2017 Project Review Meeting for Crosscutting Research

INTEGRATED HARSH ENVIRONMENT GAS / TEMPERATURE WIRELESS MICROWAVE ACOUSTIC SENSOR SYSTEM FOR FOSSIL ENERGY APPLICATIONS

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OUTLINE

I. **Introduction**
   - Motivation: Gas Sensor Need for Operation in HT / HE

II. **Methodology:**

   Microwave Acoustics Technology for HT / Gas Sensors
   - Technology accomplishments & Methodology for Gas Sensors

III. **Project Objectives**

IV. **Recap: Last Year Reported Progress**

V. **Project Progress & Current Experiments**

VI. **Conclusions & Acknowledgements**

I. Introduction

Motivation

- **High Temperature Gas Sensor FOSSIL FUEL: WHY?**
  - **Better process control ⇒ ↓ maintenance ⇒ ↓ POWER PLANT DOWNTIME**
    - Gas PP ⇒ Cost $11,000/h ⇒ $264,000/day (KCF Technologies)
    - Average Outage (2007/11) Coal Units alone (NETL / Krulla 2014) →
      - ✓ Btwn 300 - 500 hours/unit-year ⇒ Over 40 M$ (coal units alone)

Motivation

➢ **High Temperature Gas Sensor FOSSIL FUEL: WHY?**

❖ ↑ **EFFICIENCY in fuel burning by controlling combustion**

- 1% Heat rate improvement (500MW) (NETL / Romanosky 2015) ⇒
  - ✓ $780,000/unit-year;
  - ✓ Entire coal-fired fleet $340 million/yr coal cost savings
- 1% increase in availability (500MW) ⇒
  - ✓ 44 Million kWh/yr added generation ⇒ ↑ 2.6 M$ /unit-year in sales
  - ✓ More than 2GW additional power / yr from the existing fleet

❖ **Emission / Pollution?**

- 1% Heat rate improvement

  Cool fleet alone ⇒

  ↓ 13.8 billion metric tons CO_2/yr

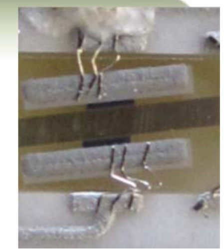
NEED

- ➢ High Temperature / Harsh Environment GAS SENSORS
  - Platform → **STABLE** in the environment over **LONG PERIODS**
  - Operate **RELIABLY** with very little or no wires
    - ✓ Wiring poses problem for reliability in harsh environments
    - ✓ Packaging restricts the use of several technologies
  - Require very little or **NO MAINTENANCE** (inaccessible locations)
    - ✓ No battery allowed →
      - ☞ Limited to 500°C
      - ☞ Frequent maintenance
      - ☞ Size restriction
      - ☞ Safety impediment for several applications
      - ☞ Compromise system operation and reliability

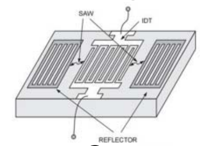
II. Methodology

Methodology

- ➢ μ~ acoustics → resilient platform for HT operation

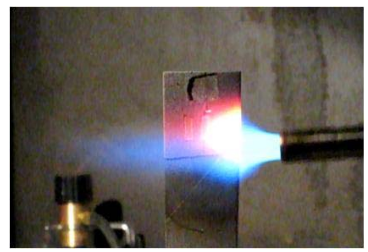


- ➢ Surface Acoustic Wave devices →

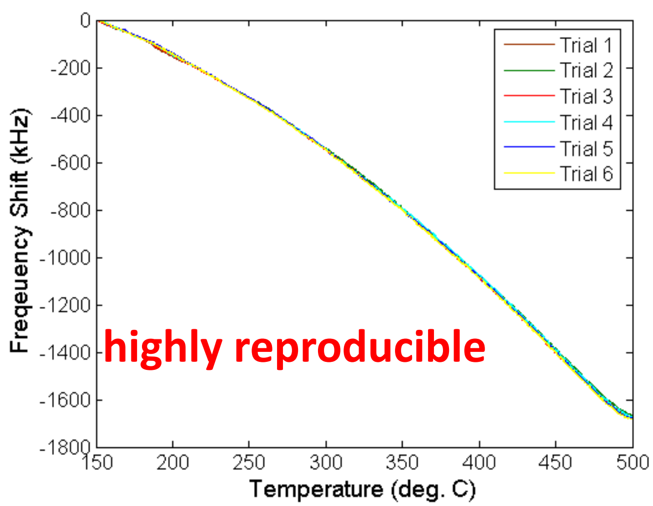


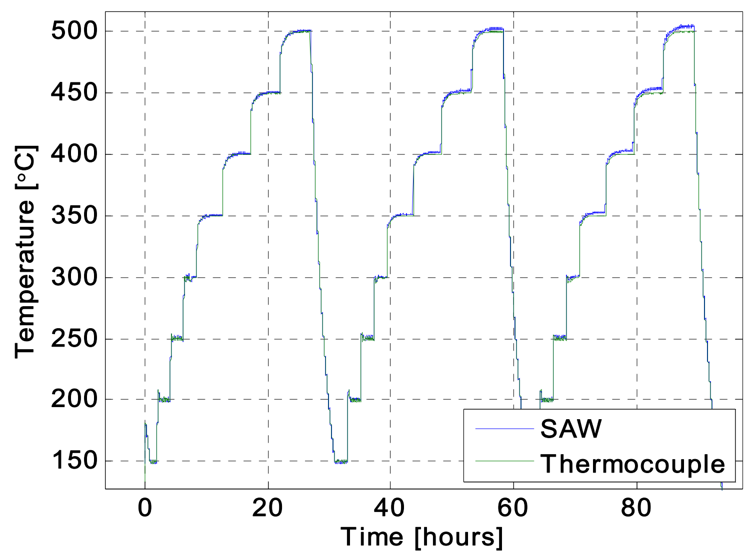
  - Platform developed & improved @ UMaine for over 15 yrs
  - Langasite $La_3Ga_5SiO_{14}$ Piezoelectric Crystal

    - ✓ Stable up to 1400°C
    - ✓ Resistant to thermal shock

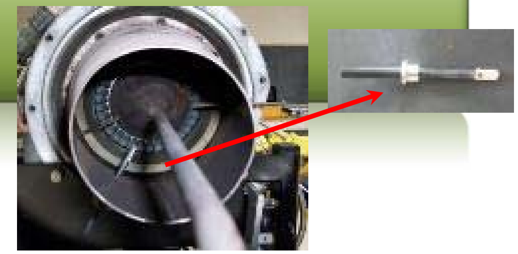


  - Stable / Repetitive operation
    - ✓ Tested over 5 ½ Mo @ 800°C

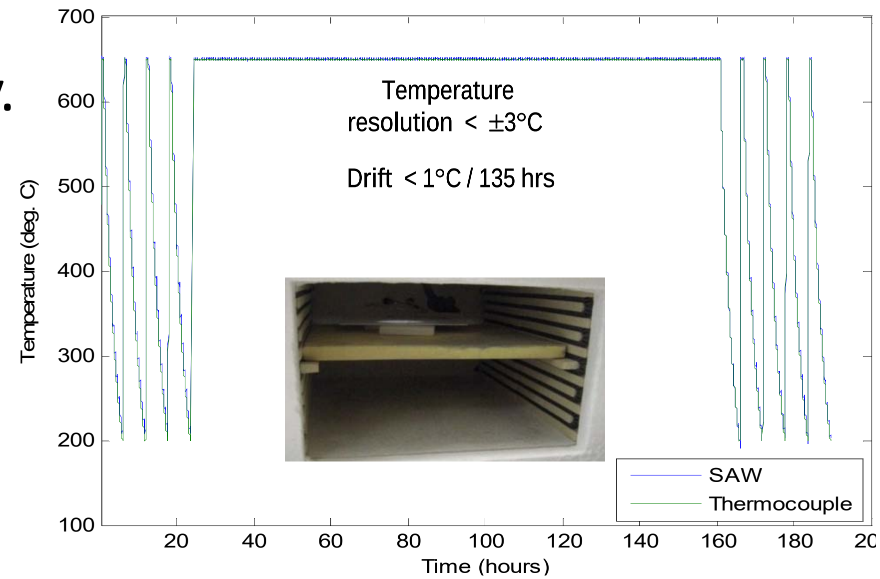


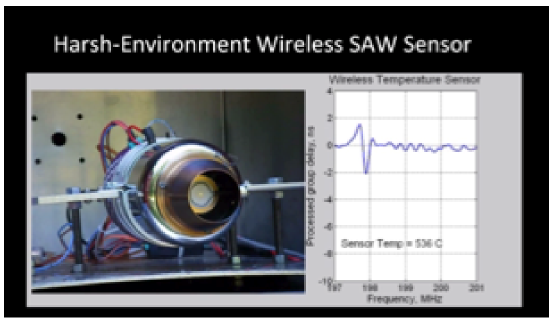


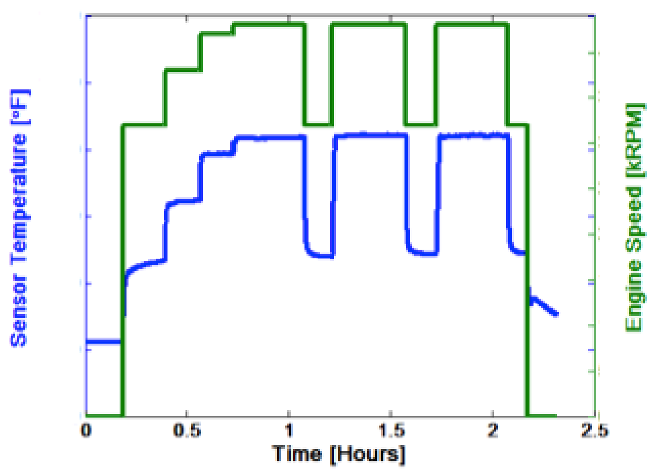
Methodology



- Surface Acoustic Wave T SENSORS →
  - Allow WIRELESS operation
  - Tested in multiple HT/Harsh Env.
    - ✓ **Sensor Turbines**



