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

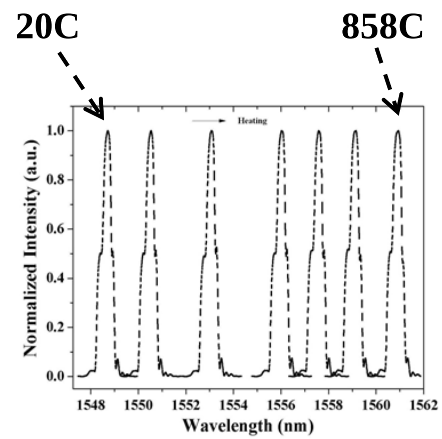
- University Coal Research Program
- Starting September 2010 (20-Months)
- Two Key Components:
  - Development of High-Temperature Sensor Platforms
  - Integration and Application of Functional Metal Oxide for Gas Sensing
- Three fiber sensor platform techniques
- Seven journal publications
- Two industrial collaborations

Research Overview

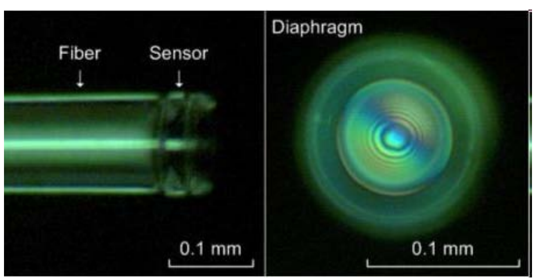
- **Point fiber sensor for high-T**
  - High performance high-T FBG point sensor (>800C) at $20/sensor
  - Chemical regenerative process
  - Integration with SnO_2 on D-Shaped fiber for NH_3 sensing
- **Distributed fiber chemical sensor**
  - First-ever demonstration of distributed fiber chemical sensing
  - Rayleigh-scattering OFDR technique
  - 1-cm spatial resolution
  - Integration with Pd/PdH for H_2 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 CO_2 and C_2H_6 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**

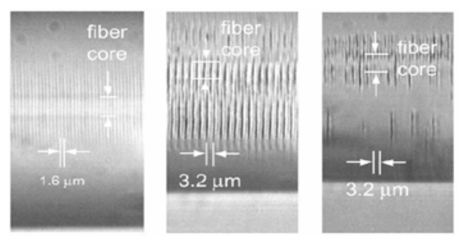


F-P Sensor



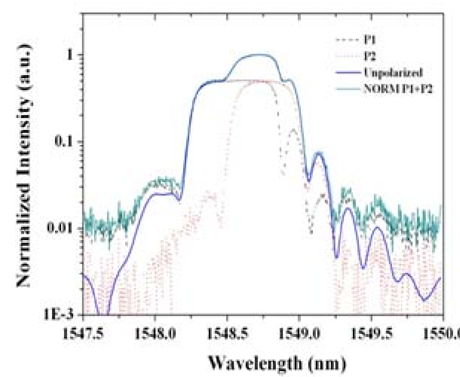
Dr. Wang's group at VT

Type II FBG



Type I IR 125 fs grating	Type II IR 125 fs grating	Type II IR 1.6 ps grating

CRC Canada



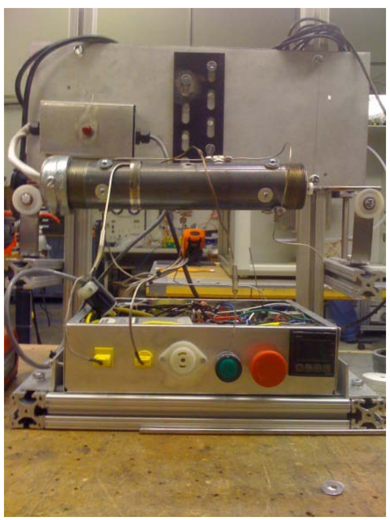
Technique: Chemical Regenerative Process

- 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 <u>no longer needed!</u>
    - Cost of high-T sensors could come down drastically!
    - Parameters that sensor can measure drastically expanded (due to the air-hole microstructural fibers.

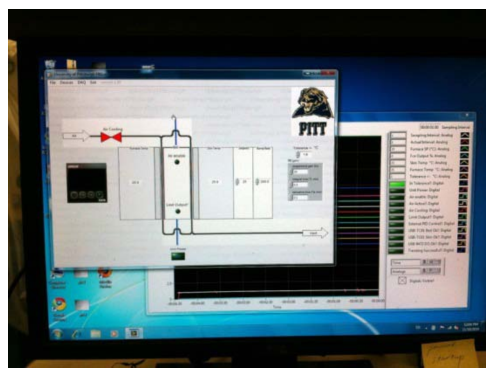
Process: Chemical Regenerative Process

- 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.

