8. Photo-electrochemistry of semiconductors
**Energetics of semiconductors: Reminder**

Quasi-Fermi levels $E^{*}_F$ for electrons ($n$) and holes ($p$):

$$E^{*}_{F,n} = E_C + kT \ln \frac{n^*}{N_C}$$
$$E^{*}_{F,p} = E_V - kT \ln \frac{p^*}{N_V}$$

where $E_C$ is the conduction band energy, $E_V$ the valence band energy, and $n^*$ and $p^*$ the concentrations of, respectively, negative and positive charge carriers out of equilibrium.

Doped semiconductor in the dark:

- **n-type** $E_F = E_C + kT \ln \frac{N_d}{N_C}$
- **p-type** $E_F = E_V - kT \ln \frac{N_a}{N_V}$

Doped semiconductor under illumination:

- **n-type** $E^{*}_{F,n} = E_C + kT \ln \frac{N_d + n^*}{N_C} \approx E_C$
- **p-type** $E^{*}_{F,p} = E_V - kT \ln \frac{N_a + p^*}{N_V} \approx E_V$
8.1 Energetics at the surface of semiconductors: Band-bending

n-type semiconductor

- Flat band
- Depletion layer
- Accumulation layer
**Space charge layer width**

![Diagram](image)

Poisson-Boltzmann:

\[
\Delta E = E_b - E_S = \frac{kT}{4} \left( \frac{w}{L_D} \right)
\]

Debye length:

\[
L_D = \sqrt{\frac{\varepsilon \cdot \varepsilon_0 \cdot kT}{2e^2 \cdot n_o}}
\]

\(\varepsilon\) and \(\varepsilon_0\) are the medium dielectric constant and the permittivity of vacuum, respectively. \(e\) is the elementary charge and \(n_0\) the carrier density (concentration).

**Example**

TiO\(_2\) is usually n-doped, due to stoechiometric oxygen deficiency

\[
n_0 = N_d = 10^{17} \text{ cm}^{-3}
\]

\[
N_C = 10^{22} \text{ cm}^{-3}
\]

\[
\varepsilon = 130
\]

\[
E_F = E_C + kT \ln \frac{N_d}{N_C}
\]

\[
E_C - E_F = 12kT \approx 0.3 \text{ eV}
\]

\[
L_D = \sqrt{\frac{\varepsilon \cdot \varepsilon_0 \cdot kT}{2e^2 \cdot n_o}}
\]

\(L_D = 30 \text{ nm}\)
8.2 Case of thin semiconductor layers

The above description is valid only for a semiconductor bulk larger than the width $w$ of the accumulation or depletion layer. If the layer thickness decreases below that limit, band bending progressively vanishes, and the conduction band level eventually coincides with the flat band potential, reflecting the fact that the electric field created by the species present on the surface extends inside the whole layer.

The potential drop between the surface and the center (bulk) of a flat semiconducting layer is obtained by solving Poisson-Boltzmann equation and can be expressed by:

$$
\Delta \phi = \phi(r) - \phi_S = \frac{k_B T}{4e} \cdot \left( \frac{r}{L_D} \right)^2
$$

$$
\Delta \phi_{\text{max}} = \phi_b - \phi_S = \frac{k_B T}{16e} \cdot \left( \frac{L}{L_D} \right)^2
$$

where $r$ is the distance to the surface, $L$ the layer's thickness, $L_D$ Debye's length and $e$ the elementary charge.
Case of nanodispersed semiconductors

For spherical particles, which radius \( r_0 \approx w \), Poisson-Boltzmann equation yields:

\[
\Delta \phi_{\text{max}} = \phi_b - \phi_S = \frac{k_B T}{6e} \left( \frac{r_0}{L_D} \right)^2
\]

A flat band situation prevails when charge migration due to the electric field in the space charge layer is negligible compared to thermal diffusion:

\[
\Delta \phi_{\text{max}} < \frac{k_B T}{e} \quad \Rightarrow \quad r < \sqrt{6} \cdot L_D
\]

In the previous example of TiO\(_2\):

\[
\begin{align*}
\varepsilon &= 130 \\
n_0 &= 10^{17} \text{ cm}^{-3} \\
L_D &= 30 \text{ nm} \quad \Rightarrow \quad r_{\text{max}} < 73 \text{ nm}
\end{align*}
\]

\[
\begin{align*}
n_0 &= 10^{19} \text{ cm}^{-3} \\
L_D &= 3 \text{ nm} \quad \Rightarrow \quad r_{\text{max}} < 7 \text{ nm}
\end{align*}
\]

It is then apparent that the electric field in semiconductor nanoparticles is usually small and/or that high dopant levels are required to produce a significant band bending inside the particle.
8.3 Potential-controlling ions

The Helmoltz layer contains ions that are specifically adsorbed onto the surface (protons on an amphoteric surface, for instance). The concentration of these ions defines the potential drop across the Helmoltz layer and controls the position of the contact potential at the surface of the solid (flatband potential $\phi_{fb}$). This potential can thus be shifted up and down by changing the solution composition.

Diagram:
- $\phi_{fb}$
- $\phi_s$
- $\Delta \phi_H$
- $\phi_{sol}$
- $E_F$
- $E_F$
- Semiconductor
- Electrolyte
- Helmoltz layer
- Diffuse (Gouy-Chapman) layer
Control of flat-band potential by specifically adsorbed ions

\[
\Delta \phi_H = \phi_{sol} - \phi_{fb} = \left(\frac{\mu_X^{*}}{F} - \left(\frac{\mu_X^{*}}{a_X}\right)\right) \geq 0
\]

\(\phi_{sol}\) the electron potential in the solution at the shear plane, \(\phi_{fb}\) the flat-band potential at
the surface of the semiconductor, and \(a_X\) the activities of an ion \(X\) that is able to
specifically adsorb onto the surface within the Helmoltz layer. If the activity of the ion on
the surface does not change with its concentration in solution (saturated surface), the
equation simplifies to the Nernstian relation:

\[
\Delta \phi_H = \text{const.} + \frac{RT}{F} \cdot \ln \left(\frac{a_X}{a_X^{*}}\right) = \text{const.} - 0.059 \ [V] \cdot pX
\]

If the potential controlling ion is \(H^+\), for instance, the flatband potential \(\phi_{fb}\) is expected to
shift cathodically by 59 mV when the \(pH\) of the electrolyte is increased by one unit:

\[
\phi_{fb} = \text{const.} - 0.059 \ [V] \cdot pH \quad \text{or} \quad E_{fb} = \text{const.} + 0.059 \ [eV] \cdot pH
\]

Oxides are generally characterized by an amphoteric surface. \(H^+\) ions are therefore potential-
controlling species for these materials.

\[
M-O^- + H^+ \Leftrightarrow MOH \quad M-OH + H^+ \Leftrightarrow M-OH_2^+
\]
The natural electric field present at the semiconductor-electrolyte junction allows for the charge separation of carriers generated by the intrinsic absorption of light. In the case of a depletion layer in a n-doped material, photoelectrons will migrate towards the interior of the solid. Holes will accumulate at the surface, where they can react with a donor in the electrolyte.

In the bulk of the solid, far from the junction, no field is existing to ensure charge separation. Electrons and holes produced there will thus recombine readily.
Light-induced charge separation at a Schottky junction

A so-called 'Schottky barrier' is formed when a n-doped semiconductor is contacted with a metal characterized by a large work function $\phi_m$ (noble metal). The situation is equivalent to a liquid junction with acceptor species in solution. This effect is used to build diode rectifiers and simple solar cells (Chapter 9).
**Light-induced charge separation efficiency**

Neglecting charge carriers recombination within the space charge layer, Gärtner proposed a simplified model of the electrical current $i$ flowing across the interface:

$$i = e \cdot I_0 \cdot \frac{1 - \exp(-\alpha \cdot w)}{1 + \alpha \cdot L_m}$$

Here, $I_0$ is the incident light intensity, $\alpha$ the absorption coefficient of the semiconducting material, $w$ the space charge layer width, and $L_m$ the mean diffusion length of majority carriers.

$$L_m = \sqrt{D \cdot \tau}$$

where $D$ is the Fick’s diffusion coefficient of carriers and $\tau$ the mean carrier lifetime before recombination.

This model predicts a rapid increase of the photocurrent for $\phi > \phi_{fb}$, as soon as a space charge layer is built-up.
8.5 Dye-sensitization of wide-bandgap semiconductors

Intrinsic absorption:

\[
\begin{align*}
SC & \xrightarrow{hv} SC(e^-\ldots h^+) \\
SC(e^-\ldots h^+) + D & \rightarrow SC(e^-) + D^+
\end{align*}
\]

Redox dye-sensitization:

\[
\begin{align*}
S & \xrightarrow{hv} S^* \\
S^* + SC & \rightarrow SC(e^-) + S^+ \\
S^+ + D & \rightarrow S + D^+
\end{align*}
\]
Interfacial ET as a way to hinder charge recombination

Interfacial back electron transfer following photoinduced charge injection can be hampered by the electric field in the semiconductor space charge layer. As a consequence the rate constant \( k_{r_{\text{int}}} \) is 2-6 orders of magnitude smaller than in the homogeneous case.

Homogeneous system

Forward ET:
\[
S^* + A \rightarrow A^- + S^+
\]

Back electron transfer:
\[
S^+ + A^- \overset{k_{r_{\text{hom}}}}{\longrightarrow} S + A
\]

Interfacial system

Forward ET:
\[
S^* + SC \rightarrow SC(e^-) + S^+
\]

Back electron transfer:
\[
SC(e^-) + S^+ \overset{k_{r_{\text{int}}}}{\longrightarrow} SC + D
\]