High Surface Area Nanostructured Films for Surface Acoustic Wave (SAW) Sensors

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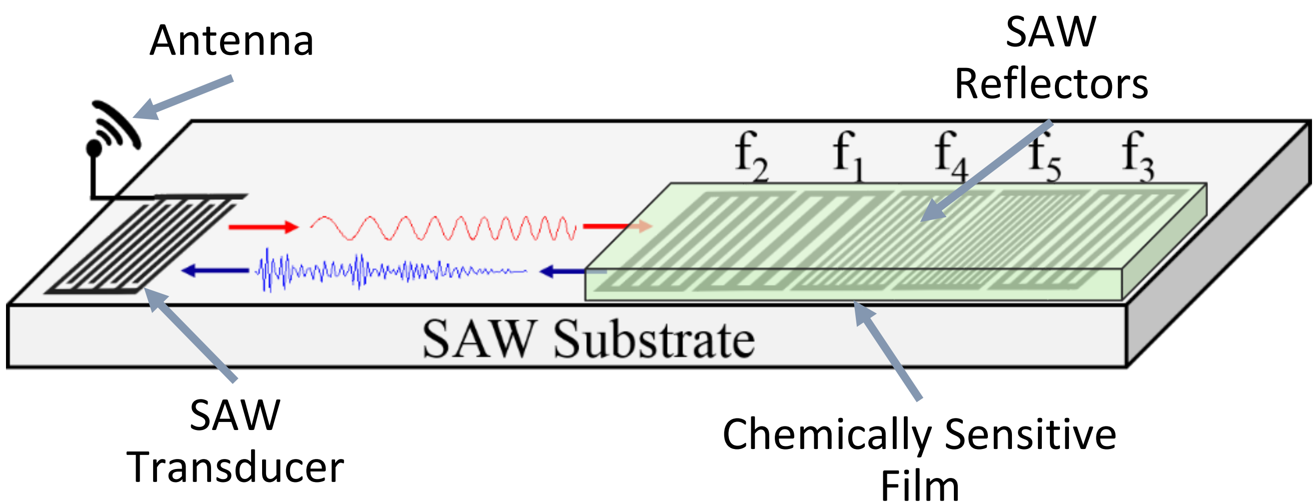
ORNL is managed by UT-Battelle, LLC
for the US Department of Energy

LDRD Program

SAW Sensor Background

- **Single Port Device**
  - Measure reflected interrogation signal (S_{11}); passive operation
  - Post-processing to determine how frequency, phase, time-delay of reflected signal is changing
  - Operation analogous to “RADAR” principals
- **10 MHz — 3 GHz Operation**
  - Fabrication tolerances limit; sensor size dominated by antenna in wireless configuration
  - Common to operate at 915 MHz or 2.4 GHz range
- **Variety of Device Embodiments**
  - Resonant, delay line (narrow or wideband)
  - Exquisitely sensitive to temperature, strain (pressure), mass loading (e.g., gas detection)
  - Radiation tolerant



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Objective & Advantages of SAW Devices

Overall Objective: Develop surface acoustic wave (SAW) based online dissolved gas analysis (DGA) systems for power transformers (i.e., off gassing in transformer indicative of aging & potential failures)

- **SAW devices w/ integrated high surface area nanostructured scaffolds + selective chemistry**

Advantages:

- Current DGA monitors are costly and slow (laboratory analysis)
  - Online systems on the order of $50,000
- SAW devices are mass produced (mostly for RF filters, delay lines, resonators)
  - A few cents to a few dollars based on production volume
  - Total system cost < $1000 (much cheaper than current DGA systems)
  - No local power source is needed for passive/wireless SAW operation; can communicate w/low cost radio electronics
- Array of SAW devices can be selectively functionalized w/appropriate chemistry to detect multiple gasses
  - Cost-effective ubiquitous monitoring of transformer health; both large & small transformers
  - Continuous monitoring reduces unforeseen failures & grid down time

Gas:	Hydrogen	Methane	Acetylene	Ethylene	Ethane	Carbon Monoxide	Carbon Dioxide
Concentration (ppm)	700-1800	400-1000	10-35	100-200	100-150	570-1400	4000-10000

Methane Sensing SAW Technology Platform

Nanostructured Materials:

Sensor performance is affected by granularity, porosity, & surface area/volume ratio of the sensing element

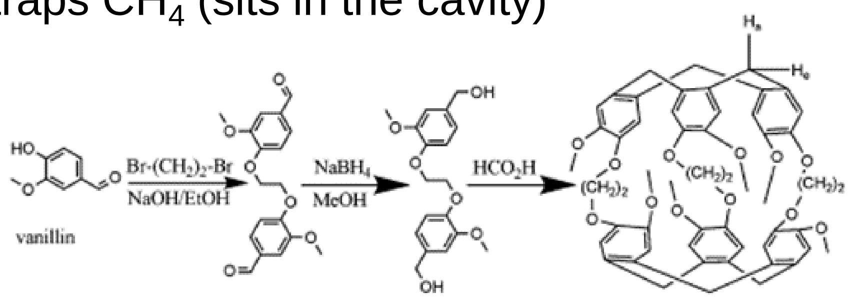
- Facilitates rapid diffusion of gases into & out of the sensing material
- Increased adsorption & reaction rate
- Improved response & recovery time
- Increased sensitivity & low detection limit
- Nanostructured surface promotes application of uniform sensing chemistry

Nanostructured Material Systems – 2 approaches:

- Spinodally phase separated silica films
- Chemically phase-separated TiO_2/Cu_2O composite films

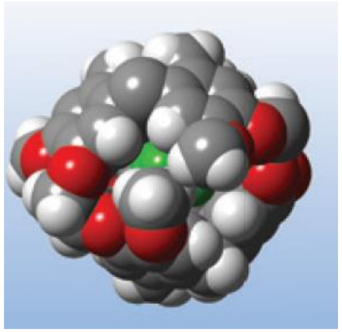
Sensing Chemistry: Cryptophane-A

- Size selective & reversible affinity for CH_4, traps CH_4 (sits in the cavity)



cryptophane-A

Cryptophane-A



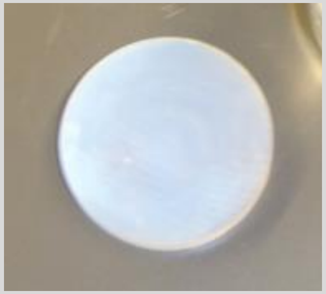
Methane encapsulated by cryptophane-A
(Chavagnac *Internat. Innovation*, 2015, 126-128)

Integration to piezoelectric QCM & SAW platforms:

- Proof-of-principal first on QCM (track frequency shift due to mass loading); then
- Integrate to YZ-$LiNbO_3$ based SAW device platform

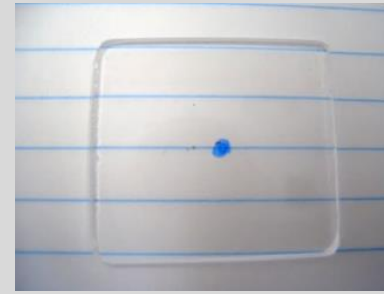
Approach 1: Nanostructured Spinodally Phase Separated Porous Silica Films

Step I: Fabrication of ***thin film glass coatings*** via industrial processes



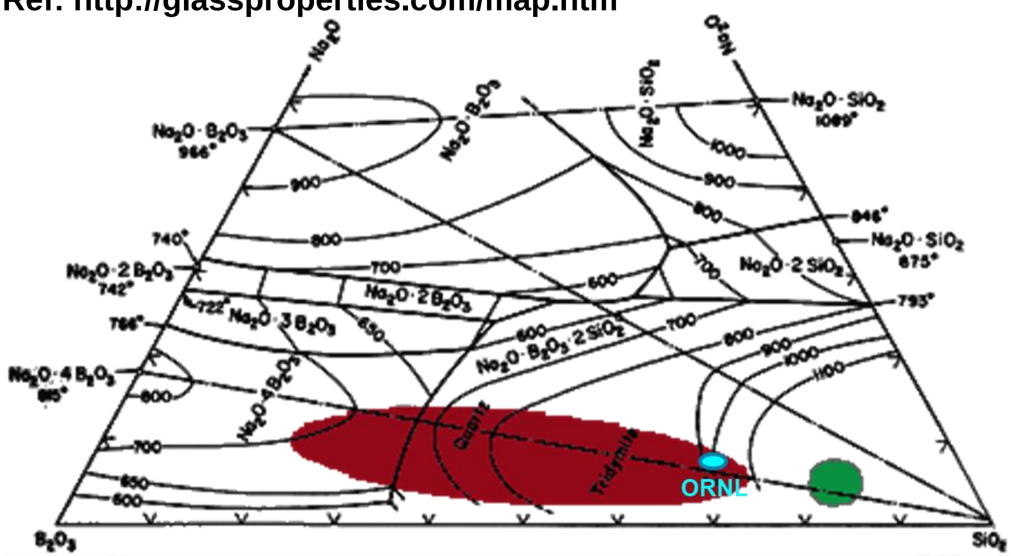
ORNL Glass target
(X% SiO_2, Y% B_2O_3, Z% Na_2O)

Glass film deposition

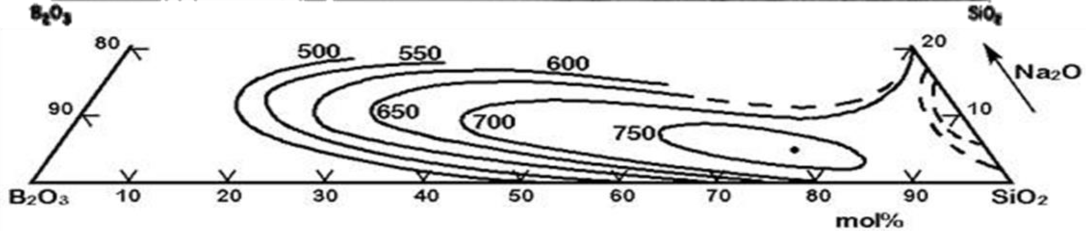


Glass film on silica

Ref: http://glassproperties.com/map.htm



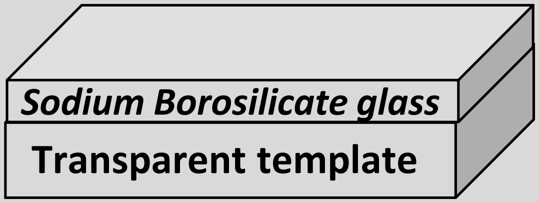
Areas of immiscibility in the SiO_2-B_2O_3-Na_2O system used to make Vycor and Pyrex



