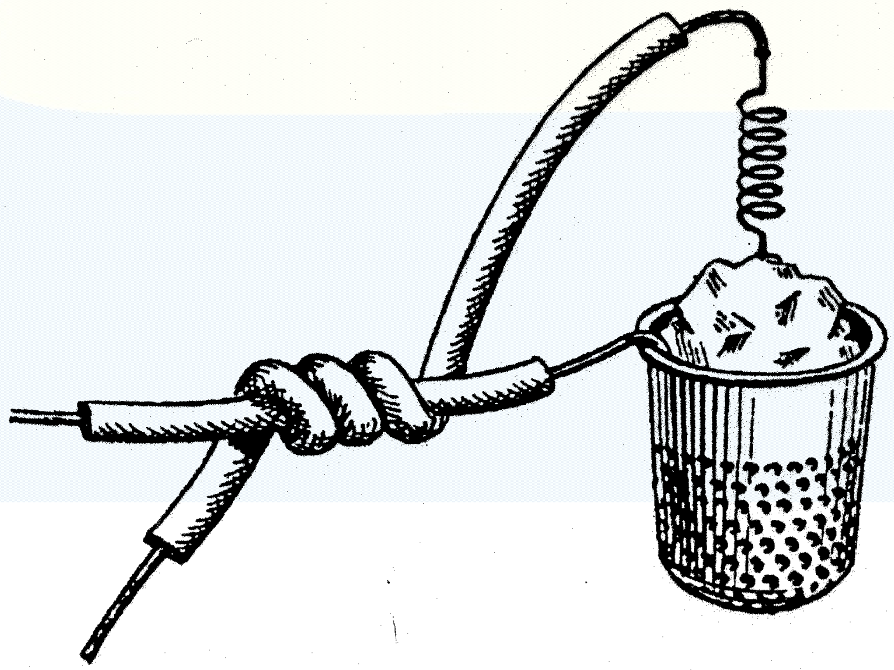
ELECTRONICS
Design Division

Sensor devices



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Outline

- **8 Chemical Sensors**
  - **Introduction**
  - **Interaction of gaseous species at semiconductor surfaces**
  - **Catalysis, the acceleration of chemical reactions**
  - **The electrical properties of compressed powders**
  - **Thin film sensors**
  - **Thick film and pressed-pellets sensors**
  - **FET devices for gas or ion sensing**

Introduction

- Discussion is mainly on detection of combustible gases such as CO, H2, alcohols, propane and other hydro-carbonates
- Can be done using semiconducting metal oxides "primarily used"
- H_2 sensing can be done with use of FET-transistors

Interaction of gaseous species at semiconductor surfaces

- Typical operation principle “one explanation”
- Resistive sensor, resistance decrease when a layer of powdered SnO_2 is exposed to combustible gas in present of ambient air.
- Oxygen in air adsorbs at semiconductor surface, oxygen dissociates to form O^-. The electron is picked up from semiconductor, which increase the resistance

$$O_2 + 2e^- \rightarrow 2O^-$$

Interaction of gaseous species at semiconductor surfaces

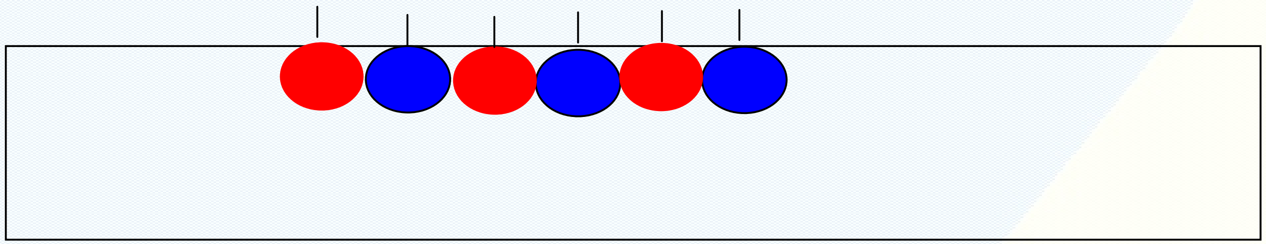
- O^- is highly reactive and easily react with combustible gases which contain hydrogen.

$$H_2 + O^- \rightarrow H_2O + e^-$$

- Hydrogen react and form water, as a result a electron is released which lower the resistance in the semiconductor
- To increase the reaction rate a catalyst is often included

