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

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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 $\Rightarrow$ ↓ maintenance $\Rightarrow$ ↓ **POWER PLANT DOWNTIME**

- Gas PP $\Rightarrow$ Cost $11,000/h \Rightarrow $264,000/day (KCF Technologies)
- Average Outage (2007/11) Coal Units alone (NETL / Krulla 2014) $\Rightarrow$
  - Btw 300 - 500 hours/unit-year $\Rightarrow$ 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)
      - 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
      - More than 2GW additional power / yr from the existing fleet

- **Emission / Pollution?**
  - 1% Heat rate improvement
    - Cool fleet alone
    - 13.8 billion metric tons CO₂/yr
GAS SENSORS capable of HTemperature Harsh-Environment oper.

- Operate **RELIABLY** with very little or no wires
  - Wiring poses problem for reliability in harsh environments
  - Packaging restricts the use of several technologies
- **NO MAINTENANCE** (inaccessible locations: no wires; no packaging deterioration; no replacement)
- Sensor → **STABLE** in the environment over **LONG PERIODS**
- **NO Battery**
  - Frequent maintenance
  - Limited to 500°C
  - 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 17 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

![Graph showing temperature and frequency shift](image)

- Highly reproducible
Methodology

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

Temperature resolution < ±3°C
Drift < 1°C / 135 hrs
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°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 → GAS SENSOR → PLATFORM
  - Provide **STABILITY & SENSITIVITY**

For GAS detection:
- **Selectivity**
- **Retention** of gas in the sensor

Selectivity:
- For HT:
  - Addressed → arrays w/ ≠ films ⇒ Multi-dimensional signatures / sensor array training & learning

Retention: To have a signature → Gas must be **detected**
- At HT → gas @ ↑ energy level ⇒ film used to **RETAIN** the gas
- In addition:
  - Other materials → 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 750°C
  - Passive operation
  - Targeting initially: detection of H₂ and O₂

- 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

- SAWR platform development & testing for gas sensor
- Check stability of bare (no film) SAW sensor platform
  - LGS crystal with Pd & Pt-Al₂O₃ electrodes fabricated & tested

Stable platforms
Pd @ 500°C
Pt-Al₂O₃ @ 750°C
In order to achieve the required gas RETENTION @ HT

- YSZ (Yttrium stabilized Zirconia) →
  - IYSZ film deposited initially on sapphire and then transitioned to LGS
- 15 to 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%$\text{Y}_2\text{O}_3$-92%$\text{ZrO}_2$ film stoichiometry: film 65.9% O, 29.0% Zr, and 5.1% Y
  - Anneal 1000°C / 1h $\Rightarrow$ $\uparrow$ crystalline quality

Post-deposition annealing improves crystalline quality
LAST YEAR REPORTED PROGRESS

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>O %</th>
<th>Y %</th>
<th>Zr %</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ Unheated / LGS</td>
<td>53.8</td>
<td>6.3</td>
<td>39.9</td>
</tr>
<tr>
<td>YSZ Heated / LGS</td>
<td>53.2</td>
<td>6.4</td>
<td>40.4</td>
</tr>
</tbody>
</table>

- After heating 850°C 1hr ⇒ Bubbles (film unde stress)
  ⇒ ISSUE RESOLVED THIS YEAR

Heated 850°C 1h, vacuum ⇒
LAST YEAR REPORTED PROGRESS

- 2016 @ NETL/Pitts:
  
  1st SAWRs platform test with 100% H₂

- Two days → Sensors exposed to:
  - 100% N₂, 5% H₂ in N₂, and 100% H₂
  - Room temperature, 300°C, and 500°C (Pd-based sensor) and 300°C and 700°C (PtAl₂O₃ - based sensor)
  - Stable platform → encouraging to develop gas detecting film

Test made in collaboration with: Paul Ohodnicki, Technical Portfolio Lead / Functional Materials Team & Robert Fryer, ORISE Postdoctoral Researcher
V. Project Progress & Current Experiments
Project Progress & Current Experiments

1) Gas Test System at UMaine

- High-Temp. High-Pressure DelTech DT-29-PV-66 Gas Furnace
  - Chamber: > 1 cubic feet \(\Rightarrow\) huge dead volume (time)

- Smaller chamber built
  - 2 chambers: (~1 in\(^3\) \(\approx\) 6.10\(^{-4}\) ft\(^3\) each)
    - \(\text{N}_2\) reference (temperature)
    - Gas sensing
    - Witness thermocouple access
Project Progress & Current Experiments

- HT Chamber → Sensors, gas delivery, & interrogation system
- System developed:
  - Real-time interrogation of up to 4 sensors (two / chamber)
  - Two thermocouples (one / chamber)
Project Progress & Current Experiments

