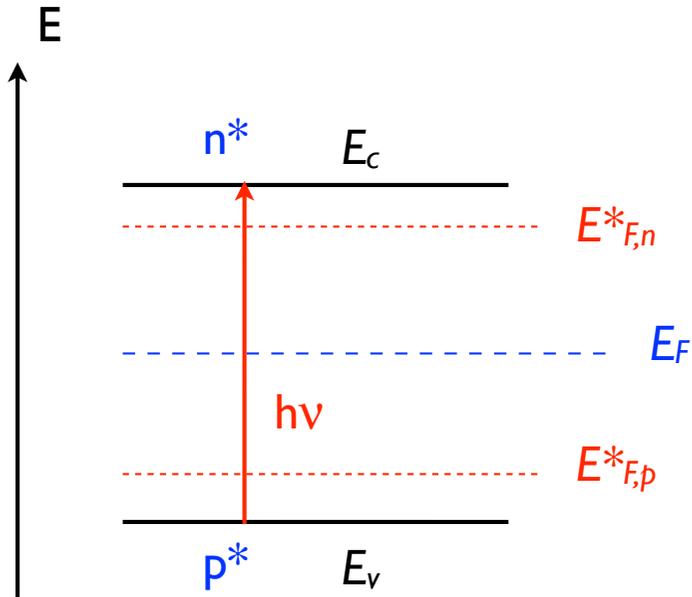


8. Photo-electrochemistry of semiconductors

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:

$$\text{n-type} \quad E_F = E_C + kT \ln \frac{N_d}{N_C}$$

$$\text{p-type} \quad E_F = E_V - kT \ln \frac{N_a}{N_V}$$

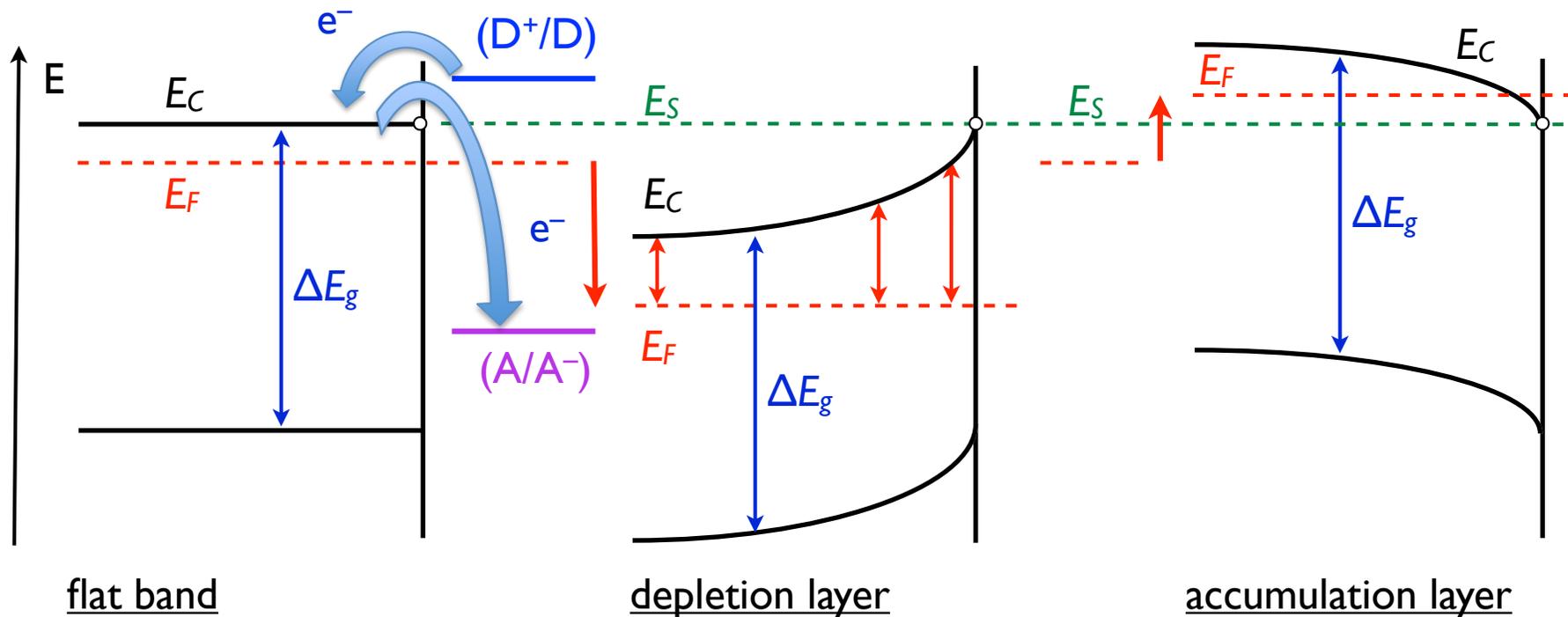
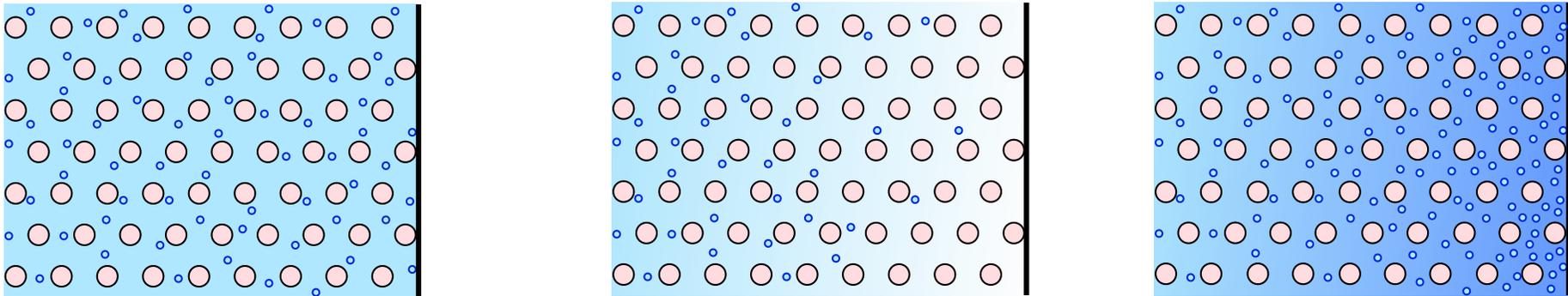
Doped semiconductor under illumination:

$$E_{F,n}^* = E_C + kT \ln \frac{N_d + n^*}{N_C} \cong E_C$$

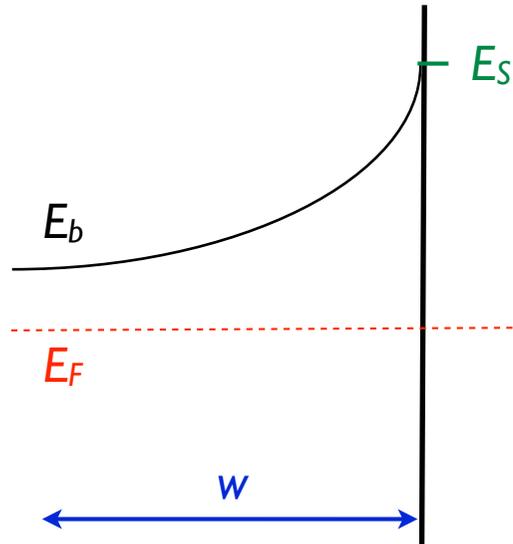
$$E_{F,p}^* = E_V - kT \ln \frac{N_a + p^*}{N_V} \cong E_V$$

