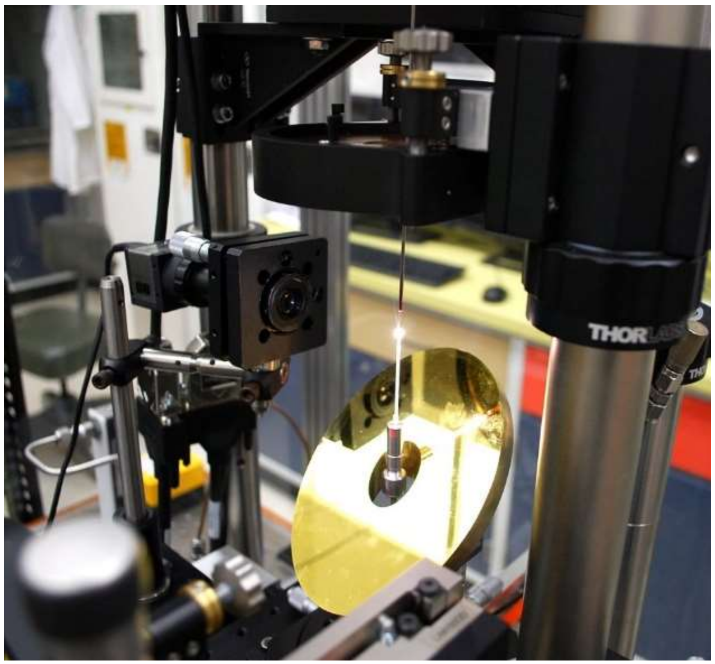
FIG. 4. Phase diagram of the binary MgO-Al_2O_3 system.[89] Reproduced with permission from B. Hallstedt, J. Am. Ceram. Soc. **75**, 1497 (1992). Copyright 1992 John Wiley & Sons, Inc.

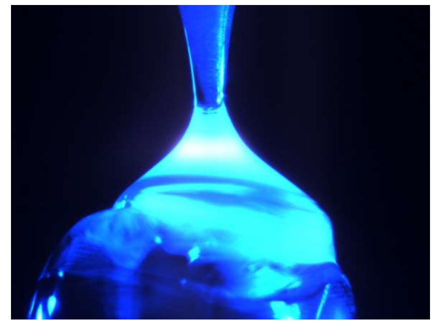


New Research Efforts Currently Being Initiated Will Target Research and Development of Cladding Layer Approaches for Sapphire Based Fibers.

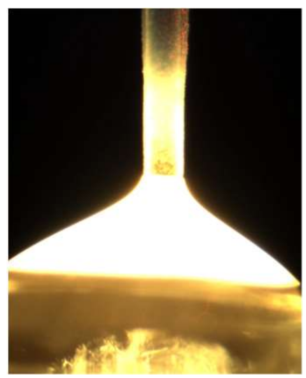
Alternative Optical Fiber Material Investigations