Metastable phase separation in the SiO_2-B_2O_3-Na_2O system (mol%)

Approach 1: Nanostructured Silica Films Cont.`d

STEP *II*: Techniques to create ***nanostructured surfaces***

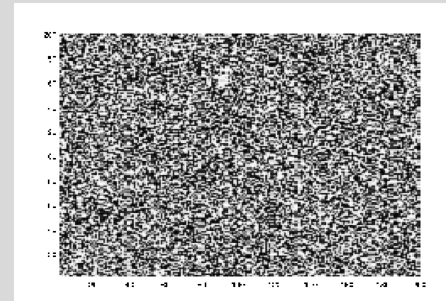


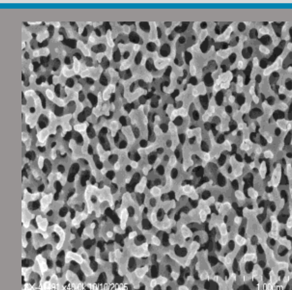
Heat Treatment

Temp:
500 - 700 °C

Phase separated spinodal decomposition
1) Sodium borate
2) Silica rich phases

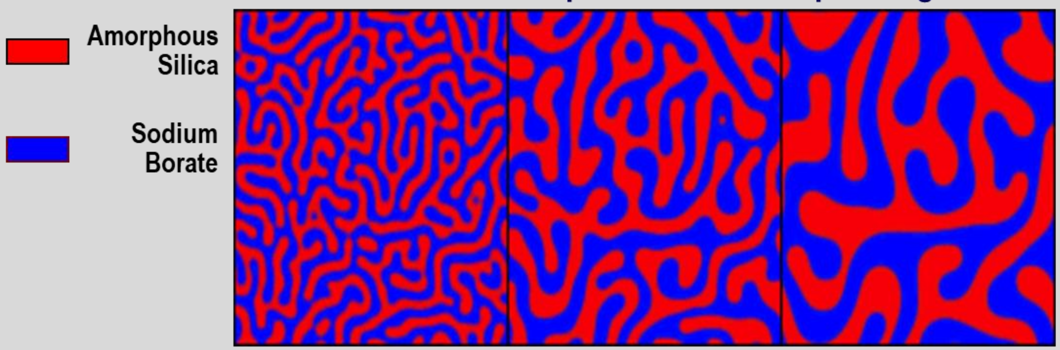
HF-based
Differential etching



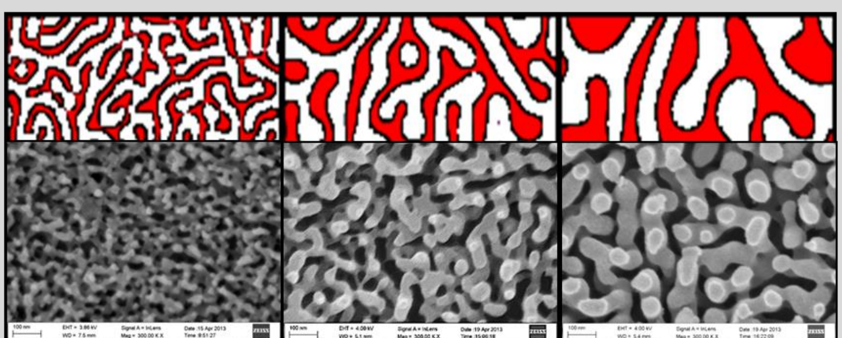


Nanostructured Material

Sodium Borosilicate Spinodal Phase Separating Glass



Heat treatment time ➔ t = 1 t = 2 t = 3



The spinodal microstructure is determined by :

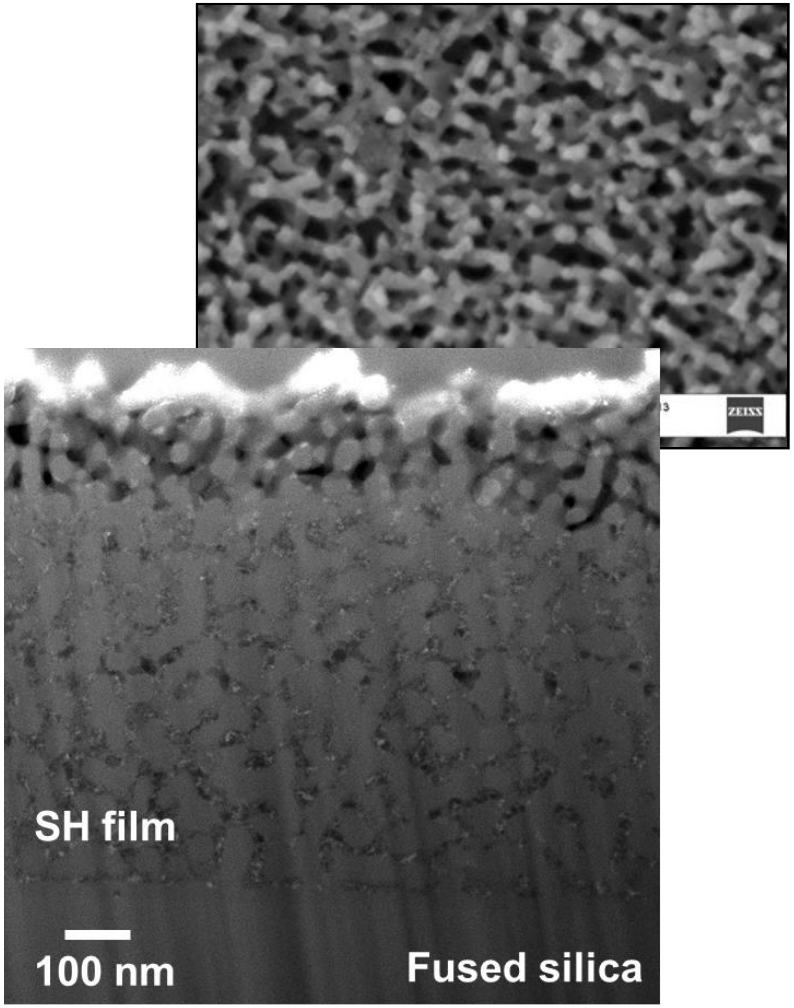
- **Heat treatment temperature & time**

And, the final etched-out nanostructure controlled by:

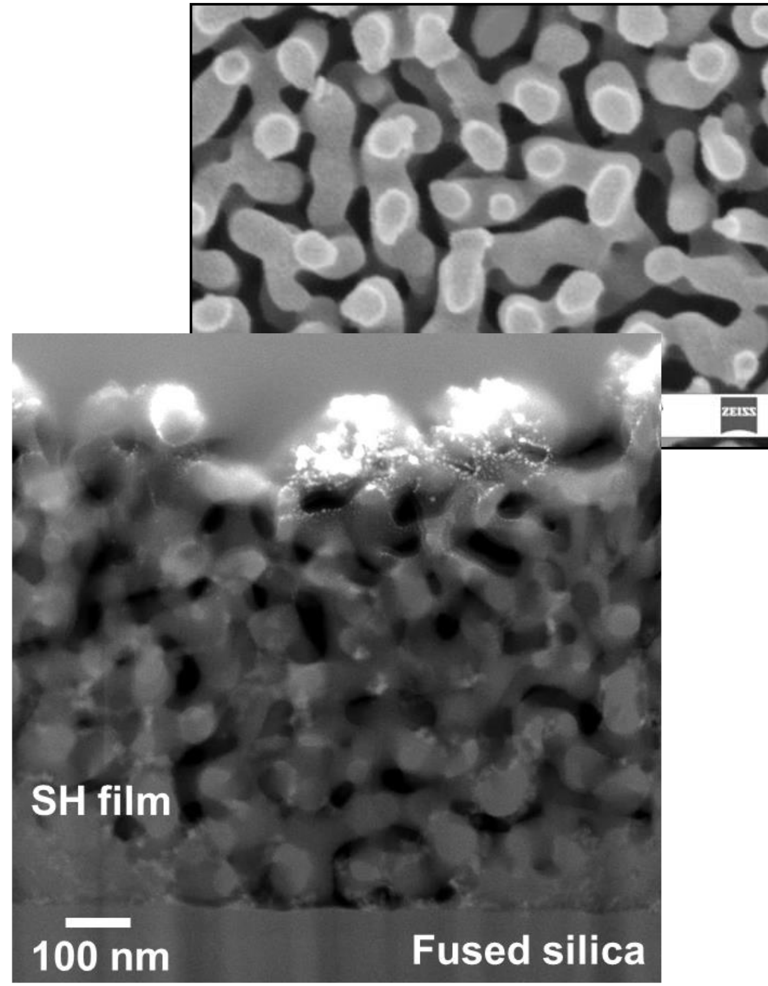
- **Etchant type, concentration & etch duration**