8.1 Energetics at the surface of semiconductors: Band-bending

n-type semiconductor



Space charge layer width



Poisson-Boltzmann:

$$\Delta E = E_b - E_s = \frac{kT}{4} \left(\frac{w}{L_D} \right)$$

Debye length:

$$L_D = \sqrt{\frac{\epsilon \cdot \epsilon_0 \cdot kT}{2e^2 \cdot n_0}}$$

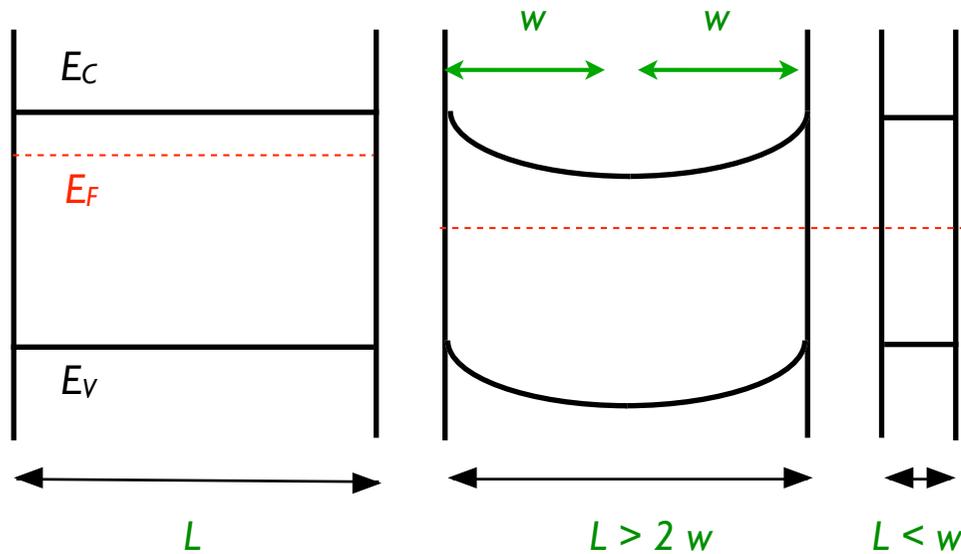
ϵ and ϵ_0 are the medium dielectric constant and the permittivity of vacuum, respectively. e is the elementary charge and n_0 the carrier density (concentration).

Example

TiO₂ is usually n-doped, due to stoichiometric oxygen deficiency

$$\left. \begin{array}{l} n_0 = N_d \approx 10^{17} \text{ cm}^{-3} \\ N_C \approx 10^{22} \text{ cm}^{-3} \end{array} \right\} \begin{array}{l} E_F = E_C + kT \ln \frac{N_d}{N_C} \\ L_D = \sqrt{\frac{\epsilon \cdot \epsilon_0 \cdot kT}{2e^2 \cdot n_0}} \end{array} \quad \begin{array}{l} E_C - E_F \approx 12 kT \approx 0.3 \text{ eV} \\ L_D = 30 \text{ nm} \end{array}$$

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:

$$\Delta\phi = \phi(r) - \phi_s = \frac{k_B T}{4e} \cdot \left(\frac{r}{L_D} \right)^2 \qquad \Delta\phi_{\max} = \phi_b - \phi_s = \frac{k_B T}{16e} \cdot \left(\frac{L}{L_D} \right)^2$$

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:

$$\Delta\phi_{\max} = \phi_b - \phi_s = \frac{k_B T}{6e} \cdot \left(\frac{r_0}{L_D}\right)^2$$

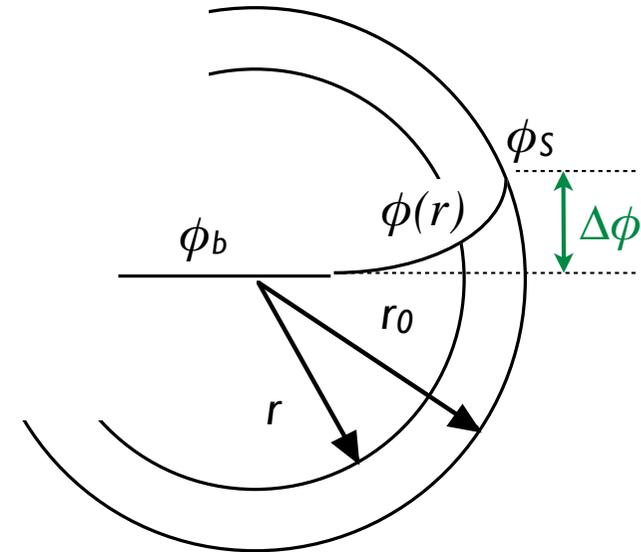
A flat band situation prevails when charge migration due to the electric field in the space charge layer is negligible compared to thermal diffusion:

$$\Delta\phi_{\max} < \frac{k_B T}{e} \Rightarrow r < \sqrt{6} \cdot L_D$$

In the previous example of TiO_2 :

$$\left. \begin{array}{l} \varepsilon = 130 \\ n_0 = 10^{17} \text{ cm}^{-3} \end{array} \right\} L_D = 30 \text{ nm} \Rightarrow r_{\max} < 73 \text{ nm}$$

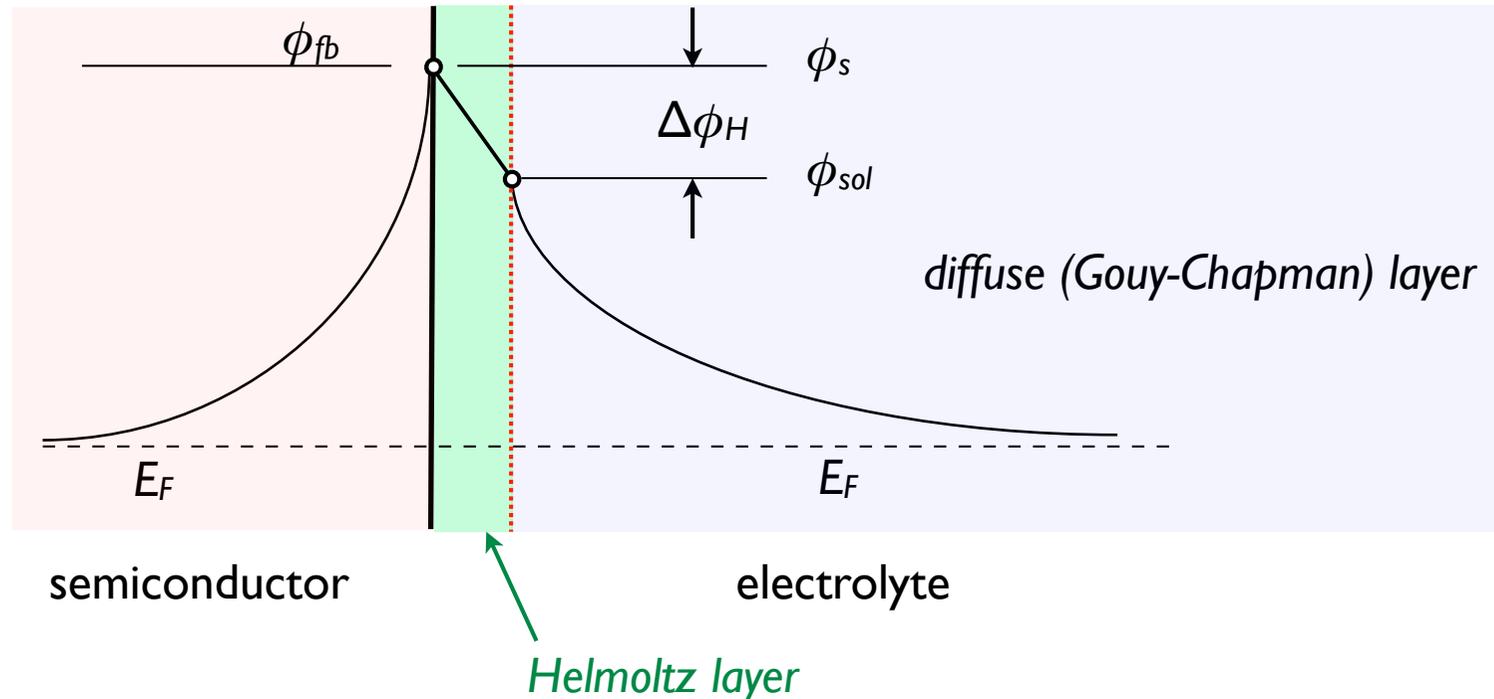
$$n_0 = 10^{19} \text{ cm}^{-3} \quad L_D = 3 \text{ nm} \Rightarrow r_{\max} < 7 \text{ nm}$$



