11

The semiconductor-electrolyte interface

11.1 Electrochemistry at semiconductors

Many naturally occurring substances, in particular the oxide films that form spontaneously on some metals, are semiconductors. Also, electrochemical reactions are used in the production of semiconductor chips, and recently semiconductors have been used in the construction of electrochemical photocells. So there are good technological reasons to study the interface between a semiconductor and an electrolyte. Our main interest, however, lies in more fundamental questions: How does the electronic structure of the electrode influence the properties of the electrochemical interface, and how does it affect electrochemical reactions? What new processes can occur at semiconductors that are not known from metals?

11.2 Potential profile and band bending

When a semiconducting electrode is brought into contact with an electrolyte solution, a potential difference is established at the interface. The conductivity even of doped semiconductors is usually well below that of an electrolyte solution; so practically all of the potential drop occurs in the boundary layer of the electrode, and very little on the solution side of the interface (see Fig. 11.1). The situation is opposite to that on metal electrodes, but very similar to that at the interface between a semiconductor and a metal.

The variation of the electrostatic potential $\phi(x)$ in the surface region entails a bending of the bands, since the potential contributes a term $-e_0\phi(x)$ to the electronic energy. Consider the case of an n-type semiconductor. We set $\phi = 0$ in the bulk of the semiconductor. If the value ϕ_s of the potential at the surface is positive, the bands band downwards, and the concentration of electrons in the conduction band is enhanced (see Fig. 11.2). This is called an *enrichment layer*. If $\phi_s < 0$, the bands bend upward, and the concentration of electrons at the surface is reduced; we speak of a *depletion layer*. On the other

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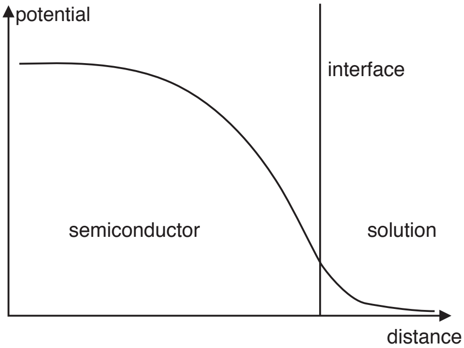

Fig. 11.1. Variation of the potential at the semiconductor-solution interface (schematic).

hand, the concentration of the holes, the minority carriers, is enhanced at the surface; if it exceeds that of the electrons, one speaks of an *inversion layer*. The special potential at which the electrostatic potential is constant (i.e., $\phi(x) = 0$ throughout the semiconductor), is the *flat-band potential*, which is equivalent to the potential of zero charge. In Chap. 4 we noted that, because of the occurrence of dipole potentials, the difference in outer potential does not vanish at the pzc; the same is true for the flat-band potential of a semiconductor in contact with an electrolyte solution.

Mutatis mutandis the same terminology is applied to the surface of p-type semiconductors. So if the bands bend upward, we speak of an enrichment layer; if they bend downward, of a depletion layer.

Just as in Gouy–Chapman theory, the variation of the potential can be calculated from Poisson's equation and Boltzmann statistics (in the nondegenerate case). As an example we consider an n-type semiconductor, and limit ourselves to the case where the donors are completely ionized, and the concentration of holes is negligible throughout – a full treatment of all possible cases is given in [1, 2]. The charge density in the space-charge region is the sum of the static positive charge on the ionized donors, and the mobile negative charge of the conduction electrons. Let n_b be the density of electrons in the bulk, which equals the density of donors since the bulk is electroneutral. Poisson's equation gives:

$$\frac{d^2\phi}{dx^2} = -\frac{n_{\rm b}}{\epsilon\epsilon_0}\left(1 - \exp\frac{e_0\phi}{kT}\right) \tag{11.1}$$

which is reminiscent of the Poisson–Boltzmann equation. An approximate analytic solution can be derived for a depletion layer; the band has a parabolic shape, and the corresponding interfacial capacitance $C_{\rm sc}$ is given by the *Mott–Schottky* equation (see Appendix), which is usually written in the form:

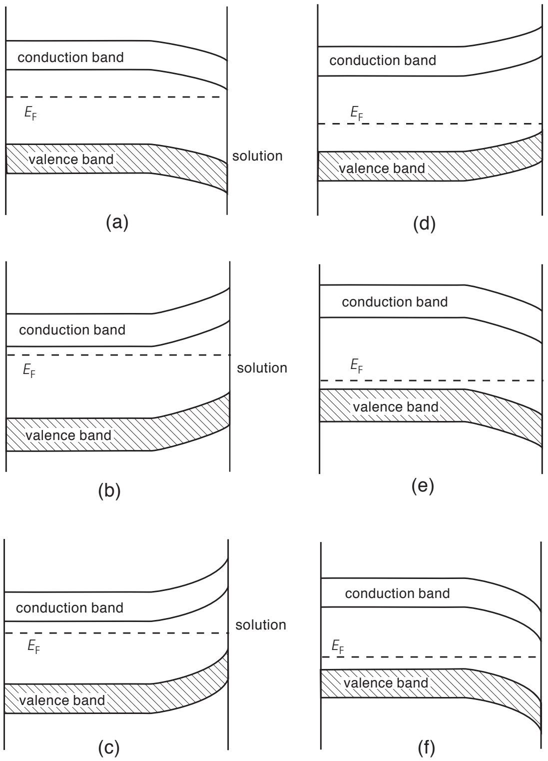

Fig. 11.2. Band bending at the interface between a semiconductor and an electrolyte solution; (**a**)–(**c**) n-type semiconductor: (**a**) enrichment layer, (**b**) depletion layer, (**c**) inversion layer; (**d**)–(**f**) p-type semiconductor: (**d**) enrichment layer, (**e**) depletion layer, (**f**) inversion layer.

$$\left(\frac{1}{C_{\mathrm{sc}}}\right)^2 = \frac{2}{\epsilon\epsilon_0 e_0 n_b}\left(|\phi_s| - \frac{kT}{e_0}\right) \tag{11.2}$$

Often, the small term kT/e_0 is neglected. The total interfacial capacity C is a series combination of the space-charge capacities C_{sc} of the semiconductor and C_{sol} of the solution side of the interface. However, generally $C_{\mathrm{sol}} \gg C_{\mathrm{sc}}$, and the contribution of the solution can be neglected. Then a plot of $1/C^2$ versus the electrode potential ϕ (which differs from ϕ_s by a constant) gives a straight line (see Fig. 11.3). From the intercept with the ϕ axis the flat-band potential is determined; if the dielectric constant ϵ is known, the donor density can be calculated from the slope. The same relation holds for the depletion layer of a p-type semiconductor.

Semiconductors that are used in electrochemical systems often do not meet the ideal conditions on which the Mott–Schottky equation is based. This is particularly true if the semiconductor is an oxide film formed in situ by oxidiz-

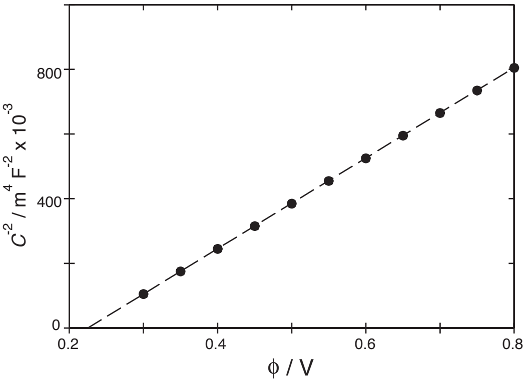

Fig. 11.3. Mott–Schottky plot for the depletion layer of an n-type semiconductor; the flat-band potential $E_{\rm fb}$ is at 0.2 V. The data extrapolate to $E_{\rm fb} + kT/e_0$.

ing a metal such as Fe or Ti. Such semiconducting films are often amorphous, and contain localized states in the band gap that are spread over a whole range of energies. This may give rise to a frequency dependence of the space-charge capacity, because localized states with low energies have longer time constants for charging and discharging. It is therefore important to check that the interfacial capacity is independent of the frequency if one wants to determine donor densities from Eq. (11.2).

11.3 Electron-transfer reactions

There is a fundamental difference between electron-transfer reactions on metals and on semiconductors. On metals the variation of the electrode potential causes a corresponding change in the molar Gibbs energy of the reaction. Due to the comparatively low conductivity of semiconductors, the positions of the band edges at the semiconductor surface do not change with respect to the solution as the potential is varied. However, the relative position of the Fermi level in the semiconductor is changed, and so are the densities of electrons and holes on the semiconductor surface.

