Thin Film Gas Sensors

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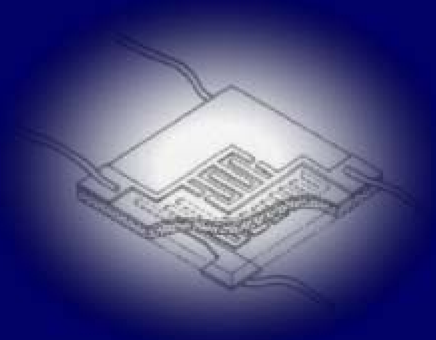
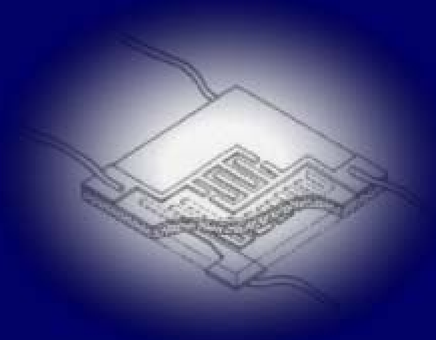
Abstract

Artificial sensors have become a vital element both in domestic life and industry. Although sensors of a great variety of types are well established in process industries, agriculture, medicine and many other areas, the development of new sensing capabilities is currently proceeding at an unprecedented rate. One of the most important fields of sensor technology is that of thin film gas sensors, since gases are the key measurands in many of the industrial and domestic activities. The purpose of this seminar is to give an introduction to sensor types and materials with a greater emphasis devoted to thin film gas sensors. Finally, I will highlight the research currently conducted on TFGS at CAPS.

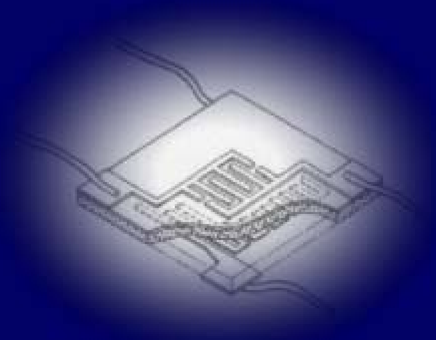


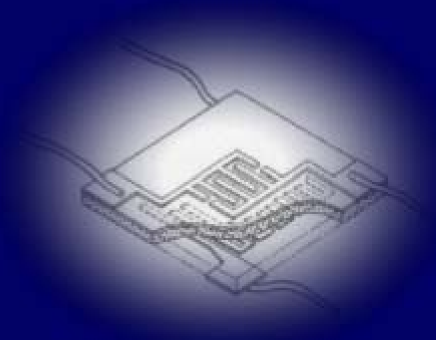


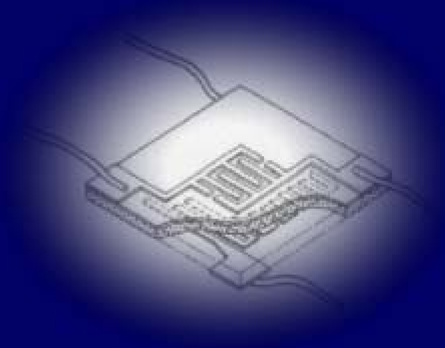
- **Part I : Sensors**

- **Part II : Thin Film Gas Sensors**

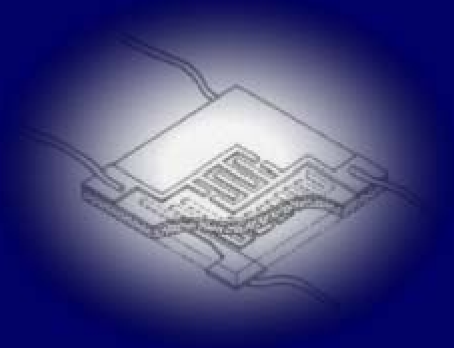
- **Part III : TFGS Research at ERC**



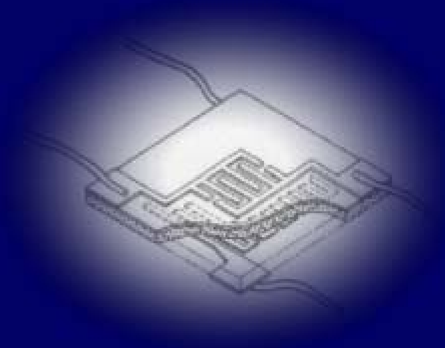


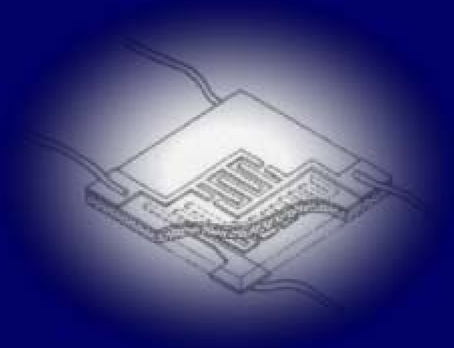


Part I



- **Sensors terminology & specifications**
- **Sensor materials**





Sensors

Terminology

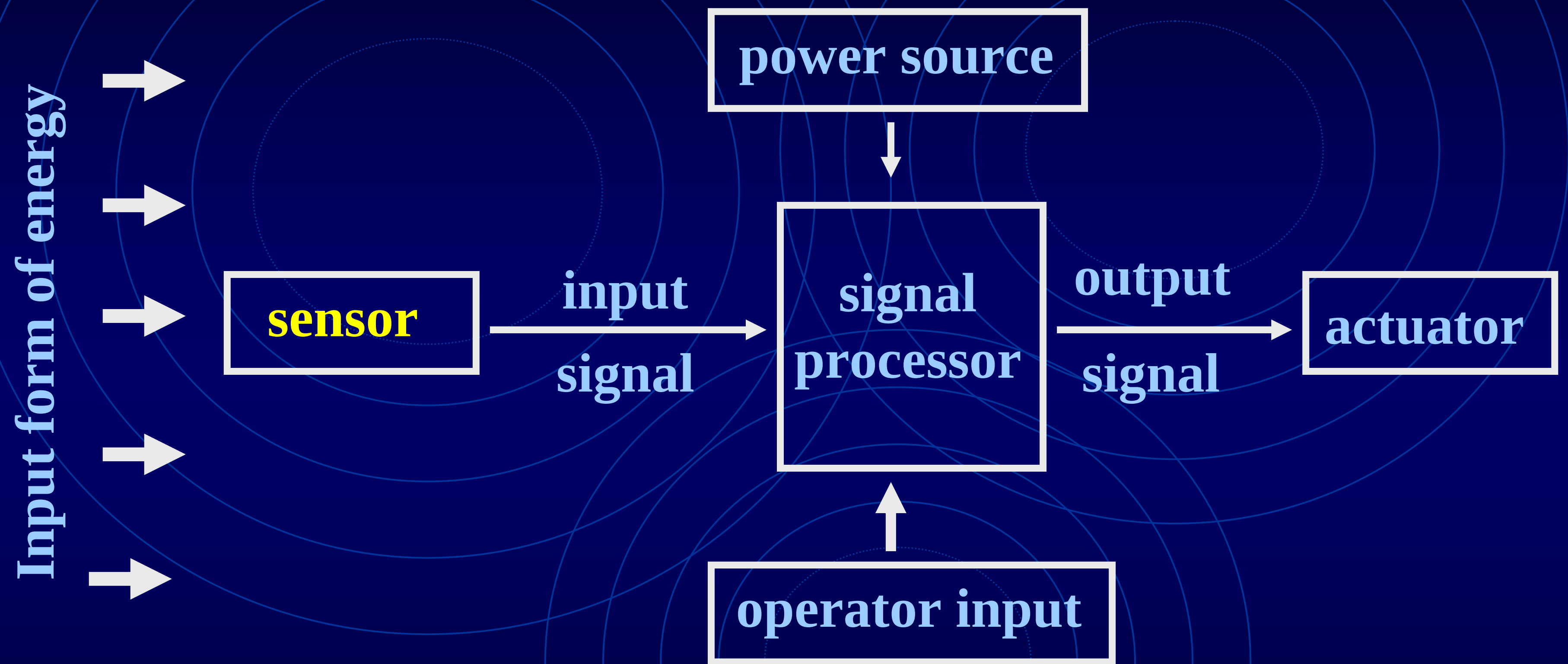
&

Specifications

Sensor Terminology

- **Sensor**: a device that detects or measures a physical quantity. Usually the output of a sensor is an electrical signal.
- **Actuator**: a device which converts a signal (usually electrical) to some action (usually mechanical)
- **Transducer**: a device that converts energy from one form into another

➢ Sensors and actuators are forms of transducers.


Input form of energy
sensor
input
signal
power source
signal
processor
output
signal
actuator
operator input

Types of Sensors

- **Active** Sensor: one that can generate a signal without the need for any external power supply (photovoltaic cell).
- **Passive** Sensor: needs an external source of energy (electrical).

The forms of energy involved in the sensing operation can be conveniently divided into six categories:

- **Chemical** (concentration, reaction rate)
- **Electrical** (current, voltage, resistance)
- **Magnetic** (moment, permeability)
- **Mechanical** (position, force, stress)
- **Radiant** (energy, phase, polarization)
- **Thermal** (heat, temperature)

Sensor Requirements

- Low cost
- Structurally & chemically reliable
- Selectivity
- Sensitivity
- Ruggedness

Sensed Quantities

- Strain & pressure
- Position, direction, distance & motion
- Light & associated radiation
- Temperature
- Sound, infrasound & ultrasound
- Liquids & gases
- Environment (moisture, acidity, radioactivity, pollution)

Sensor

Materials

Metals

- Metals consist of fixed ion cores surrounded by a sea of free electrons (free electron gas).
- They have closed-packed structures.
- They have the following properties:
  - High electrical conductivity
  - High thermal conductivity
  - High strength

Applications

- Thermal expansion devices
- Shape memory alloys
- Thermocouples
- Strain gauges
- Catalysts
- Electrodes (interface to sensing elements)

Semiconductors

Semiconductors are characterized by :

- A bandgap in their band structure
- Have two types of charge carriers
- Can be doped
- Can form rectifying or ohmic contacts

This leads to :

- Ability to control their conductivity
- Ability to modify their structures
- Ability of semiconductors to respond to light

Applications

- Thermistors
- Optical detection
- Gas-sensitive resistors
- Charge-coupled devices
- Position and displacement sensors

Dielectrics

- Have high electrical resistivity
- Can be polarized in an electric field
- Dielectrics include the following classes:
  - Piezoelectric materials: strain – electric field
  - Pyroelectric materials: temperature gradient – electric field
  - Ferroelectric materials
- Examples: Quartz – PZT – Polymers

Applications

- Crystal oscillators
- Radiation detection
- Vibration monitors
- Air bags
- Intrusion alarms
- ABS in cars
- Fuel level monitor
- Leak detection
- Optical shutters

- NDT
- Particle size dist.
- Large area display
- Ultrasonic imaging
- Airport control
- Earthquake detection
- Touch panels
- Thermography
- Motion detection

Magnetic Materials

- Classes of magnetic materials:
  - Diamagnetic materials
  - Paramagnetic materials
  - Ferromagnetic materials
  - Antiferromagnetic materials
  - Ferrimagnetic materials
  - Superconductors
- These materials respond differently to an external magnetic field.

