High-Temperature Nano-Derived Micro-$H_2$ and -$H_2S$ Sensors

Christina Wildfire, Engin Ciftyurek, Edward M. Sabolsky

Energy Materials Program
Department of Mechanical and Aerospace Engineering
West Virginia University

Annual DOE-NETL University Coal Research Project Review
May 30-31, 2012
Outline

• Objectives
• Background and proposed work plan
• Synthesis of nanomaterials
• Evaluation of H$_2$ nanomaterials
• Micro-patterning techniques
• Stable micro-interdigitized electrodes (µIDEs)
• Conclusions
• Future Work
Objectives

• Develop micro-scale, chemical sensors composed of nano-derived, metal-oxide materials which display stable performance within high-temperature environments (>500°C).

• **Short term**—Develop high-temperature H₂ and H₂S sensor using low cost, easily reproducible methods with 3D porous nanomaterials.

• **Long term**—Develop high-temperature micro-sensor arrays to detect gases such as NOₓ, SOₓ, H₂S, H₂, HCs.

• Collaboration with NexTech Materials, Ltd. (Lewis Center, OH).
Proposed Work Plan

Task 2.0  Synthesis and Characterization of Nano-Composite Electrodes.  Doped-tin oxide, ceria and zirconate (perovskite and pyrochlore) nanomaterials will be synthesized using hydrothermal and/or glycine-nitrate processes and characterized.


Task 4.0  Fabrication of Micro-Sensors and Arrays.  Fabricate functional hydrogen micro-sensors and micro-sensor arrays.  In addition, stable IDEs for high-temperature applications must be developed.

Task 5.0  Micro-Sensor and Sensor Array Testing.
Micro-sensors will be first characterized for baseline resistance using external furnace heat at temperatures ranging from 500°C to at least 1100°C.  Key tests include:

- Hydrogen sensitivity and selectivity
- Humidity sensitivity (0-10% H₂O)
- O₂ requirements (0.1-20%)
- CO cross-sensitivity (ppm-% CO)
- Temperature sensitivity (500-1200°C)
- Poison effects (<200 ppm PH₃, H₂S, HCl)
## Proposed Work Schedule

### Schedule of tasks and milestones

<table>
<thead>
<tr>
<th>Task/Milestone</th>
<th>Quarter after Project Initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

#### Task 1. Project Management and Planning (Q1-Q12)

**Subtask 1.1:** Kick-Off Meeting and Sensor Design at WVU.
- → MS: Sensor and Array Established

**Subtask 1.2:** Project Meetings and Reporting
- → DL: Quarterly Reports
- → DL: Annual Progress Reports
- → DL: Final Technical Report

#### Task 2. Synthesis and Characterization of Nano-Composite Electrodes. (Q1-Q7)

**Subtask 2.1:** Synthesis of Zirconate Electrode Compositions
- → MS: Process for synthesizing $ABO_3$ and $A_2B_2O_7$ nano-powder established

**Subtask 2.2:** Composite Selective Electrodes
- → DL: NexTech nano-catalyst delivered to WVU for stability testing

**Subtask 2.3:** Electrode Characterization
- → MS: Stability of $H_2$ and $H_2S$ nano-composites electrodes defined to 1200°C

#### Task 3. Lost-Mold Microcasting of the Selective Electrode Structure. (Q5-Q11)
<table>
<thead>
<tr>
<th>Task/Milestone</th>
<th>Quarter after Project Initiation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 3. Lost-Mold Microcasting of the Selective Electrode Structure.</strong> (Q5-Q11)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 3.1:</strong> Micro-Mold Fabrication</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>MS:</strong> Microcasting process defined</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>DL:</strong> Micro-molds delivered to NexTech for commercial microcasting demonstration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 3.2:</strong> Lost-Mold Microcasting and Sintering of Micro-Selective Electrode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 3.3:</strong> Selective Electrode (SE) Characterization.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 4. Fabrication of Micro-Sensors and Arrays (Q6-Q12)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 4.1:</strong> Pt Interconnect and Counter-Electrode (CE) Deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 4.2:</strong> Selective Electrode (SE) Deposition/Sintering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>MS:</strong> Micro-sensor fabricated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 4.3:</strong> H₂-H₂S Micro-Sensor Array Fabrication</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>MS:</strong> Micro-sensor array fabricated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 5. Micro-Sensor and Sensor Array Testing (Q8-Q12)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 5.1:</strong> Testing of H₂ micro-sensors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>MS:</strong> Micro-sensor specification targets achieved</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>DL:</strong> Delivery of sensors to NexTech for testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Subtask 5.2:</strong> Testing of H₂S micro-sensors and H₂-H₂S array</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ <strong>MS:</strong> Micro-sensor array specification targets achieved</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Proposed Milestones