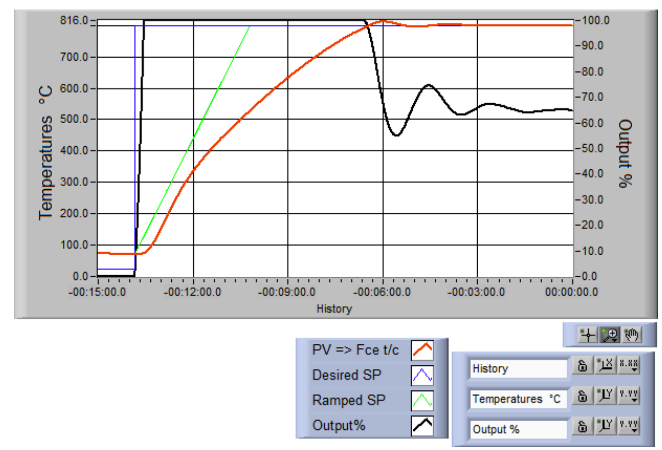
Miniaturized Furnace



Control Software

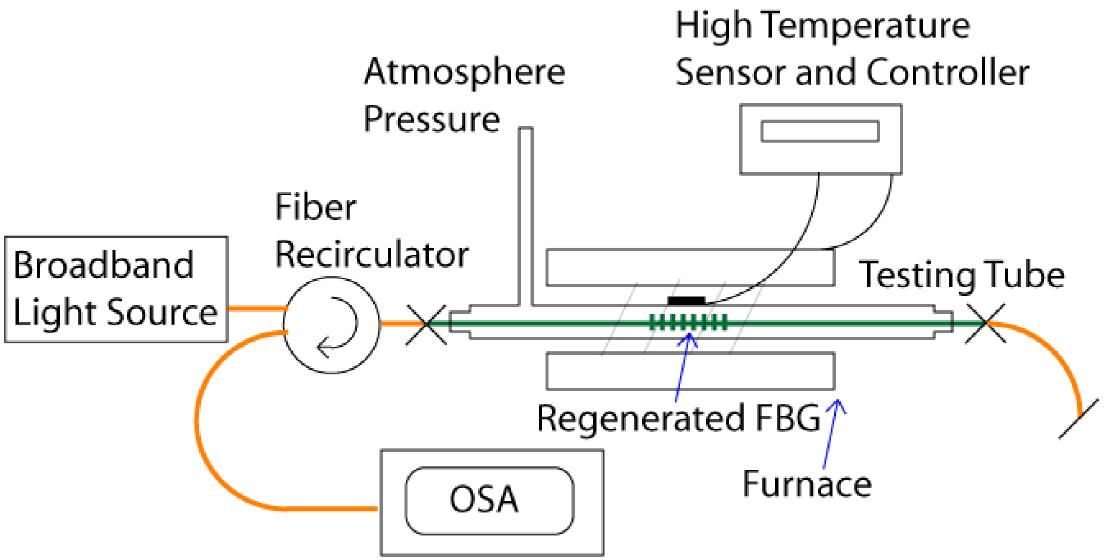


Sample Run

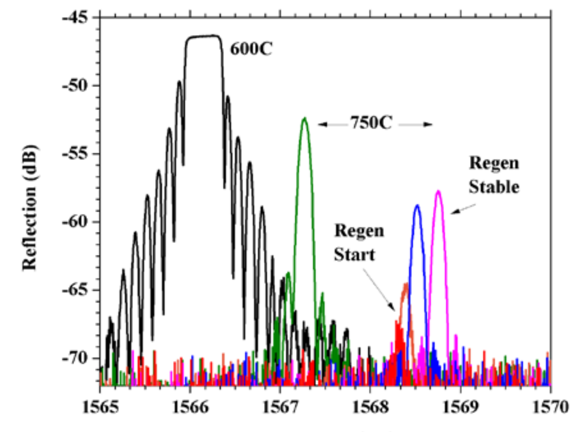


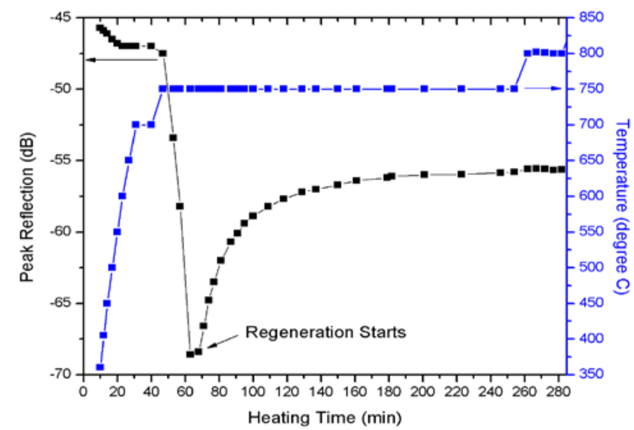
Process: Chemical Regenerative Process

Experimental Setup

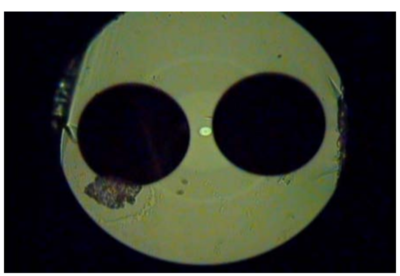


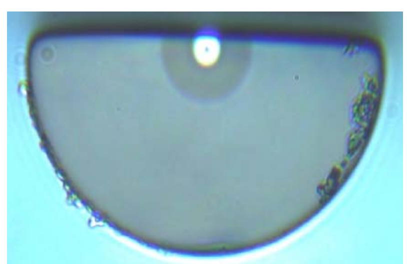
Typical Regenerative Process





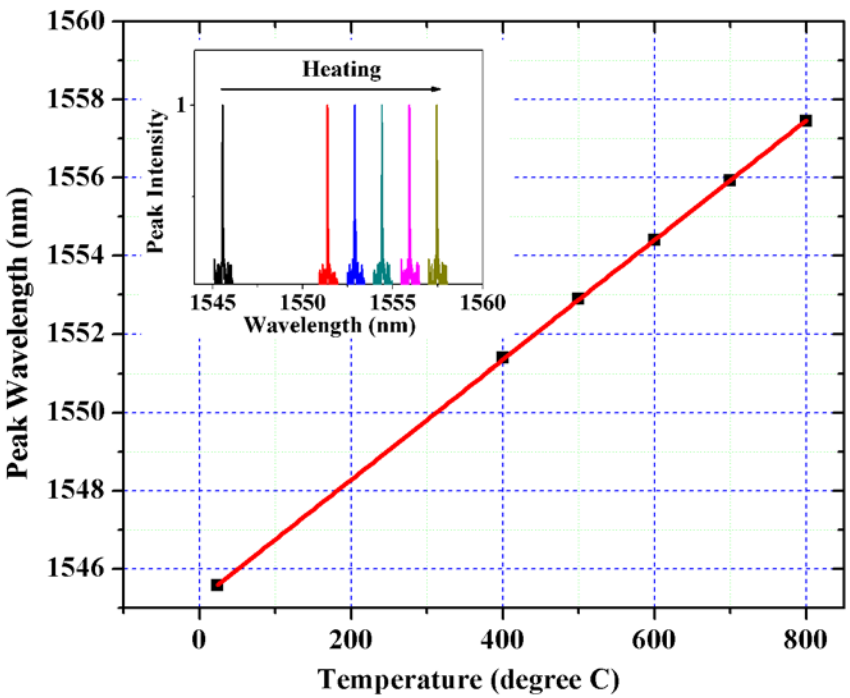
Fibers Used for this work



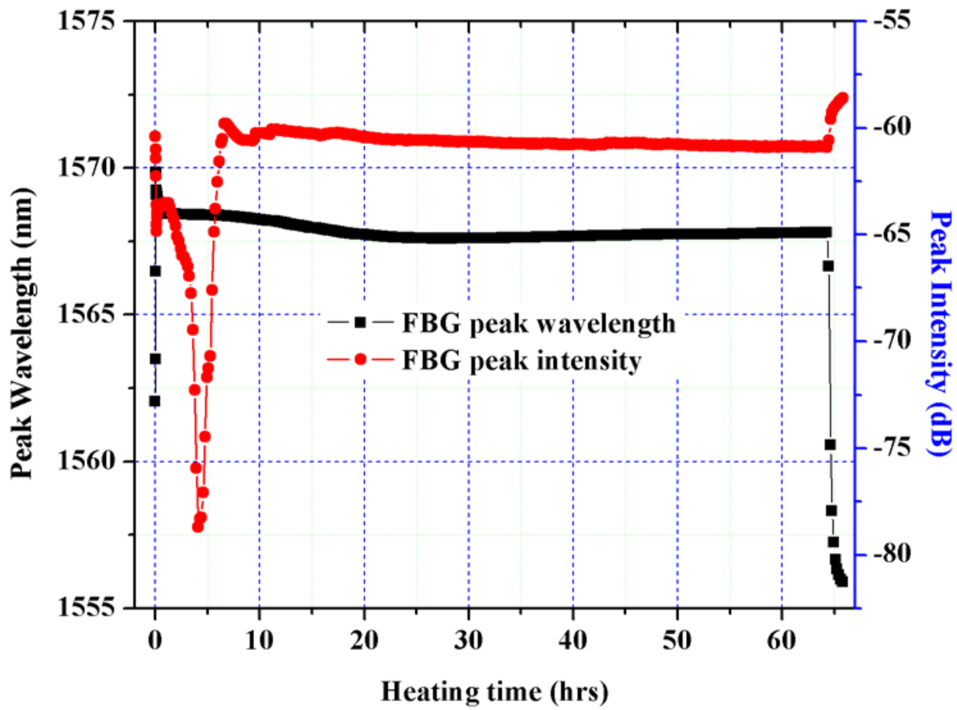


Regenerated Grating in Twin-hole Fiber

Temperature Cycles



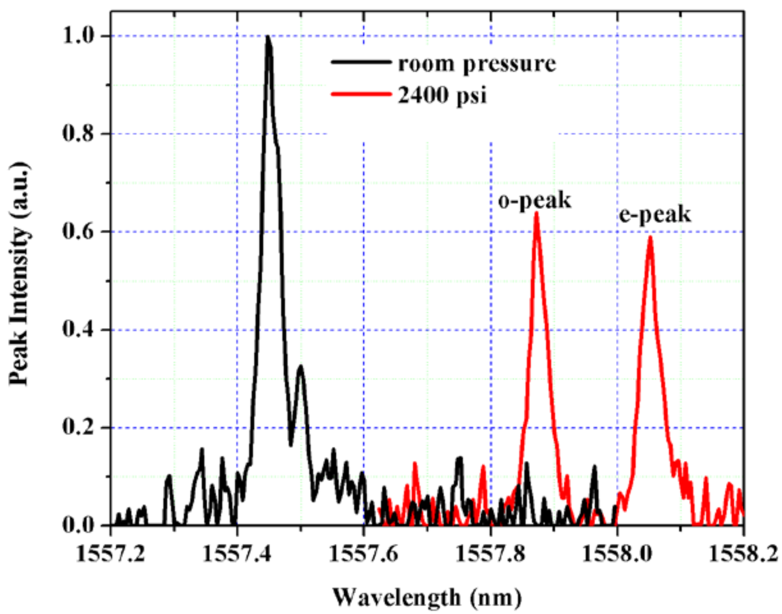
Stability Testing

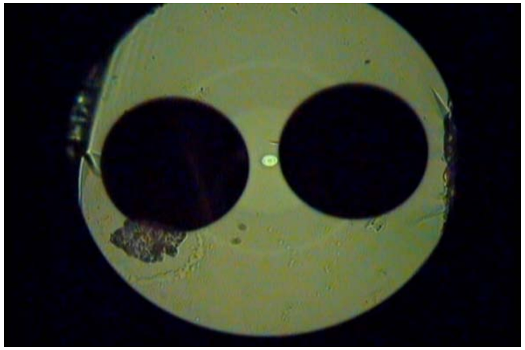


High-T Thermal Drift: 0.013 K/hour (Best case)
0.045 K/hour (Worse)

