The Application of Metal Oxide Nanomaterials for Chemical Sensor Development

Jennifer C. Xu*, Gary W. Hunter, and Laura J. Evans
NASA Glenn Research Center
Cleveland, OH 44135

Randy L. Vander Wal and Gordon M. Berger
USRA/NASA Glenn Research Center
Cleveland, OH 44135

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 (SnO_2) 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 (CO_2) sensing material using doped nanocrystalline SnO_2 will be discussed. Nanocrystalline SnO_2 coated solid electrolyte CO_2 sensors and SnO_2 nanorod and nanofiber hydrogen (H_2) sensors operated at reduced or room temperatures will also be discussed.

The Application of Metal Oxide Nanomaterials for Chemical Sensor Development

Jennifer Xu, Gary Hunter, and Laura Evans
NASA Glenn Research Center
Randy VanderWal and Gordon Berger
National Center for Space Exploration Research

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**

  H_2, CH_4, C_2H_4, C_3H_6, CO_2, CO, NOx, and N_2H_4
  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

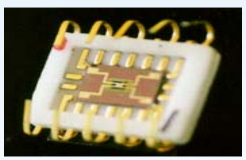
Background and Applications

Multi Species Fire Sensors for Aircraft Cargo Bays

R&D 100 award and NASA Turning Goal into Reality Award (2005)

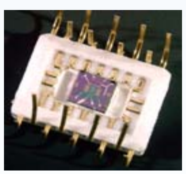
"Lick and Stick" Space Launch Vehicle Leak Sensors with Power and Telemetry

R&D 100 award (1995) and NASA Turning Goal into Reality Award (2003)

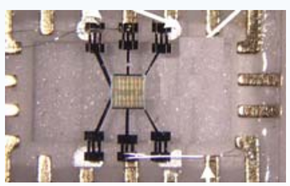


Oxygen Sensor

SiC Hydrocarbon Sensor



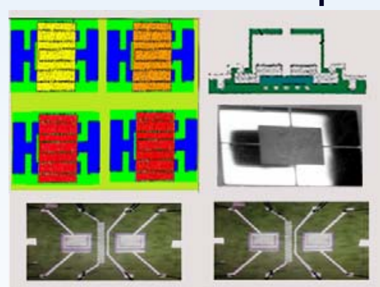
H2 Sensor

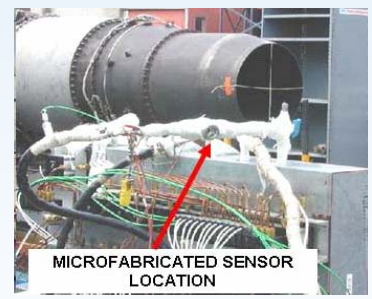


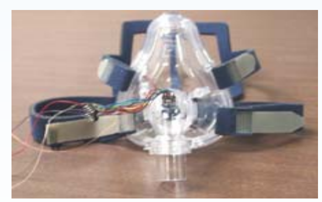
Nanocrystalline Tin Oxide NOx and CO Sensor

BASE PLATFORM SENSOR TECHNOLOGY

Aircraft Propulsion Exhaust High Temperature Electronic Nose







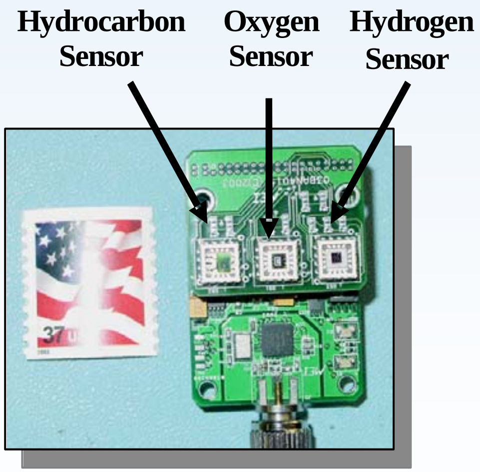
Sensor Equipped Prototype Medical Pulmonary Monitor

Hydrazine EVA Sensors (11 ppb Detection)

Goal

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

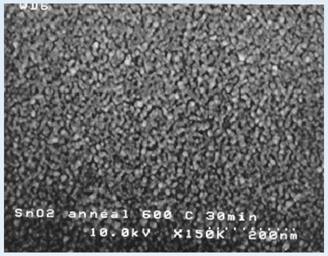
"Lick and Stick" Leak Sensor System: Sensors, Signal Processing, Communication, Power all in one package