• Sensor and Sensor Array design established – Q2
• Process for synthesizing nanomaterials established – Q4
• Stability of H₂ and H₂S nano-composites electrodes defined to 1200°C – Q6
• Micro-casting process defined – Q6
• Micro-sensors fabricated – Q8
• Micro-sensor array fabricated – Q9
• Micro-sensor specification targets achieved – Q11
• Micro-sensor array specification targets achieved – Q12
Proposed Deliverables

1) Quarterly and annual progress reports to DOE
2) Subtask 2.2- industrial partner delivers nanomaterials to WVU for stability testing (Q3)
3) Subtask 3.1- Micro-molds delivered to industrial partner for commercial microcasting demonstration (Q5-8)
4) Subtask 5.1- Delivery of micro-sensors to industrial partner for testing (delivery start of each quarter Q7-Q11)
5) Subtask 5.2- Delivery of arrays to industrial partner for testing (delivery start of each quarter Q7-Q12)
Presentations of this Work


Publications of this Work

Sensor Background
Background - Chemiresistive Sensors

- Ceramic Substrate
- Thermally Stable Interdigitized Electrode (IDE)
- Nano Metal-Oxide Sensing Material (Chemiresistive Bridge)

- Metal-oxide’s shape, size, composition, and surface characteristics controls the selectivity and sensitivity.
- Nanomaterials provide ultra-high surface area which will enhance encounter of chemical species with sensing material.
Current High-Temp $H_2$ Sensors

- Industrial applications above 500°C
- Special interest from DOE for harsh environment sensors (turbine engines, gasifiers, etc)
- Not for RT and ambient safety purposes
- Example of industrial environment

Slagging gasifier:
(at 1315°C exit)

39.2% $H_2$, 40.3% $CO$, 0.11% $CH_4$, 17.3% $CO_2$, 0.87% $H_2S$+Sulfides, 0.41% $H_2O$, 0.78% $O_2$ *

Refractory Nanomaterials

Pyrochlore $A_2B_2O_7$ (focus on $A=\text{Gd}$ and $B=\text{Zr, Sn, Ti}$)

- Not prone to carbonate formation or CO adsorption (i.e. low CO interference).
- Dopants in A-site ($\text{Sm, Y, Yb, Ca, Sr}...$) increase $V_0^{\text{2-}}$ concentration, and thus, ionic conductivity.
- Mixed-ionic conductor ($O^{2-}$ and $H^+$ conduction).
- Humidity required for proton conduction.
- Ionic and electronic contribution can be controlled by substitution and oxygen partial pressure.

*Highly resistant to sintering and coarsening*
Sensing Mechanisms

Ionic Conductor

\[ \text{Gd}_2\text{Zr}_2\text{O}_7 \] (Ionic)
\[ \text{Gd}_2\text{Zr}_2\text{O}_7 - \text{SnO}_2 \] (Ionic – Semiconductor composite)
\[ \text{Gd}_2(\text{Zr}_x\text{Sn}_{(1-x)})_2\text{O}_7 \] (mixed conduction solid solution)
\[ \text{Gd}_2\text{Ti}_2\text{O}_7 \] (Mixed Semiconductor)

n-Type Conductor

\[ \text{Gd}_2\text{Ti}_2\text{O}_7 \]


Tuller, Solid State Ionics (1992)
Nanomaterial Synthesis and Sensor Testing
Synthesis of Nanomaterials

