Functionalized SAW Sensors for Chemical Sensing in Fossil Energy Applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

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PWST, Dec 11 - 13, 2018

What is the National Energy Technology Lab?

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL is the Only Government Owned Government Operated DOE Laboratory

MISSION
Advancing energy options to fuel our economy, strengthen our security, and improve our environment

Oregon

Pennsylvania

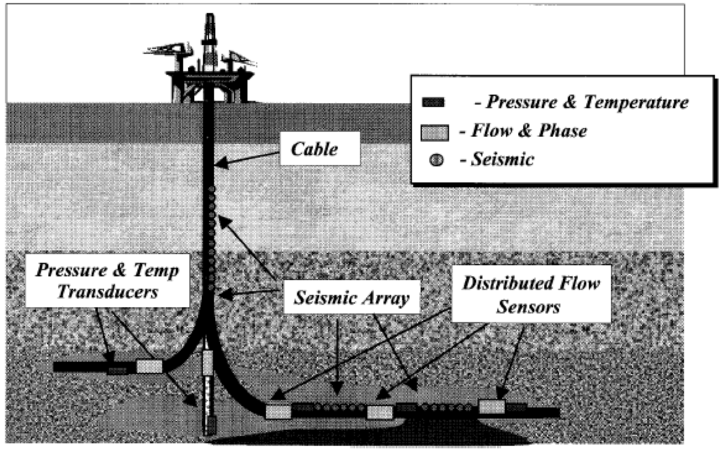
West Virginia

NETL Researchers Work Closely with Program Staff in Support of the Mission.

Embedded Sensing Fossil Energy Applications

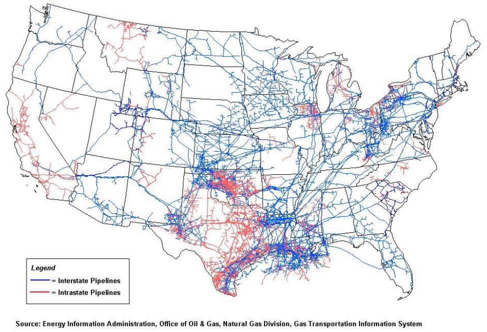
Needs for increased visibility span all aspects of the US Energy Infrastructure

Power Generation

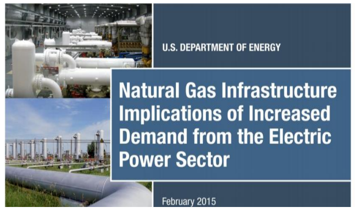


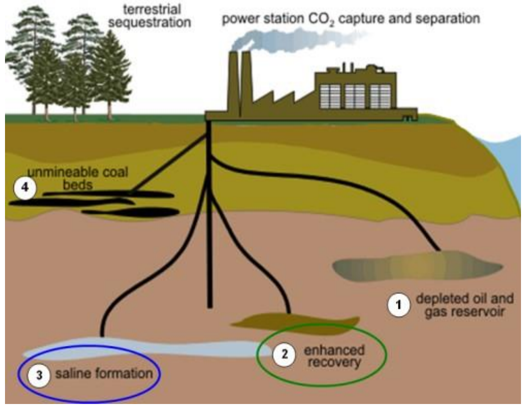
Unconventional Oil & Gas

Natural Gas Infrastructure



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





CO_2 Sequestration

Ubiquitous Embedded Sensors Combined with Geo-spatial Data Analytics is a Requirement to Achieve Desired Visibility Across the Entire Fossil Energy Infrastructure : *NETL Initiative*

Engagements with Extramural Programs

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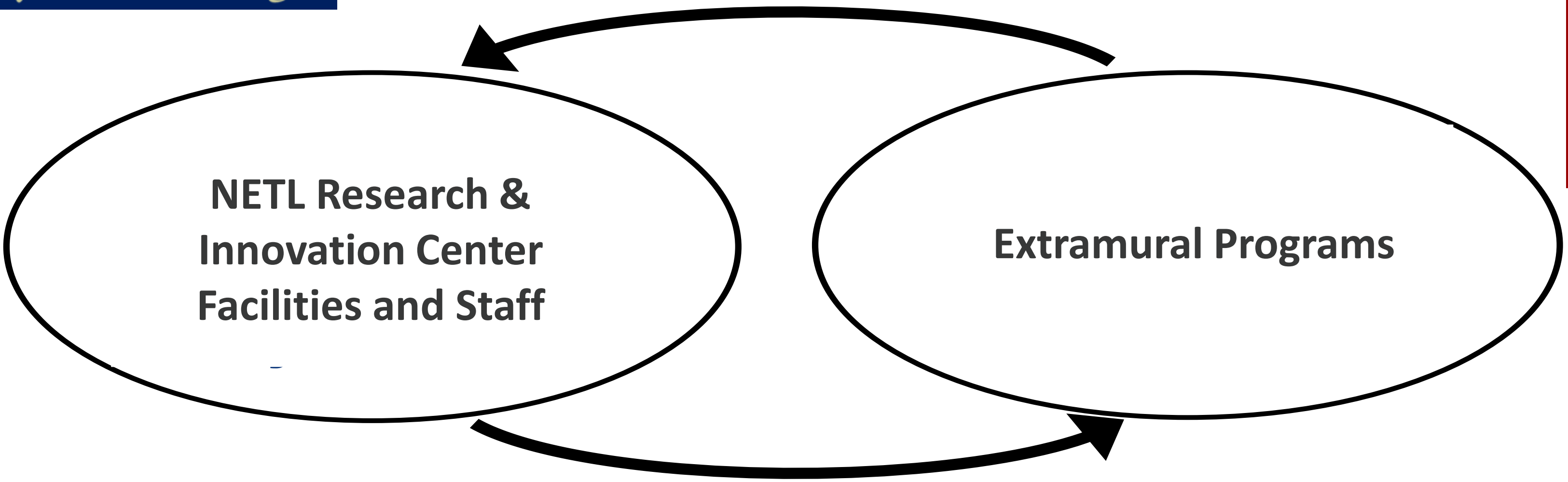
University of Pittsburgh

University of Cincinnati

Virginia Tech Invent the Future®

Carnegie Mellon University



STEVENS INSTITUTE of TECHNOLOGY THE INNOVATION UNIVERSITY®

OSU Oregon State UNIVERSITY

UCONN UNIVERSITY OF CONNECTICUT

COLLEGES OF NANOSCALE SCIENCE AND ENGINEERING SUNY POLYTECHNIC INSTITUTE

The Team Seeks Synergistic Interactions with a Broad Range of Extramurally Supported NETL Funded Projects to Help Drive the FE Mission in Support of Our Program Offices.

Reliability & Resiliency of Natural Gas Infrastructure

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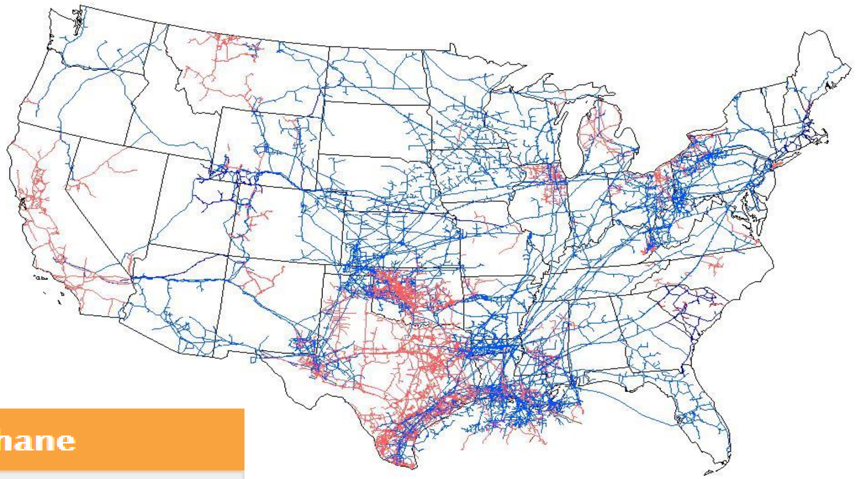

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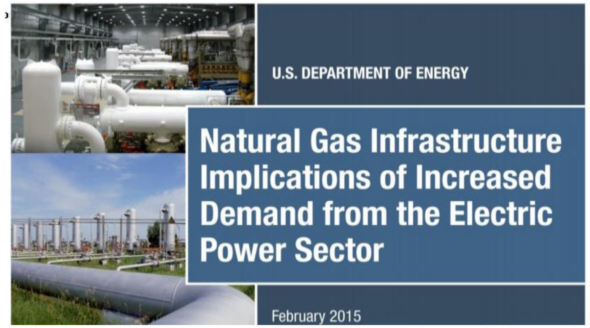
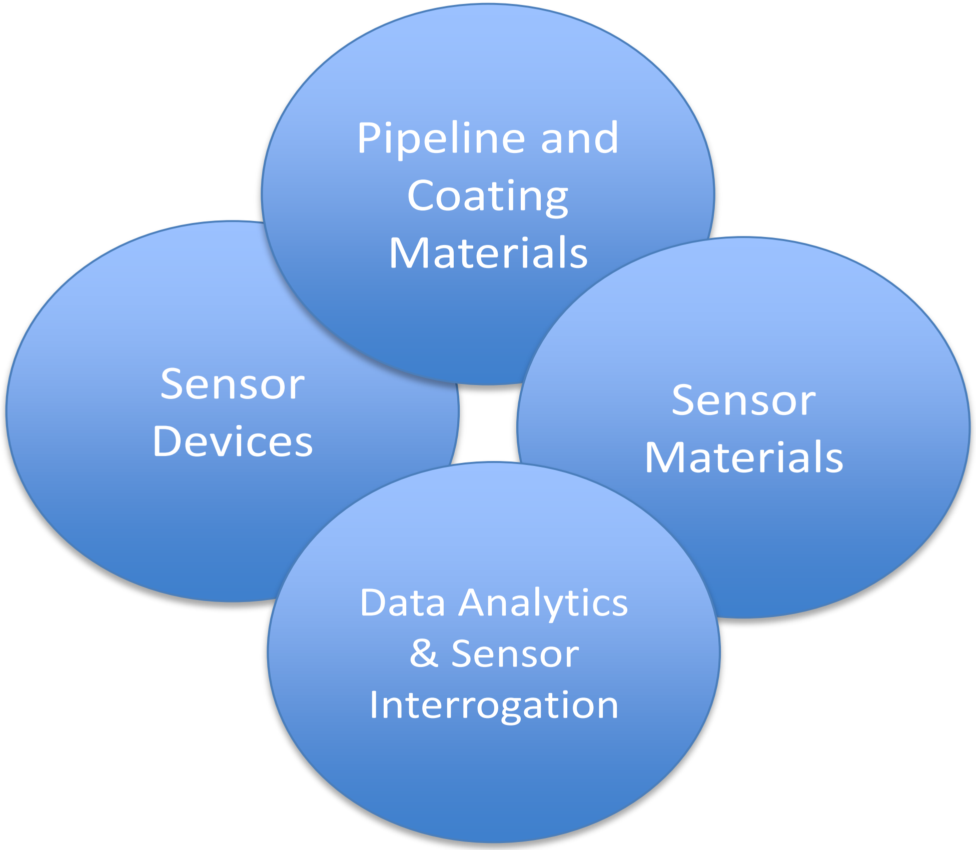


http://energy.gov/sites/prod/files/2015/02/f19/DOE%20Report%20Natural%20Gas%20Infrastructure%20V_02-02.pdf



In 2016, A Program was Established to Develop New Sensor and Material Technologies for Monitoring, Detection, and Mitigation of Failures and Events in Natural Gas Infrastructure.

Existing Midstream Oil & Gas Sensing Technology

Pipeline Explosion Caused by Corrosion

http://wvpublic.org/post/ntsb-determines-cause-december-2012-sissonville-pipeline-explosion#stream/0

Existing Technologies : Detecting Presence of Leaks and Failures

- Internal Leak Detection Systems: Measured Flow Rates and Computational Models
- Periodic In-Line Inspections
- Monitoring of Local Geohazards (Ground Movements and Seismic Events)
- External Inspections, Including Aerial Surveys
- Optical Fiber Based Leak Detection Systems: Indirect Measurement (Temperature, Strain, Acoustic)

Conventional Pipeline Monitoring Techniques Identify Leaks and Events Once they Have Occurred, But are Limited in Capability to Identify Failures Before they Occur.

Data Analytics, Sensors & Materials Technology

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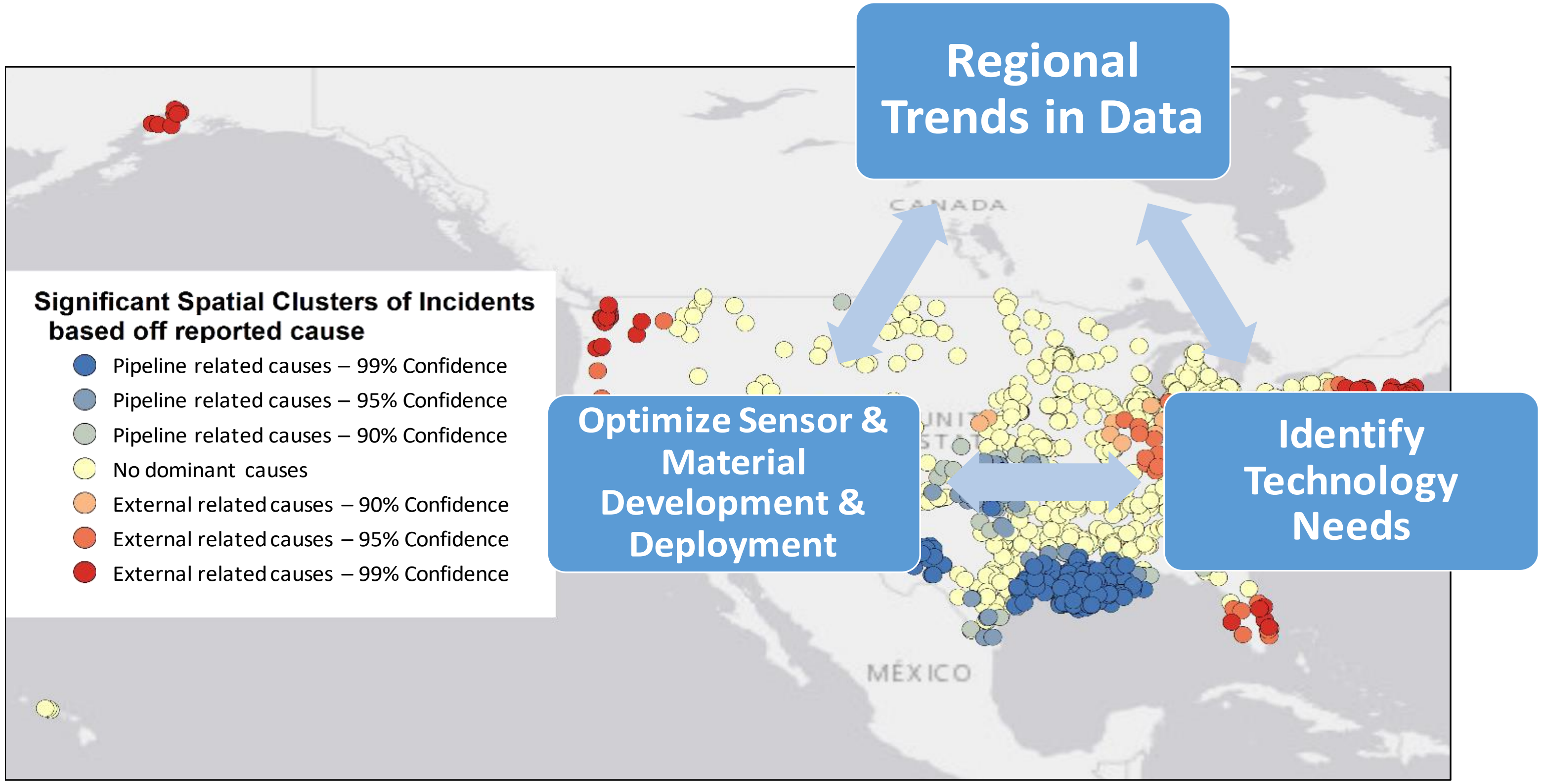
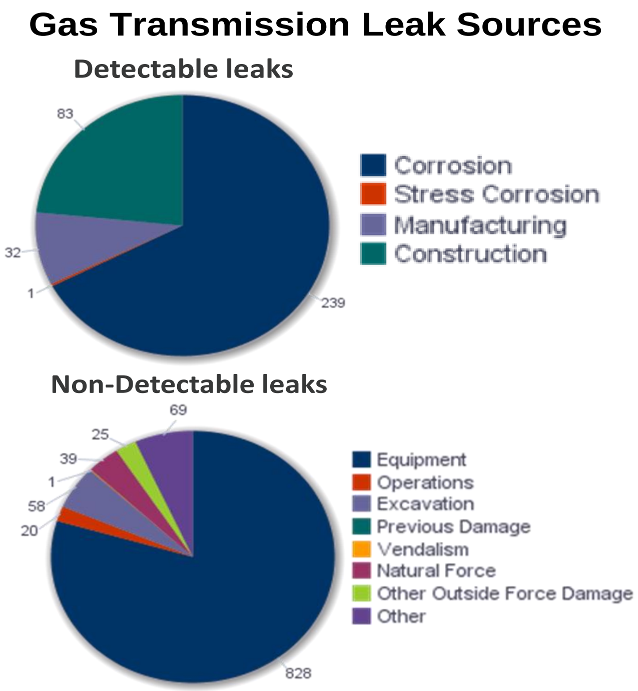
Goal = Optimized Sensor Selection and Placement

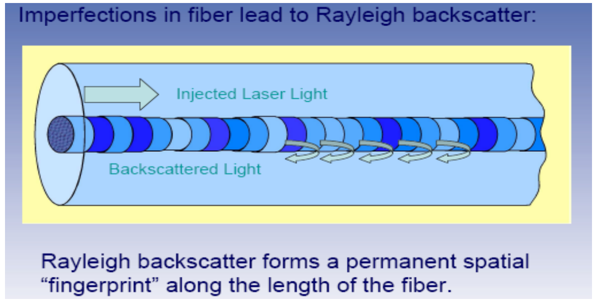




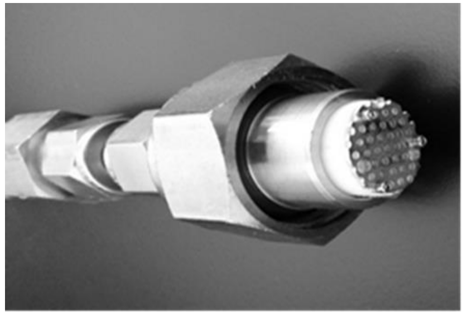
Analytics Methodologies can Be Developed and Applied in Parallel with New Sensor and Materials Research and Development Efforts to Impact Infrastructure Risks and Resiliency.