Applications

- **Position & movement sensors**
- **Coded sensors (credit cards, smart cards)**
- **Hall effect sensors**
- **SQUIDS: measurement of extremely small magnetic fields (human brain)**

Other Materials

- Radiant materials (IR detection)
- Solid electrolytes
- Optical fiber sensor materials

PART II

- TFGS
- Sensing Mechanism
- Sensor Variables
- Sensor Parameters
- Advantages
- Applications
- Problems & Limitations

Thin Film Gas Sensors

Thin Film Gas Sensors

- Thin films of a semiconductor metal oxide (e.g. SnO_2) show a substantial conductivity change when only small concentrations of combustible gases (e.g. CO) are present in a large excess of oxygen (e.g. air).

- The conductance is controlled by surface processes.

- **There is a large number of semi-conducting metal oxides sensitive to gas composition in this way.**

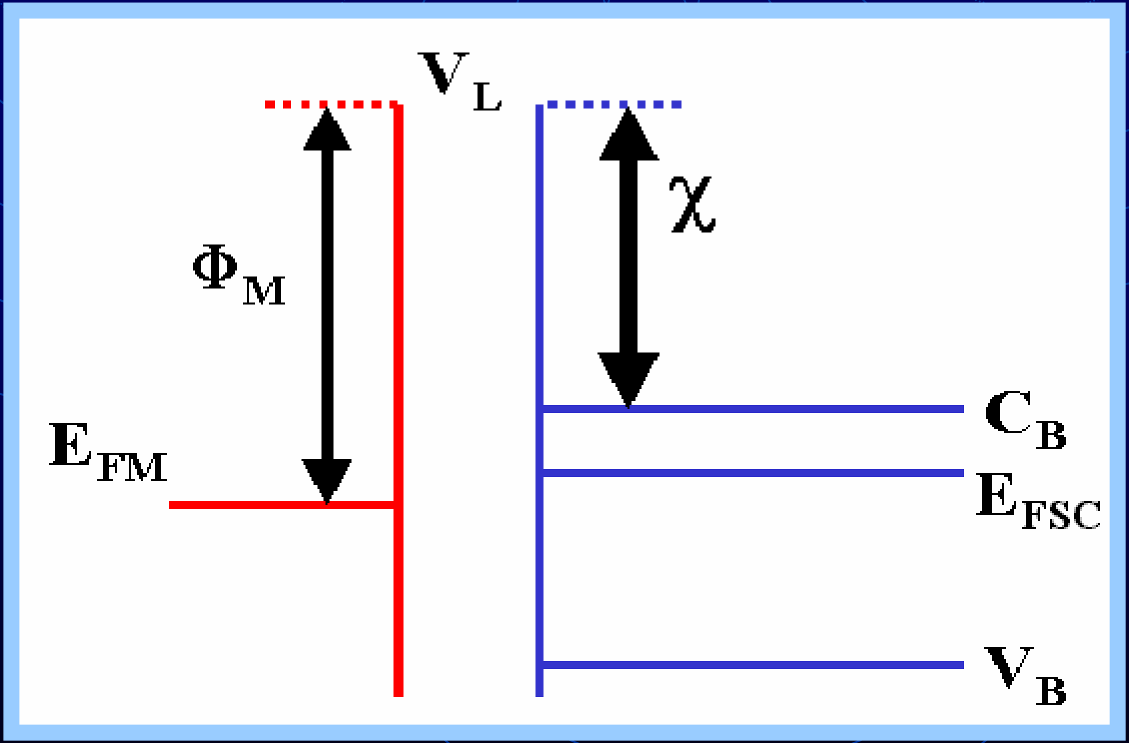
- **These include SnO_2 , ZnO , WO_3 , Fe_2O_3 , TiO_2 , In_2O_3 and Ga_2O_3.**

- **These films are sensitive to a range of combustible gases (H_2 , CO , and CH_4).**

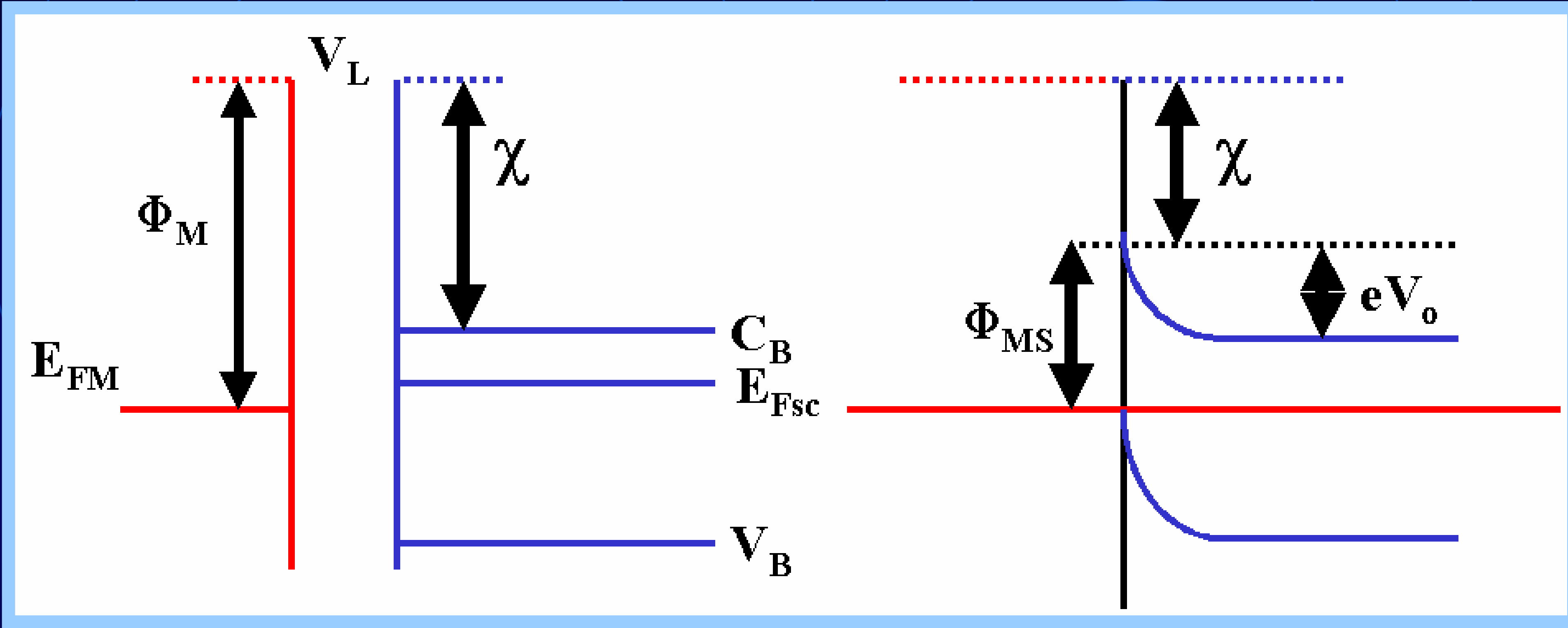
Sensing Mechanism

Metal – Semiconductor Junctions

- Consider the contact between an n-type semiconductor and a metal where $\chi < \Phi_m$



- When equilibrium is reached, the band diagram looks like



- There will be a barrier to electron flow from semiconductor to metal of magnitude:

$$\Phi_{SB} = \Phi_m - \chi$$ { Schottky barrier }

- **Additionally, there will be a built-in potential of magnitude:**

$$eV_o = \Phi_{SB} - E_{FSC}$$

- **Forward bias increases S – M current (reduce eV_o)**
- **Reverse bias decreases S – M current (increase eV_o)**
- **M – S current is the same (reverse saturation current)**
- **Such a junction behaves as a diode (rectifying)**

Behavior of Gas Sensors

- Many sensors are made from polycrystalline materials made up of grains.

- Unmodified SnO_2 is oxygen-deficient and, consequently, is an n-type semiconductor.

- The I – V characteristics of SnO_2 sensors have shown that the conductivity is determined by a Schottky barrier mechanism.