Interaction of gaseous species at semiconductor surfaces

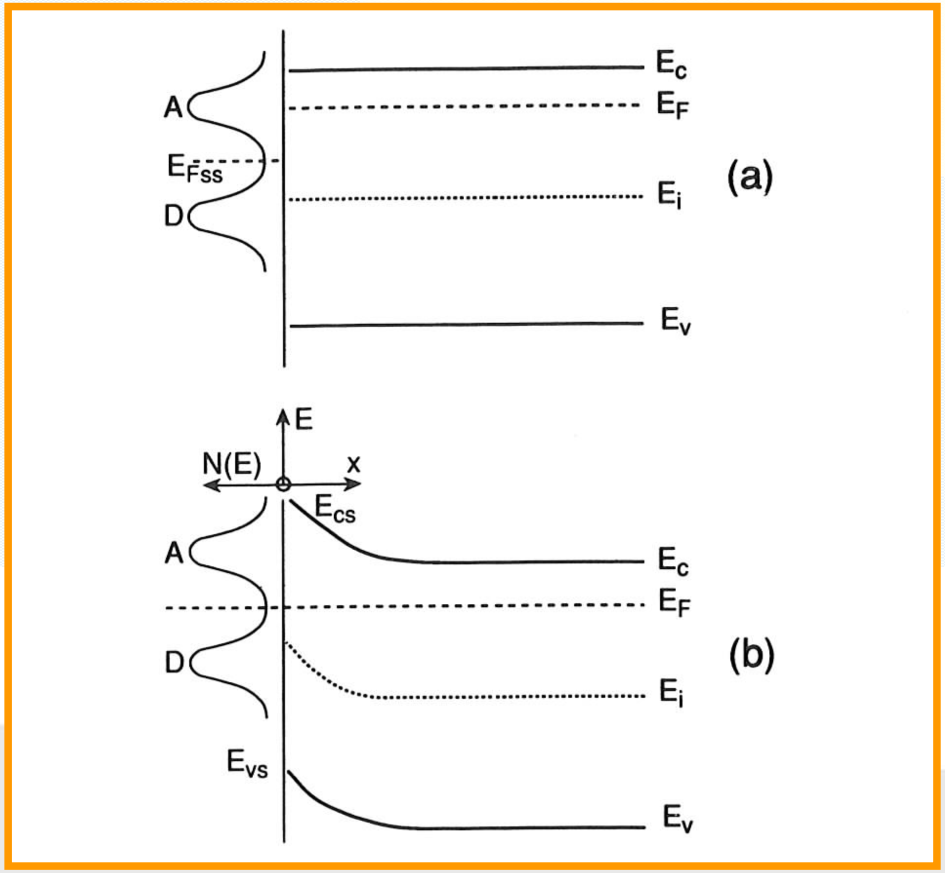
- Normally n-type semiconductor is used, p type is more unstable.
- SnO_2 is an ionic crystal, Sn^{2+}or Sn^{4+} (Cations), O^{2-} (Anions)
- At surface, Sn^{4+} easily can attract electrons caused by the dangling bonds
- On the other hand can O^{2-} at the surface, easily pick up holes or release electrons to the bulk



- Because the capability to attract positive and negative charge on the surface, also ions as OH^- and H^+ can be adsorbed on the surface.

Interaction of gaseous species at semiconductor surfaces

- Humidity change the response of the detector, at higher temperature the water is evaporated from the surface, which leave the surface exposed for the mesurand (gas)



a) No charge exchange

b) After charge exchange

Interaction of gaseous species at semiconductor surfaces

- High ratio of O^- is needed! O^- is the catalytic active ion

$$[O^-]/[O_2^-] = [O_2]^{-1/2} \exp[(-E_{O_2} - E_O - \Delta G/2)/kT]$$

- High temperature gives high ratio of O^-
- ZnO above 180 ºC, TiO_2 above 400 º C and SnO_2 above 150 ºC

Catalysis, the acceleration of chemical reactions

- Catalyst is needed to increase the sensitivity and accelerate the reaction in metal-oxide gas sensor
- A catalyst is not consumed and lower the activation energy for the reactions
- Without the catalyst, the reaction have a high activation energy:

$$H_2 \rightarrow 2H$$

$$O_2 \rightarrow 2O$$

$$2H + O \rightarrow H_2O.$$

Catalysis, the acceleration of chemical reactions

Hydrogen is adsorbed on a platinum surface (“group of”)

With Platinum as a catalyst

$$H_2 + 2Pt \rightarrow 2Pt{-}H$$

$$O_2 + 2Pt \rightarrow 2Pt{-}O$$

$$2Pt{-}H + Pt{-}O \rightarrow 3Pt + H_2O.$$

The activation energy is drastic reduced

The electrical properties of compressed powders

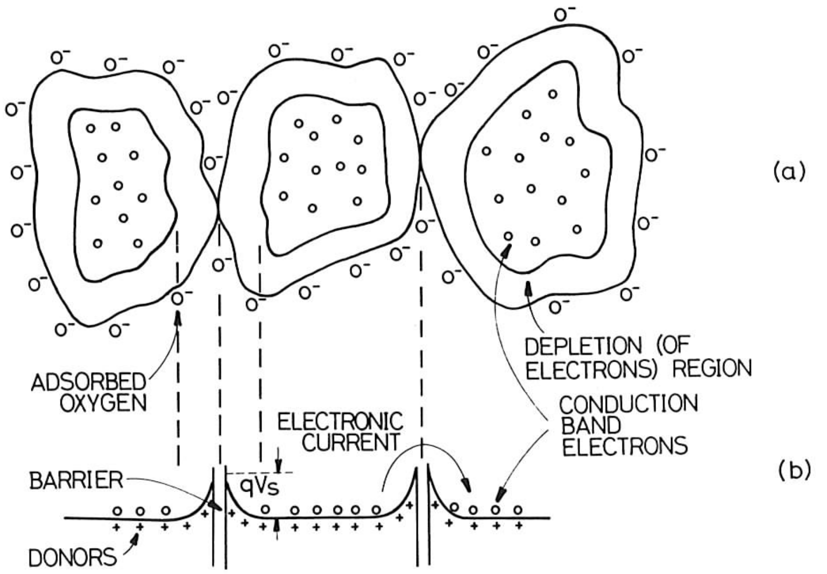


Fig. 3 Barriers at intergranular contacts on a pressed pellet. (a) Three gains with adsorbed oxygen providing surface depletion layers. The depleted layers cause a high contact resistance. (b) The corresponding band model for a more quantitative analysis where, for conductance, electrons must cross over the surface barriers.

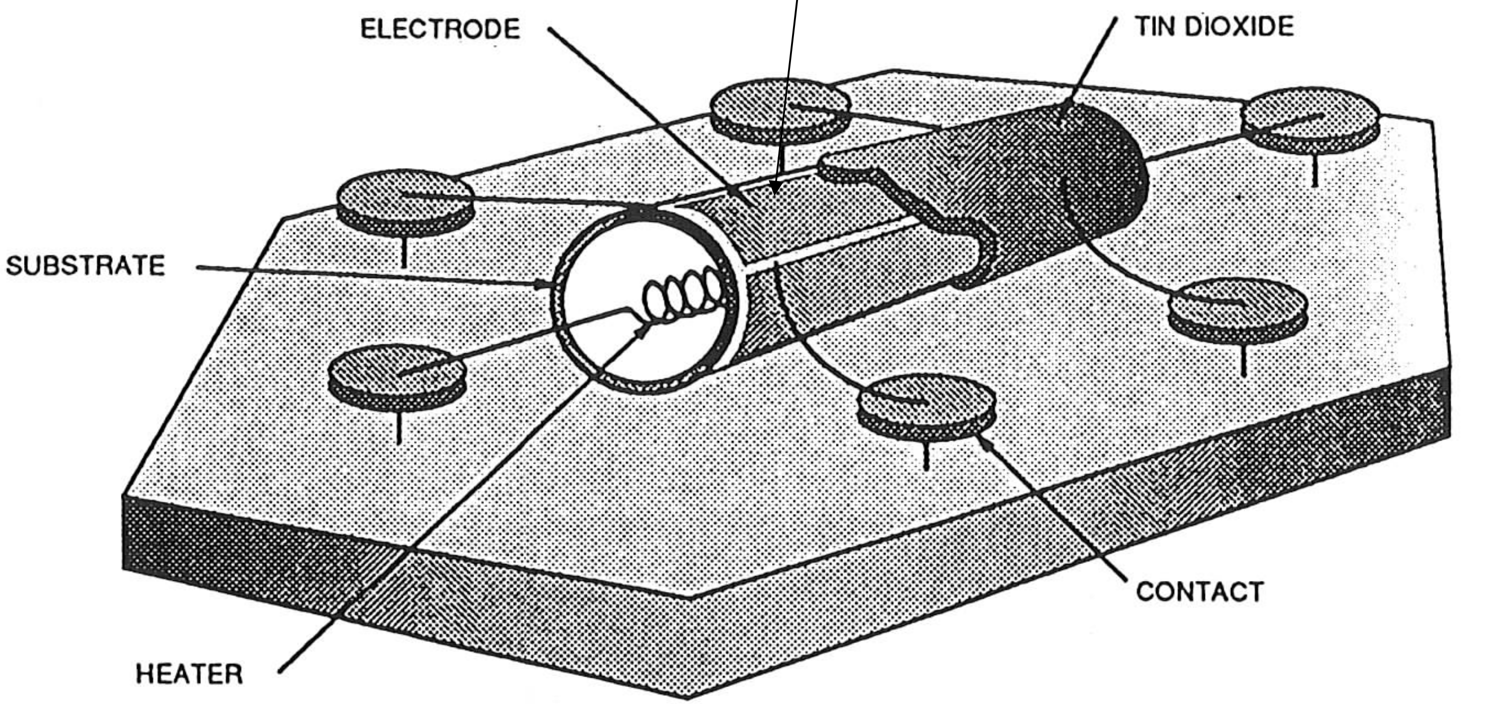
The grains result in a potential barrier in between the grains, which reduce the sensitivity