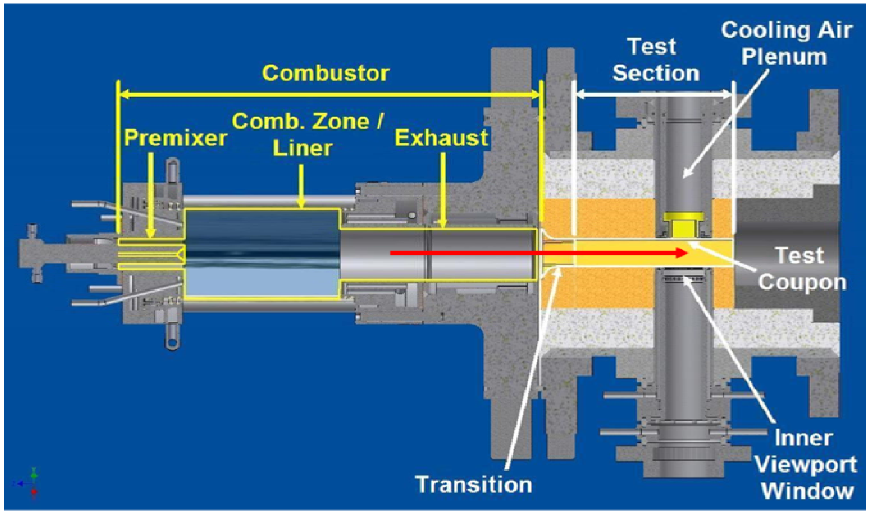




Methodology

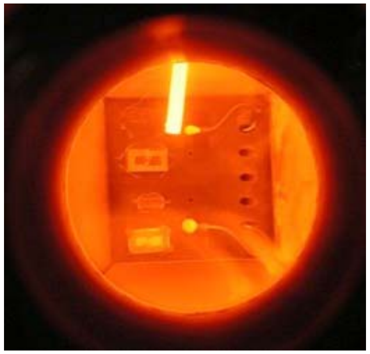
➢ Surface Acoustic Wave Temp. SENSORS (cont.) →

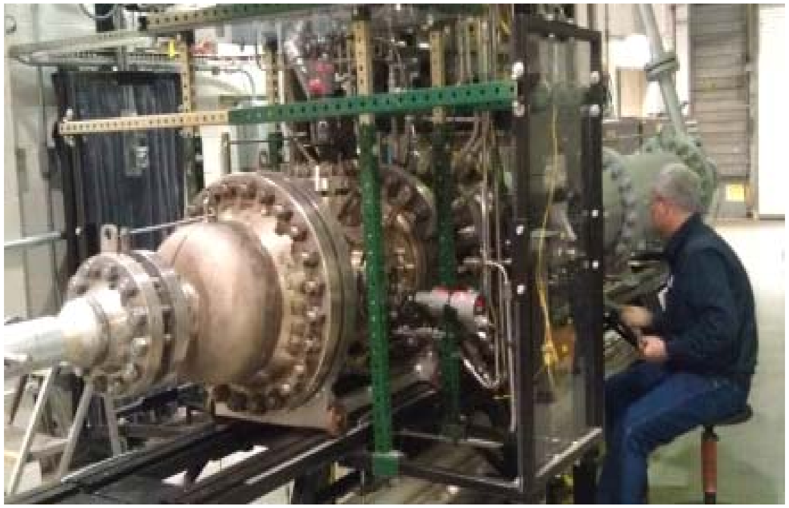
- WIRELESS operation
- Tested in multiple HT/Harsh Env.
  - ✓ **NETL Aerothermal Facility**



Sensor Performance Tests

- Sensor operation demonstrated in a combustor environment
- Multiple wired and wireless sensor designs tested up to 1100^{o}C gas temp.
- All sensors survived entire test





Methodology

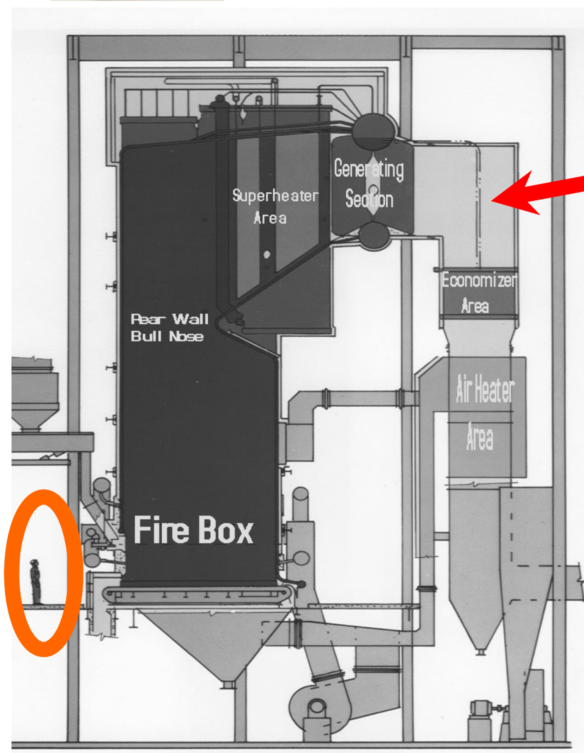
➢ Surface Acoustic Wave Temp. SENSORS (cont.) →

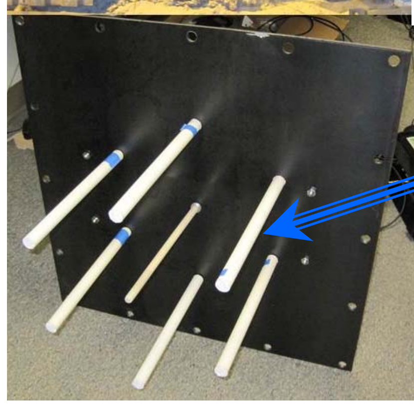
- WIRELESS operation → Tested in multiple HT/Harsh Env.

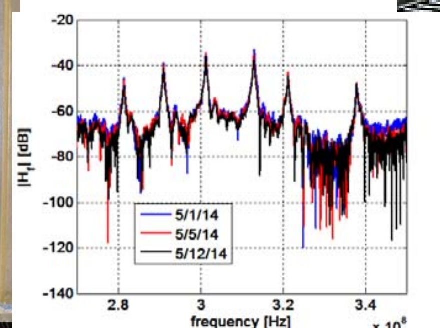
Penobscot Energy Recovery Company (PERC)

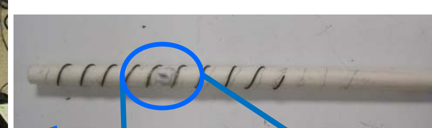
- Power plant: burns municipal **SOLID WASTE**

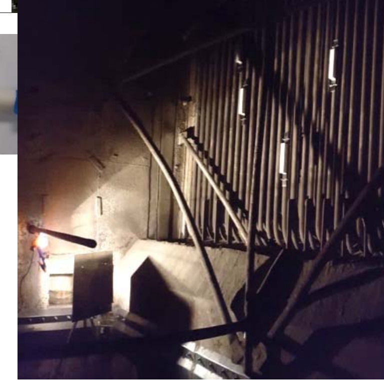
Installed in the boiler tubes → slag detection & removal











Methodology

- SAW $\rightarrow$ GAS SENSOR $\rightarrow$ **PLATFORM**
  - Provide **STABILITY** & **SENSITIVITY**
- For GAS detection :
  - **Selectivity**
  - **Retention** of gas in the sensor
- Selectivity:
  - For HT:
    - ✓ Addressed $\rightarrow$ arrays w/ $\neq$ films $\Rightarrow$ Multi-dimensional signatures / sensor array training & learning
- Retention: To have a signature $\rightarrow$ Gas must be **detected**
  - At HT $\rightarrow$ gas @ $\uparrow$ energy level $\Rightarrow$ film used to **RETAIN** the gas
  - In addition:
    - ✓ Other materials $\rightarrow$used to **ATTRACT** the gas to sensor

III. PROJECT OBJECTIVES

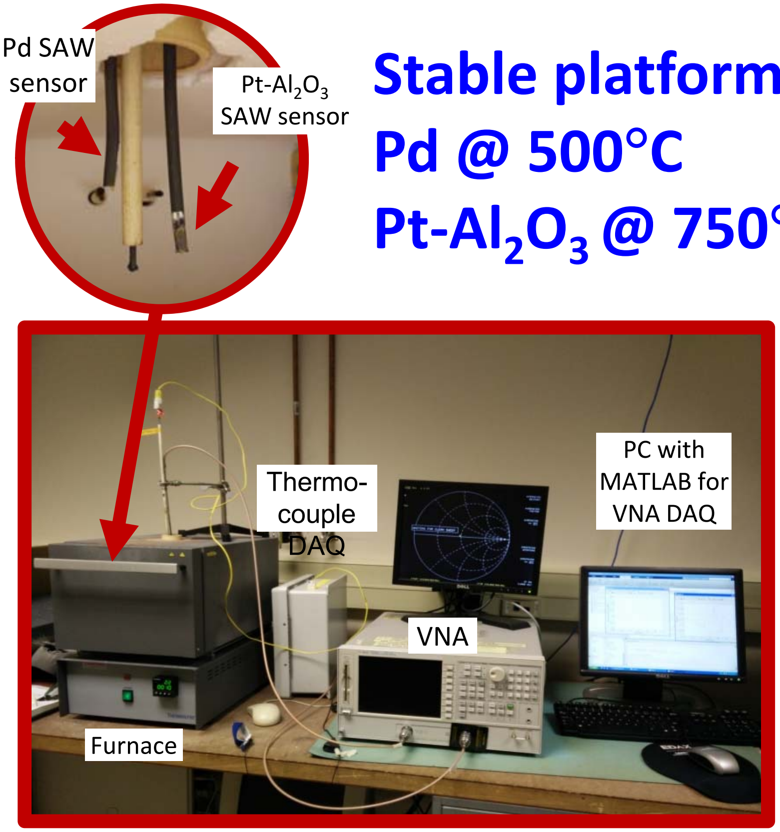
Project Objectives

- Demonstrate → Performance μ~ acoustic sensor (SAW) for GAS SENSOR applications in power plant environments
  - Coal gasifiers, combustion turbines, solid oxide fuel cells, and advanced boiler systems
  - HT → in the range 350°C and 1000°C
  - Passive operation
  - Targeting initially: detection of H_2, O_2, and/or NO_x
- Major project targets:
  - Establish SAW gas sensor (platform + film) **STABILITY**
  - Establish adequate **RETENTION** for HT gas detection
- Thus functional sensor for long-term maintenance-free operation
  - @ power plant: ↑ **fuel burning efficiency**; ↓ **gaseous emissions**, and ↓ **maintenance costs & downtime** through condition-based monitoring