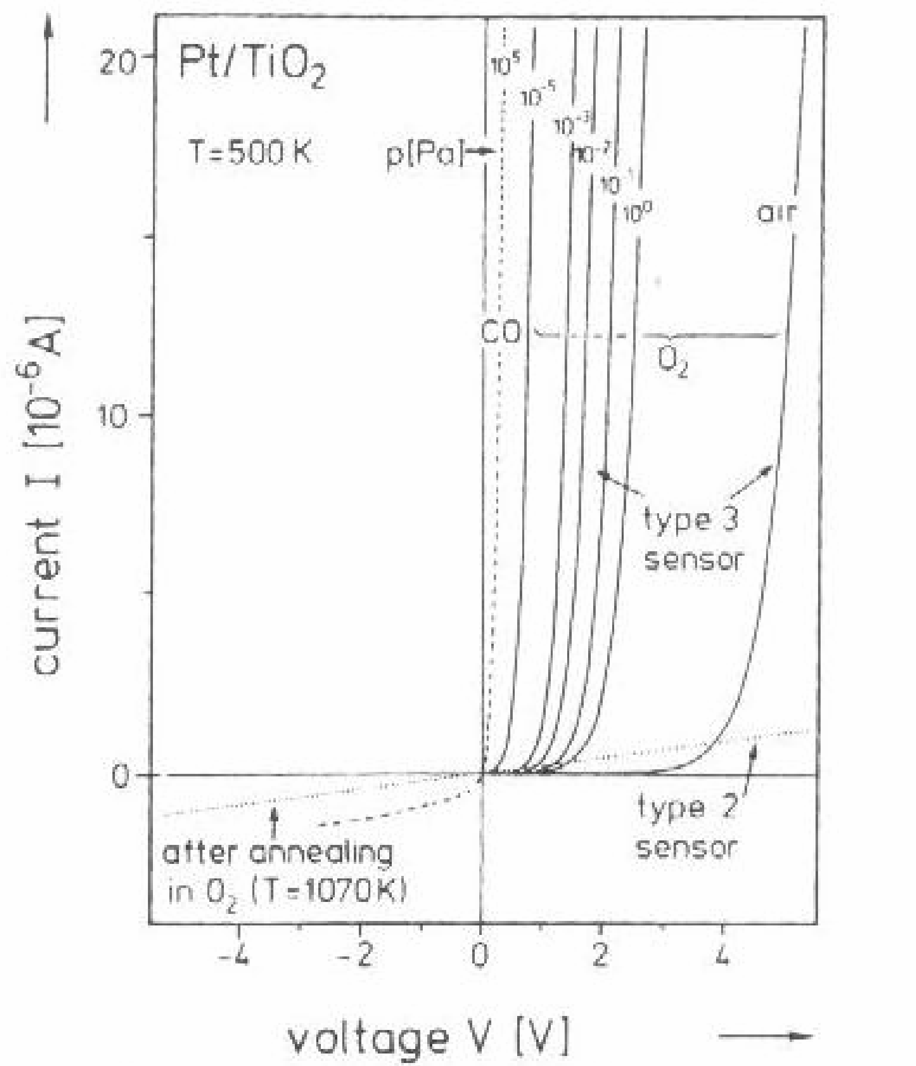
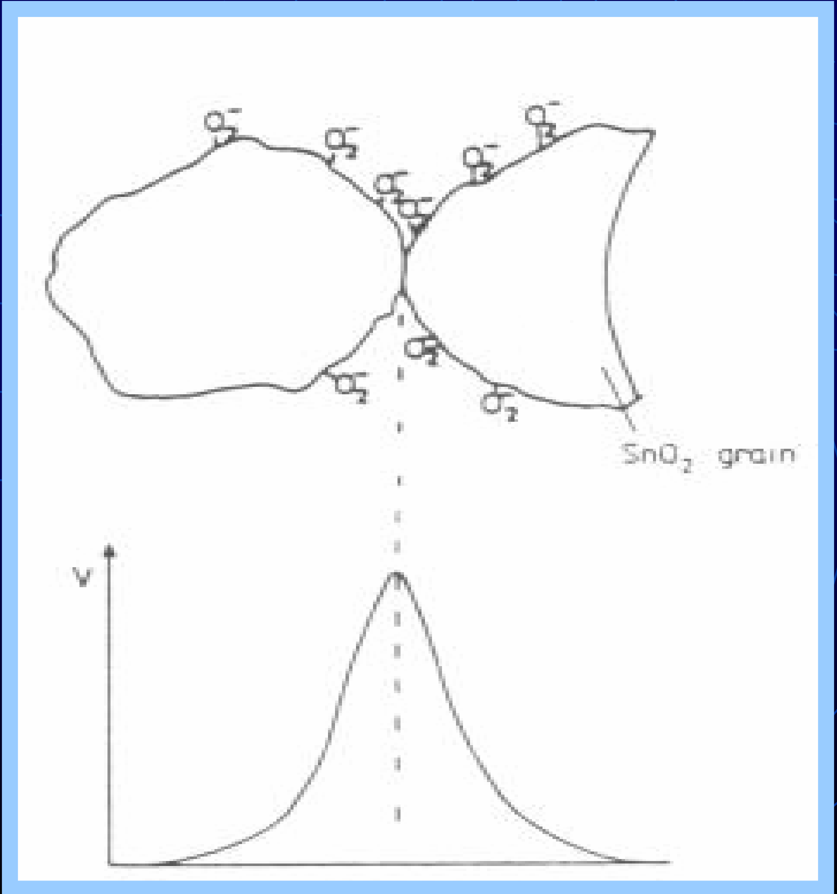
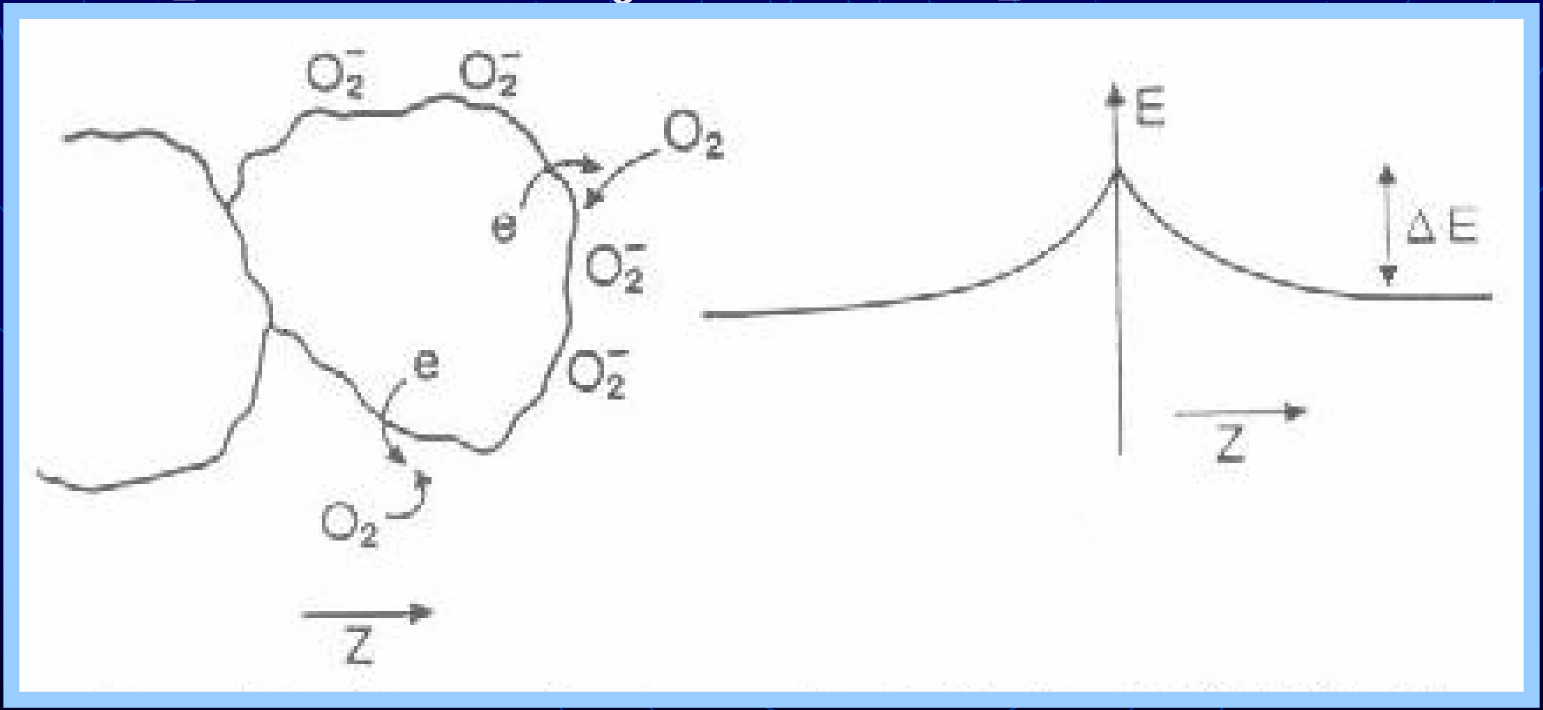


Figure 4.10 Current voltage curves of a Pt–TiO$_2$ Schottky diode for different partial pressures of oxygen at $T = 500$ K (solid curves) and for pure carbon monoxide (dashed curve). (Schierbaum *et al* 1991.) (Reproduced from *Sensors Actuators* 1991 **B 4** 87–94, with kind permission of Elsevier Science.)

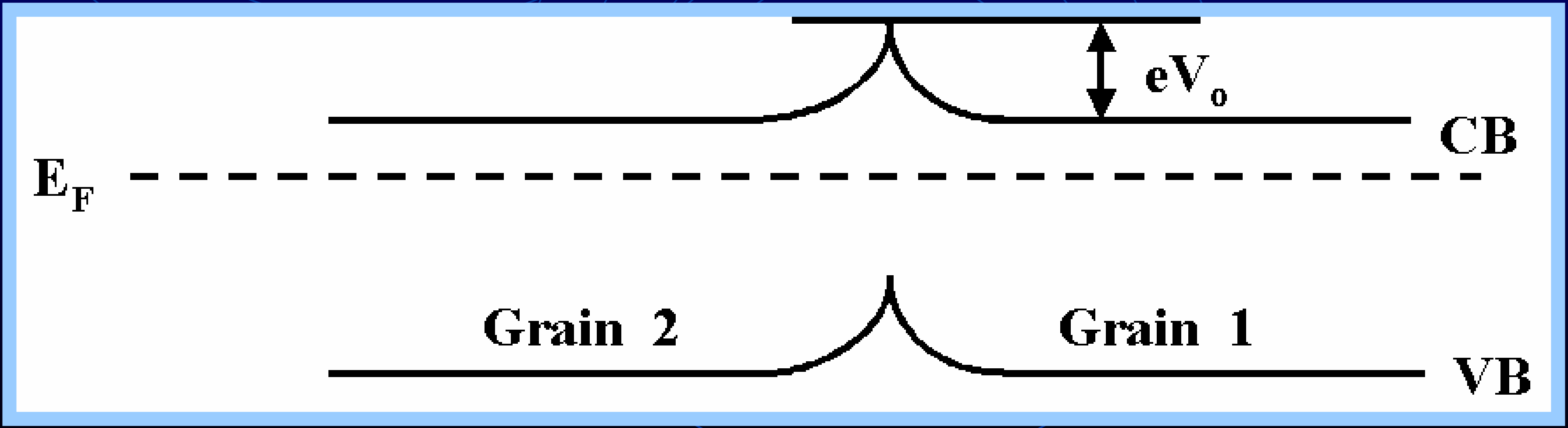
- Oxygen adsorbed on the oxide surface (grain boundaries) can remove an electron from the semiconductor to from either $(O_2)^-$ or O^-, so reducing the # of current carriers (oxygen is a surface trap for electrons).

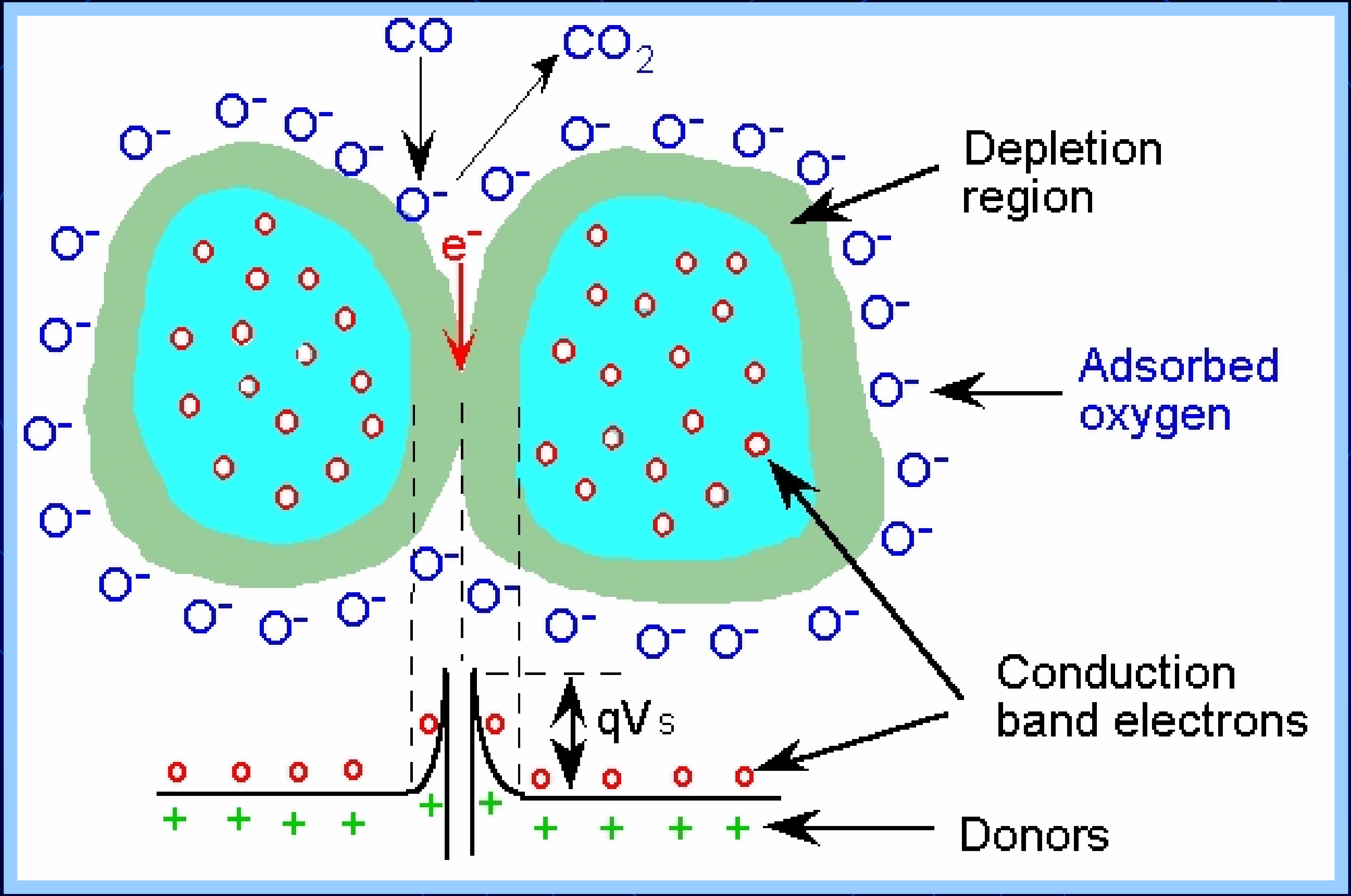


- **Since the electrons are drawn from ionized donors via the CB, the charge carrier density at the interface is reduced.**
- **Therefore, an energy barrier to charge transport ΔE (eV_o) is developed**



- As the surface charge grows, the adsorption of further oxygen is inhibited.
- At the junction between the grains of the solid, the depletion layer and associated potential barrier make for high resistance.
- This can be considered as a back-to back Scottky diode.