Approach 1: Coating Engineering

Longer the annealing time, larger the size of the phase separated film structure

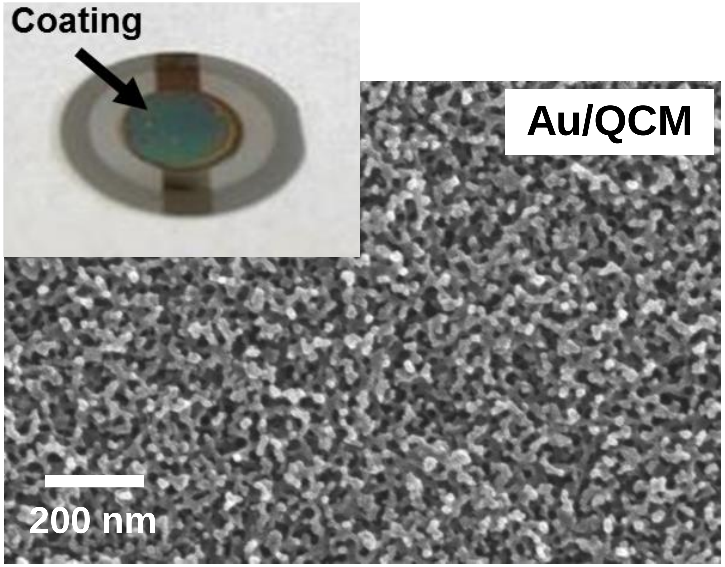


Heat treatment temperature = 710 ^{o}C
Heat treatment time = 5 min

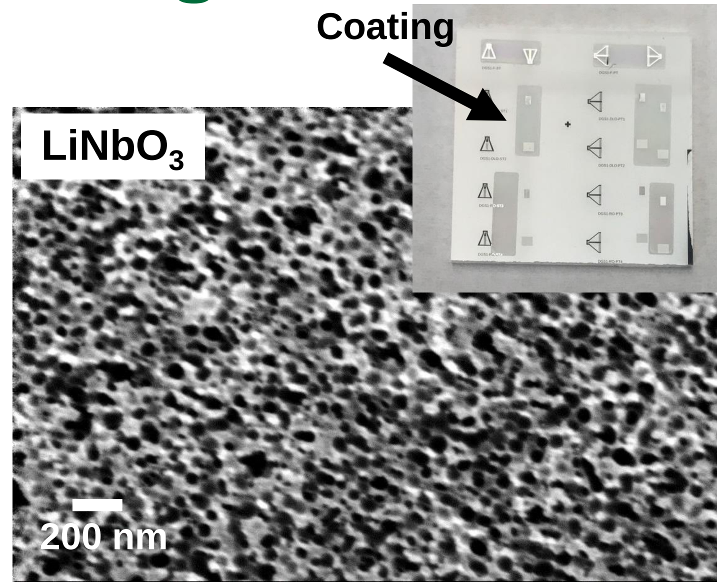


Heat treatment temperature = 710 ^{o}C
Heat treatment time = 120 min

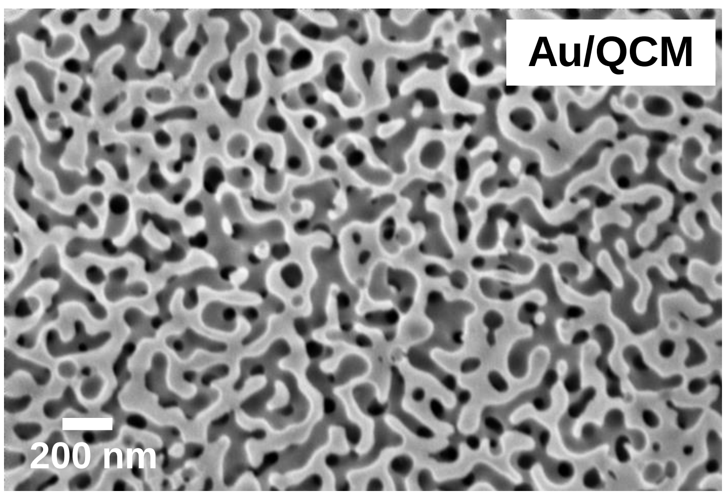
Approach 1: Coating Engineering Cont`d



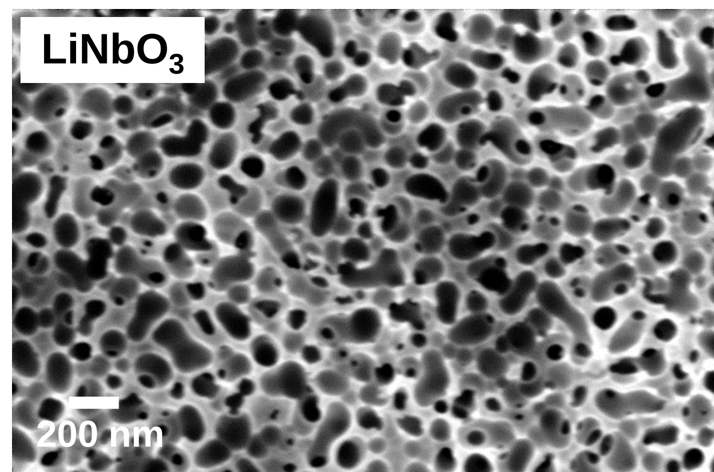
Heat treatment temperature = 700 ^{o}C
Heat treatment time = 1 min



Heat treatment temperature = 600 ^{o}C
Heat treatment time = 240 min



Heat treatment temperature = 700 ^{o}C
Heat treatment time = 12 min

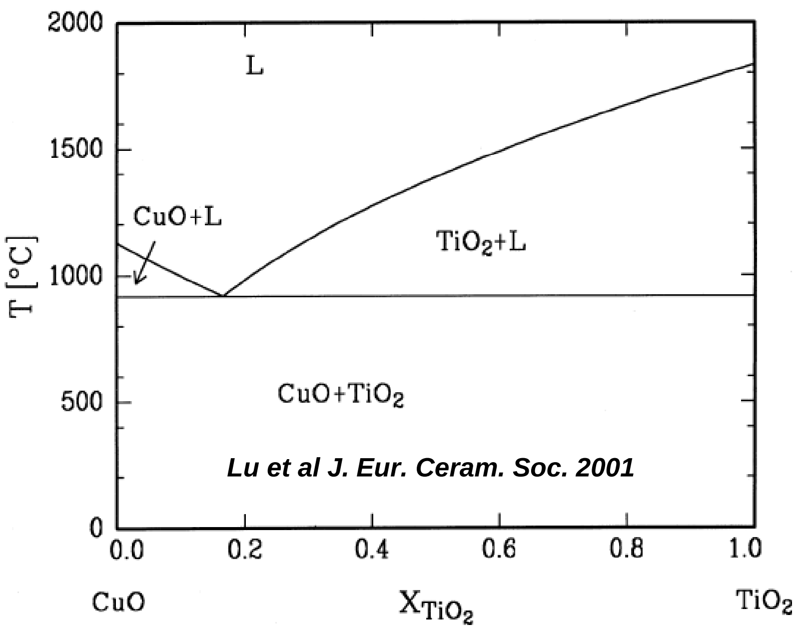


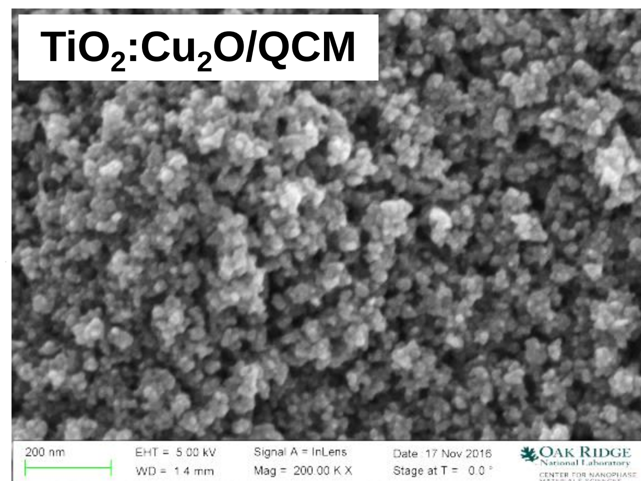
Heat treatment temperature = 700 ^{o}C
Heat treatment time = 12 min

Approach 2: Phase Separated Metal-Oxide TiO_2:Cu_2O Nanocomposite Films

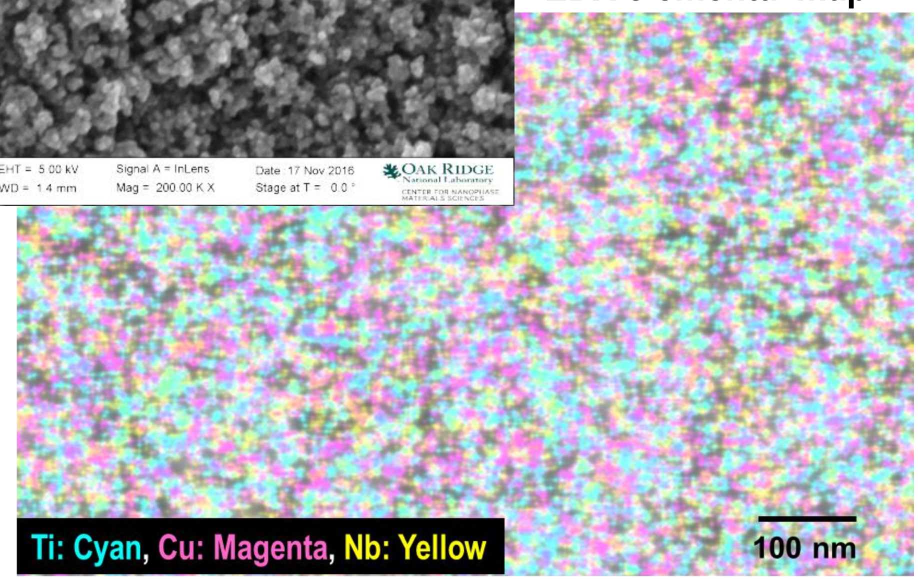
Exploits phase separation in oxide materials: a new composite based on TiO_2-Cu_2O

- Phase separation is driven by thermodynamic stability combined w/ insolubility between TiO_2 & Cu_2O
- Nanostructural transformation is governed by the minimization of the lattice misfit strain (~12%) between TiO_2 & Cu_2O
- Material system is naturally abundant, non-toxic, inexpensive, chemically & environmentally stable



