The Application of Metal Oxide Nanomaterials for Chemical Sensor Development

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NASA Glenn Research Center (GRC) has been developing miniature chemical sensors for a variety of applications including fire detection, emissions monitoring, fuel leak detection, and environmental monitoring. Smart “Lick and Stick” sensor technology which integrates a sensor array, electronics, telemetry, and power into one microsystem are being developed. These microsystems require low power consumption for long-term aerospace applications. One approach to decreasing power consumption is the use of nanotechnology. Nanocrystalline tin oxide (SnO₂) carbon monoxide (CO) sensors developed previously by this group have been successfully used for fire detection and emissions monitoring. This presentation will briefly review the overall NASA GRC chemical sensor program and discuss our further effort in nanotechnology applications. New carbon dioxide (CO₂) sensing material using doped nanocrystalline SnO₂ will be discussed. Nanocrystalline SnO₂ coated solid electrolyte CO₂ sensors and SnO₂ nanorod and nanofiber hydrogen (H₂) sensors operated at reduced or room temperatures will also be discussed.
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Outline

• Background of Chemical Sensors at NASA GRC

• Metal Oxide Nanomaterials for Chemical Sensors
  - Nanocrystalline tin oxides
  - Tin oxide nanorods and nanofibers

• Summary
Background of Chemical Sensors at NASA GRC

• Sensors and platforms
  H₂, CH₄, C₂H₄, C₃H₆, CO₂, CO, NOx, and N₂H₄
  Schottky diodes, resistors, and electrochemical cells

• Approaches
  Microfabrication, small size, low weight, cost, and power consumption. Batch fabrication, sensor arrays, and use as “Lick and Stick”

• Applications
  Engine health and emissions monitoring, fuel leak detection, low false alarm fire detection, and environmental monitoring
Background and Applications

Multi Species Fire Sensors for Aircraft Cargo Bays
R&D 100 award and NASA Turning Goal into Reality Award (2005)

“Lick and Stick” Space Launch Vehicle Leak Sensors with Power and Telemetry
R&D 100 award (1995) and NASA Turning Goal into Reality Award (2003)

Oxygen Sensor
SiC Hydrocarbon Sensor
H2 Sensor
Nanocrystalline Tin Oxide NOx and CO Sensor

Aircraft Propulsion Exhaust High Temperature Electronic Nose

Sensor Equipped Prototype Medical Pulmonary Monitor

Hydrazine EVA Sensors (11 ppb Detection)
Goal

To improve sensor performance and reduce power consumption for integration into “Lick and Stick” smart sensor systems

“Lick and Stick” Leak Sensor System: Sensors, Signal Processing, Communication, Power all in one package
Metal Oxide Nanomaterials for Chemical Sensors

dresentation will concentrate on three basic material types

• Nanocrystalline SnO₂
  - Sol gel process
  - SnO₂-CuO: Resistor CO₂ sensing material
  - Nanocrystalline SnO₂: CO₂ sensor improved

• SnO₂ Nanorods
  - CVD process
  - Pd Doping: Reduced temperature H₂ detection

• SnO₂ Nanofibers
  - Electrospun process
  - Pd Doping: Room temperature H₂ detection
Review of Fabrication of CuO Doped SnO$_2$ Carbon Dioxide Sensor

Synthesis of SnO$_2$ Sol Gel

- Precipitate formation
  \[ \text{SnCl}_4 + 4\text{NH}_4\text{OH} \rightarrow \text{Sn(OH)}_4\downarrow + 4 \text{NH}_4\text{Cl} \]
- Removal of $\text{NH}_4^+$ and $\text{Cl}^-$ by washing with D. I. H$_2$O
- Dissolve Sn(OH)$_4$ in NH$_3$.H$_2$O overnight
- Reflux the solution and the SnO$_2$ sol gel formed.

