Metal oxide sensing materials integrated with high-temperature optical sensor platforms for real-time fossil fuel gas composition analysis

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Program Overview

- University Coal Research Program
- Starting September 2010 (18-Months)
- Two Key Components:
  - Development of High-Temperature Sensor Platforms
  - Integration and Application of Functional Metal Oxide for Gas Sensing
- Three fiber sensor platform techniques
- Five journal publications
- Two industrial collaborations
Research Overview

- **Point fiber sensor for high-T**
  - High performance high-T FBG point sensor (>800°C) at $20/sensor
  - Chemical regenerative process
  - Integration with SnO₂ on D-Shaped fiber for NH₃ sensing

- **Distributed fiber chemical sensor**
  - First-ever demonstration of distributed fiber chemical sensing
  - Rayleigh-scattering OFDR technique
  - 1-cm spatial resolution
  - Integration with Pd/PdH for H₂ sensing

- **Coherent Anti-Stokes Raman (CAR) sensor**
  - One-laser pulse CARS measurement using temporal pulse shaping
  - Integration with hollow-core fiber
  - >1000 enhancement beyond spontaneous Raman
  - Aiming for CO₂ and C₂H₆ measurement
**Topic I: Point Fiber Sensor for high-T**

- **Current State of the Art**
  - Single-mode F-P interferometer on the fiber tip
  - Fiber Bragg grating in single-mode fiber by the ultrafast laser fabrication

- **Challenge**
  - Packaging is key (Expensive and difficult)
  - Poor spectral performance
  - Expensive

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**F-P Sensor**

- Dr. Wang’s group at VT

**Type II FBG**

- CRC Canada
Technique: Chemical Regenerative Process

- Turn a dollar commercially off-shelf fiber Bragg grating ($20) into a high-temperature sensors beyond 800C.

- **Extended this process to air-hole microstructural fibers, expand capability of fiber sensor beyond only temperature or strain measurements.**
  - Specially laser fabrication equipment for high-T grating fabrication no longer needed!
  - Cost of high-T sensors could come down drastically!
  - Parameters that sensor can measure drastically expanded (due to the air-hole microstructural fibers.)
Process: Chemical Regenerative Process

- A Strong Type I FBG in optical fiber by UV laser.
- Rapid thermal annealing to anneal UV-induced defect.
  - Customer furnace development
- Stress induced on the fiber core-cladding interface during defect erasure.
Process: Chemical Regenerative Process

Experimental Setup

Typical Regenerative Process

Fibers Used for this work
Regenerated Grating in Twin-hole Fiber

Temperature Cycles

Stability Testing

High-T Thermal Drift: 0.013 K/hour (Best case)
0.045 K/hour (Worse)
Regenerated Grating in Twin-hole Fiber

Pressure Test

Pressure Testing

FEA Simulation
Simultaneous Measurement of T and P

\[
\begin{align*}
\Delta \lambda_o & = 1.532 \times 10^{-2} \Delta T + \left( 2.521 \times 10^{-4} - 9.185 \times 10^{-8} \Delta T \right) \Delta P \\
\Delta \lambda_e & = 3.526 \times 10^{-4} - 1.232 \times 10^{-7} \Delta T \\
\Delta \lambda_{o,e} & = \lambda - 1545.25\text{nm} \\
\Delta T & = T - 0^\circ C \\
\Delta P & = P - 0\text{psi}
\end{align*}
\]
High-T Chemical Sensing

- Oxide-coated FBG stable up to 800°C
- Metal Oxide Coating: TiO$_2$, SnO$_2$, ZnO$_2$
- Gas under tests: NH$_3$
- Testing Range: <1 ppm
- Oxide coating need optimization
- NETL Collaborator: Paul Ohodnicki
Progress Update: high T FBG sensors

- **Success in sensor platform development**
  - FBG sensors with superior spectral characteristics at high T
  - Demonstrate high-T stable FBG sensor derived from standard single-mode fiber
  - Low cost
  - Potential commercialization
  - >1000C operation possible using silica-core fiber

- **Successful fiber coating development**
  - SnO₂, TiO₂, and ZnO₂
  - Integration with D-shaped fiber
  - Coated FBG successfully regenerated at 700C

- **Fiber sensor testing**
  - NH₃, NOₓ
  - Sensor response need optimization
Topic II: Distributed Fiber Sensor

• Current State of the Art
  • Brillouin Scattering – OTDR
    • Sub-meter resolution
    • Limited to Temperature and Strain measurement (0.1°C and 1 µε)
    • Long distance (up to km)
  • Rayleigh Scattering – OFDR
    • mm-resolution
    • Limited to Temperature and Strain measurement (0.1°C and 1 µε)
    • ~100 meter distance

Schematic illustration of Brillouin scattering and (b) Rayleigh scattering.
Technique: Active Distributed Fiber Sensor