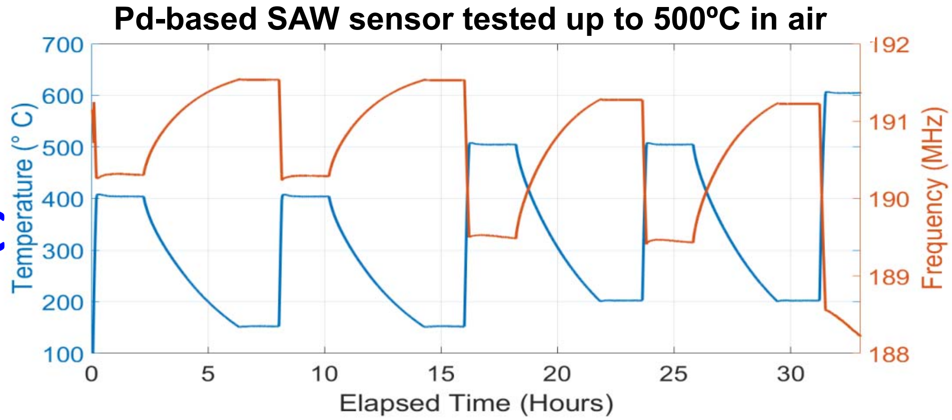
IV. RECAP: LAST YEAR REPORTED PROGRESS

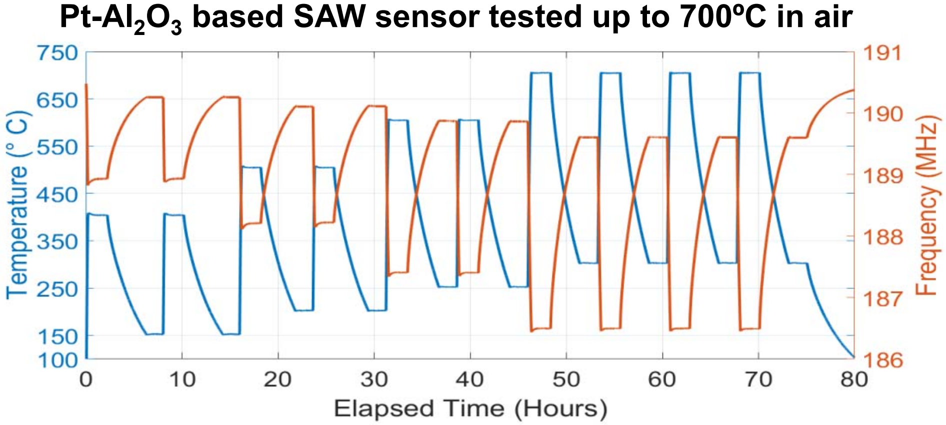
LAST YEAR REPORTED PROGRESS

- Poster 2016 (after six months work)
- Check stability of bare (no film) SAW sensor platform
  - LGS crystal with Pd & Pt-Al_2O_3 electrodes fabricated & tested



Stable platforms
Pd @ 500°C
Pt-Al_2O_3 @ 750°C



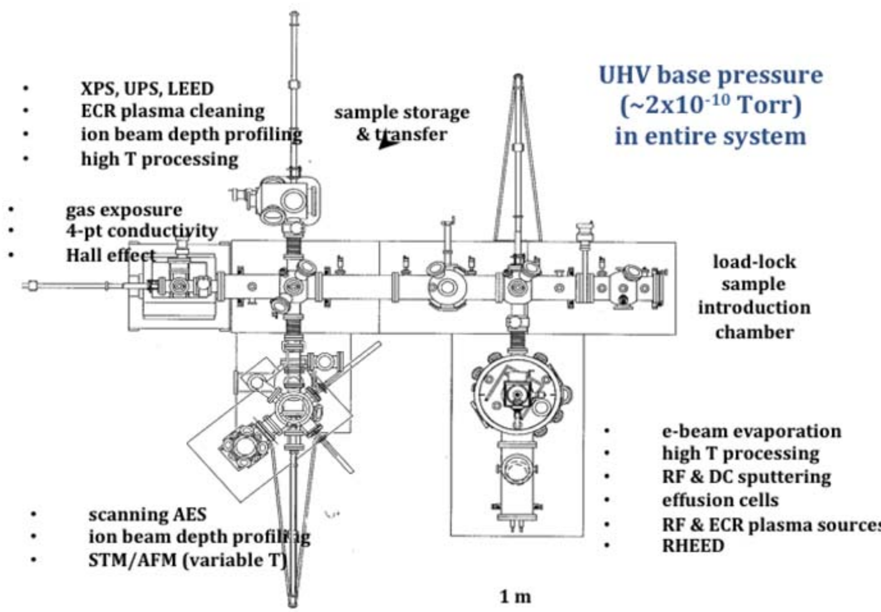


LAST YEAR REPORTED PROGRESS

- In order to achieve the required gas RETENTION @ HT
  - YSZ (Yttrium stabilized Zirconia) →
    - ✓ Initial YSZ film deposition and testing on **sapphire**
  - 30nm (reactive magnetron sputter deposition)

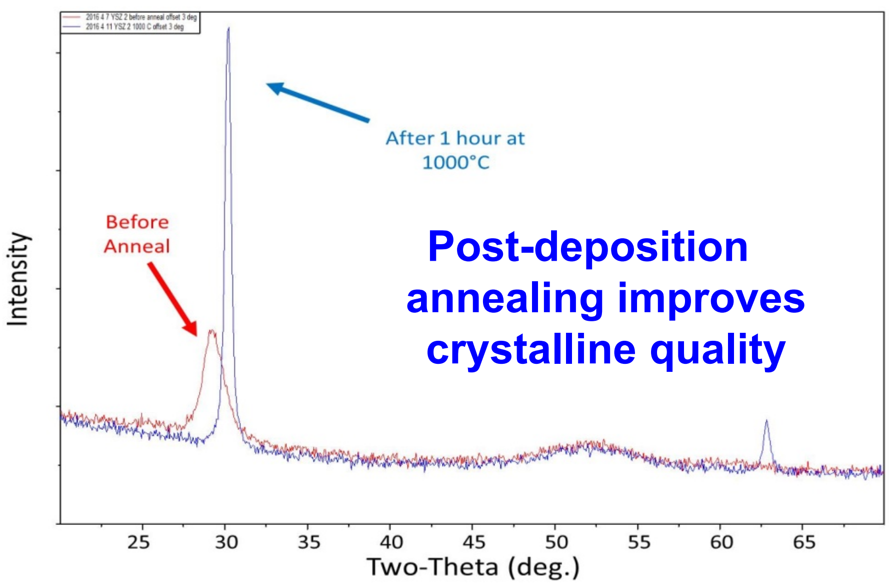
Photo & schematic:

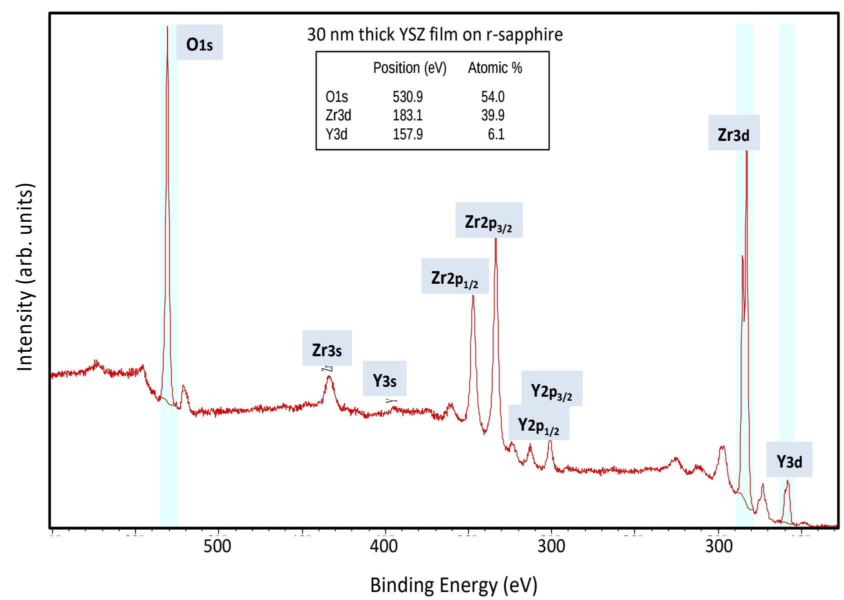
Thin Film Deposition, Processing, and Characterization Facility at the UMaine used to synthesize and analyze thin film materials for the SAW sensor devices