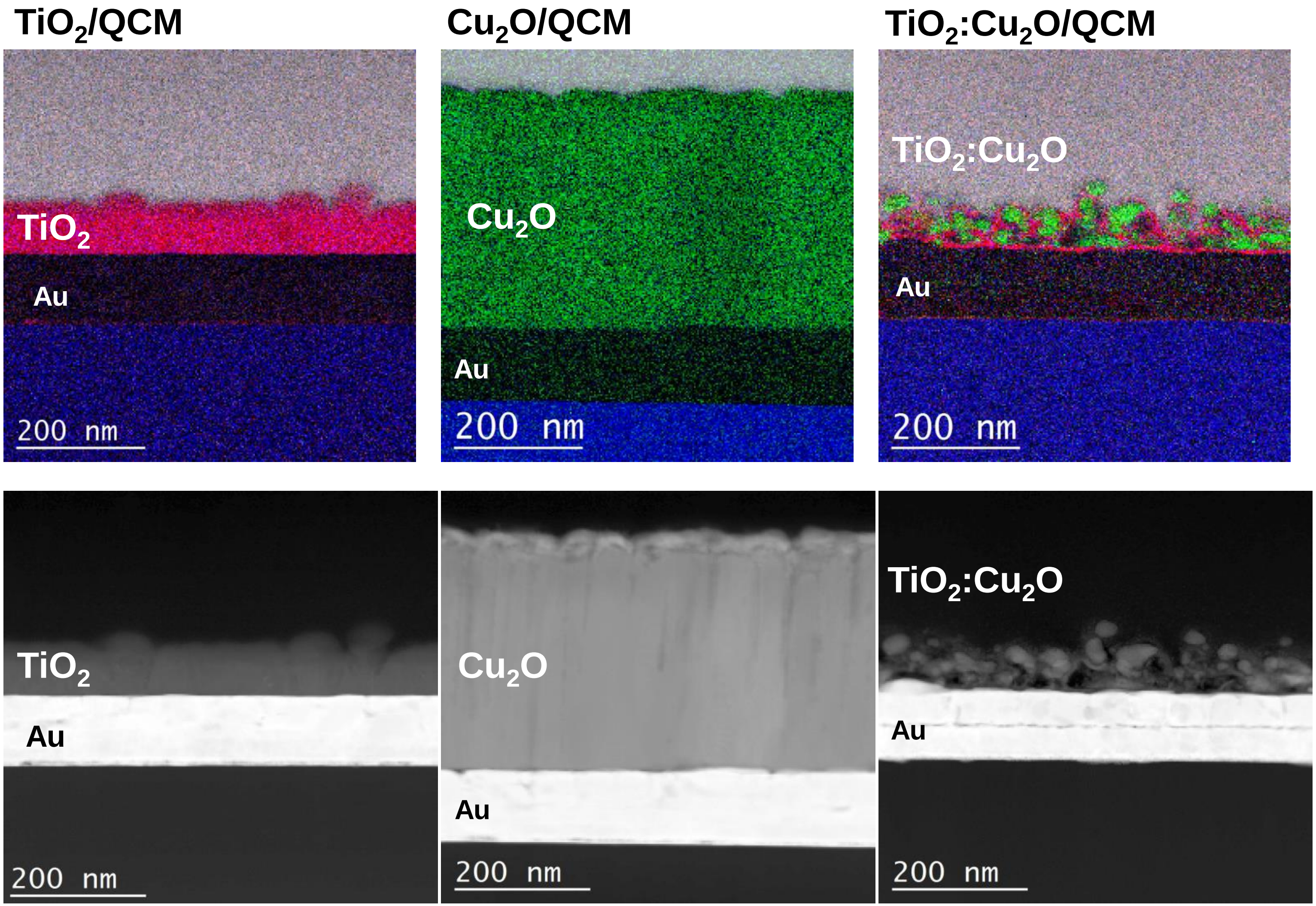


EDX elemental map



Color combined elemental map reveals nanoscale phase separation between TiO_2 & Cu_2O phases

Cross-sectional Z-Contrast STEM & Integrated EELS Reveal Nanostructured Phase Separation in TiO_2:Cu_2O Composite



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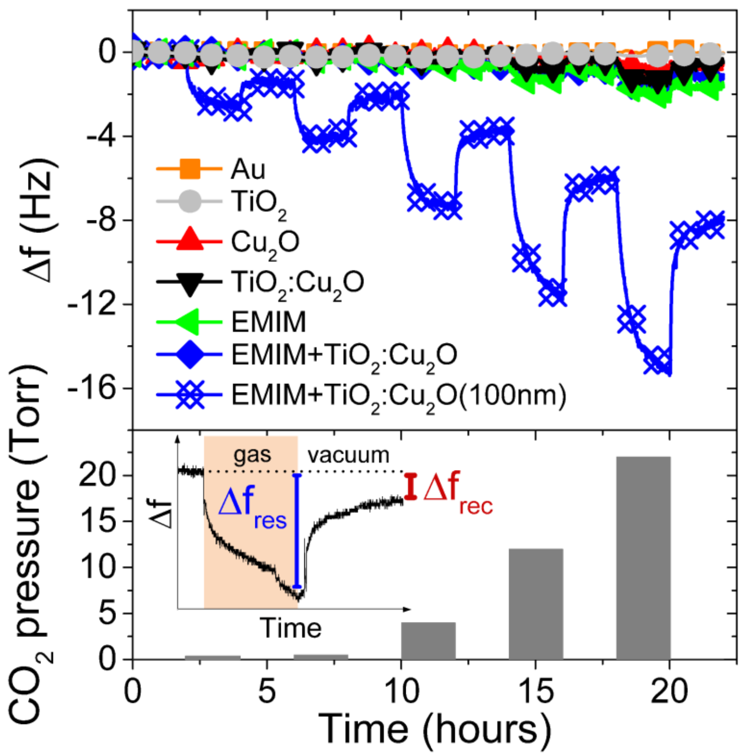
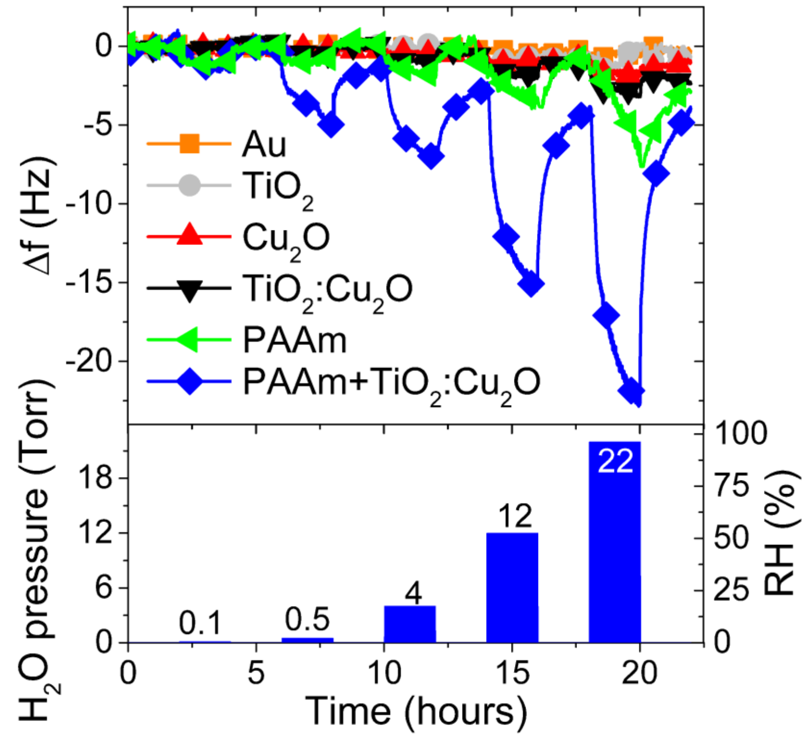
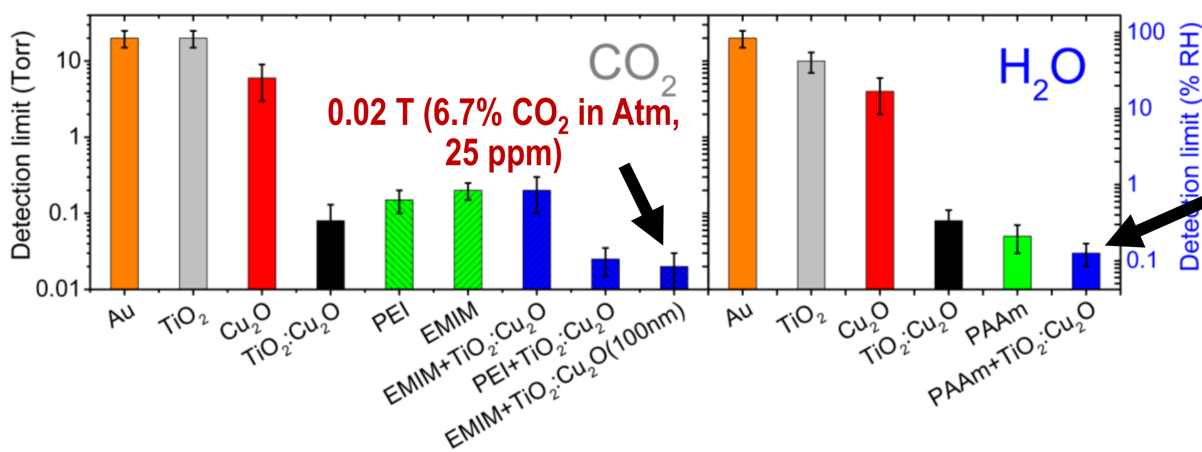
Demonstrated low detection limits for CO_2 & Humidity Sensing for TiO_2:Cu_2O Coated QCM

Chemistry (CO_2) : 1-ethyl-3-methylimidazolium (EMIM)



Chemistry (H_2O): polyacrylamide (PAAm)





0.13% RH
(0.03 T of H_2O pressure)

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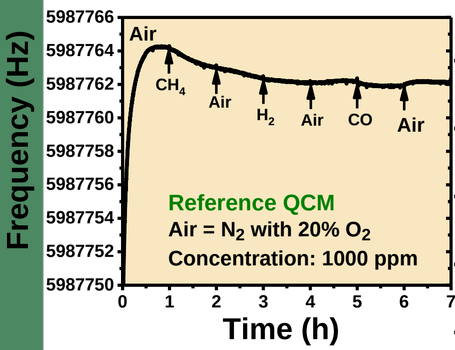
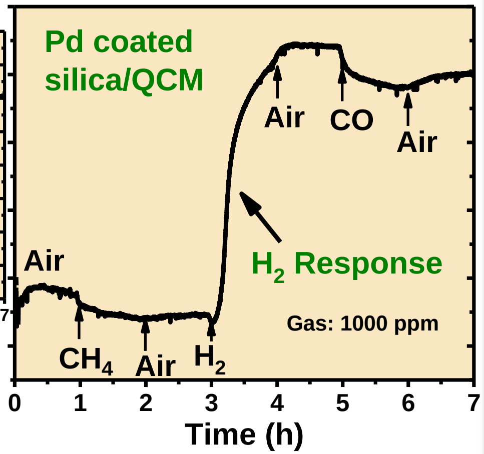
High Surface Area Porous Nanostructured Sensor Films: QCM & $LiNbO_3$