Metal Oxide Nanomaterials for Chemical Sensors

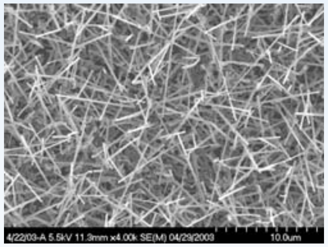
Presentation will concentrate on three basic material types

- **Nanocrystalline SnO_2**
  - Sol gel process
  - SnO_2-CuO: Resistor CO_2 sensing material
  - Nanocrystalline SnO_2: CO_2 sensor improved



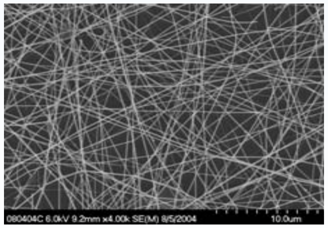
Nanocrystalline SnO_2

- **SnO_2 Nanorods**
  - CVD process
  - Pd Doping: Reduced temperature H_2 detection



SnO_2 Nanorods

- **SnO_2 Nanofibers**
  - Electrospun process
  - Pd Doping: Room temperature H_2 detection



SnO_2 Nanofibers

Review of Fabrication of CuO Doped SnO_2 Carbon Dioxide Sensor

Synthesis of SnO_2 Sol Gel

- Precipitate formation

  $SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4\downarrow + 4\ NH_4Cl$
- Removal of NH_4^+ and Cl^- by washing with D. I. H_2O
- Dissolve $Sn(OH)_4$ in $NH_3.H_2O$ overnight
- Reflux the solution and the SnO_2 sol gel formed.