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 Helmholtz 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 Helmholtz layer and controls the position of the contact potential at the surface of the solid (flatband potential ϕ_{fb}). This potential can thus be shifted up and down by changing the solution composition.



Control of flat-band potential by specifically adsorbed ions

$$\Delta\phi_H = \phi_{sol} - \phi_{fb} = \frac{(\mu_X^*)_{sol} - (\mu_X^*)_s}{F} + \frac{RT}{F} \cdot \ln \left[\frac{(a_X)_{sol}}{(a_X)_s} \right] \geq 0$$

ϕ_{sol} the electron potential in the solution at the shear plane, ϕ_{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 Helmholtz 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:

$$\Delta\phi_H = \text{const.} + \frac{RT}{F} \cdot \ln (a_X)_{sol} = \text{const.} - 0.059 [\text{V}] \cdot pX$$

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

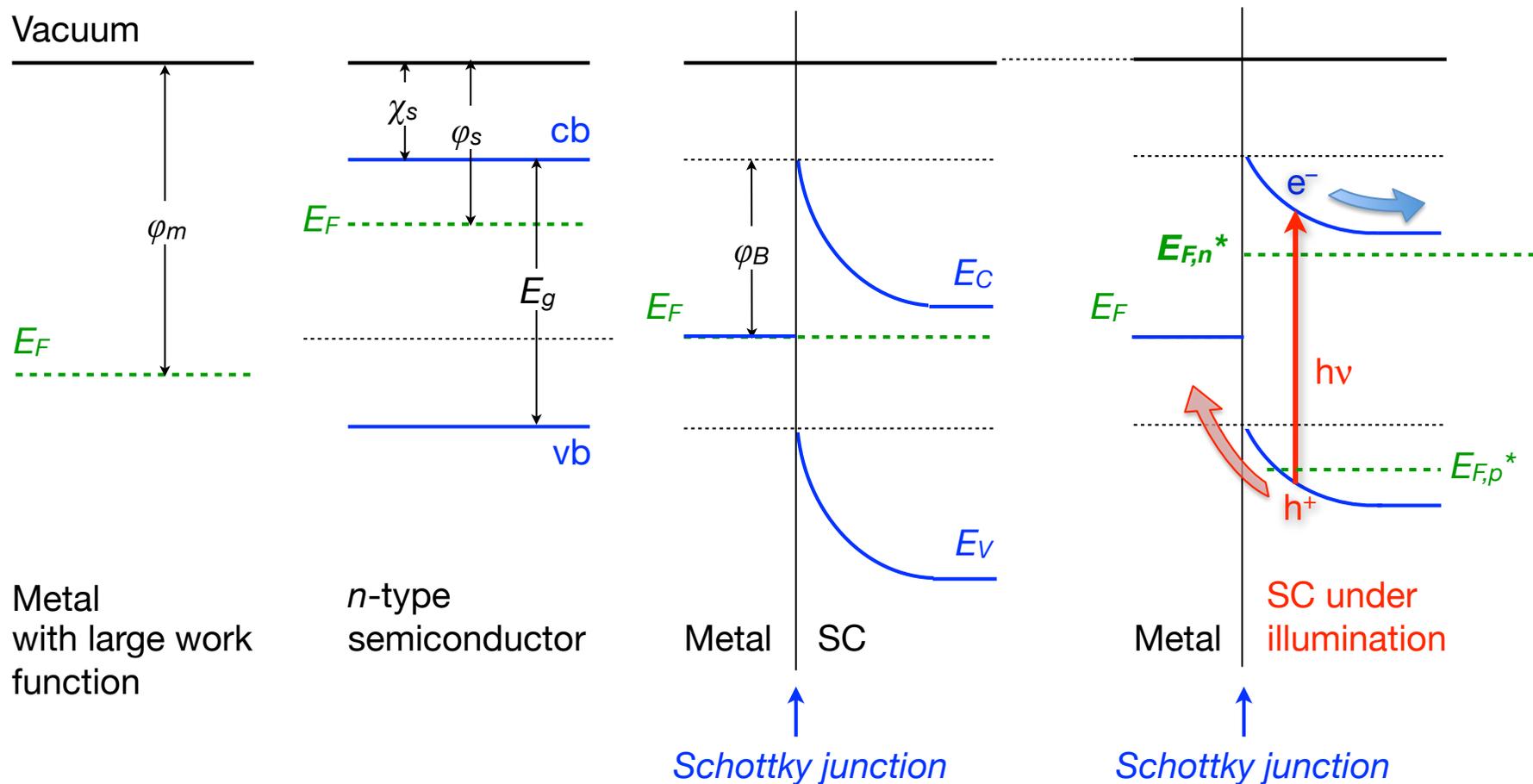
$$\phi_{fb} = \text{const.} - 0.059 [\text{V}] \cdot pH \quad \text{or} \quad E_{fb} = \text{const.} + 0.059 [\text{eV}] \cdot pH$$