NETL Sensor Development : Natural Gas Infrastructure

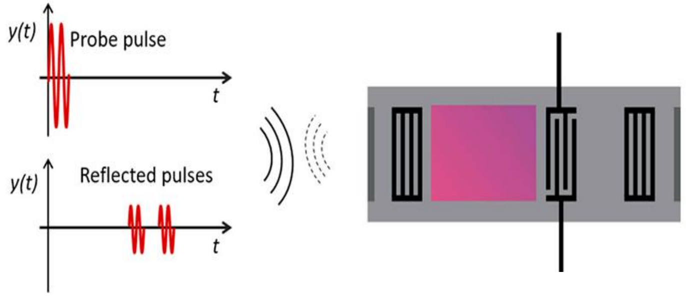
Distributed Optical Fiber Sensors



Advanced Electrochemical Sensors



Surface Acoustic Wave Sensors



	Geospatial Attributes	Cost	Targeted Function
Distributed Optical Fiber Sensors	Linear Sensor Adjustable Distance and Resolution	Varies, Dominated by Interrogation Technique Cost Per Sensor "Node" Can Be Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, etc.) Early Corrosion Detection
Surface Acoustic Wave Sensors	Point Sensor	Extremely Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, etc.) Early Corrosion Detection
Advanced Electrochemical Sensors	Point Sensor	Moderate	Humidity and Corrosion Rate Monitoring

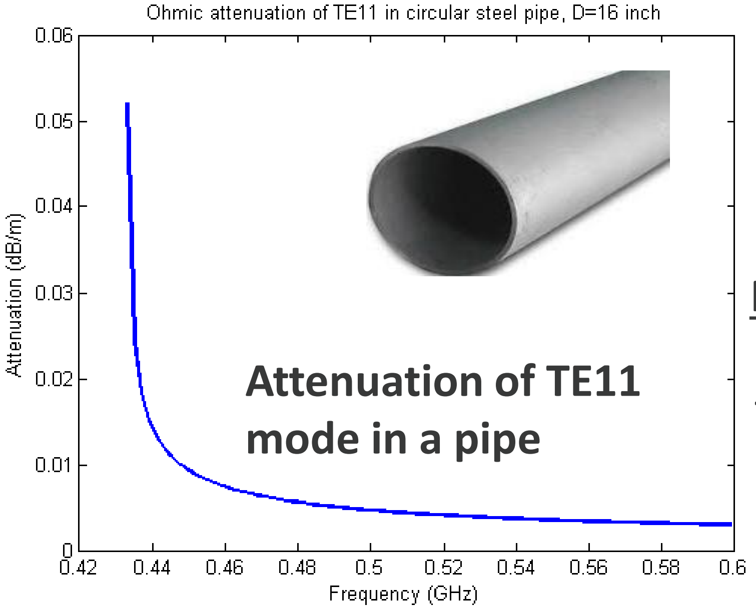
Three Synergistic Sensor Platforms with Complementary Cost, Performance, and *Geospatial Characteristics* are Being Developed with an Emphasis on Corrosion & Gas Composition.

RF and Microwave Technique for Pipelines and Tubing

Common pipe / tubing sizes for fossil energy infrastructure

Pipe Type	Diameter (inch)	TE11 Cut off Freq (MHz)
Mainline	16 – 48	433 – 144
Interstate	24, 36	288, 192
Lateral	6 – 16	1153 – 432
Wellbore casing	~4.5	1537
Wellbore tubing	~2.5	2767

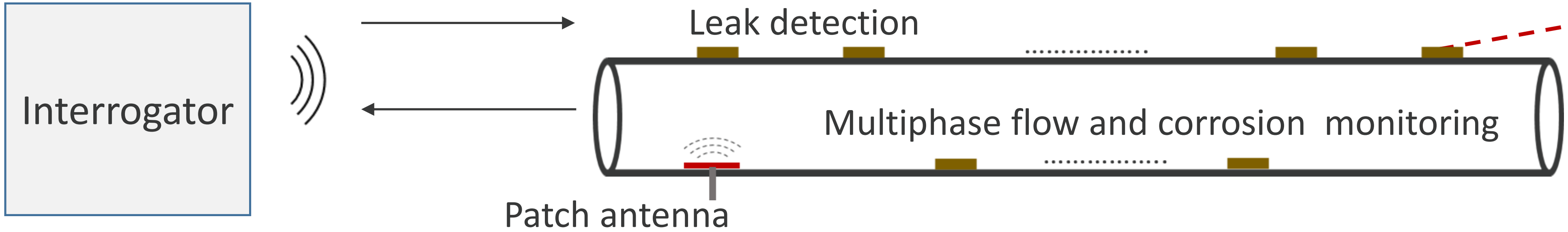
16 inch steel pipe:

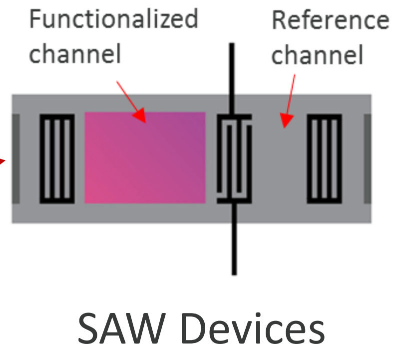


Launch Frequency
~ 500 MHz
Conducting Loss
< 0.01 dB/m

Relative Signal Intensity at 1km

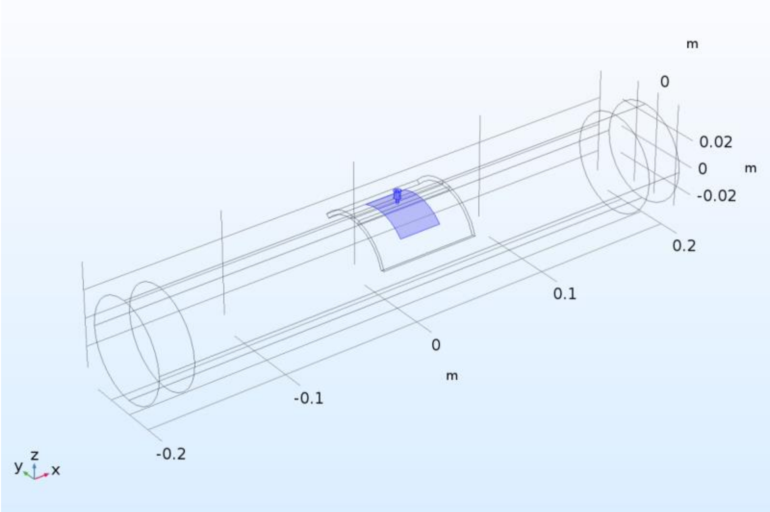
Free Space (isotropic): 86.42dB
TE11 Mode in Pipe: 10dB

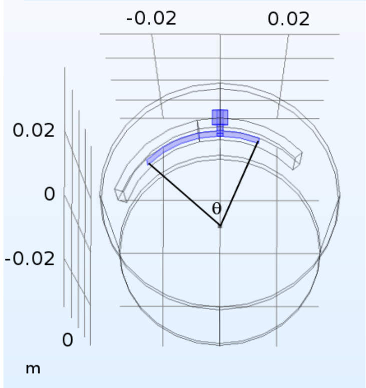


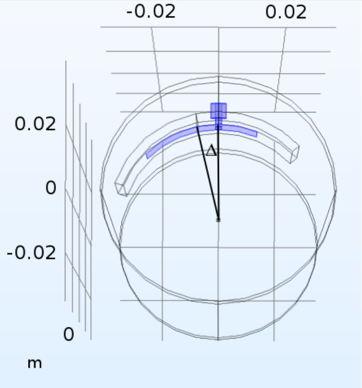


One Example Mode of Telemetry for Pipeline / Tubing Instrumented Wireless Sensors.

Launching RF into Pipes

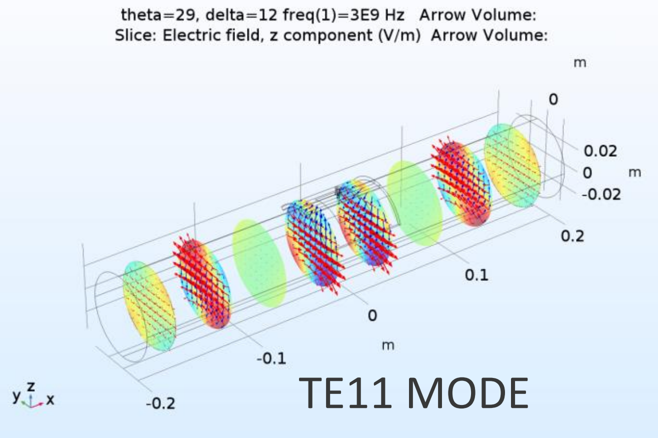




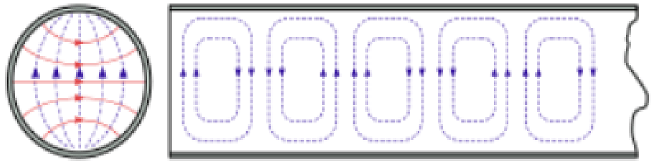


To be investigated:

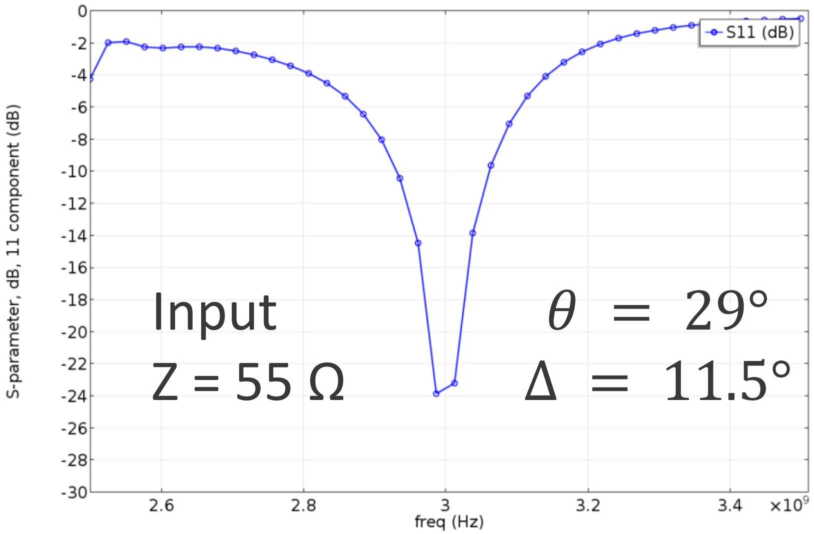
- Angular size of the patch (θ)
- Feed offset (Δ)



Blue arrows: Magnetic field in the transverse plane
Red arrows: Electric field (Color: Y-component of the electric field)



Field patterns of TE_{11} mode

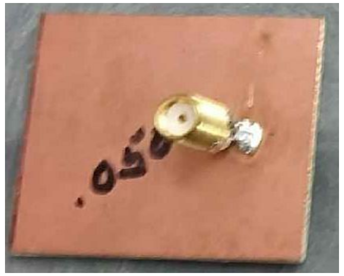


An antenna radiation into a metal pipe

Preliminary Test

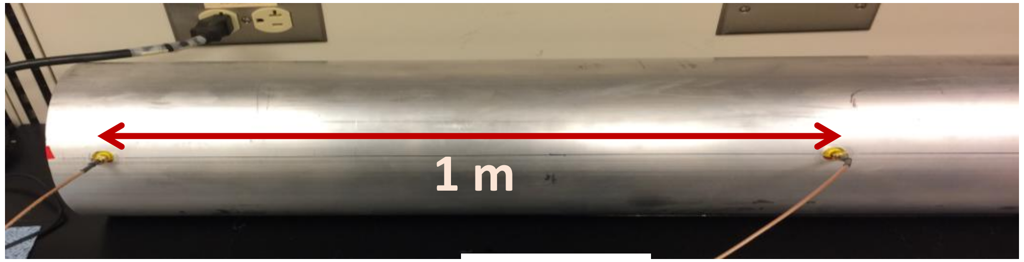
Antenna:
Dielectric Material: FR4
Patch: Copper foil
Frequency: 3 GHz
Feed: Coaxial feed at 1/3rd of the patch length

Patch

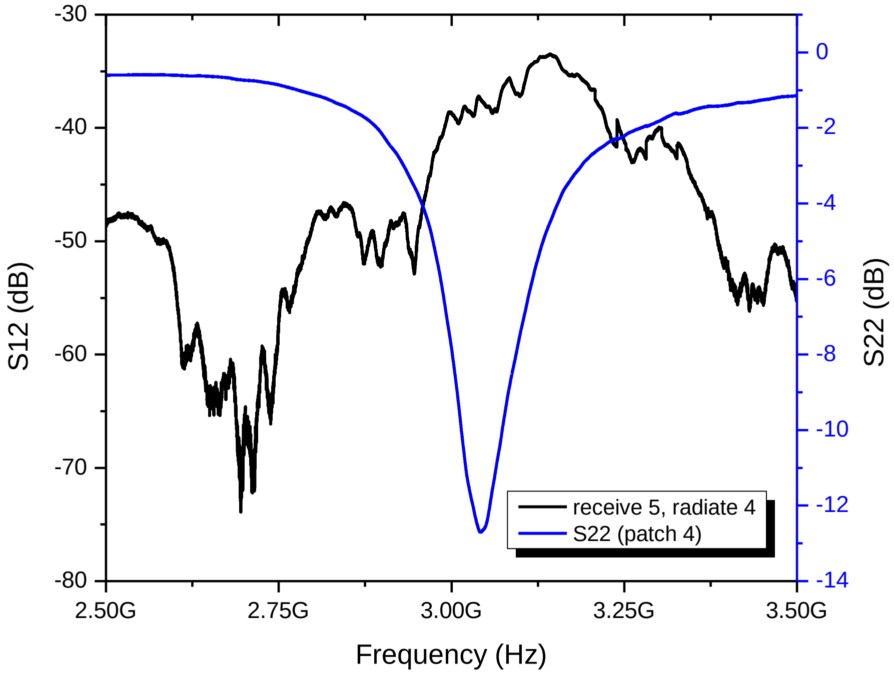


Ground/Feed

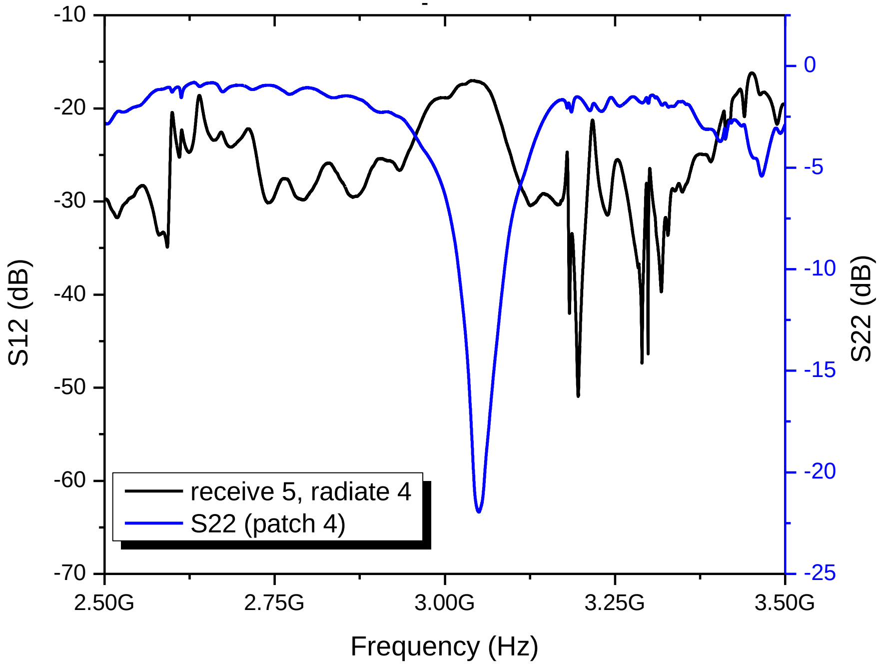
Pipe:
Material: Aluminum
Diameter: 7 cm
End: Open
Feed: End and/or Middle



Free Space



Pipe



Patch antennas can launch RF into and receive from arbitrary locations in metal pipes.