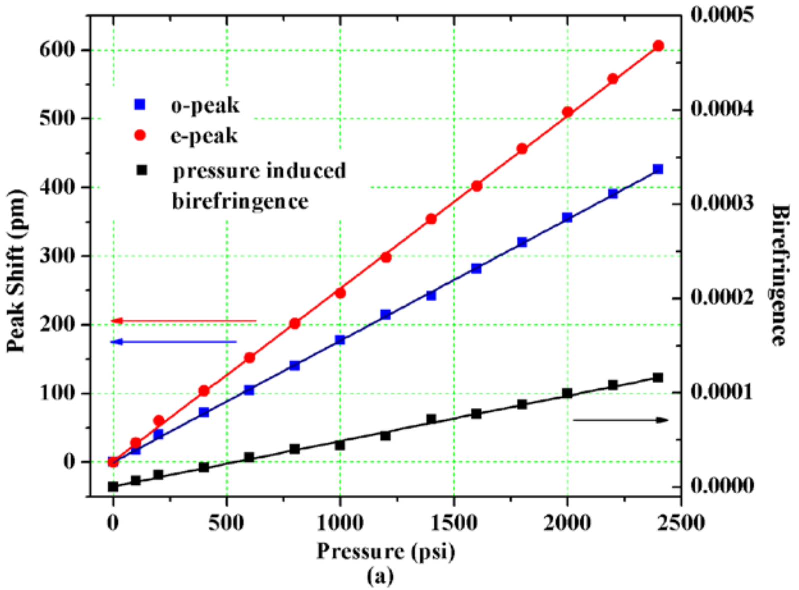
Regenerated Grating in Twin-hole Fiber

Pressure Test

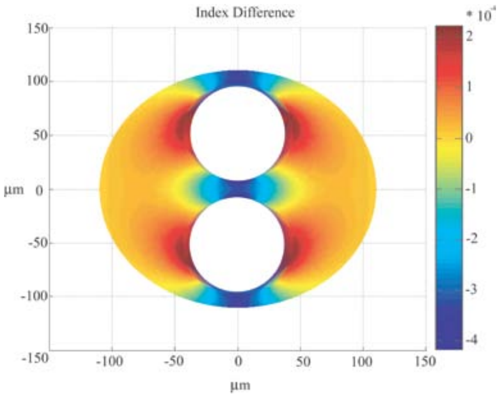




Pressure Testing

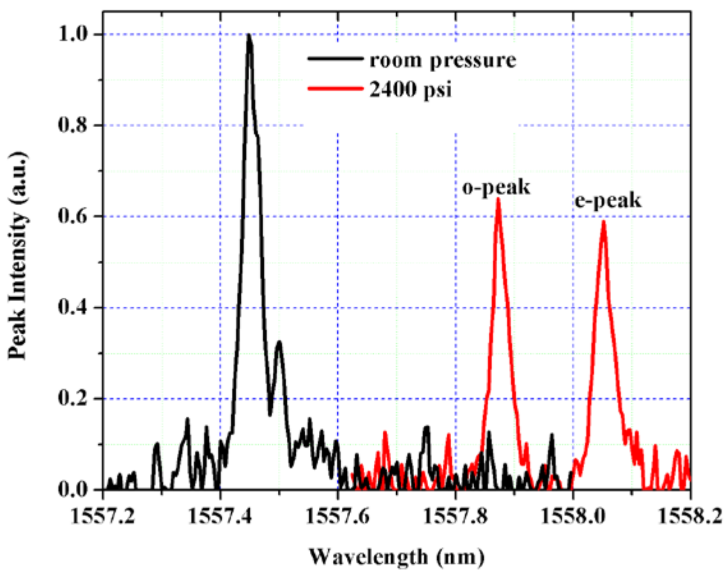


FEA Simulation

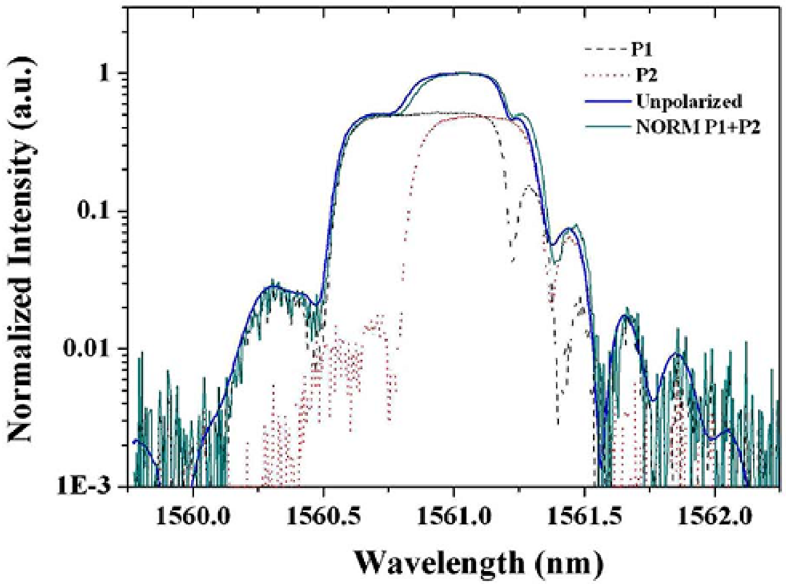


Regenerated Grating in Twin-hole Fiber

Regenerative FBG



Ultrafast Laser FBG



Simultaneous Measurement of T and P

$$\begin{pmatrix} \Delta\lambda_o \\ \Delta\lambda_e \end{pmatrix} = 1.532 \times 10^{-2} \Delta T + \begin{pmatrix} 2.521 \times 10^{-4} - 9.185 \times 10^{-8} \Delta T \\ 3.526 \times 10^{-4} - 1.232 \times 10^{-7} \Delta T \end{pmatrix} \Delta P$$

$$\Delta\lambda_{o,e} = \lambda - 1545.25nm$$

$$\Delta T = T - 0°C$$

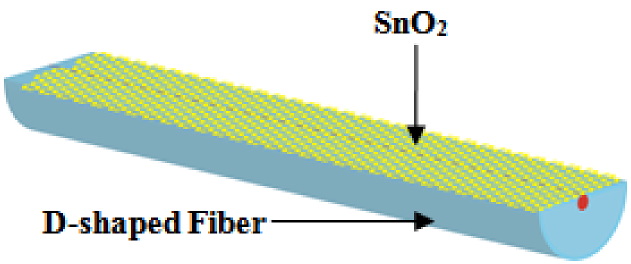
$$\Delta P = P - 0psi$$

Regenerated Grating in Twin-hole Fiber

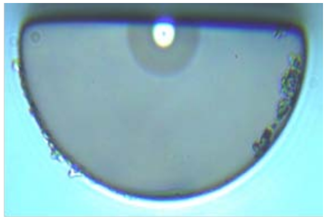
Industry Collaborator: Lakeshore Crytronics