LAST YEAR REPORTED PROGRESS

- X-ray diffraction(XRD) & X-ray photoelectron spectroscopy (XPS)
  - ✓ 8%Y_2O_3-92%ZrO_2 film stoichiometry: film 65.9% O, 29.0% Zr, and 5.1% Y
  - ✓ Anneal 1000°C / 1h ⇒ ↑ crystalline quality





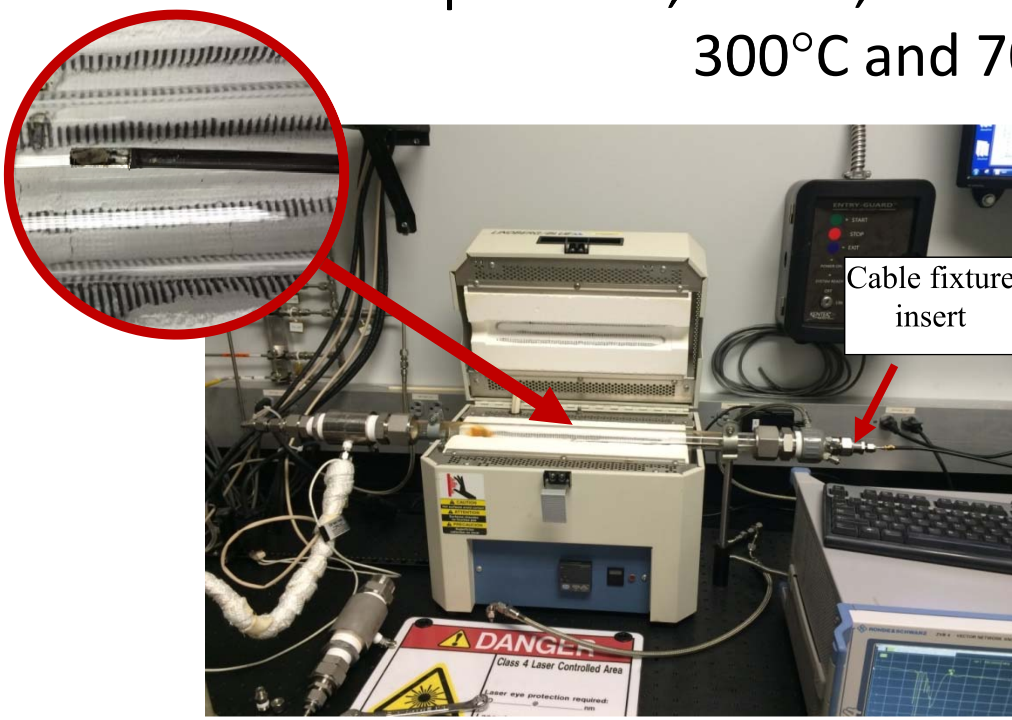
V. Project Progress & Current Experiments

Project Progress & Current Experiments

1) Test performed 2016 @

   NETL Research and Innovation Center, Pittsburgh, PA

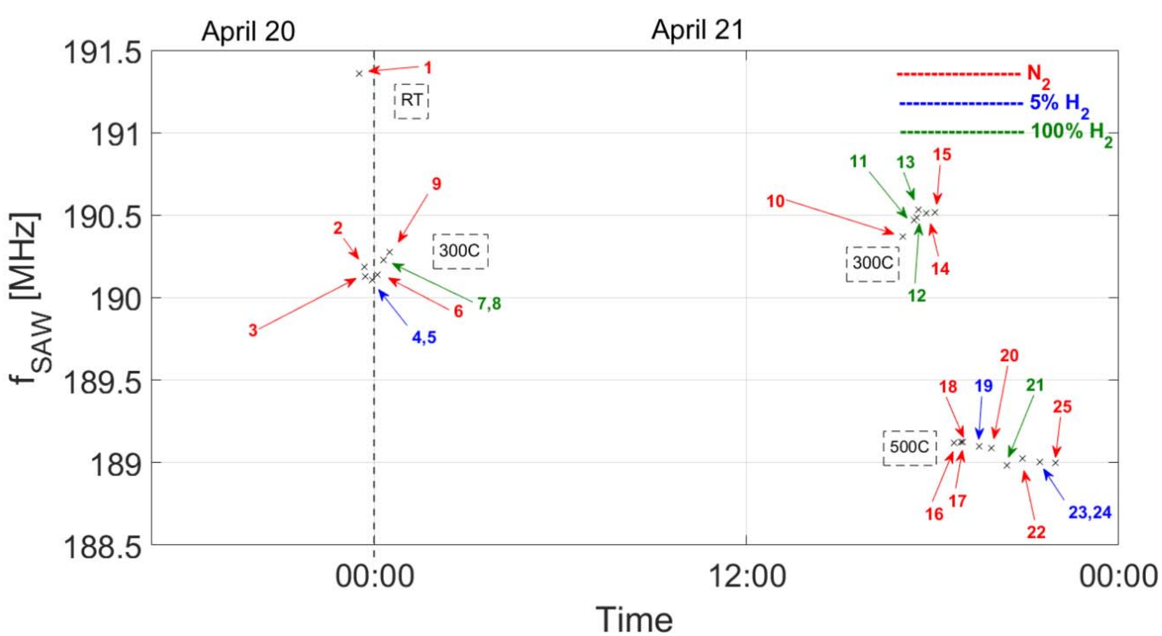
- Two days → Sensors exposed to:
  - 100% N_2, 5% H_2 in N_2, and 100% H_2
  - Room temperature, 300°C, and 500°C (Pd-based sensor) and 300°C and 700°C ($PtAl_2O_3$ - based sensor)

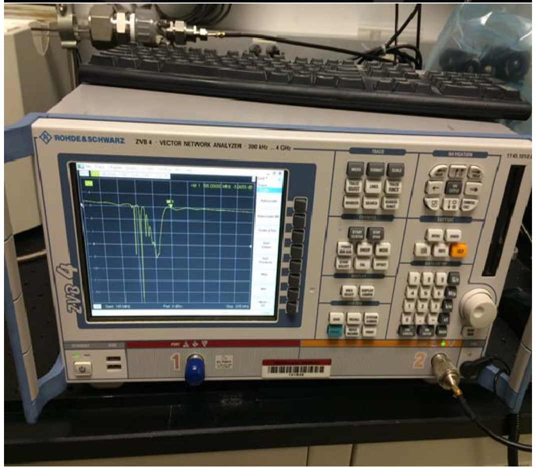


Test made in collaboration with: Paul Ohodnicki, Technical Portfolio Lead / Functional Materials Team

Project Progress & Current Experiments

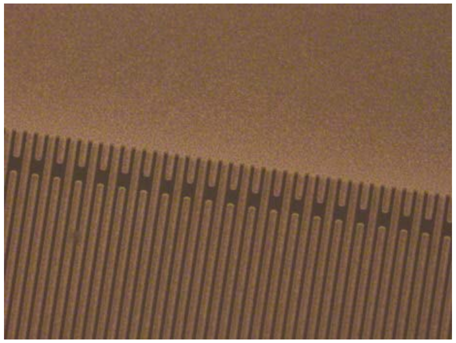
- RF measurements: VNA Rohde & Schwarz ZVB 4
- For Pd-based bare SAW platform:
  - Exposure to $H_2 \rightarrow$ both $\uparrow$ & $\downarrow$ in freq.
  - Multiple phenomena @ bare crystal :
    - ✓ Surface cleaned or reacting with H_2
    - ✓ Pd electrodes reacting with H_2