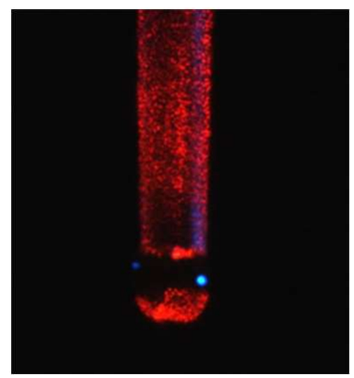
Laser Heated Pedestal Growth Processing

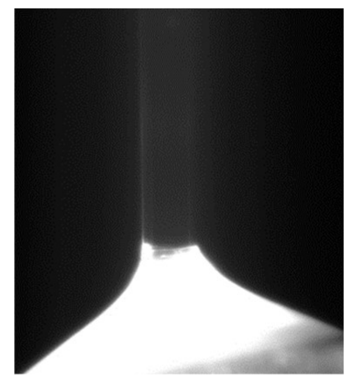




Novel Sensor Fabrication Through LHPG Process Controls



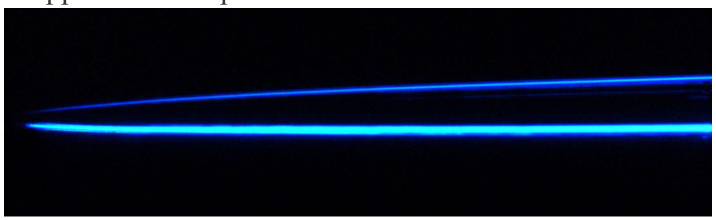




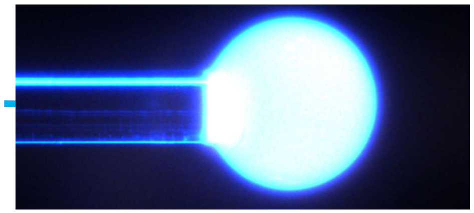
Laser Heated Pedestal Growth Facilities Were Established to Support Sapphire Fiber Development, Including In-Line Processing for Cladding Integration.

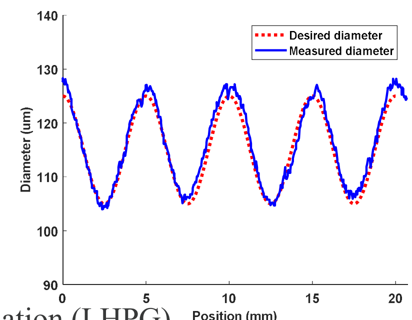
Alternative Optical Fiber Material Investigations

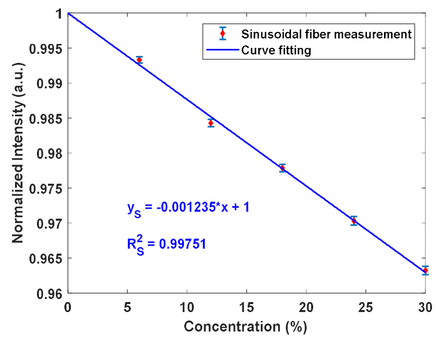
Sapphire fiber taper



Sapphire ball lens (reduces end reflections)

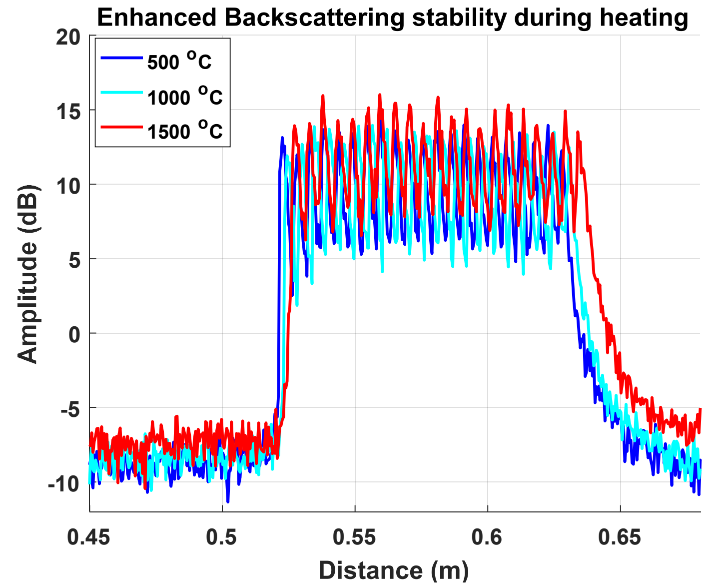






Periodic Variation (LHPG)

$$\Delta L = C \cdot L \cdot \Delta T$$



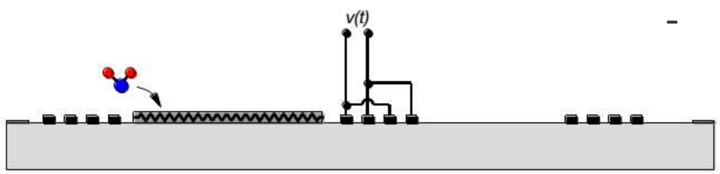
Significant Accomplishments Include (1) Optimized Process Control for Long Sapphire Growth and Custom Shapes and (2) fs-laser Processed Sapphire Fibers for Distributed Interrogation.

