Annual 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

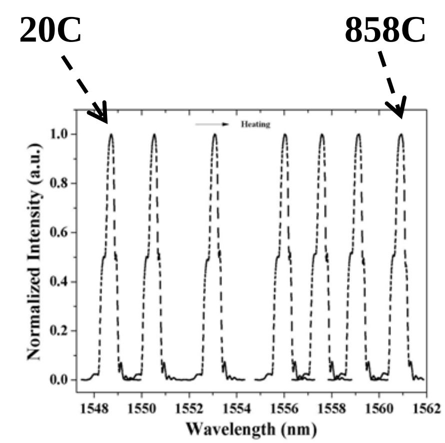
- University Coal Research Program
- Starting September 2010
- Two Key Components:
  - Development of High-Temperature Sensor Platforms
  - Integration of Functional Metal Oxide Nano-Materials for Gas Sensing
- Two fiber sensor platform techniques
- Twelve journal publications
- One pending patent
- Two industrial collaborations

Research Overview

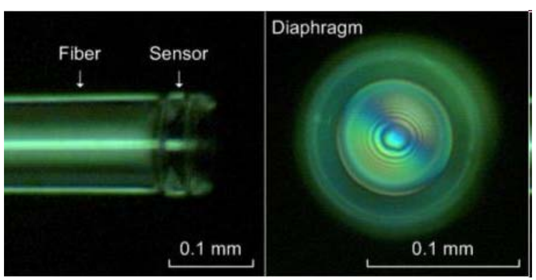
- **Point fiber sensor for high-T**
  - High performance high-T fiber Bragg grating point sensor (1200^{o}C) at $20/sensor
  - Chemical regenerative process
  - Single-mode fiber laser sensors rated at 750^{o}C
- **Distributed fiber chemical sensors**
  - First-ever demonstration of distributed fiber chemical sensing
  - Rayleigh-scattering OFDR technique
  - 1-cm spatial resolution
  - Integration with Pd/PdH for H_2 sensing
- **Functional Metal Oxide Nanomaterials**
  - Engineering porosity to control refractive index for on-fiber integration
  - Integration with high-T fiber sensors
  - Real-time characterization of refractive index change/Optical loss
  - NH_3 measurements

Topic I: Fiber Point Sensor for high-T

- Current State of the Art
  - F-P interferometer on the sapphire fiber tip
  - Fiber Bragg grating in single-mode fiber by the ultrafast laser fabrication
- Challenge
  - Packaging is key (Expensive and difficult)
  - Multi-mode fiber (No cladding)
  - Poor spectral performance
  - **Expensive**

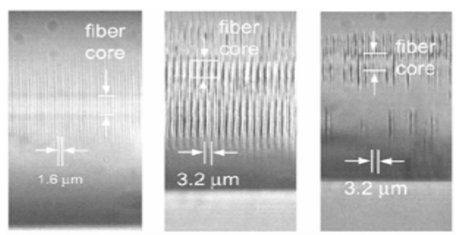


F-P Sensor



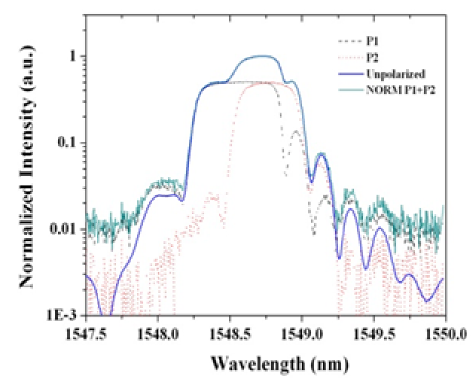
Dr. Wang's group at VT

Type II FBG



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

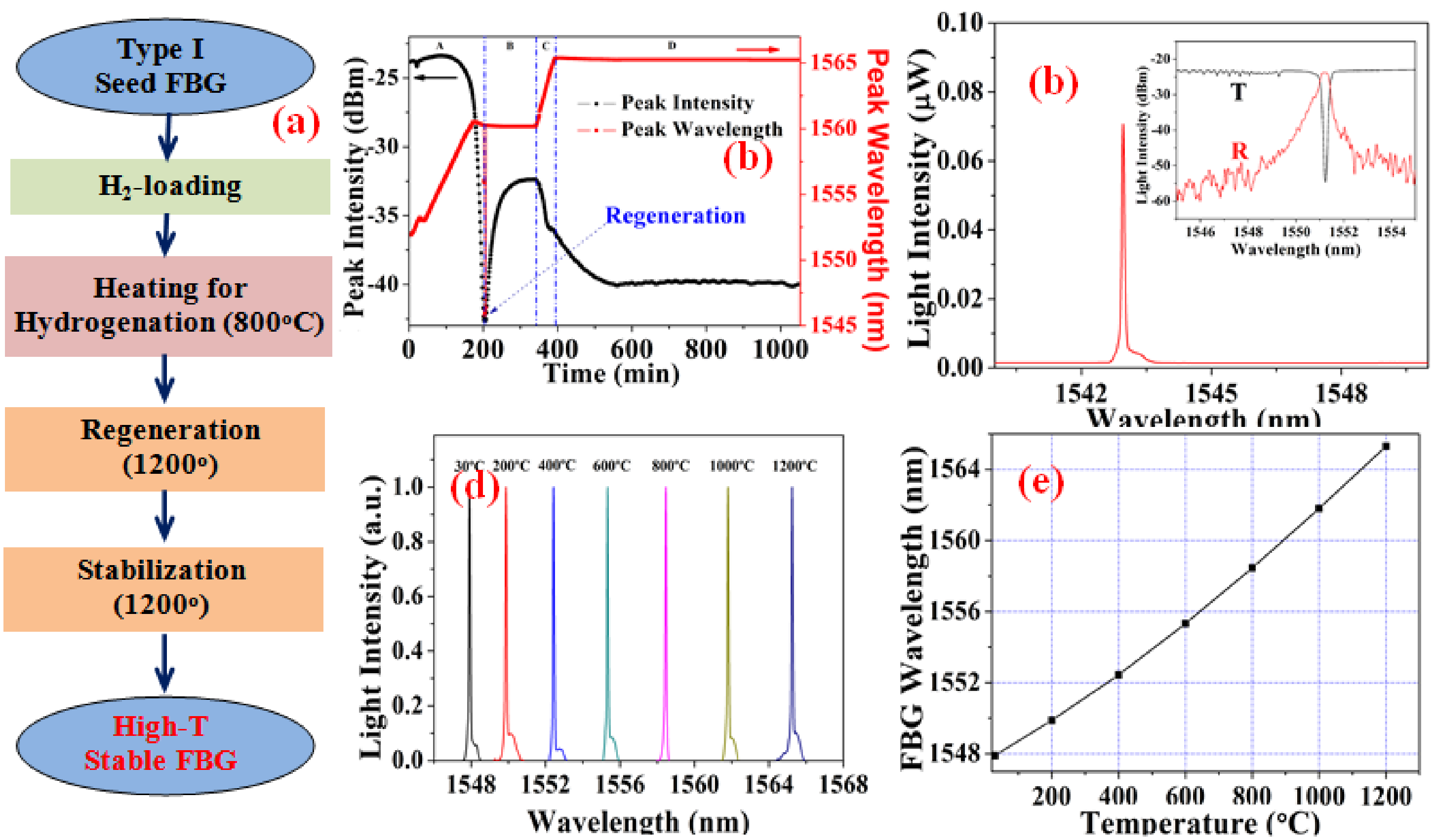
CRC Canada



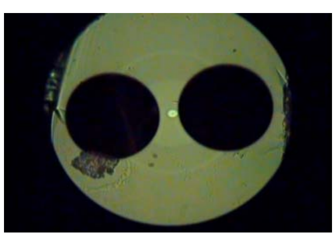
Technique: Chemical Regenerative Process

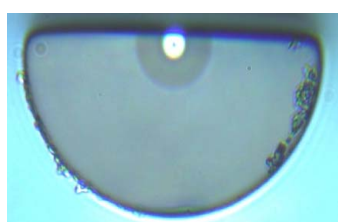
- Turn a $20 dollar commercially off-shelf fiber Bragg grating into a high-temperature sensors beyond 1000^{o}C.
- **Extended this fabrication process to air-hole microstructural fibers (multi-functional measurements), active fibers (lasers), and high attenuation fibers (active sensors).**
- **Expand 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 wide applicability).