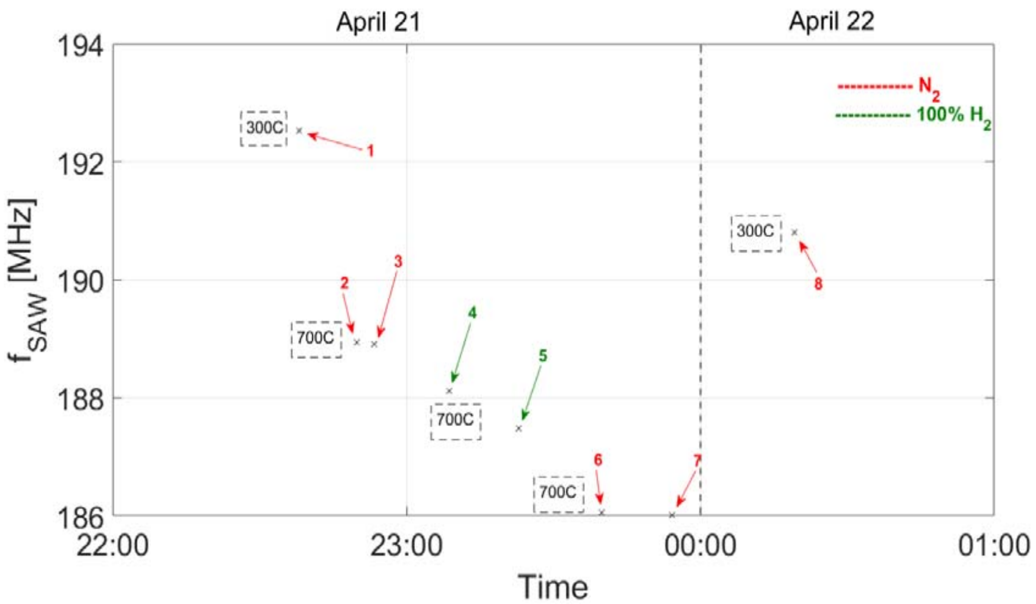


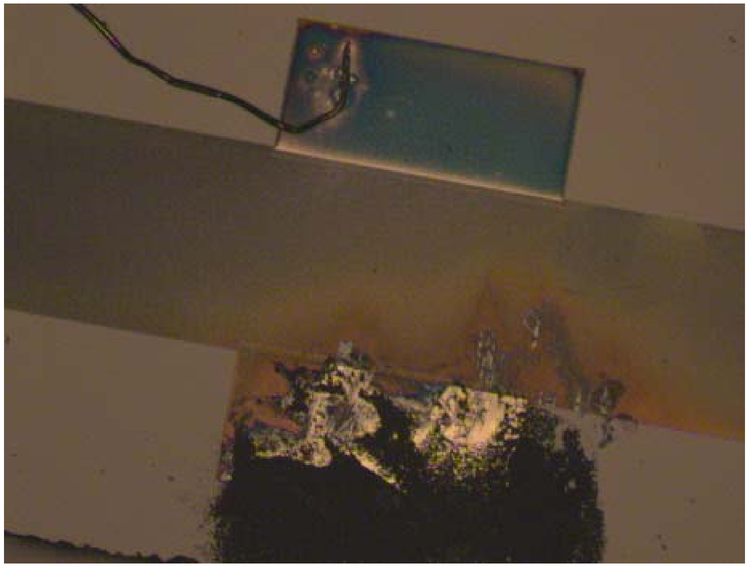


Project Progress & Current Experiments

- For $PtAl_2O_3$ - based bare SAW platform:
  - Device bonding damaged due to transport
  - Fixed with Ag paste @ NETL →
    - ✓ Pasted reacted with electrodes @ HT / H_2 environment
    - ✓ Frequency response affected by paste
    - ✓ Permanent damage to the device

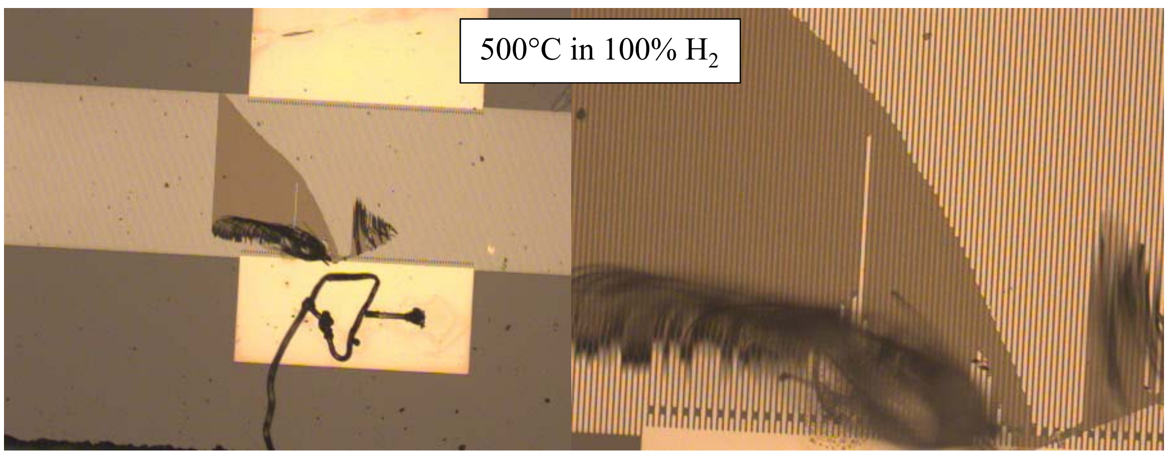


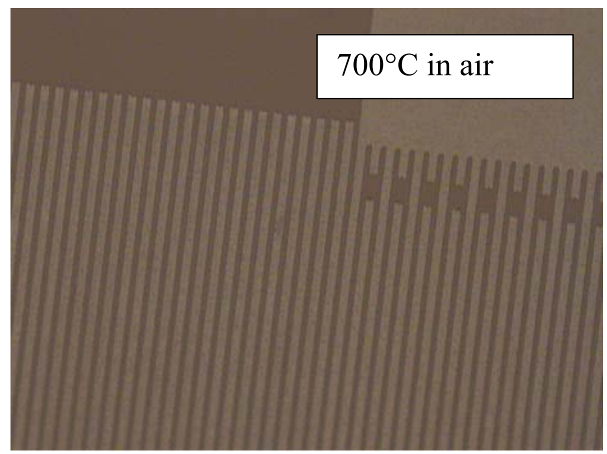




Project Progress & Current Experiments

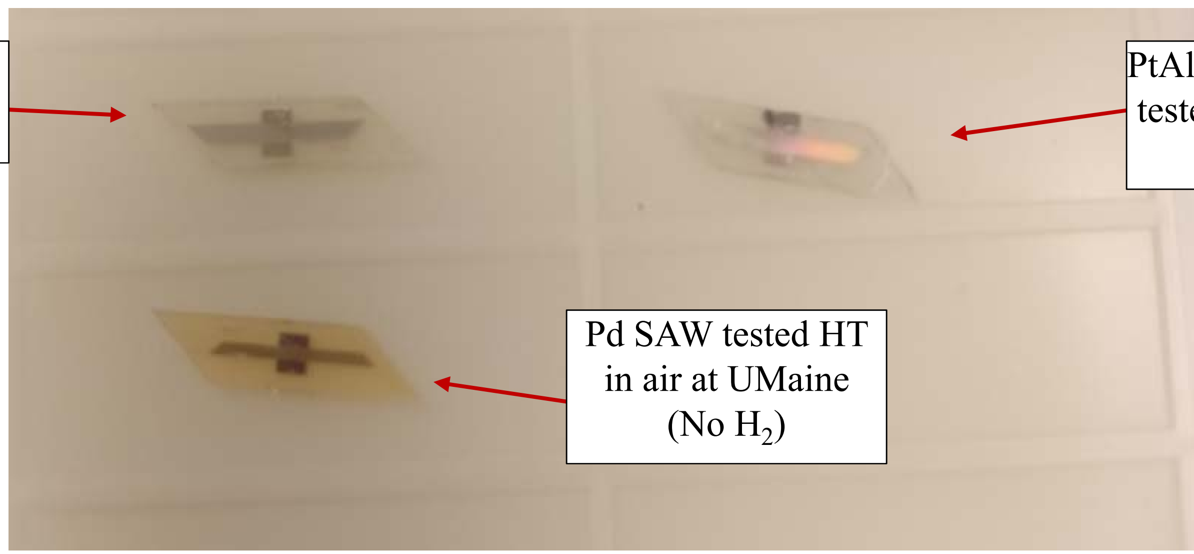
- Back to the Laboratory for analysis:
- Pd-based bare SAW platform:
  - H_2 & HT stressed significantly the Pd film → delamination
  - Delamination occurred btwn Pd and Zr adhesion layer (not surface cleaning problem)
  - Phenomenon does NOT repeat under HT alone (same batch)
    - ✓ Normal agglomeration due to the de-wetting phenomenon





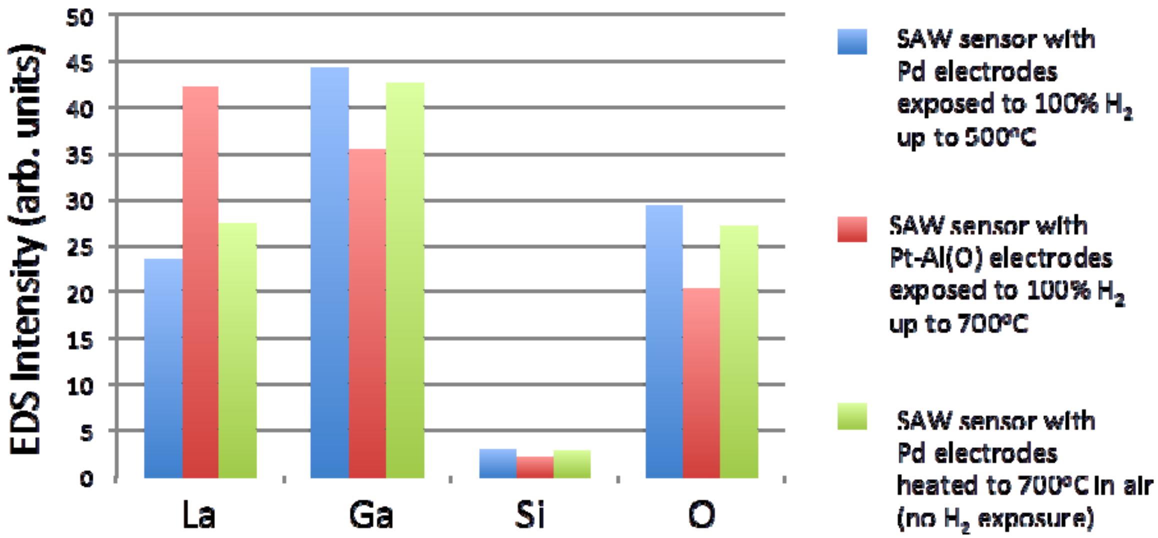
Project Progress & Current Experiments

- Regarding the LGS substrate:
  - Exposure to H_2 at high temperature $\rightarrow$ changed color of substrate
  - Phenomenon is NOT observed when material is exposed to high temperature in AIR