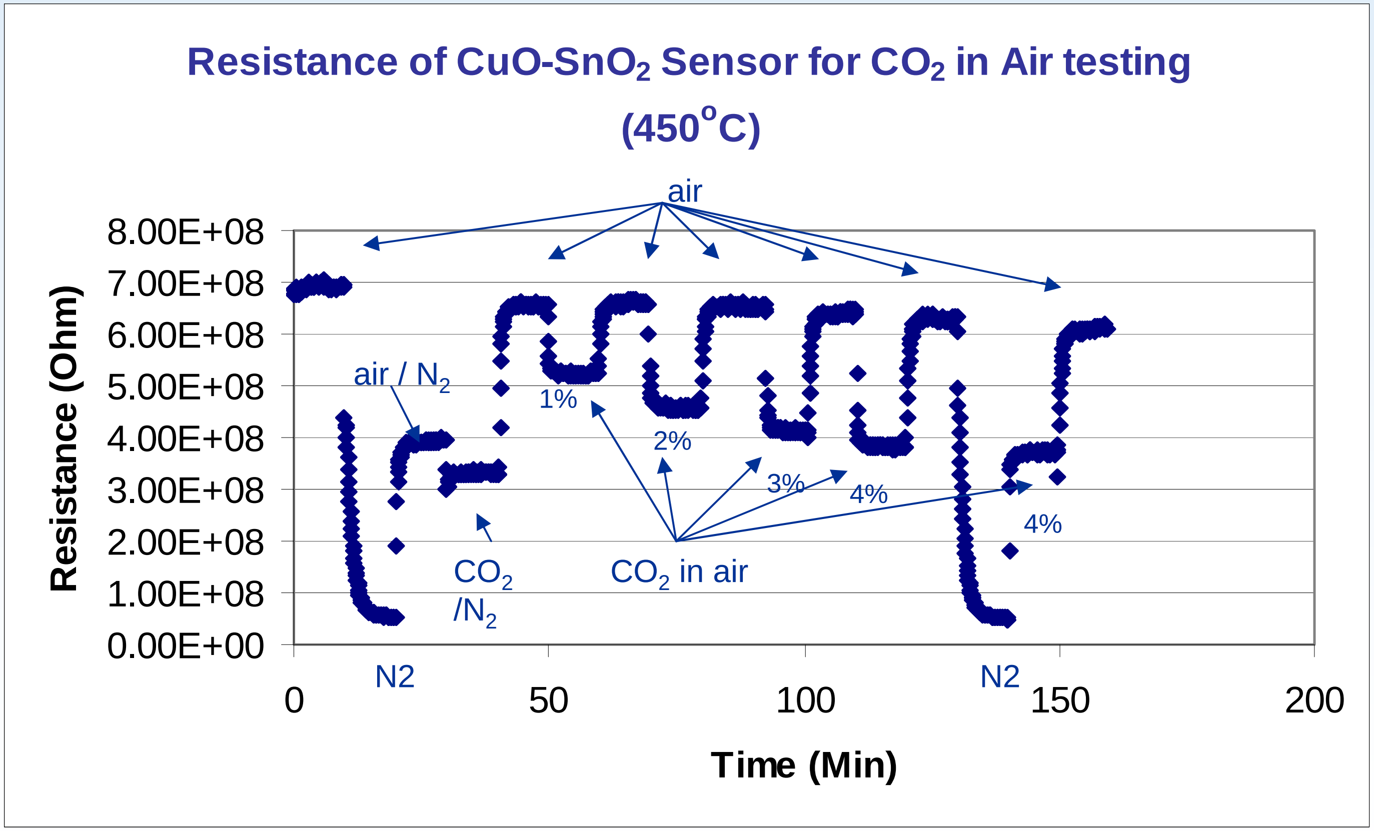
Freshly Deposited CuO Synthesis

- $CuCl_2 + 2NaOH \rightarrow CuO\downarrow + 2NaCl$
- Removal of Na^+ and Cl^- by washing with D. I. H_2O
- Dissolve CuO in $NH_3.H_2O$
- $Cu(NH_3)_4^{2+} \xrightarrow[\textbf{heat}]{} CuO\downarrow$

Mixture of SnO_2 sol gel and CuO at 8:1 molar ratio

Nanocrystalline Tin Oxide: Copper Doping Significantly Changes Sensing Mechanism

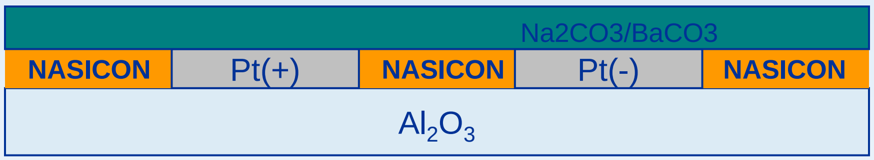
- CO_2 Detection achieved, sensor resistor based
- CuO Doping yields significantly different sensor response from standard SnO_2
- Mechanism still being investigated



Nanocrystalline Tin Oxides Used as a Coating to Modify Solid Electrolyte Carbon Dioxide Sensors

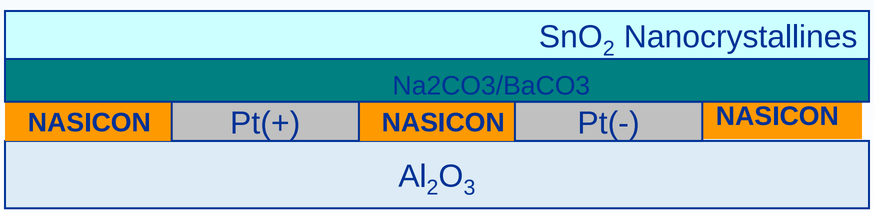
Side view of microfabricated CO_2 sensor

(Simplified with two electrodes, new tech. disclosed, patent filed)

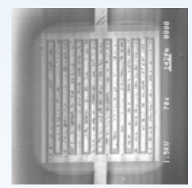


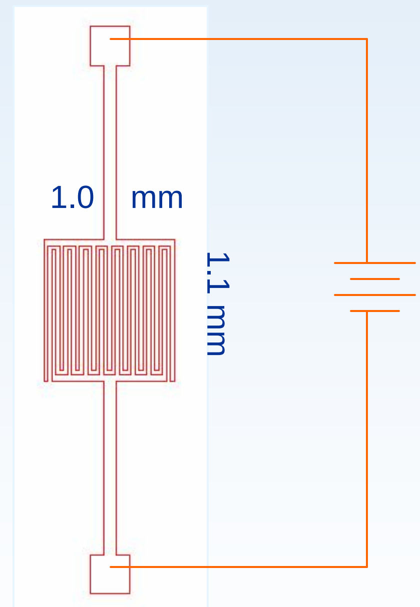
Coated with SnO_2 sol gel, heated at 500°C for 2 hr