UCR Outreach Program : Formalized Collaborations

NATIONAL ENERGY TECHNOLOGY LABORATORY

Promoting Development of High Temperature Wireless Sensor Technology

e.g. Surface Acoustic Wave Based Sensors



NETL Research & Innovation Center

- 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

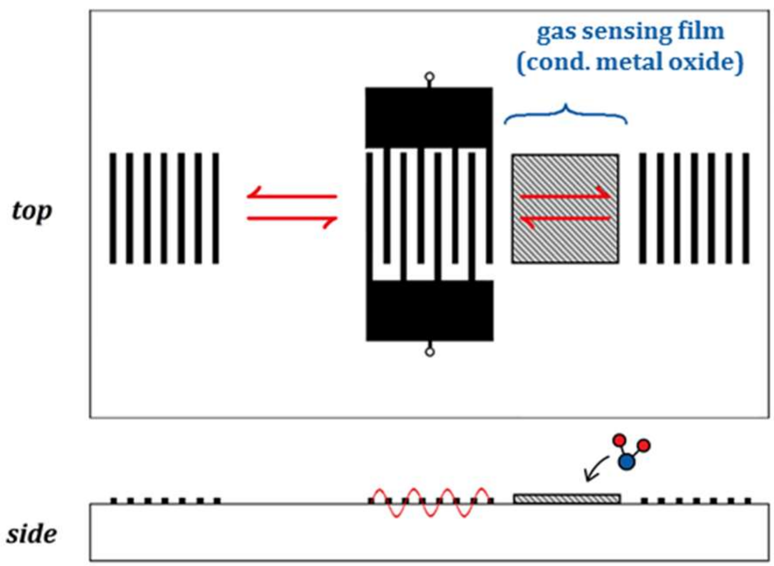
Dr. Robert Fryer, ORISE Researcher

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.

UCR Outreach Program : Formalized Collaborations

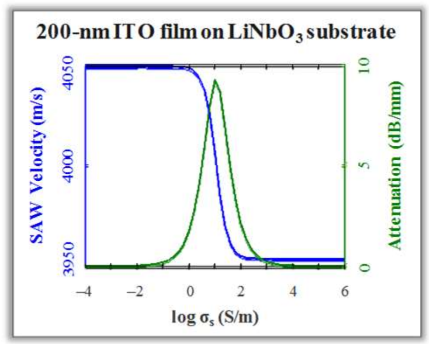


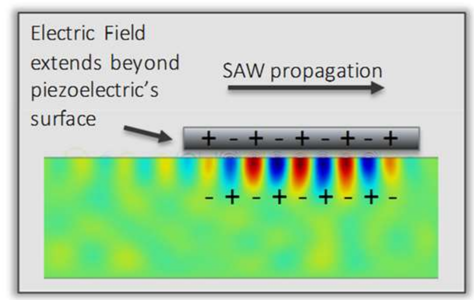
$$\frac{\Delta v}{v_0} \cong \frac{1}{V_p}\left(\frac{\delta v}{\delta T}\Delta T + \frac{\delta v}{\delta \varepsilon}\Delta \varepsilon + \frac{\delta v}{\delta E}\Delta E + \frac{\delta v}{\delta \sigma}\Delta \sigma + \frac{\delta v}{\delta m}\Delta m + \frac{\delta v}{\delta p}\Delta p + \ldots\right)$$

Δv = change in velocity
v_0 = velocity without surface layer
K^2 = electromechanical coupling coeff.
σ_s = sheet conductivity of sensing layer
ε_{eff} = effective dielectric permittivity

Contributions from varying surface layer's film conductivity:

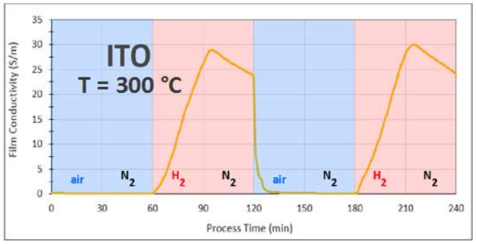
$$\frac{\Delta v}{v_0} = -\frac{K^2}{2}\frac{\sigma_s^2}{\sigma_s^2 + (v_0 \varepsilon_{eff})^2}$$