The general shape of the current-potential curves for a perfect, nondegenerate semiconductor, for which the Fermi level lies well within the band gap, is easily derived. We first consider electron exchange with the conduction band. Since concentration of electrons in this band is very low, electron transfer from a redox couple in the solution to this band is not impeded by them. Further, since the relative position of the electronic levels in the solution and the semiconductor surface do not change with potential, the anodic current is constant, and we call its density j_0^c, the superscript indicating the conduction band. On the other, application of a negative overpotential η brings the band edge at the surface by an amount $e_0\eta$ closer to the Fermi level, and the concentration of electrons increases exponentially. Noting that for $\eta = 0$ the total current must vanish, we can write the current density passing through the conduction band as:

$$j^c = j_0^c \left[1 - \exp\left(-\frac{e_0\eta}{kT}\right)\right] \tag{11.3}$$

Obviously, this current-potential characteristics has rectifying properties (see Fig. 11.5).

Conversely, the valence band is practically full, and electron transfer from this band to the solution is constant; the corresponding current density we call $-j_0^v$. Electron transfer from the solution to the valence band is proportional to the density of holes in this band, which increases exponentially with $e_0\eta$. Therefore we obtain for the current through the valence band:

$$j^v = j_0^v \left[\exp\frac{e_0\eta}{kT} - 1\right] \tag{11.4}$$

Gerischer's terminology is popular in semiconductor electrochemistry, and it is instructive to calculate the currents in this model. This implies that the transfer is non-adiabatic, which seems plausible in view of the fact that the surface orbitals of semiconductors are less extended than those of metals.

We start from Eq. (10.14) for the rate of electron transfer from a reduced state in the solution to a state of energy ϵ on the electrode, and rewrite it in the form:

$$k_{\text{ox}}(\epsilon) = A' \int \left[1 - f(\epsilon)\right] W_{\text{red}}(\epsilon, \eta) d\epsilon \tag{11.5}$$

using Gerischer's terminology; Fig. 11.4 shows a corresponding plot. We have introduced $A' = A\Delta/\hbar$ for brevity. We still have to specify the integration limits. There are two contributions to the anodic current density, j_a^v from the valence and j_a^c from the conduction band. Denoting by E_v, E_c the band edges at the surface, we write for the current density:

$$j_a^v = FA'c \int_{-\infty}^{E_v - E_F} d\epsilon \ \left[1 - f(\epsilon)\right] W_{\text{red}}(\epsilon, \eta) \tag{11.6}$$

$$j_a^c = FAc \int_{E_c - E_F}^{\infty} d\epsilon \ \left[1 - f(\epsilon)\right] W_{\text{red}}(\epsilon, \eta) \tag{11.7}$$

Strictly speaking, the integrals should extend over the two bands only; however, far from the band edges the integrands are small; so the integration regions may safely be extended to infinity. The band edges E_v and E_c are measured with respect to the Fermi level of the electrode, and move with the overpotential; they are fixed with respect to the Fermi level of the redox couple in the solution. Writing $\Delta E_v = E_F - E_v(\eta = 0)$ and $\Delta E_c = E_c(\eta = 0) - E_F$, we have: $E_v - E_F = -\Delta E_v + e_0\eta$, $E_c - E_F = \Delta E_c + e_0\eta$. In the valence band $[1 - f(\epsilon)] \approx \exp[\epsilon/kT]$, in the conduction band $[1 - f(\epsilon)] \approx 1$, both approximations hold for nondegenerate semiconductors only. This gives:

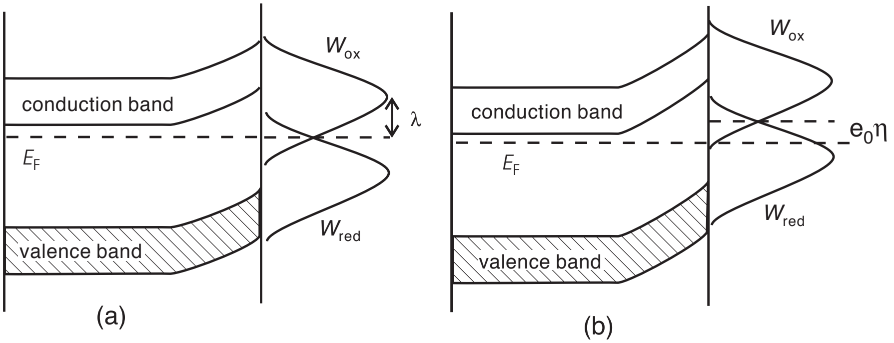

Fig. 11.4. Gerischer diagram for a redox reaction at an n-type semiconductor: (**a**) at equilibrium the Fermi levels of the semiconductor and of the redox couple are equal; (**b**) after application of an anodic overpotential.

$$j_a^v = FA'c \int_{-\infty}^{-\Delta E_v + e_0\eta} d\epsilon \ \exp \frac{\epsilon}{kT} \ W_{\text{red}}(\epsilon, \eta) \tag{11.8}$$

$$j_a^c = FA'c \int_{\Delta E_c + e_0\eta}^{\infty} d\epsilon \ W_{\text{red}}(\epsilon, \eta) \tag{11.9}$$

We substitute $\xi = \epsilon - e_0\eta$, and note that $W_{\text{red}}(\epsilon, \eta) = W_{\text{red}}(\epsilon - e_0\eta, 0)$:

$$\begin{aligned} j_a^v(\eta) &= FA'c \int_{-\infty}^{-\Delta E_v} d\xi \exp \frac{\xi + e_0\eta}{kT} W_{\text{red}}(\xi, 0) \\ &= j_a^v(\eta = 0) \exp \frac{e_0\eta}{kT} \qquad (11.10) \\ j_a^c(\eta) &= FA'c \int_{\Delta E_c}^{\infty} d\xi \ W_{\text{red}}(\xi, 0) = j_a^c(\eta = 0) \qquad (11.11) \end{aligned}$$

So, as already discussed above, the contribution of the valence band to the anodic current increases exponentially with the applied potential, because the number of holes that can accept electrons increases. In contrast, the anodic current via the conduction band is unchanged, since it remains practically empty. These equations hold independent of the particular form of the function W_{red}. Similarly the contributions of the valence and conduction bands to the cathodic current densities are:

$$\begin{aligned} j_c^v(\eta) &= FA'c \int_{-\infty}^{-\Delta E_v} d\xi \ W_{\text{ox}}(\xi, 0) \\ &= j_c^v(\eta = 0) \qquad (11.12) \\ j_c^c(\eta) &= FA'c \int_{\Delta E_c}^{\infty} d\xi \exp\left(-\frac{\xi + e_0\eta}{kT}\right) \ W_{\text{ox}}(\xi, 0) \\ &= j_c^c(\eta = 0) \exp\left(-\frac{e_0\eta}{kT}\right) \qquad (11.13) \end{aligned}$$

The contribution of the valence band does not change when the overpotential is varied, since it remains practically completely filled. In contrast, the contribution of the conduction band decreases exponentially with η (or increases exponentially with $-\eta$) because of the corresponding change of the density of electrons (Fig. 11.5). All equations derived in this section hold only as long as the surface is nondegenerate; that is, the Fermi level does not come close to one of the bands.

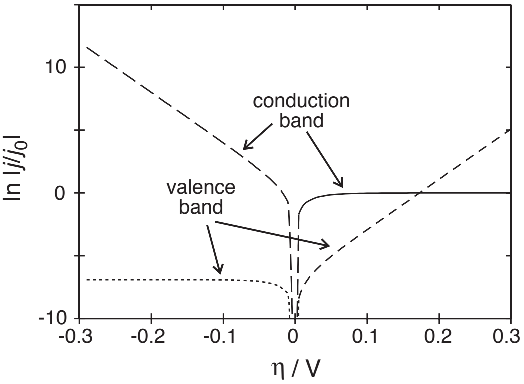

Fig. 11.5. Current-potential characteristics for a redox reaction via the conduction band or via the valence band. The current was normalized by setting $j_0^v = 1$. In this example the redox system overlaps more strongly with the conduction than with the valence band.

