PhotoElectroChemistry
Theoretical Background

M. Skocic

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1 Basics

PEC takes advantage of the photovoltaic effect, discovered by Becquerel [3] in 1839, that occurs at the interface of a semiconductor and an electrolyte. In fact, the first experience showed the occurrence of a photopotential and a photocurrent under illumination when a silver electrode, covered with an oxide layer, was immersed in an acidic medium and connected to a platinum electrode. Nonetheless, the first studies focused on the understanding of the interfacial processes were performed much later [4–6].

The basics of photoelectrochemistry and application examples are presented in the following sections and they are largely described in the literature [7–12]. Several hypotheses are needed in order to apply the theoretical concepts:

- semiconductor are considered to be ideal i.e. crystallized and homogeneous

- the dielectric constant of the semiconductor is independent of the light wavelength

- the capacity of the Helmholtz layer is greater than the capacitance of the space charge capacitance

- the potential drop in the Helmholtz layer is independent of the applied potential and is negligible

The hypotheses are rarely fully respected in the case of oxides or passive films formed on industrial alloys. Nonetheless, the literature shows that the developed models can be applied to non-ideal systems such as oxides and passive films.

1.1 Electronic Band Structure

Solids are generally classified into three groups: conductors, semiconductors and isolators. Each category can be illustrated with a specific band structure as shown in figure 1. Valence and conduction bands correspond to allowed energy states for the electrons. The lowest energy level of the conduction band is labeled E_c and the highest energy level of the valence band is labeled E_v. They are separated by a band gap, E_g, with no allowed energy states. The repartition of the electrons among both bands are described by the position of the Fermi Level, E_F, which represents the highest energy state that can be occupied level at 0K. It is equivalent to the electrochemical potential in solid phases.
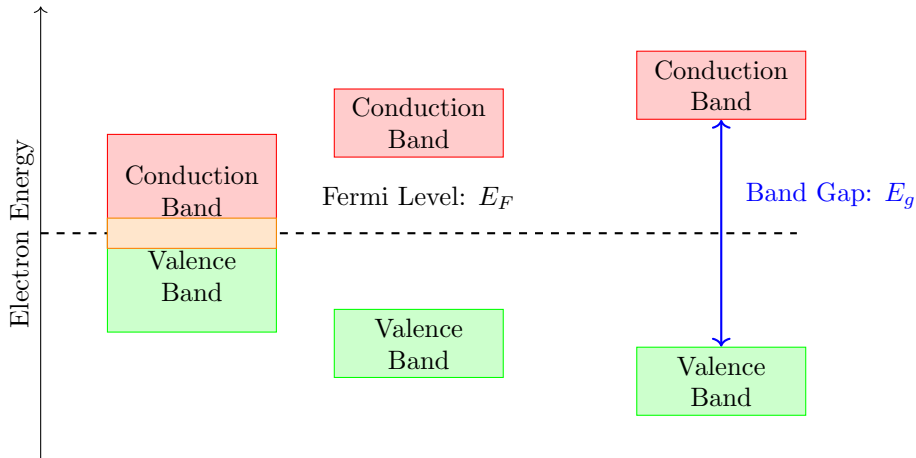

Figure 1: Schematic representation of the electronic band structure [1]: a) conductor, b) semiconductor, c) isolator

The electronic conduction is due to the movement either of the negatively charged electrons in the conduction band or of the positively charged holes in the valence band or both simultaneously. Consequently, the conduction depends on the number of available charge carriers in the conduction band and in the valence band. In conductors, an overlap of the conduction and the valence bands occurs which means that the highest allowed energy band is partially filled. The distinction between a semiconductor and an isolator is less obvious because the conduction depends on the band gap and the energy provided by the environment to the electrons from the valence band in order to jump into the conduction band.

In semiconductors, charge carriers can be generated by three mechanisms: *thermal excitation, photoexcitation and doping* as shown in figure 2. In the case of very low band gaps, thermal excitation can be enough in order to eject an electron from the valence band to the conduction band. Photoexcitation ejects electrons from the valence band to the conduction band when an incident photon, with energy greater than the band gap, is absorbed. Doping introduces additional energy level located in between the conduction and valence bands.

Doping occurs when the stoichiometry is altered or when impurities are introduced in the crystallographic lattice of the semiconductor. In the case of n-type semiconductors, the donor energy levels E_d lie just under the conduction band. The electrons from the donor levels are ejected by thermal excitation. Consequently, the majority charge carriers are negatively charged electrons in the band conduction. Similarly, the acceptor energy levels E_a, of p-type semiconductors, lie just above the band valence. The latter trap electrons from the valence band and therefore create holes. Consequently, the majority charge carriers are positively charged holes.
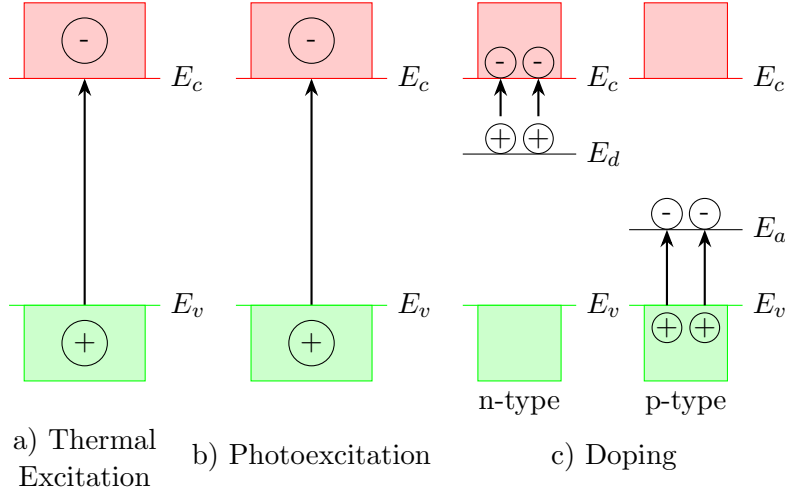

Figure 2: Schematic representation of the mechanisms generating charge carriers in semiconductors [2]: a) thermal excitation, b) photoexcitation, c) doping

The Fermi level E_F in intrinsic semiconductors is located at the mid-gap. The n-type and p-type doping shift the Fermi level towards band edges E_c and E_v, respectively. The figure 3 shows the position of the Fermi level with respect to the semiconductor type.

1.2 Semiconductor/electrolyte interface in dark condition

A potential gradient occurs when a semiconductor comes into contact with an electrolyte as shown in figure **??**.

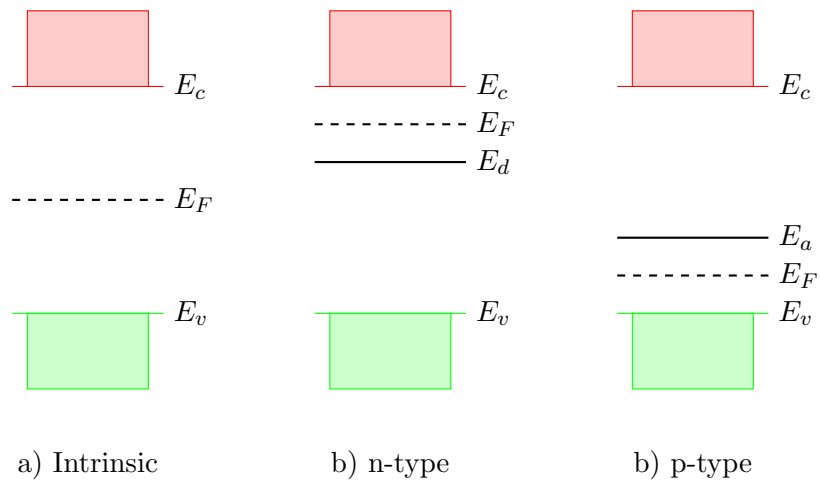## 1.3 Semiconductor/electrolyte interface under illumination

Figure 3: Schematic representation of the Fermi level with respect to the semiconduction type [2]: a) intrinsic, b) n-type, c) p-type.

References

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