Sensors and Actuators
(เซนเซอร์และตัวขับเร้า)

Chapter 2: BIO(CHEMICAL) SENSORS

By

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Bio(Chemical) Sensors

- Bio(chemical) sensor is a device that responds to a particular analyte in a selective way and transforms input chemical quantity, ranging from the concentration of a specific sample component to a total composition analysis, into an analytically electrical signal.

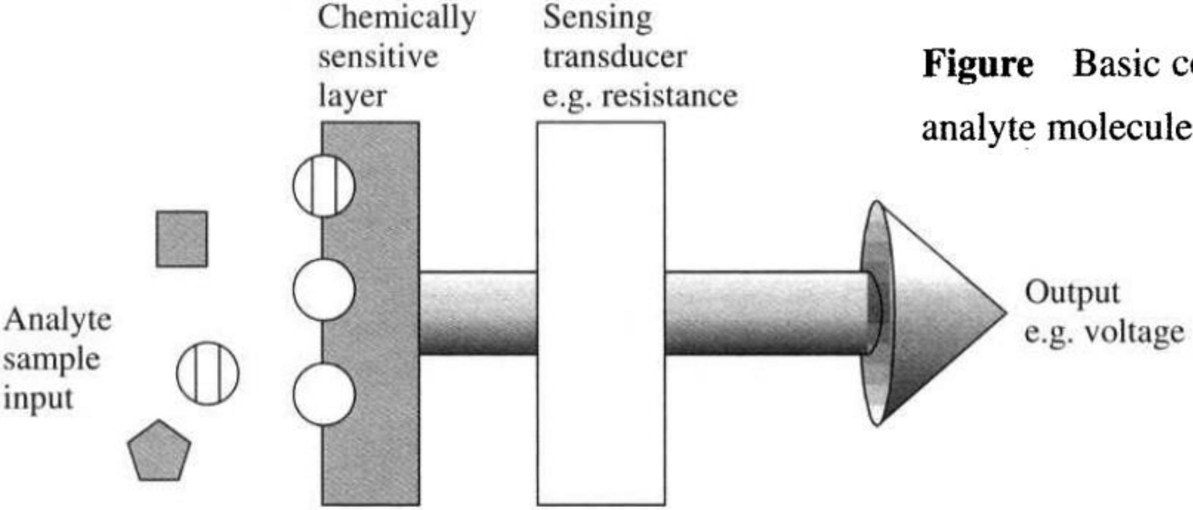
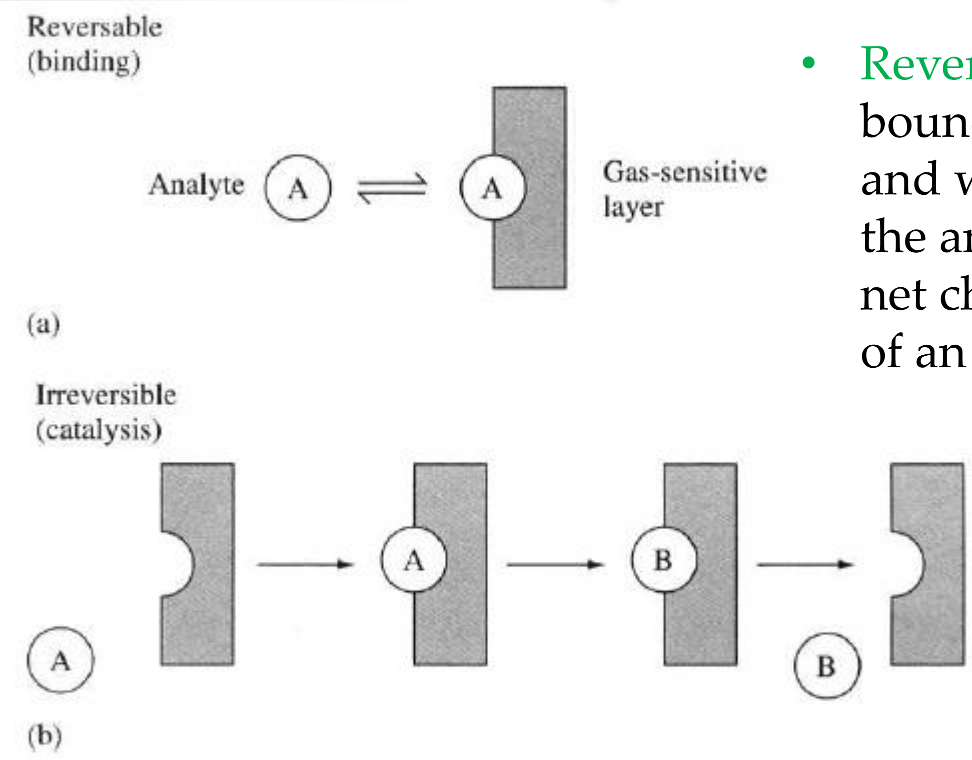


Figure Basic components of a bio(chemical) sensor: analyte molecules, chemically sensitive layer, and transducer.

- The analyte molecules interact with the chemically sensitive layer and produce a physical change that is detected by the sensing transducer and are converted into an electrical output signal.
- The nature of this interaction is determined by the type of material used and can be either a reversible process or an irreversible reaction

Bio(Chemical) Sensors



- Reversible reaction : The analyte A is typically bound to specific sites within the sensitive layer, and when the external concentration is removed, the analyte molecules dissociate and there is no net change. EX. the adsorption and desorption of an organic vapor in a polymeric material.

- Irreversible reaction : The analyte A undergoes a chemical reaction catalysed by the sensitive layer and is consumed in the process.

- However, the poor stability of biological materials makes them unsuitable for use in a real sensor that operates many thousands or millions of times with a lifetime of a year or more but more suited to a single measurement, that is, a disposable sensor.

