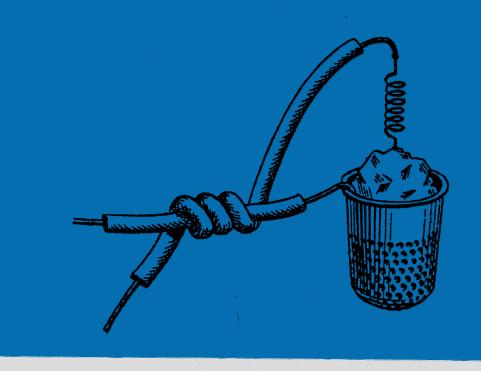




Sensor devices Chemical Sensors







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"
- H₂ sensing can be done with use of FET-transistors





- 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 the semiconductor, which increases its resistance.

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





• O⁻ is highly reactive and easily react with combustible gases which contain hydrogen.

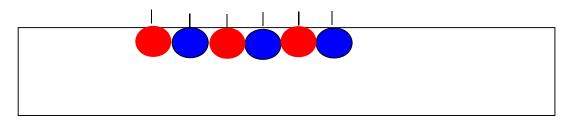
$$H_2 + O^- \rightarrow H_2O + e^-$$

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





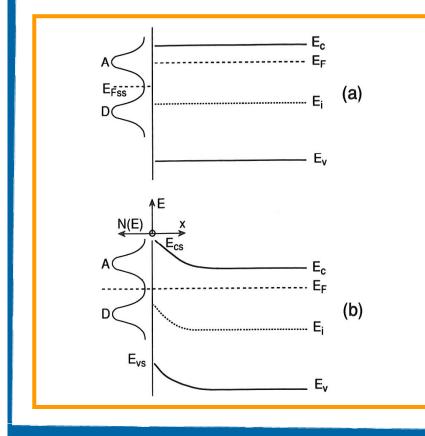
- Normally n-type semiconductor is used, p type is more unstable.
- SnO₂ is an ionic crystal, Sn²⁺or Sn⁴⁺ (Cations), O²⁻ (Anions)
- At surface, Sn⁴⁺ easily can attract electrons caused by the dangling bonds
- On the other hand can O^{2-} at the surface, easily pick up holes or release electrons to the 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.







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

a) No charge exchange

b) After charge exchange





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 °C, TiO $_2$ above 400 ° C and SnO $_2$ above 150 °C



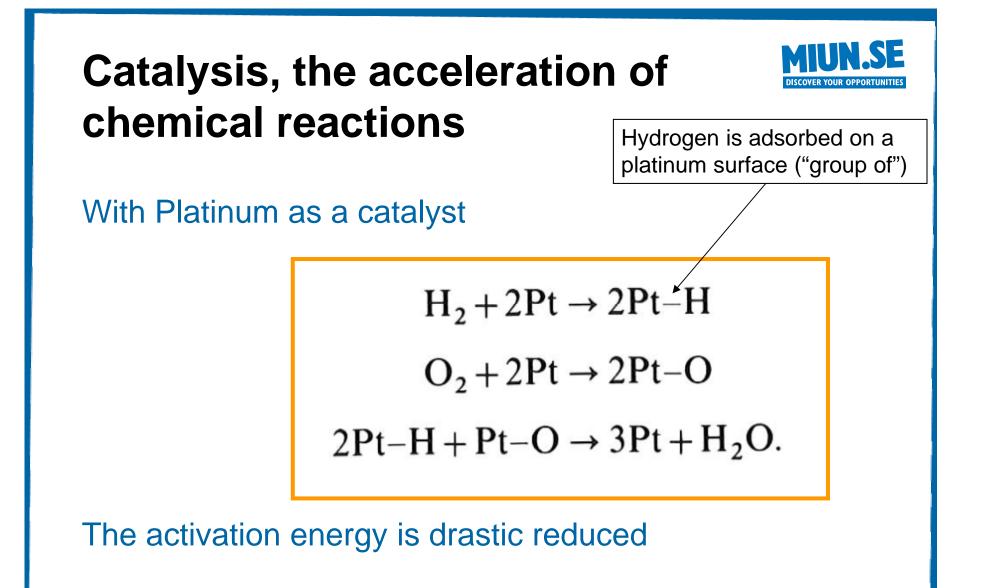
Catalysis, the acceleration of chemical reactions



- 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:

$$H_2 \rightarrow 2H$$
$$O_2 \rightarrow 2O$$
$$2H + O \rightarrow H_2O.$$







The electrical properties of compressed powders

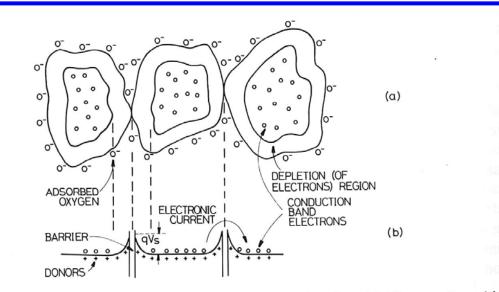


Fig. 3 Barriers at intergranular contacts on a pressed pellet. (a) Three gains with adsorbed oxygen providing surface depletion layers. The depleted layers cause a high contact resistance. (b) The corresponding band model for a more quantitative analysis where, for conductance, electrons must cross over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