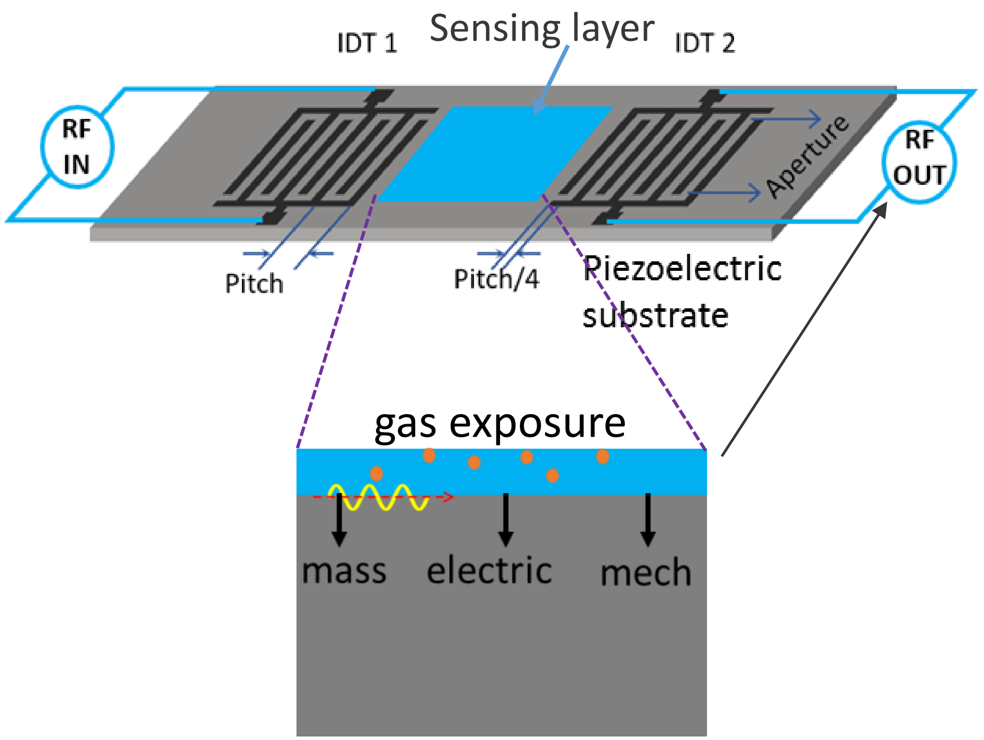
Surface Acoustic Wave Sensors

- Passive, Wireless Sensors Requiring No Active Power (Harsh Environment Compatible, Reduced Maintenance)
- Possible to Develop for Multi-Function Parameter Operation (Temperature, Chemistry, Other Parameters)
- Matured Technique: Millions of SAW Filters Produced for Use in Mobile Phones & Commercialized for Temperature Sensing
- SAW Devices Can be Functionalize for Other Parameters Through Integration with Functional Sensing Layers

SAW velocity can be recorded in terms of time delay, frequency or phase and correlated with a parameter of interest.

$$\frac{\Delta v}{v_0} = \Delta_{temp} + \Delta_{pressure} + \Delta_{mass} + \Delta_{conductivity} + \Delta_{mech} + \ldots\ldots$$

$$\frac{\Delta v}{v_0} = \frac{\Delta f}{f_0} = -\frac{\Delta \phi}{\phi_0}$$



e.g. Working principle of SAW gas sensors.

Functionalized SAW Sensors for Chemical Sensing

sensors
MDPI

Review

SAW Sensors for Chemical Vapors and Gases

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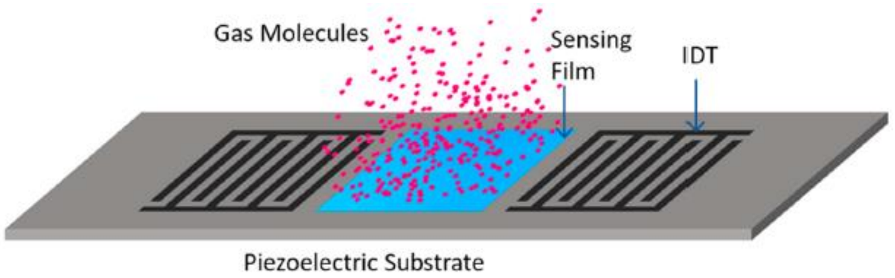
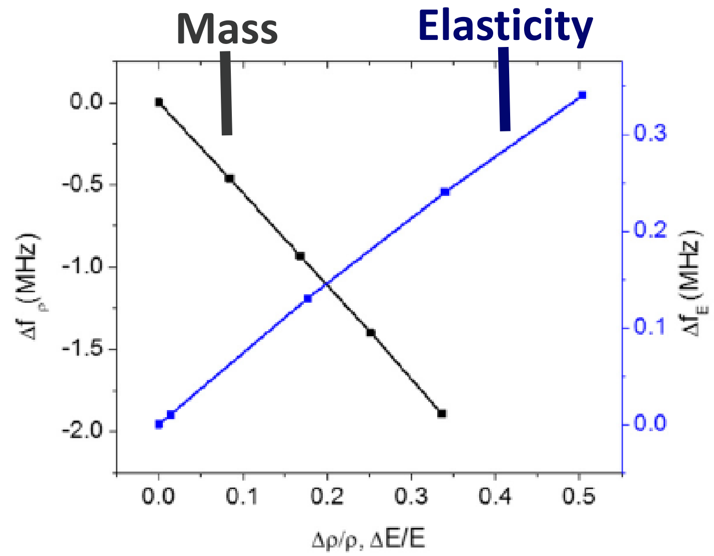
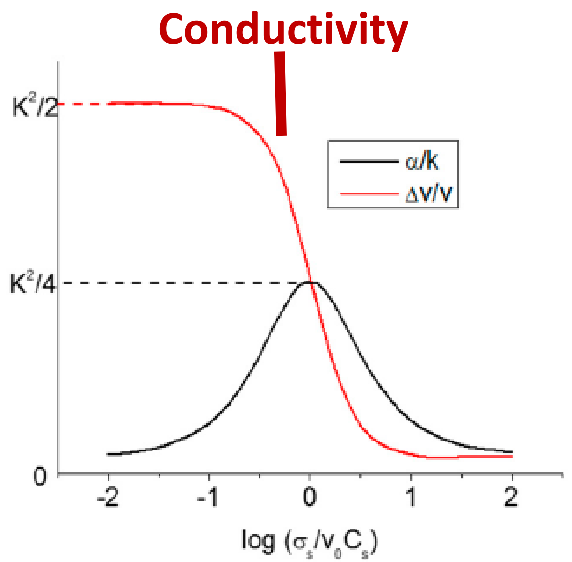
Table 1. Some common piezoelectric materials for SAW chemical sensors. An (*) is for a SAW other than Rayleigh mode and a (†) is for a measured velocity.

Substrate Material	Reported SAW Velocity (m/s)	K^2 (%)	TCF (ppm/C)	ε	T_{max} (C)
ST-X Quartz	3159.3 [30]	0.11	0	3.7	573
Y-Z $LiNbO_3$	3487.7 [30]	4.80	94		
128Y-X $LiNbO_3$	3992 [43]	5.6	75	83	1150
64Y-X $LiNbO_3$	4742.5 * [54]	11.3	80		
Y-Z $LiTaO_3$	3230 * [42]	0.74	35		
X-112Y $LiTaO_3$	3301 * [45]	0.64	18	52	665
(0, 138.5, 26.8) $La_3Ga_5SiO_{14}$	2734 † [44]	0.34	~0	18	1470
(0001) AlN	5607 [55]	0.30	19	8.5	2200
(001)-<110> GaAs	2864 [52]	0.07	35	12.9	
ZnO	2645 [47]	1.8	15	10	1170



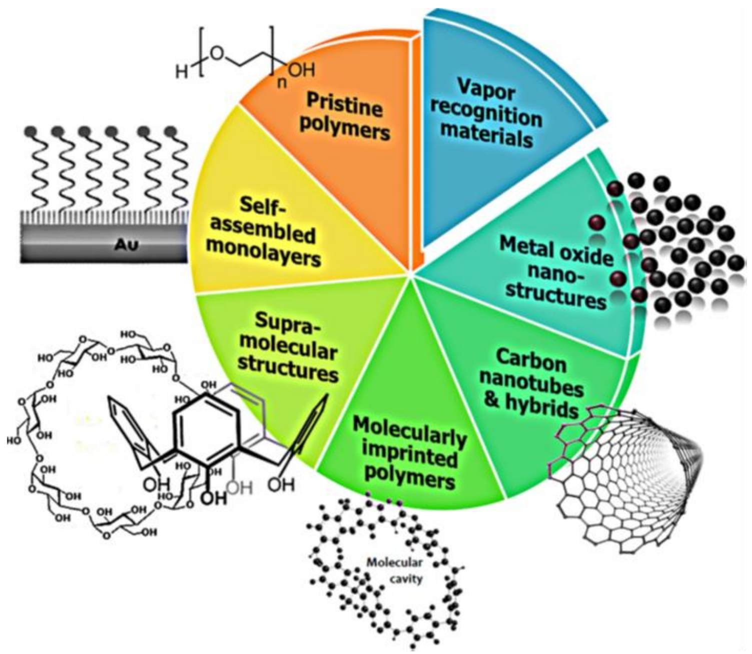
Delay Line SAW Devices





Materials for Methane and In-Pipe Gas Sensing

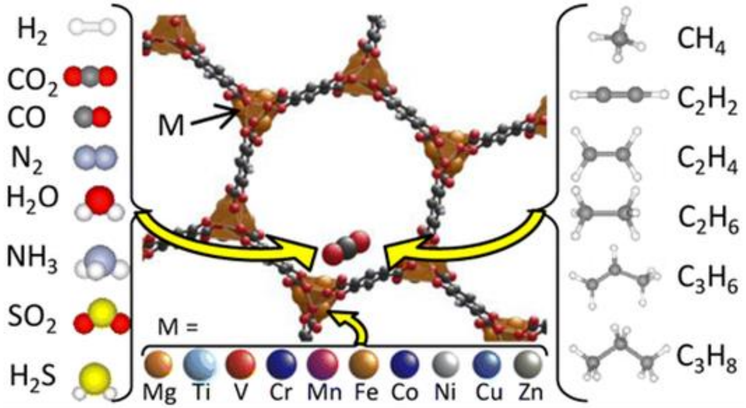
Popular vapor sensing materials for acoustic devices



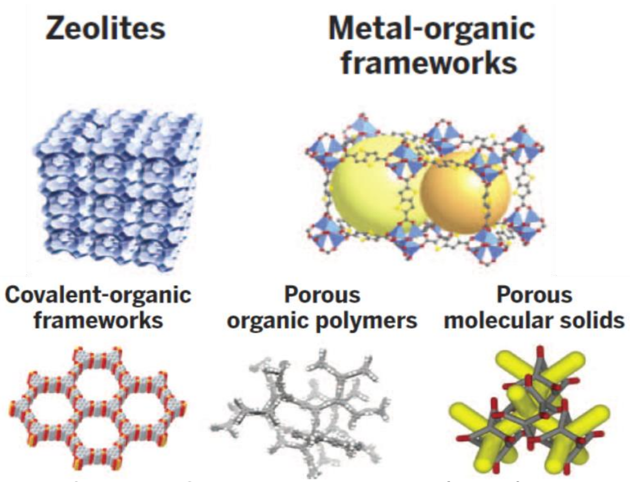
Afzal et al., Anal. Chim. Acta 787 (2013) 36–49

- Metal oxides, semiconductors
- Metals
- Polymers
- Graphene, carbon nanotubes
- Composite/hybrid materials

Porous materials?



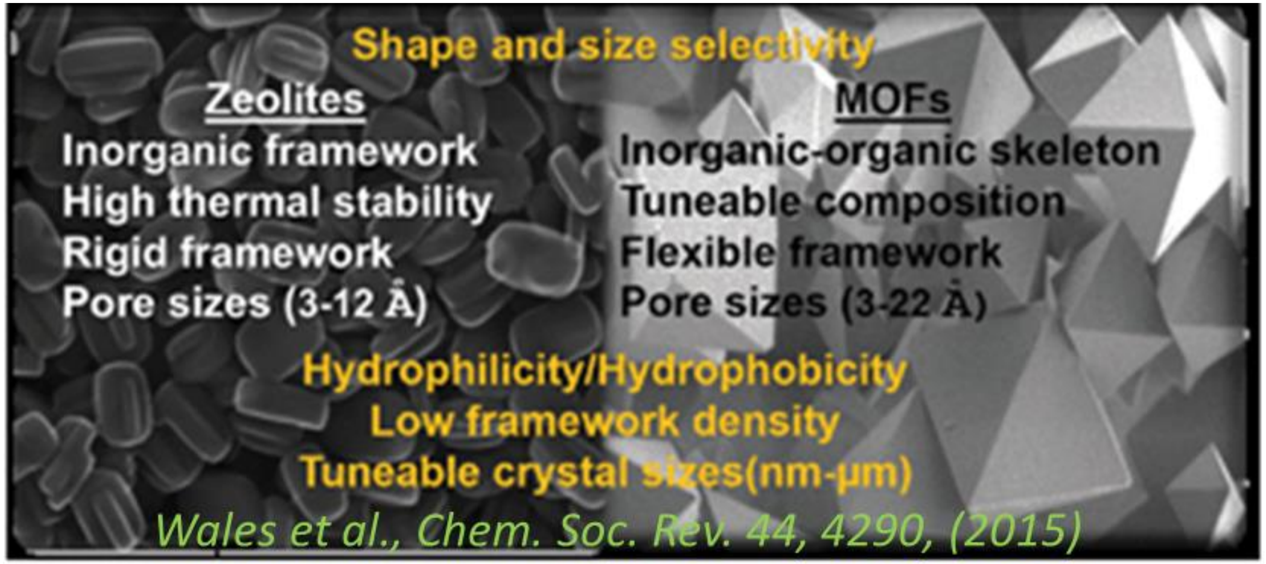
Lee et al., Chem. Mater. 27, 668, (2015)

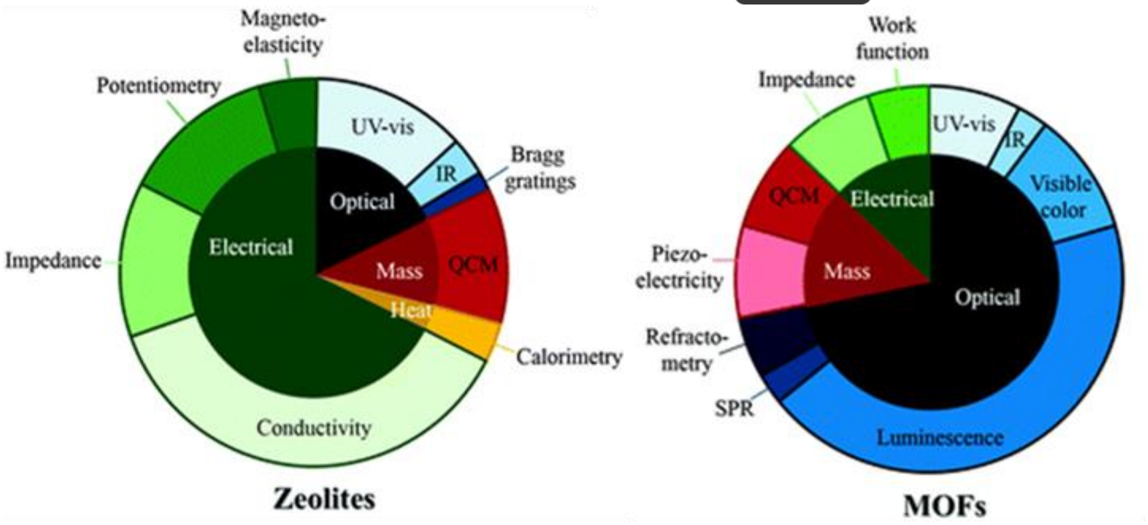


Slater et al., Sci. 348, aaa8075 (2015)

- **Key component for sensor's performance**
- Interaction with analytes: physisorption/chemisorption (rate, reversibility, strength, selectivity)
- Coupling with transducers: adhesion and other interfacial properties

Integrating Porous Materials w/ Functional Devices





Wales et al., Chem. Soc. Rev. 44, 4290, (2015)

Can these materials be integrated with functional devices?

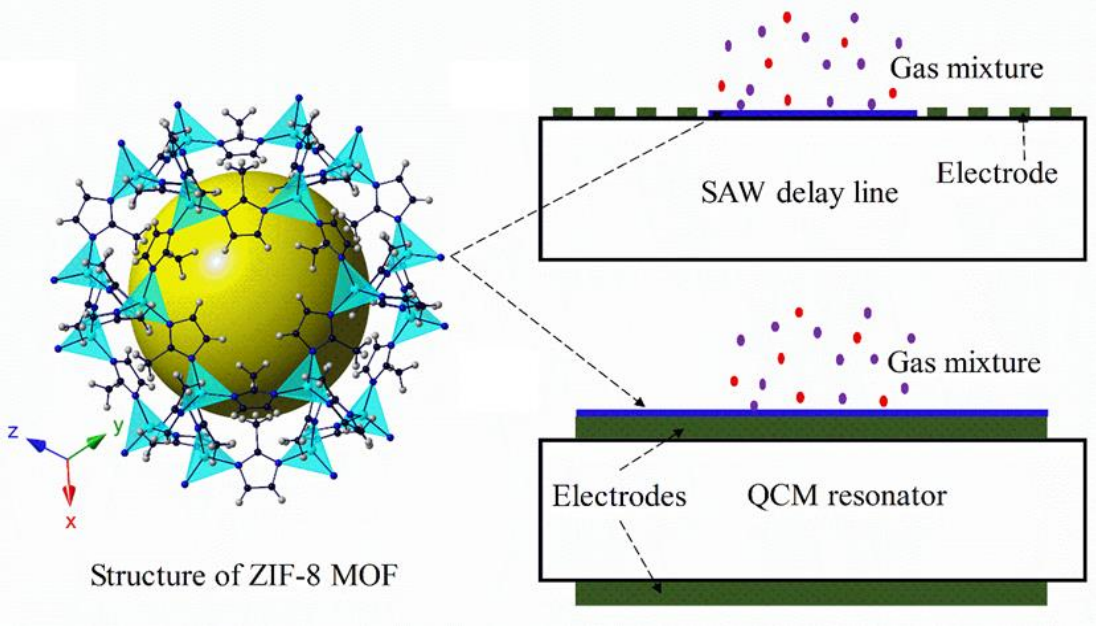
- ***Compatibility***: Growth of the materials suitable forms
- ***Methods***: Easy/Difficult? Fast/Slow?
- ***Quality***: Smooth/Rough? Mechanically adhesive?

- Thousands of MOFs and Zeolites are yet to be characterized.
- Integration with sensitive transducers can open up a possibility of developing robust sensors.

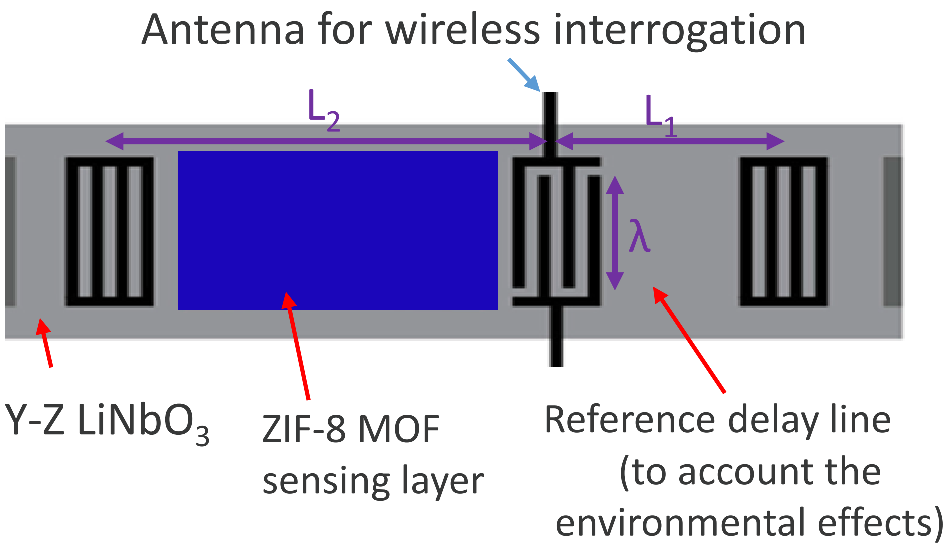
MOF-Coated SAW Devices

MOF sensing layers (Typical):
- Non-Conducting, stiff
- High gas adsorption capacity with tunable pores

Demonstrative Experiment:

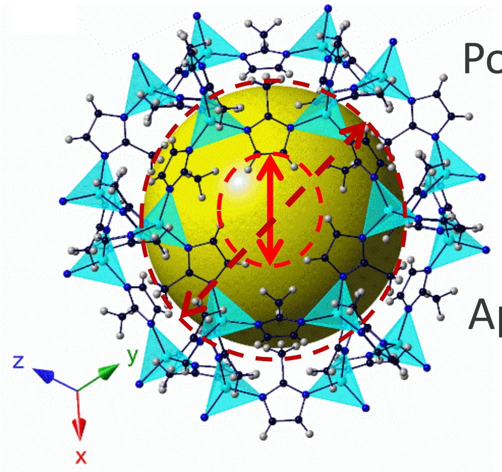


Mass loading plays dominant role: $\frac{\Delta v}{v_0} = -C_m f_0 h \left(\frac{\Delta m}{A}\right)$



SAW Device Specifications:
- One port delay line
- Center frequency: f_0 = 436 MHz
- Two channels: L_1 = 2.38 mm, L_2 = 3.08 mm
- Aperture: 780 µm
- IDT electrodes: Al (120 nm)
- Device Dimension: < 10 mm X 5 mm

Gas Adsorption Properties of ZIF-8

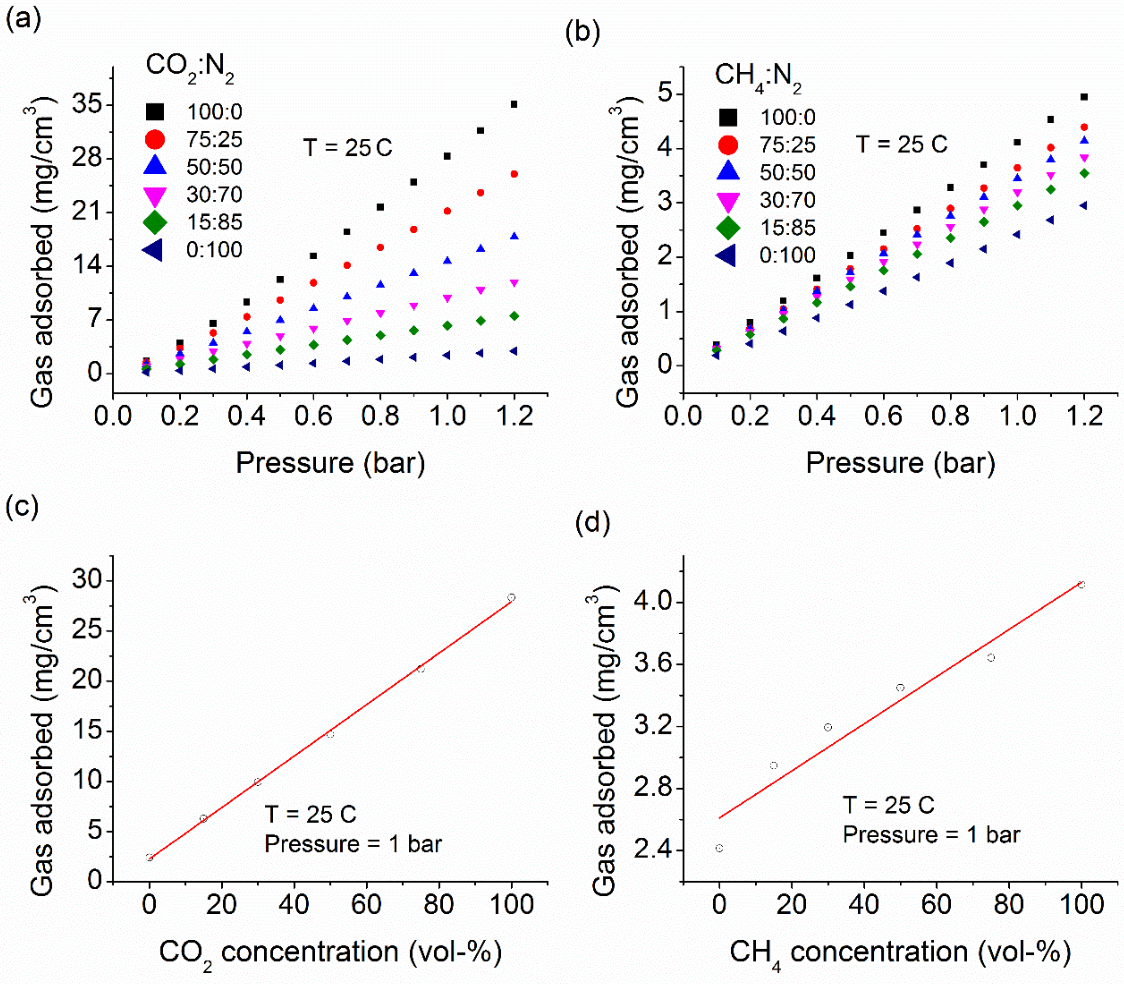


Pore size: ~ 11.6A

Aperture: ~ 3.4A

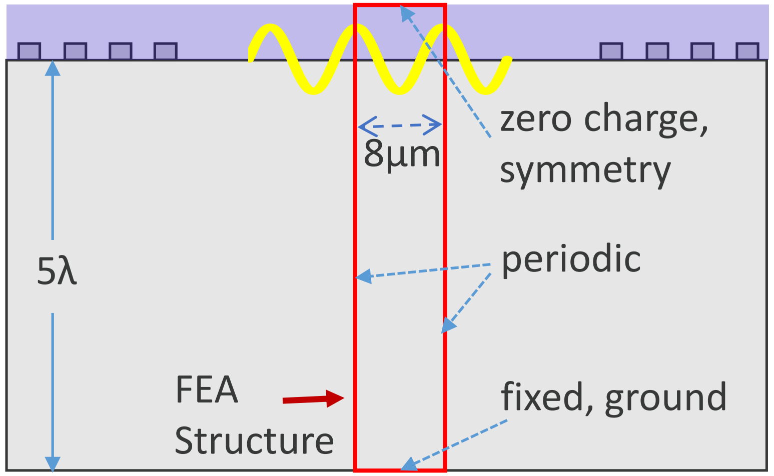
- Structural and gas adsorption properties are known
- Methods to grow as films are known
- Relatively hydrophobic and stable

Gas	Kinetic Diameter (Å)	Critical Temp. (°C)
CO_2	3.30	31.0
CH_4	3.80	-82.6
N_2	3.64	-140.9



Bulk gas adsorption isotherms measured by gravimetric methods

Finite Element Analysis of SAW Devices with ZIF-8 Layer

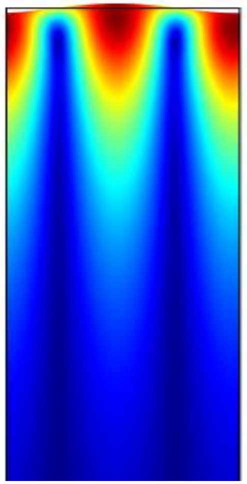


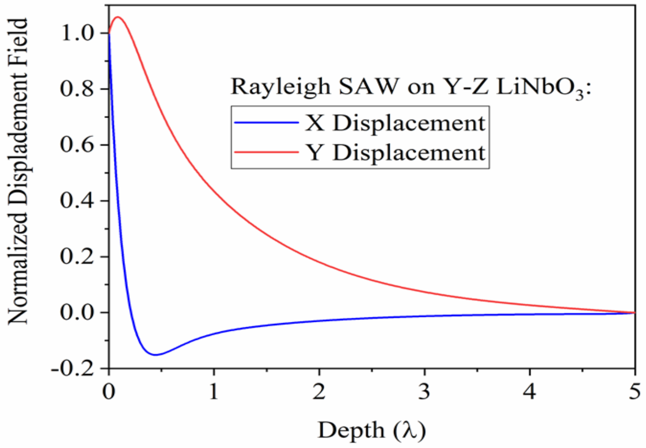
Predicted f_0 = 436.27 MHz

Y-Z LiNbO3:
SAW velocity = 3487.8 m/s
(parameters from COMSOL's inbuilt library)

ZIF-8 parameters from literature

Displacement on free surface





Predicted for a **200nm ZIF-8 Sensing Layer**

$$\frac{\Delta v}{v} = 189.3 \text{ X } 10^{-6}\ (CO_2)$$

$$\frac{\Delta v}{v} = 25.6 \text{ X } 10^{-6}\ (CH_4)$$

Modeling gas sensing response:

- The ZIF-8 mass density change upon gas adsorption was modeled as

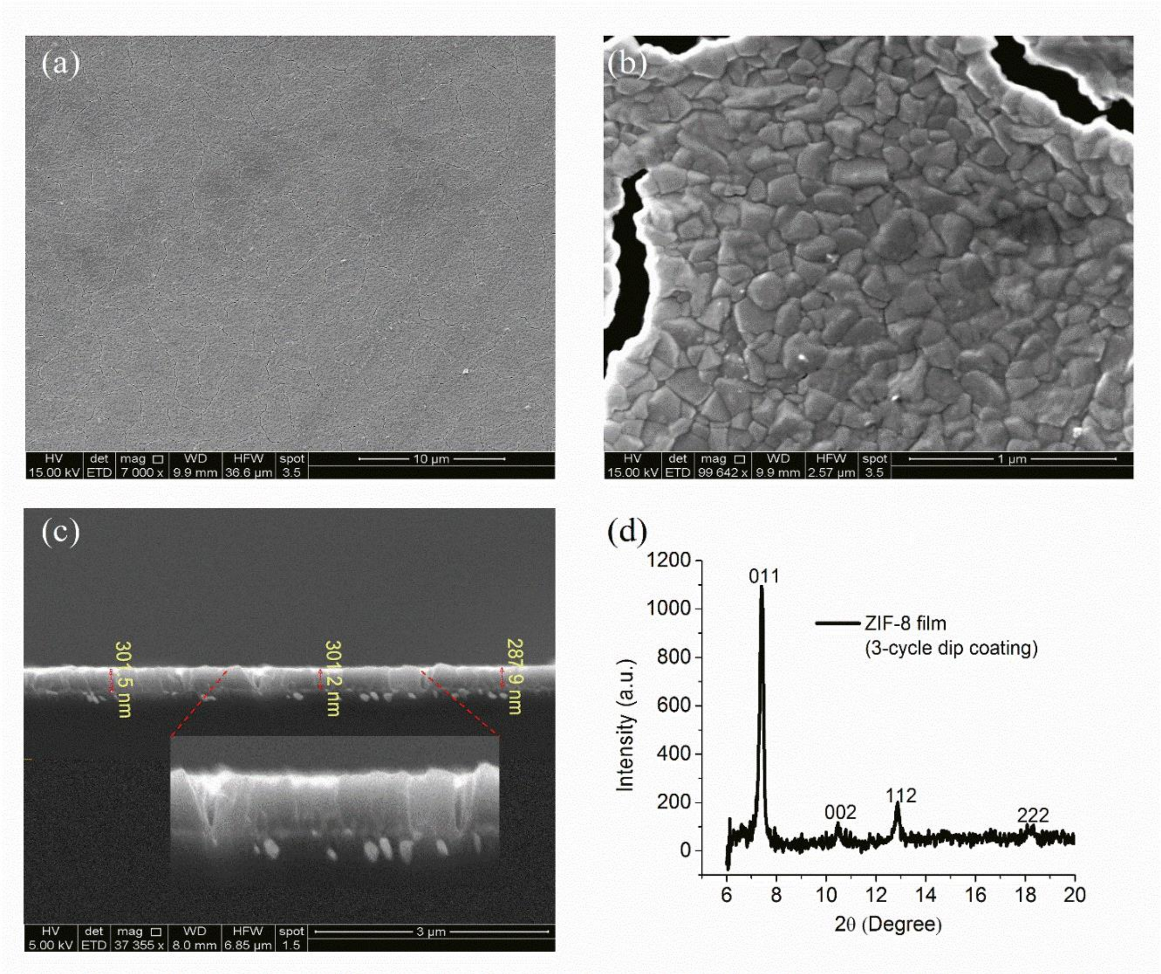
$$\rho_{net} = \rho + \Delta\rho = \rho + \boldsymbol{K}C_v$$

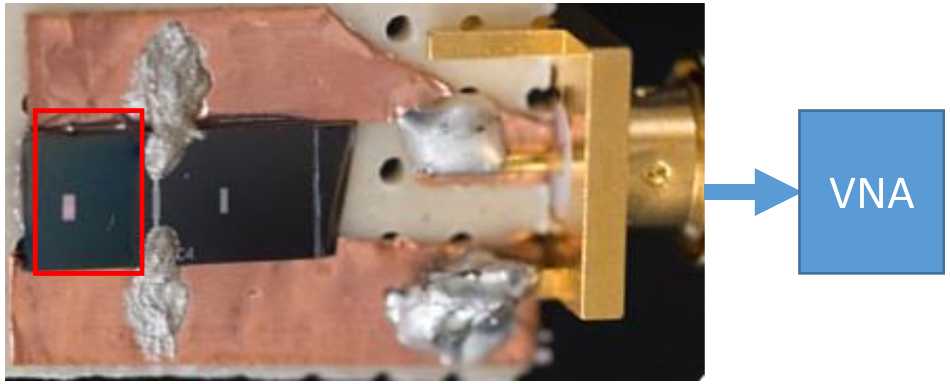
- Dimensionless Henry's constant as the partition coefficient $\boldsymbol{K} = \frac{C_s}{C_v}$.