- For this reason, we concentrate predominantly on chemical sensors;

Bio(Chemical) Sensors

- Chemical sensor can be classified into many types such as optical, electrochemical, mass, magnetic, and thermal.
- Optical chemical sensor is based on the changes in optical phenomena analysis arising from the interaction between the analyte and the receiver.
- Electrochemical sensor utilizes electrochemical effect among the analytes and featured electrodes.
- Mass sensor depends on the quality change induced by the mass loading from the adsorption toward the analyte by the special modification of sensor surface.
- Magnetic sensor is based on the magnetic properties in analyte adsorption.
- Thermal sensor utilizes the thermal effect generated by the specific chemical reaction or adsorption process.
- Another way to categorize the chemical sensors is based on the object to be detected

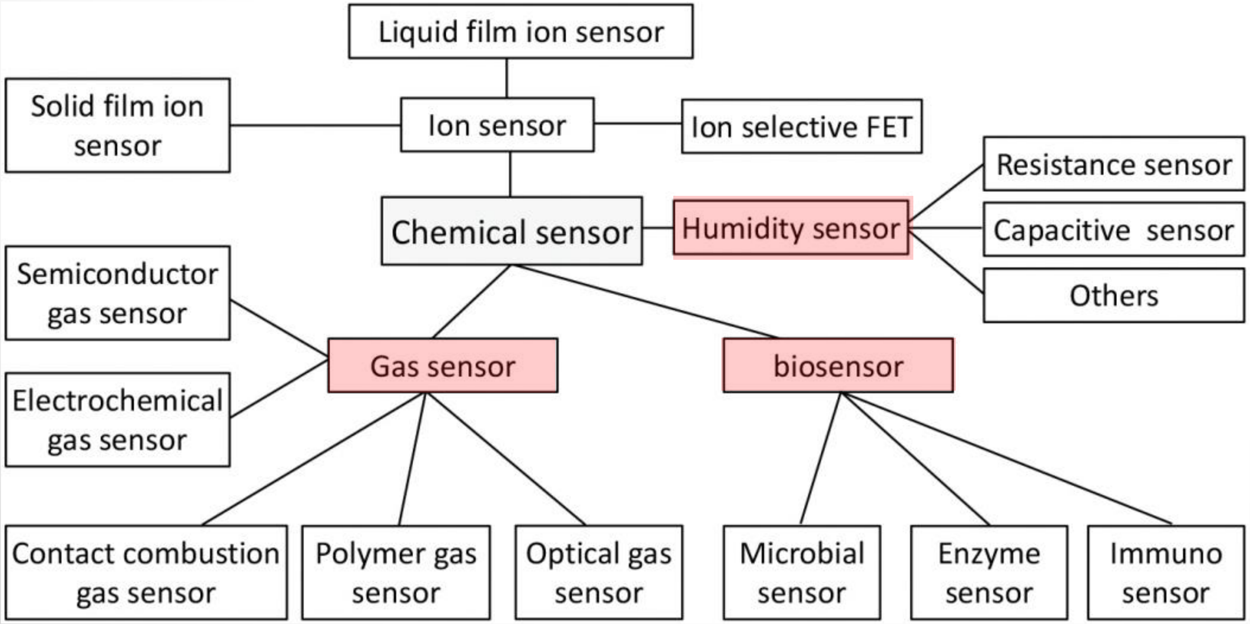


Figure. Classification of chemical sensors based on sensing objects

Bio(Chemical) Sensors

- *Semiconductor gas sensor* is made by metal oxides or metal semiconductor oxide materials. As regards the electrical conductivity sensors, the resistance of their active sensing layer changes due to contact with the gas to be detected. The semiconductor gas sensors have been widely used gas sensors.
- *Electrochemical gas sensor* can be categorized into *galvanic cell type*, *controlled potential electrolysis type*, *coulometric type*, and *ion-selective electrode type*.
  - ✓ *Galvanic cell gas sensor* evaluates the target gas composition by measuring the shift in current.
  - ✓ *Controlled potential electrolysis gas sensor* senses the target gas by measuring the electrolytic current. Furthermore, the oxygen in blood can also be detected in addition to CO, NO, NO_2 , and SO_2.
  - ✓ *Coulometric gas sensor* detects the target species by measuring the current generated by the interaction between the gas and the electrolyte.
  - ✓ *Ion-selective electrode gas sensor* has appeared earlier, and it detects the gas by measuring the ion current with high sensitivity and excellent selectivity.

Bio(Chemical) Sensors

- *Contact combustion gas sensor* includes direct contact sensor with the combustion and catalysis combustion sensor. The platinum wire (Pt) coil used in the detection element. In general, the electrical resistance of metal is affected by temperature changes (T↑ R↑, T↓ R↓). The contact combustion type gas sensor uses this to electrically capture the temperature change of the element that has risen due to the catalytic combustion reaction of the detection element as the change in electrical resistance and detect the gas. Since the range of change in electrical resistance is proportional to the gas concentration, the gas concentration can be easily measured. It is widely used for sensing combustible gas in petroleum chemical plant, shipyards, mine tunnels, kitchens, and bathrooms.


https://sensor.nemoto.co.jp/

- *Optical gas sensors* include infrared absorption sensors, spectrum absorptive sensors, fluorescence sensors, and fiber sensors, in which, the infrared absorption sensor is the most widely used for sensing gas by measuring and analyzing the infrared absorption peak from various gas adsorption.

Bio(Chemical) Sensors

- *Polymer gas sensor* The polymer gas sensitive materials play an important role in sensing trace poisonous gas because of its easy operation, simple process, good selectivity at normal temperature, low price, and easy to combine with the micro-structure or surface acoustic wave (SAW) devices.
- *Enzyme biosensors* Enzymes interact specifically with some substrates, and can be used for the detection of these substrates as, for example, glucose by glucose oxidase, creatinine by creatinine amidohydrolase, or urea by urease. Among these analytes, urea and creatinine have received considerable attention leading to the development of many potentiometric biosensors for use in clinical, food, and environmental areas.
- *Immuno sensors* When potentiometric sensors are based on antibodies used as molecular biorecognition elements through the formation of a stable complex, the device is called immunosensor. In essence, immunosensing can encompass a broader spectrum of target analytes in comparison to enzyme-based biosensing. Immunosensing is also selective because of the high specificity of immunoreactions. Consequently, immunosensors constitute an attractive method for clinical diagnosis, environmental monitoring, and food analysis. The strategy of potentiometric immunosensors is based on the change in the potentiometric response before and after antigen-antibody reaction.