Project Progress & Current Experiments

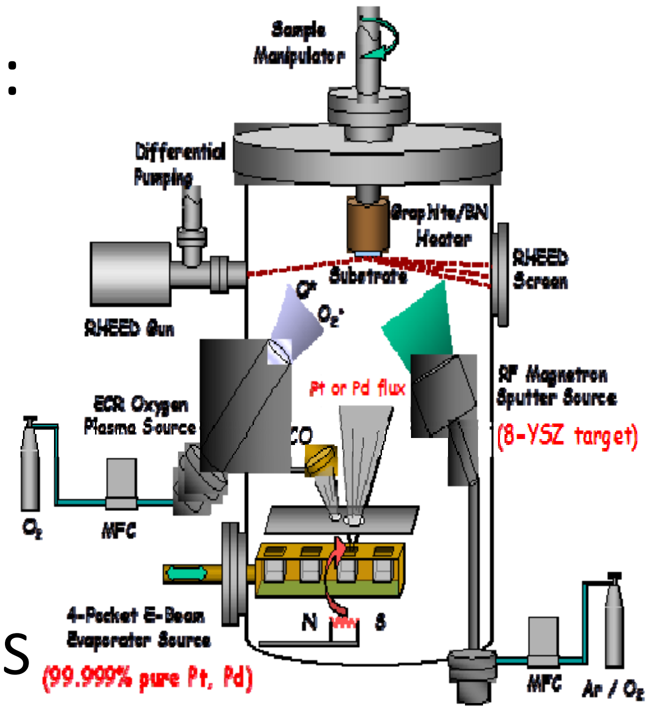
- XPS analysis of the samples exposed to 100% H_2@ NETL
- H_2 → reducing gas → potential to affect $La_3Ga_5SiO_{14}$ surface
  - Thus the SAW response (~90% energy within 1λ from surf.)
  - Preliminary analysis of the devices tested at NETL 2016
    - ✓ No significant difference for the Pd-based SAW sensor
    - ✓ Apparent depletion of Ga for the $PtAl_2O_3$ - based SAW sensor
    - ✓ More data is required for statistical analysis



Project Progress & Current Experiments

2.) YSZ deposition → Initially on sapphire; now on LGS

- Reactive magnetron sputtering using:
  - An 8%Y_2O_3-92%ZrO_2 target;
  - Argon/Oxygen ratio of 95%/5%;
  - 6 mTorr total pressure



- Films grown both at RT and @ 600°C on LGS

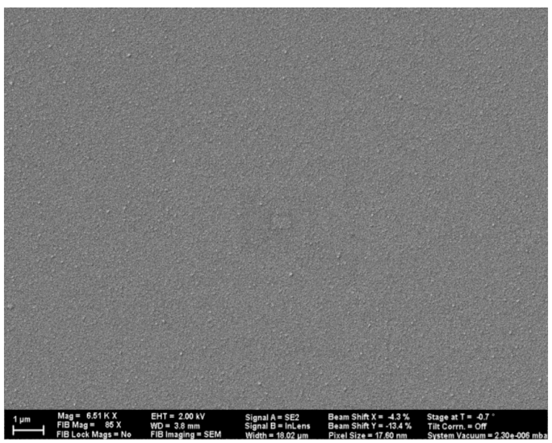
- Initial thickness investigated: 200 nm

Project Progress & Current Experiments

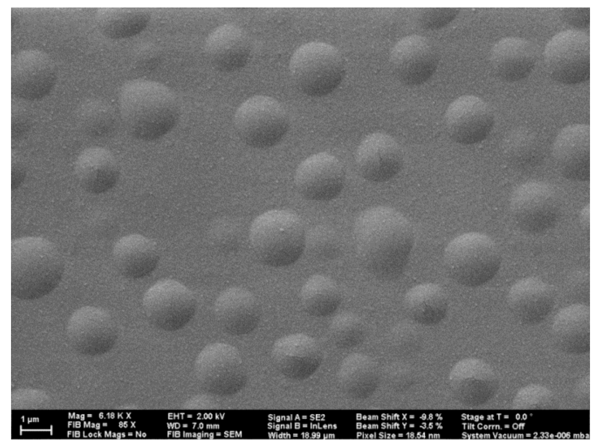
- Stoichiometry: before & after 850°C 1hr
  - No detectable ≠ in stoichiometry

Sample	O %	Y %	Zr %
YSZ Unheated / LGS	53.8	6.3	39.9
YSZ Heated / LGS	53.2	6.4	40.4

- After heating 850°C 1hr ⇒ Bubbles (film under stress)



Heated 850°C 1h, vacuum ⇒

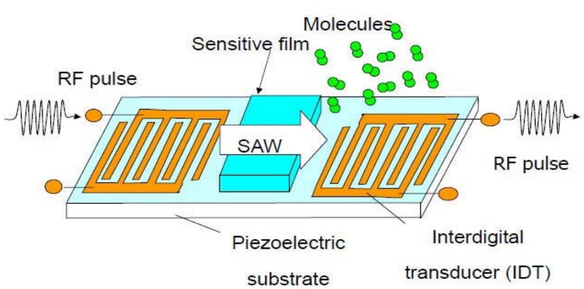


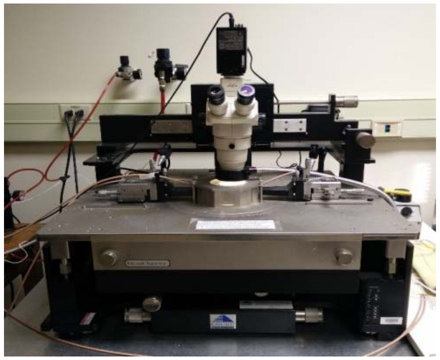
- Phenomenon also observed:
  - If film is annealed in air & if film is grown @ 600 °C
- Other growth conditions being currently analyzed

Project Progress & Current Experiments

3.) LGS SAW platform tested with YSZ film deposited on top

- Bare SAW platform → not expected ↑ sensitivity to H_2
  - Low sticking coefficient to H_2
- YSZ proposed. Though question:
  - How does the YSZ film affect LGS SAW platform response?
  - Operational? Stable after HT exposure?
- 200 nm YSZ film deposited on LGS SAW devices
- Room temperature frequency responses measured:
  - Before & after deposition





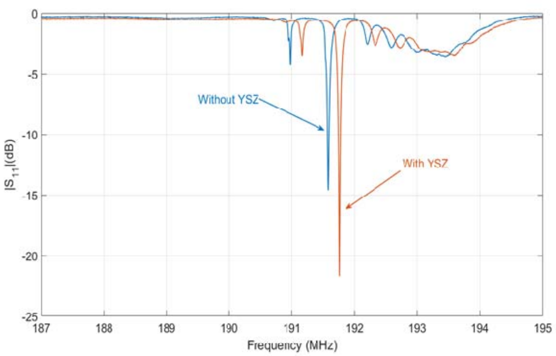
SAW Sensors with YSZ on Top

➢ Pd & $PtAl_2O_3$ – based electrodes

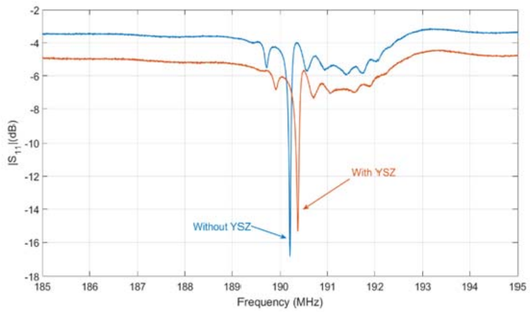
a) Room Temperature tests before and after deposition

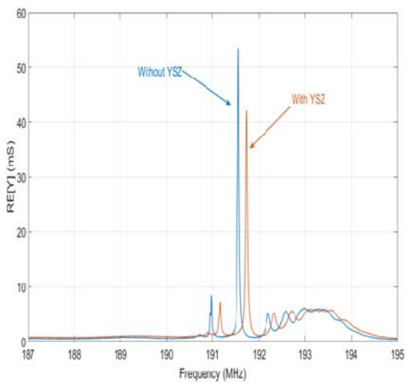
- Devices operational, response consistent with the type of film

