

# PhotoElectroChemistry for Corrosion

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# Introduction

- ▶ Photoelectrochemical techniques have been shown to be useful tools for characterizing oxidation layers.
- ▶ Interdisciplinary theoretical underpinnings were built [1–5] such as the Gärtner-Butler model [6, 7] which has been proven to be a simple and robust model for the photocurrent generation.
- ▶ Technical progresses were achieved, allowing to study oxide layers at macroscopic, mesoscopic, and microscopic scales [8, 9], or in-situ in high temperature corrosion conditions [10, 11].

# Hypotheses

Several hypotheses are needed in order to apply the theoretical concepts:

- ▶ semiconductors 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

## Warning

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.

# Band Model I

- ▶ Solids: conductors, semiconductors and insulators.
- ▶ Valence and conduction bands correspond to allowed energy states for the electrons.
- ▶  $E_c$  is the lowest energy level of the conduction band.
- ▶  $E_v$  is the highest energy level of the valence band.
- ▶  $E_g$  is the band gap with no allowed energy states.
- ▶  $E_F$  is the Fermi Level which describes the distribution of the electrons among both bands.

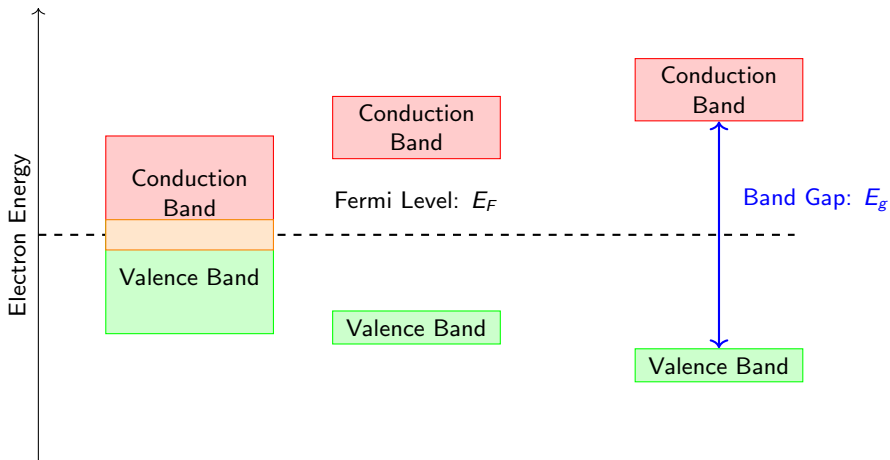
## Fermi Level

The Fermi Level represents the highest energy state that can be occupied level at 0K. It is equivalent to the electrochemical potential in solid phases.

## Band Model II

- ▶ The electronic conduction = movement of electrons and/or holes in conduction/valence band.
- ▶ The conduction depends on the number of available charge carriers in the conduction band and in the valence band.
- ▶ In conductors: overlap of the conduction and the valence bands occurs.
- ▶ In semiconductor and insulator: 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.

# Band Model III



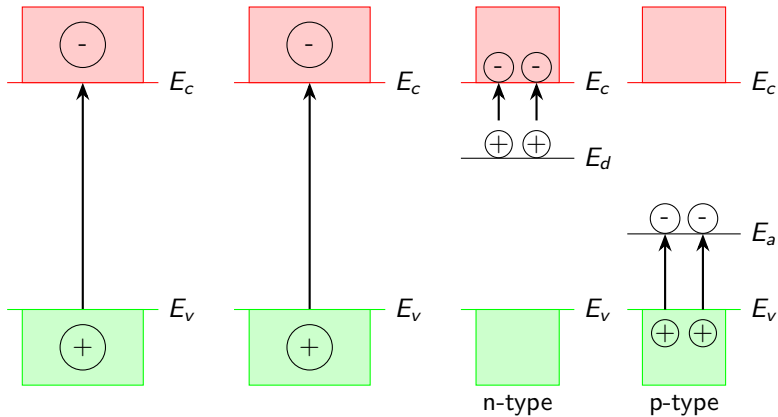
# Excitation carrier I

In semiconductors, charge carriers can be generated by three mechanisms:

- ▶ thermal excitation: 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.



## Excitation carrier II

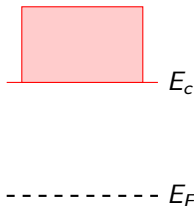


a) Thermal  
Excitation

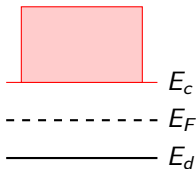
b) Photoexcitation

c) Doping

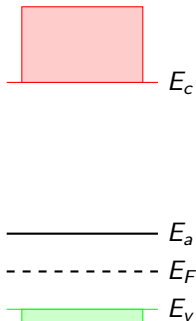
# Fermi Position



a) Intrinsic



b) n-type



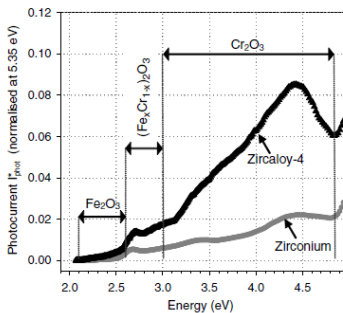
b) p-type

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  $E_v$ .

# Identification of minor oxides I

- ▶ Benaboud et al. [8] showed that the photoelectrochemical characterization is robust for detecting the presence of minor oxides.
- ▶ Alloying elements Fe, Sn and Cr, present in Zircaloy4, form precipitates which can be oxidized into minor oxides during the oxidation process.
- ▶ The strong photocurrent observed at around 5 eV reveals the major oxide i.e. monoclinic zirconia.
- ▶ The photocurrent at energy lower than 5 eV is not null and reveals the presence of minor oxides even in “pure” zirconium despite the very low concentration of impurities.
- ▶ The slope changes provided an estimation of the band gaps where the author identified the presence of hematite, chromia and a solid solution of  $(Fe_xCr_{1-x})O_3$ .

## (a)



**Figure:** Photocurrent spectra measured on zirconia oxide layer formed on Zircaloy4 and “pure” zirconium oxidized for 1h at 470°C in oxygenated atmosphere[8]: a) complete spectrum b) close-up view on the minor contributions.

# Identification of minor oxides

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