FBG Sensor in Silica Fiber Rated at 1200°C



Fibers Used for this work



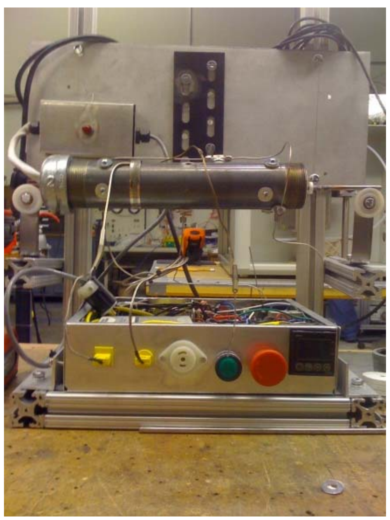


- Air-hole fibers.
- D-shape fibers.
- Active fibers for lasers
- High-attenuation fibers for active sensing

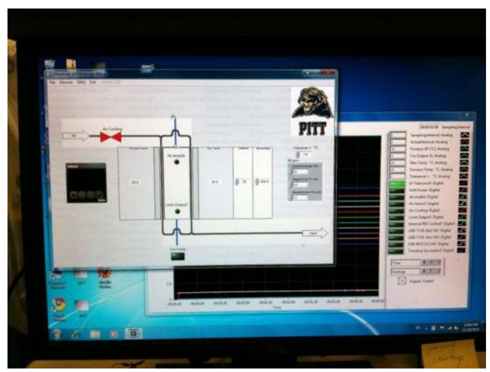
Process: Chemical Regenerative Process

- 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.

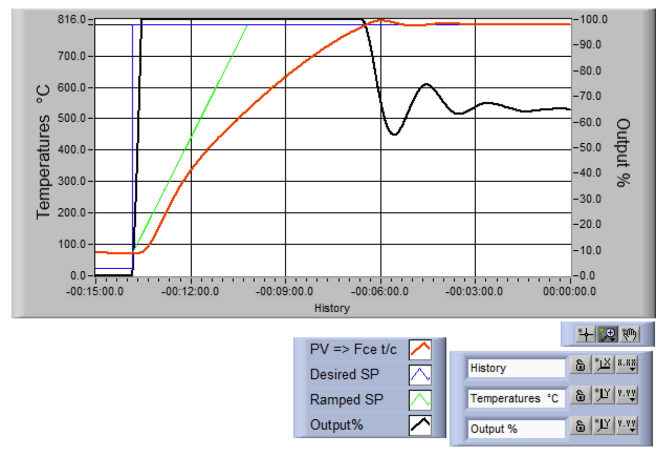
Miniaturized Furnace



Control Software

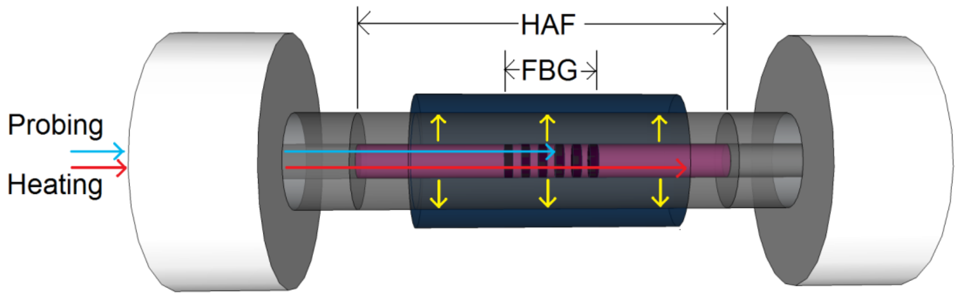


Sample Run



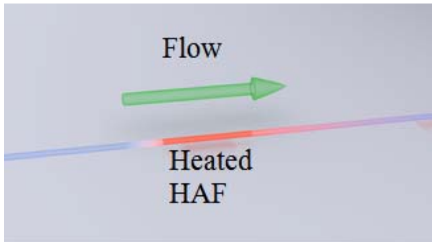
Application I: Optical Flow Sensors at 1000^{o}C

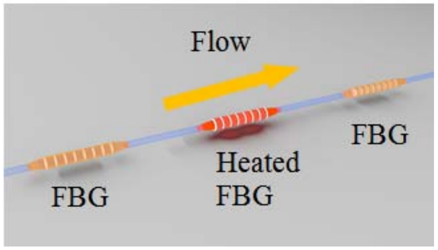
High-Attenuation Fiber



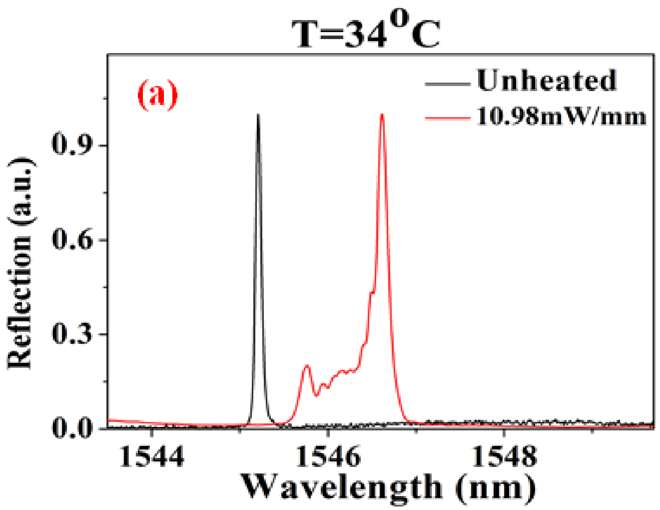
- Co-doped core to absorb guided laser light.
- Attenuation 0.1-1 dB/cm
- **Application: multiplexible flow sensors**

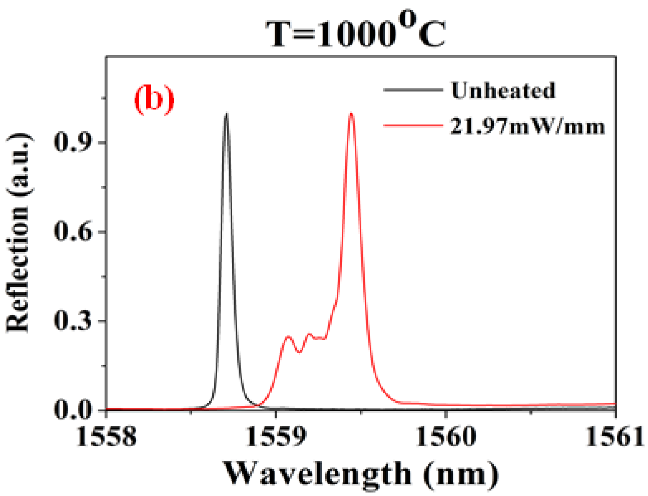
Fiber Optical Flow Sensors





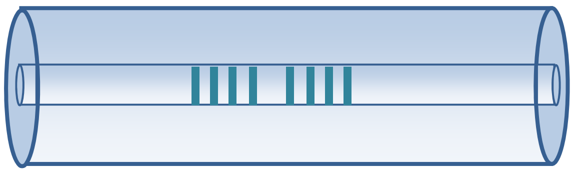
Optical Heating at 1000^{o}C

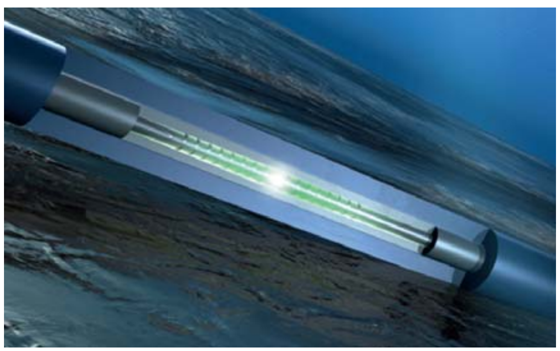




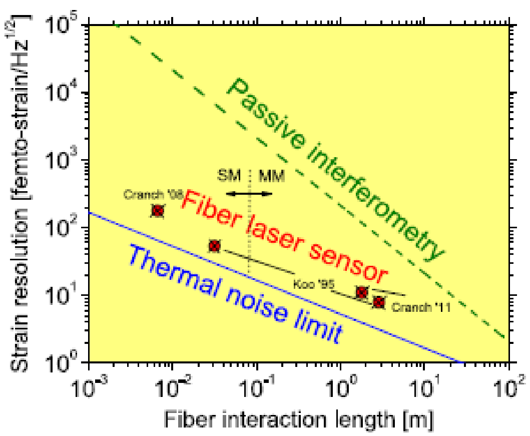
Fiber Laser Operated at 750ºC

High-T FBG in Er-doped Fibers

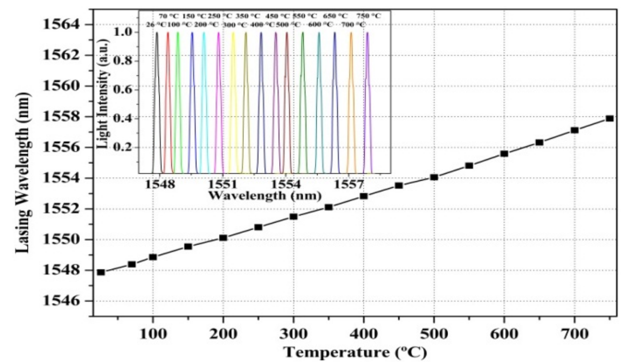




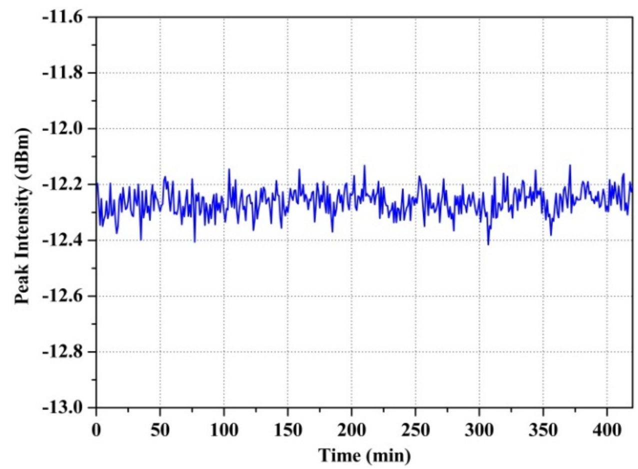
- Fiber laser with highest operation temperature.
- >10,000 better sensitivity than passive FBG sensors