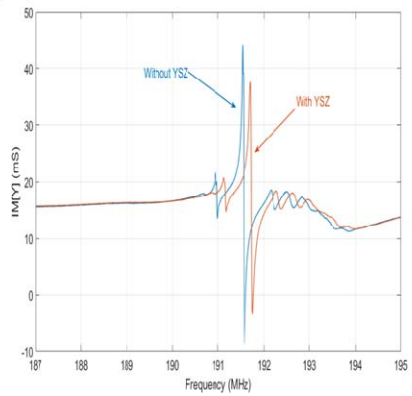
Pd –based Electrodes

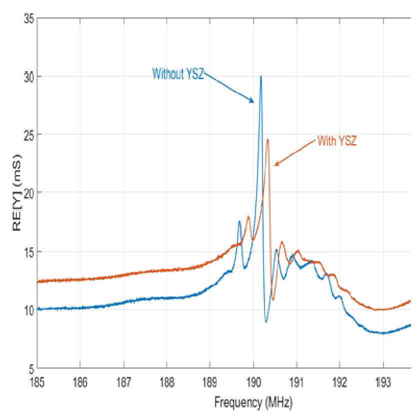


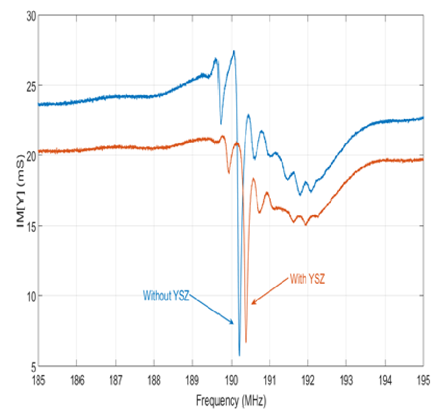
$PtAl_2O_3$ –based Electrodes









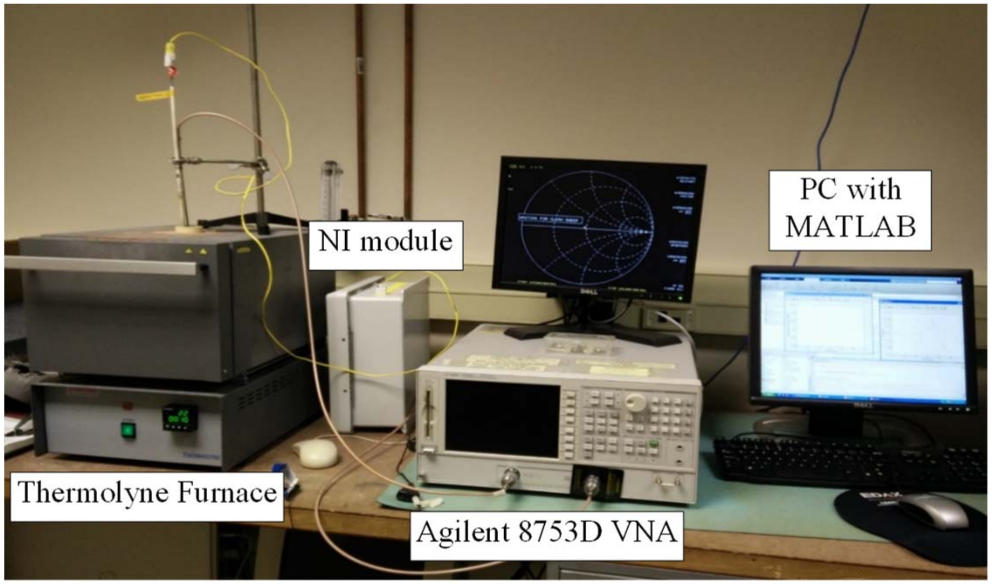


SAW Sensors with YSZ on Top

b) High temperature **monitoring** tests

- Pd & $PtAl_2O_3$ – based electrode sensors
  - YSZ film on top
  - Tested up to 700°C in air
  - Temperature profile & Experimental setup for HT stability testing

Temperature	# of Cycles
150°C-400°C	2
200°C-500°C	2
250°C-600°C	2
300°C-700°C	4

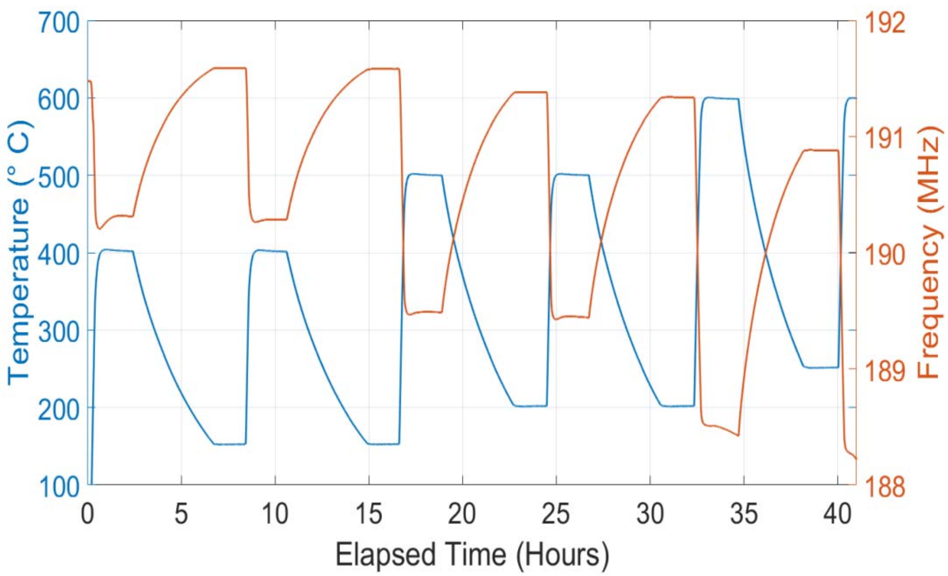


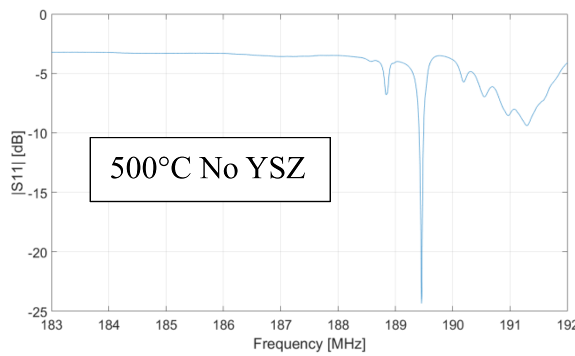
SAW Sensors with YSZ on Top

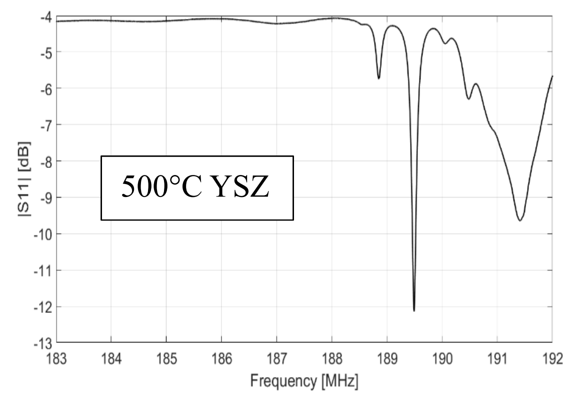
➢ Pd & $PtAl_2O_3$ – based electrode sensors

b) High temperature tests

- **Pd –based Electrode SAW Sensors** YSZ film on top
- Tested up to 600°C in air
  - ✓ Stable @ 500°C; Deteriorating @ 600°C
  - ✓ Stronger radiation to the bulk due to YSZ



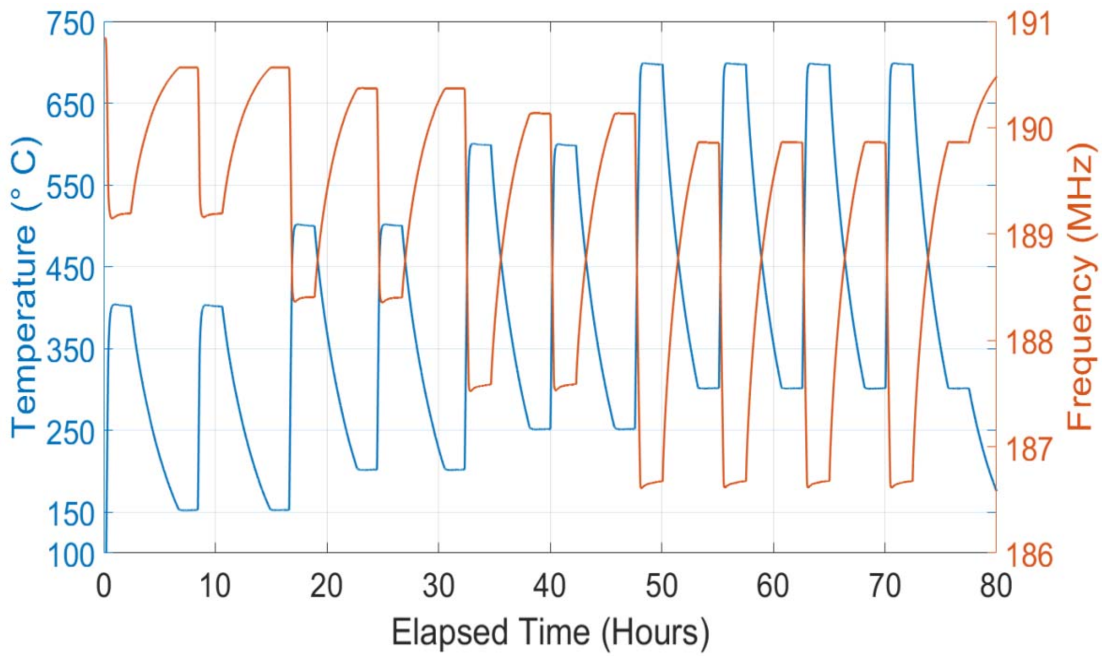


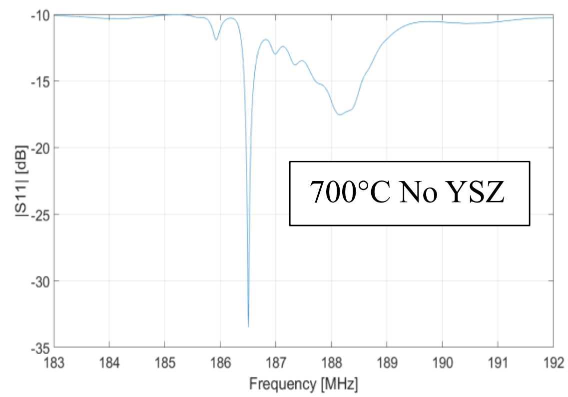


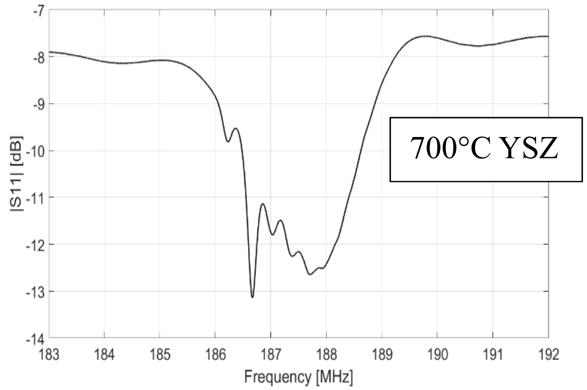
SAW Sensors with YSZ on Top

b) High temperature tests (cont.)

