**Measurement of Gas Sensor Performance**

- **Gas sensing materials:**
  1. Sputtered ZnO film (150 nm) (Massachusetts Institute of Technology)
  2. Sputtered SnO₂ film (60 nm) (Fraunhofer Institute of Physical Measurement Techniques)

- **Target gases:**
  \( \text{H}_2, \text{CO}, \text{NH}_3, \text{NO}_2, \text{CH}_4 \)

- **Operating temperature:**
  320 - 460 °C

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**Mechanisms in Semiconducting Gas Sensor**

- **Bulk:** Change in stoichiometry
  \[ O_O^- = 2e^- + V_{O^2}^- + \frac{1}{2} \text{O}_2(g) \]
  
  → *Induce shallow donors: density related to \( \text{PO}_2 \)*)
  
  \[ n^2 [V_{O^2}^-] \text{PO}_2^{1/2} = K_R(T) \Rightarrow \] \[ n = (2 K_R(T))^{1/3} \text{PO}_2^{-1/6} \]

  modulate
  
  Bulk electronic conduction
Resistive Oxygen Sensors Based on SrTiO₃

\[ \sigma \propto e^{\frac{E_A}{kT} pO_2^{\frac{1}{m}}} \]

Influence of Dopants on Electrical Conductivity of SrTiO₃

\[ \log(\sigma / (\Omega \cdot cm)^{-1}) T = 800 \, ^\circ C \]

Donors: Nb, Ta, Sb, Y, La, Ce, Pr, Nd, Pm, Sm, Gd

Acceptors: Al, Ni, Fe
Temperature Independence: High Acceptor Concentration in SrTiO$_3$

![Graph showing electrical conductivity versus $pO_2$ for Sr(Ti$_{0.65}$Fe$_{0.35}$)O$_3$ at various temperatures.]

Response times $T / °C$ $t_{90} / ms$
- 900°C: 6.5
- 800°C: 26
- 750°C: 83
- 700°C: 185


Oxygen Sensor in Thick Film Technology
Mechanisms in Semiconducting Gas Sensor

• Interface - Gas adsorption

\[ 2e^+ + O_2(g) = 2O(s) \]

→ Induce space charge barrier

modulate

1. Surface conduction

2. Grain boundary barrier
Sensor Configuration

A single 9 mm² chip sensor array with:

- four sensing elements with interdigitated structure electrodes
- heater
- temperature sensor
**Resistance Response to Gas Environment**

**Schematic of Gas Sensor Structure**

- ZnO film (150 nm)
- Electrode: Pt(200 nm)/Ta(25 nm) film
- Insulation layer: SiO$_2$ layer (1 µm)
- Substrate: Si wafer

**MicroElectroMechanical Systems - MEMS**

- Bulk Micromachining
- Surface Micromachining

Micromachining - Application of microfabrication tools, e.g. lithography, thin film deposition, etching (dry, wet), bonding
Gas Sensors and MEMS

- Miniaturization
  - Reduced power consumption
  - Improved sensitivity
  - Decreased response time
  - Reduced cost

- Arrays
  - Improved selectivity

- Integration
  - Smart sensors

Microhotplate
Microhotplate Sensor Platform

NIST Microhotplate Design

Microhotplate Characteristics

- Milli-second thermal rise and fall times
  - programmed thermal cycling
  - low duty cycle
- Low thermal mass
  - low power dissipation
- Arrays
  - enhanced selectivity
Harsh Environment MEMS

- High temperatures
- Oxidation resistant
- Chemically inert
- Abrasion resistant

Wide band gap semiconductor/insulator

Photo Electro-chemical Etching - PEC

Features:

- materials versatility e.g. Si, SiC, Ge, GaAs, GaN, etc.
- precise dimensional control down to 0.1 mm through the use of highly selective p-n junction etch-stops
- fabrication of structures with negligible internal stresses
- fabrication of structures not constrained by specific crystallographic orientations
Photo Electro-chemical Etching - PEC

- Electro-chemical etching

\[ \text{Light source} \]
\[ \text{electrolyte} \]
\[ \text{n-type} \]
\[ \text{h}^+ \text{semiconductor} \]
\[ \text{h}^+ \]
\[ \text{p-type} \]
\[ \text{h}^+ \text{h}^+ \text{h}^+ \text{h}^+ \text{semiconductor} \]

- Photo electro-chemical etching

Examples ...