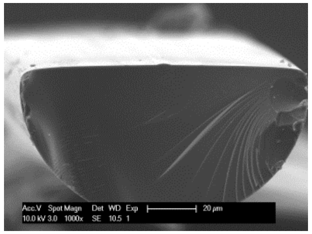
High-T Chemical Sensing

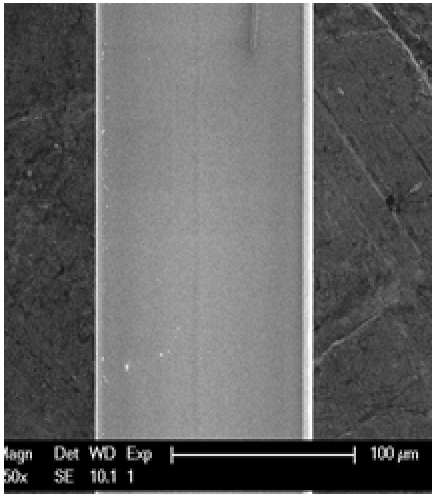
D-Shaped Fiber



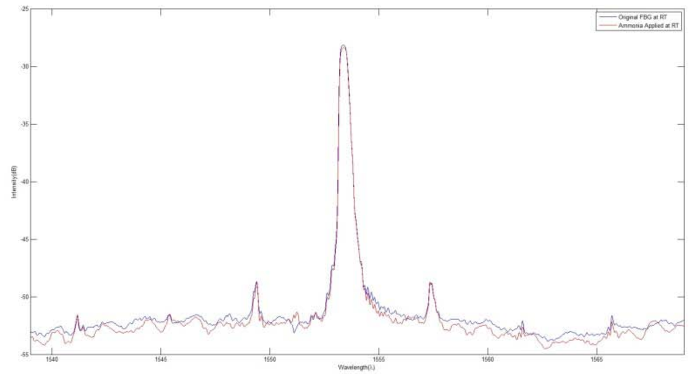
SnO_2 Dip Coating







5ppm Ammonia Testing



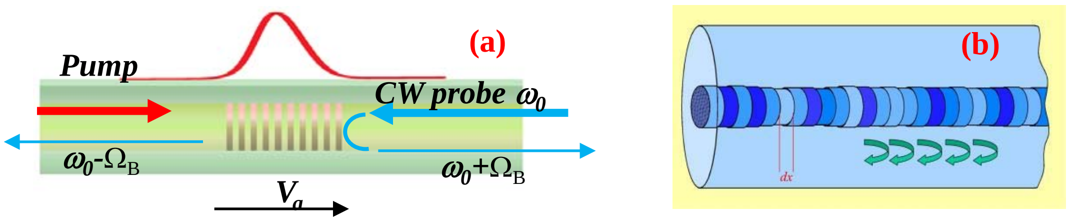
- Oxide-coated FBG stable up to 800C
- Metal Oxide Coating: TiO_2, SnO_2, ZnO_2
- Gas under tests: NH_3
- Testing Range: <1 ppm
- Oxide coating need optimization

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
  - SnO_2, TiO_2, and ZnO_2
  - Integration with D-shaped fiber
  - Coated FBG successfully regenerated at 700C
- Fiber sensor testing
  - NH_3, NO_x
  - 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 (0.1C and 1 με)
    - Long distance (up to km)
  - Rayleigh Scattering – OFDR
    - mm- resolution
    - Limited to Temperature and Strain measurement (0.1C and 1 με)
    - ~100 meter distance



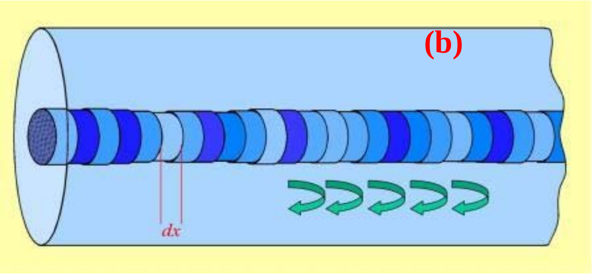
Schematic illustration of Brillouin scattering and (b) Rayleigh scattering.

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



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

OFDR Scheme

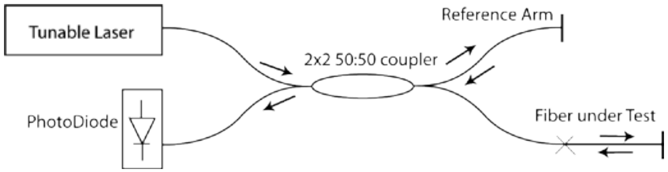
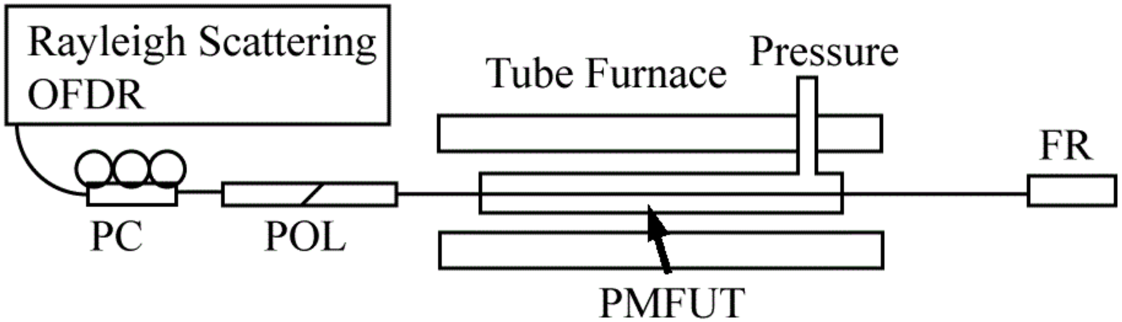
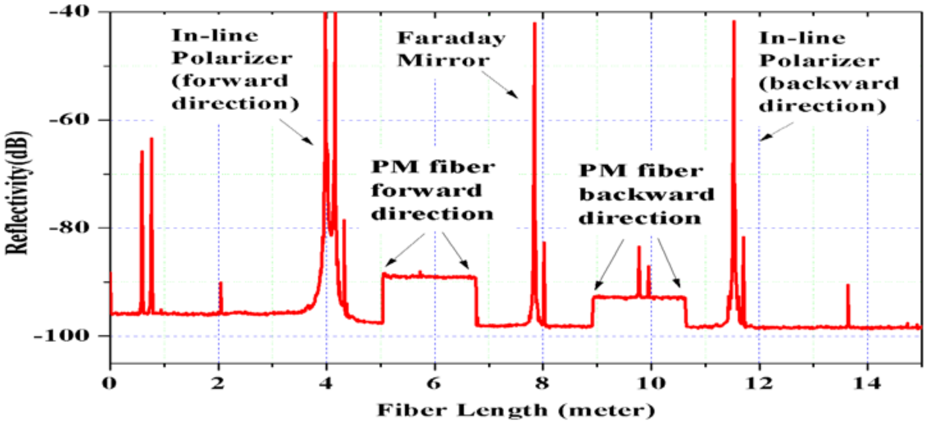


Fig. 3: Schematic sketch illustration of the OFDR operation principle [20].

- ✓ **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**
- o **Cost, Response Time, Cross Talk**

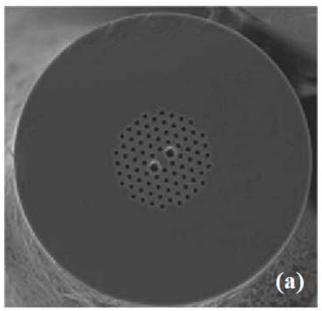
Distributed Pressure Measurement

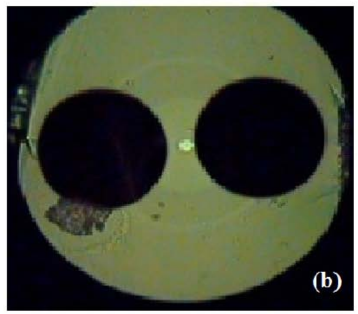


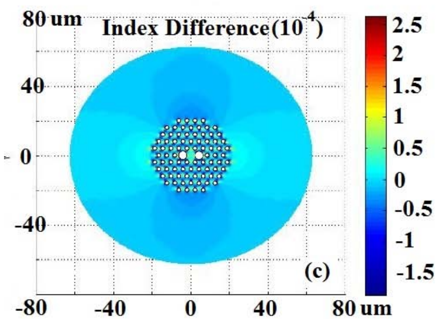


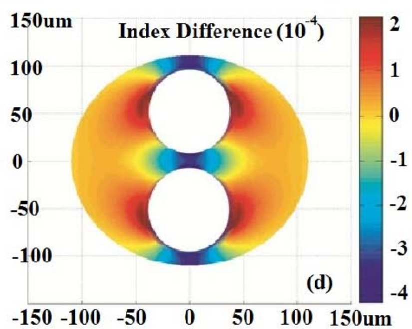
OFDR Measurement Results
Two-Hole Fibers: 2000 psi