1. Acid Solution of Gadolinium Carbonate
2. Acid Solution of Dopants
3. Acid Solution of Zr, Sn, Ti Chloride

- Basic Solution (modify pH)
- Solution washed until conductivity < 10 mS/cm³
- Solution placed in autoclave at 150-260°C (100-700 psi)
- Solution is dried while washing in IPA and sieved through 200 mesh
Structural Characterization (XRD)

- Higher temps or longer dwell times needed for pyrochlore phase
- Broad peaks due to particle sizes in nano range

Gd$_{1.8}$Y$_{0.1}$Zr$_2$O$_7$

pH=11

* TMAOH
Structural Characterization (XRD)

Gd$_2$Sn$_2$O$_7$

- pH was adjusted from 6 to 11
- pH > 8 creates secondary phase of Gd(OH)$_3$
- pH = 6 creates single pyrochlore phase
Thermal Stability of Nano-GZ

- Particle size increases from 4 nm to <70 nm.
- Structure necks at 1200 °C, but nano-network remains highly porous (nanoporous).

Calcined 1200 °C for 10 hours

<table>
<thead>
<tr>
<th></th>
<th>Sintered 1 Hour</th>
<th>Sintered 24 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area</td>
<td>3.5 m²/g (244nm)</td>
<td>3.6 m²/g (234nm)</td>
</tr>
<tr>
<td>Adsorption SA of pores</td>
<td>2.639 m²/g</td>
<td>2.793 m²/g</td>
</tr>
<tr>
<td>Volume of pores (adsorption)</td>
<td>0.0107 cm³/g</td>
<td>0.00654 cm³/g</td>
</tr>
</tbody>
</table>
Compositional Testing Protocol

Macro-Sensor Fabrication:
- Alumina substrates polished
- Pt-IDEs sputtered and annealed at 1200°C
- Sensing material printed onto electrodes and sintered at 1200°C (~80-100 µm thick)
Macro-Sensor Testing ($SnO_2$)

WVU Nano-$SnO_2$ Ordered Agglomerates

- WVU nano-$SnO_2$ has high level of sensitivity to ppm levels of $H_2$ at higher temperatures.
- Degradation or “drift” in sensor due to sintering/coarsening (3 nm to ~0.5 μm).
Macro-Sensor Testing ($Gd_{2-x}A_xZr_2O_7$)

$Gd_{1.8}Y_{0.1}Zr_2O_7$

- Doped zirconate sensor shows sensitivity to H$_2$ in air at 600°C (no humidity).
- Surface reduction at lower temperature results in n-type dominated response.
- Steam formation dominates at higher temperature (low H$_2$ adsorption and reaction with zirconate surface).

H$_2$/N$_2$, 20% Oxygen
Compositional Testing
(50% SnO$_2$-50%Gd$_{1.8}$Y$_{0.1}$Zr$_2$O$_7$)

- Dispersed nano-suspensions combined to make composite.
- Addition of SnO$_2$ allows for H$_2$ adsorption at higher temperatures.
- Zirconate limits amount of “drift” seen throughout testing.
Compositional Testing
(10%-SnO$_2$-90%-Gd$_{1.8}$Y$_{0.1}$Zr$_2$O$_7$)

- SnO$_2$ increases H$_2$ adsorption.
- Surface O$^-$ reaction or O$_6^x$ junction reduction leads to n-type like response.
- Decreased ionic conduction across contact junctions.
- Enough oxygen in atmosphere for reaction without assistance from bulk.
- Vacancy conc. change at contacts.
- Oxygen/vacancy diffusion into bulk increases conductivity to cause $\Omega$ relaxation.
- Stabilization change is limited due to available oxygen.

---

$\Omega$

21000
20400
19800
75000
72000
69000
168000
162000
156000
150000
100000
50000

Time (Hours)

500 ppm
2500 ppm
5000 ppm
2500 ppm
500 ppm
500
2500
5000
2500
500

No Humidity

1000°C

20% Oxygen
10% Oxygen
1% Oxygen
0% Oxygen
Comparison of Composite Sensors

20% Oxygen Atmosphere

- Addition of SnO$_2$ increases sensitivity at elevated temperatures but decreases stability as temperature increases.
- 10% SnO$_2$ composite shows more sensitivity than composites with higher % of SnO$_2$.
Comparison of Sensing Materials

20% Oxygen Atmosphere

- Fully replacing Zr with Sn decreases sensitivity and increases drift
- Doping Zr site with 10% SnO₂ results in lower sensitivity than a 10% composite mixture but lower drift
1) **Pattern of high-temperature, stable, thin film electrodes:**
   - Platinum (Pt)-based sputtered electrodes.
   - Wet-etch or lift-off.