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



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 ϕ_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:

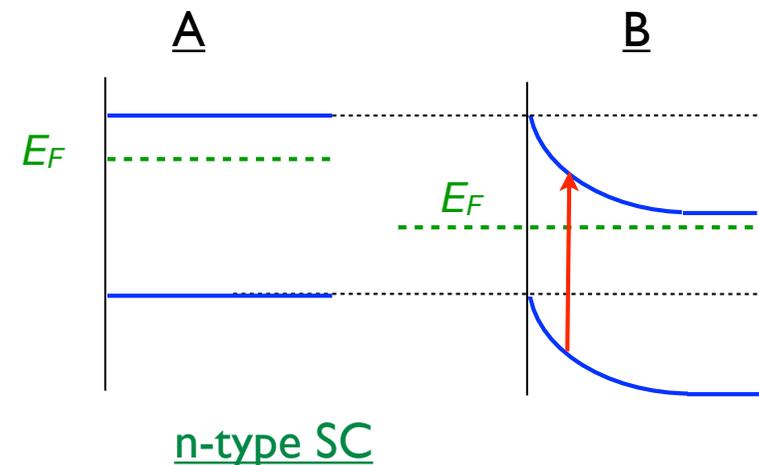
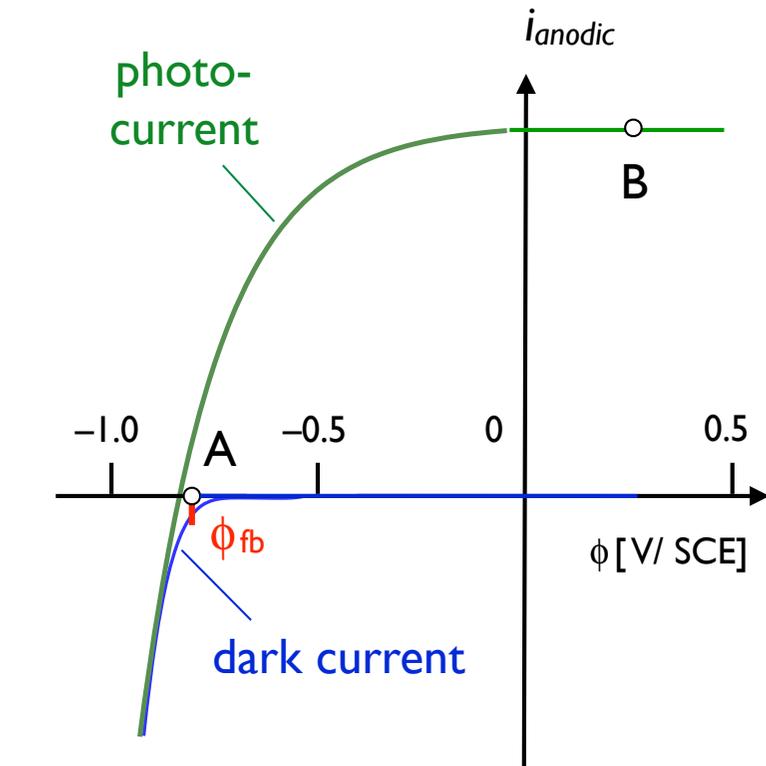
$$i = e \cdot I_0 \cdot \frac{1 - \exp(-\alpha \cdot w)}{1 + \alpha \cdot L_m}$$