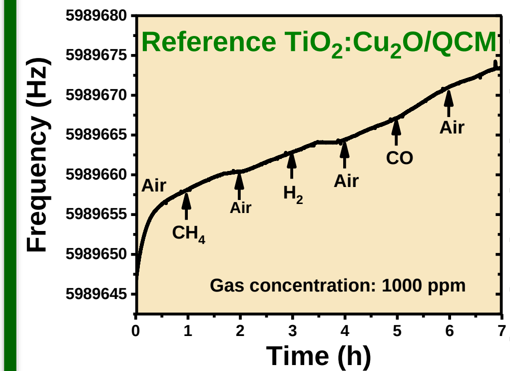
Collaboration with
Paul Ohodnicki (NETL)

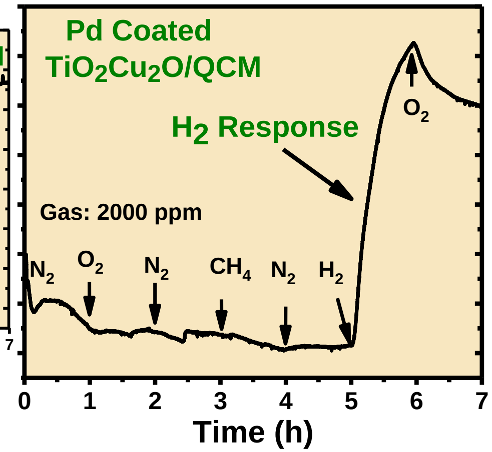
QCM: H_2 Sensing (Pd)





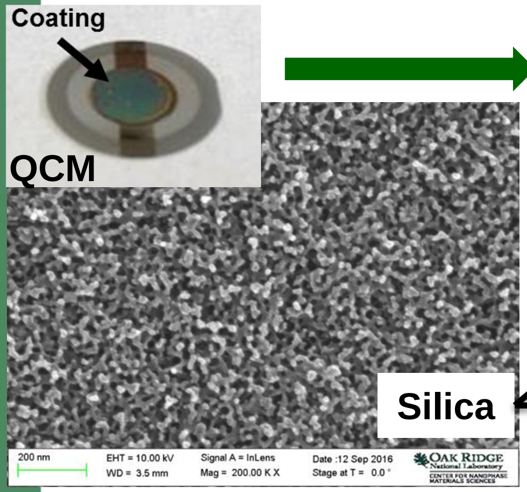
QCM: H_2 Sensing (Pd)



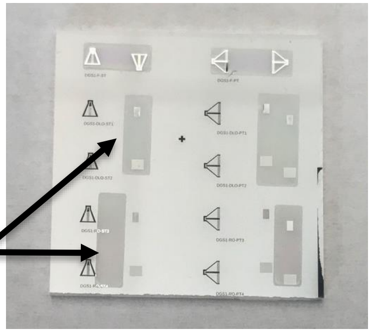


Approach 1: Nanostructured silica films

Exploits spinodal phase decomposition in glass materials

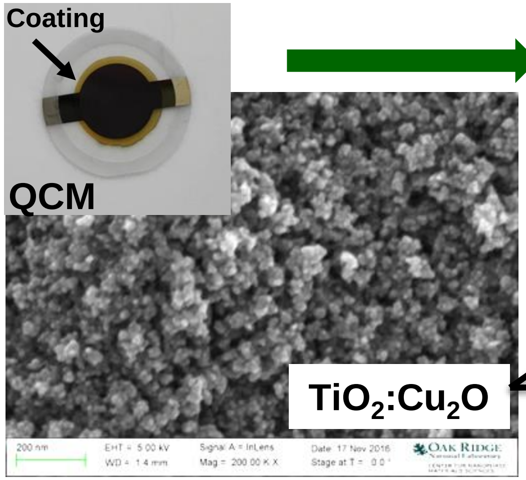


Integrated onto $LiNbO_3$ SAW devices

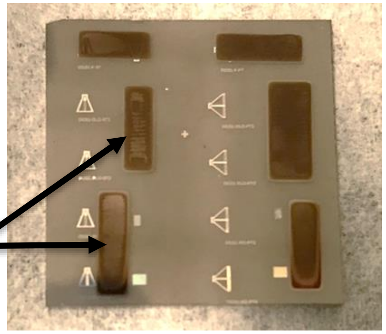


Approach 2: Nanostructured TiO_2-Cu_2O films

Exploits control of materials phase separation in metal oxide systems



Integrated onto $LiNbO_3$ SAW devices



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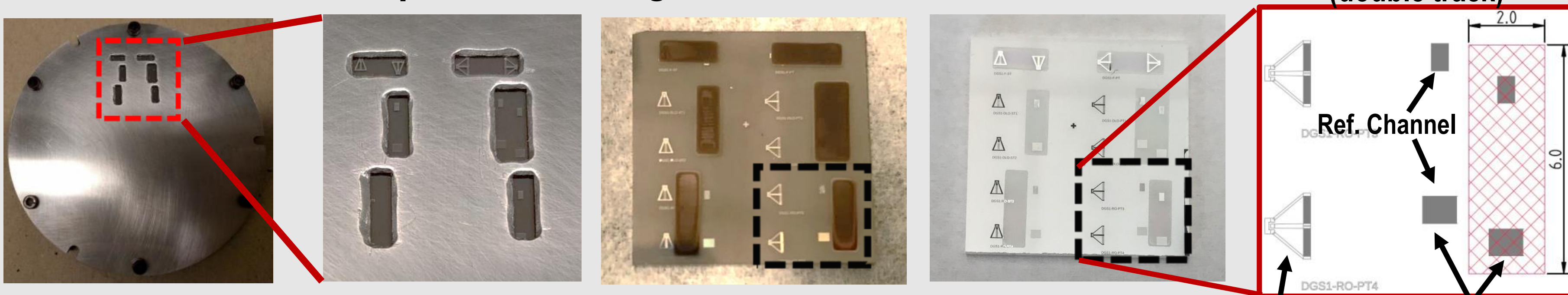
SAW Design (250 MHz)

Nanostructure film deposition through shadow mask

SAW schematic (double track)



