

## 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** ٠

- \* H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, CO<sub>2</sub>, CO, O<sub>2</sub>, NOx, and N<sub>2</sub>H<sub>4</sub>
- \* 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



**NASA GRC Sensors and Electronics Branch cleanroom** 







#### **Example of smart** sensor system

### **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





### **Two Approaches to Deposit ITO Sensing Materials**

- Sputter Deposition
  - \* ITO Sputter Target: 90% In<sub>2</sub>O<sub>3</sub> and 10% SnO<sub>2</sub> (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

In(OC<sub>3</sub>H<sub>7</sub><sup>i</sup>)(C<sub>7</sub>H<sub>15</sub>COO)<sub>2</sub> + Sn(OC<sub>3</sub>H<sub>7</sub><sup>i</sup>)<sub>2</sub>(C<sub>7</sub>H<sub>15</sub>COO)<sub>2</sub>  $\xrightarrow{550^{\circ}\text{C}, 2 \text{ hr}}$ Oven

ITO [90%  $In_2O_3$  and 10%  $SnO_2$  (by weight) ]+  $CO_2 + H_2O$ 

\* 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:



- Adsorption: O<sub>2</sub> and NO adsorbed on the ITO surface, deplete surface electrons, increase film resistance: O<sub>2</sub> + e → O<sub>2</sub><sup>-</sup>; NO + e → NO<sup>-</sup>
- Reaction: NO react with  $O_2^-$ , release electrons back to ITO, decrease resistance: NO +  $O_2^- \rightarrow NOx (NO_2 + N_2O_3 + N_2O_5...) + ne$



#### Sputtered ITO Microsensor Response to Nitric Oxide Gas (ppm)



Note: 1200 A ITO thin film deposited in sputter system. NO concentration: 100 ppm NO in  $N_2$  gas. The NO was diluted with  $N_2$  and Air to match base gas  $N_2$  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  $N_2$  gas. The NO was diluted with  $N_2$  and Air to match base gas:  $N_2$  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  $N_2$  gas. The NO was diluted with  $N_2$  and Air to match baseline  $N_2$  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  $N_2$  gas. The NO was diluted with  $N_2$  and Air to match base gas  $N_2$  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  $N_2$  gas. The NO was diluted with  $N_2$  and Air to match base gas  $N_2$  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: NO+ O<sub>2</sub><sup>-</sup>→ NOx (NO<sub>2</sub> +N<sub>2</sub>O<sub>3</sub> +N<sub>2</sub>O<sub>5</sub>...) + 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/