Lasing Performance (750ºC)



Stability (~1%)



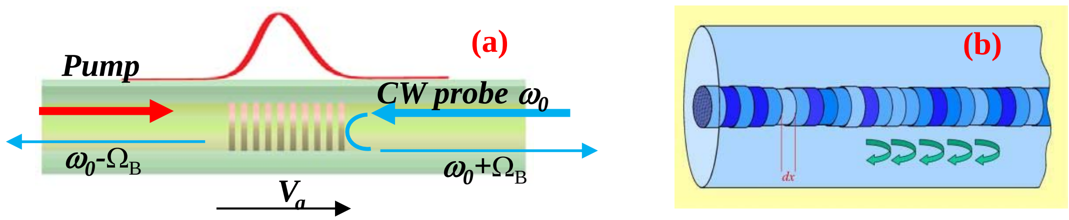
Miller, Gary A., Geoffrey A. Cranch, and Clay K. Kirkendall. "High-Performance Sensing Using Fiber Lasers." *Optics and Photonics News* 23.2 (2012): 30-36.

Regenerated Grating in Twin-hole Fiber

Industry Collaborator: Lakeshore Crytronics

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



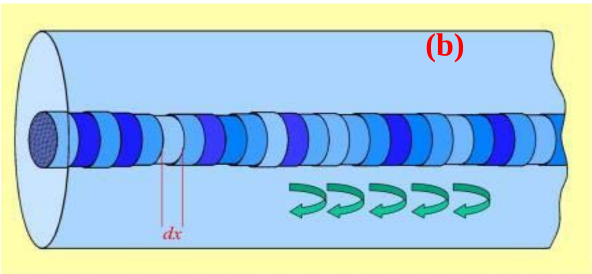
Schematic illustration of Brillouin scattering and (b) Rayleigh scattering.

Technique: Active Distributed Fiber Sensor

- Expand Rayleigh scattering distributed sensing beyond T and Strain measurements
  - Active fiber sensing scheme for environmental adaptability.
  - Air-hole microstructural fiber for multi-parameter measurements
  - 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

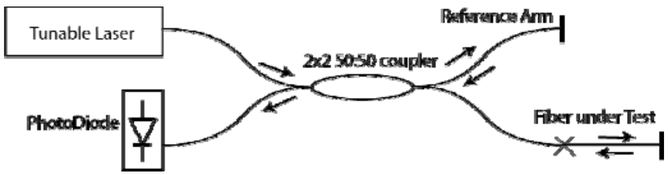
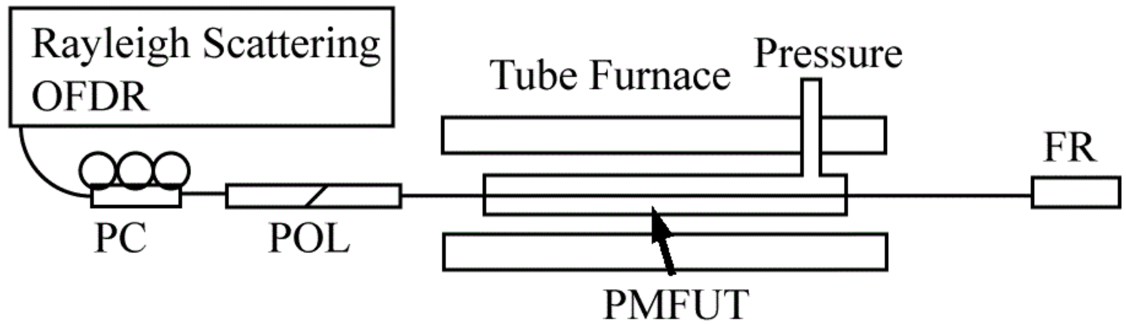
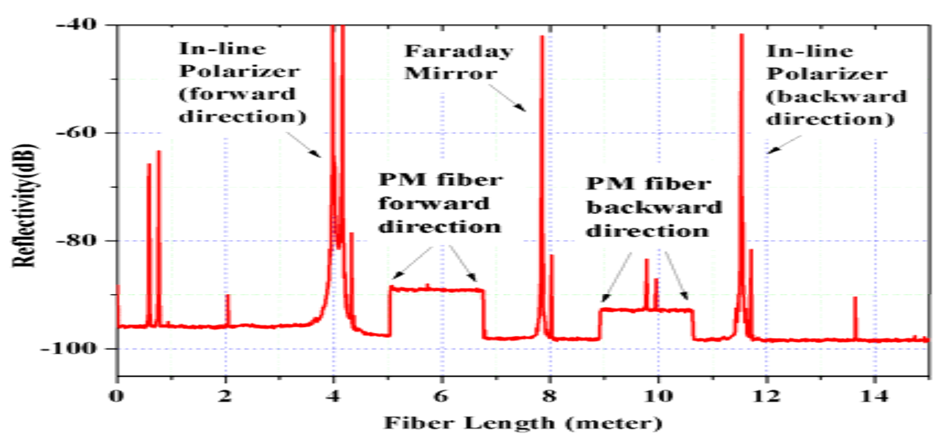


Fig. 3: Schematic sketch illustration of the OFDR operation principle [20].

- ✓ **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**

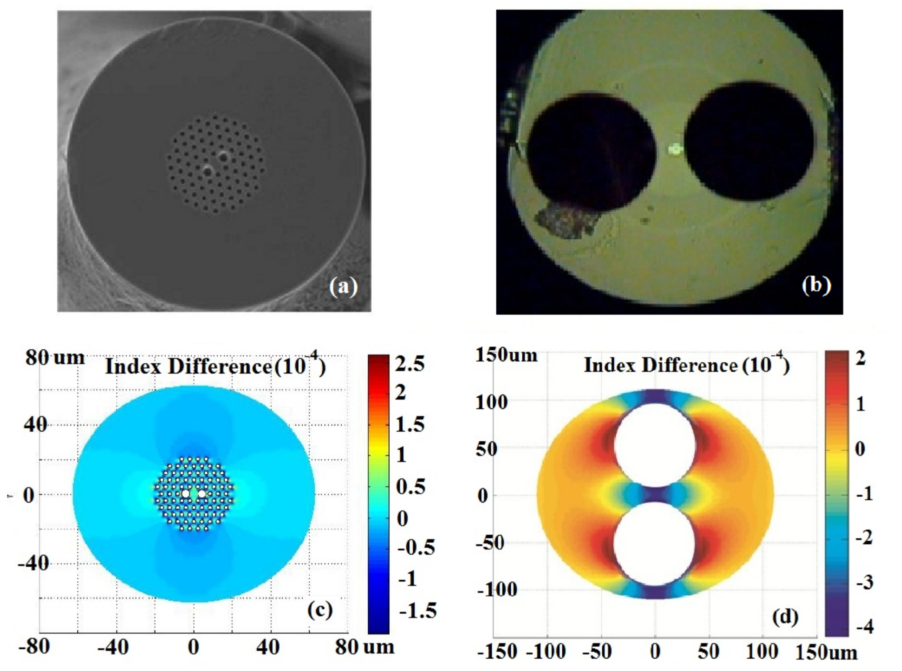
Distributed Pressure Measurements

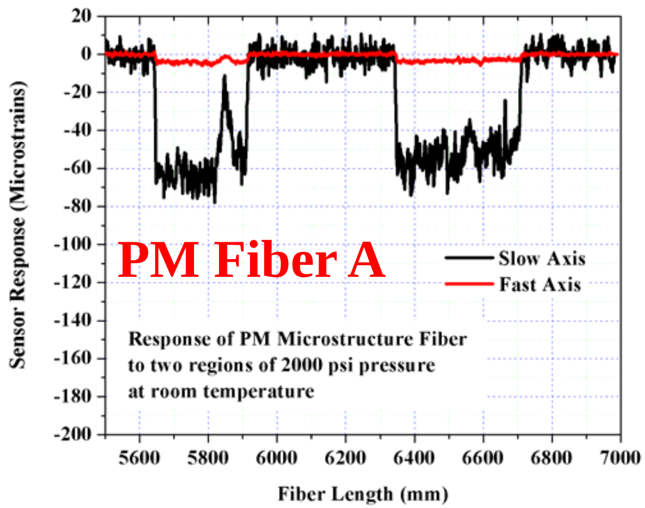


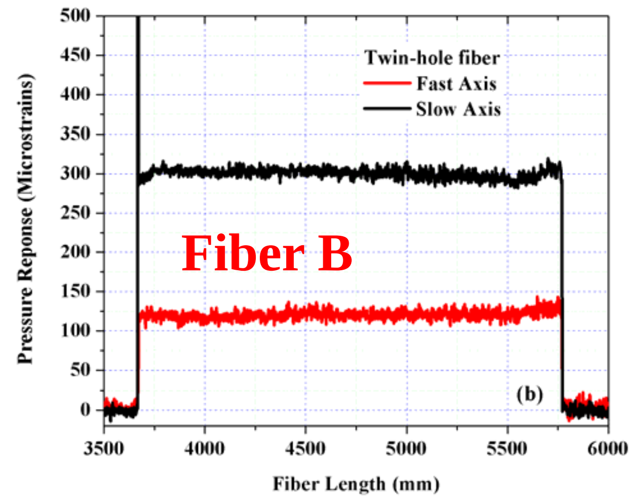


OFDR Measurement Results Two-Hole Fibers: 2000 psi

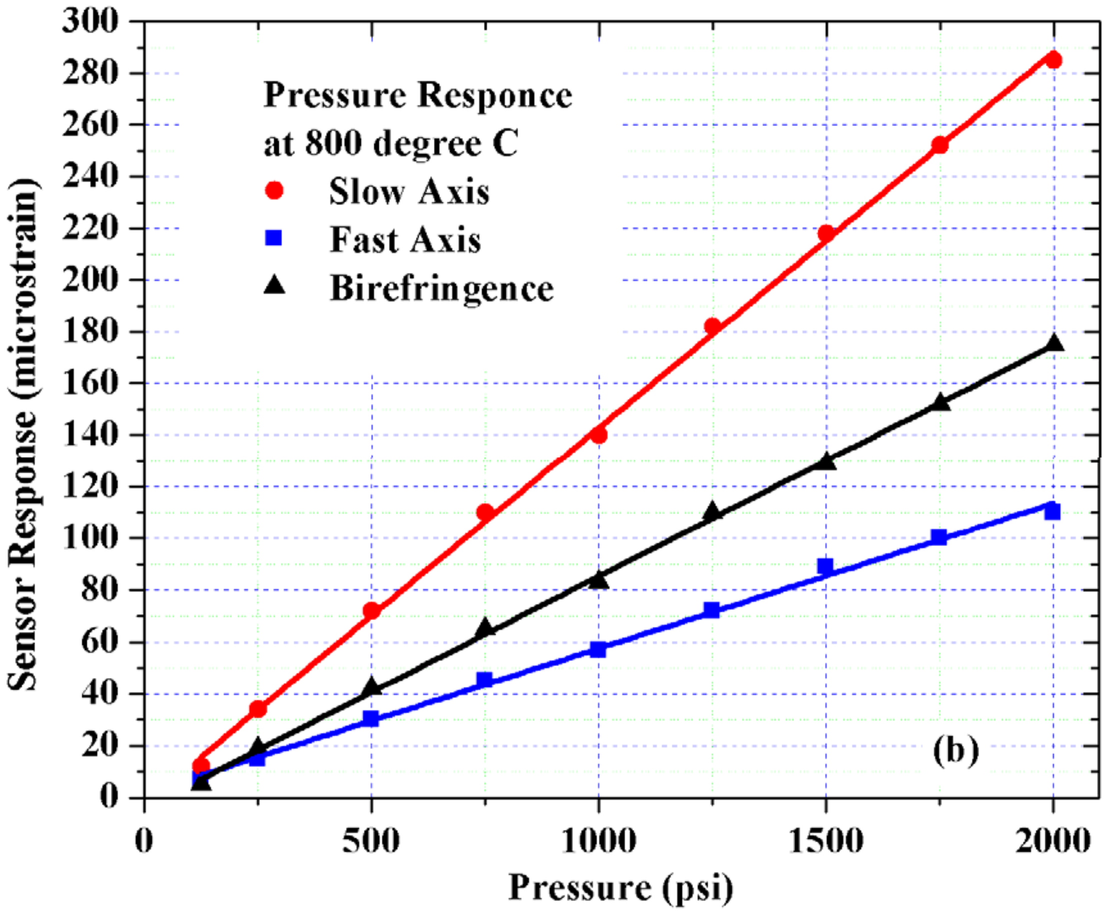
PM Fiber A **Two-Hole Fiber B**





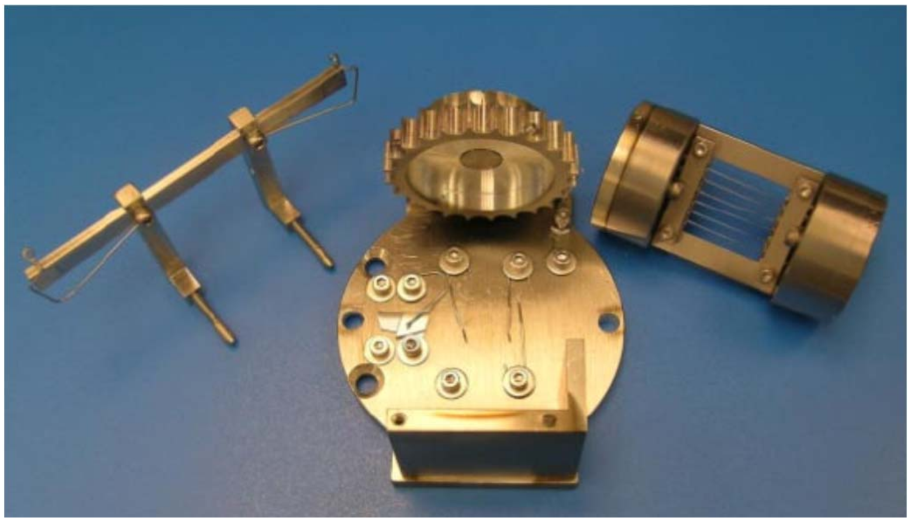


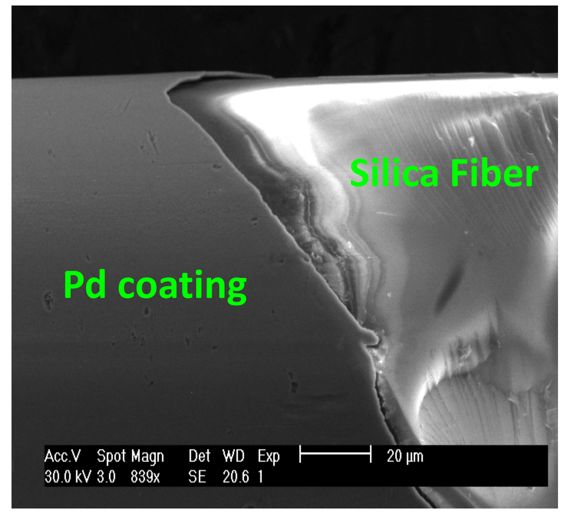
OFDR Measurement Results 800^{o}C