Bio(Chemical) Sensors

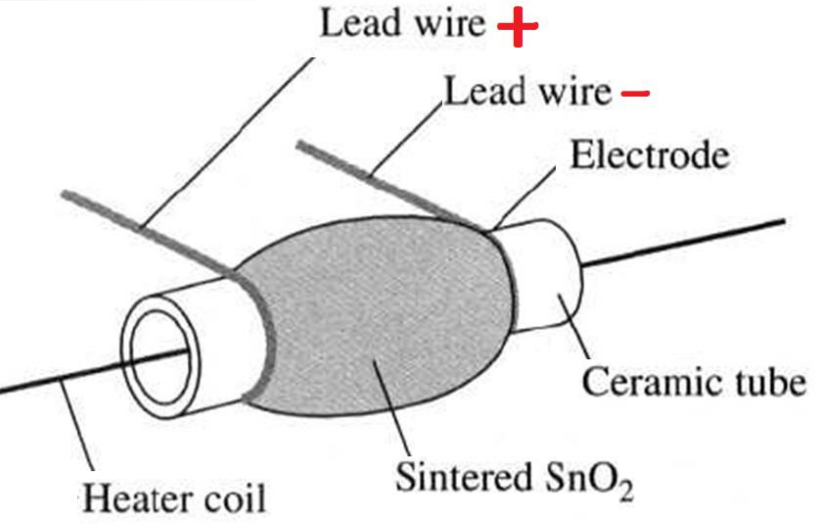
- *Microbial Sensor* is a device which combines microorganism(s) and a physical transducer, capable of generating a signal proportional to the concentration of some analyte. Many microbial biosensors have been developed recently for applications in environment, food, or medicine. Optical microbial sensors use fluorescent, bioluminescent, and colorimetric sensing techniques. Electrochemical microbial sensors use amperometry, impedancemetry, or potentiometry. Potentiometric microbial biosensors are generally sensitive to pH changes or CO_2 release. They can consist of modified electrodes or field-effect transistors. Another potentiometric biosensor was developed for the identification of β-lactam residues in milk. This analytical device consisted of Bacillus stearothermophilus and a CO_2-sensitive electrode, which measured its release by the microorganisms.

Conductimetric Sensors

- Conductimetric gas sensors are based on the principle of measuring a change in the electrical resistance (resistance (DC case) or impedance (AC case)) of a material upon the introduction of the target gas.

- The most common type of gas sensor employs a solid-state material as the gas-sensitive element. The principal class of material used today is semiconducting metal oxides, with tin oxide (SnO_2) being the most popular.

- The device consists of a wire-wound platinum heater coil inside a ceramic former onto which a thick layer of porous SnO_2 is painted manually. The electrical resistance (conductance) of the sintered film is then measured by a pair of gold electrodes and basic potential divider circuit.



Bio(chemical) sensor is a device which is capable of converting a chemical (or biological) quantity into an electrical signal

Conductimetric Sensors
(Selectivity Enhancement by Doping)

- SnO_2 devices are operated at various high temperatures and *doped* with different materials to enhance their specificity. The response of a SnO_2 sensor, in terms of its relative conductance G_s/G_0, where G_s is conductance of a gas of fixed concentration and G_0 is conductance in air.
- First, the chemical reaction is at higher temperatures
- Second, the reaction kinetics are much faster in just a few seconds.
- Finally, operating the device well above a temperature of 100 °C ameliorates the effect of humidity upon its response - a critical factor for many chemical sensors.