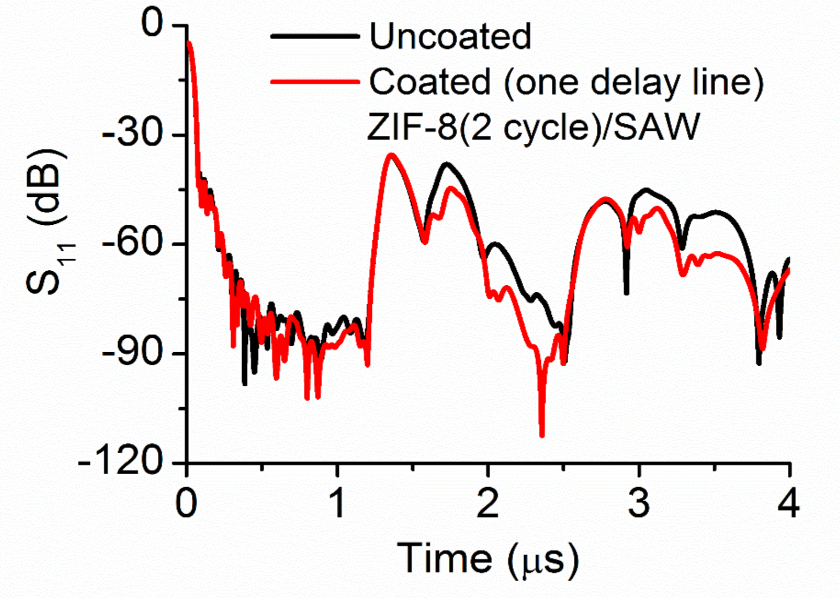
From Bulk Isotherms

Integration of ZIF-8 with SAW/QCM Devices

One cycle dip coating produces ~100 nm thick ZIF-8 layer

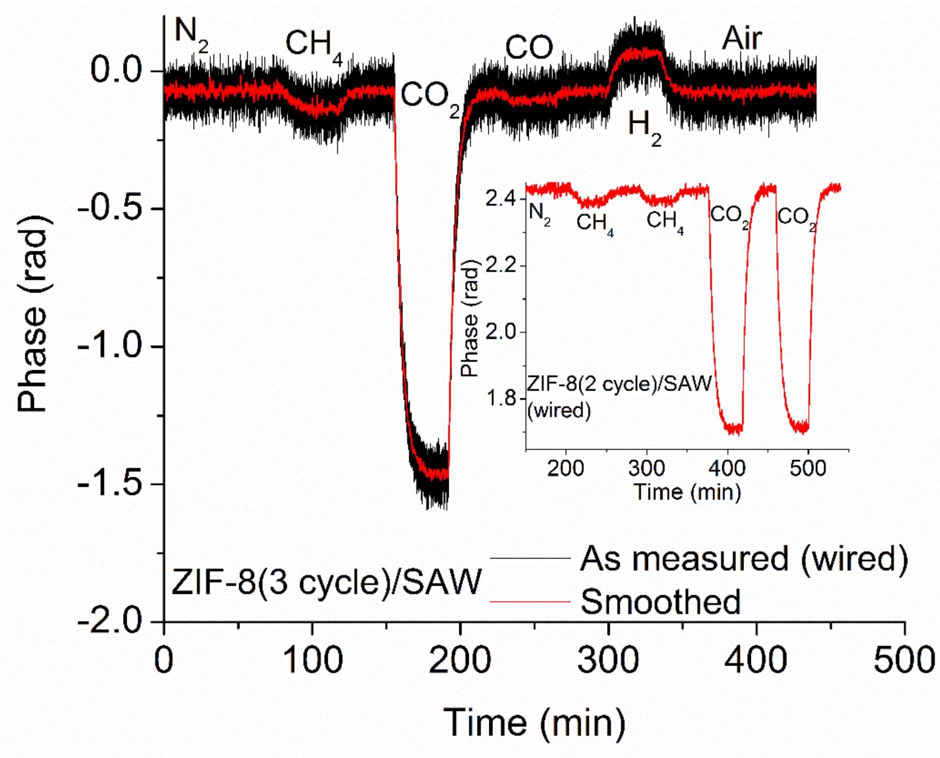






SAW delay line coated with 200-nm thick ZIF-8

Response of ZIF-8-Coated SAW Delay Line to Gases

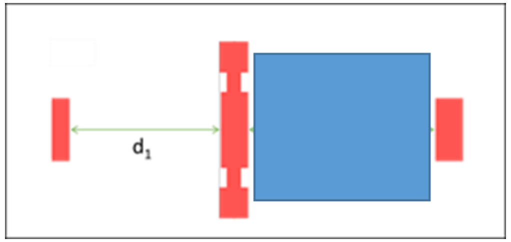


- **Distinct response to various gases with good reversibility and repeatability.**
- Response determined by the adsorption potential and molecular weight of the gases.
- Response to lighter H_2 molecules in opposite direction.

Predicted for a **200nm ZIF-8 Sensing Layer**

$$\frac{\Delta v}{v} = 189.3 \text{ X } 10^{-6} \ (CO_2)$$

$$\frac{\Delta v}{v} = 25.6 \text{ X } 10^{-6} \ (CH_4)$$



Specifications:

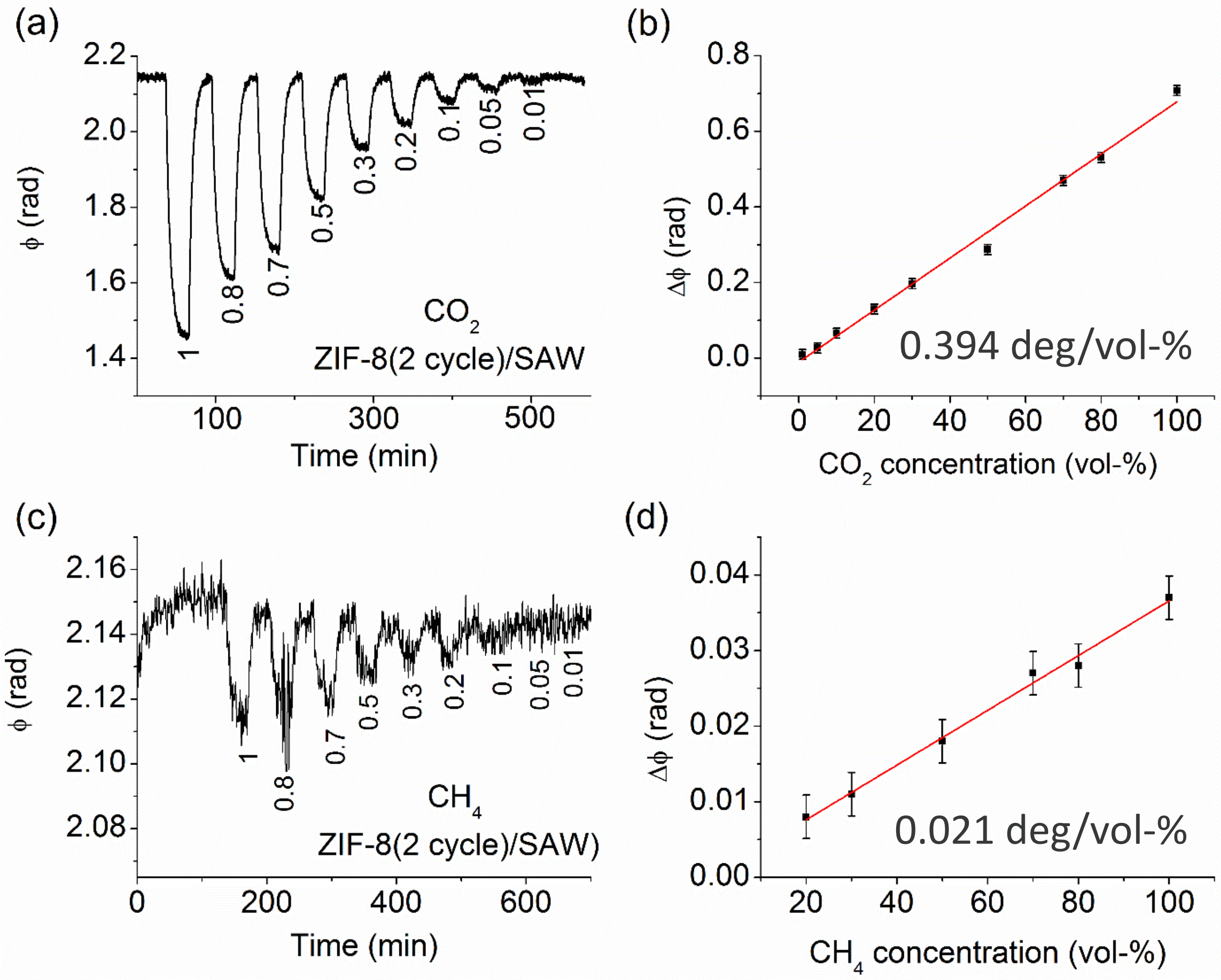
- One port delay line
- Center frequency, f_0 = 431.4 MHz
- Active area: 2.464 mm^2
- **Wired measurement**

Experimental for a **200nm ZIF-8 Sensing Layer**

$$\frac{\Delta v}{v} = 152.66 \text{ X } 10^{-6} \ (CO_2)$$

$$\frac{\Delta v}{v} = 8.48 \text{ X } 10^{-6} \ (CH_4)$$

ZIF-8 SAW Delay Line for CO_2 and CH_4



- **SAW sensor output**
  CO_2:CH_4 ratio ~18
- **Gravimetric isotherm**
  CO_2:CH_4 uptake : ~17

Mass uptake (mg/cm^3-vol-%)

Technique	CO_2	CH_4
Gravimetric	0.257	0.015
QCM	0.595	0.025
SAW	0.304	0.016

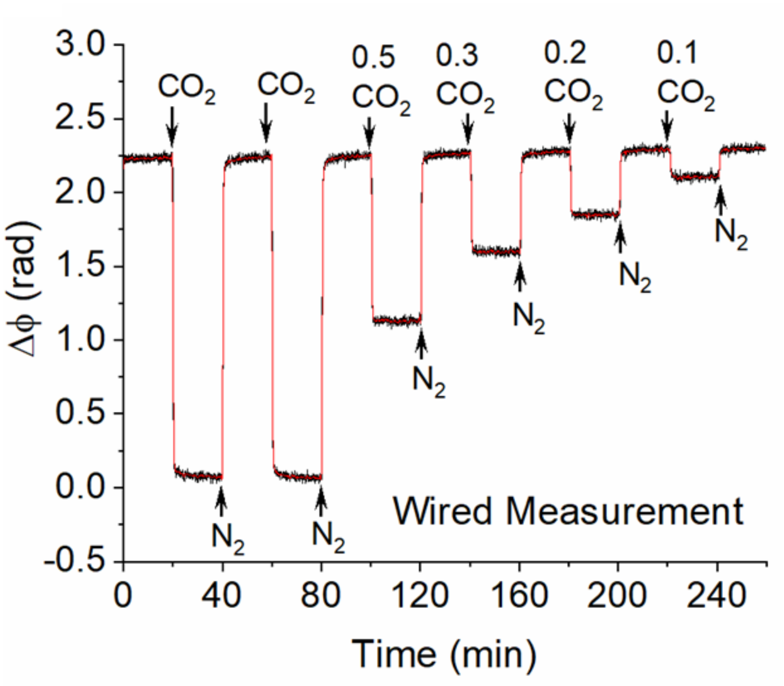
SAW

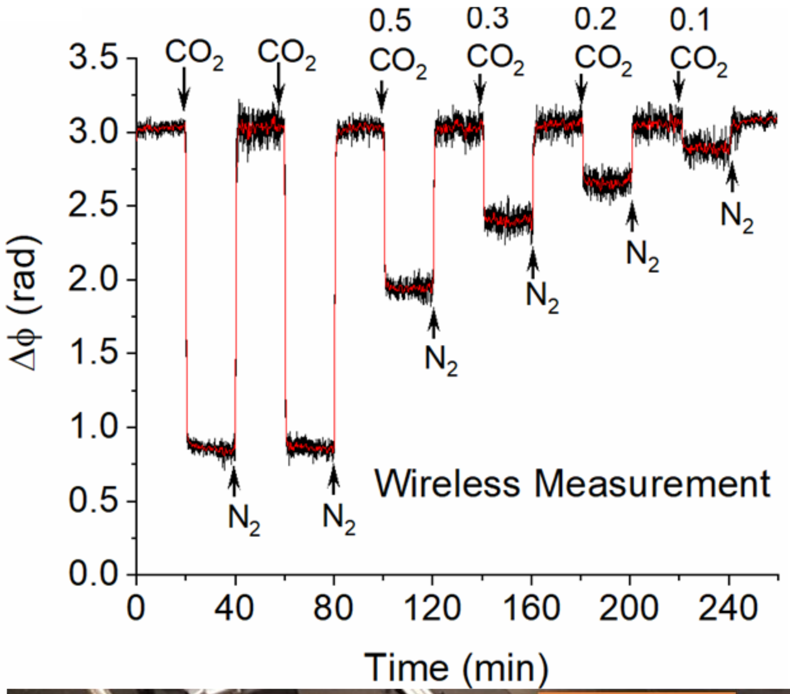
$$\frac{\Delta v}{v_0} = -c_m f_0 \left(\frac{\Delta m}{A}\right)$$

QCM

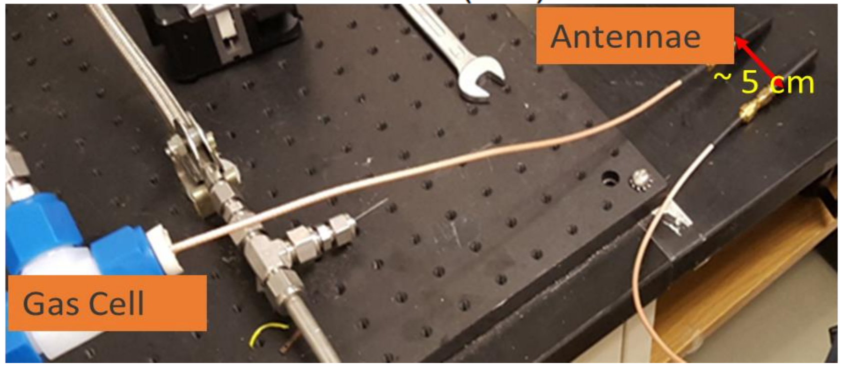
$$\frac{\Delta f}{f_0} = -\frac{2}{\sqrt{\rho\mu}} f_0 \left(\frac{\Delta m}{A}\right)$$

Wireless SAW with ZIF-8 Layer for CO_2

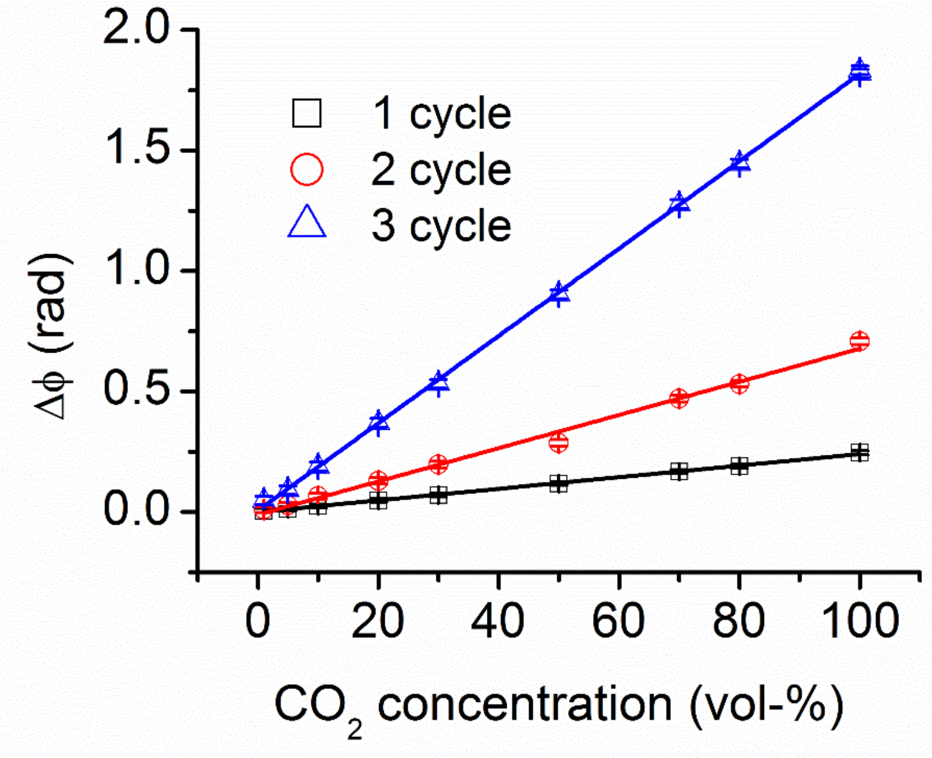


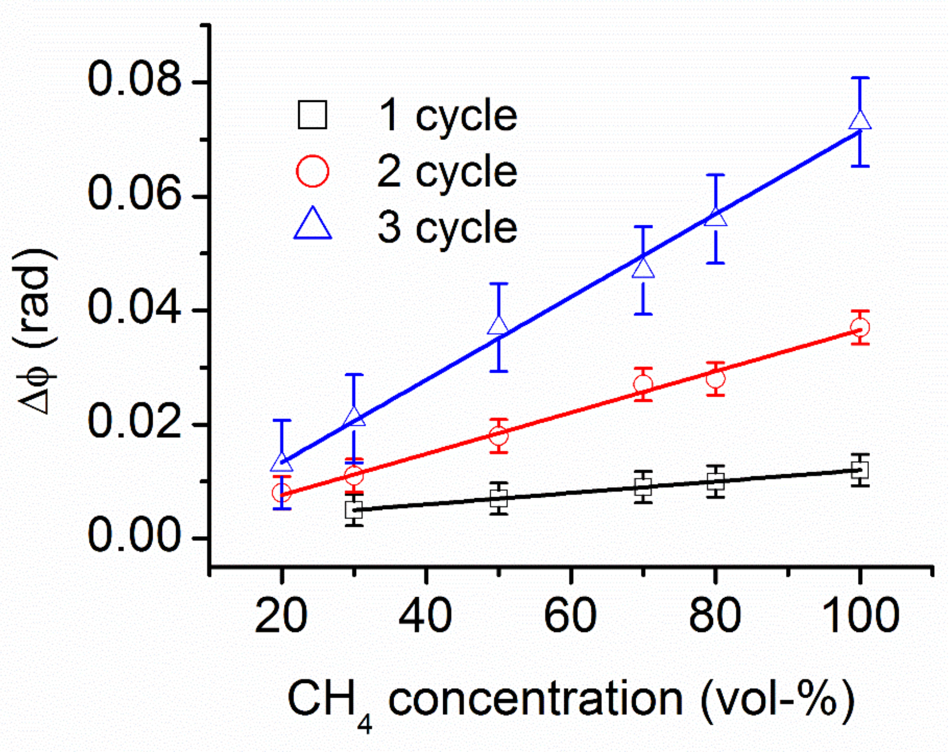


Response of a 500 nm thick ZIF-8 film coated SAW sensor to CO_2 via wired and wireless measurements



