Nitric Oxide Microsensors for Engine Emissions, Environmental, and Human Health Monitoring Applications

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Outline

• Background of Chemical Sensors at NASA GRC

• Development of Nitric Oxide (NO) Microsensors
  ♦ Harsh environment engine emission and environmental monitoring
  ♦ Human health monitoring

• Summary

NASA Glenn Research Center
Chemical Sensor Development at NASA GRC

- **Microsensors and platforms**
  - $\text{H}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_4$, $\text{C}_3\text{H}_6$, $\text{CO}_2$, $\text{CO}$, $\text{O}_2$, NOx, and $\text{N}_2\text{H}_4$
  - Orthogonal technology: different sensing mechanism
  - Schottky diodes, resistors, and electrochemical cells

- **Applications**
  - **Propulsion system, fuel depot leak detection**
  - **Low false alarm fire detection.**
  - **Harsh environment engine emissions and environmental monitoring**
  - **Human health monitoring and potential astronaut health evaluation**

- **Approaches**
  - **Smart sensor system**: sensor arrays, signal processing and conditioning components, power and telemetry
  - **“Lick and Stick”** for full-field view of environment
  - **Nanotechnology and batch microfabrication**
  - **Small size, low weight, cost, and power consumption**
Development of Nitric Oxide Microsensors

• Harsh environment engine emission and environmental monitoring
  * Detection limit required: ppm level

• Human health monitoring application
  * Detection limit required: 10 ppb; e.g. Asthma patient.

• Parallel Approaches
  * Electrochemical cells
  * SiC based sensors
  * Resistor based sensors

  ◆ N-type semiconductor Indium Tin Oxides (ITO): sensitive materials for reducing gases
  ◆ Two types of films investigated: sputter deposition and polymer precursor
Pt interdigitated electrodes fabricated on a 2-inch alumina wafer

Electrode structure and schematic of gas testing setup

Gas testing chamber: Probe contact

ITO sensing material
Two Approaches to Deposit ITO Sensing Materials

• **Sputter Deposition**

  * ITO Sputter Target: 90% In$_2$O$_3$ and 10% SnO$_2$ (by weight)
  
  * 1200 Å ITO

• **ITO organic precursors**

  * Mixture of 2-ethylhexenoic acid modified indium isoproxide and tin isoproxide
  
  * Drop deposit on the interdigitated electrode, heat treat

\[ \text{In(OC}_3\text{H}_7\text{i})(\text{C}_7\text{H}_{15}\text{COO})_2 \ + \ \text{Sn(OC}_3\text{H}_7\text{i})_2(\text{C}_7\text{H}_{15}\text{COO})_2 \xrightarrow{550^\circ\text{C, 2 hr}} \text{ITO [90% In}_2\text{O}_3 \text{ and 10% SnO}_2 \text{ (by weight)] + CO}_2 + \text{H}_2\text{O} } \]

  * Thickness in the micro range
Sensing Mechanism

- **Sputter ITO Thin film: at 450°C, 1V, NO sensing involves two processes:**
  
  * Low concentration (ppb to low ppm): adsorption
  
  * High concentration (ppm): adsorption and NO oxidation reaction:

  \[
  \text{O}_2, \ NO \text{ from air grab electrons from ITO surface, deplete ITO surface}
  \]

  
  ♦ Adsorption: \( \text{O}_2 \) and NO adsorbed on the ITO surface, deplete surface electrons, increase film resistance: \( \text{O}_2 + e \rightarrow \text{O}_2^- ; \ NO + e \rightarrow \text{NO}^- \)

  ♦ Reaction: NO react with \( \text{O}_2^- \), release electrons back to ITO, decrease resistance: \( \text{NO} + \text{O}_2^- \rightarrow \text{NOx} (\text{NO}_2 + \text{N}_2\text{O}_3 + \text{N}_2\text{O}_5 \ldots ) + \text{ne} \)
Sputtered ITO Microsensor Response to Nitric Oxide Gas (ppm)

0 10 20 30 40 50 60 70 80 90

Current (A)

1.68E-02 1.70E-02 1.72E-02 1.74E-02 1.76E-02 1.78E-02 1.80E-02 1.82E-02 1.84E-02 1.86E-02

450°C, 1V

60 ppm NO
40 ppm NO
20 ppm NO
10 ppm NO
4 ppm NO

N₂/Air (60:40)

(1. Adsorption)

(2. Chemical reaction)

Time (min)

Note: 1200 Å ITO thin film deposited in sputter system.
NO concentration: 100 ppm NO in N₂ gas. The NO was diluted with N₂ and Air to match base gas N₂ and Air ratio (60 : 40). Total flow is 2500 sccm.
Sputter Deposited Nitric Oxide Microsensor Response to Nitric Oxide Gas (ppb-ppm)

Note: Original NO concentration: 3.97 ppm NO in N₂ gas. The NO was diluted with N₂ and Air to match base gas: N₂ and Air ratio (60 : 40). Total flow is 2500 sccm.
Nitric Oxide Microsensor (ITO from polymer precursor) 
Response to Nitric Oxide Gas (ppm)

Note: ITO sensing material from ITO polymer precursor, heat-treated at 550°C for 2 hr 
NO concentration: 100 ppm NO in N₂ gas. The NO was diluted with N₂ and Air to match baseline N₂ and Air ratio (60 : 40). Total flow is 2500 sccm.
Nitric Oxide Microsensor (ITO from polymer precursor) Response to Nitric Oxide Gas (ppm)

- **550°C, 1V**
- **Base gas N₂/Air (60:40)**

Note: ITO sensing material from ITO polymer precursor, heat-treated at 550°C for 2 hr
NO concentration: 100 ppm NO in N₂ gas. The NO was diluted with N₂ and Air to match base gas N₂ and Air ratio (60 : 40). Total flow is 2500 sccm.
Nitric Oxide Microsensor (ITO from polymer precursor)
Response to Nitric Oxide Gas (ppm)

Note: ITO sensing material from ITO polymer precursor, heat-treated at 550°C for 2 hr
NO concentration: 100 ppm NO in N₂ gas. The NO was diluted with N₂ and Air to match base gas N₂ and Air ratio (60 : 40). Total flow is 2500 sccm.
Sensing Mechanism
(with ITO from organic precursor)

• High temperatures, 450°C to 550°C, involve one process:
  NO oxidation reaction: \( \text{NO} + \text{O}_2 \rightarrow \text{NOx} \) (NO\(_2\), N\(_2\)O\(_3\), N\(_2\)O\(_5\), \ldots) + ne

• Low temperature: 250°C, 2V, involves two processes (like sputtered film in ppb level NO gases):
  NO adsorption and NO oxidation reactions

♦ Next: Film surface morphology analysis to understand different NO sensing behavior
Summary

• Resistor based nitric oxide microsensor being developed for aerospace applications: engine emission and health monitoring

• Two approaches used for the ITO sensing materials exploration. Preliminary data showed NO detection from ppm to ppb achieved. Improvement in detection limit needed

• Two sensing mechanisms involved: adsorption and chemical reaction. ITO films from different processes have different behaviors. More investigation needed to develop practical NO sensors

• Extensive testing and surface morphology studies to be conducted

• Provide potential simple and sensitive NO sensors: low cost, small size, batch fabrication, high yield, and easy use

• Provide quick information for selecting NO sensing materials for nano-structure NO sensor development.
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Thank You!

Please visit:

http://www.grc.nasa.gov/WWW/sensors/