- Complete test setup: Chamber, devices mounted & respective equipment
2) Design, fabrication, and experimental verification of alternate orientations on LGS plane

- Simulations carried out on commercial LGS wafer:
  - Two orientations identified: temperature compensation
    - 175°C & 300°C ⇒ insensitive to temp. ⇒ ↓ cross-sensitivity
    - Acceptable electromechanical coupling for SAWR sensor
    - Power flow angle addressed in the mask design

- Photomask generated & devices fabricated
Responses for the 175°C & the 300°C TCs SWRs

- $|S_{11}|$ and admittance at room temp.
Project Progress & Current Experiments

- Experimental verification of temperature compensation at temperatures above 150°C
  - Two orientations compensated at higher temperatures
  - Publication on method of selection and verification of TC orientations on LGS at HT

3) Gas Delivery Measurements

- TC SAWR 175°C → Gas response @ Room Temperature

- Conditioning the device surface: oxygen exposure

- Exposure to hydrogen causes desired changes in resonant frequency
Project Progress & Current Experiments

- TC SAWR 175°C → Gas response @ 200°C

Hydrogen Exposures, ~30kHz shift in resonant frequency
Project Progress & Current Experiments

- TC SAWR 300°C → Gas response @ 300°C

Hydrogen Exposures,
~6kHz shift in resonant frequency
4) YSZ material development

- YSZ deposited at room temperature
  - Bubbles after HT annealing (700°C) and cycling (750°C)
  - Issue more severe for thicker layers
  - Could affect sensor stability over time
Materials Development

- High-temperature deposition of YSZ (25 nm @ 850°C)
  - Releases stress ⇒ PROBLEM SOLVED!!!

RT deposited YSZ, after HT cycling up to 750°C

850°C deposited YSZ, after HT cycling up to 750°C
Materials Development

- **PtAl<sub>2</sub>O<sub>3</sub> – based electrode sensors**
  - Develops stress hillocks much like YSZ
  - PtAl<sub>2</sub>O<sub>3</sub> deposited @ ↓ temp. → photoresist (lift-off process)
  - Exploration of different interfacial layers to diminish stress

Heated 800°C 1h, air

- ZrO<sub>2</sub> / Zr interfacial layer
- Zr / ZrO<sub>2</sub> interfacial layer
5) Capacitive coupling $\rightarrow$ YSZ deposited @ HT

- No photoresist necessary to define contacts
SAW Sensors with YSZ on Top

Fabrication of SAW resonators with YSZ deposited at HT

- Bare Device
- Device with 15 nm of YSZ

Bare SAWR TC 175°C

300°C

N₂

⇒

YSZ on Top SAWR TC 175°C

300°C

N₂

⇒
6) Collaborations with NETL/Pittsburgh

- Robert Fryer / Paul Ohodnicki
- Confirmation of SAWR platform stability (no detecting film)
6) Collaborations with NETL/Pittsburgh

- Investigation of stability of UMaine Pt-decorated YSZ film on LGS
  - GOAL: Verification of chemical composition and morphology of Pt-doped YSZ films deposited onto LGS substrates
  - Process A = Temp. cycling (750–300°C, 750°C dwell, 750–300°C); fixed gas (air)
  - Process B = Gas cycling (O$_2$, N$_2$, H$_2$, N$_2$, H$_2$, N$_2$, O$_2$, N$_2$, H$_2$); fixed temperature (700°C)
  - Planned measurements:
    - In situ 4-point electrical conductivity during annealing
    - XPS and SEM before and after annealing
    - XPS depth profiling as a control for the Pt-doped
VI. CONCLUSIONS & ACKNOWLEDGEMENTS
CONCLUSIONS

- Previous period activities & progress → HT μ~ SAW Gas Sensor
- The presentation started with the:
  - Motivations, Methodology, and Project Objectives
- Last year project developments → reviewed
- This year’s activities & advances:
  1. Gas Test System at UMaine → new ↓ vol./↓ dead vol. ⇒ fast response
  2. Design, fab., and experim. verification → TC 175°C and 300°C LGS orientations
  3. Gas Delivery Measurem. (O₂ / H₂ / N₂): successful gas tests up to 500°C
  4. YSZ Pt-decorated film developed & fabricated: film stress → bubbles
     - Problem solved by HT deposition of YSZ
  5. Electrical access → capacitive coupling technique developed at UMaine
  6. Samples sent to NETL/Pitt. → Pt-YSZ / LGS → Stability → chem. comp. & morph

- Successful H₂ detection. Encouraging results wrt:
  - Sensor stability/endurance
  - Temperature compensation at 175°C and 300°C → explored with Pt-YSZ SAWR
  - Capability of detecting with H₂ tested up to 500°C
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