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

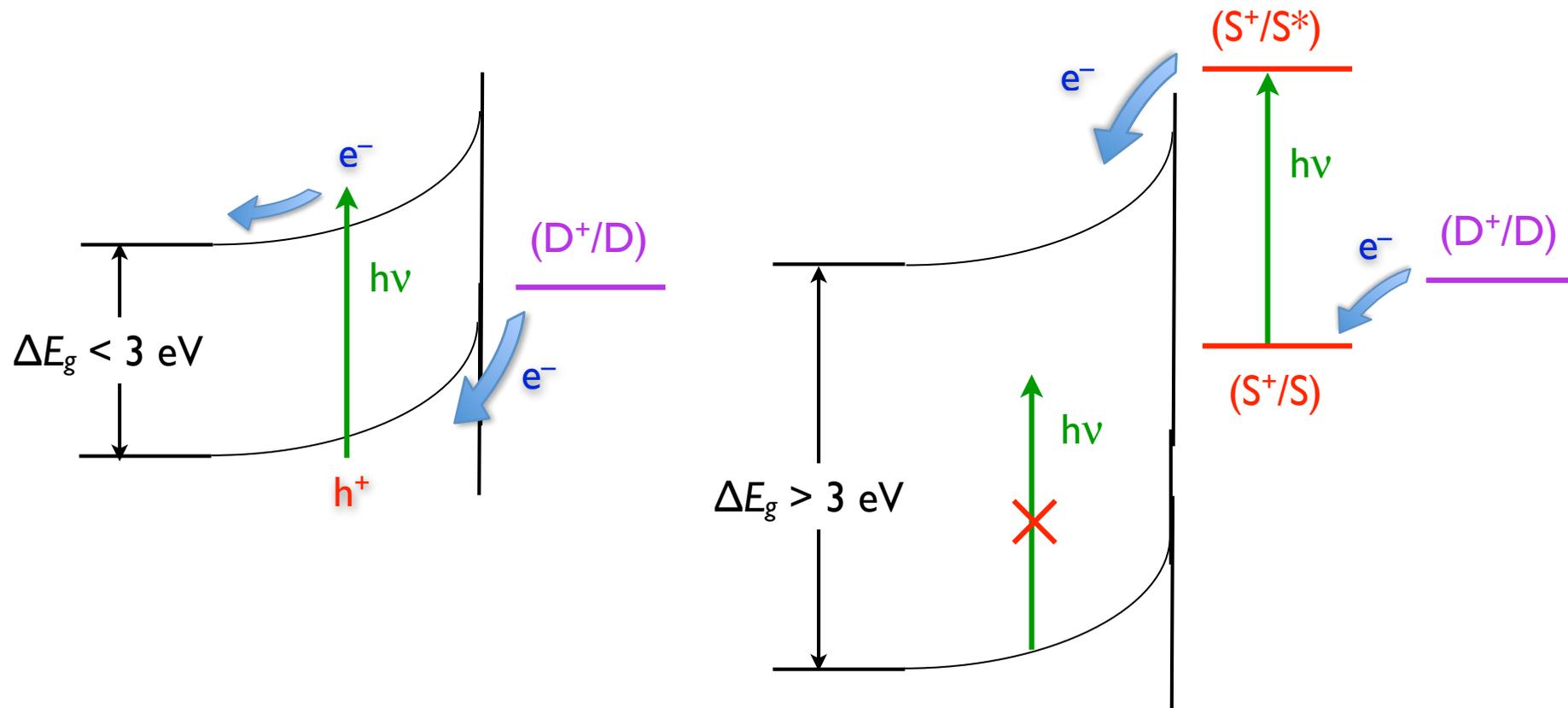
$$L_m = \sqrt{D \cdot \tau}$$

where D is the Fick's diffusion coefficient of carriers and τ the mean carrier lifetime before recombination.

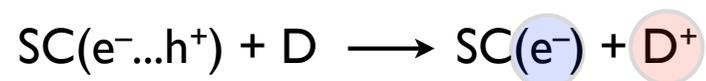
This model predicts a rapid increase of the photocurrent for $\phi > \phi_{fb}$, as soon as a space charge layer is built-up.



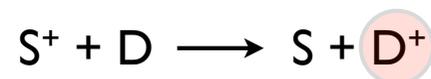