Thin film sensors

- A thin film produced by evaporation or sputtering
- Sensors are difficult to produces as thin films because of
  - High resistance in grain boundary
  - Risk for consuming all available electrons because of thin film
  - However, material with high defect mobility such as bismuth molybdate, the grain boundary does not influence the resistance substantially

Thick film and pressed-pellets sensors

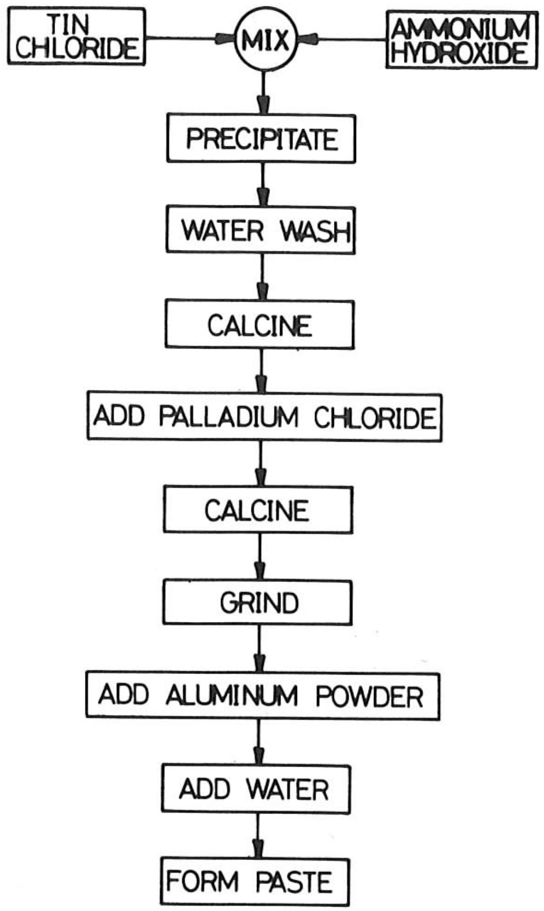
Gold



Structure of a Taguchi gas sensor

Fig. 4 The Taguchi sensor, a ceramic tube with a $SnO_2 + Pd$ paste deposited on the outside, a heater element on the inside.

Thick film and pressed-pellets sensors



Preparation of SnO_2 for thick film sensors

TABLE 1 Example Combinations of Semiconductor/Additive/Gas Combinations for Metal-Oxide Sensors

Semiconductor	Suggested Additives	Gas to be Detected
SnO_2	Pt + Sb	CO
SnO_2	Pt	alcohols
SnO_2	Sb_2O_3 + Au	H_2, O_2, H_2S
ZnO	V, Mo	halogenated hydrocarbons
WO_3	Pt	NH_3
Fe_2O_3	Ti-doped + Au	CO

It has been suggested in the literature that these catalyst/promoter combinations may provide some degree of selectivity for the gas indicated.