2) **Multiple techniques available to pattern sensing nanomaterial particulates in suspension/ink:**
   - LIGA
   - Stamping
   - Embossing
   - Micro-casting
   - Dip-pen nanolithography

**Note:** depositing nano-particulates, and not using typical CVD or PVD processes to deposit/pattern thin films.
Patterning of Nano-Derived Micro-Sensors
**Micro Molding - Nanomaterials**

**Lost-Mold Micro-casting**
- SU8 is processed into molds onto substrate.
- Mold is removed during thermolysis and casted material bonds onto substrate.
- Feature thickness >20 µm can be demonstrated.
- Antolino et al. produced dense free-formed zirconia bars.

Micro-Casting Nanomaterials

- Negative Lithography for Micro-Molds
  - SU8-25 (Microchem)
    - From 20-90 µm depth depending on spin rate
  - OAI UV Flood Exposure System
  - SU8 developer
- Sensing Material is casted into mold
- Mold is burned off and material is sintered
Micro-Casting

Stenciling with screenprinter

• Clean surface obtained
• Controlled pressure, squeegee speed
• Average viscosity of 300 poise at 8/s

Micro-casting variables:

• Particle size
• Ink dispersion
• Rheology
• Mold geometry/dimensions
• Binder system
Micro-Casting - SEM

- Casted single layer on YSZ substrate

- Casted double layer on YSZ substrate
Micro-Casting—Aqueous Epoxy

- Aqueous epoxy system (Beckopax and Dicynex)
- Evidence of shrinkage
- Uniform particle packing
- Adequate shape retention.

![Micro-Casting images](image-url)
Micro-Casting – Aqueous Epoxy

Variation of solids loading and sintering temperature

• Compared 12%, 20%, and 30 vol% solids loading in water-based epoxy system
  – Single casting
  – Noticed increased stability with solids loading (left)

• Sintered at 1200°C and 1300°C
  – Significant shrinkage increase with temperature increase (right)
• Critical particle loading is reached, capillary force pulls liquid in and fights surface tension.
• Therefore, there is a limitation on particle loading due to particle interaction.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>12 vol%</th>
<th>20 vol%</th>
<th>30 vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>55.792 θ</td>
<td>52.640 θ</td>
<td></td>
</tr>
<tr>
<td>YSZ</td>
<td>46.975 θ</td>
<td>50.868 θ</td>
<td></td>
</tr>
<tr>
<td>SU-8</td>
<td>61.721 θ</td>
<td>61.587 θ</td>
<td></td>
</tr>
</tbody>
</table>
Micro-casting –
Aqueous Acrylate and Terpineol-based Systems

- SEM revealed water based (MAM:MBAM) gel casting did not cup but collapsed due to air bubble (Left).
- SU8 seems to attract terpineol-based ink suspension forming hollow cylinders (Right).
Wetting Measurements
(Terpineol-based System)

<table>
<thead>
<tr>
<th></th>
<th>0 wt%</th>
<th>5 vol%</th>
<th>10 vol%</th>
<th>15 vol%</th>
<th>25 vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>19.341</td>
<td>18.670</td>
<td>27.001</td>
<td>30.352</td>
<td>48.720</td>
</tr>
<tr>
<td>YSZ</td>
<td>19.269</td>
<td>18.478</td>
<td>23.199</td>
<td>25.537</td>
<td>44.361</td>
</tr>
<tr>
<td>SU-8</td>
<td>20.732</td>
<td>19.646</td>
<td>22.576</td>
<td>25.904</td>
<td>46.425</td>
</tr>
</tbody>
</table>

- Binder system wets SU-8 mold very well.
- Wicking of solvent into SU-8 results in well-packed molded features (similar to slip-casting).
**Micro-Patterning Techniques**

**Dip Pen Nanolithography (DPN)**

- Direct drawing delivers multiple materials onto a single substrate.
- Typically used to deposit organic material (DNA, cells, peptides, polymers).