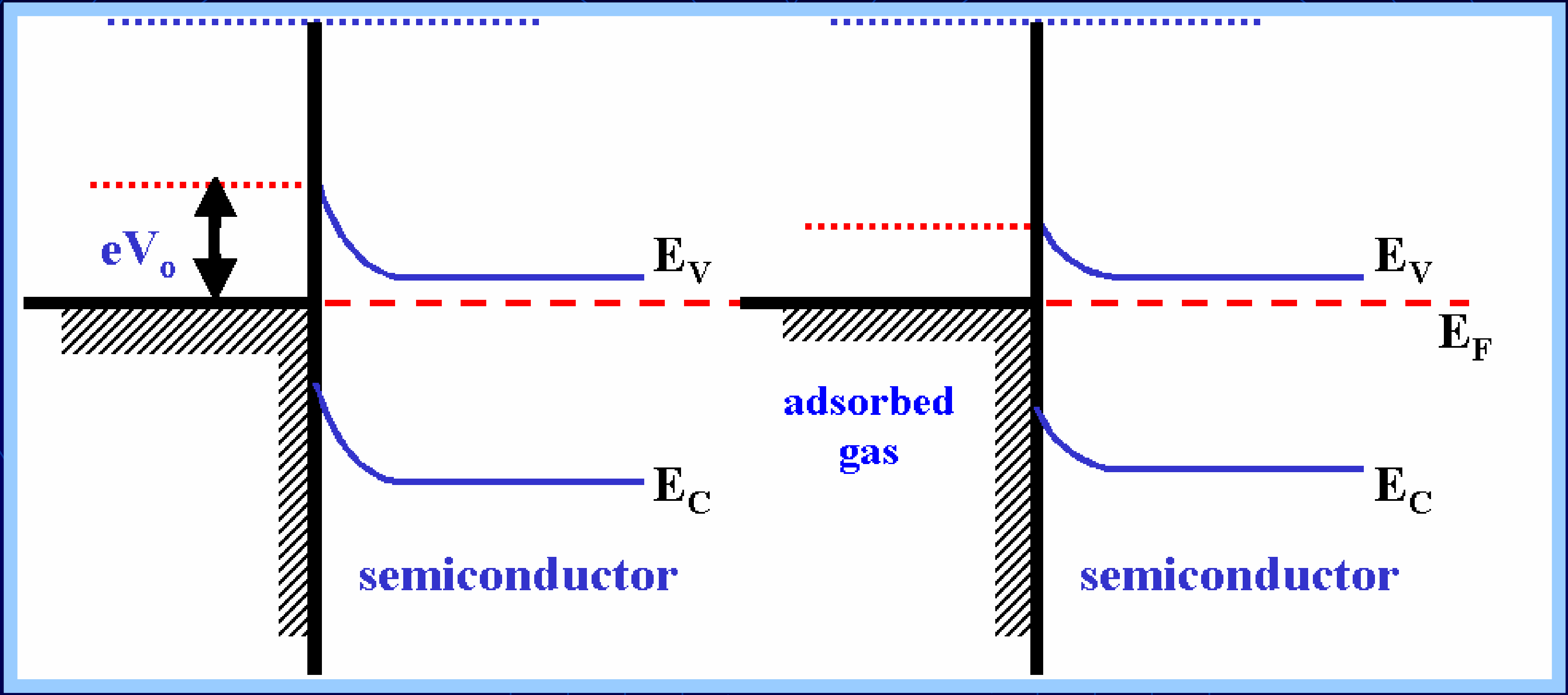



CO
CO2
O⁻
e⁻
Depletion region
Adsorbed oxygen
qVs
Conduction band electrons
Donors

- **Reducing gases (e.g. CO) may then react with the oxygen ions according to reactions such as:**

  $(O2)^{-} + 2\ CO = 2\ CO_2 + e^{-}$

- **As a result, the charge carrier density in the n-type semiconductor is replenished (increasing the conductivity) and the height of the Schottky barrier (eV_o) reduced.**



eV_o
E_V
E_C
semiconductor
adsorbed gas
E_V
E_F
E_C
semiconductor

Sensor Variables

SENSOR VARIABLES

The major factors affecting the operation of a semiconductor gas sensor are:

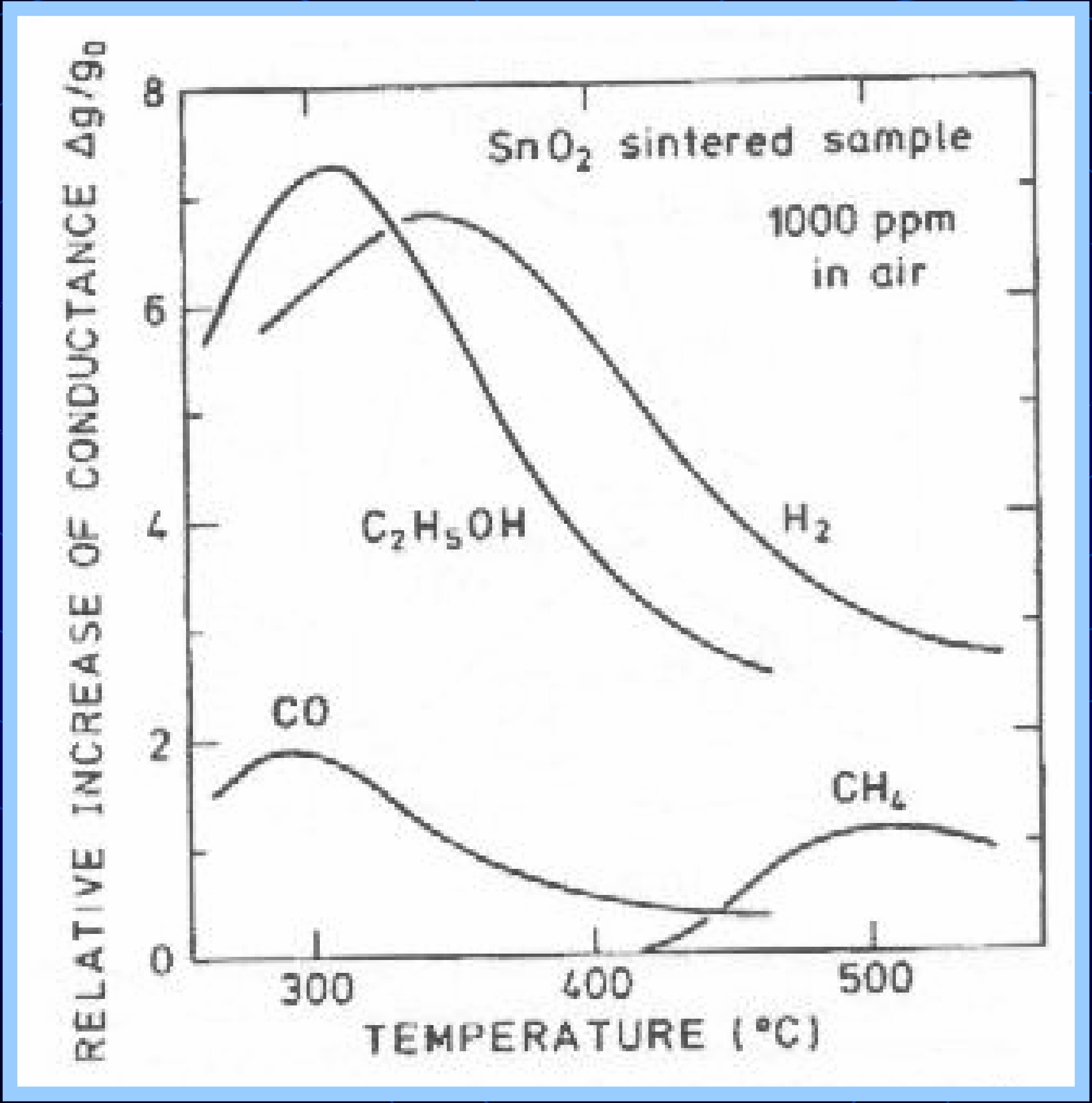
1. Sensor material
2. Temperature
3. Analyte gases (composition & concentration)
4. Sensor Geometry

1. Sensor Material

- Choice of the material: physical & chemical properties of the sensor
- Method of preparation
- Growth conditions and post-deposition treatment
- Additives (dopants / catalysts)

2. Temperature

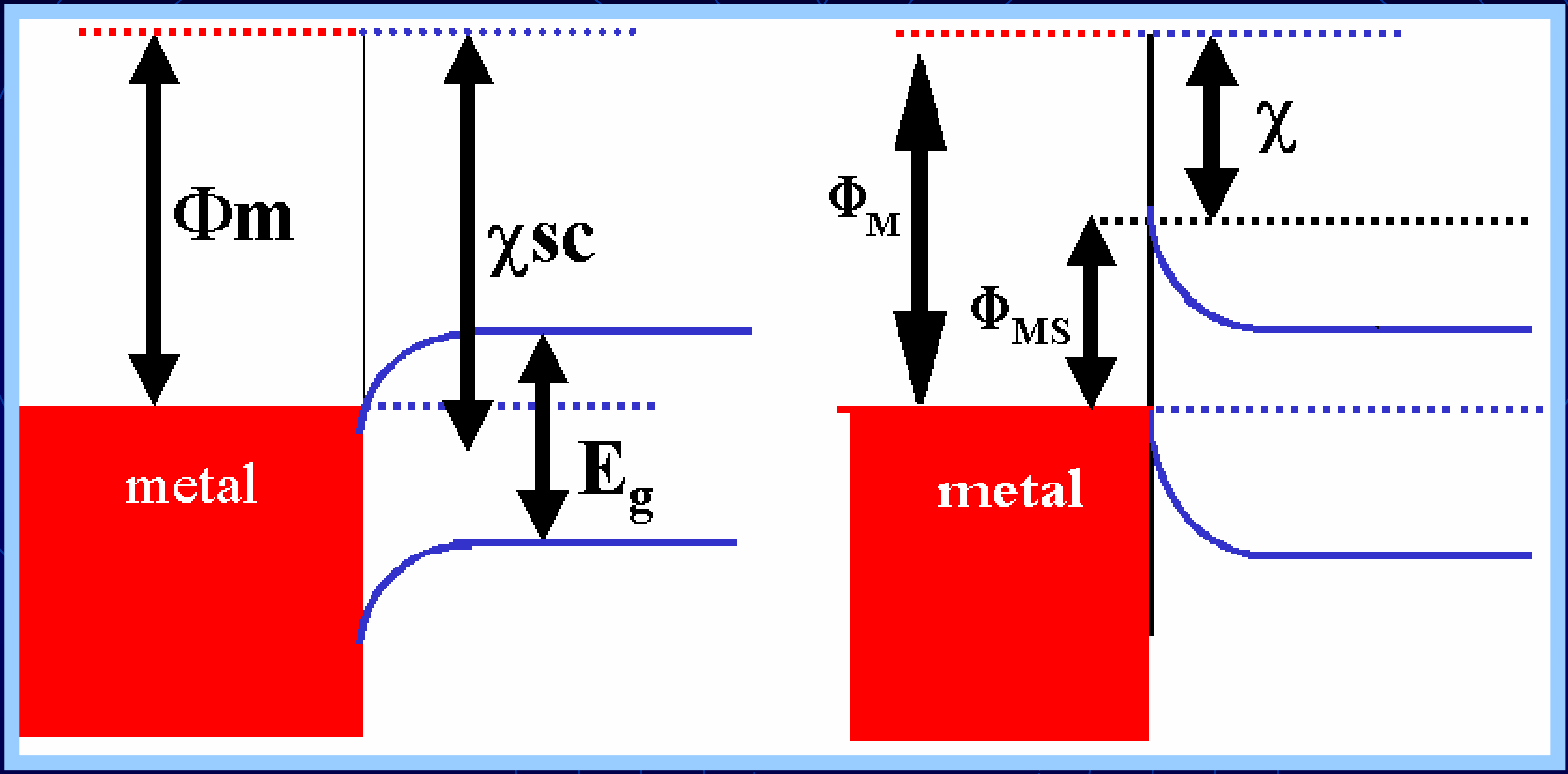
- The gases are discriminated by causing a maximum response at different temperatures.
- Maximum sensitivity occurs at different temperatures for different gases and different oxides.



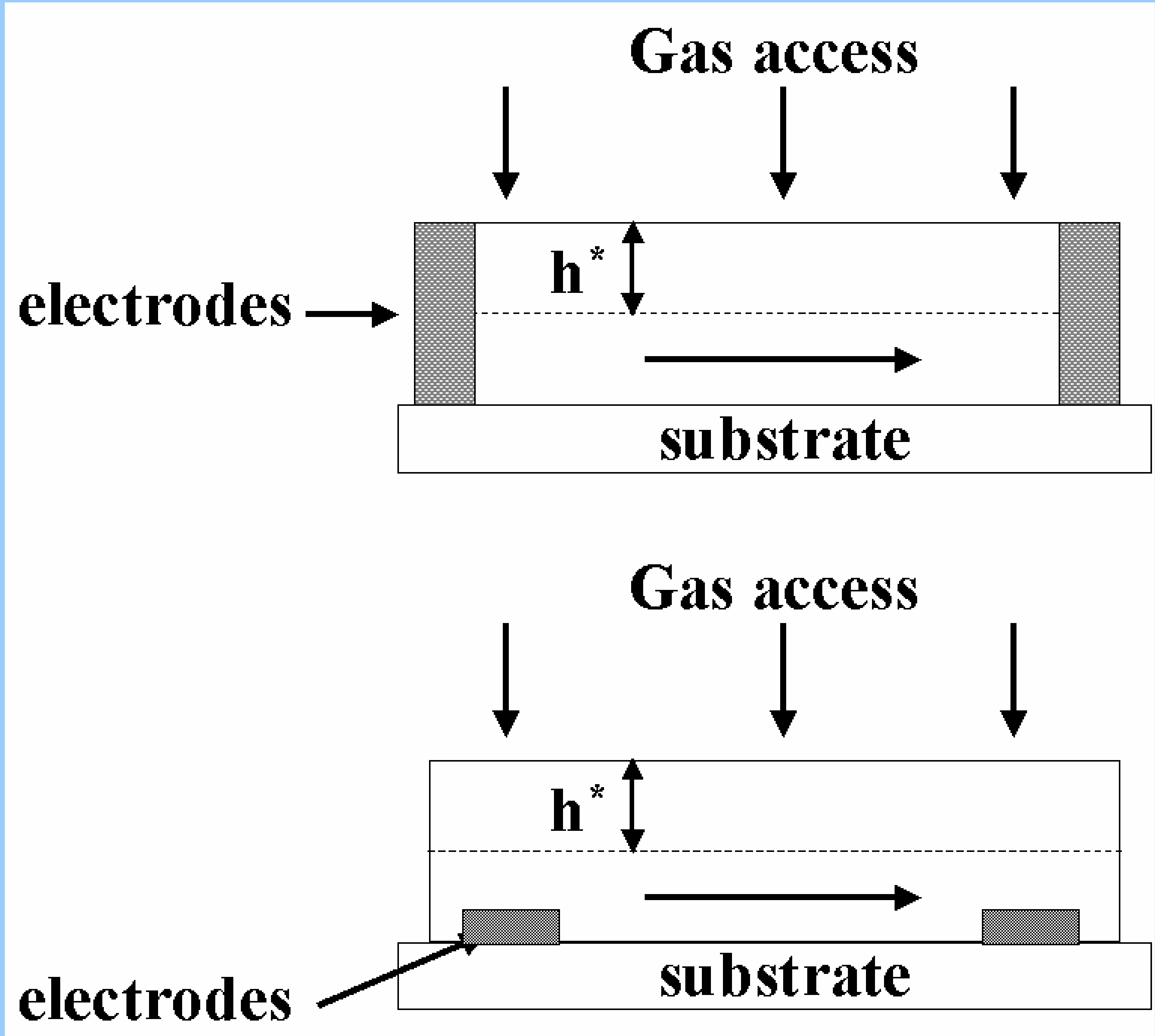
RELATIVE INCREASE OF CONDUCTANCE Δg/g₀
8
6
4
2
0
300
400
500
TEMPERATURE (°C)
SnO₂ sintered sample
1000 ppm
in air
C₂H₅OH
H₂
CO
CH₄

4. Sensor Geometry

- The sensor geometry affects the response of the sensor.
- The choice of electrodes affects the S-M barrier height.
- The placement of the electrodes affects the characteristic reaction depth.



Φm
χsc
metal
Eg
ΦM
ΦMS
χ
metal


Gas access
electrodes
h*
substrate
Gas access
h*
substrate
electrodes

Sensor Parameters

Sensor Parameters

1. Conductance
2. Base line
3. Selectivity & Sensitivity
4. Calibration curve
5. Response time
6. Reproducibility
7. Spread of variables

1. **Conductance**
    - Conductance = reciprocal of resistance
    - All the operating characteristics of the sensor are derived from this one measurement
2. **Base line**
    - Conductance in clean dry air, or humid air of controlled humidity

3. Sensitivity and selectivity

- $S = \{[\sigma(gas) - \sigma(air)]/\sigma(air)\} \times 100$

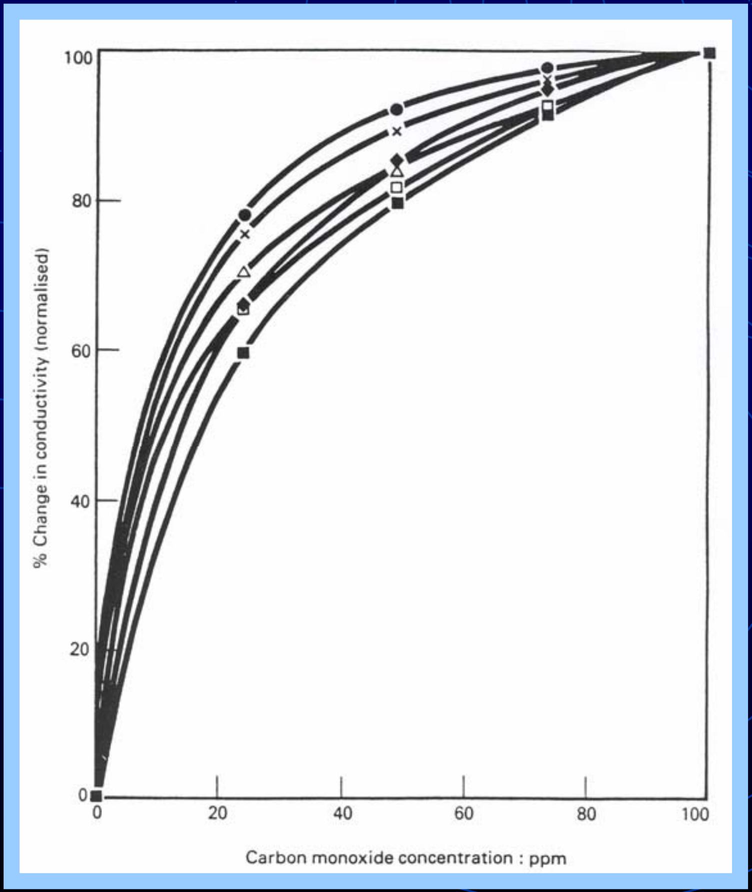
- For a given sensor , S_{max} and the temperature at which S_{max} occurs are gas-dependent.

- This can be used as the basis for selectivity of a certain gas among a mixture of gases.

- Selectivity = *sensitivity of gas 1/ sensitivity of gas 2* , for equivalent concentrations of both gases.

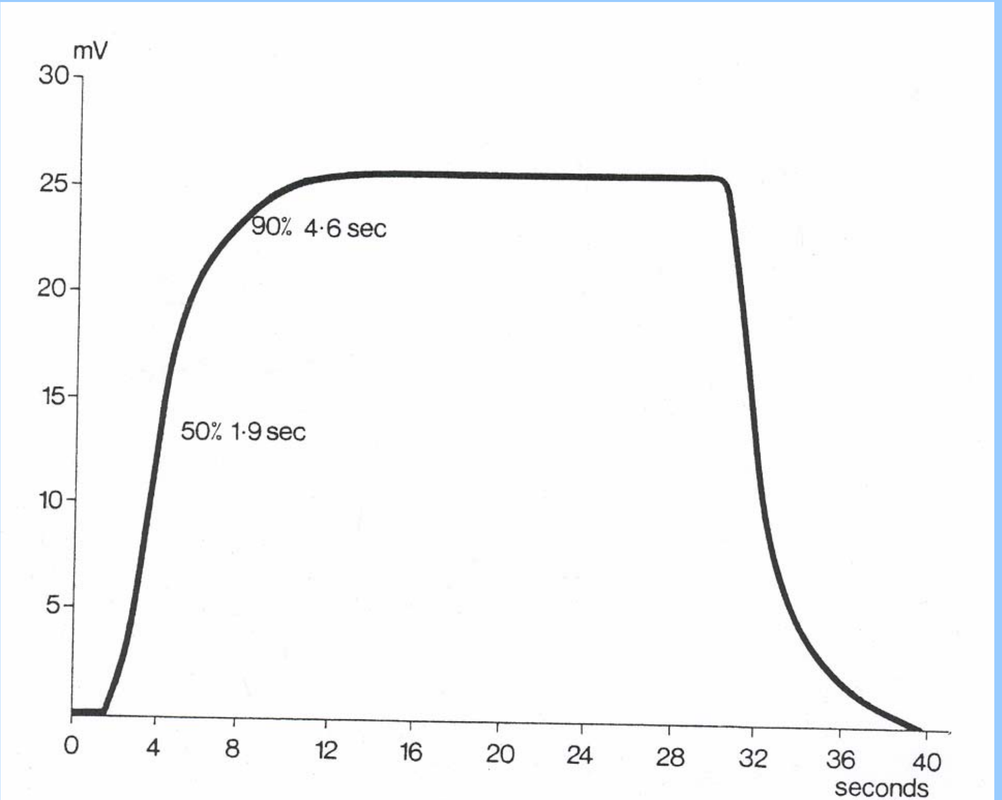
4. Calibration curve

- Sensitivity plotted as a function of the concentration.
- The temperature may be set at the value of S_{max}.