Shadow mask

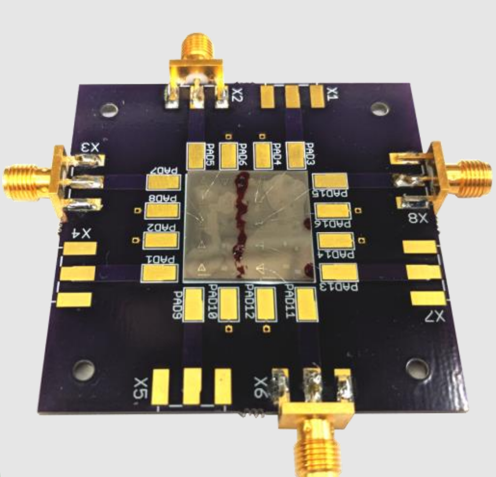
Metal-oxide on $LiNbO_3$

Silica on $LiNbO_3$

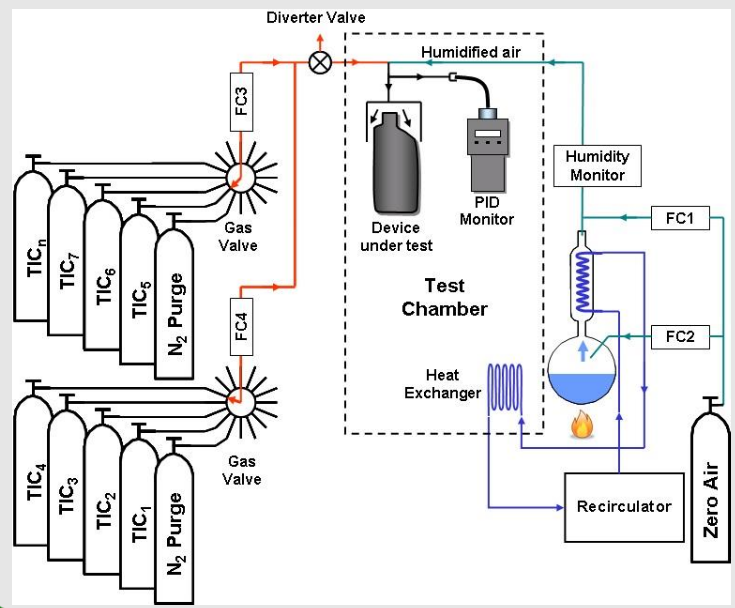
Transducers

Reflectors

Sensor test module/Gas chamber

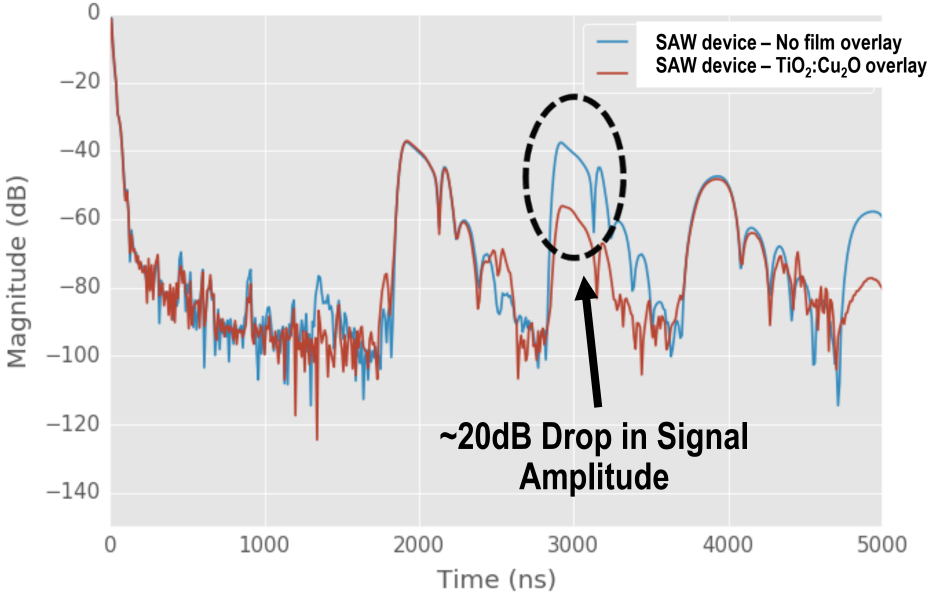


Gas sensing test setup



Influence of Film Morphology on SAW Performance

TiO_2/Cu_2O Film

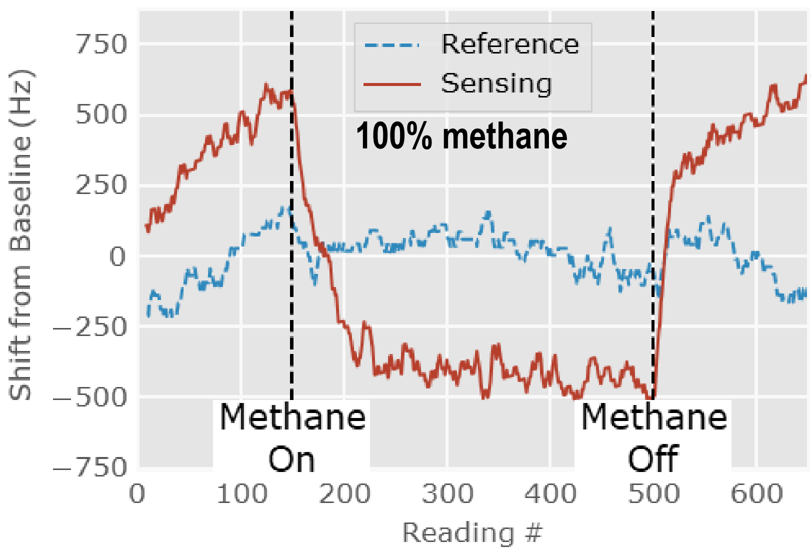


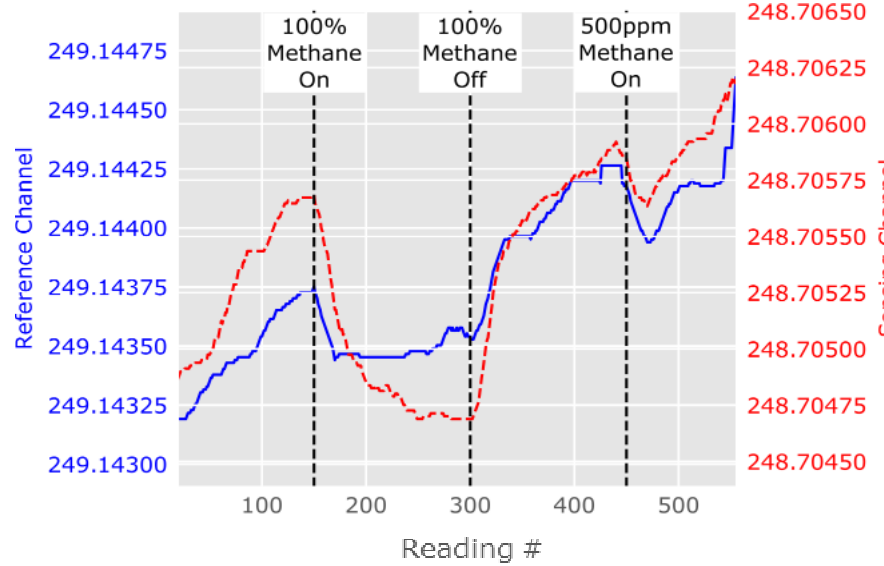
SiO_2 Film

- Deposition process/methods did not seem to adversely affect SAW performance of transducers/reflectors that do not have film overlay
- Silica thin films show no affect on SAW device performance **(Low Loss)**
- TiO_2:Cu_2O films initially showed attenuation. Process has been optimized

CH_4 Sensing Experiments w/250 MHz Device

- Exposed sensor to 100% and 500 ppm (desired sensitivity) methane
- Sensor has reference (temp.) and sensing (methane) channel
  - Sensing channel shows larger freq. shift than ref. channel when exposed to 100% methane
  - For 500 ppm observed similar shift for both channels (likely dominated by temperature) ➡ low sensitivity to methane





- Solution: Increase device frequency to increase the sensitivity (i.e., mass on surface)
  - Design SAW devices for 915 MHz operation ➡ predict 500-1000% increase in sensitivity

$$\Delta f = \boxed{(k_1 + k_2) f_0^2 h p_f} - k_2 f_0^2 h \left\{ \frac{4\mu'(\lambda' + \mu')}{v_0^2(\lambda' + 2\mu')} \right\}$$

Mass loading **Stress**

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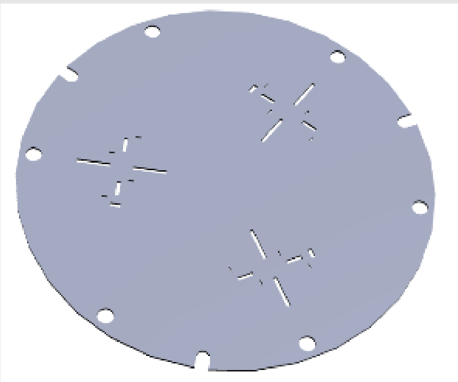
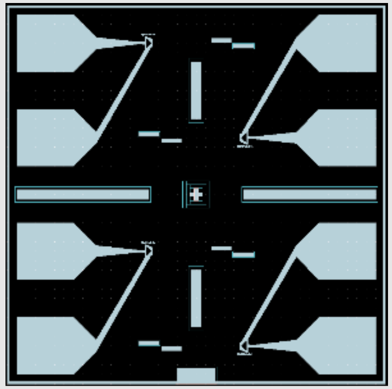
SAW Design (915 MHz)

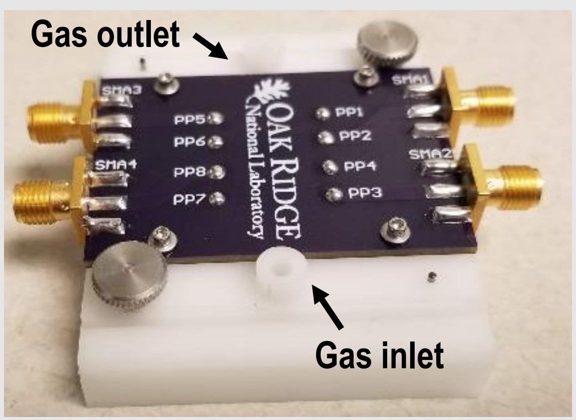


Shadow mask
(laser cut)



SAW die w/915 MHz devices
(double track)

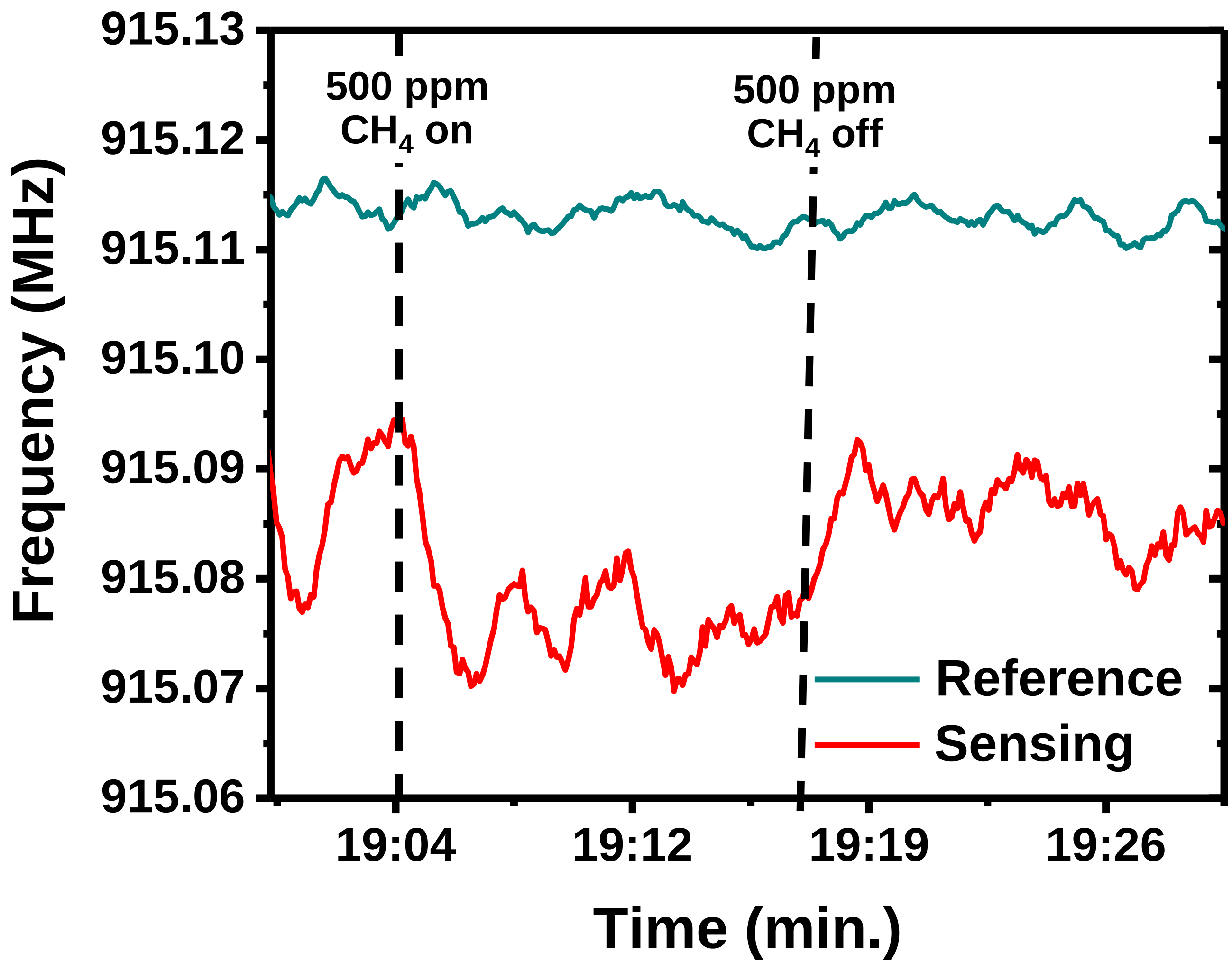
Sensor test module



Pogo pin connections
(no wire bonds)