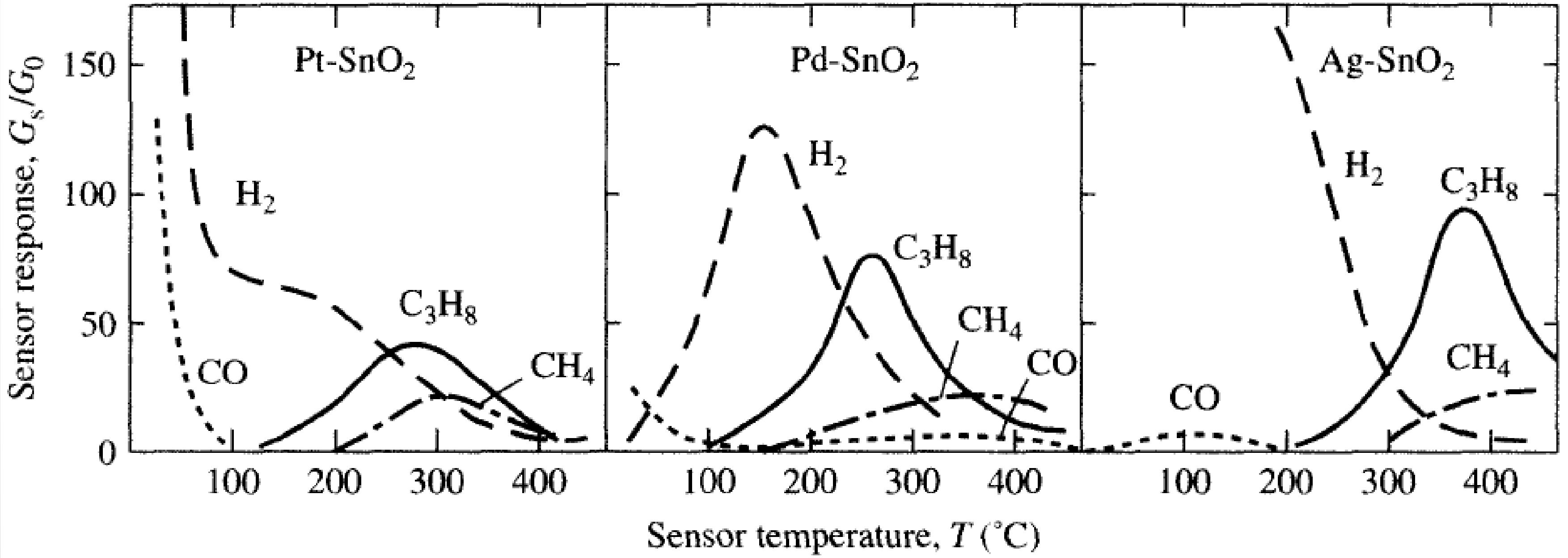


Fig. Variation of the response of three doped tin oxide gas sensors with temperature for four different gases.

Conductimetric Sensors

- First, vacant sites within the SnO_2 lattice react with atmospheric O_2 to remove electrons out of the conduction band of the SnO_2 creating chemisorbed oxygen sites such as $\mathbf{O^-}, \mathbf{O_2^-}, \mathbf{O_m^-}$.

$$\frac{1}{2}\mathbf{mO_2} + \begin{Bmatrix} \mathbf{vacancy} \\ \mathbf{SnO_2\ lattice} \end{Bmatrix} + \mathbf{e^-} \xleftrightarrow{k_1} \{\mathbf{O_m^-}\}$$

- Second, reversible reaction is disturbed when the analyte molecule **A** reacts with $\mathbf{O_m^-}$ to release electrons $\mathbf{e^-}$

$$\mathbf{A} + \{\mathbf{O_m^-}\} \xrightarrow{k_2} \{\mathbf{AO_m}\} + \mathbf{e^-}$$

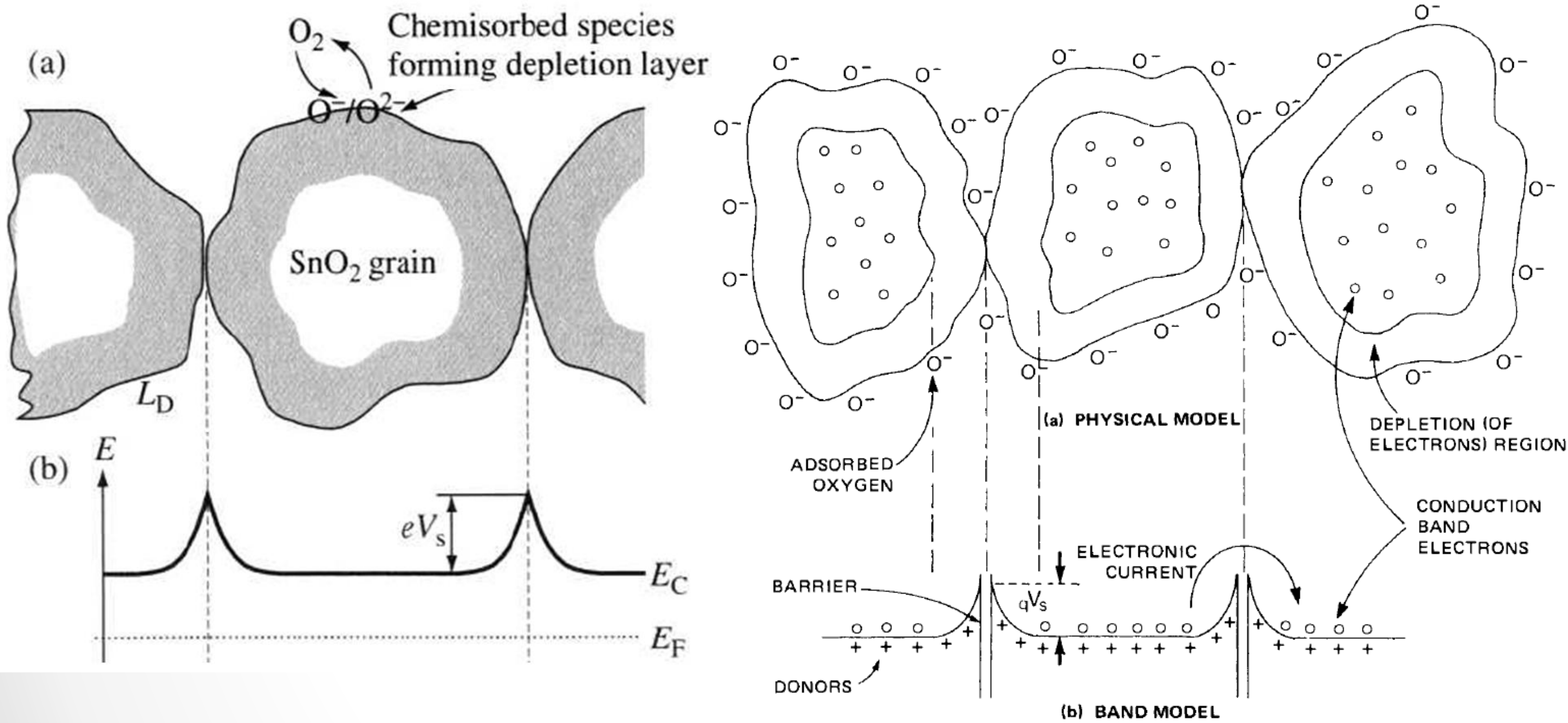
- In a simple description, the SnO_2 behaves like an *n-type* semiconductor and, there is an increase in the electron carrier density n, and hence in the electrical conductivity σ of the material with increased gas concentration where μ_n is the electron mobility (250 $cm^2\ V^{-1}\ s^{-1}$), $e = 1.6 \times 10^{-19}$ coulombs.

