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# PhotoElectroChemistry for Corrosion

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$\mathcal{E}$lectrochemistry $\chi$pertise $\mathcal{C}$orrosion

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# Contents

## 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.

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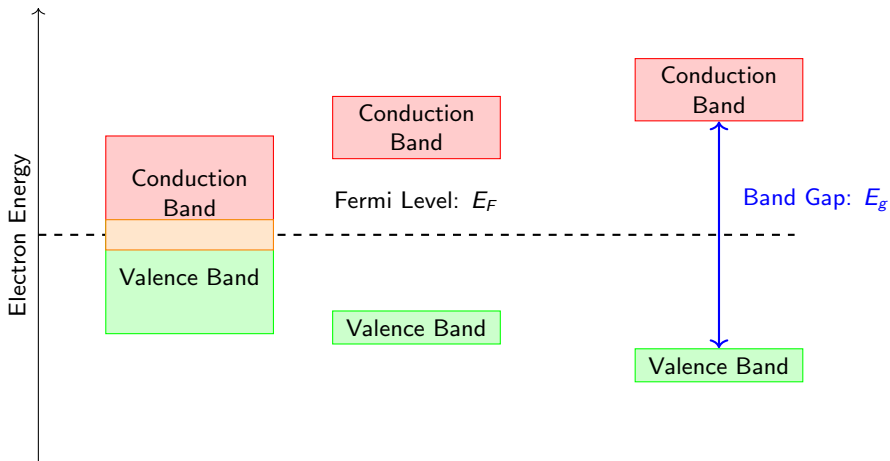
## Fermi Level
The Fermi Level represents the highest energy state that can be occupied level at 0K. It is equivalent to the electrochemical potential in solid phases.

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# 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.

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# Band Model III

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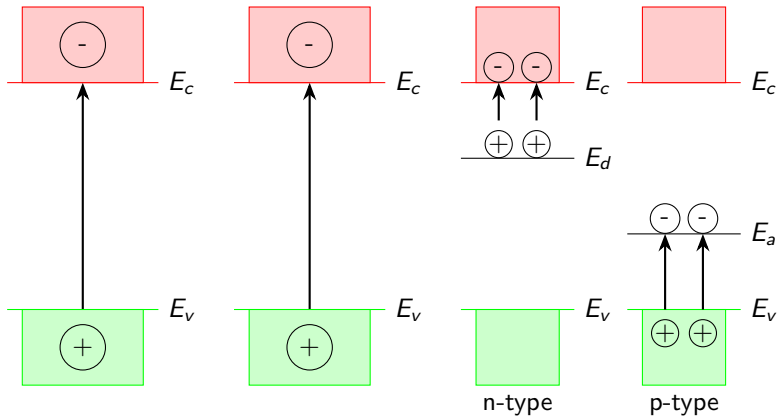
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# Excitation carrier I

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.

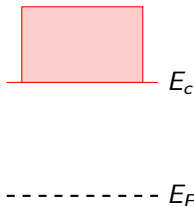▶ doping: introduces additional energy level located in between the conduction and valence bands.

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# Excitation carrier II



a) Thermal Excitation

b) Photoexcitation

c) Doping

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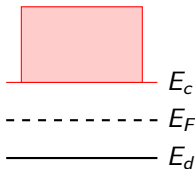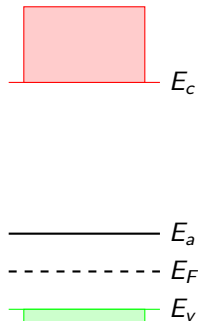
# Fermi Position



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 $E_v$.

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Semiconductor/electrolyte interface under illumination

# Electron/hole pairs

The illumination of the semiconductor/electrolyte interface, with photons having an energy greater than the band gap, $E_g$, creates electron/hole pairs in the semiconductor. By applying the adequate potential the pairs can be separated. As a consequence, the majority charge carriers are attracted to the semiconductor bulk whereas the minority charge carriers are drawn to the semiconductor/electrolyte interface where they can be transferred to a RedOx species creating an additional current called photocurrent.

Figure 1 illustrates schematically the mechanism leading to the creation of a photocurrent. n-type (p-type) semiconductors generate anodic (cathodic) photocurrents where the electrons (holes) move towards the external circuit whereas the holes (electrons) move towards the interface. The photocurrent is significant when the semiconductor/electrolyte junction is in depletion. Figure 2 shows the anodic (cathodic) photocurrent for a GaAs n-type (p-type) semiconductor.

Therefore, the applied potential on n-type (p-type) semiconductors is greater (lower) than the flat band potential.
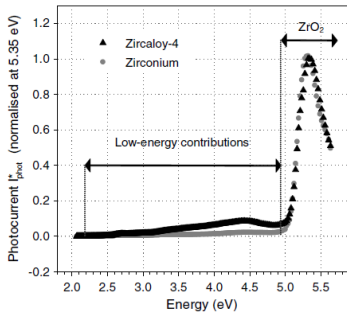
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Semiconductor/electrolyte interface under illumination

# Semiconductor/electrolyte interface under illumination I

▶ The linear transform with respect to the energy is used for determining the band gaps.