Effect of Sensing Layer Thickness





- 1 cycle ZIF-8 ≡ 100 nm
- Sensor sensitivity increased with ZIF-8 film thickness.
  (Sensitivity to CO2: 0.14 deg/vol-% 100 nm, 1.26 deg/vol-% 500 nm)

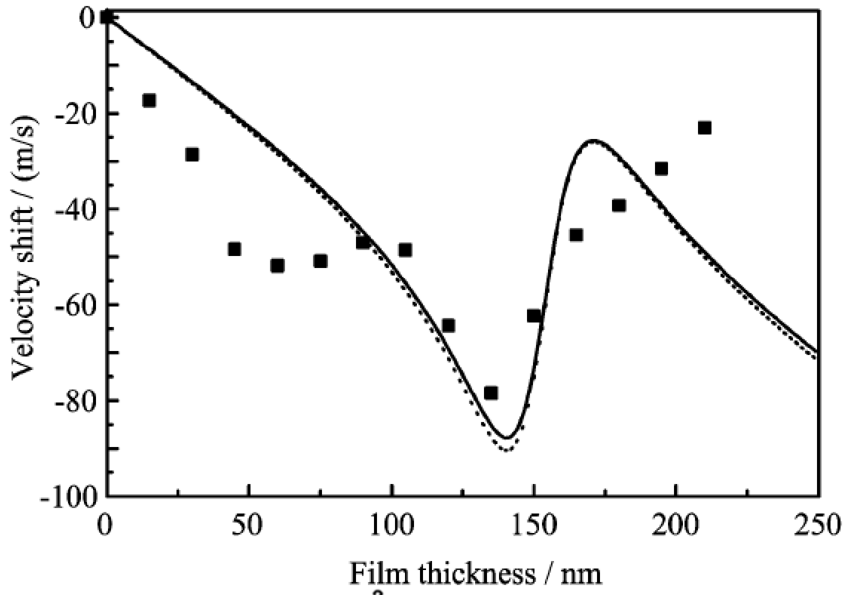
- **Can we increase sensitivity indefinitely by increasing thickness?**

Devkota, Ohodnicki et al., Nanoscale 2018, 10 (17), 8075 - 8087

SAW Dependence on Sensing Layer Thickness

“Rubbery” Polymer Sensing Layer

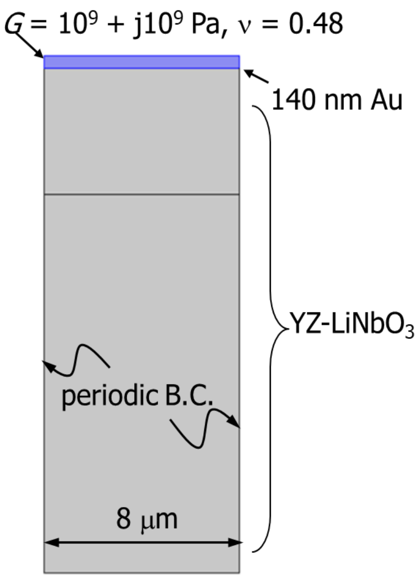
Analytic Solution

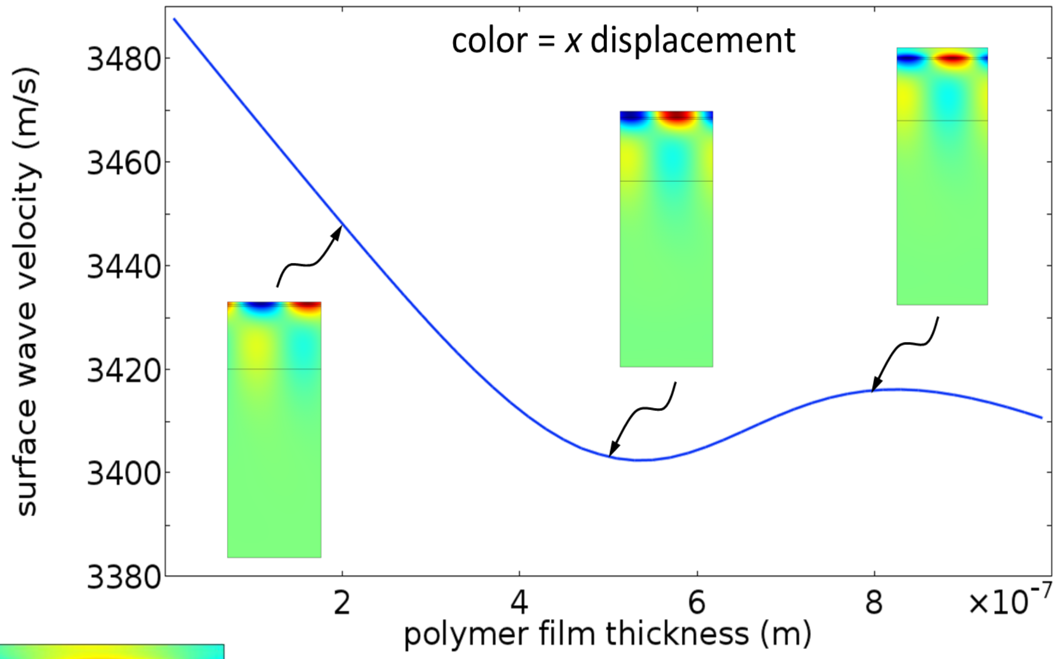


$$\frac{\Delta\gamma}{k_0} = \frac{\Delta a}{k_0} - j\frac{\Delta V}{V} = j\sum_{i}^{3} c_i' \frac{\alpha_i M^i}{\omega} \tan[\alpha_i(h_1 - h)]$$

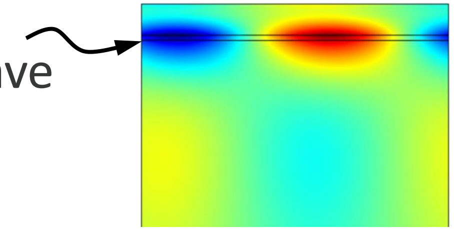
Wen Wang, Shi-tang He, Yong Pan, Chinese J. Chem. Phys. 19 47-53 (2006).

Finite Element Modeling





Transverse wave in polymer

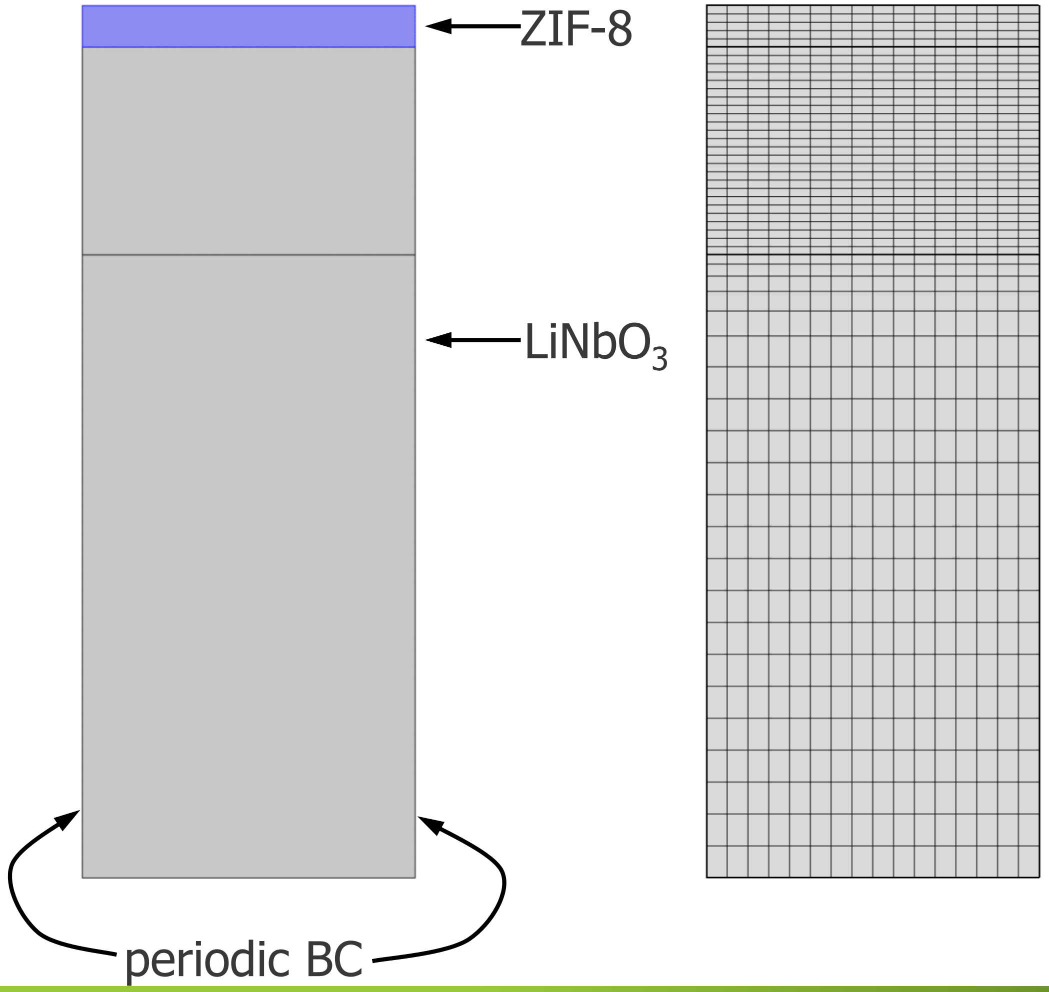


0.8 µm sensing layer

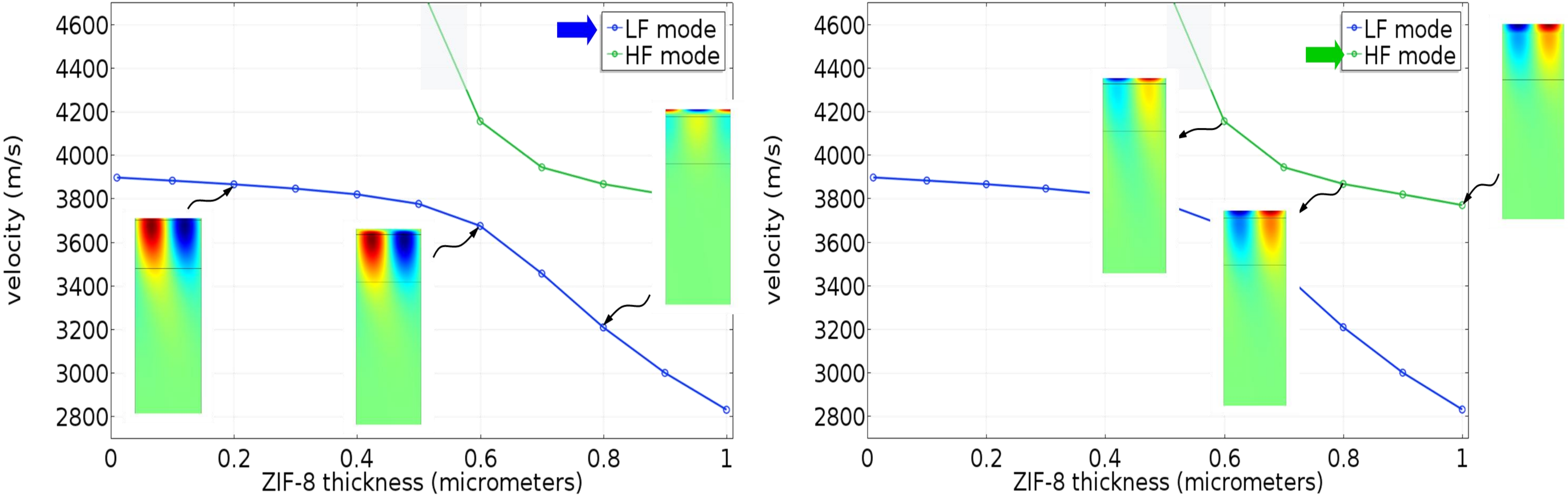
Simulation with Thicker ZIF-8 Sensing Layer

- simulated using COMSOL 5.3a
- eigenmode simulation
- coupled solid (piezo) mechanics and electrostatics
- YZ-$LiNBO_3$
- varying ZIF-8 thickness
  - E = 3 GPa
  - ν = 0.4
  - ρ = 950 kg/m^3

Note: Elastic properties of MOF-based materials are not well characterized in the literature



Two Surface Wave Modes in Thicker Films

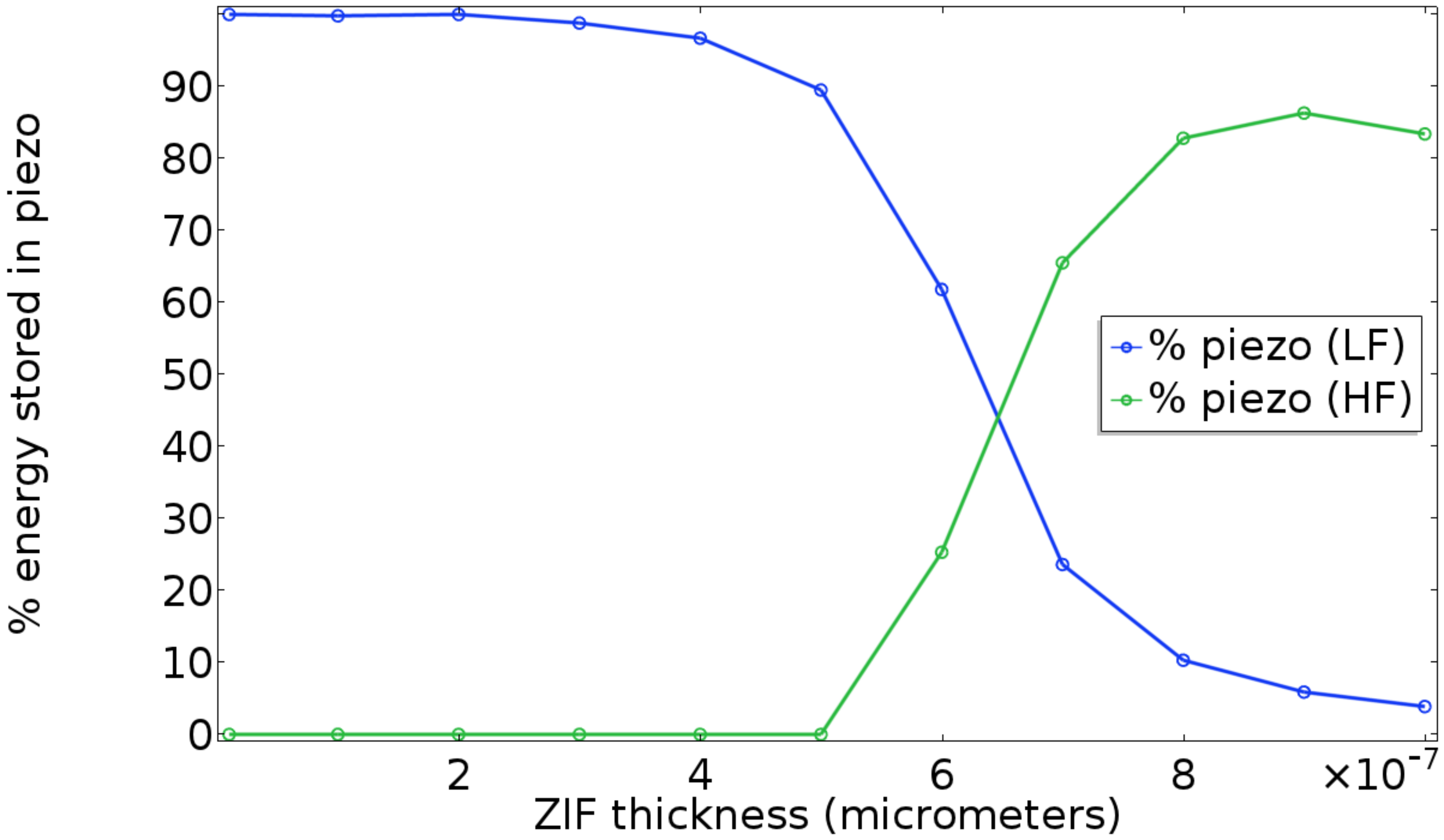


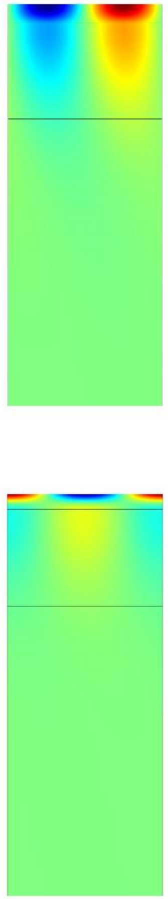
color = *y* displacement

Beyond ~0.5 Microns New Propagation Modes Become Possible

High Frequency Mode → Greater Energy Storage and Propagation Within the Sensing Layer

Energy Stored in Piezoelectric Substrate

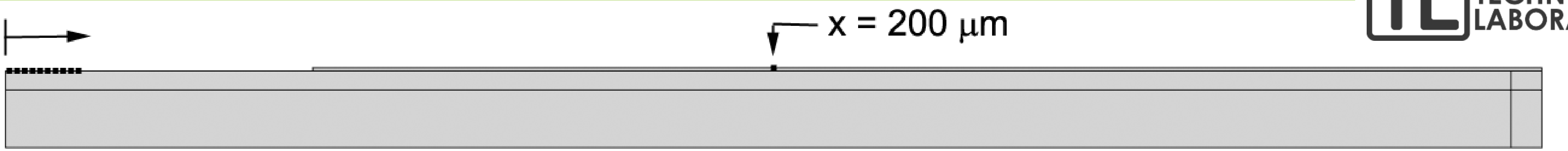


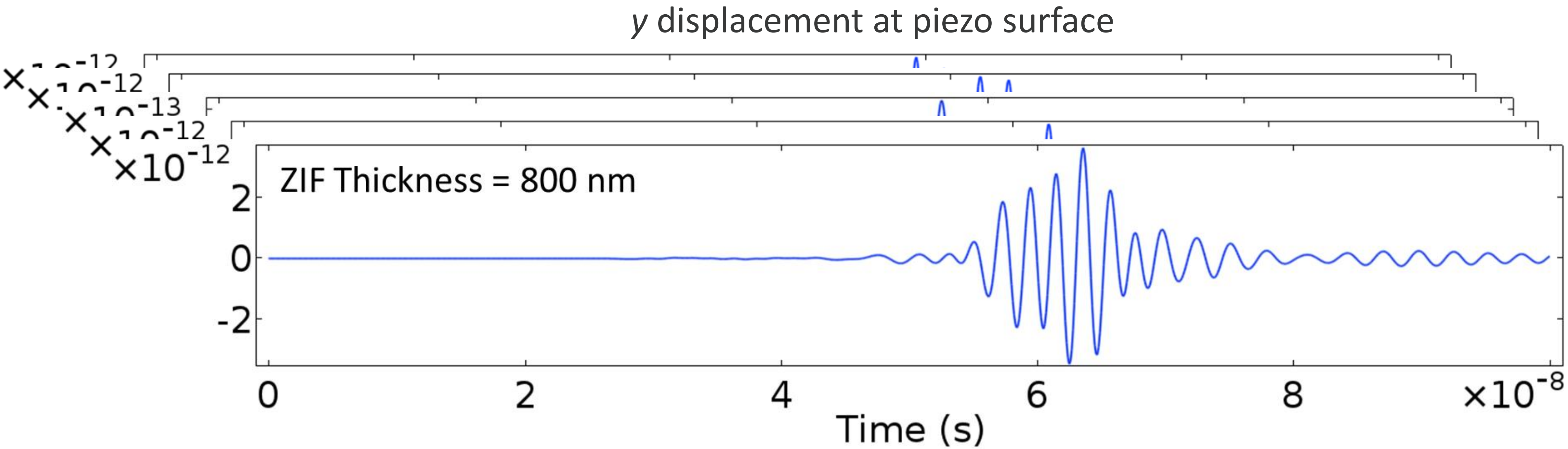


color =
y displacement

Greater Energy Propagation Within the Sensing Layer and Larger Displacements May Also Be More Sensitive to Surface Roughness and Film Quality (Under Investigation)

Pulse Propagation

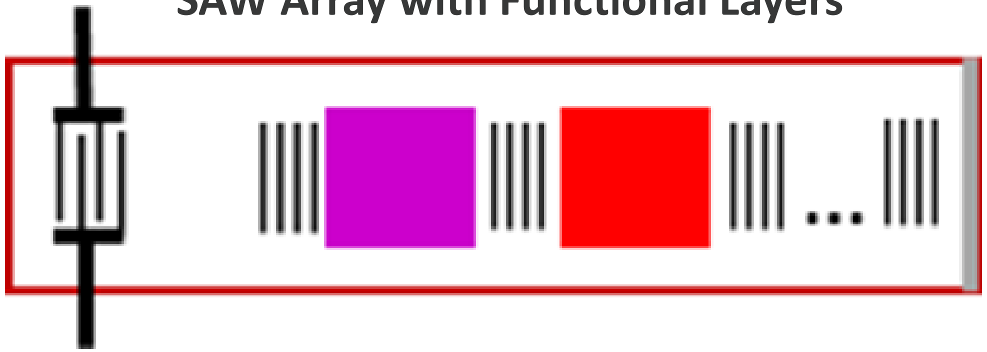




- Unusual behavior can be observed in SAW sensors for thicker sensing layers
- For ZIF-8, sensing layers thicker than ~0.5 μm begin to show complex behavior
- More detailed investigations are required, including for non-ideal film microstructure

SAW Sensor Array for Gas Components Analysis

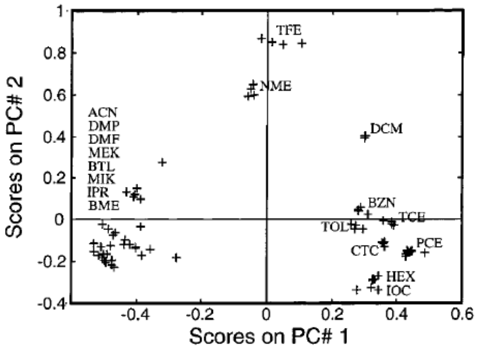
SAW Array with Functional Layers



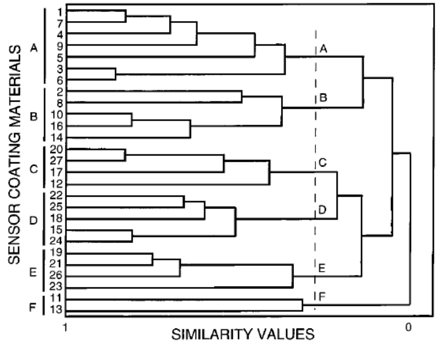
Data Analysis

Statistical and Neural Network Techniques

Principal Component Analysis

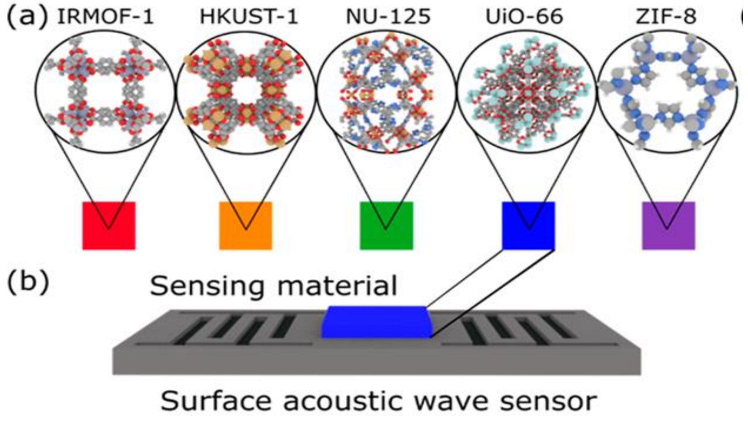


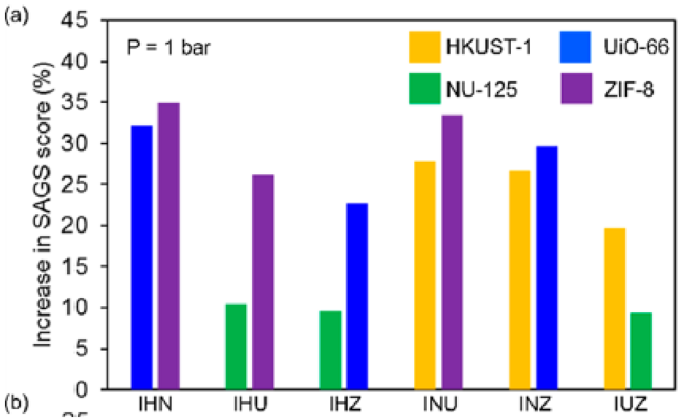
Cluster analysis



Grate, Chem. Rev. 2000, 100, 2627 – 2648

Computational Design of MOF arrays for Gas sensing (Grand Monte Carlo Simulation : RASPA Software)

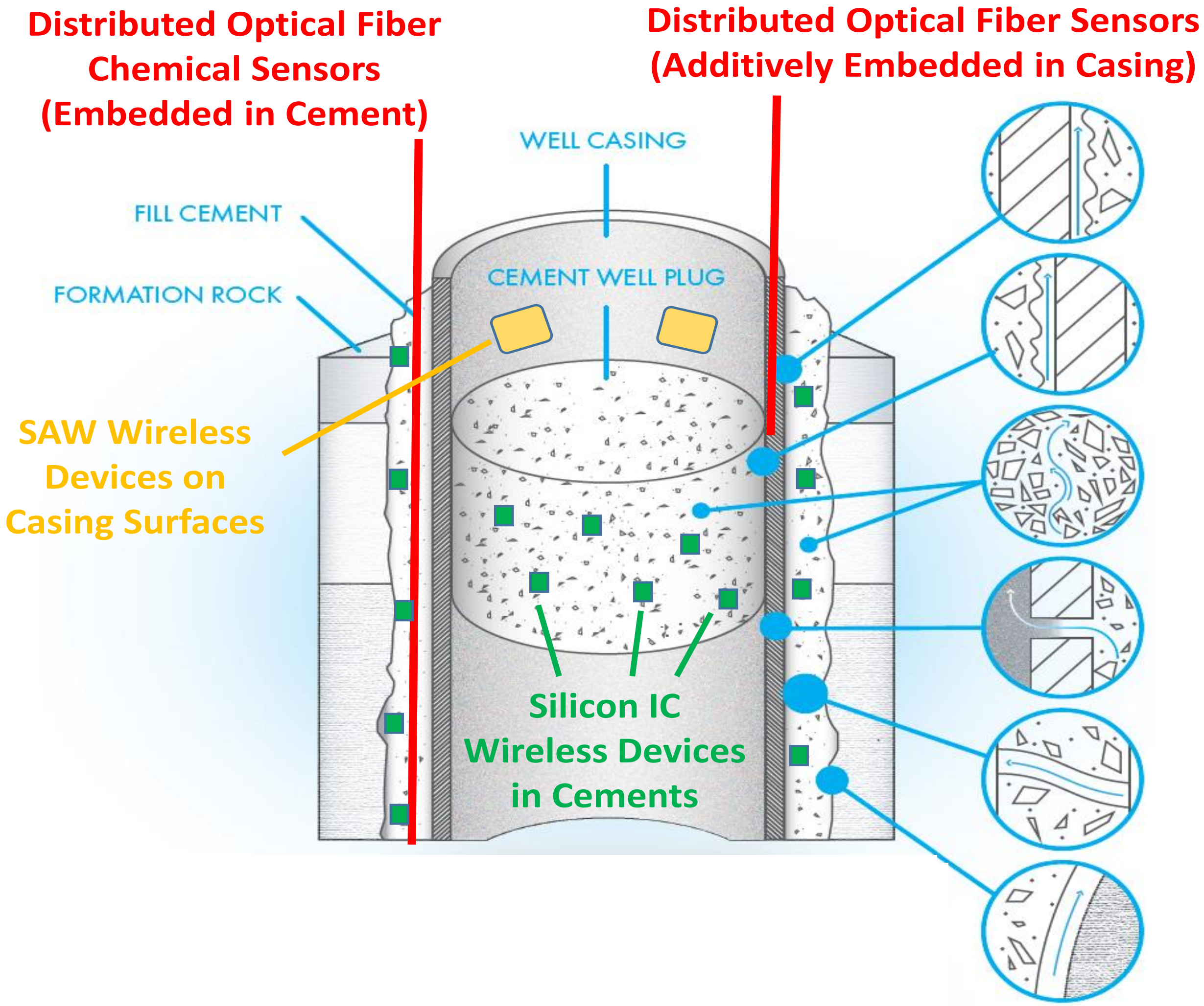




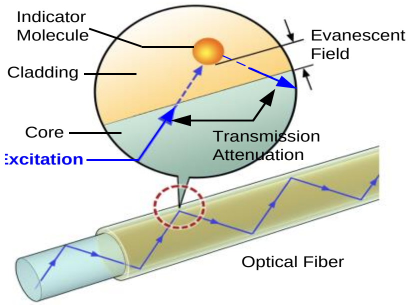
Percent increase in sensor performance score with addition of an MOF in an existing 3-MOF sensor array.

Gustafson and Wilmer, J. Phys. Chem. C 2017, 121, 6033- 6038

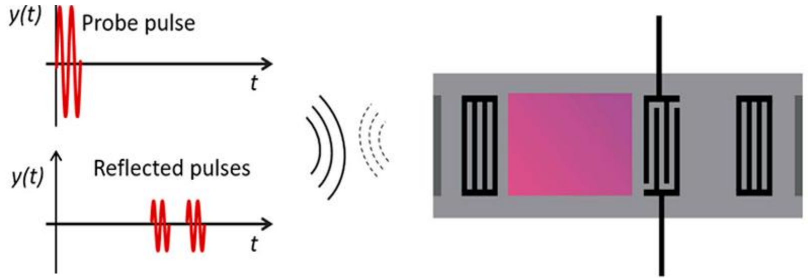
Wellbore Integrity Monitoring Sensor Technology

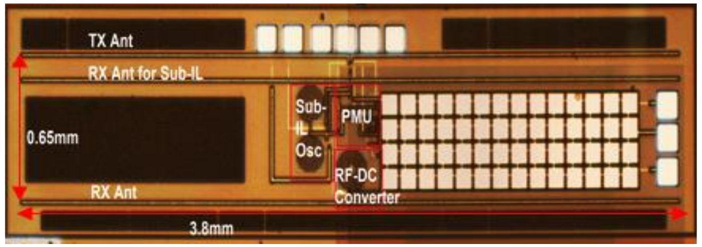


Fiber Optic Chemical Sensor



Functionalized Surface Acoustic Wave Sensor



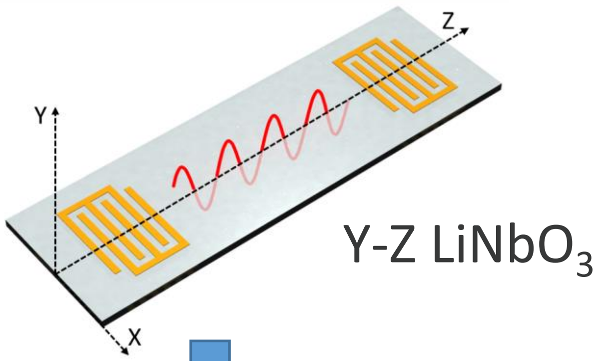


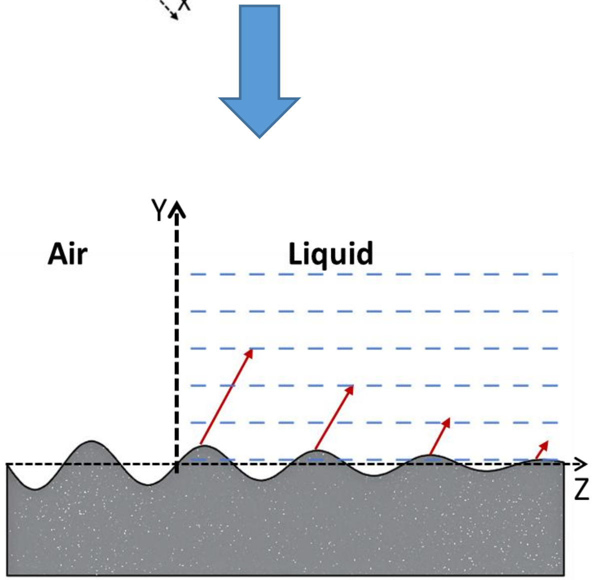
Silicon Integrated Circuit Sensor

A Suite of Well-Bore Sensing Technologies are Being Pursued For Carbon Storage Applications.