- Expand Rayleigh scattering distributed sensing beyond T measurement
- Active fiber sensing scheme for environmental adapability.
- Air-hole microstructural fiber for multi-parameter measurement
- Functional coating on-fiber for chemical sensing with –cm resolution
Rayleigh Scattering and OFDR

Rayleigh Scattering

\[ \alpha (z)_{Rayleigh} = \frac{8\pi}{3\lambda^4} \left[ n(z)^8 p^2 \right] (kT_f) \beta \]

OFDR Scheme

- Optical Frequency Domain Reflectometry (Swept-Wavelength Interferometry) for Sub-mm spatial resolution over tens of meters
- In-fiber Rayleigh scattering highly sensitive to local perturbation
- All-temperature operation
- Further Functionality improvement possible
  - Cost, Response Time, Cross Talk

Fig. 3: Schematic sketch illustration of the OFDR operation principle [20].
Distributed Pressure Measurement
OFDR Measurement Results
Two-Hole Fibers: 2000 psi

PM Fiber A
Two-Hole Fiber B

PM Fiber A
Response of PM Microstructure Fiber to two regions of 2000 psi pressure at room temperature

Fiber B
OFDR Measurement Results
Room Temperature

![Graph showing sensor response (microstrain) vs. pressure (psi)](image)

- PM PCF (Fiber A)
- Twin-hole Fiber (Fiber B)
OFDR Measurement Results
Two-Hole Fibers at 800C

Response of Twin-hole fiber to 2000 psi at 800 degree C

Pressure Response
at 800 degree C
Slow Axis
Fast Axis
Birefringence

(b)

Sensor Response (microstrain)
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300

Pressure (psi)
0 500 1000 1500 2000
Distributed Hydrogen Sensing

Sputtering Coating of Pd on fiber
Chemical Sensing: H2 sensing Case using FBG

FBG Wavelength Shift due to Pd Hydrogen Absorption

![Graph showing FBG wavelength shift due to Pd hydrogen absorption](image1)

Intensity (A.U.)

![Graph showing intensity vs. wavelength for original and 10% H2](image2)

Wavelength (nm)

![Graph showing FBG shift vs. H2 concentration](image3)

H2 Concentration (%)

![Graph showing percentage of hydrogen concentration over time](image4)
Distributed Chemical Sensing
Heating of on-fiber Pd Coating to Speed up sensor performance

![Graph showing temperature change with varying heating power density.]
Distributed Sensor Response (10% hydrogen)
Progress Update: Distributed Sensing

• Distributed Fiber Sensing **Beyond T and Strain Measurements**
  • Demonstration of distributed pressure sensing
  • Demonstration of distributed chemical sensing
  • Spatial resolution of 1-cm achieved
  • High temperature capability demonstrated at 800C
    • >1000C operation possible (depends on fiber)

• Further development
  • Improve distributed chemical measurement distance > 1 km
  • Enhance sensitivity and response time
  • Expand distributed measurement species
**Topic III: CARS Chemical Sensors**

- **Current State-of-the-Art**
  - Spontaneous Raman spectroscopy in hollow core fibers
  - Sensitivity enhancement by spatial confinement
  - Gas exchange hampers the response time and sensitivity ("residual gas issue")

- **Coherence Anti-Stokes Raman**
  - Enhance signal up to $10^5$
  - Reduce the length of hollow-core fiber from ~ meter to ~ cm
  - Single-beam CARS for easy optical measurement
  - Use of broadband ultrafast lasers for multi-gas measurement
Single Beam CARS

- Eliminate the need of alignment of multiple beams
- No need for accurate time-delay control
- Broadband spectrum provide wide range of available resonant energy levels.
- Single-shot multiplexible measurements
- Combine with hollow-core fiber spatial confinement for ultimate enhancement
Broadband Laser Development

- Ti:Sapphire laser
- Chirped mirror technology
- Laser Bandwidth 1100 cm$^{-1}$
- Pulse duration down to $\sim$10 fs
Experimental Setup

- Spatial light modulator pulse shaper
- Background-free detection
- PCF as gas cell
- Intended Gas: CO₂ and C₃H₈
Experimental Setup

Spontaneous Raman: $C_3H_8$

- Spontaneous Raman: 200-mW, 776-nm single wavelength, 10s integration.
- CARS: 20 mW (70 nm bandwidth, 0.3 s integration)
- Hollow core scheme see 150 time enhancement on CARS signal
Progress Update: Raman

• **CARS in hollow core fibers**
  • Successful development of custom ultrafast laser with wide bandwidth
  • Complete construction of gas sensing set up
  • Confirmed signal enhancement using CARS vs. spontaneous process
  • Confirmed CARS signal enhanced by hollow-core fibers

• **Further development (in this program)**
  • Optimization of phase match condition inside PCF
  • Complete all gas measurement (CO₂ and C₃H₈)
  • Data process