$$\boldsymbol{\Delta\sigma = \mu_n e \Delta n}$$

It is then a reduction in the height of the intergranular barriers Vs that increases the electron hopping mobility and hence the conductance of the tin oxide film (Williams 1987). This change in device conductance can be approximately related to the gas concentration C from the chemical rate constants $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$,where the $\boldsymbol{r}$ has a value between 0.5 and 0.9 and depends on the kinetics of the reaction.

$$\boldsymbol{\Delta G \propto \frac{k_1}{k_2} C^r}$$

Conductimetric Sensors

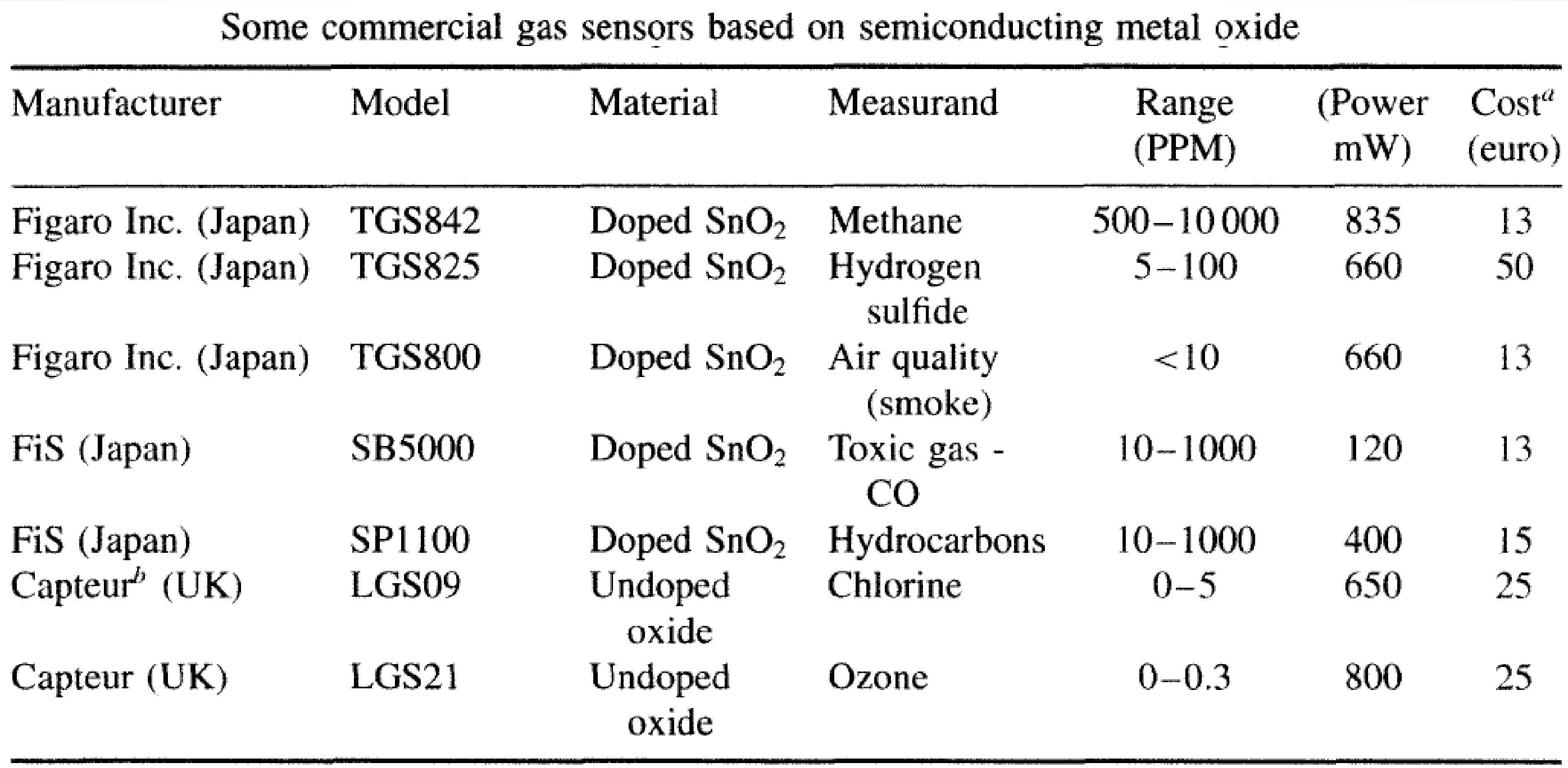


(a) Schematic diagram showing a series of nanometre-sized grains in a SnO_2 film

(b) band diagram showing the effect of the oxygen-induced depletion regions.

Conductimetric Sensors

- lists some tin oxide gas sensors that are commercially available together with their properties.



Some commercial gas sensors based on semiconducting metal oxide

Manufacturer	Model	Material	Measurand	Range (PPM)	(Power mW)	Cost[a] (euro)
Figaro Inc. (Japan)	TGS842	Doped SnO_2	Methane	500–10 000	835	13
Figaro Inc. (Japan)	TGS825	Doped SnO_2	Hydrogen sulfide	5–100	660	50
Figaro Inc. (Japan)	TGS800	Doped SnO_2	Air quality (smoke)	<10	660	13
FiS (Japan)	SB5000	Doped SnO_2	Toxic gas - CO	10–1000	120	13
FiS (Japan)	SP1100	Doped SnO_2	Hydrocarbons	10–1000	400	15
Capteur[b] (UK)	LGS09	Undoped oxide	Chlorine	0–5	650	25
Capteur (UK)	LGS21	Undoped oxide	Ozone	0–0.3	800	25

- The requirement to run this type of gas sensor at a high temperature causes the power consumption of about 0.8 W of a Taguchi-type device to be a problem for handheld units.