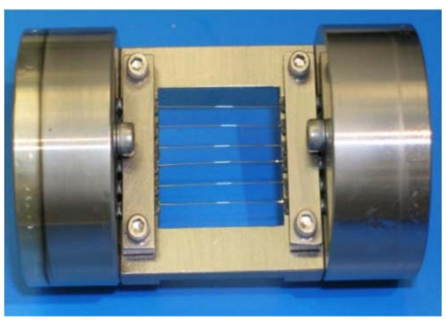


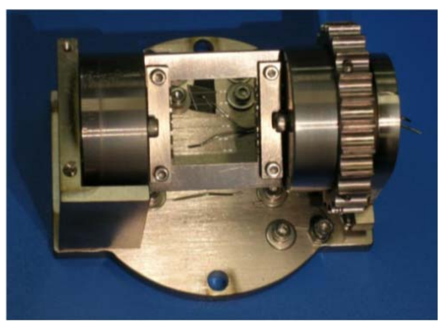
Distributed Hydrogen Sensing

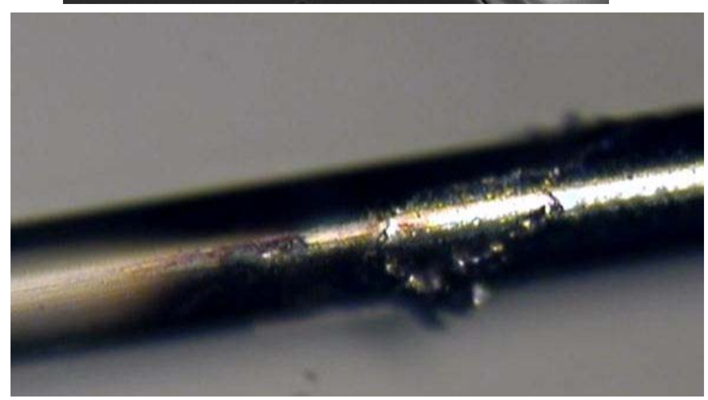
Sputtering Coating of Pd on fiber



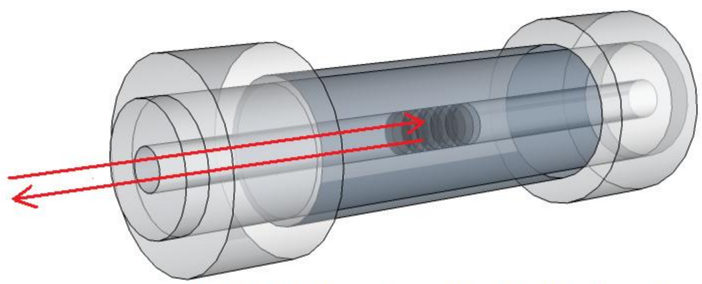




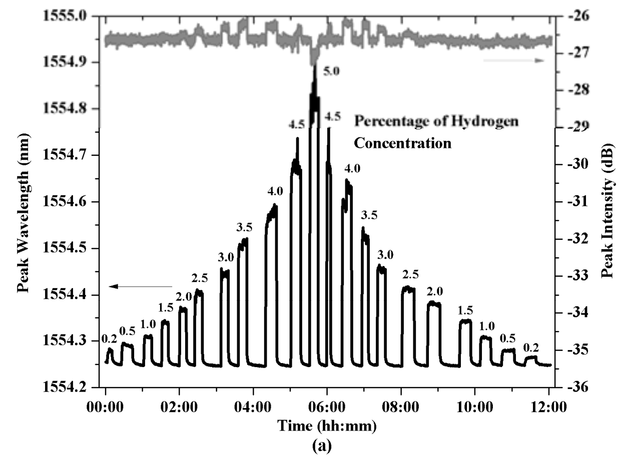


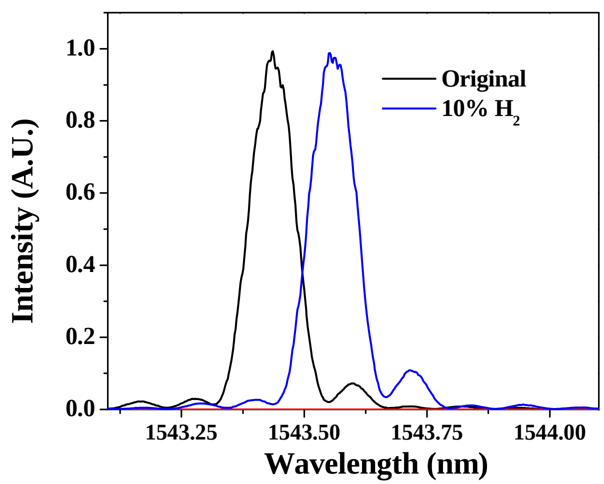


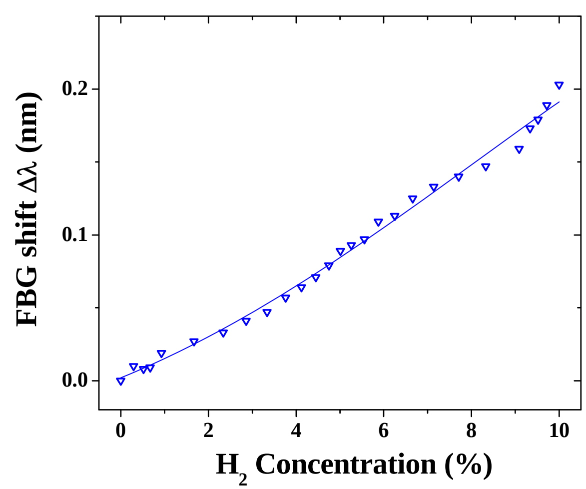
Chemical Sensing: H2 sensing Case using FBG



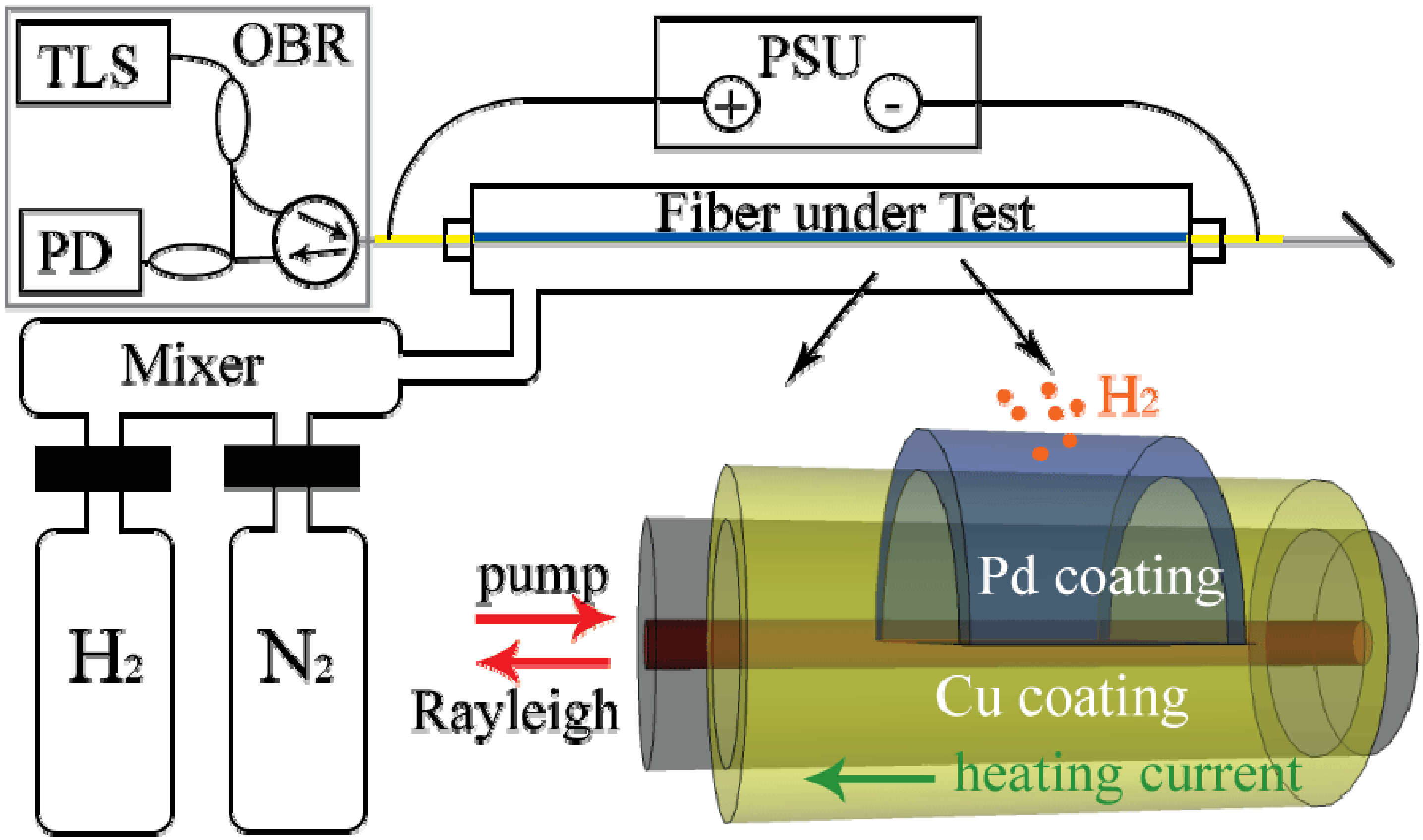
FBG Wavelength Shift due to Pd Hydrogen Absorption



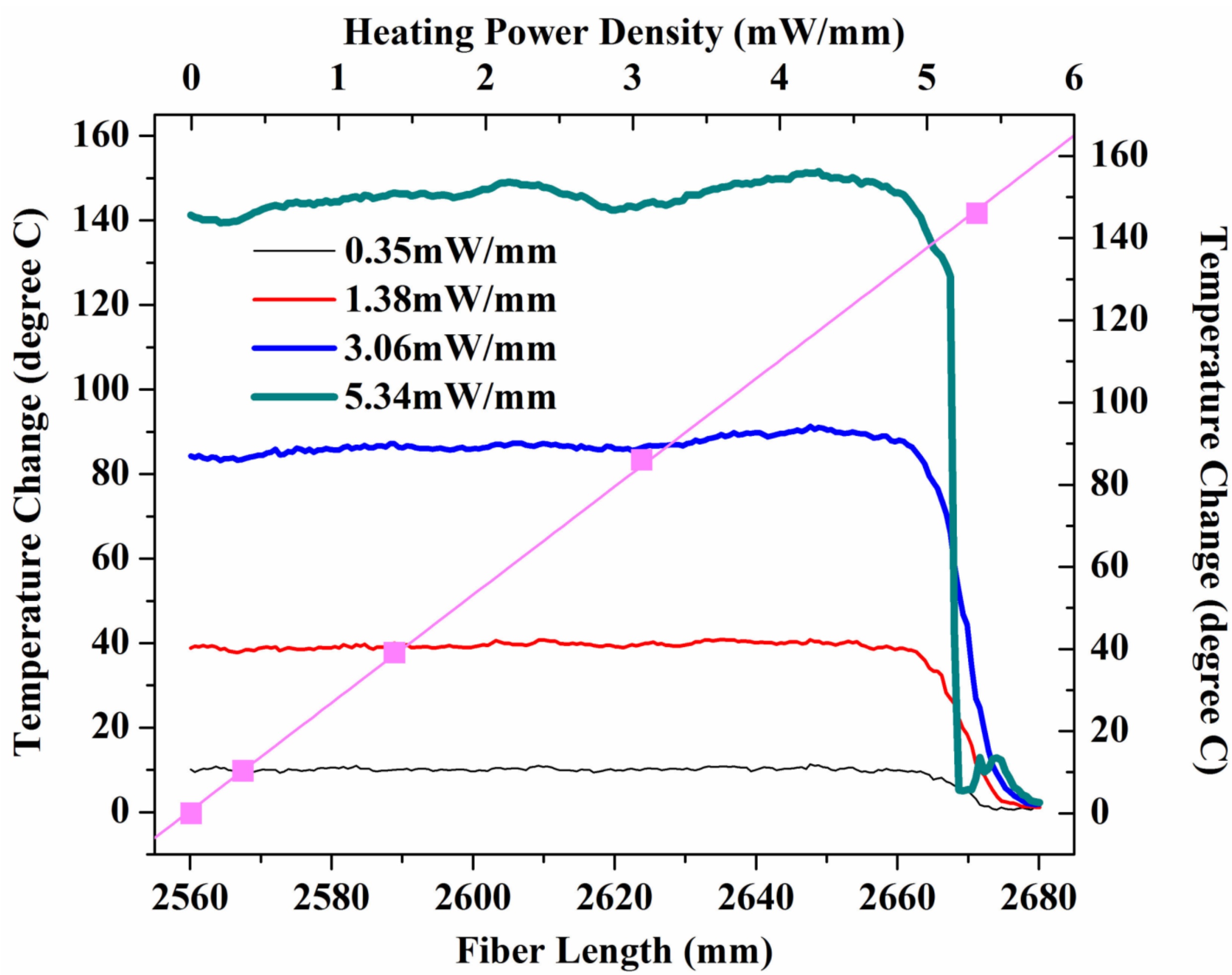




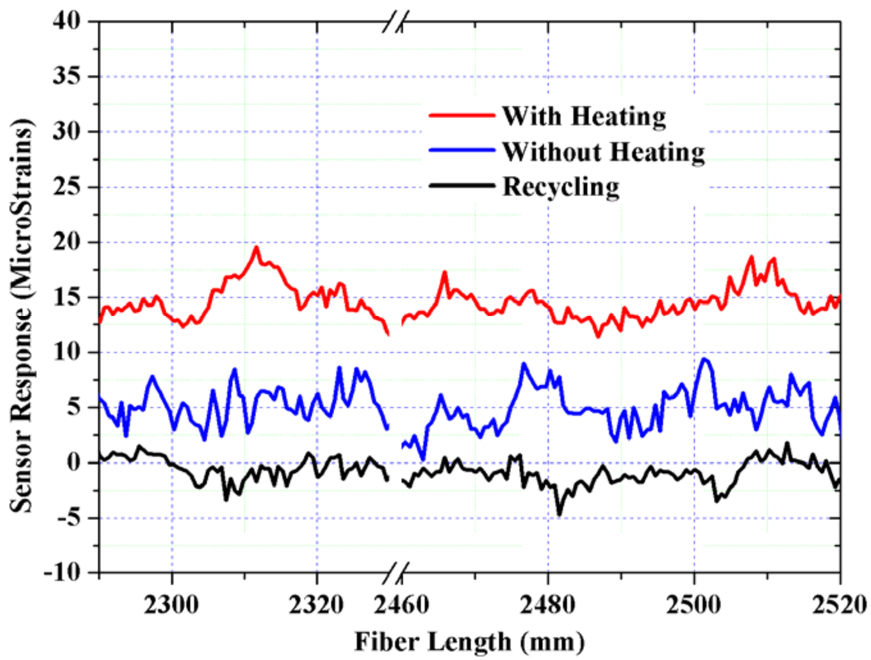
Distributed Chemical Sensing

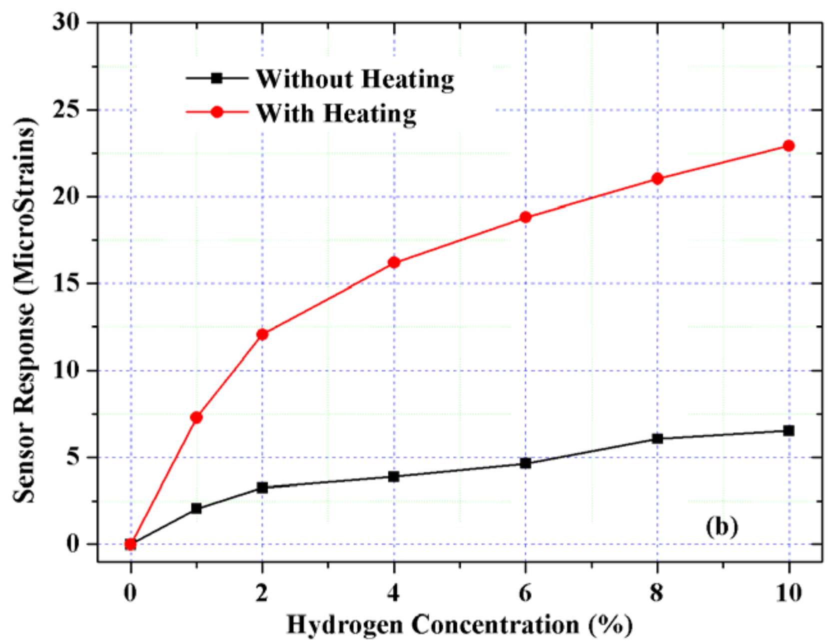


Heating of on-fiber Pd Coating to Speed up sensor performance



Distributed Sensor Response (10% hydrogen)