Nanocrystalline tin oxide layer added



Pt interdigitated finger electrode on Al_2O_3 substrate



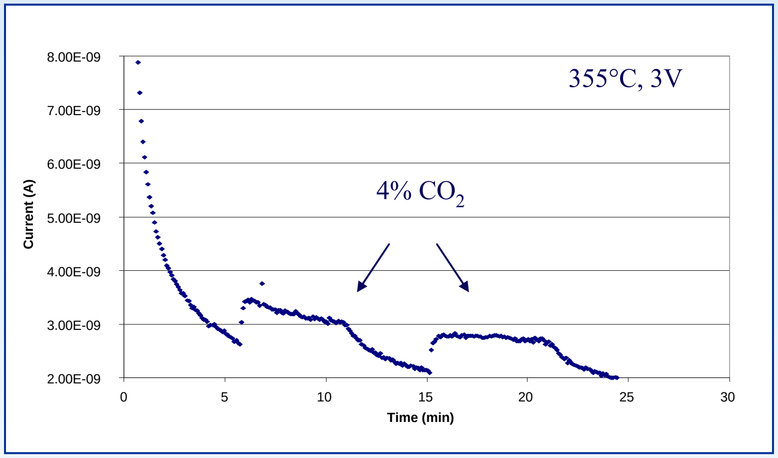


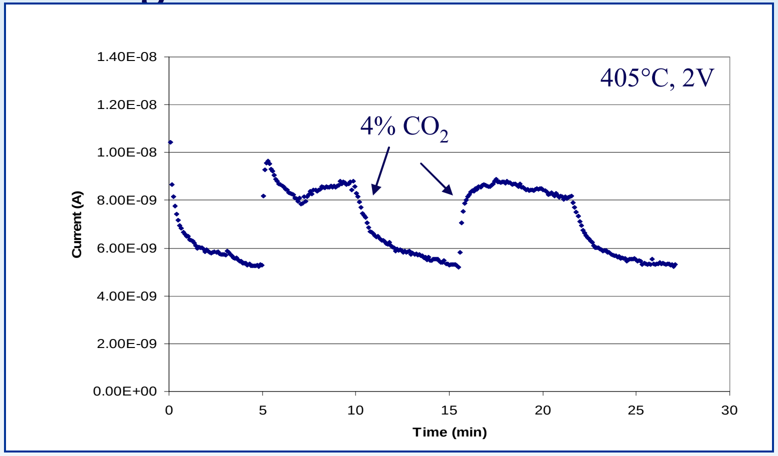
SEM image of a fabricated CO_2 sensor

Nanocrystalline Tin Oxide Improves Solid Electrolyte Carbon Dioxide Sensor Performance

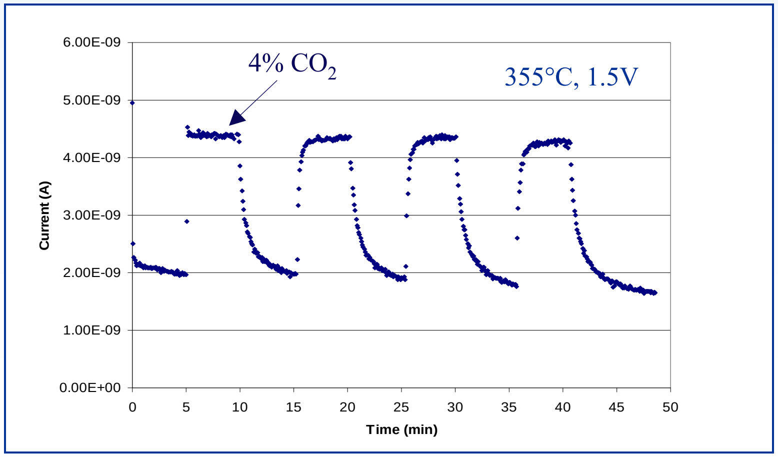
Sensor Responses Significantly Changed with Nanocrystalline Coating

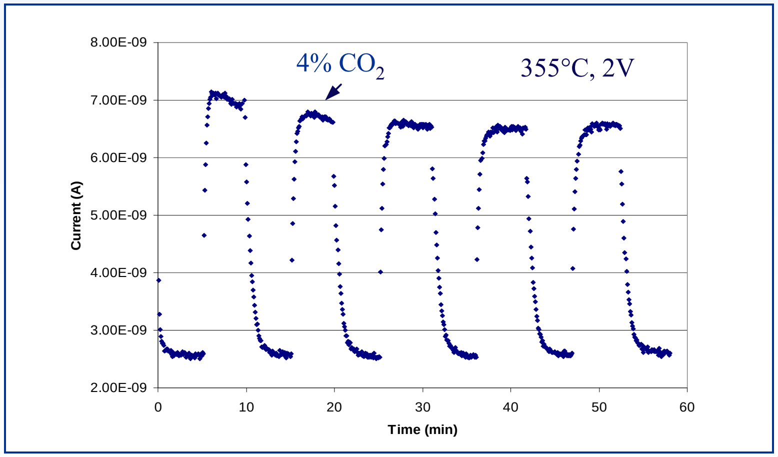
Sensors without tin oxide sol gel addition





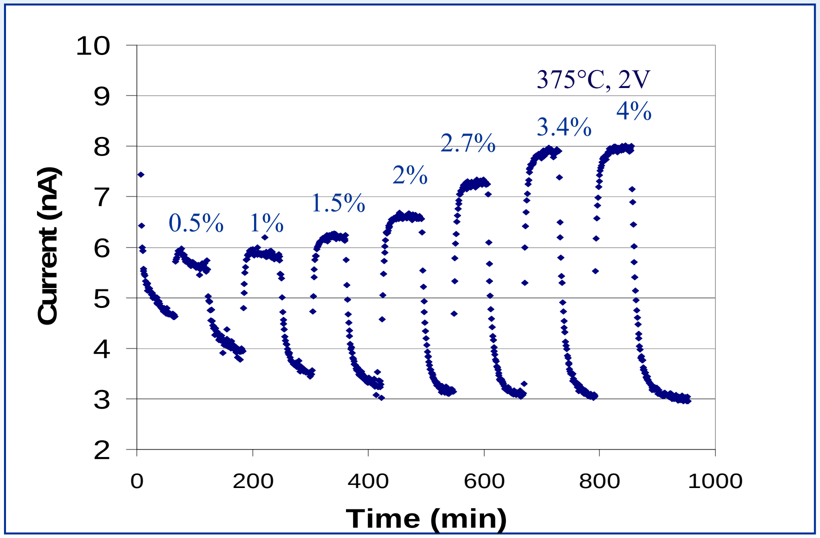
Sensors after tin oxide sol gel addition



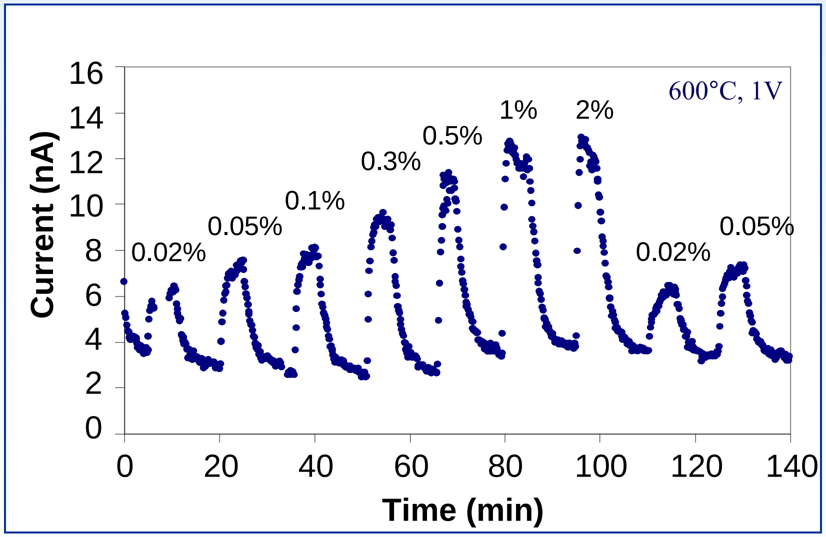


Nanocrystalline Tin Oxides Improve Solid Electrolyte Carbon Dioxide Sensor by Decreasing Power Consumption