5. Response Time

- The time required to achieve (90 % , 70 % or 50 %) of the final change in conductance following a step change in gas concentration.

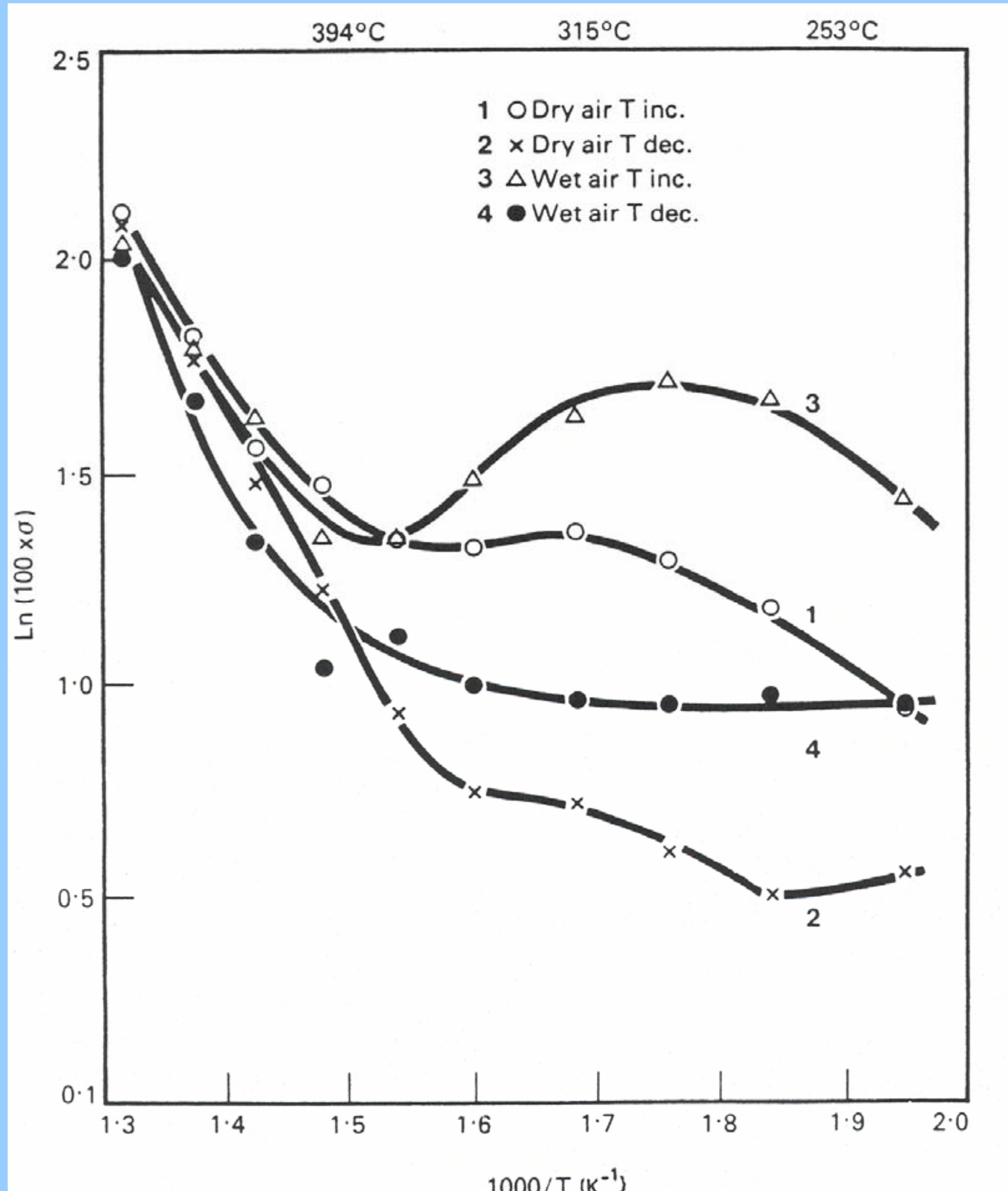


- Response times are very temperature-dependent (shorter for higher T).

6. Reproducibility

- The ability of the sensor to reproduce readings when the same environment is applied to it consecutively under the same conditions.

- Sensors are dependent on surface chemical effects which are notoriously irreproducible.


394°C
315°C
253°C
1 ○ Dry air T inc.
2 × Dry air T dec.
3 △ Wet air T inc.
4 ● Wet air T dec.
2·5
2·0
1·5
1·0
0·5
0·1
Ln (100 xσ)
1·3
1·4
1·5
1·6
1·7
1·8
1·9
2·0
1000/T (K⁻¹)
1
2
3
4

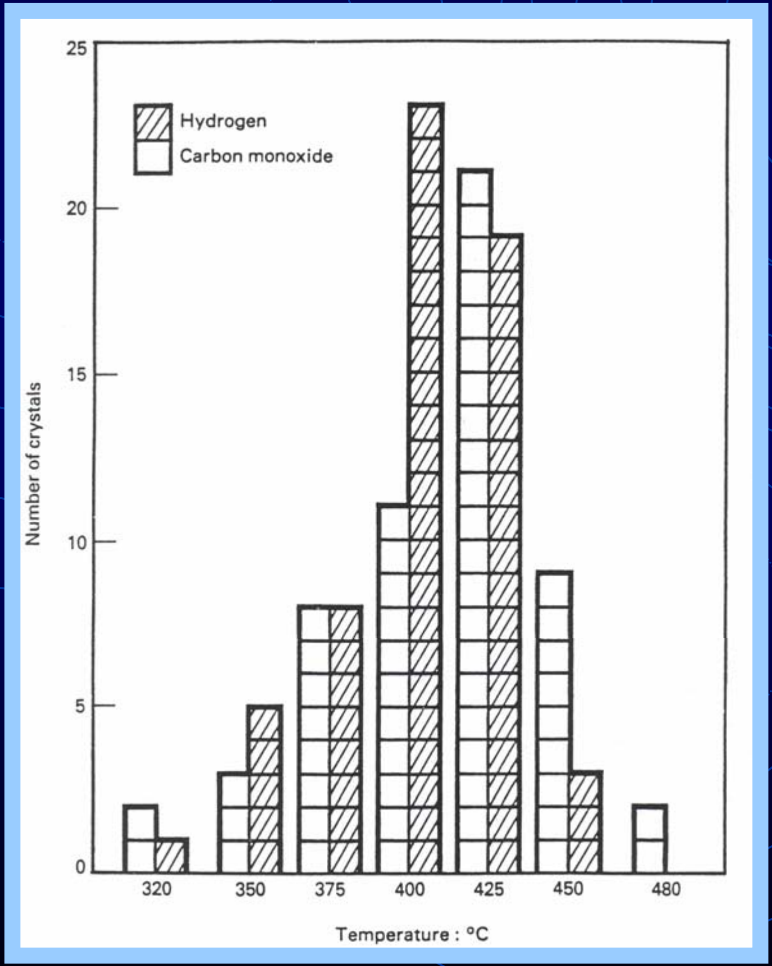
- **Therefore, the time history of the sensor can severely limit its function.**

- **This effect could be attributed to the adsorption of species on the surface which are not easily desorbed.**

- **Fortunately, for this case, the differences at T > 400 ºC are small, and the optimum T (S_{max}) is 400 – 450 ºC.**

7. Spread of Variables

- The range of variables taken by a certain parameter (e.g. conductance) for different sensors



Advantages

Advantages

- Large selection of materials and variables
- Possibility of material engineering
- Measurable response
- Ruggedness – harsh environments
- Potential for miniaturization

APPLICATIONS

Applications

- Automobile engine management – O_2
- Industrial boiler & furnace control – O_2
- Refrigerated food storage – NH_3
- Oil rigs – hydrocarbons & H_2S
- Domestic gas alarms – hydrocarbons
- Steel industry – CO & O_2
- Chemical industry - hydrocarbons

Problems

&

Limitations

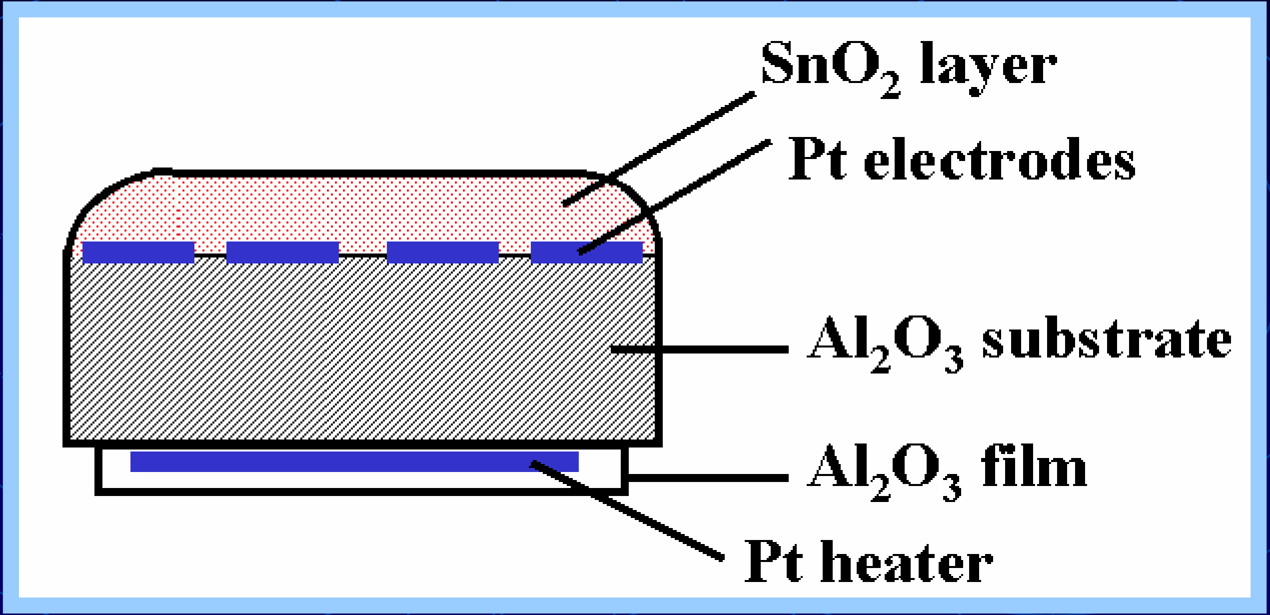
Problems & Limitations

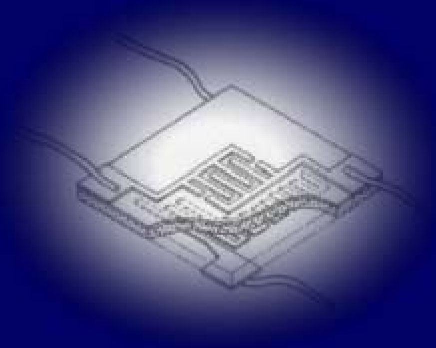
1. Poor understanding of surface & interface chemistry
2. Poor selectivity
3. Temperature instability: turbulent flow
4. Very high (PPB) sensitivity for certain gases
5. Adsorption and desorption of chemical species (long-term effects)
6. Irreproducibility
7. Environmental degradation
8. Water vapor