- **$PtAl_2O_3$ – based Electrode Sensors** / YSZ film on top
- Tested up to 700°C in air → Stable response
- Stronger radiation to the bulk due to YSZ



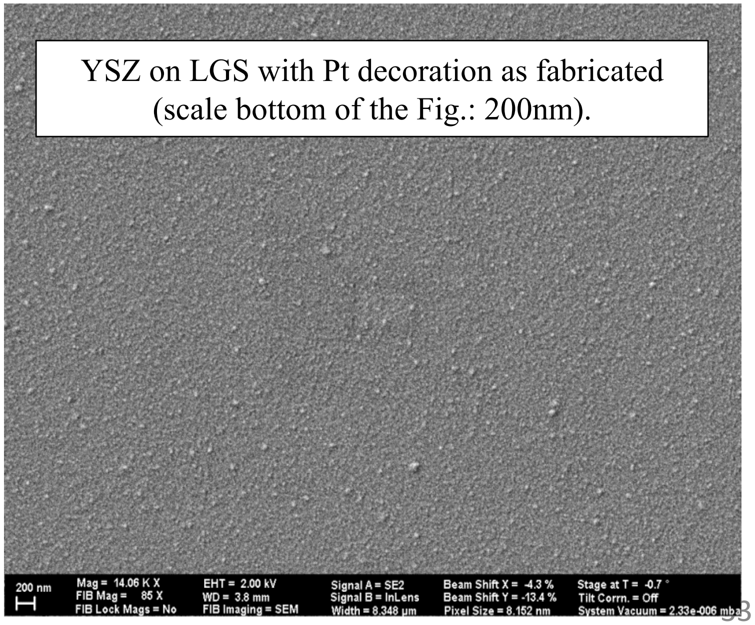




Project Progress & Current Experiments

4.) Decoration of the YSZ surface with Pt or Pd

- Goal: catalytically enhance the chemical reaction @ H_2 gas / SAW sensor interface
- 0.5nm of Pd or Pt deposited
  - Metal clusters (surface not completely covered)
  - Annealed in air @ 1000°C for 2h in air
  - YSZ composition: unaltered by the presence of the decoration
- Pd or Pt decoration →
  - Concern:Compromise layer insulation?
  - No increase in conductivity measured
  - Pd & Pt diffused into the YSZ film
- XPS analysis:
  - Ga diffused into the YSZ layer;
  - Y moved towards the surface



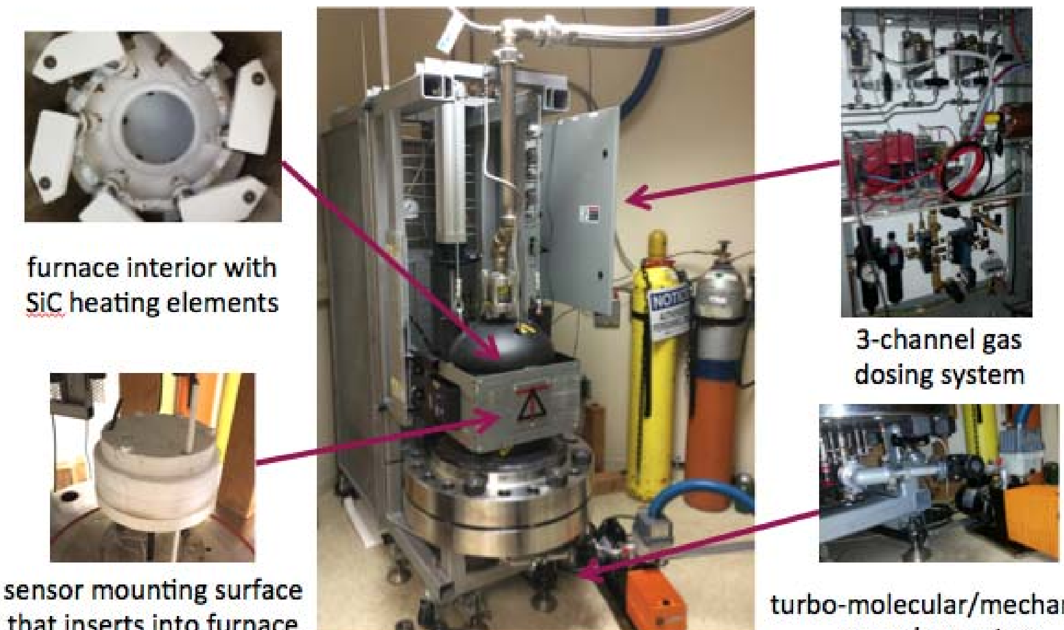
YSZ on LGS with Pt decoration as fabricated (scale bottom of the Fig.: 200nm).

Project Progress & Current Experiments

5.) Gas tests at UMaine:

- Adaptation of a Gas Furnace for 4% H_2/N_2 Gas tests
- Deltech DT-29-PV-66 furnace
  - Internal volume of the chamber > 1 cubic ft ⇒ huge dead volume (time)
  - Decision to build
    - ✓ Smaller chamber

    (work in progress)



furnace interior with SiC heating elements

sensor mounting surface that inserts into furnace

Deltech DT-29-PV-66 controlled pressure high temperature furnace

3-channel gas dosing system

turbo-molecular/mechanical pumping system

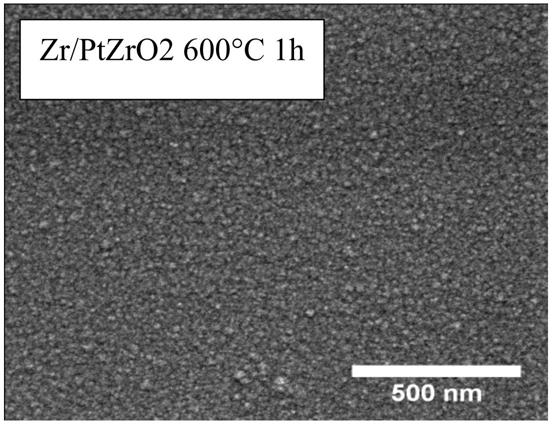
Project Progress & Current Experiments

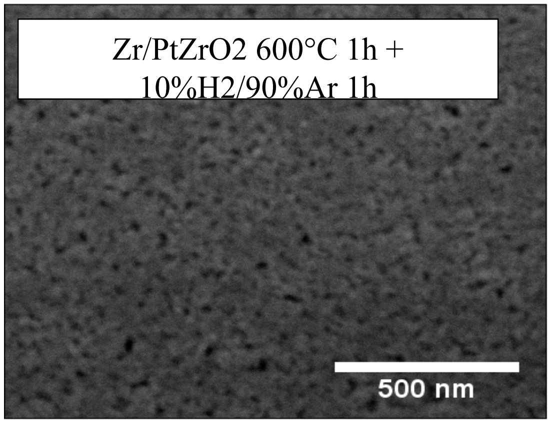
6.) 1st Series of Film Tests with NETL / Pittsburgh:

- Samples sent to perform film analysis:
  1. Sample 1: 200 nm of YSZ / LGS
  2. Sample 2: 10 nm Zr / 150 nm of co-evaporated Pt and ZrO_2
  3. Sample 3: 10 nm Zr / 150 nm of co-evaporated Pt and Al_2O_3.
  4. Sample 4: 10 nm Zr / 150 nm of Pd.
  5. Sample 5: bare LGS for witness.
- Goal: **verification of stable films for sensor fabrication**
- Exposure to AIR vs. 10%H2/90%Ar @ 600°C
  - Comparison by SEM for
    - ✓ ≠s in morphology
    - ✓ ≠s in electrical properties
    - ✓ ≠s in crystalline properties

Project Progress & Current Experiments

- Preliminary findings (exposure to AIR vs. 10%H2/90%Ar @ 600°C):
  - No major morphological changes regarding the YSZ film
  - Signs of film delamination found: consistency with UMaine (slide 27)
  - Particle aggregation identified for both Pd and Pt-Al2O3
  - PtZrO2 thin film seems to reveal voids



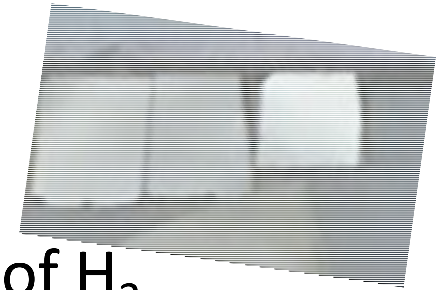


- New tests are under way for further
  - Verification of the performance of these films
  - Identification of possible substrate and film changes
  - Corrective actions in film fabrication / selection for stable sensors

Project Progress & Current Experiments

7.) Collaboration with NETL / Pittsburgh (ongoing activity):

- 2nd Series of Film sent to NETL / Pittsburgh
- Goal: **verification of stable films for sensor fabrication**
  - Ongoing tests of YSZ films
  - Ongoing tests of metal particles decorated YSZ films
  - Ongoing tests of electrode & retention layer on LGS surface



- Tests to be performed under exposure to
  - HT in air vs. modest and high concentrations of H_2
  - Temperature cycling & long term exposure

VI. CONCLUSIONS & ACKNOWLEDGEMENTS

CONCLUSIONS

- Past year activities & progress $\rightarrow$ HT μ~ SAW Gas Sensor Project
- The presentation started with the:
  - Motivations, Methodology, and Project Objectives
- A couple slides $\rightarrow$ reviewed last year project developments
- This year's advances:
  1. Preliminary SAW platforms test @ NETL Pittsburgh (100%H_2 & 700°C)
  2. YSZ grown on LGS @RT and 600°C : morphology & stress analyzed
  3. YSZ grown & tested SAW platform: before/after deposition & HT cycling
  4. YSZ/LGS wafer decorated $\rightarrow$ Pt & Pd investigated: YSZ consistency verified
  5. UMaine Gas test equipment updated & new chamber under development
  6. 2nd Semester 2016: 1st Series of Film Tests with NETL / Pittsburgh
  7. 1st Semester 2017: 2nd Series of Samples sent to NETL / Pittsburgh
- Project progressing as planned. Encouraging results wrt:
  - Sensor endurance; stability; capability of changing with H2

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ELECTRICAL & COMPUTER ENGINEERING Orono, Maine

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

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