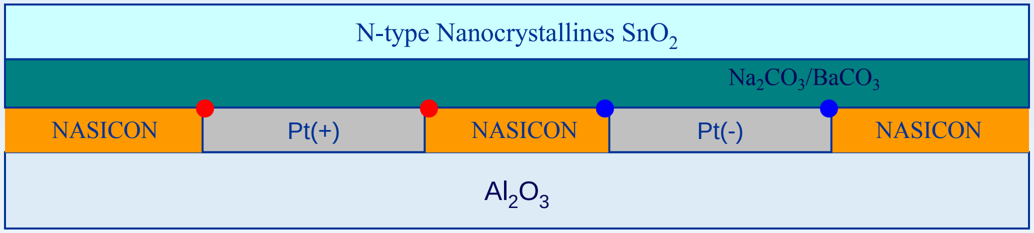
Solid Electrolyte CO_2 Sensor with Nanocrystalline SnO_2
(Detection temperature greatly reduced)



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 site**
- **Oxidation site**

- Reduction reaction at Pt(-) electrodes

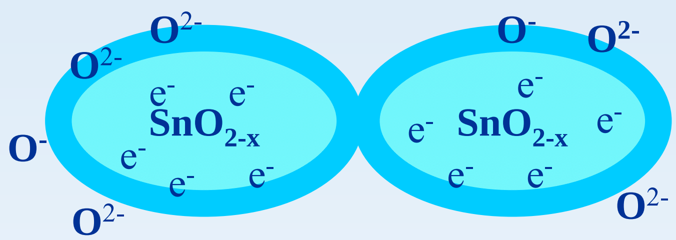
$$2Na^{+} + CO_2 + 1/2\ O_2 + 2e \rightarrow 2Na_2CO_3$$

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

- Results: Power consumption reduced

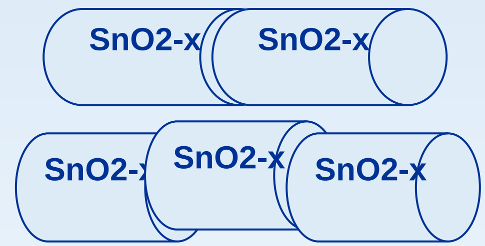
Metal Oxide Nanomaterials for Reducing Gas Sensing