Effect of Humidity

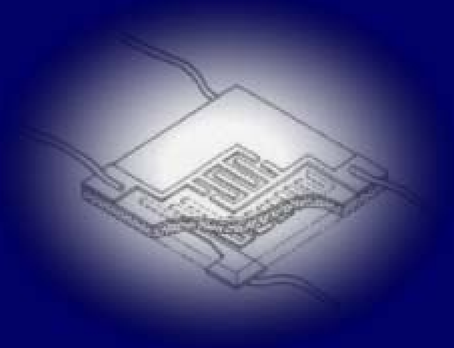
- Semiconductor gas sensors are sensitive to water vapor and their response to combustible gases is affected by the ambient humidity.
- Chemisorption of water introduces surface electron states.
- The effect of water vapor is the increase of surface conductance and the effect is reversible.
- The effects of water vapor could most certainly account for some of the aging and irreproducibility in practical devices.

Typical Gas Sensors

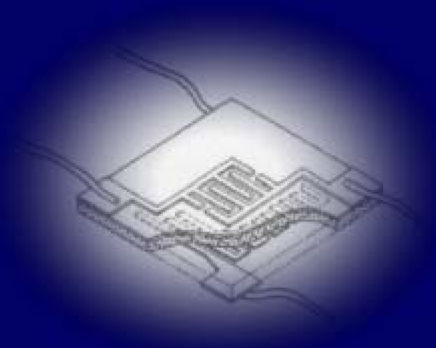


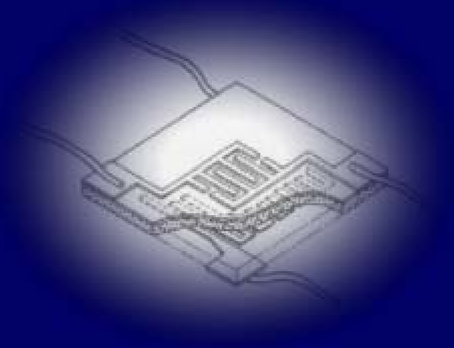


PART III



- Research on TFGS at ERC
- Some recent results





Research

on

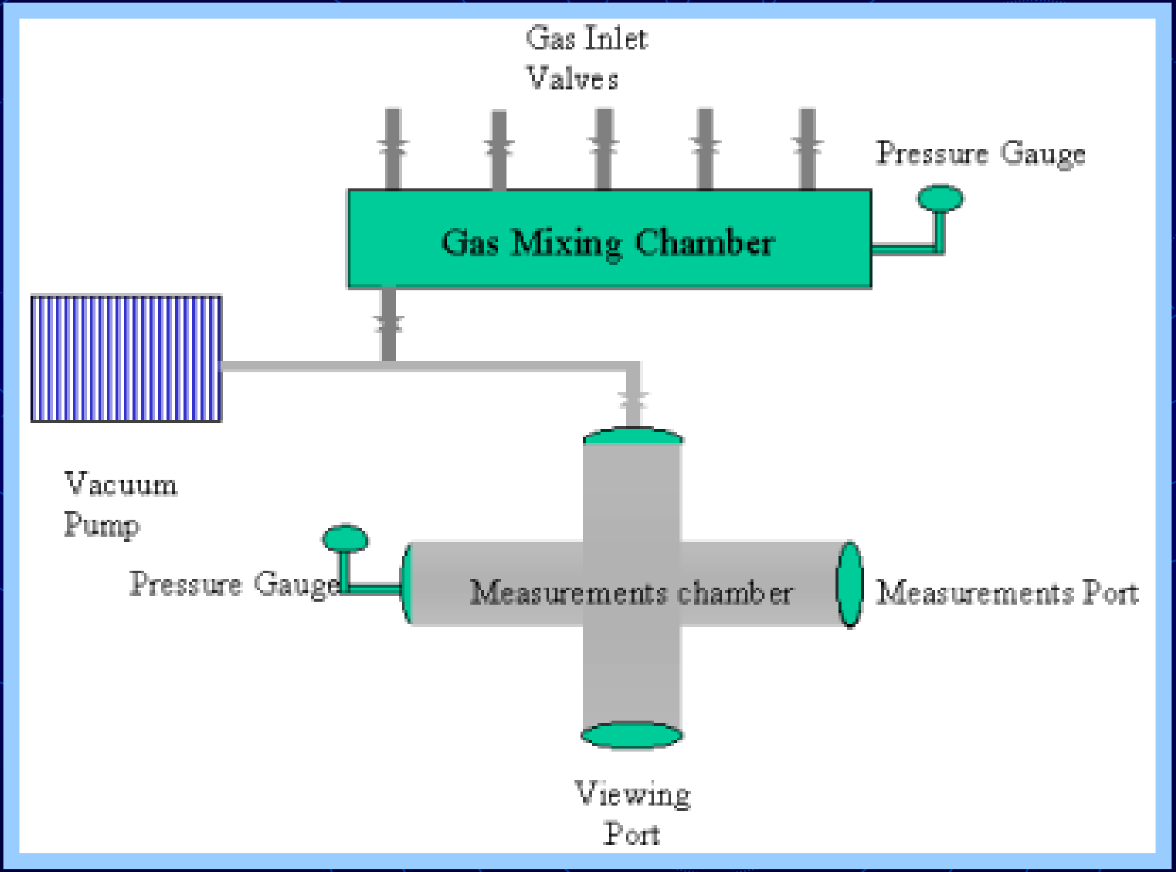
TFGS

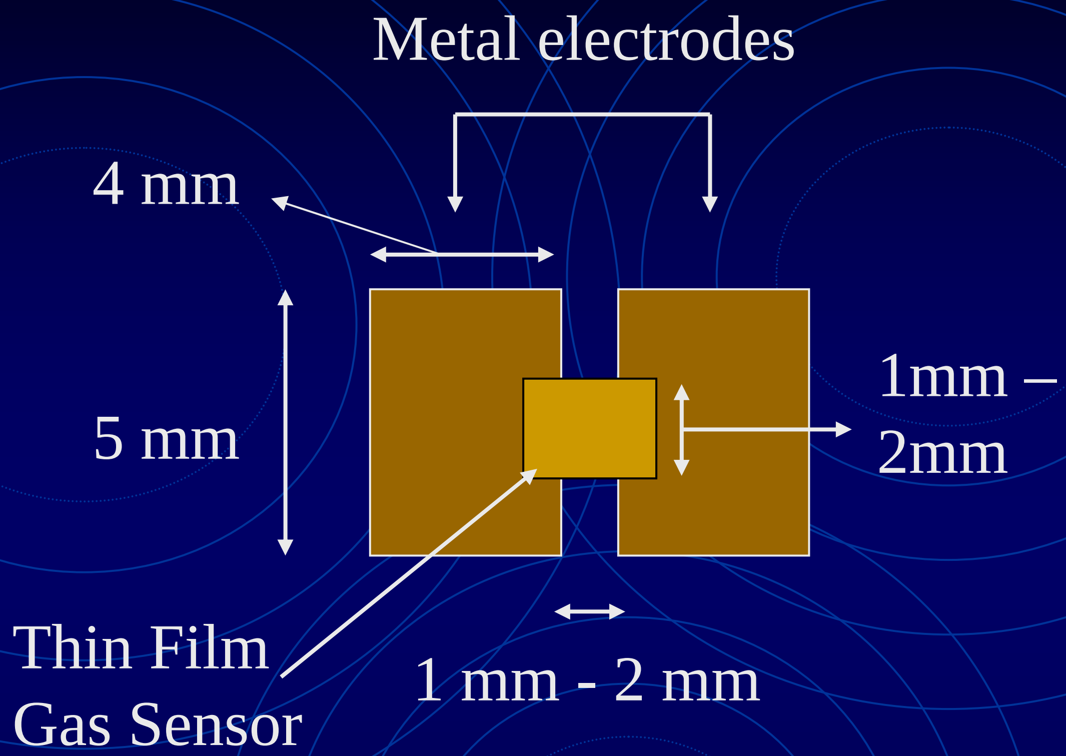
at

ERC

- **Recently established research on TFGS**
- **Members:**
  - **S. M. A. Durrani**
  - **E. E. Khawaja**
  - **M. F. Al-Kuhaili**
  - **E. Bakhtiari**
- **Task: Detection of CO using SnO_2**
- **SABIC Project**