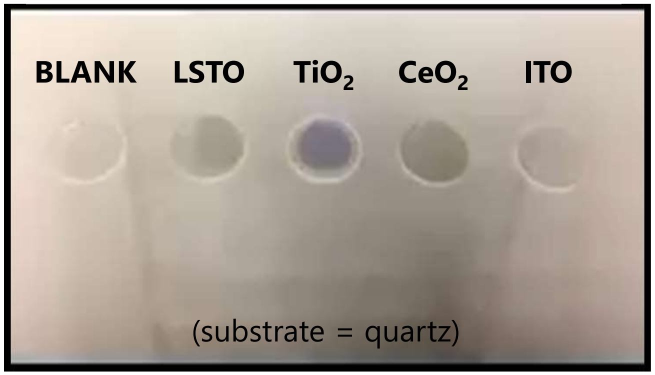




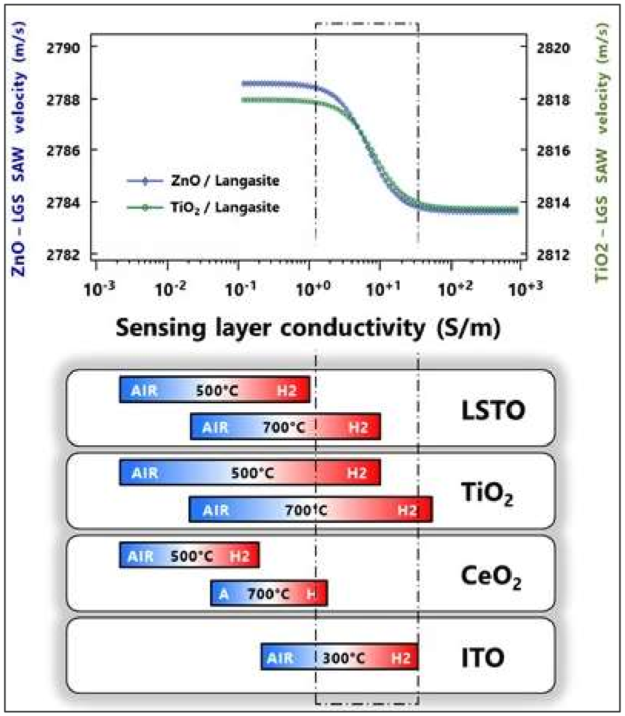
The Collaboration is Focused on (1) Developing New Sensing Materials for High Temperature SAW Sensing and (2) Collaborating with Partners to Leverage NETL Expertise and Facilities.

UCR Outreach Program : Formalized Collaborations

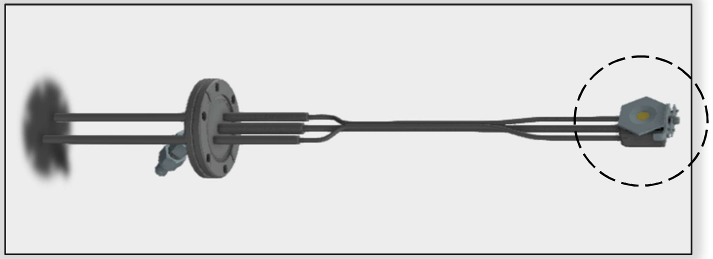


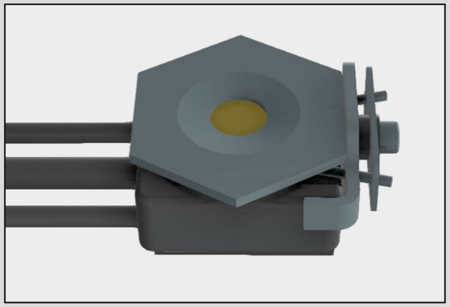


2-Point Electrical Conductivity Measurements of Various Films



High Temperature QCM





Key Successes to Date Include Screening of Several Candidate Sensing Layers for SAW Sensing Applications and Establishment of New Laboratory Capabilities.

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**