Conductimetric Sensors

- Semiconducting metal oxides (SnO_2, ZnO, Fe_2O_3) are commonly used (e.g., SnO_2 for CO, alcohol, H_2, H_2S, …etc)

- The increase and decrease of resistance affected by:
  - Adsorption of O_2 on surface: $O_2 + 2e^-$ (due to vacant sites in SiO_2) → $2O^-$ (then R increases)
  - Reaction with combustible gases H_2: $H_2 + O^- \rightarrow H_2O + e^-$ (then R decreases)

- The devices are operated at high temperatures (typ. 300 – 400 °C)
  - Speed up the chemical reaction
  - Ameliorate the humidity effect
  - Consume a few hundred mW

Potentiometric Sensors

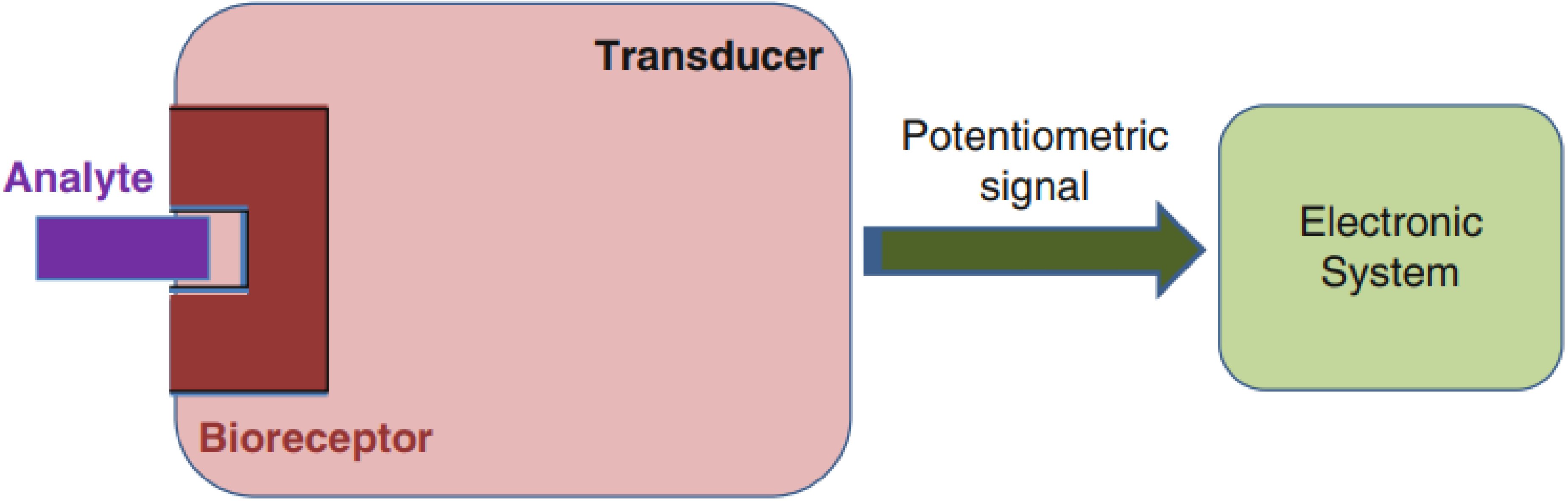


Fig. Potentiometric Biosensors, Schematic presentation of a potentiometric biosensor

Potentiometric Biosensors, Sami Yunus, Alain M. Jonas & Boris Lakard

Potentiometric Sensors

- The signal is measured as the potential difference between reference and indicator electrode.
- The indicator electrode's potential must depend on the concentration of the analyte in the gas or solution phase. The reference electrode is needed to provide a defined reference potential.
- The principles of potentiometric measurements are found in the Nernst equation,

$$E = E_0 + \frac{RT}{z_i F} \ln\left(\frac{a_i^{sample}}{a_i^{ref}}\right)$$

- where E_0 is the standard electrode potential of the sensor electrode, a_i^{sample} is the activity of the ion in the sample, a_i^{ref} is the activity of the ion in the reference of the sensor electrode, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant (9.65×10^4 C·mol^{-1}.), and z_i is the number of electrons implied in the elementary redox reaction.

Potentiometric Sensors

- ➢There are two basic devices, as illustrated in Figure, in which the structure is configured as either metal-insulator semiconductor field-effect transistor (MISFET) or metal-insulator semiconductor gas-sensitive capacitor (MISCAP).
- ➢The main types of potentiometric sensors are membrane-based Ion-Selective Electrodes (ISE), Screen-Printed Electrodes, Ion-Selective Field Effect Transistors (ISFET), Solid-State devices, and Chemically modified electrodes (using, e.g., metal oxides or electrodeposited polymers as sensitive layers).

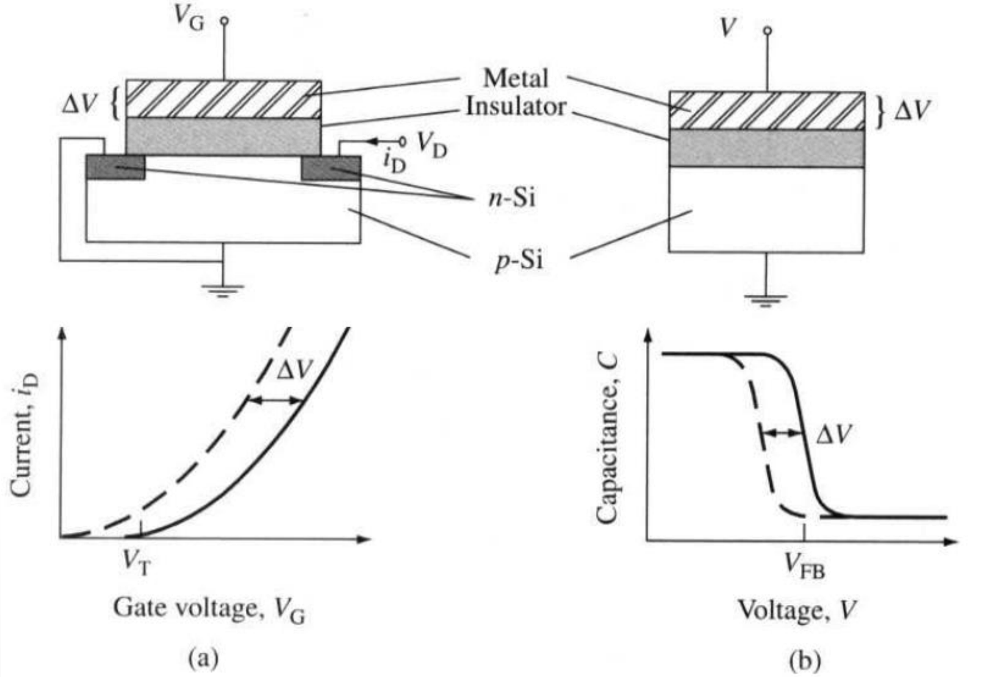


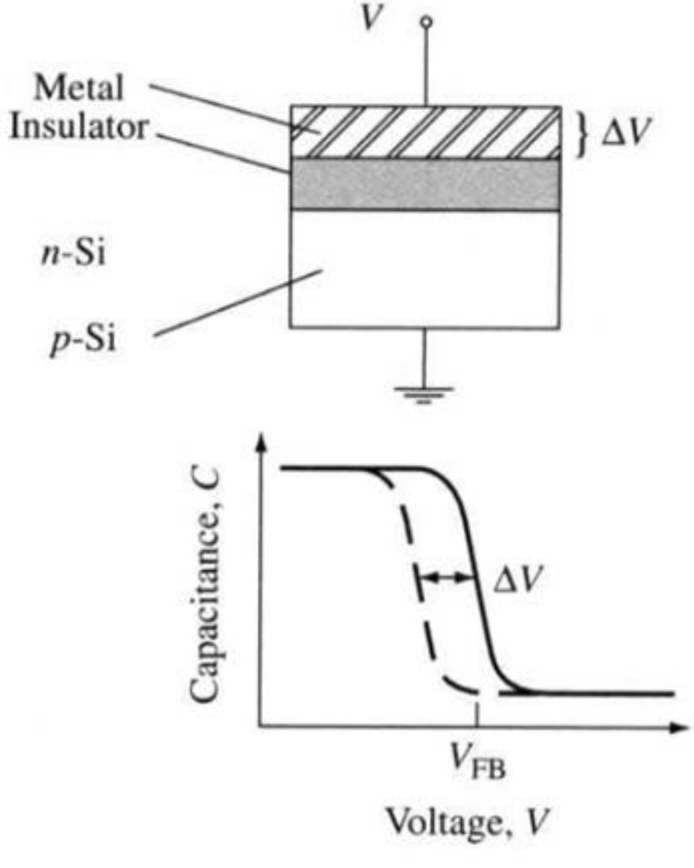
Figure Two types of potentiometric gas microsensors (a) n-channel MISFET (b) MISCAP. From Lundström *et al.* (1992)

Potentiometric Sensors

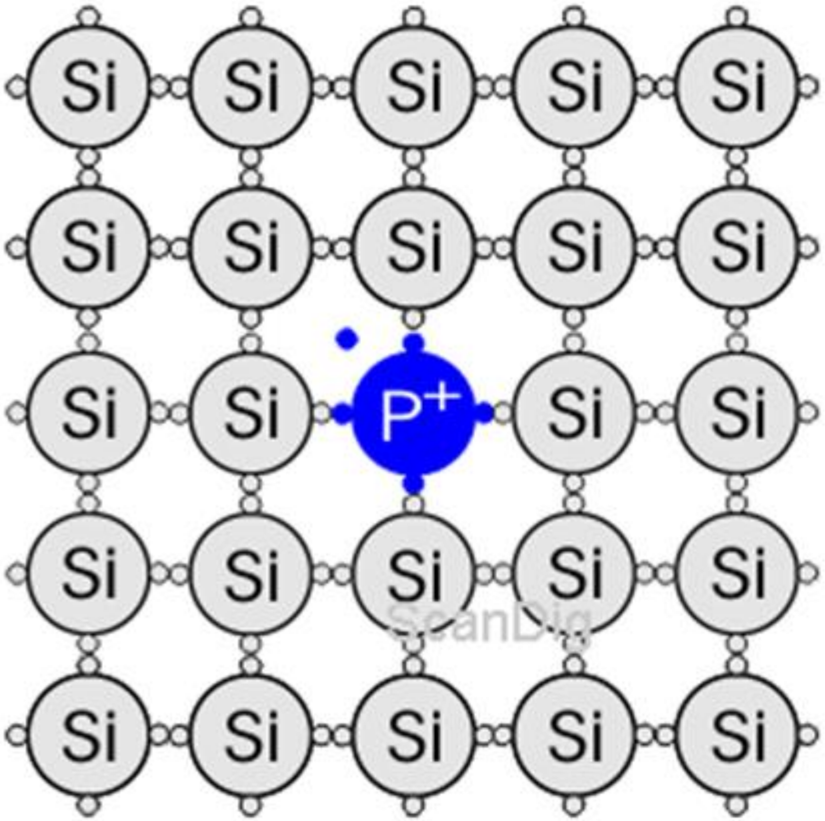
- ➢The most common device is an *n*-channel metal oxide semiconductor field-effect transistor MOSFET device configured in a common source mode, as shown in Figure.
- ➢When the device is in saturation, drain current i_D is simply related to the gate voltage V_{GS} by