Freshly Deposited CuO Synthesis

- \[ \text{CuCl}_2 + 2\text{NaOH} \rightarrow \text{CuO}\downarrow + 2\text{NaCl} \]
- Removal of $\text{Na}^+$ and $\text{Cl}^-$ by washing with D. I. H$_2$O
- Dissolve CuO in NH$_3$.H$_2$O
- \[ \text{Cu(NH}_3)_4^{2+} \rightarrow \text{CuO}\downarrow \text{heat} \]

Mixture of SnO$_2$ sol gel and CuO at 8:1 molar ratio
Nanocrystalline Tin Oxide:
Copper Doping Significantly Changes Sensing Mechanism

- CO₂ Detection achieved, sensor resistor based
- CuO Doping yields significantly different sensor response from standard SnO₂
- Mechanism still being investigated

![Graph showing the resistance of CuO-SnO₂ sensor for CO₂ in air testing at 450°C.](image)
Nanocrystalline Tin Oxides Used as a Coating to Modify Solid Electrolyte Carbon Dioxide Sensors

Side view of microfabricated CO$_2$ sensor
(Simplified with two electrodes, new tech. disclosed, patent filed)

<table>
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<tr>
<th>Na$_2$CO$_3$/BaCO$_3$</th>
<th>NASICON</th>
<th>Pt(+)</th>
<th>NASICON</th>
<th>Pt(-)</th>
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<tr>
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Coated with SnO$_2$ sol gel, heated at 500°C for 2 hr

Nanocrystalline tin oxide layer added

<table>
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<tr>
<th>SnO$_2$ Nanocrystallines</th>
<th>Na$_2$CO$_3$/BaCO$_3$</th>
<th>NASICON</th>
<th>Pt(+)</th>
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</table>

Pt interdigitated finger electrode on Al$_2$O$_3$ substrate

SEM image of a fabricated CO$_2$ sensor
Nanocrystalline Tin Oxide Improves Solid Electrolyte Carbon Dioxide Sensor Performance

*Sensor Responses Significantly Changed with Nanocrystalline Coating*

**Sensors without tin oxide sol gel addition**

**Sensors after tin oxide sol gel addition**
Nanocrystalline Tin Oxides Improve Solid Electrolyte Carbon Dioxide Sensor by Decreasing Power Consumption

Solid Electrolyte CO\(_2\) Sensor with Nanocrystalline SnO\(_2\)
(Detection temperature greatly reduced)

Solid Electrolyte CO\(_2\) Sensor without Nanocrystalline SnO\(_2\)
(Carbon dioxide detection at 600 °C)
Sensing Mechanism of Solid State Electrochemical Sensors for Carbon Dioxide Gases

- Reduction reaction at Pt(-) electrodes
  \[2Na^+ + CO_2 + \frac{1}{2} O_2 + 2e \rightarrow 2Na_2CO_3\]

- N-type metal oxides: supply more electrons or enhance electrons flow

- Results: Power consumption reduced
Metal Oxide Nanomaterials for Reducing Gas Sensing

Sensing Mechanisms Being Investigated for Nanostructured Materials

- Polycrystal SnO\textsubscript{x} nanofibers by electrospun process
- Nanocrystallines SnO\textsubscript{x} by sol gel process
- Sensing mechanism unknown
- Increased nano grain boundary contact
- More controlled crystalinity
- Single crystal nanorods by CVD
Palladium Doped SnOx Nanorods Detect Hydrogen at Reduced Temperature

100°C, 0.2V

0.5%H₂

air, N₂, 0.5% C₃H₆, N₂, air, N₂, N₂, air

Time (min)

Current (A)
Palladium Doped SnOx Nanofibers Detect Hydrogen at Room Temperature

23ºC, 2V

Air, N₂, 0.5% H₂, Air, N₂, CH₄, Air, 0.5% H₂, Air

0 10 20 30 40 50 60 70 80
0 1.00E-03 2.00E-03 3.00E-03 4.00E-03 5.00E-03 6.00E-03

Time (min)

Current (A)
Summary

• Nanotechnology enabled new sensing material development, improved sensor performance, and decreased sensor power consumption

• Resistor-based CO₂ sensing materials (CuO-SnO₂) developed through uniform doping of CuO in SnO₂ sol gel at 8:1 molar ratio

• Solid electrolyte CO₂ sensor improved and sensor power consumption decreased through addition of n-type SnO₂ sol gel

• Hydrogen detection at reduced temperature achieved by using palladium coated single crystal SnOx nanorods

• Room temperature hydrogen detection achieved by using palladium coated SnOx nanofibers

• Micro-nano contacts still a challenge for nanostructure application in sensors and electronics devices development

• Nano-based metal oxides can enable miniaturized sensing systems but further development is necessary and will be conducted
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