Mirken group (Northwestern Univ.) work with AFM writing in 1999.


### DPN on Untreated Substrate

<table>
<thead>
<tr>
<th></th>
<th>Cu Ink #1</th>
<th></th>
<th>Cu Ink #2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet</td>
<td>Dry</td>
<td>Wet</td>
<td>Dry</td>
</tr>
<tr>
<td>Glass</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
<tr>
<td></td>
<td>66 μm</td>
<td>66 μm</td>
<td>66 μm</td>
<td>66 μm</td>
</tr>
<tr>
<td>Alumina</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
<td>[Image]</td>
</tr>
<tr>
<td></td>
<td>66 μm</td>
<td>66 μm</td>
<td>66 μm</td>
<td>66 μm</td>
</tr>
</tbody>
</table>

- Ink shows $\theta \approx 35^\circ$ on both substrates.
- Uniform size and shape dots (5-10 μm) possible on alumina substrate.
- Ink #2 dots on alumina substrate retain shape through drying.
- Direct-writing of continuous line not possible on neither substrates (contact angle too high, >25° for line drawing).
Electroded Ceramic Alumina Substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pattern with Ink #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>No coating</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>CTAB coating</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- Patterning on ceramic (polycrystalline) substrate with metallic electrodes.
- Difficult due to difference in wetting characteristics of each grain and metal vs. ceramic.
- Cu ink pattern on a substrate *without a coating* shows the ink stumbling over the metallic/ceramic interchanges.
- CTAB coating provides a single chemistry surface over the IDEs on multigrain ceramic substrate.
- CTAB coating enables patterning Cu sol-gel inks.
Fabrication of Stable Micro-IDEs
Current sensor technology is limited to operate at low temperature due to:

- Sensing material composition
- Processing
- Incapable electrodes

Breaks Apart !!!
Solution In Order to Hinder Degradation of the Pt Thin Film

• Using intermediate layer i.e. adhesion layer so-called glue layer.

• Using second phase precipitation.

Grain Boundary Pinning Hinders Coarsening.

- Pt grain
- Second phase grain

Surface tension

Combat

Coarsening/Sintering

Coarsening
Objectives

1) High-temperature degradation of Pt thin films deposited onto alumina substrates.

2) Effect of Ti, Ta, Zr, and Hf adhesion layers on hillock formation and coarsening/sintering.

3) Zener-pinning effect and combination with suitable adhesion layer.
Experimental Procedure: Processing

Deposition method:
- DC Magnetron Sputtering deposition on Al₂O₃ wafer
- Alumina wafer characteristics, Rₐ=34 nm

Deposition parameters:
- Primary gas pressure (Argon): 60 mTorr
- Deposition Power : 100 watt
- Deposition temperature: 200°C

Thicknesses regardless of coating type:
- Pt=425 nm
- Adhesion layer=35 nm

<table>
<thead>
<tr>
<th>Adhesion layer (35 nm)</th>
<th>Identification of the coating architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>Pure Pt</td>
</tr>
</tbody>
</table>

**BILAYER COATING ARCHITECTURES**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>Ti+Pt</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Ta+Pt</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr+Pt</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hf+Pt</td>
</tr>
</tbody>
</table>

**MULTILAYER COATING ARCHITECTURES**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium</td>
<td>L-Zr+Pt</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hf+L-Zr+Pt</td>
</tr>
</tbody>
</table>
Experimental Procedure: Characterizations

High-temperature stability testing:
• Isothermal annealing in N₂ to 800-1200°C for 1-48 hours.
• SEM and XPS completed on annealed sample surface.