8.5 Dye-sensitization of wide-bandgap semiconductors



Intrinsic absorption:

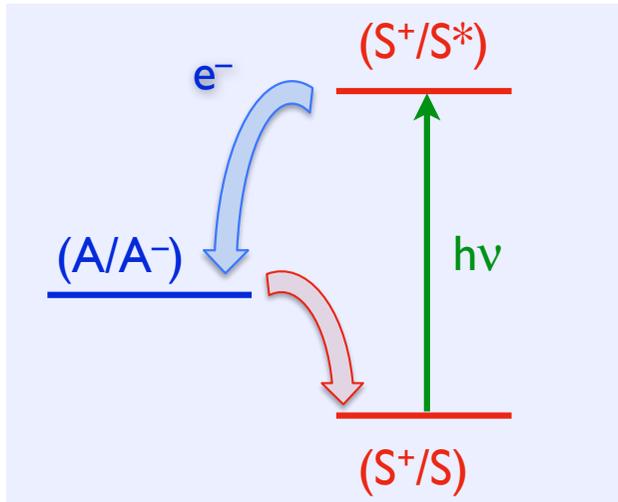


Redox dye-sensitization:



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_int} is 2-6 orders of magnitude smaller than in the homogeneous case.

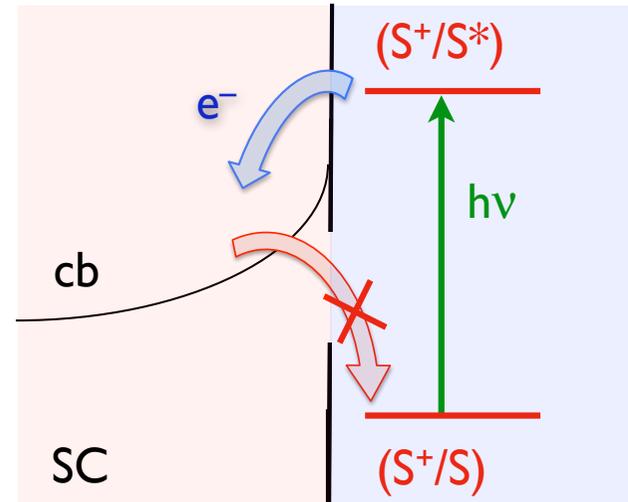
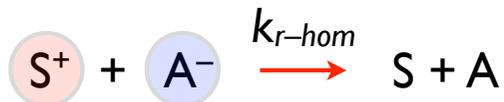


Homogeneous system

Forward ET:



Back electron transfer:



Interfacial system

Forward ET:



Back electron transfer:

