Progress Report
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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 (20-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
• Seven 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

Dr. Wang’s group at VT

CRC Canada
Technique: Chemical Regenerative Process

- Turn a $20 dollar commercially off-shelf fiber Bragg grating 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.

Miniaturized Furnace  | Control Software  | Sample Run
Process: Chemical Regenerative Process

Experimental Setup

- Atmosphere Pressure
- Fiber Recirculator
- High Temperature Sensor and Controller
- Testing Tube
- Regenerated FBG
- Furnace
- OSA

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
Regenerated Grating in Twin-hole Fiber

Regenerative FBG

Ultrafast Laser FBG

Simultaneous Measurement of T and P

\[
\left( \frac{\Delta \lambda_o}{\Delta \lambda_e} \right) = 1.532 \times 10^{-2} \Delta T + \left( \frac{2.521 \times 10^{-4} - 9.185 \times 10^{-8} \Delta T}{3.526 \times 10^{-4} - 1.232 \times 10^{-7} \Delta T} \right) \Delta P
\]

\[
\Delta \lambda_{o,e} = \lambda - 1545.25\text{nm}
\]

\[
\Delta T = T - 0^\circ C
\]

\[
\Delta P = P - 0\text{psi}
\]
Regenerated Grating in Twin-hole Fiber

Industry Collaborator: Lakeshore Crytronics
High-T Chemical Sensing

D-Shaped Fiber

SnO₂ Dip Coating

5ppm Ammonia Testing

- Oxide-coated FBG stable up to 800°C
- Metal Oxide Coating: TiO₂, SnO₂, ZnO₂
- Gas under tests: NH₃
- Testing Range: <1 ppm
- Oxide coating need optimization
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 adaptability.
- Air-hole microstructural fiber for multi-parameter measurement
- Functional coating on-fiber for chemical sensing with –cm resolution
Rayleigh Scattering and OFDR

**Rayleigh Scattering**

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

**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

Diagram:
- Rayleigh Scattering OFDR
- Tube Furnace
- Pressure
- FR
- PC
- POL
- PMFUT

Graph:
- Reflectivity (dB) vs Fiber Length (meter)
  - In-line Polarizer (forward direction)
  - Faraday Mirror
  - PM fiber forward direction
  - PM fiber backward direction
  - In-line Polarizer (backward direction)
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 vs. pressure for PM PCF (Fiber A) and 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

Fiber Length (mm)

Pressure Response (Microstrains)

Fast Axis
Slow Axis
800C region

Sensor Response (microstrain)

Pressure Response
at 800 degree C
- Slow Axis
- Fast Axis
- Birefringence

(b)
Distributed Hydrogen Sensing

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

FBG Wavelength Shift due to Pd Hydrogen Absorption

Intensity (A.U.) vs Wavelength (nm)

H2 Concentration (%) vs FBG shift ∆λ (nm)

Percentage of Hydrogen Concentration vs Time (hh:mm)
Distributed Chemical Sensing

- TLS
- OBR
- PD

Mixer

PSU

Fiber under Test

H₂

N₂

Pd coating

Cu coating

Pump

Rayleigh

Heating current
Heating of on-fiber Pd Coating to Speed up sensor performance
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 800°C
  • Demonstration of distributed flow sensing
  • Working on Chemical sensing (pH sensing).
  • >1000°C operation possible (depends on fiber)

• Further development
  • Improve distributed chemical/pressure/flow measurement distance > 1 km at high T
  • Enhance sensitivity and response time
  • Expand distributed measurement species
Metal Oxide Optical Sensor Development

- Integration of Metal Oxide with Sensor Platform
  - Nano-structural Engineering on functional metal oxide to control refractive index
    - Reduce $n$ from 2.2 to $\sim$1.45
  - Integration of functional metal oxide on high-T fiber sensor platform
  - 3D nano-fabrication of functional metal oxide.
  - Testing at high Temperature.
  - Development of distributed sensing scheme.
Metal Oxide Optical Sensor Development

- D-shape Fiber Sensor
Metal Oxide Optical Sensor Development

- D-shape Fiber Sensor
  - Evanescent field interact with metal oxide
  - SnO₂ metal oxide for NH₃ measurements
  - Metal oxide porosity control to reduce refractive index

\[ \varepsilon_r \quad \varepsilon \quad \varepsilon \]

\( m \quad i \quad e \quad ff \)

inhomogeneous medium \rightarrow effective medium

![Intensity Counts](image)

- Started Air
- Started Ammonia

![SEM Image](image)

- Initial Air Flow
- Started Ammonia

![Additional SEM Image](image)

- 20 \( \mu \)m scale
- 180 \( \mu \)m scale
Summary

- Success in high-T point sensor development
  - Greatly reduce the cost of high-T FBG sensor
  - Operation T > 800C
  - High T FBG sensor in air-hole microstructured fiber with superior performance
  - (Future) DFB fiber laser sensor for > 800C operation.

- **Extraordinary** success in distributed sensor development
  - First ever demonstration of distributed chemical sensor
  - First ever demonstration of distributed flow sensor
  - First ever demonstration of distributed pressure sensor for high temperature
  - (Future development for >10 km distributed measurement)

- Metal oxide integration (need more works)
  - Success in metal oxide porosity and index refraction control
  - Complete metal oxide fiber integration
  - Need to improve test results.