- **New test fixture for rapid testing**
  - Old design required wire bonding & adhesive bonding to PCB
  - New fixture routes RF signal to pogo pins; chip is placed into chamber & pogo pins make direct connection
- **Wide-band, multi-chip (reflector) design for improved SNR (pulse compression gain)**

Initial CH_4 Sensing Experiments w/915 MHz Device



- For 500 ppm CH_4, observed ~30 KHz shift for sensing channel
- Processing protocols of nanostructured films & sensing chemistry are being optimized to achieve higher sensitivity

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Contact Information

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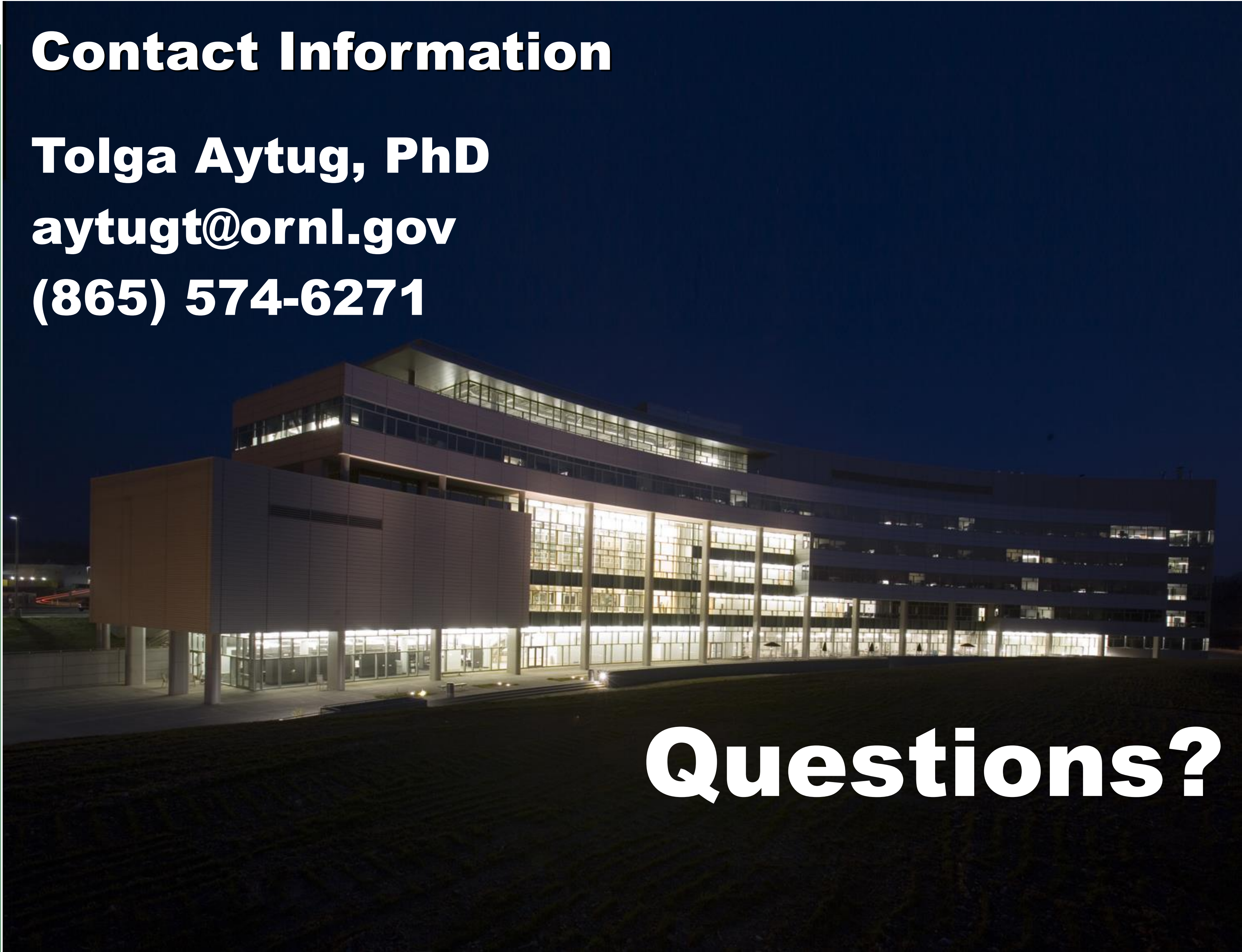
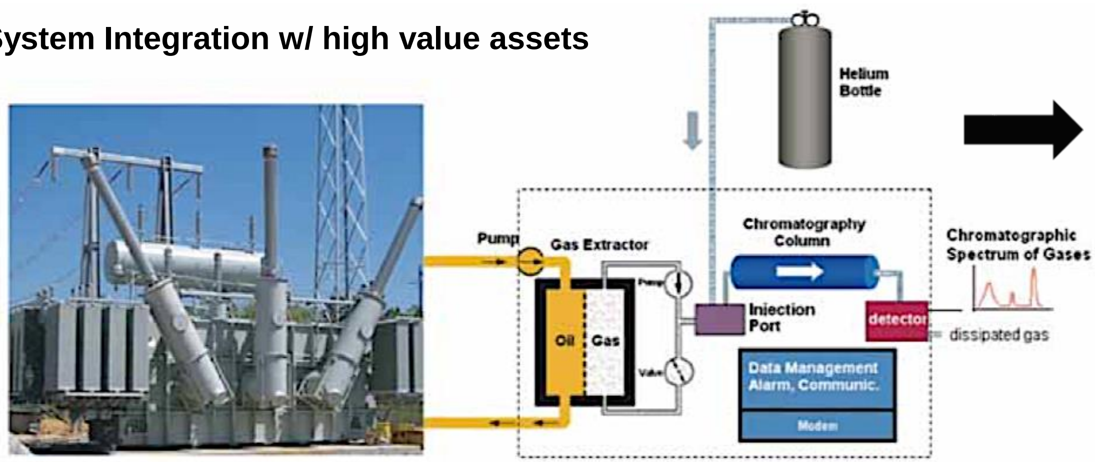


Questions?

State-of-the-art Technology – Siemens GAS-Guard® 8

System Integration w/ high value assets



Accurate and repeatable measurement of eight (8) critical fault gases

Gas		Accuracy[1]	Repeatability[2]	Range[3]
Hydrogen	H_2	+/-5% or +/-2 ppm	<2%	2-3,000 ppm
Oxygen	O_2	+/-5% or +30/-0 ppm	<1%	30-5,000 ppm
Methane	CH_4	+/-5% or +/-10 ppm	<1%	10-5,000 ppm
Carbon Monoxide	CO	+/-5% or +/-3 ppm	<1%	3-10,000 ppm
Carbon Dioxide	CO_2	+/-5% or +/-5 ppm	<1%	5-30,000 ppm
Ethylene	C_2H_4	+/-5% or +/-3 ppm	<1%	3-5,000 ppm
Ethane	C_2H_6	+/-5% or +/-5 ppm	<1%	5-5,000 ppm
Acetylene	C_2H_2	+/-5% or +/-1 ppm	<2%	1-3,000 ppm

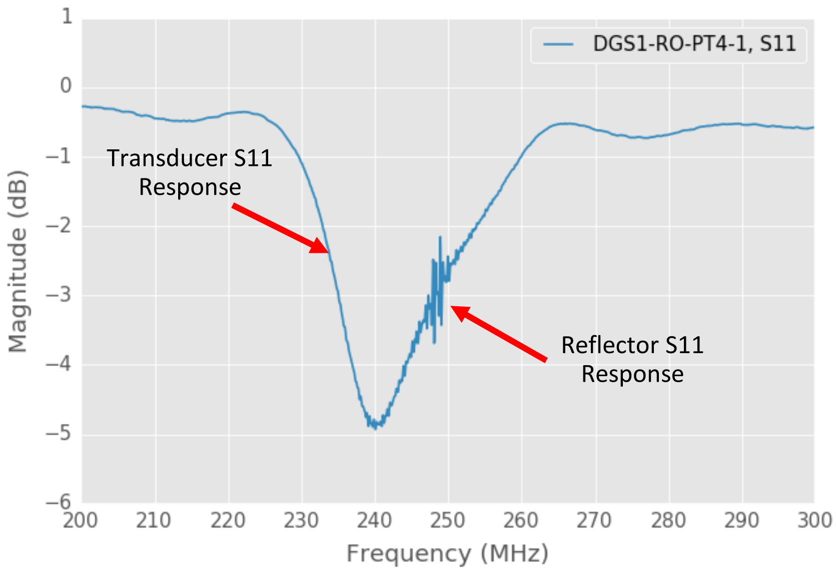
NOTES: All specifications are independent of oil temperature and gas pressure level.
1 Percent of ppm - whichever is greater
2 At gas calibration level
3 Gas-in-oil

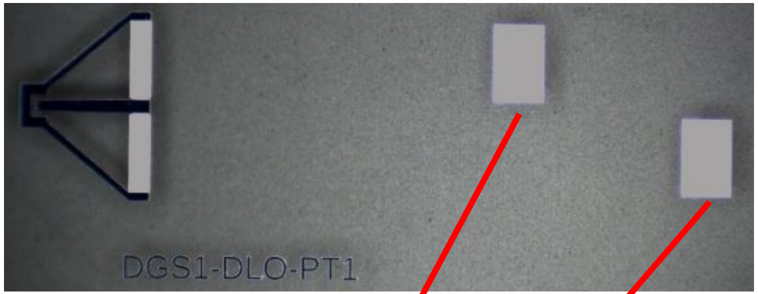
SAW Design Parameters (250 MHz)