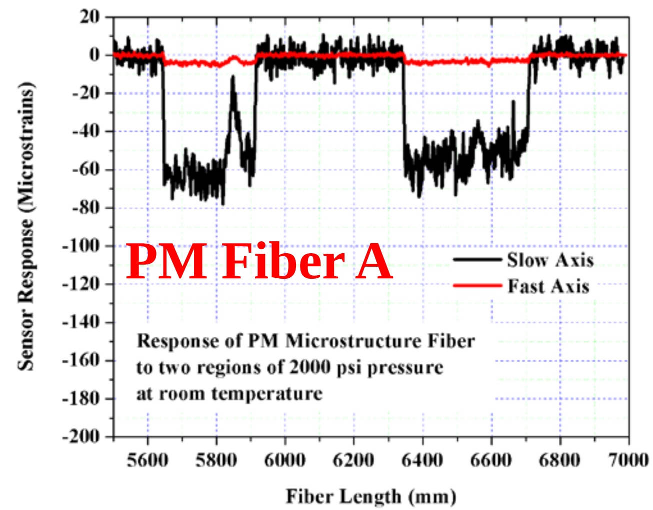
PM Fiber A **Two-Hole Fiber B**

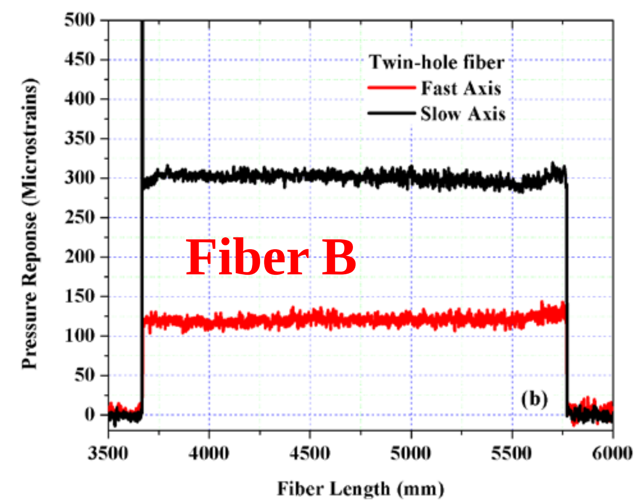




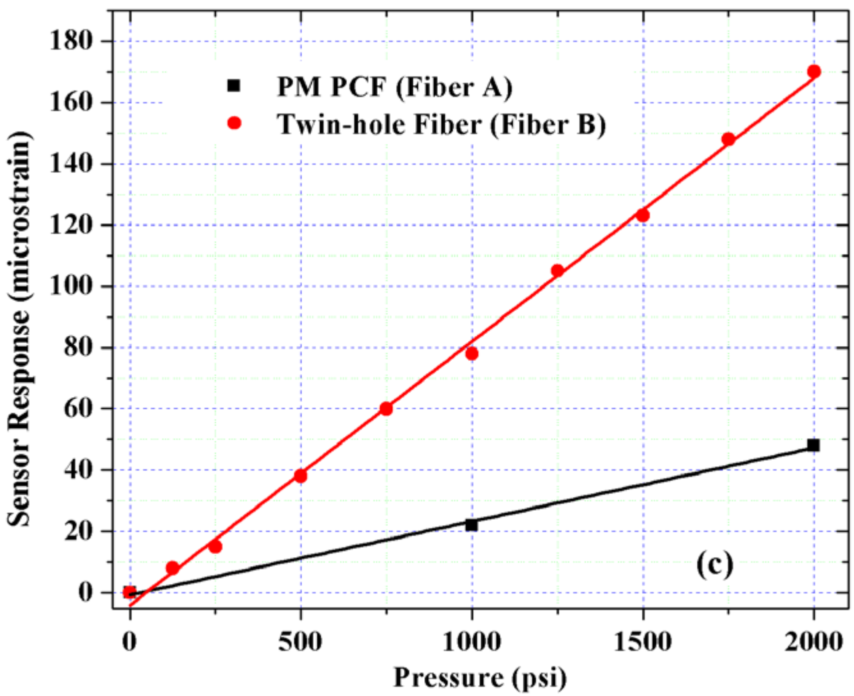




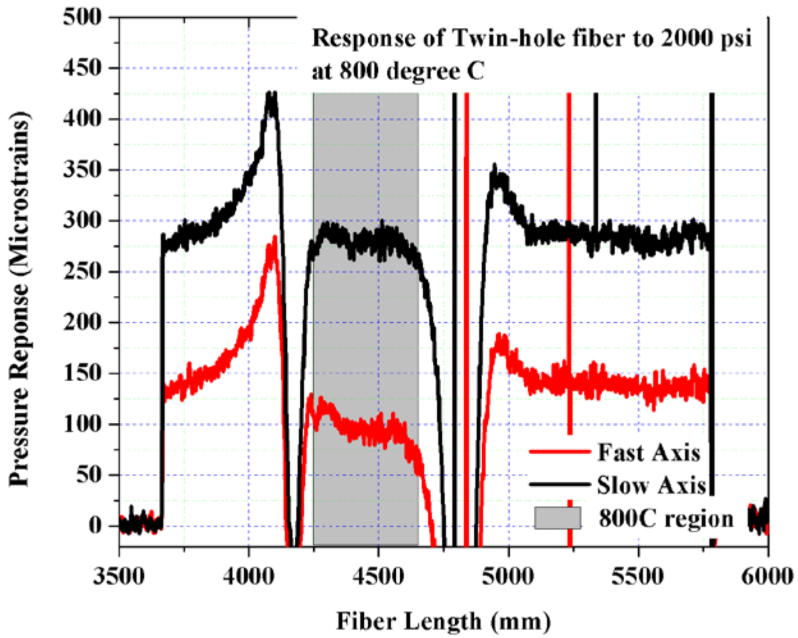


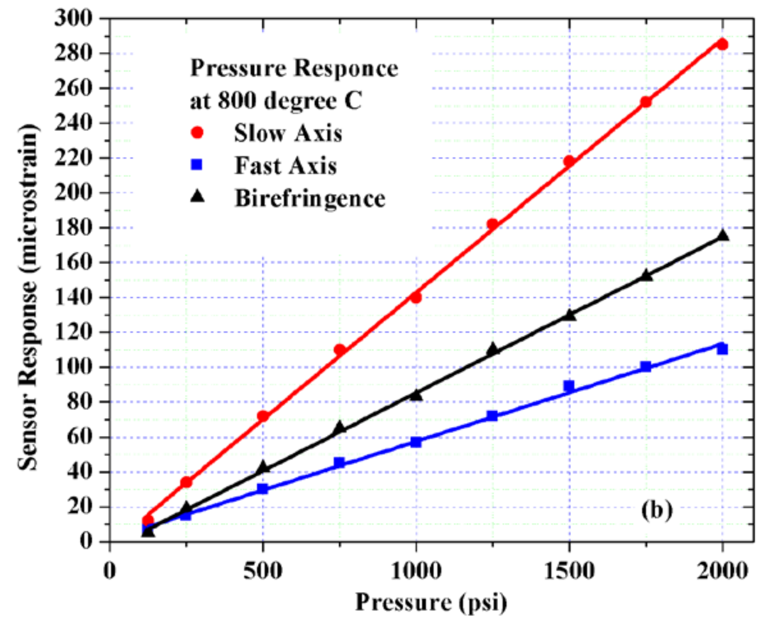


OFDR Measurement Results
Room Temperature



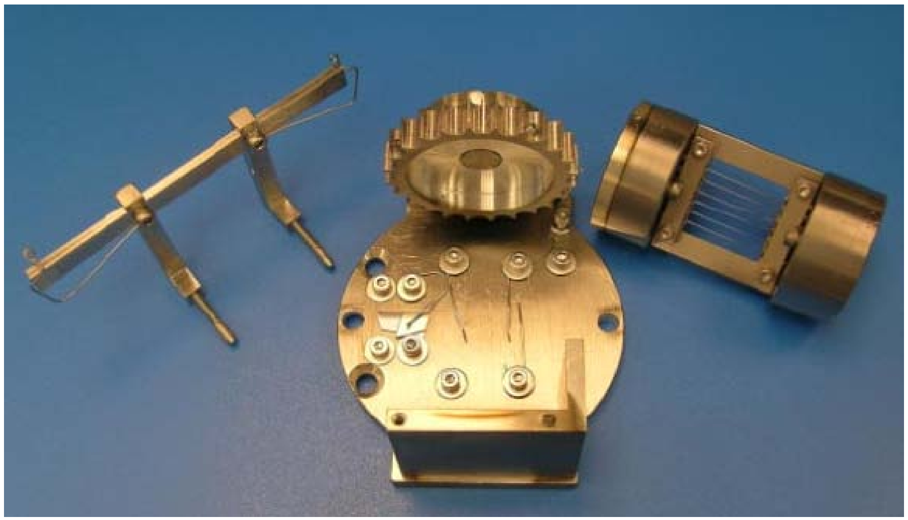
OFDR Measurement Results Two-Hole Fibers at 800C