$$i_D = \mu_n C_{ox} \frac{w}{l} (V_{GS} - V_T)^2$$

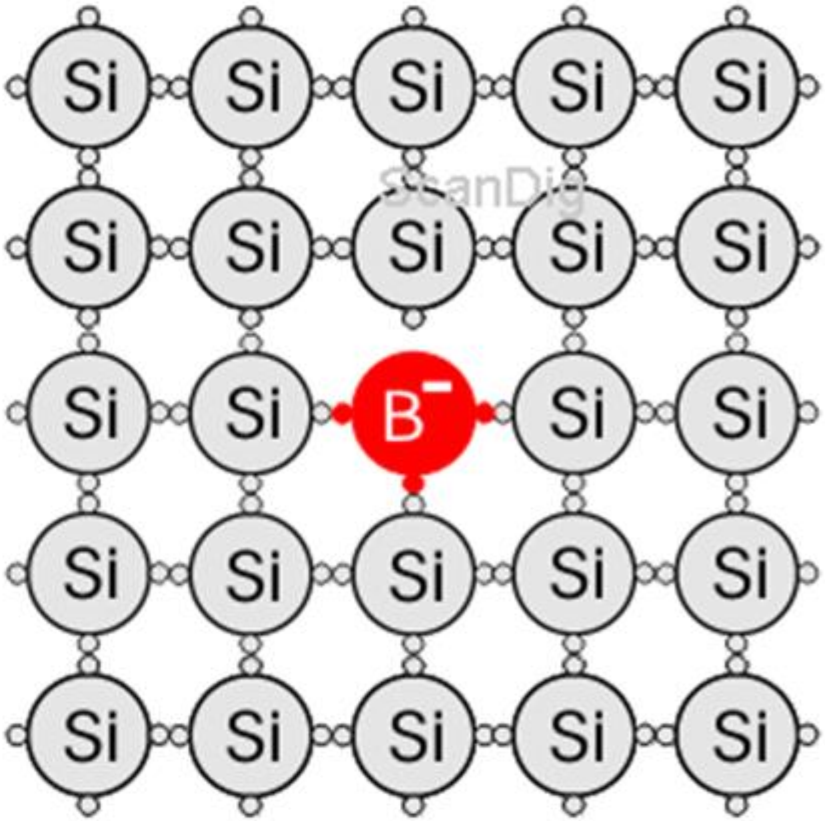
- ➢where μ_n is the electron mobility, C_{OX} is the capacitance per unit area of the oxide, *w* and *l* are the channel width and length, respectively, and V_T is the threshold voltage (about 0.7 V for Si).



n-type and p-type

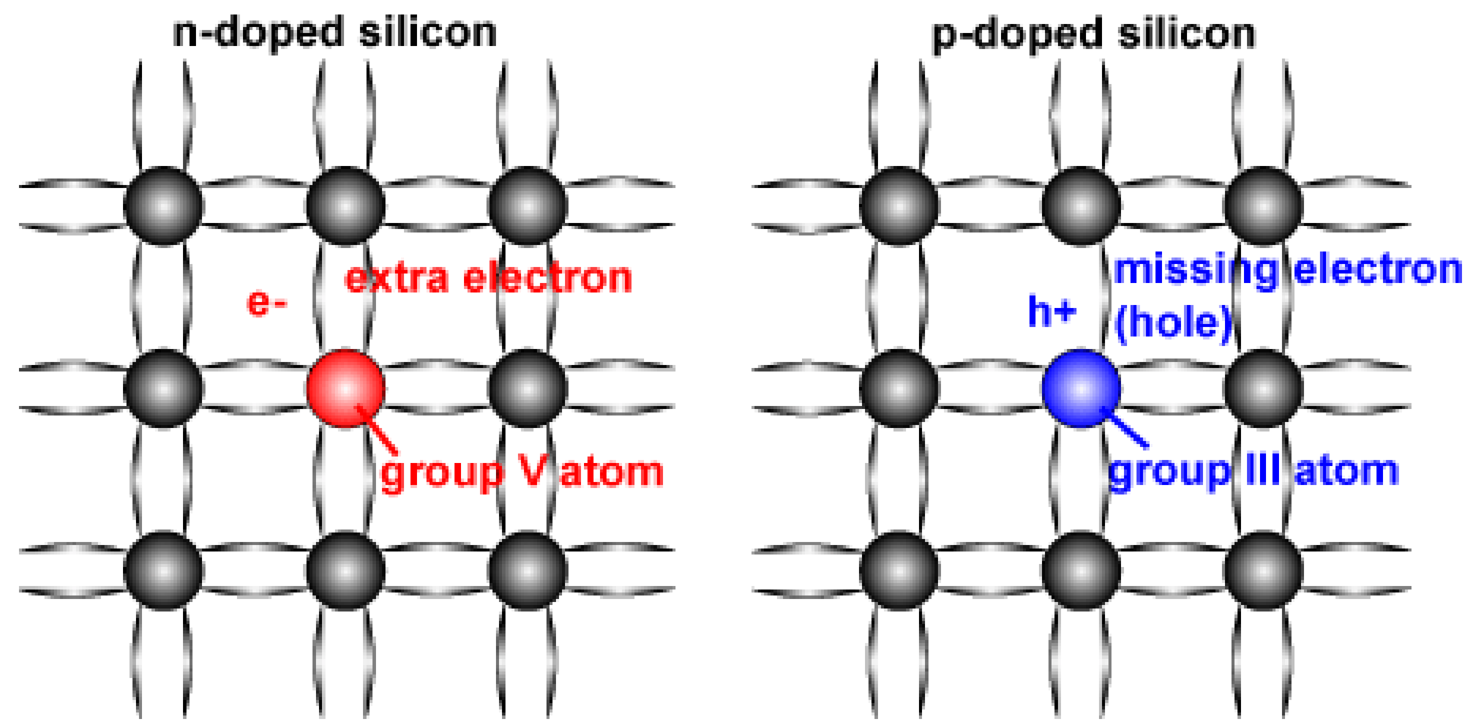


n-typed



p-typed

n-type and p-type



Schematic of a silicon crystal lattice doped with impurities to produce *n*-type and *p*-type semiconductor material.

	N-type (negative)	**P-type (positive)**
Dopant	Group V (e.g. Phosphorous)	Group III (e.g. Boron)
Bonds	Excess Electrons	Missing Electrons (Holes)
Majority Carriers	Electrons	Hole
Minority Carriers	Holes	Electrons