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
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)

http://prs-jobs.com/energy/
Motivation

- **High Temperature Gas Sensor FOSSIL FUEL: WHY?**
  - **EFFICIENCY** in fuel burning by controlling combustion
    - 1% Heat rate improvement (500MW) \(\text{(NETL / Romanosky 2015)}\)  
      - $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 \(\Rightarrow \uparrow 2.6 \text{M}$ /unit-year in sales  
      - More than 2GW additional power / yr from the existing fleet
  - **Emission / Pollution?**
    - 1% Heat rate improvement  
      - Cool fleet alone \(\Rightarrow \downarrow 13.8\) 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 $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ Piezoelectric Crystal
    - Stable up to 1400°C
    - Resistant to thermal shock
  - Stable / Repetitive operation
    - Tested over 5 ½ Mo @ 800°C

![Graph showing frequency shift vs. temperature](chart1.png)

- Highly reproducible

![Graph showing temperature vs. time](chart2.png)
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
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°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 1000°C
  - Passive operation
  - Targeting initially: detection of H₂, O₂, and/or NOₓ

- 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$_2$O$_3$ electrodes fabricated & tested
    - Pd SAW sensor tested up to 500°C in air
    - Pt-Al$_2$O$_3$ based SAW sensor tested up to 700°C in air

Stable platforms
Pd @ 500°C
Pt-Al$_2$O$_3$ @ 750°C
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%Y₂O₃-92%ZrO₂ film stoichiometry: film 65.9% O, 29.0% Zr, and 5.1% Y
  - Anneal 1000°C / 1h ⇒ ↑ crystalline quality
V. Project Progress & Current Experiments
1) Test performed 2016 @
NETL Research and Innovation Center, Pittsburgh, PA

➢ 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)

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 $H_2$
For PtAl$_2$O$_3$ - 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
Back to the Laboratory for analysis:

Pd-based bare SAW platform:

- H₂ & HT stressed significantly the Pd film → delamination
- Delamination occurred between 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
Regarding the LGS substrate:

- Exposure to H₂ at high temperature → changed color of substrate
- Phenomenon is NOT observed when material is exposed to high temperature in AIR

Pd SAW tested at DOE (H₂)

PtAl₂O₃ based SAW tested at DOE (H₂)

Pd SAW tested HT in air at UMaine (No H₂)
Project Progress & Current Experiments

- XPS analysis of the samples exposed to 100% H₂@ NETL
- H₂ → reducing gas → potential to affect La₃Ga₅SiO₁₄ 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 PtAl₂O₃ - based SAW sensor
    - More data is required for statistical analysis
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

<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 under stress)

- Phenomenon also observed:
  - If film is annealed in air & if film is grown @ 600 °C
- Other growth conditions being currently analyzed
3.) LGS SAW platform tested with YSZ film deposited on top

- Bare SAW platform → not expected ↑ sensitivity to H₂
  - Low sticking coefficient to H₂

- 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$_2$O$_3$ – based electrodes
  a) Room Temperature tests before and after deposition
    • Devices operational, response consistent with the type of film
SAW Sensors with YSZ on Top

b) High temperature monitoring tests

- Pd & PtAl$_2$O$_3$ – based electrode sensors
  - YSZ film on top
  - Tested up to 700°C in air
  - Temperature profile & Experimental setup for HT stability testing

<table>
<thead>
<tr>
<th>Temperature</th>
<th># of Cycles</th>
</tr>
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<tbody>
<tr>
<td>150°C-400°C</td>
<td>2</td>
</tr>
<tr>
<td>200°C-500°C</td>
<td>2</td>
</tr>
<tr>
<td>250°C-600°C</td>
<td>2</td>
</tr>
<tr>
<td>300°C-700°C</td>
<td>4</td>
</tr>
</tbody>
</table>
SAW Sensors with YSZ on Top

- Pd & PtAl$_2$O$_3$ – 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
b) High temperature tests (cont.)
- PtAl₂O₃ – based Electrode Sensors / YSZ film on top
- Tested up to 700°C in air → Stable response
- Stronger radiation to the bulk due to YSZ
4.) Decoration of the YSZ surface with Pt or Pd

- Goal: catalytically enhance the chemical reaction @ H₂ 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
5.) Gas tests at UMaine:

- Adaptation of a Gas Furnace for 4% $\text{H}_2/\text{N}_2$ Gas tests
- Deltech DT-29-PV-66 furnace
  - Internal volume of the chamber $> 1$ cubic ft $\Rightarrow$ huge dead volume (time)
  - Decision to build
    - Smaller chamber
      - (work in progress)
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$_2$O$_3$.
  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%H$_2$/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
7.) Collaboration with NETL / Pittsburgh (ongoing activity):

- 2<sup>nd</sup> 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<sub>2</sub>
  - Temperature cycling & long term exposure
VI. CONCLUSIONS & ACKNOWLEDGEMENTS
CONCLUSIONS

- Past year activities & progress → HT μ~ SAW Gas Sensor Project
- The presentation started with the:
  - Motivations, Methodology, and Project Objectives
- A couple slides → reviewed last year project developments
- This year’s advances:
  1. Preliminary SAW platforms test @ NETL Pittsburgh (100%H₂ & 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 → 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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