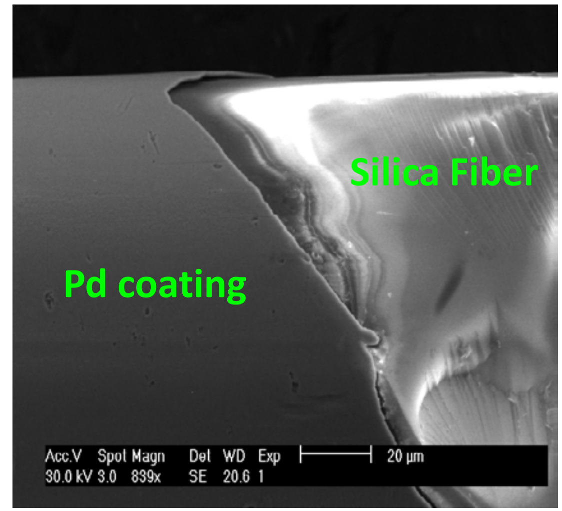


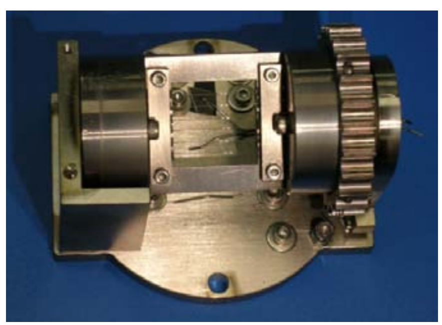


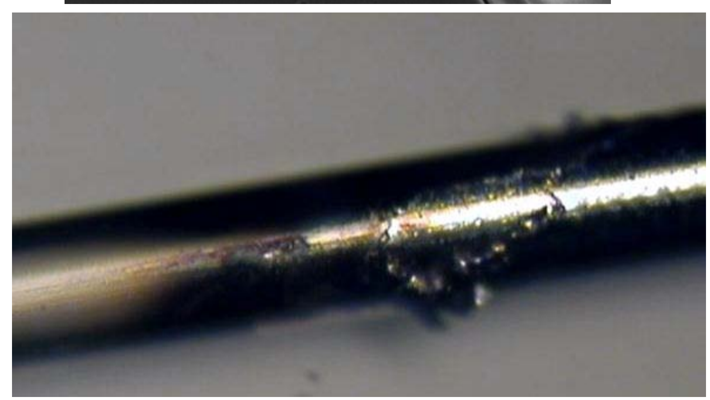
Distributed Hydrogen Sensing

Sputtering Coating of Pd on fiber

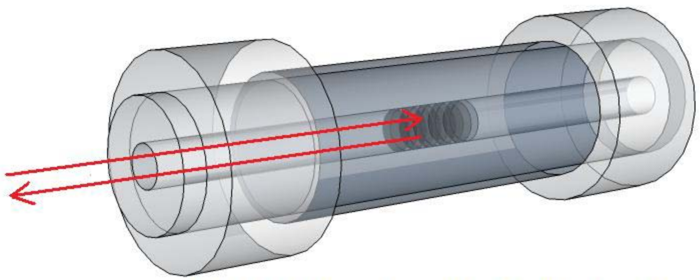




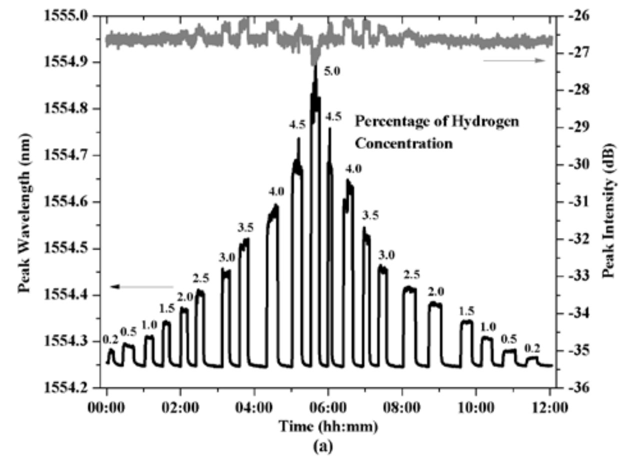


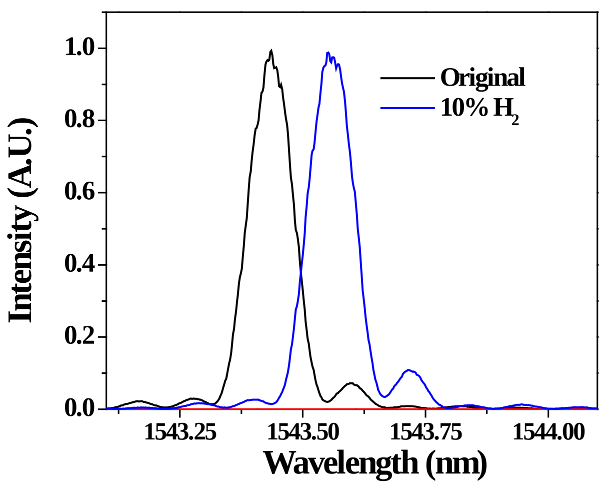


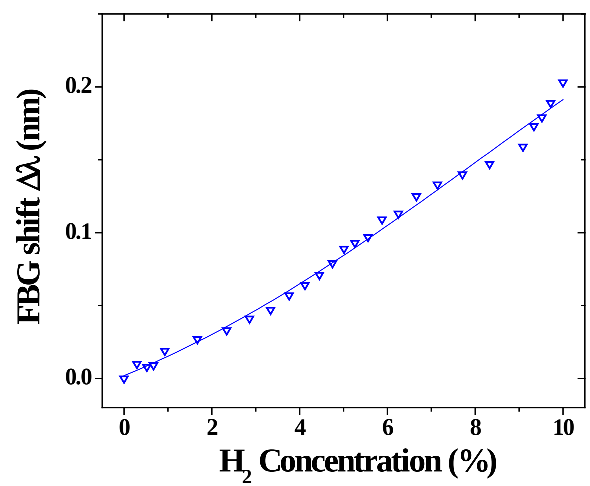
Chemical Sensing: H2 sensing Case using FBG



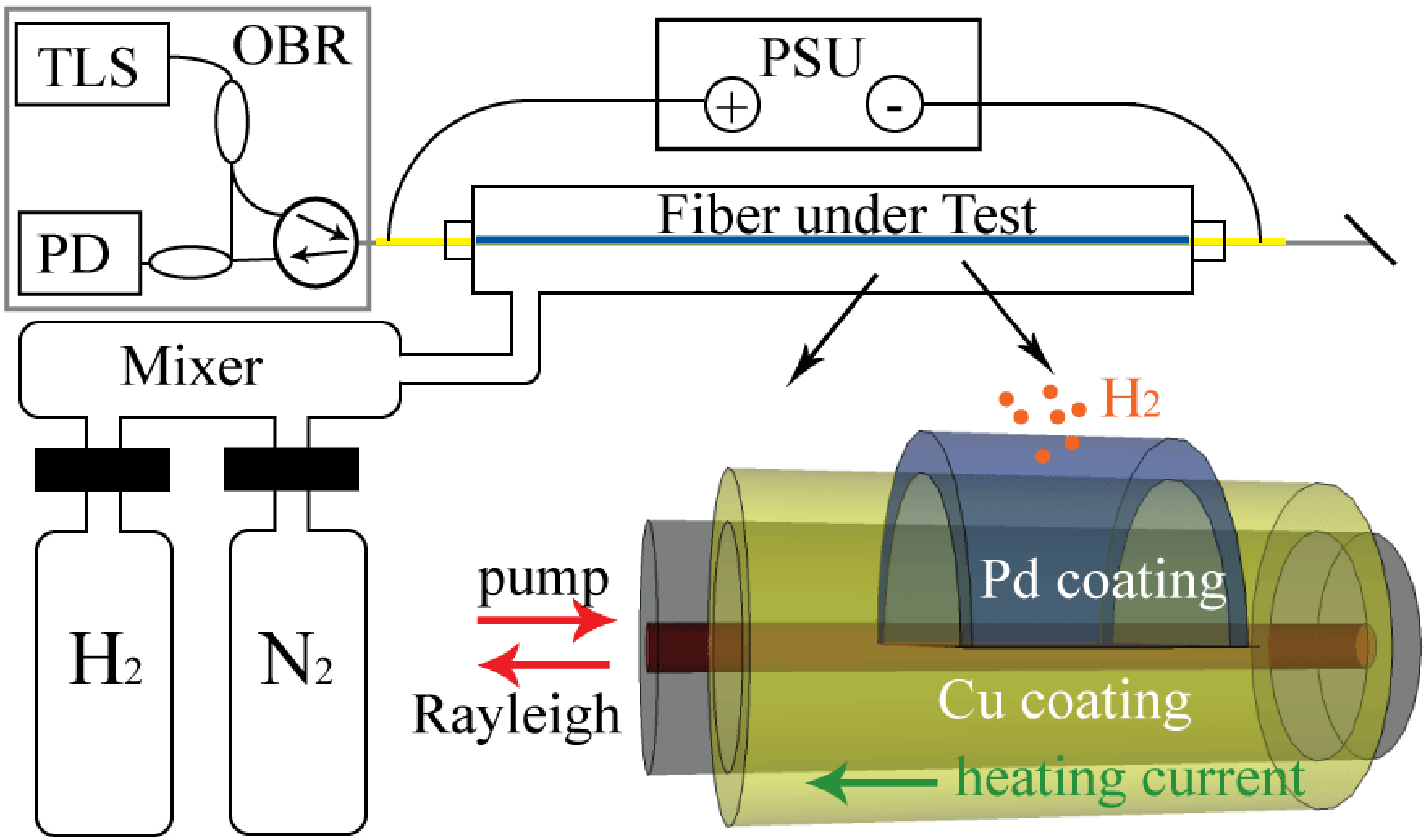
FBG Wavelength Shift due to Pd Hydrogen Absorption