Sensing Mechanisms Being Investigated for Nanostructured Materials

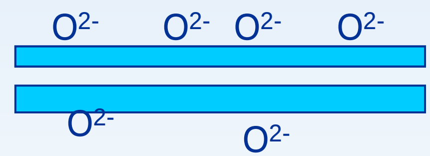


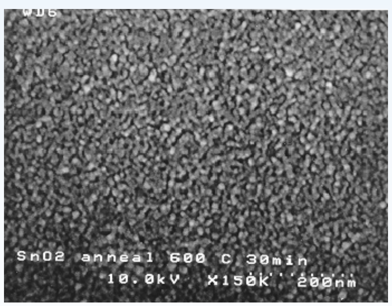
Increased nano grain boundary contact

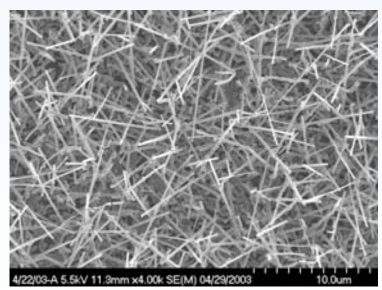
Sensing mechanism unknown

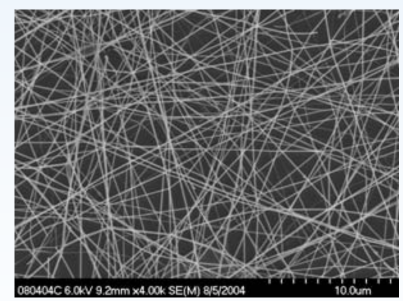


More controlled crystalanity







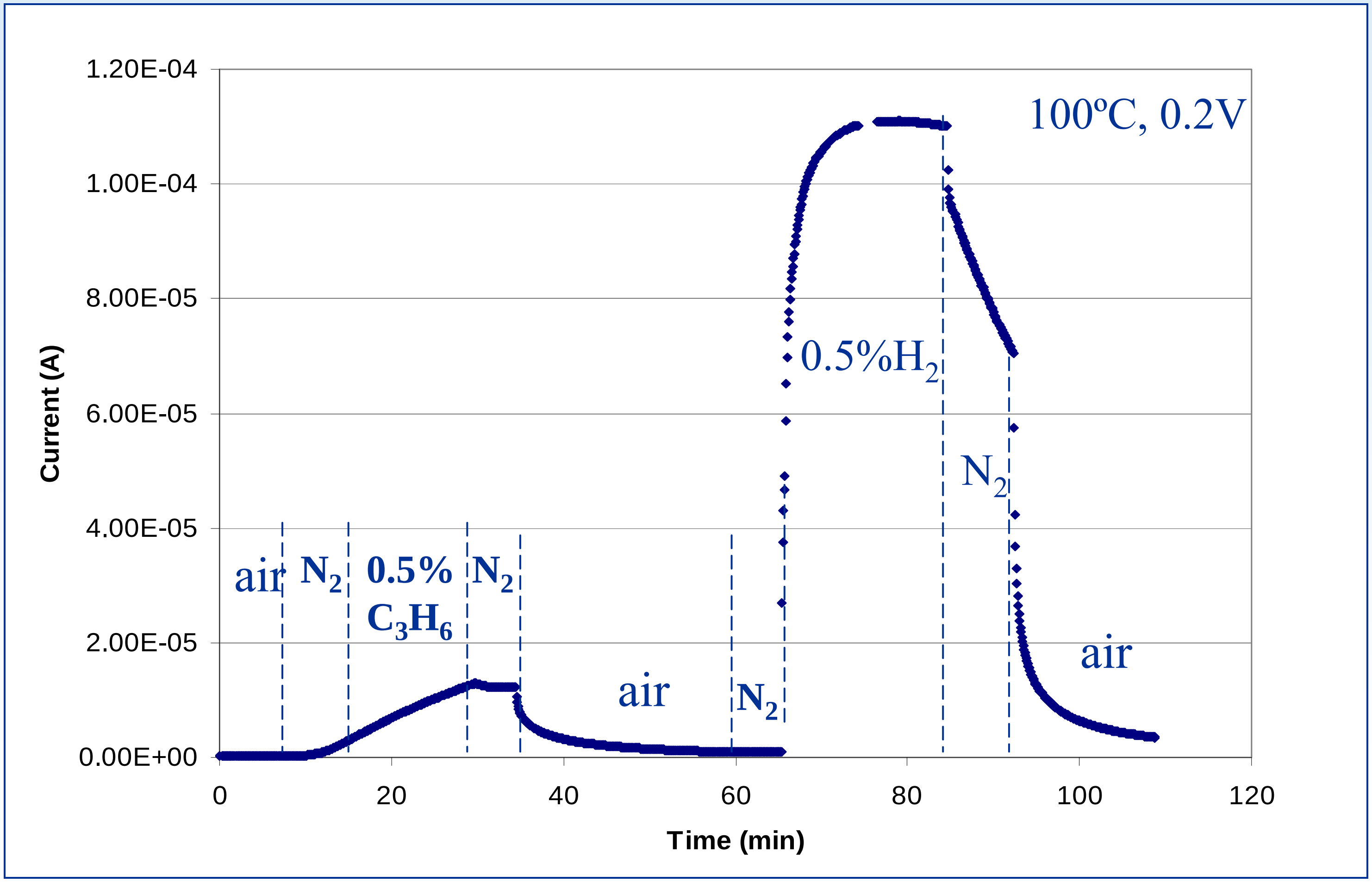


Nanocrystallines SnOx by sol gel process

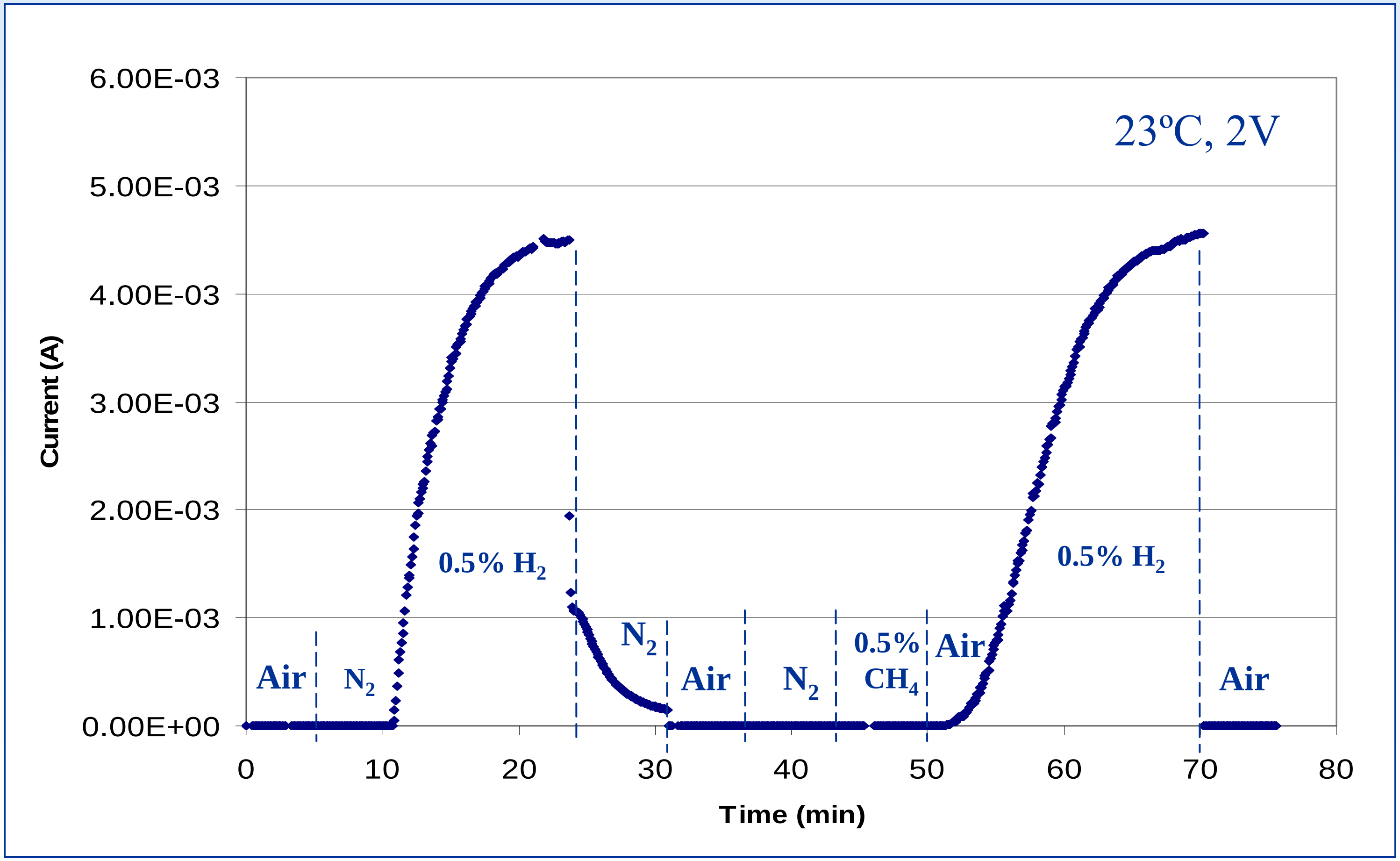
Polycrystal SnOx nanofibers by electrospun process

Single crystal nanorods by CVD

Palladium Doped SnOx Nanorods Detect Hydrogen at Reduced Temperature



Palladium Doped SnOx Nanofibers Detect Hydrogen at Room Temperature



Summary

- Nanotechnology enabled new sensing material development, improved sensor performance, and decreased sensor power consumption
- Resistor-based CO_2 sensing materials ($CuO-SnO_2$) developed through uniform doping of CuO in SnO_2 sol gel at 8:1 molar ratio
- Solid electrolyte CO_2 sensor improved and sensor power consumption decreased through addition of n-type SnO_2 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

Acknowledgements

Mike Artale, Peter Lampard, and Drago Androjna
Dorothy Lucko and Beth Osborn
Lawrence Matus and Mary Zeller

NASA Aviation Safety Program/IVHM Project
NASA ETDP/Space Fire Prevention Task