- Arrays of stress free 4.2 µm thick cantilever beams.

- Photoelectrochemically micromachined cantilevers are not constrained to specific crystal planes or directions.

- Similar structures successfully micromachined from SiC by Boston MicroSystems personnel.
**Smart Gas Sensor**

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**A Self Activated Microcantilever-based Gas Sensor**

1. A device capable of sensing a change in environment and responding without need for a microprocessor.
2. A device has both gas sensing and actuating function by integration of semiconducting oxide and piezoelectric thin films.

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**Smart Gas Sensor**

   - *Microstructure (Nano-Structure) and Composition*
2. Piezoelectric thin films for providing actuating function.
3. Thin film electroceramic deposition methods for integrating with silicon microcantilever beam.
   - *Compatibility with Si micromachining technology*
   - *High performance in chemical environment*
Resonant Gas Sensor

- Resonant Frequency: \( f_R = \frac{1}{2l} \left( \frac{\mu_o}{\rho_o} \right)^{1/2} \)
  where \( l \) = resonator thickness, \( \mu_o \) = effective shear modulus and \( \rho_o \) = density

- Mass change causes shift in resonant frequency: \( \frac{(m_0 - \Delta m)}{m_0} \approx \frac{(f + \Delta f)}{f} \)

Gas Sensor elements :

(I) Active layer interacts with environment
- stoichiometry change translates into mass change

(II) Resonator transduces mass change into resonance frequency change

Choice of Piezoelectric Materials

- Temperature limitations of piezoelectric materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Max Operating Temperature (°C)</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>450</td>
<td>High loss</td>
</tr>
<tr>
<td>LiNbO(_3)</td>
<td>300</td>
<td>Decomposition</td>
</tr>
<tr>
<td>Li(_2)B(_4)O(_7)</td>
<td>500</td>
<td>Phase transformation</td>
</tr>
<tr>
<td>GaPO(_4)</td>
<td>933 (?)</td>
<td>Phase transformation</td>
</tr>
<tr>
<td>La(_2)Ga(_5)SiO(_4) (\text{(Langasite)})</td>
<td>1470 (?)</td>
<td>Melting point</td>
</tr>
</tbody>
</table>

- Choice of Piezoelectric Materials
**Design Considerations**

- **Bulk conductivity** dependent on temperature and PO$_2$
  → contributes to resonator electrical losses

  Modify bulk conductivity - how?

- **Stability** to oxidation and reduction process
  → limited oxygen non-stoichiometry
  → slow oxygen diffusion kinetics

  Defect chemistry and diffusion kinetics study

- $f_r (T)$: Temperature dependence of resonant frequency
  → need to differentiate from mass dependence

  Minimize @ intrinsic and device-levels

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**Langasite: Bulk Electrical Properties**

- Single activation energy in the temperature range 500 - 900 °C
- Extrapolated room temperature conductivity: $\sigma = 4.4 \times 10^{-18}$ S cm$^{-1}$

  ![Graph of electrical properties](image)

  $\sigma_0 = 2.1$ S cm$^{-1}$
  $E_A = 105$ kJ mol$^{-1}$
Temperature dependence of the resonance frequency ($f_R$) of a resonator device with different mass loads.

- **Resonator (Langasite) -- H. Seh & H. Fritze**
  - Defect chemistry
  - Oxygen diffusion/exchange studies
  - Bulk conductivity dependence on T and PO$_2$

- **Active Layer (PCO) -- T. Stefanik**
  - Transport-Defect chemistry correlations

- **Gas Sensor --**
  - Add active layer (PCO) using PLD ⇒ nanocrystalline vs microcrystalline
  - Sensor testing