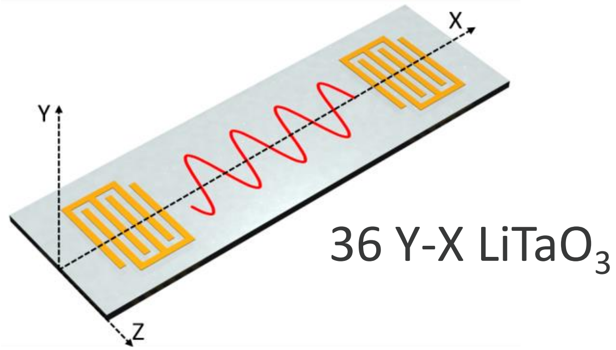
SAW Devices for Liquid Phase Applications

Rayleigh SAW



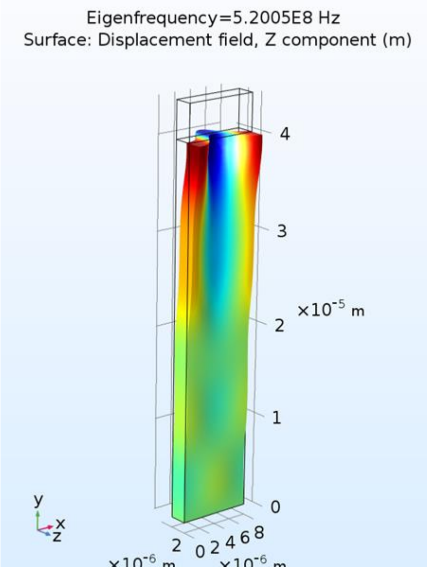


Shear Horizontal-SAW

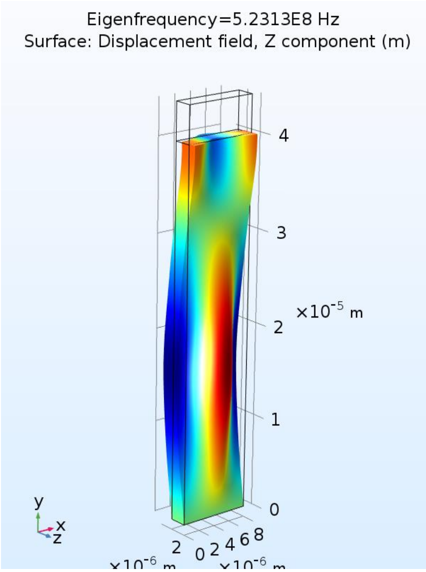


Specifications:

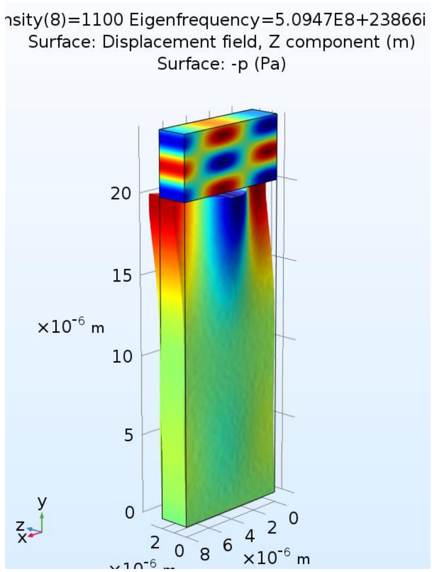
- One port delay line, two channels
- Center frequency: f_0 = 520 MHz
- Al IDT: aperture 780 µm, thickness 120 nm; width 2 µm; spacing 2 µm
- Device Dimension: < 10 mm X 5 mm



Leaky SH-SAW 4160 m/s

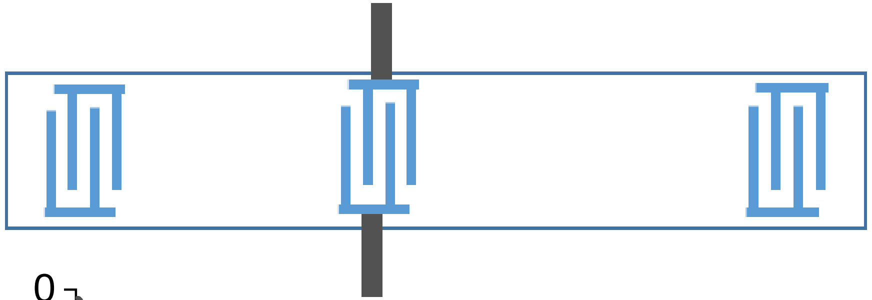


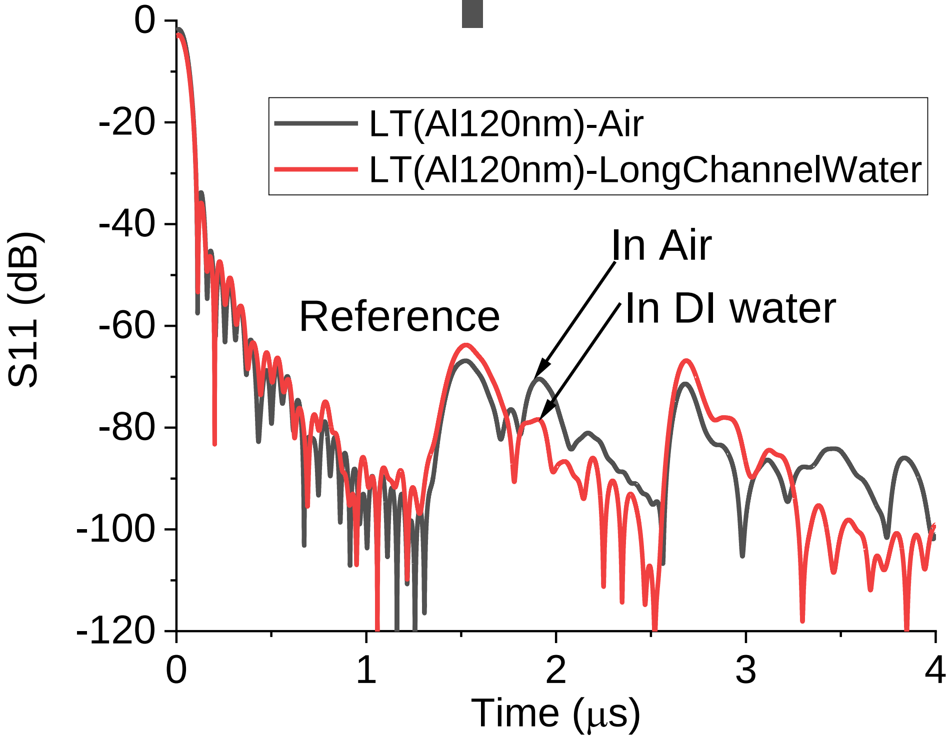
Surface-skimming bulk 4185 m/s



Surface wave on substrate in contact with water

Fabricated SH-SAW Devices





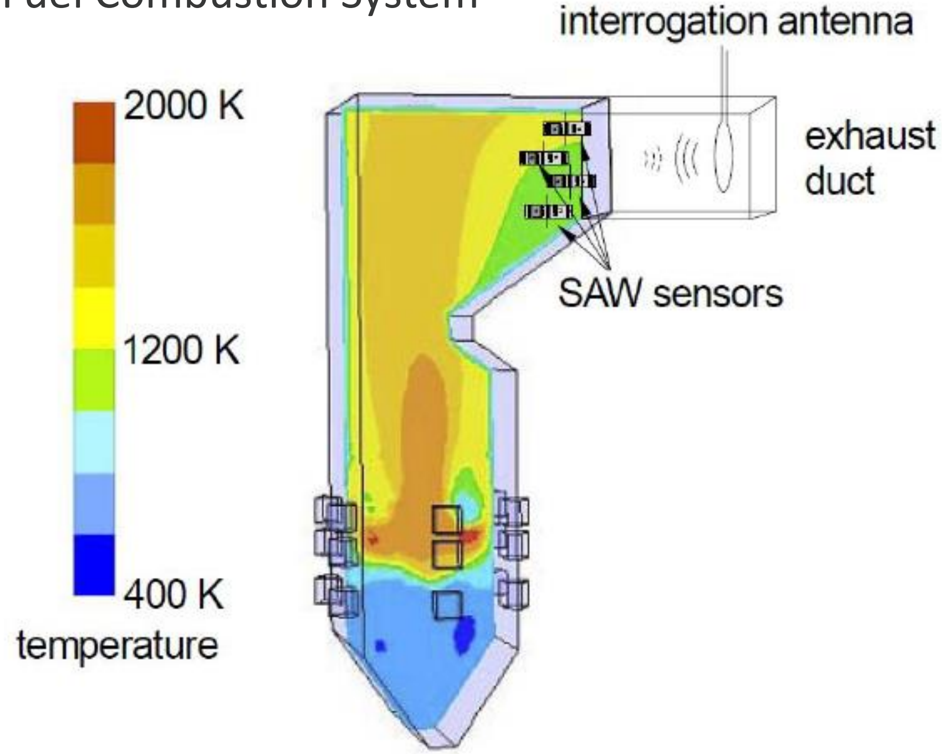
SAW Devices Compatible with Aqueous Sensing Are Being Functionalized for pH Sensing.

Harsh Environments Sensors for Power Generation

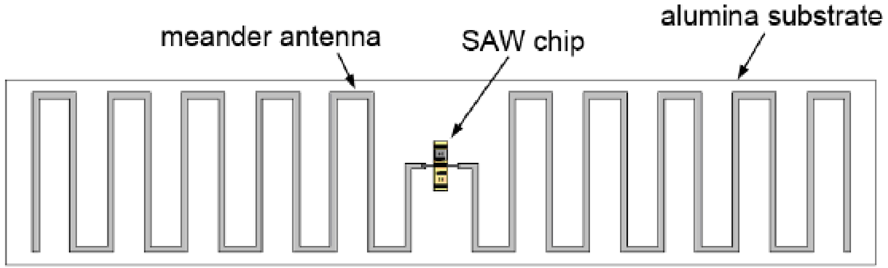
Power Generation (Combustion, Fuel Cells, Turbines, etc.)

	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

e.g. Oxy-Fuel Combustion System



Conceptual Design: SAW Gas Sensor For Harsh Environment



Greve, Ohodnicki et al., Sensors 2013, 13, 6910 - 6935

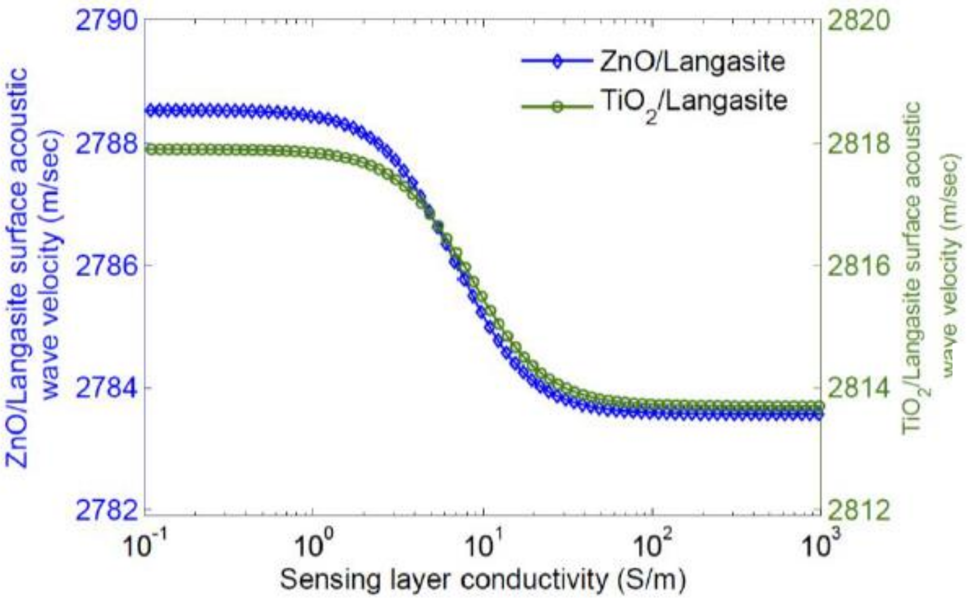
Oxygen Sensing at High Temperatures

NATIONAL ENERGY TECHNOLOGY LABORATORY

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]

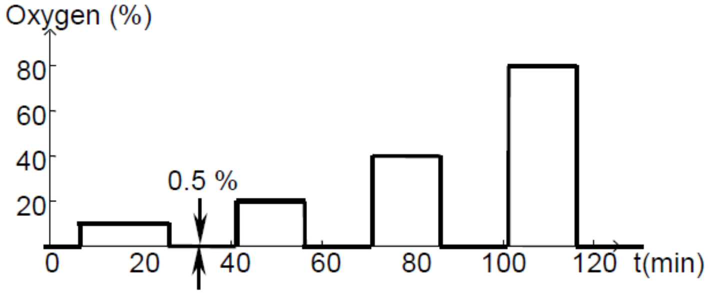
SAW devices with conducting sensing layers

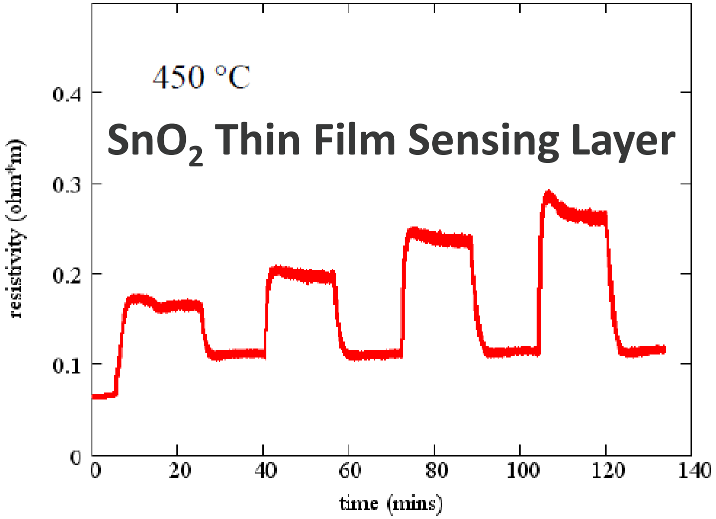


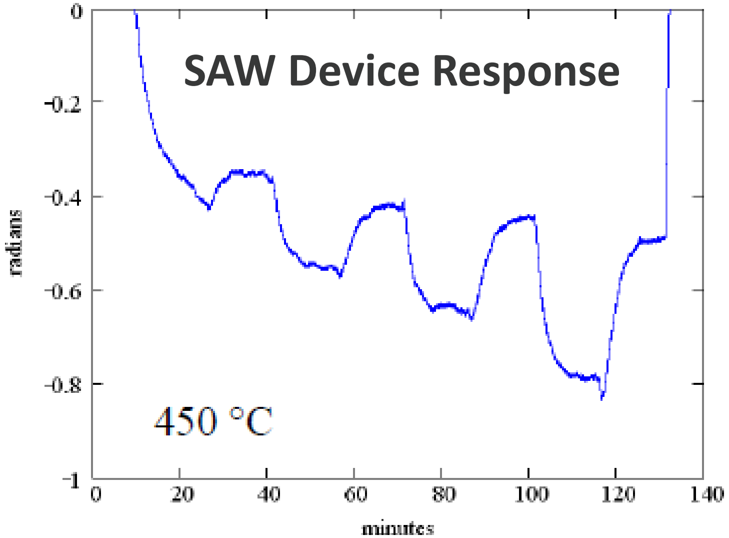
(Thickness = 100 nm)

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

Wired measurement of a SnO_2 (100 nm)/LGS SAW response to various concentrations of Oxygen



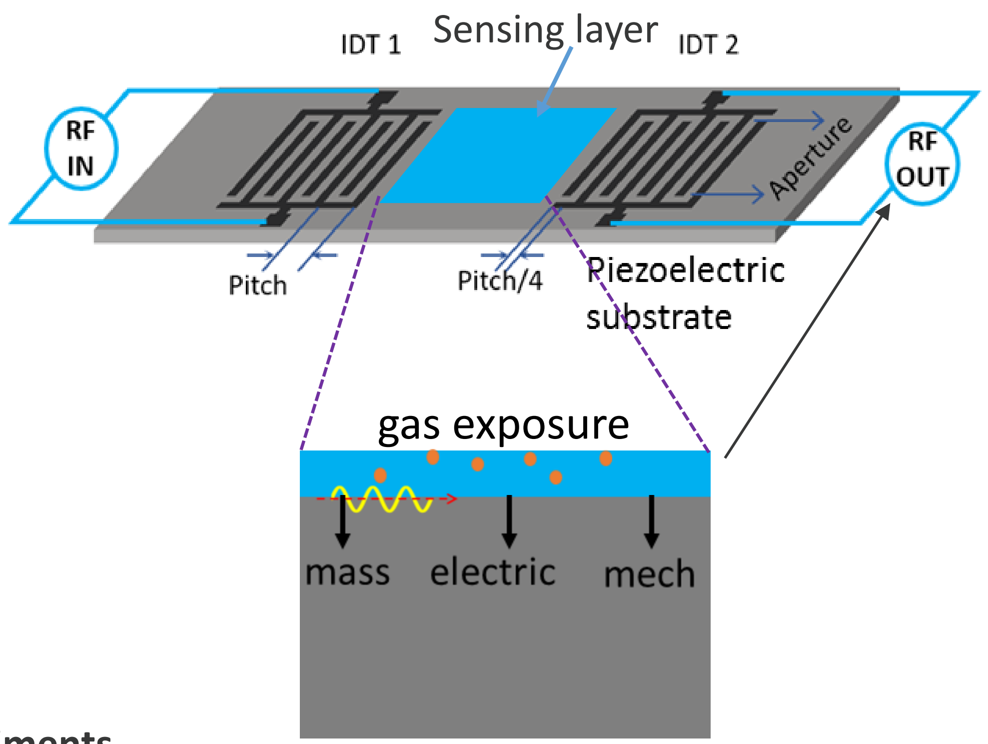




Key Take-Away Messages

- **NETL Has an Established Program on Sensor Technology Development Across the Fossil Energy Infrastructure**
  - **Oil & Gas (Emphasis Natural Gas Infrastructure)**
  - **Carbon Storage**
  - **Power Generation**

- **Surface Acoustic Wave Sensor Technology is Being Developed**
  - **Emphasis on Chemical Sensing**
  - **Integrated Sensing Layers**
  - **Device Design, Optimization, and Fabrication**
  - **Wireless Telemetry**



- **Key Accomplishments**
  - **Wireless CO_2 and CH_4 Sensing**
  - **Aqueous Phase SAW Devices Using SH-SAW**
  - **Simulated Wireless Telemetry Strategies to Be Confirmed with Experiments**
  - **Multi-Element Array Development Integrating Computational Chemistry**