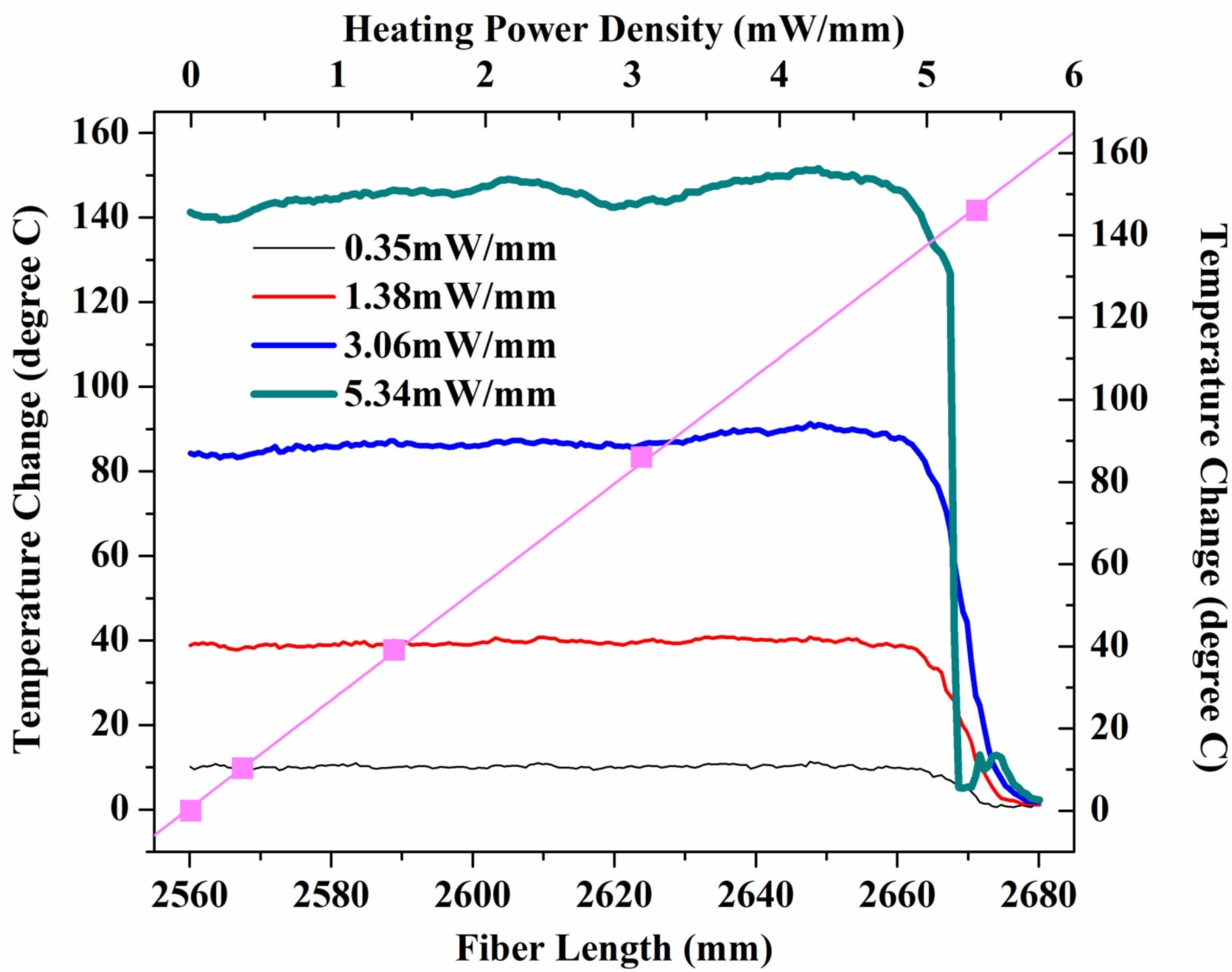




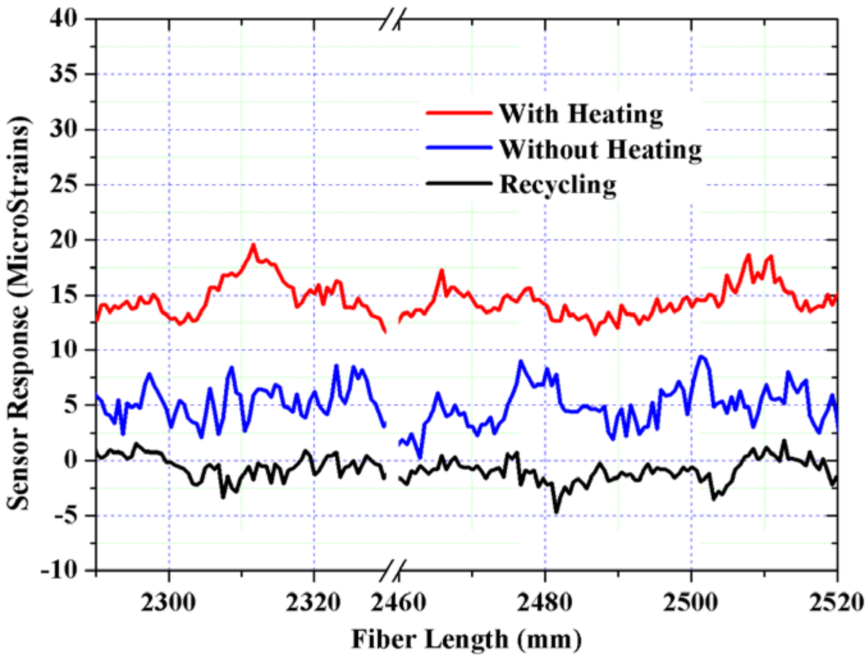
Distributed Chemical Sensing

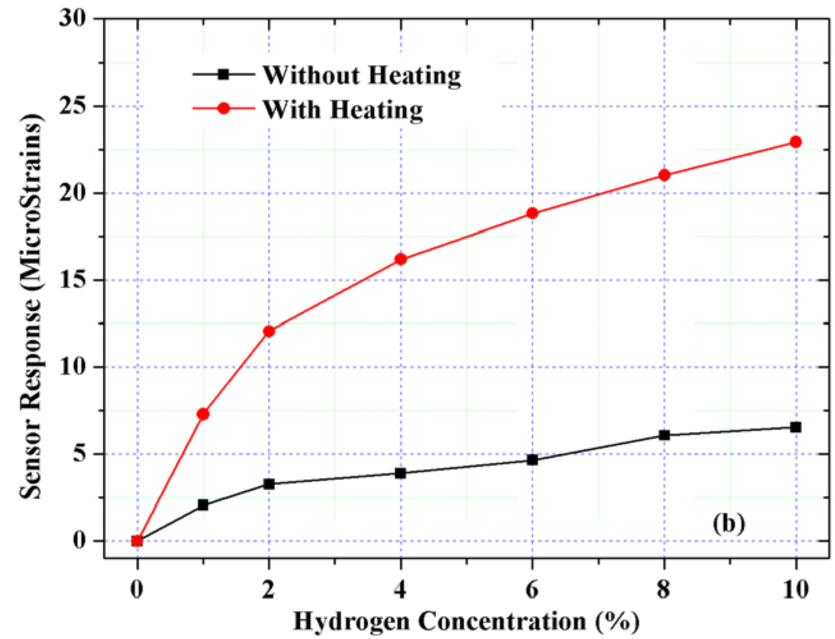


Heating of on-fiber Pd Coating to Speed up sensor performance



Distributed Sensor Response (10% hydrogen)