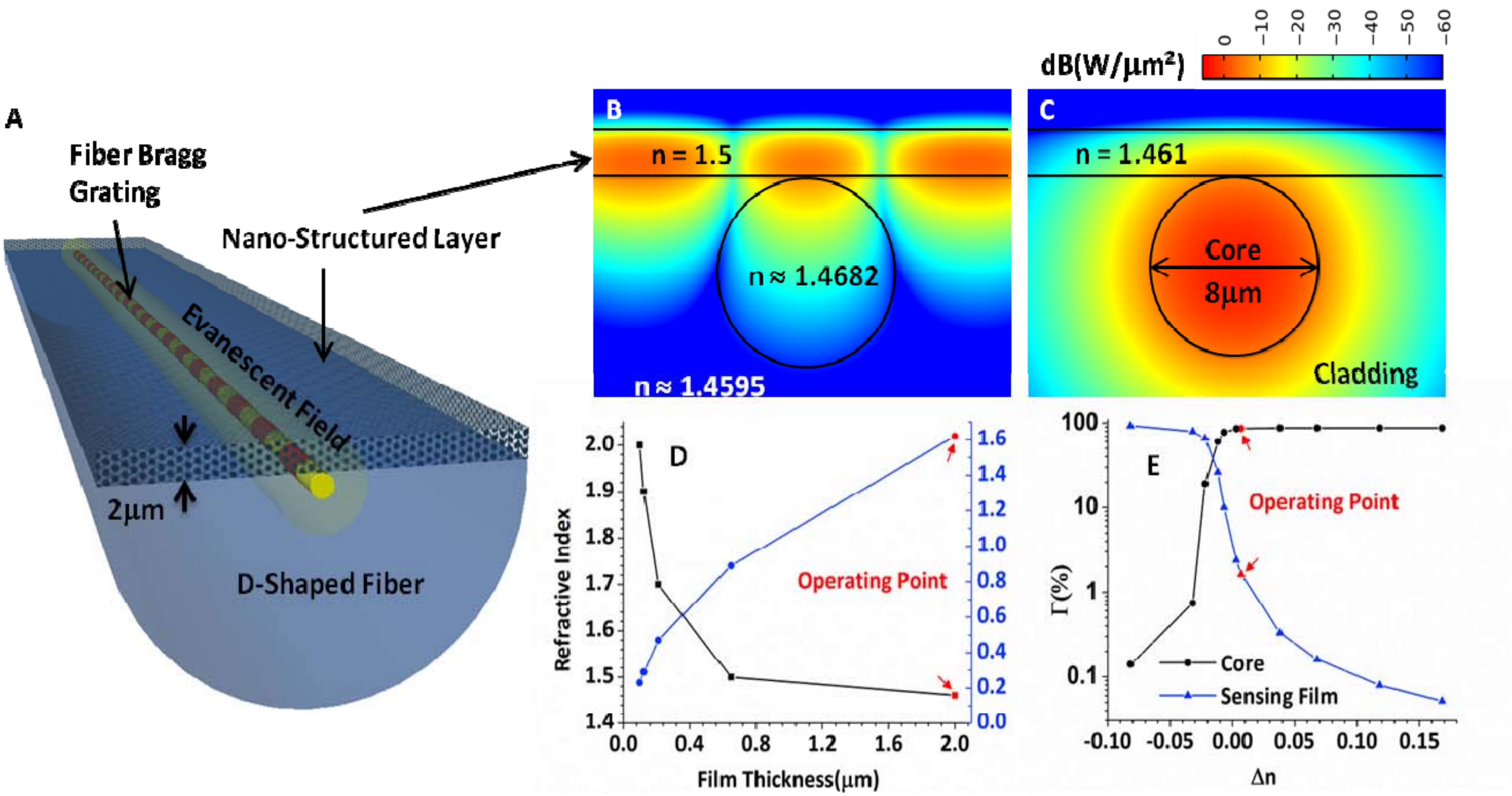
Progress Update: Distributed Sensing

- 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

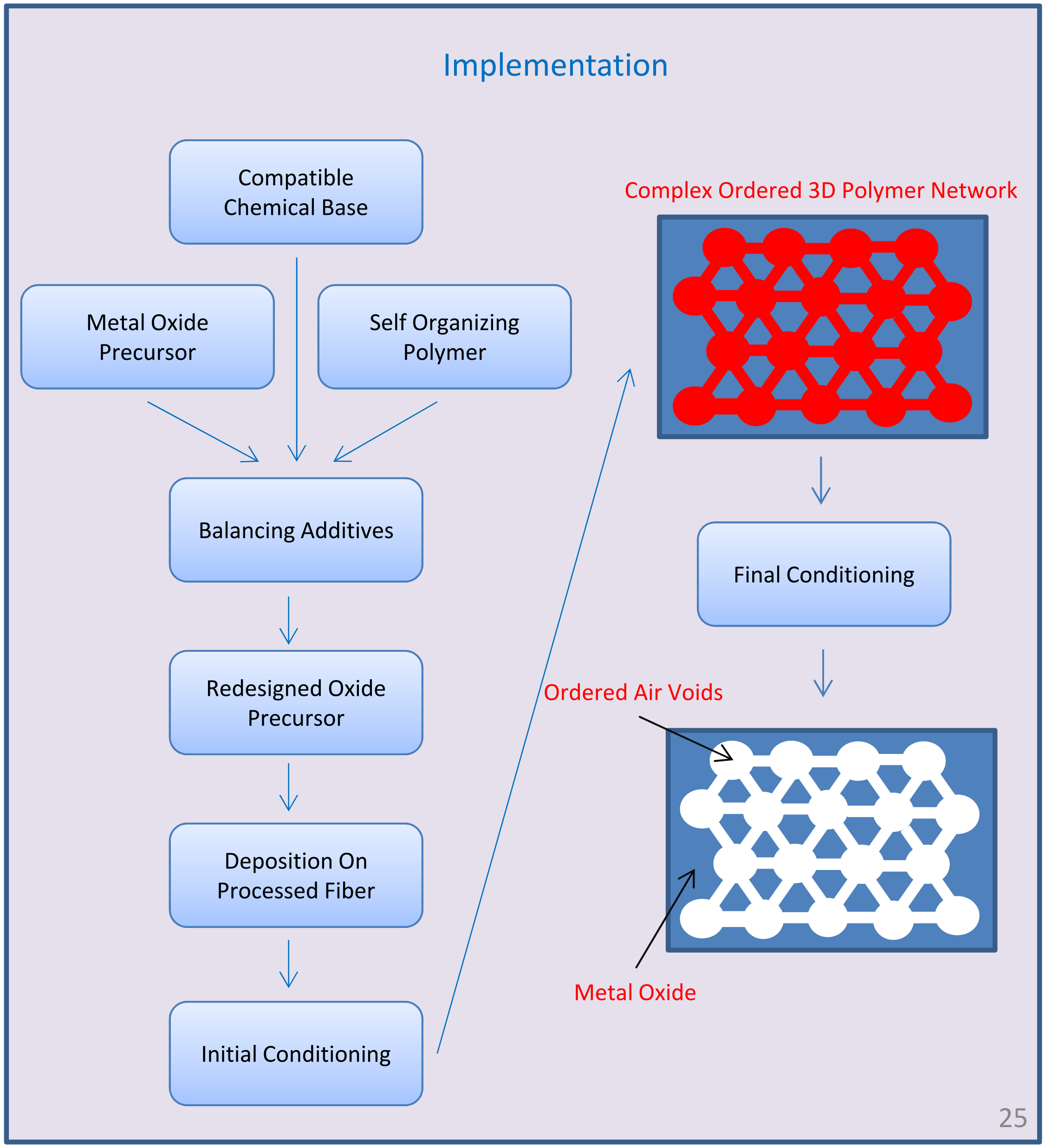
Topic III: Nanostructured Metal Oxide Sensing Material Developments

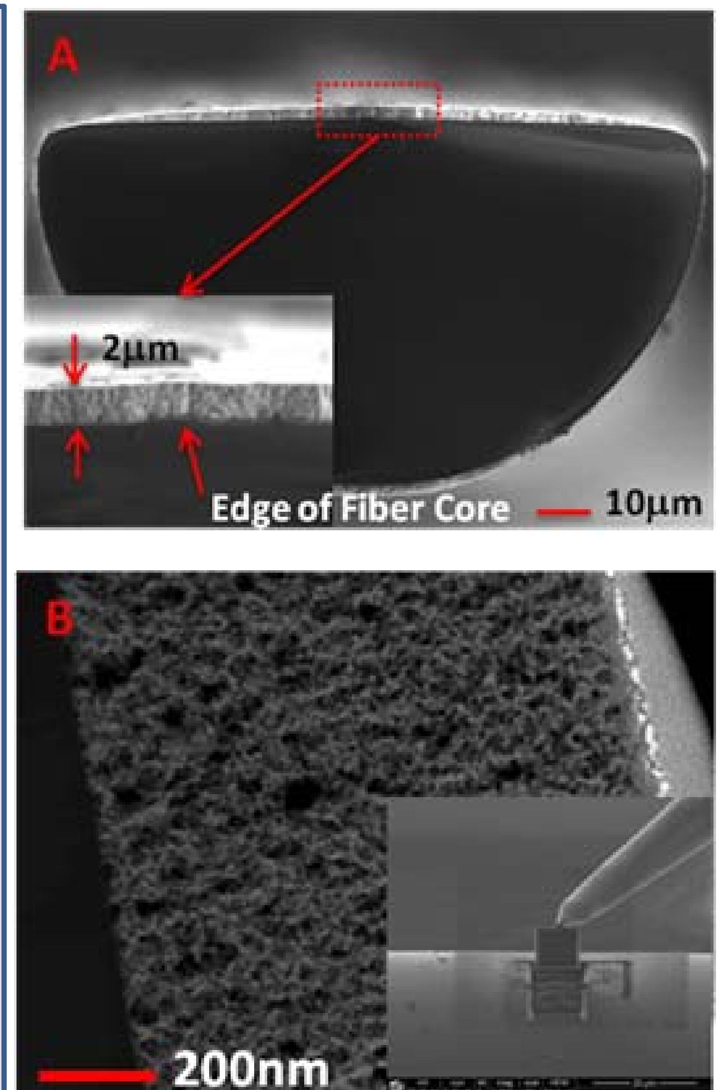
- Nano-Engineering on Refractive Index of Metal Oxide SnO_2
    Reduce index from n=2.2 to n=1.4 for on-fiber integration
- Develop high-T FBG sensor in D-shaped Fibers
- Integration of nano-engineered SnO_2 with FBG on D-shaped Fibers to characterize NH_3-induced optical properties change
- **Simultaneous determination** of refractive index change and absorption of metal-oxide FBG sensor induced by NH_3 exposure from 20^{o}C to 600^{o}C