- Substrate: YZ-$LiNbO_3$
- SAW Velocity: 3488 m/s
- Wavelength (250MHz): 13.95 µm
  - $\frac{1}{4} \cdot \lambda = 3.4875$ µm
- Beamwidth: $50 \cdot \lambda = 697.5$ µm
- Transducer Electrode Pairs: 11
  - τ=44ns; NBW = 45 MHz
- Reflector Electrodes: 65

Dual Channel SAW Device (1-Port)

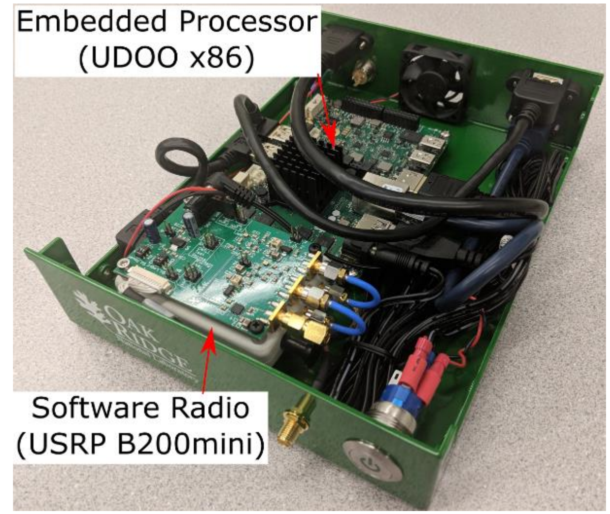
- SAW device can be split into multiple tracks
  - E.g. reference and sensing track

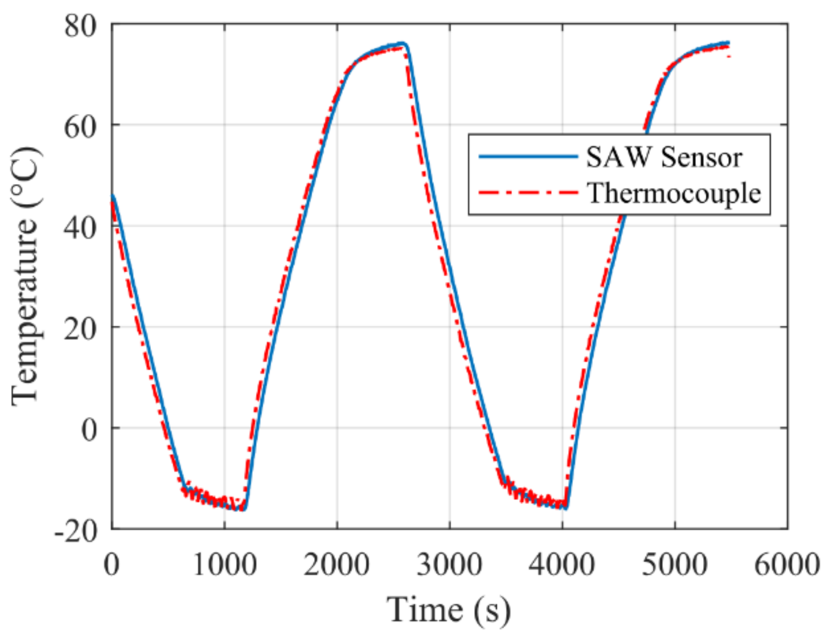


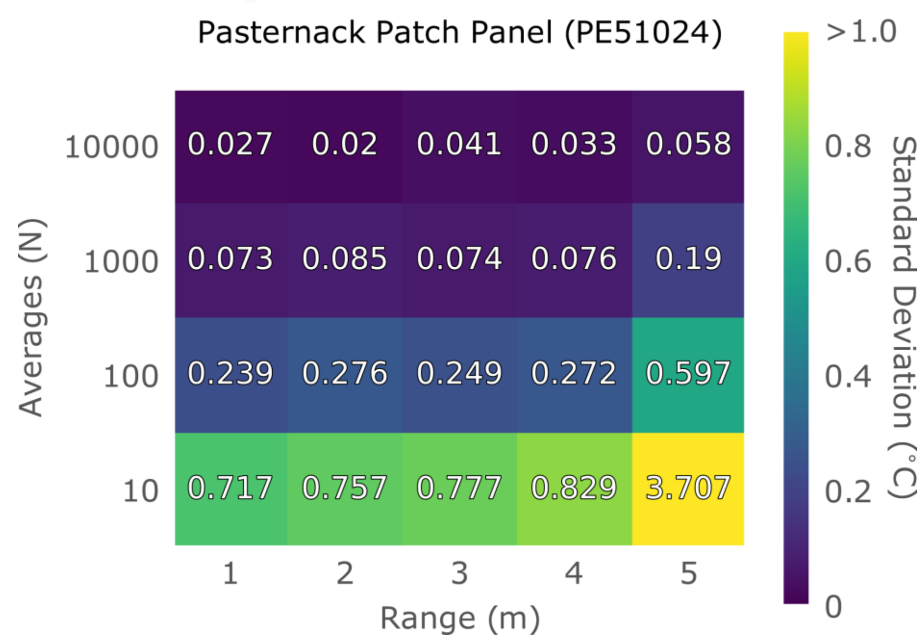


SAW Field Validation

- Embedded interrogation systems with Udoo x86
- Wireless SAW temperature sensor testing in anechoic chamber
- SAW sensor temperature cycling in environmental chamber



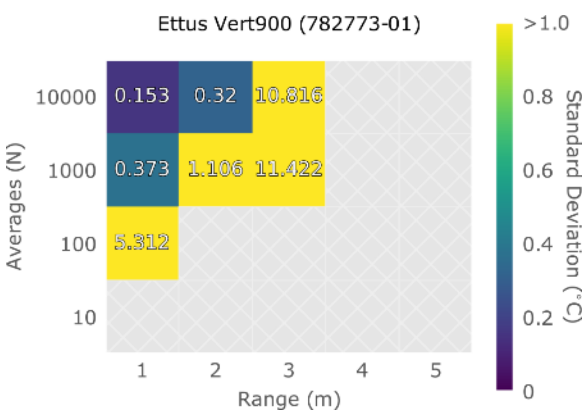


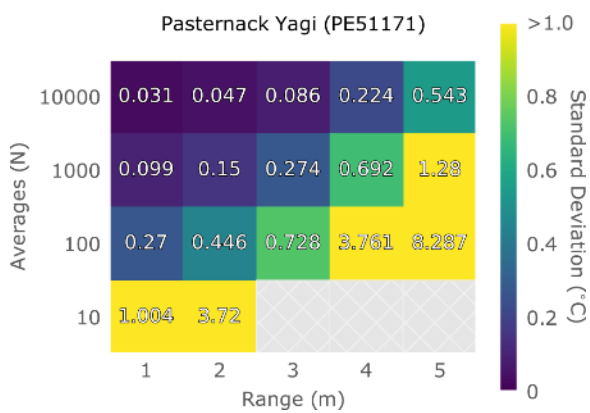


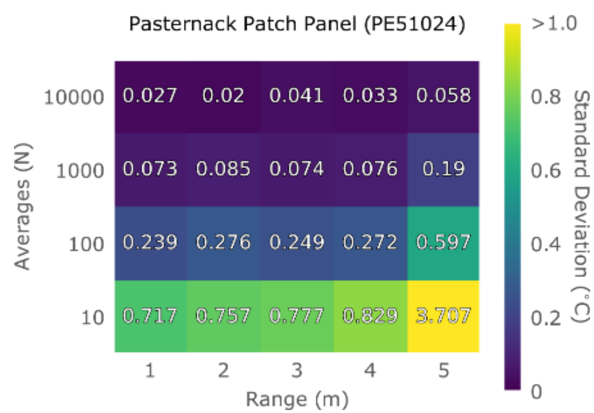
OAK RIDGE
National Laboratory

Anechoic Chamber Results

- Monopole, Yagi, and Patch Panel antennas tested
- Sensor can operate up to 5 meters (Limited by chamber length)
- Measurement precision down to 0.027°C observed
- Best performance observed with Patch Panel antenna

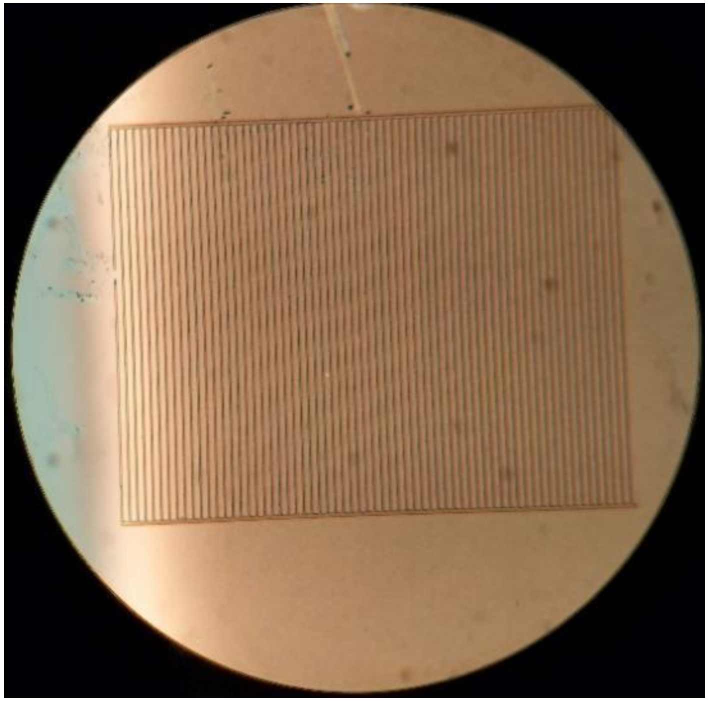






Nanostructuring on SAW Reflectors

TiO_2/Cu_2O Film



SiO2 Film