THE EXPERIMENTAL SYSTEM





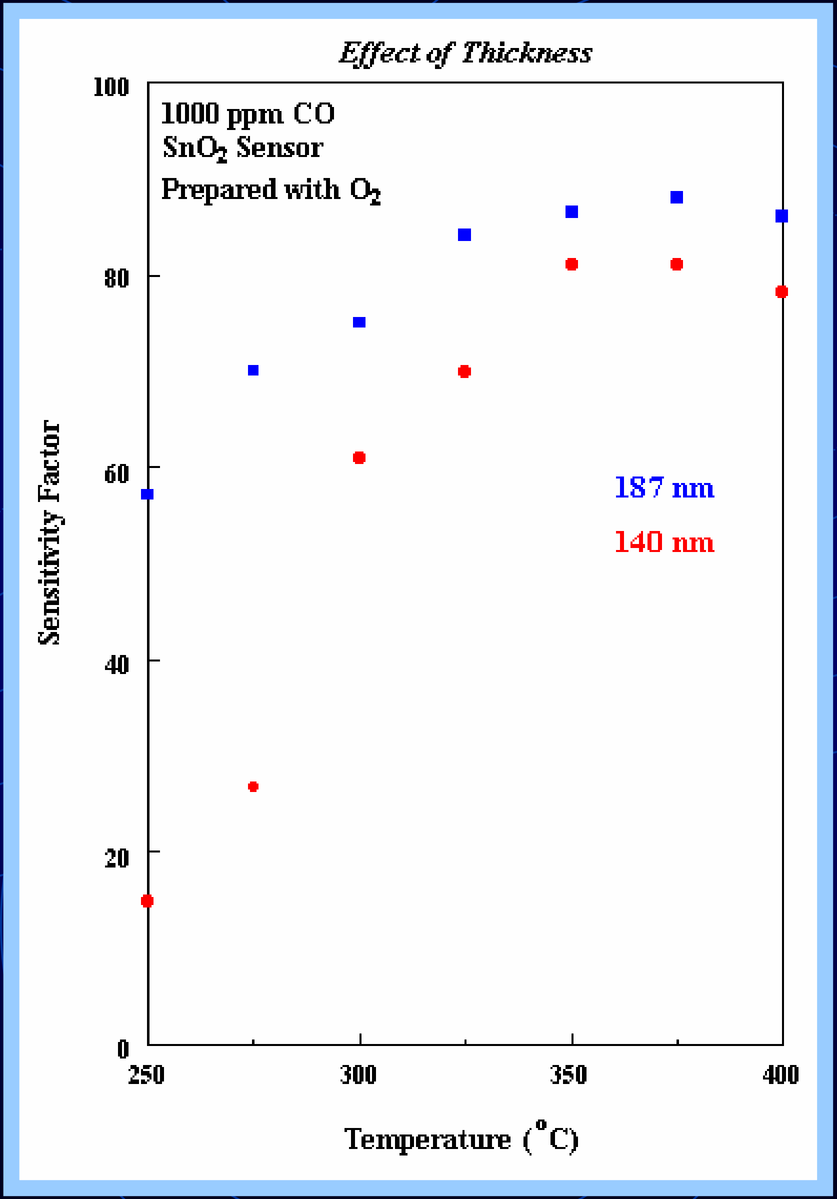
Thin film sensor

- **Materials : SnO_2 , Ga_2O_3 , HfO_2**

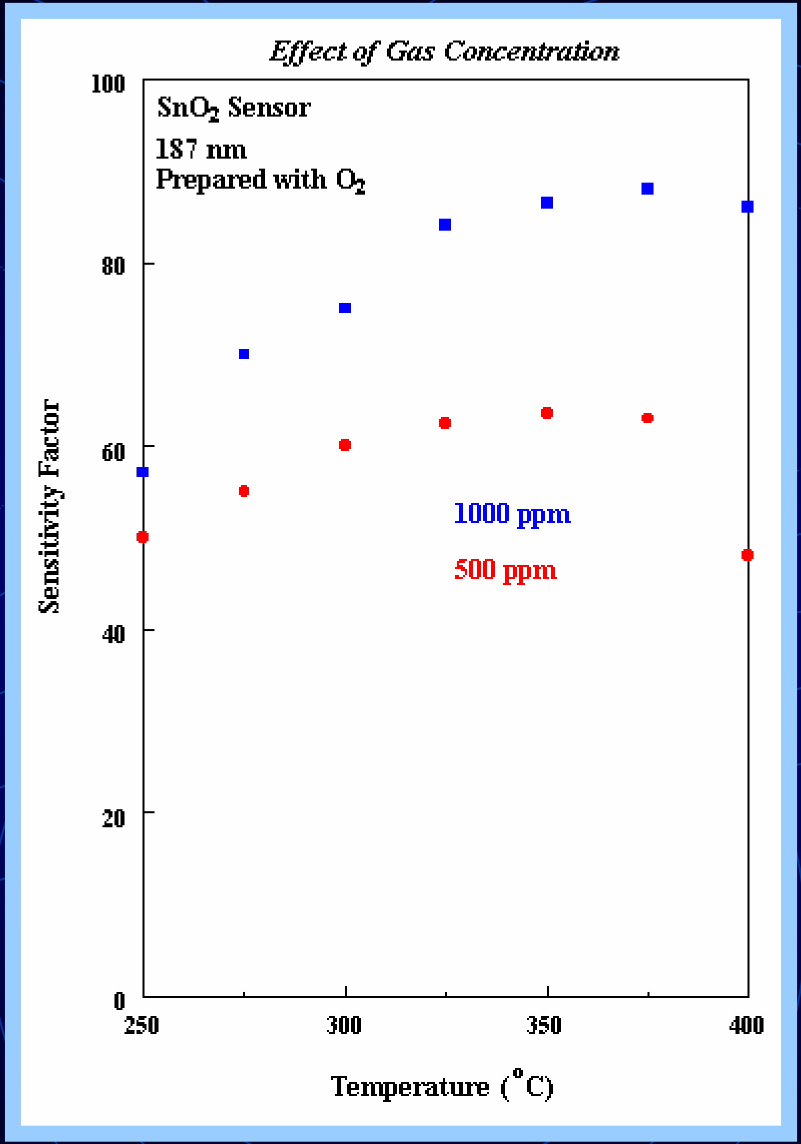
- **Method : Thermal & E-Beam Evaporation**

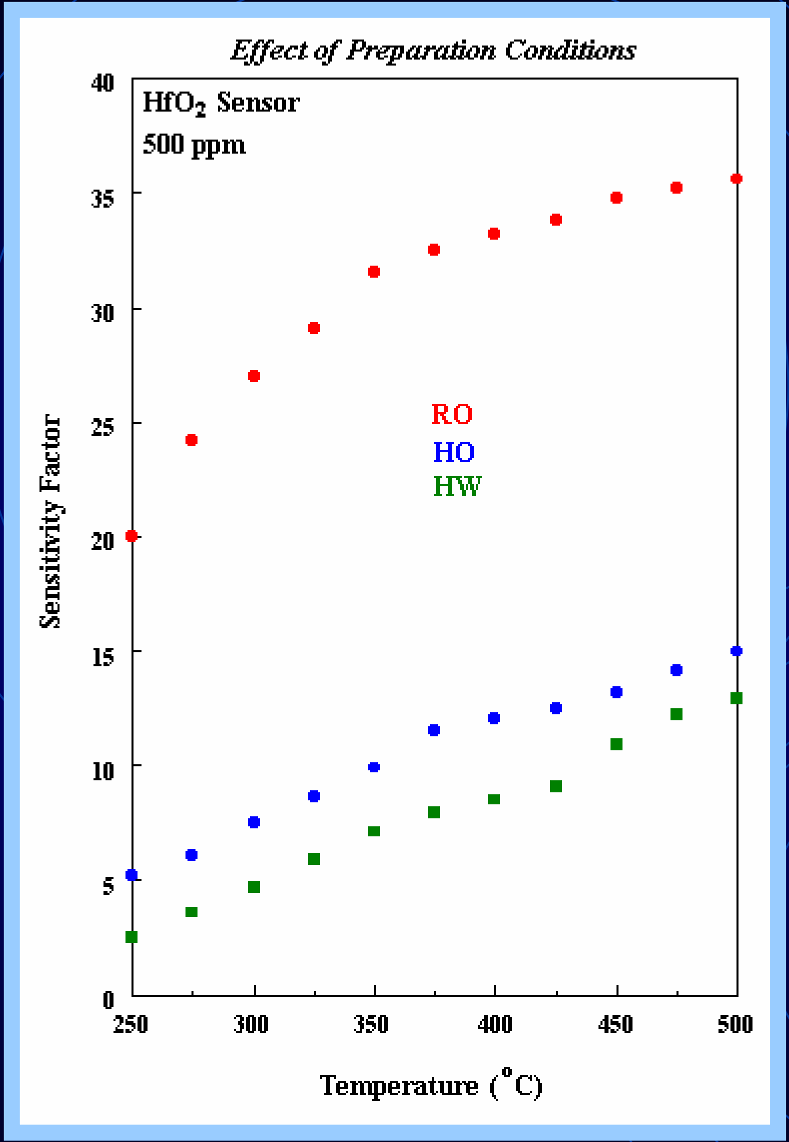
- **Different growth conditions:**
  - **Oxygen partial pressure**
  - **Substrate temperature**
  - **Annealing: temperature & atmosphere**

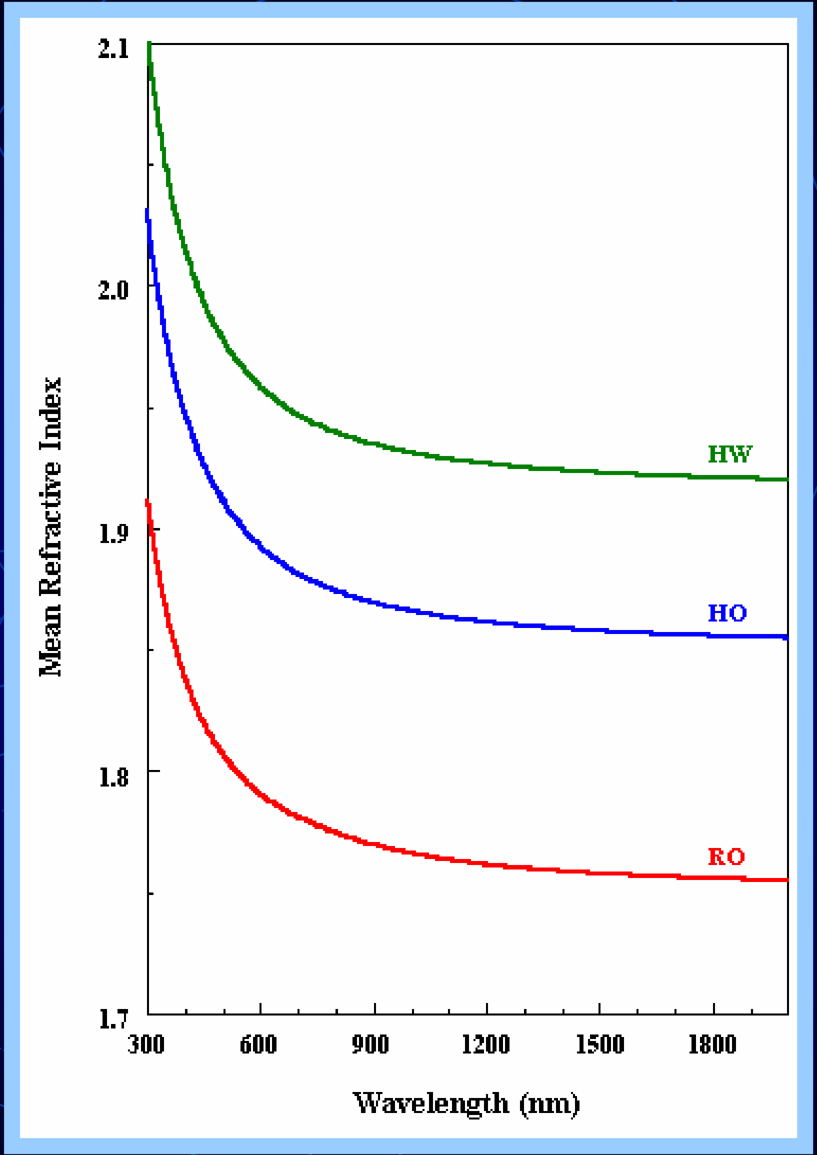
- **Different electrode materials & geometries**
- **Base line measurement**
- **Different experimental parameters**
- **Different gases**
- **Characterization techniques:**
  - **Optical**
  - **XRD**
  - **XPS**



Effect of Thickness
1000 ppm CO
SnO_2 Sensor
Prepared with O_2
187 nm
140 nm
Sensitivity Factor
Temperature (°C)
0
20
40
60
80
100
250
300
350
400


Effect of Gas Concentration
SnO2 Sensor
187 nm
Prepared with O2
1000 ppm
500 ppm
Sensitivity Factor
Temperature (°C)
0
20
40
60
80
100
250
300
350
400


Effect of Preparation Conditions
HfO_2 Sensor
500 ppm
RO
HO
HW
Sensitivity Factor
Temperature (°C)
0
5
10
15
20
25
30
35
40
250
300
350
400
450
500


Mean Refractive Index
Wavelength (nm)
HW
HO
RO
1.7
1.8
1.9
2.0
2.1
300
600
900
1200
1500
1800

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