Importance of Refractive Index Control



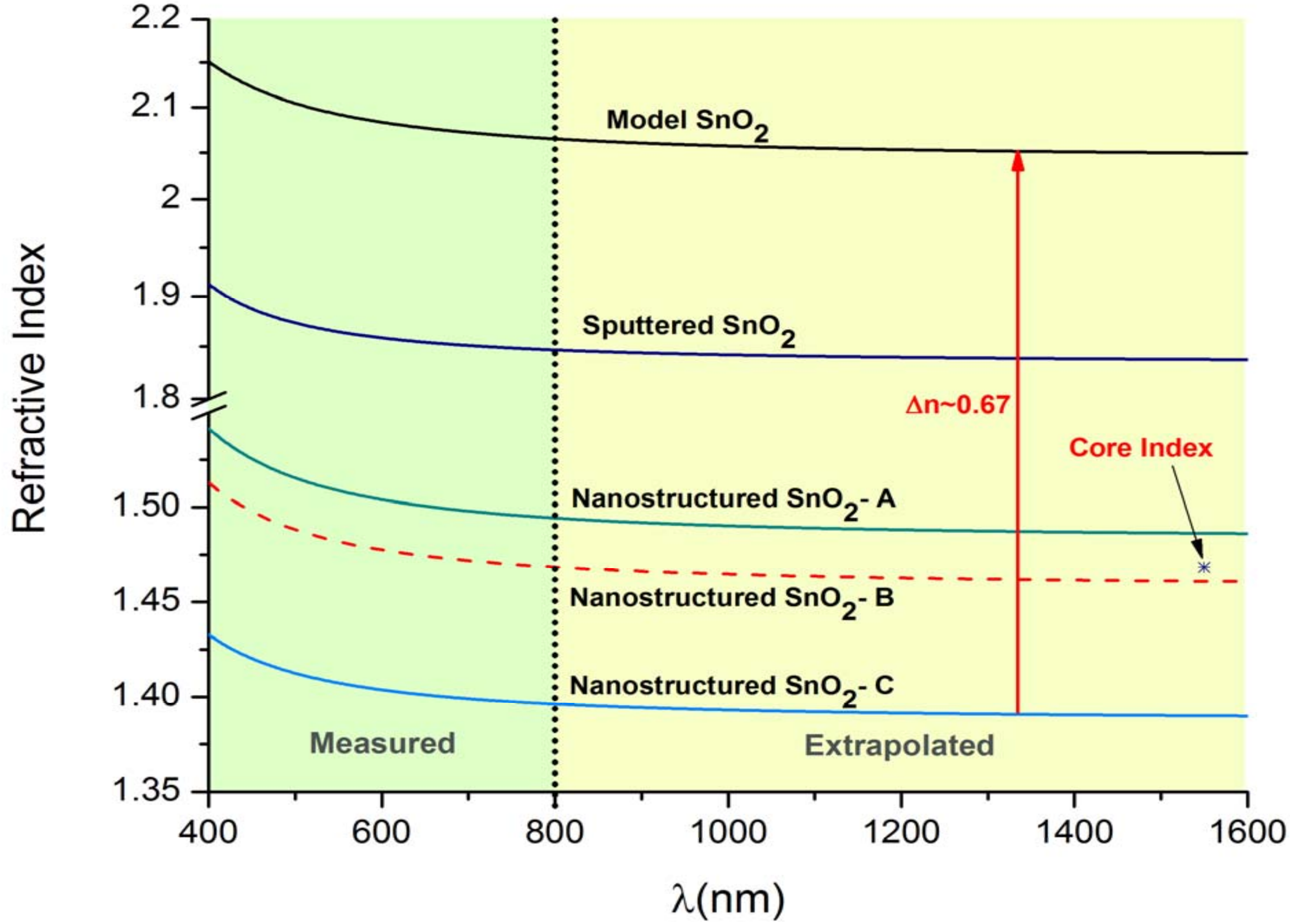
Metal Oxide Nanomaterial Development





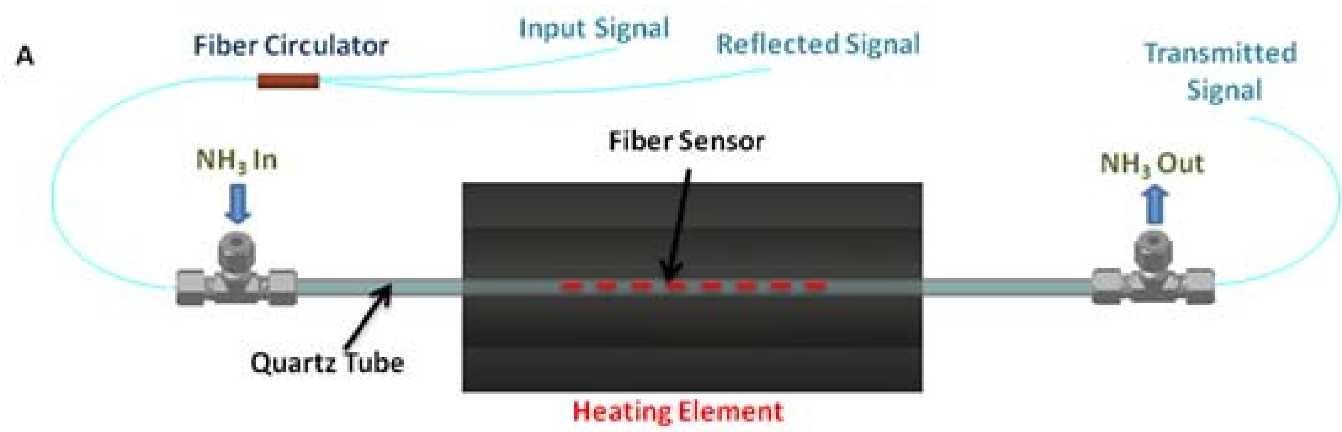
Metal Oxide Optical Sensor Development

SnO_2 Refractive Index Measurements (by Ellipsometer)

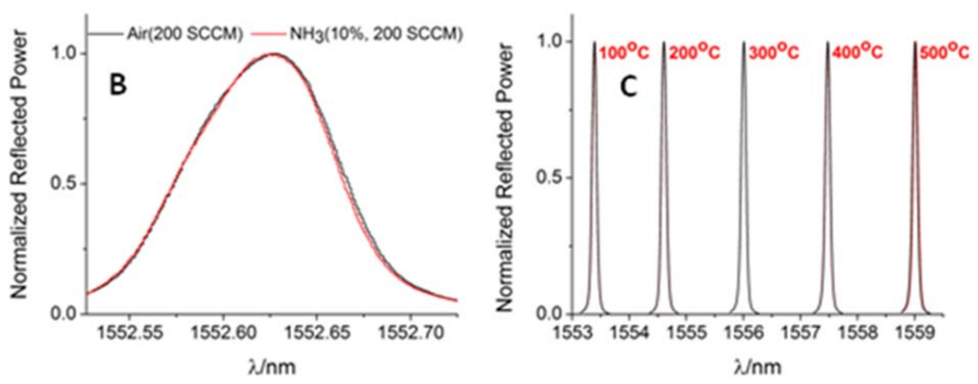


Sensor Characterization in NH_3

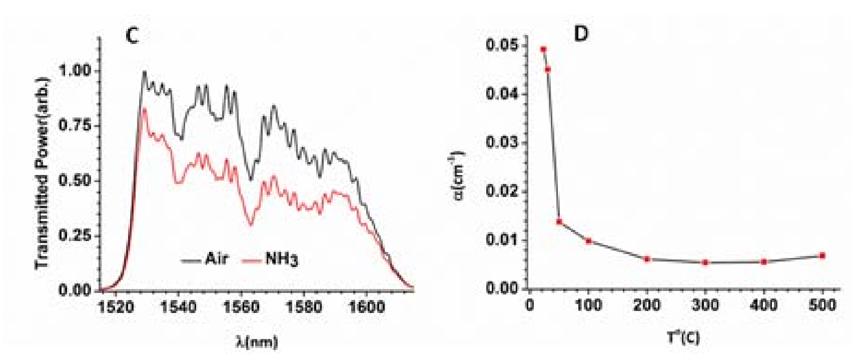
Experimental Setup



FBG Peak Shifts (RT to 500°C)



Absorption (RT to 500°C)



Summary

- Strong evidence support
  - **NH_3 reaction with metal oxide does NOT induce refractive index change**
  - **NH_3 reaction with metal oxide DOES induce strong absorption**
- **Implication for sensing application**
  - Metal-oxide fiber sensor based on measuring stimuli-induced index change MIGHT NOT Work
  - Evanescence-field fiber absorption sensors can be very sensitive!
  - Nano-engineering to reduce refractive index of metal oxide critical!!!
    - High-quality (i.e. high uniformity) metal-oxide MIGHT NOT WORK
    - Sol-gel approach might be better than other coating techniques such as sputtering
- Future works
  - Explore different oxides (SnO_2, TiO_2, VO_2, etc)
  - Sensitization of oxide by doping to improve sensitivity and selectivity
  - More sensitive fiber sensing scheme

Program Summary

- Success in high-T point sensor development
  - Greatly **reduce the cost** of high-T FBG sensors in **a wide varieties of fibers**
  - Operation T ~ 1200C
  - **Optical flow sensor rated for 1000^{o}C**
  - **DFB fiber laser sensor for 750C 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 nano-materials integrations
  - Success in metal oxide porosity and index refraction control
  - Complete metal oxide fiber integration
  - Real-time gas sensing demonstrated