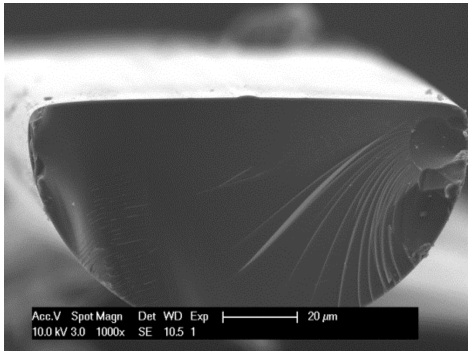


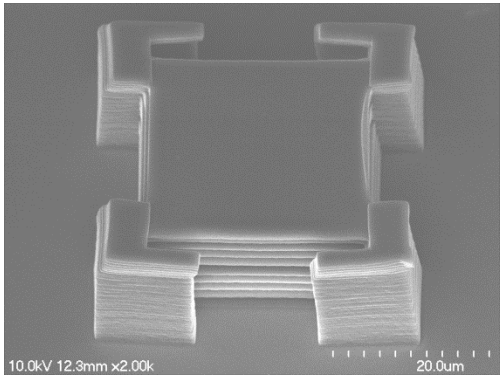
Progress Update: Distributed Sensing

- 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 800C
  - Demonstration of distributed flow sensing
  - Working on Chemical sensing (pH sensing).
  - >1000C 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

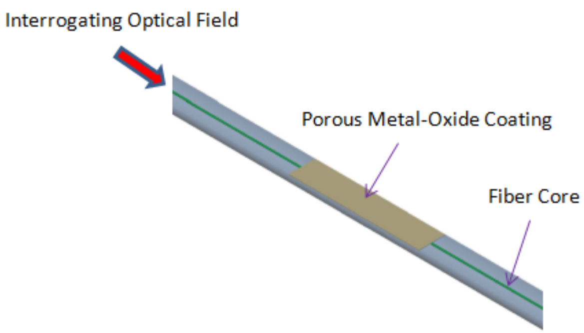
- Integration of Metal Oxide with Sensor Platform
  - Nano-structural Engineering on functional metal oxide to control refractive index
    - Reduce n from 2.2 to ~1.45
  - Integration of functional metal oxide on high-T fiber sensor platform
  - 3D nano-fabrication of functional metal oxide.
  - Testing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

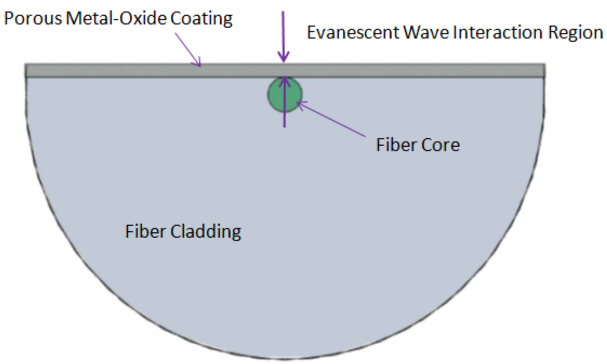


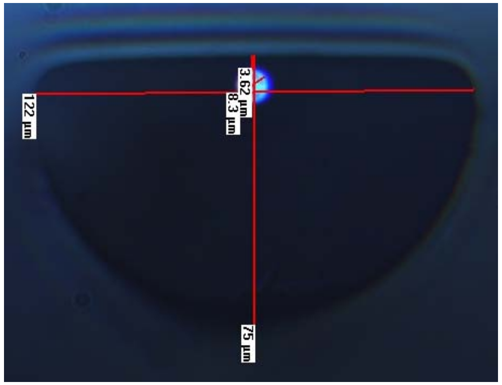


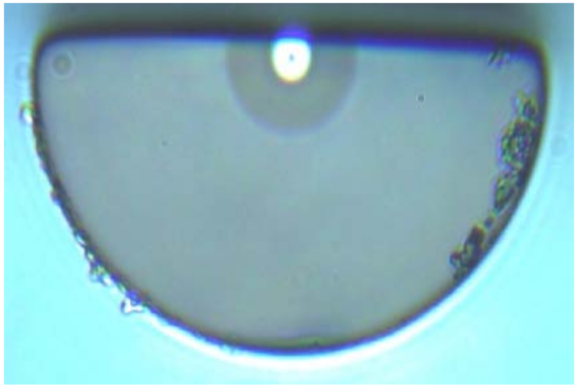
Metal Oxide Optical Sensor Development

- D-shape Fiber Sensor



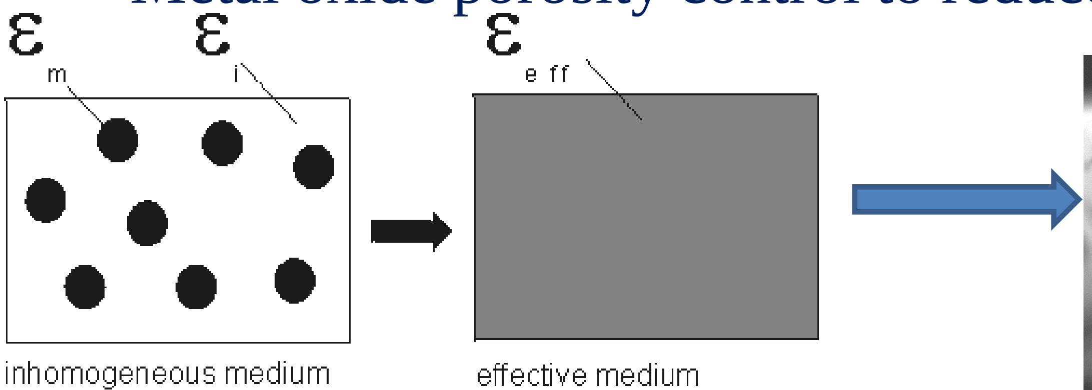


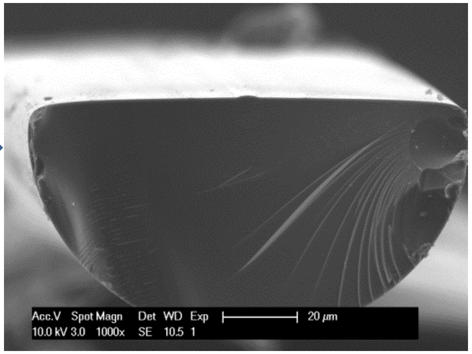


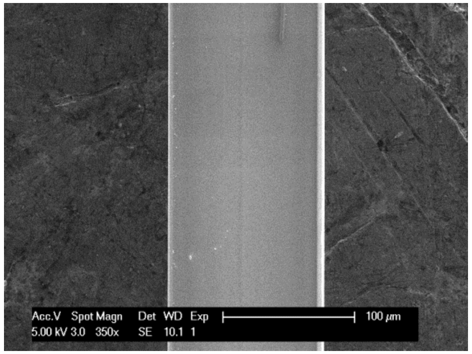


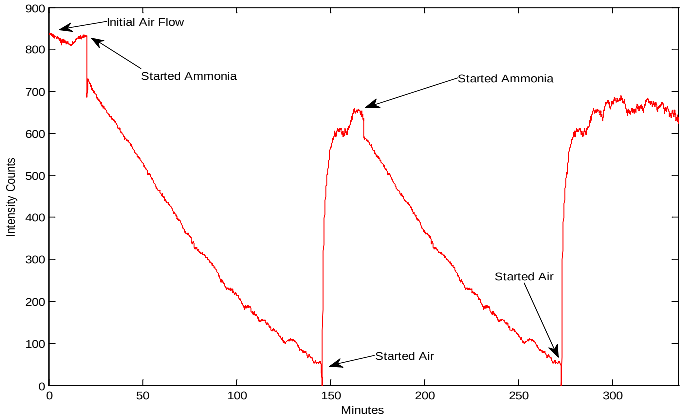
Metal Oxide Optical Sensor Development

- D-shape Fiber Sensor
  - Evanescent field interact with metal oxide
  - SnO_2 metal oxide for NH_3 measurements
  - Metal oxide porosity control to reduce refractive index









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.