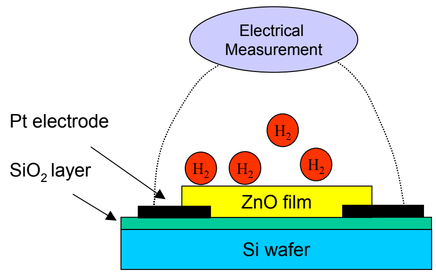
Measurement of Gas Sensor Performance

- Gas sensing materials:
  1. Sputtered ZnO film (150 nm
     (Massachusetts Institute of Technology)
  2. Sputtered SnO_2 film (60 nm)
     (Fraunhofer Institute of Physical Measurement Techniques)
- Target gases:
  H_2, CO, NH_3, NO_2 , CH_4
- Operating temperature:
  320 - 460 °C



Mechanisms in Semiconducting Gas Sensor

- Bulk: Change in stoichiometry

$$O_O = 2e' + V_O^{\cdot\cdot} + 1/2\ O_2(g)$$

→ *Induce shallow donors: density related to PO_2*

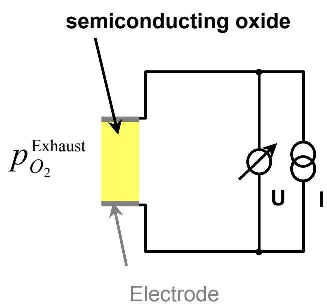
$$n^2\,[V_O^{\cdot\cdot}]\,PO_2^{\,1/2} = K_R(T) \Rightarrow \boxed{n = (2\,K_R(T))^{1/3}\,PO_2^{\,-1/6}}$$

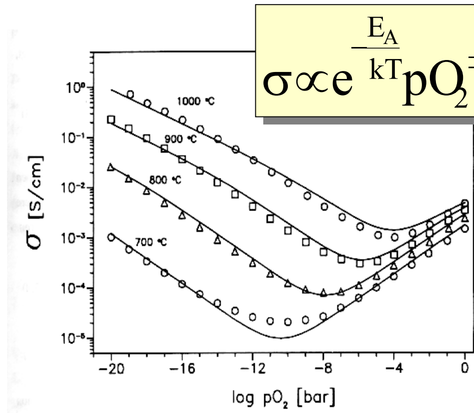
modulate

↓

Bulk electronic conduction

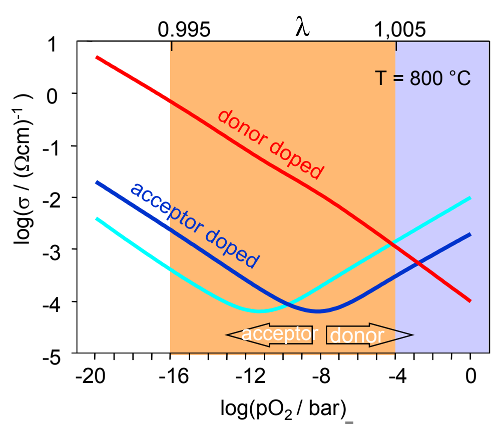
Resistive Oxygen Sensors Based on $SrTiO_3$





$$\sigma \propto e^{-\frac{E_A}{kT}} pO_2^{\pm\frac{1}{m}}$$

Influence of Dopants on Electrical Conductivity of $SrTiO_3$

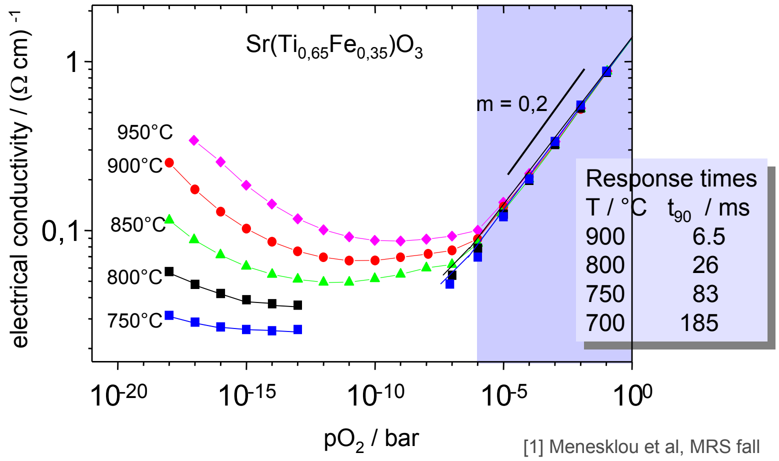


Sr^{2+} Ti^{4+} O^{2-}_3

Acceptors: Al, Ni, Fe

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

Temperature Independence: High Acceptor Concentration in $SrTiO_3$

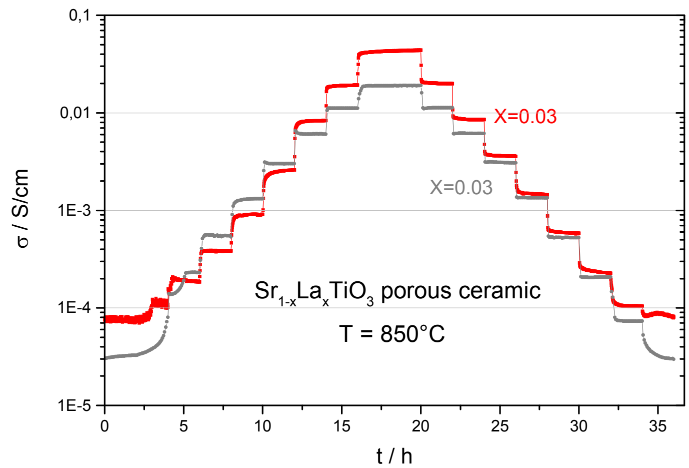


[1] Menesklou et al, MRS fall meeting, Vol. 604, p. 305-10 (1999).

Oxygen Sensor in Thick Film Technology

Transient Behavior of Porous $Sr_{1-x}La_xTiO_3$ for x=0.005 and x=0.03

T = 850 °C

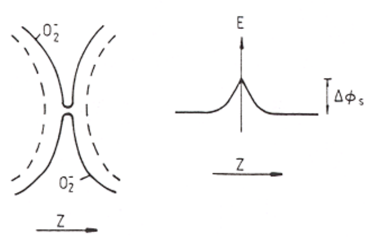


Mechanisms in Semiconducting Gas Sensor

- Interface - Gas adsorption

$$2e' + O_2(g) = 2O(s)'$$

→ *Induce space charge barrier*



Grain boundary barrier

modulate

↓

1. Surface conduction

2. Grain boundary barrier

Sensor Configuration

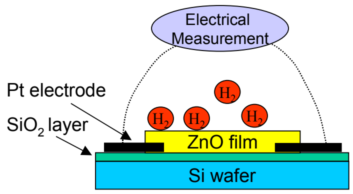
A single 9 mm^2 chip sensor array with:

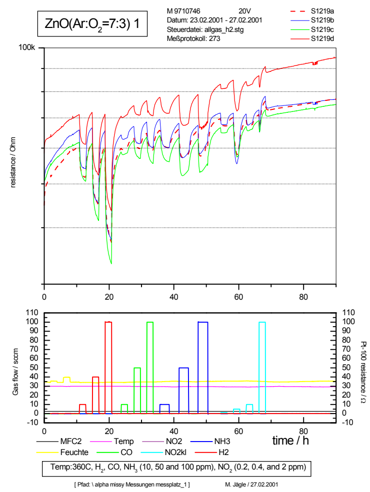
- four sensing elements with interdigitated structure electrodes
- heater
- temperature sensor

Schematic Cross Section of Mounted Sensor

Resistance Response to Gas Environment

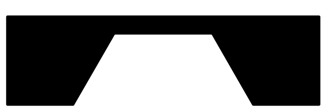
Schematic of Gas Sensor Structure



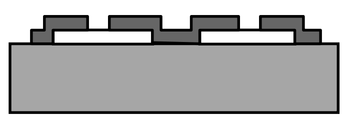


- ZnO film (150 nm)
- Electrode: Pt(200 nm)/Ta(25 nm) film
- Insulation layer: SiO_2 layer (1 μm)
- Substrate: Si wafer

MicroElectroMechanical Systems - MEMS



Bulk Micromachining



Surface Micromachining

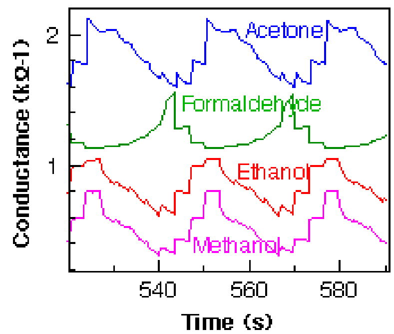
Micromachining - Application of microfabrication tools, e.g. lithography, thin film deposition, etching (dry, wet), bonding

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

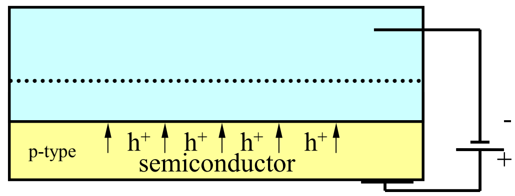
Photo Electro-chemical Etching - PEC

Features:

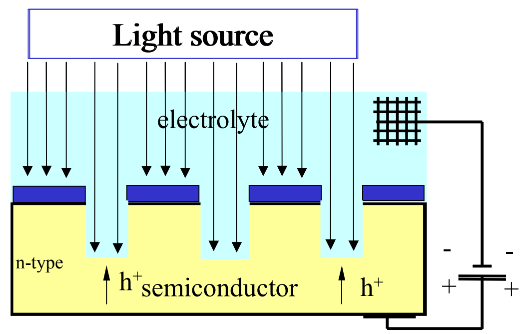
- *materials versatility* e.g. Si, SiC, Ge, GaAs, GaN, etc.
- precise dimensional control down to 0.1 mm through the use of highly selective *p-n junction etch-stops*
- fabrication of structures with *negligible internal stresses*
- fabrication of structures *not constrained by specific crystallographic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

Photo Electro-chemical Etching - PEC

- Electro-chemical etching



- Photo electro-chemical etching



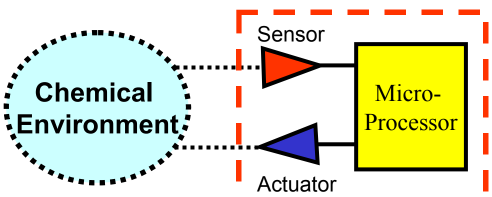
Examples ...

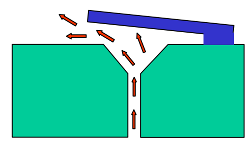
- **Arrays of stress free 4.2 μm thick cantilever beams.**
- **Photoelectrochemically micromachined cantilevers are not constrained to specific crystal planes or directions.**
- **Similar structures successfully micromachined from SiC by Boston MicroSystems personnel**

Smart Gas Sensor

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.





Microfluidic structure

Smart Gas Sensor

1. Semiconducting oxide thin films for high gas sensitivity
   : ***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***
4. Microcantilever structures for the self activated gas sensor
   : ***High performance in chemical environment***

Resonant Gas Sensor

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

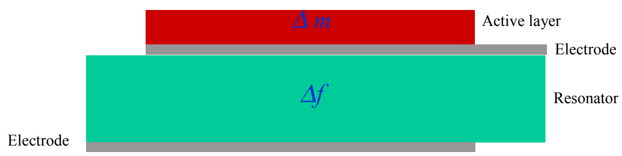
- Mass change causes shift in resonant frequency : $(m_o - \Delta m) / m_o \approx (f + \Delta f) / f$

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

Material	Max Operating Temperature (°C)	Limitations
Quartz	450	High loss
$LiNbO_3$	300	Decomposition
$Li_2B_4O_7$	500	Phase transformation
$GaPO_4$	933 ?	Phase transformation
$La_2Ga_5SiO_4$ (Langasite)	1470 ?	Melting point

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

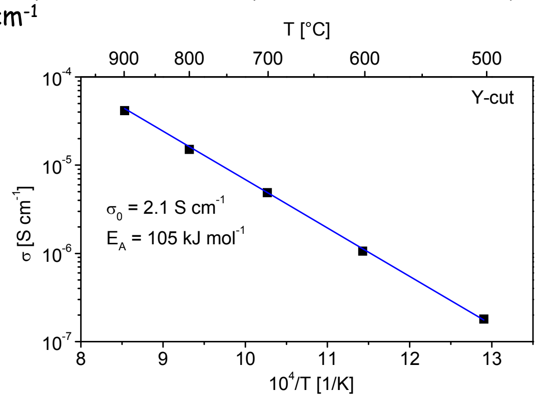
Defect chemistry and diffusion kinetics study

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

Minimize @ intrinsic and device-levels

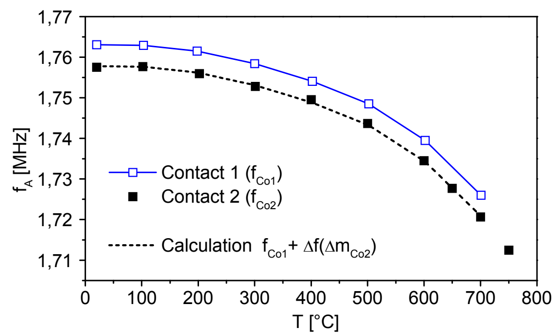
Langasite : Bulk Electrical Properties

- Single activation energy in the temperature range 500 - 900 °C
- Extrapolated room temperature conductivity: $\sigma = 4.4\times10^{-18}$ S cm^{-1}



Langasite : f_R (T)

- Temperature dependence of the resonance frequency (f_R) of a resonator device with difference mass loads.



Ongoing Activities

- **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