Electrical resistivity testing:
• Van der Pauw method
  [Philips Research Reports 13 1-9, 1952]
Definition of Coating Architectures

**Schematic Representations**

**MULTILAYER COATING ARCHITECTURES**

- Zirconium: L-Zr+Pt
- Hafnium: Hf+L-Zr+Pt

**BILAYER COATING ARCHITECTURES**

- Titanium: Ti+Pt
- Tantalum: Ta+Pt
- Zirconium: Zr+Pt
- Hafnium: Hf+Pt
**Pure Pt on Alumina**

**Platinum Layer**

**Ceramic Substrate**

**Consequences:**

- Grain growth
- Device failure

\[ \rho = \infty \left(10^{-9} \, \Omega \cdot m\right) \]

Pt on ceramic without adhesion layer, after 1200°C 1 h inert atmosphere annealing

\[ \rho = 185 \left(10^{-9} \, \Omega \cdot m\right) \]

Bulk resistivity of Pt, \( \rho = 106 \left(10^{-9} \, \Omega \cdot m\right) \)
Bilayer Coatings; Ti+Pt and Ta+Pt

1 hour 1200 °C, $\rho = 561 \times 10^{-9} \Omega \cdot m$

5 hours 1200 °C, $\rho = \infty \times 10^{-9} \Omega \cdot m$

LOST OF ADHESION LAYER

XPS of Ti+Pt film surface after 800 °C

Match well with TiO$_2$

1 hour 1200 °C, $\rho = 442 \times 10^{-9} \Omega \cdot m$

5 hours 1200 °C, $\rho = \infty \times 10^{-9} \Omega \cdot m$
Bilayer Coatings; Zr+Pt

A few researchers worked with Zr as an adhesion layer;


1 hour 800 °C

1 hour 1200 °C, \( \rho = 234 \times 10^{-9} \ \Omega \cdot m \)

15 hours 1200 °C, \( \rho = \infty \times 10^{-9} \ \Omega \cdot m \)
Bilayer Coatings; Hf+Pt

1 hour 1200 °C, $\rho = 244 \times 10^{-9} \Omega.m$

5 hours 1200 °C, $\rho = \infty \times 10^{-9} \Omega.m$

- Slow diffusion of Hf in Pt.
- Improved durability in adhesion layer.
Bilayer Coatings; Diffusion Behaviors of Hf and Zr

After 1200°C 1 h of Hf+Pt film surface

Hf 4.5% of the Hf+Pt film

After 1200°C 1 h of Zr+Pt film surface

Zr 13.5% of the Zr+Pt film
### Summary of Adhesion Layer Study

<table>
<thead>
<tr>
<th>Adhesion layer (35 nm)</th>
<th>Identification of the coating architecture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum (not reliable $&gt;700 , ^\circ C$)</td>
<td>Pure Pt</td>
</tr>
<tr>
<td>Titanium (moves all the way up)</td>
<td>Ti+Pt</td>
</tr>
<tr>
<td>Tantalum (better but not sufficient)</td>
<td>Ta+Pt</td>
</tr>
<tr>
<td>Zirconium (for intermediate layers)</td>
<td>Zr+Pt</td>
</tr>
<tr>
<td>Hafnium (very stable adhesion layer)</td>
<td>Hf+Pt</td>
</tr>
<tr>
<td>Layer by Layer Zirconium</td>
<td>L-Zr+Pt</td>
</tr>
<tr>
<td>Hafnium based Layer by Layer Zirconium</td>
<td>Hf+L-Zr+Pt</td>
</tr>
</tbody>
</table>

**Objective 1:** Effect of Ti, Ta, Zr, and Hf adhesion layers on hillock formation and coarsening

**Conclusions:**
- All show hillock formation and diffusion
- Zr adequate for adhesion layer
- Hf shows best stability

**NEXT STEP:** Multilayer coatings in order to hinder coarsening
Multilayer Coatings; L-Zr+Pt

5 hours 1200 °C

15 hours 1200 °C, $\rho = 315 \times 10^{-9} \, \Omega.m$

24 hours 1200 °C, $\rho = 391 \times 10^{-9} \, \Omega.m$

48 hours 1200 °C, $\rho = \infty \times 10^{-9} \, \Omega.m$

Extended high temperature service life !!!
Multilayer Coatings; Hf+L-Zr+Pt

- Better performance.
- Durable adhesion layer.
- The most stable intermetallic, HfPt$_3$.