▶ The linear transform with respect to the potential is used for determining the semiconducting type, the flat band potential, and the number of majority charge carrier.
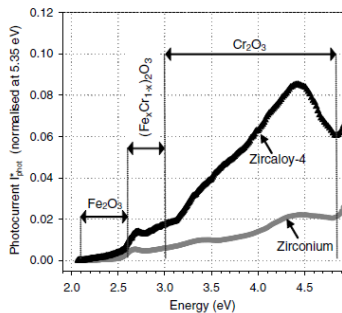
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Minor oxides

# 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 $(Fe_x Cr_{1-x})O_3$.

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Minor oxides

# Identification of minor oxides II



(a)                                                    (b)

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.

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# Semiconduction type I

- ▶ Loucif et al. [15] showed the effect of hydrogen pressure on the semiconduction type on Ni-based alloy 600 oxidized in simulated PWR.
- ▶ The "V-shape" of the normalized photocurrent reveals an isolating behavior of the oxide layer at high hydrogen pressure.
- ▶ The monotonous increase of the normalized photocurrent towards more anodic potentials reveals n-type semiconduction.

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Semiconducting type

# Semiconduction type II



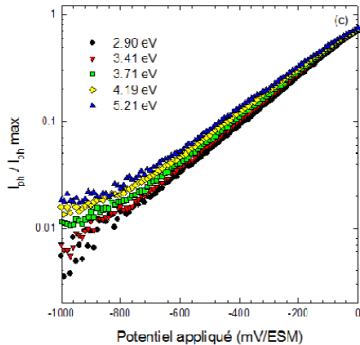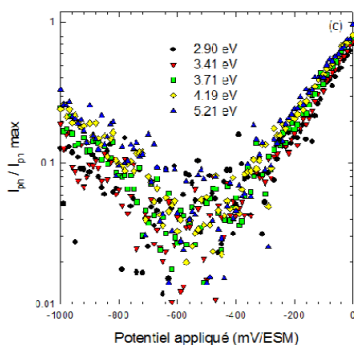(a)                                                                    (b)

Figure: Photocurrent with respect to the potential for an Ni-based alloy 600 polished and oxidized in simulated PWR for 500 h [15]: a) $P_{H_2}$=6.5 bar, b) $P_{H_2}$=0.05 bar.

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High temperature PEC

# High temperature PEC I

▶ The majority of photoelectrochemical characterizations are performed at room temperature in simple glass/Plexiglas cells where the signal/noise ratio is very good.

▶ High temperature photoelectrochemical characterizations require sophisticated metallic cells and transparent windows able to withstand the arch environment.

▶ Despite the need to improve the signal/noise ratio, the feasibility of the in-situ photoelectrochemical characterizations was demonstrated by Bojinov et al. [10] in 2002 and more recently by Skocic [11] in 2015

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High temperature PEC

# High temperature PEC II
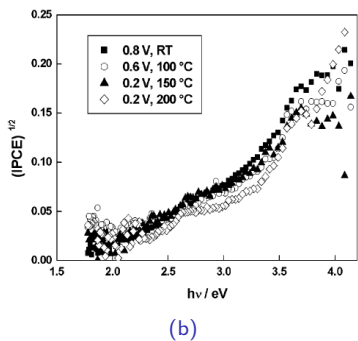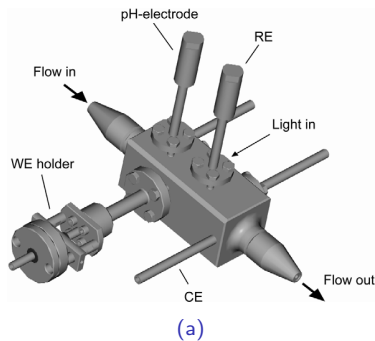


(a)                              (b)

Figure: a) Schematic representation of the metallic cell developed by Bojinov et al. [10]. b) Photocurrent spectra performed on iron oxides at different temperatures (up to 200°C) obtained by Bojinov et al. [10].

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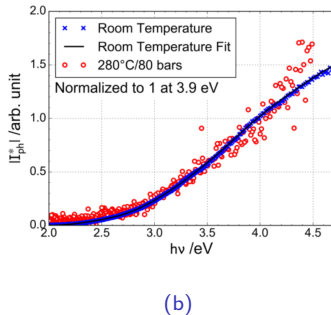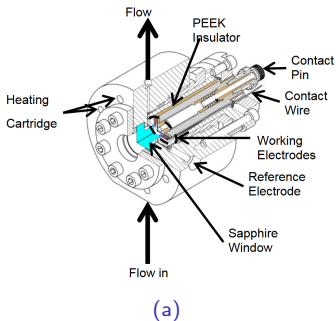
# High temperature PEC III



(a)

(b)

Figure: a) Schematic view of the photoelectrochemical cell developed by Skocic [11]. b) Photocurrent energy spectra of an X750 specimen recorded at room temperature and in 280°C/80 bar water [11]

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