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



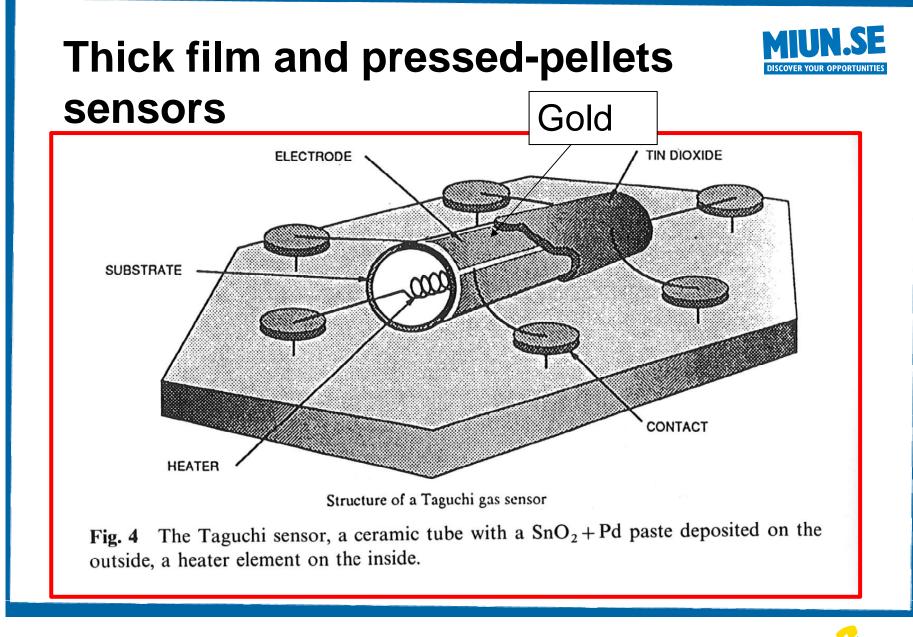


Thin film sensors



- 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







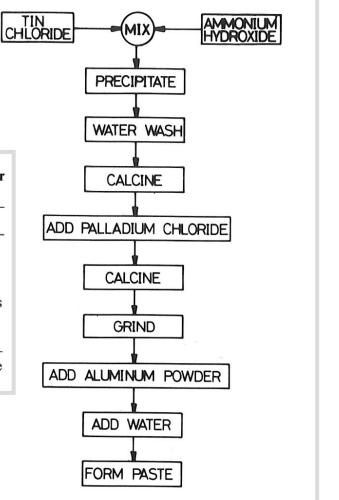
Thick film and pressed-pellets sensors

Preparation of SnO₂ 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	СО
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 ₂ O 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
 - SiO₂ is used as filter for rejecting H_2





Thick film and pressed-pellets sensors

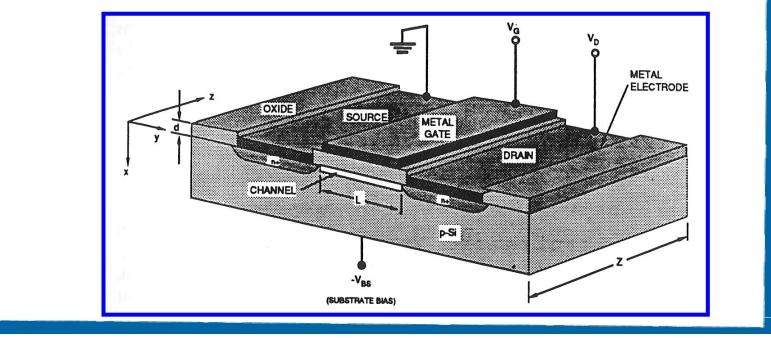


- The sensor should be stable and reversible
 - -SnO₂ show good stability, however after been kept in room temperature and the heated up to operation temperature a high conductive spike is observed.
 - An correct functional sensor is indicated by a drop in the current after a few minutes
 - A rest current 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, H₂ 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

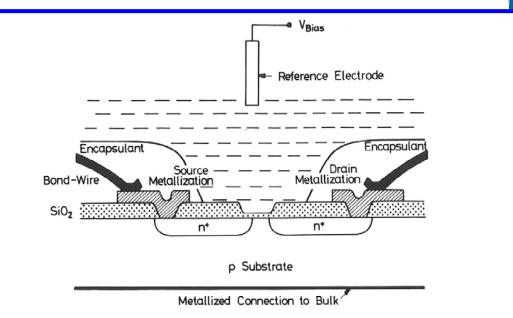


Fig. 7 A simple ISFET. The metal gate is removed from the MOSFET of Fig. 6, a voltage to induce a channel is applied, if necessary, to the reference electrode, and the adsorbing species to be measured induces a double-layer voltage across the oxide that coats the channel.