[P. Ficalora et al. Department of the Navy Mar. 1971]
Multilayer Coatings; Hf+L-Zr+Pt

- Broadening due to intermetallic formation of HfPt$_3$ and ZrPt$_3$.
- (~0.67%) higher than the value found in the literature work for HfPt$_3$.

Summary: Improvement

1 hour 1200°C, ρ=∞ (10^{-9} \, \Omega \cdot m)

Hf+L-Zr+Pt

Pure Pt

48 hours 1200°C, ρ=624 (10^{-9} \, \Omega \cdot m)
Summary: High-Temperature Electrode

Simple **Lift-off** process for electrode manufacturing.

Micro-electrode
Micro-Sensor Testing

(10\% \textit{SnO}_2-90\% \textit{Gd}_{1.8} \textit{Y}_{0.1} \textit{Zr}_2 \textit{O}_7)

- Micro-sensor shows higher sensitivity to H\textsubscript{2} and more stability than macro-sensor.
- Response time also decreases at higher temperature.
Micro Casting of SnO$_2$
Summary

• Hydrothermal processes for synthesis of ionic and mixed-conducting zirconate, stannate, and titanate pyrochlores (3-10 nm).

• Screenprinted macro-sensors of composite nanomaterials sense 500-4000 ppm H₂ (in air) at 600-1000°C.

• Zirconate and MOS/zirconate composites displayed enhanced stability
  – From 0.792%/hr to 0.016%/hr

• Developed Pt-based micro-IDEs that are stable to 1200°C.

• Initiated development of micro-casting, templated hydrothermal, and DPN processes for fabricating micro-sensor arrays.
Future Work

• Impedance testing to further understand conduction mechanisms of sensing materials
• CO cross-sensitivity testing
• Synthesis and test materials for NO\textsubscript{x} sensing
• Co-Sputter deposition of adhesion material with platinum in order to obtain infinite layer structure and characterization
• AEM and TEM characterization for further information about Hf+L-Zr+Pt.
Acknowledgments

• Funding by US Department of Energy, University Coal Research (UCR) program under contract DE-FE0003872.

• Adrienne McGraw, Zachary Santer

• Oak Ridge Institution for Science and Education (ORISE)

• ORAU (Oak Ridge Associated Universities)

• WVU Shared Research Facilities.

• The authors also would like to acknowledge Dr. Kolin Brown, Dr. Wei Ding. Mr. Harley Hart for their assistance.
Additional Information
5 hours 1200 °C \( \rho = \infty \ (10^{-9} \ \Omega.m) \)
5 hours 1200 °C \( \rho = \infty \left(10^{-9} \, \Omega \cdot m\right) \)
Detailed XPS scan for the (a) Hf 4f peak positions in the Hf/L-Zr+Pt sample (b) Zr 3d peak positions in the L-Zr+Pt sample, both annealed at 1200°C for 48 h.
Detailed XPS scan for the (a) Hf 4f peak positions in the Hf/L-Zr+Pt sample (b) Zr 3d peak positions in the L-Zr+Pt sample, both annealed at 1200°C for 48 h.
Zirconium, Hafnium, Th,

Room temp. sputtering with possible lowest power and highest possible pressure to maximize the mean freem path

Transition Region

Highest possible sputtering temperature, lowest possible sputtering pressure
Compositional Testing ($\text{Gd}_{2-x}\text{A}_x\text{Zr}_2\text{O}_7$)

- $800^\circ\text{C}$
  - $\text{Gd}_{1.8}\text{Y}_{0.1}\text{Zr}_2\text{O}_7$
  - 0.289%/hr

- $1000^\circ\text{C}$
  - 0.036%/hr

$\text{H}_2/\text{N}_2$, 0% Oxygen, 0% Humidity

- Sensitive to $\text{H}_2$ down to 500 ppm level with less than 1 min response time.
- Surface defect state altered in reducing atmosphere (response independent of $\text{H}_2$ concentration).
- Spike in resistance due surface reduction and stabilization due to bulk oxygen movement and reordering at surface/junction?