Thick film and pressed-pellets sensors

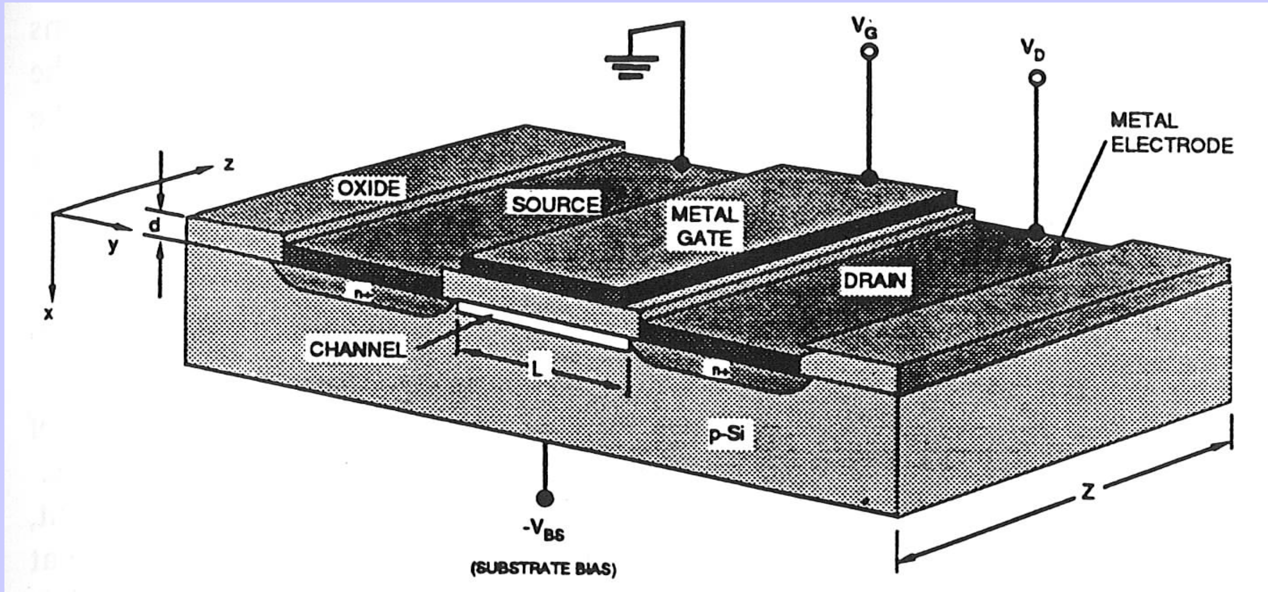
- Selectivity
  - The catalyst
  - The promoter
  - The temperature
    - Oxidation of gas is temperature depended, CO and alcohols are easy to oxidise
  - Use of gas-filter
    - SiO_2 is used as filter for rejecting H_2

Thick film and pressed-pellets sensors

- The sensor should be stable and reversible
  - SnO_2 show good stability, however after been kept in room temperature and the heated up to operation temperature a high conductive spike is observed.
  - An correct functional sensor is indicated by a drop in the current after a few minutes
  - A rest current is still observed which can remain for weeks, therefore it is recommended to burn in the sensor before use.

FET devices for gas or ion sensing

- FET-transistor can be sensitive to some gases or ions if the gate is exposed
- The metal gate can be of Pd, H_2 dissolves in the Pd an change the gate voltage



FET devices for gas or ion sensing

- ISFET as pH sensor
  - **At low pH, hydrogen (protons) are absorbed**
  - **At high pH, OH^- are absorbed**
  - **The current in the channel, reflecting the pH value in the liquid**

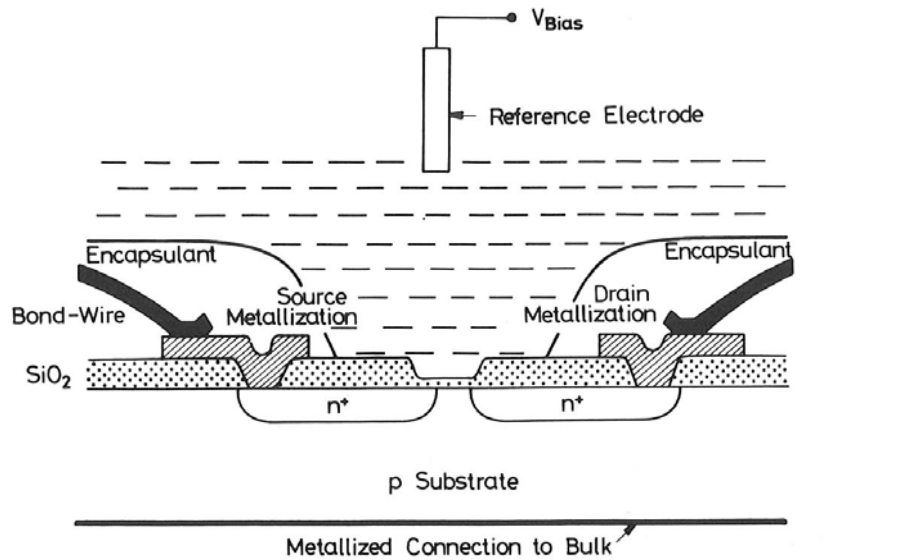


Fig. 7 A simple ISFET. The metal gate is removed from the MOSFET of Fig. 6, a voltage to induce a channel is applied, if necessary, to the reference electrode, and the adsorbing species to be measured induces a double-layer voltage across the oxide that coats the channel.