Typically the contributions of the two bands to the current are of rather unequal magnitude, and one of them dominates the current. Unless the electronic densities of states of the two bands differ greatly, the major part of the current will come from the band that is closer to the Fermi level of the redox system (see Fig. 11.4). The relative magnitudes of the current densities at vanishing overpotential can be estimated from the explicit expressions for the distribution functions $W_{\rm red}$ and $W_{\rm ox}$:

$$\begin{aligned} j_0^v &= FA'c \int_{-\infty}^{-\Delta E_v} d\xi \; W_{\rm ox}(\xi, 0) \\ &= 2FA'c \; \mathrm{erfc} \frac{\lambda + \Delta \mathrm{E_v}}{(4\lambda \mathrm{kT})^{1/2}} \end{aligned} \tag{11.14}$$

$$\begin{aligned} j_0^c &= FA'c \int_{\Delta E_c}^{\infty} d\xi \; W_{\rm red}(\xi, 0) \\ &= 2FA\rho_c \; \mathrm{erfc} \frac{\lambda + \Delta \mathrm{E_c}}{(4\lambda \mathrm{kT})^{1/2}} \end{aligned} \tag{11.15}$$

If the electronic properties of the semiconductor – the Fermi level, the positions of the valence and the conduction band, and the flat-band potential – and those of the redox couple – Fermi level and energy of reorganization – are known, the Gerischer [3] diagram can be constructed, and the overlap of the two distribution functions W_{ox} and W_{red} with the bands can be calculated.

Both contributions to the current obey the Butler–Volmer law. The current flowing through the conduction band has a vanishing anodic transfer coefficient, $\alpha_c = 0$, and a cathodic coefficient of unity, $\beta_c = 1$. Conversely, the current through the valence band has $\alpha_v = 1$ and $\beta_v = 0$. Real systems do not always show this perfect behavior. There can be various reasons for this; we list a few of the more common ones:

1. Electronic surface states may exist at the interface; they give rise to an additional capacity, so that the band edges at the surface change their energies with respect to the solution.
2. When the semiconductor is highly doped, the space-charge region is thin, and electrons can tunnel through the barrier formed at a depletion layer.
3. At high current densities the transport of electrons and holes may be too slow to establish electronic equilibrium at the semiconductor surface.
4. The semiconductor may be amorphous, in which case there are no sharp band edges.

An example of an electron-transfer reaction on a semiconductor electrode will be given in the next chapter.

11.4 Photoinduced electron transfer

Semiconducting electrodes offer the intriguing possibility to enhance the rate of an electron-transfer reaction by photoexcitation. There are actually two different effects: Either charge carriers in the electrode or the redox couple can be excited. We give examples for both mechanisms.

11.4.1 Photoexcitation of the electrode

If light of a frequency ν, with $h\nu \geq E_g$, is incident on a semiconducting electrode, it can excite an electron from the valence into the conduction band, so that an electron-hole pair is created. In the space-charge region the pair can be separated by the electric field, which prevents recombination. The electrical field produces a force F in the x direction perpendicular to the surface, and the equation of motion for an electron is given by:

$$F = -e_0 E_x = \hbar \frac{dk}{dt} \tag{11.16}$$

where k is the wavevector of the electron, and $\hbar k$ its momentum. For a hole, the force is in the opposite direction.

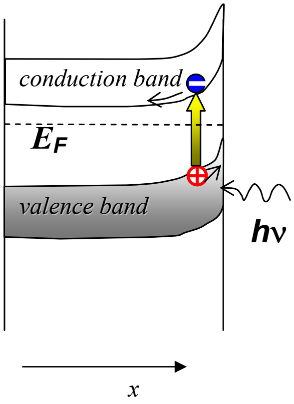

Fig. 11.6. Photogeneration of holes at the depletion layer of an n-type semiconductor.

Depending on the direction of the field, one of the carriers will migrate toward the bulk of the semiconductor, and the other will drift to the surface, where it can react with a suitable redox partner. These concepts are illustrated in Fig. 11.6 for a depletion layer of a n-type semiconductor. Holes generated in the space-charge region drift towards the surface, where they can accept electrons from a reduced species with suitable energy. According to the momentum balance for the system consisting of the electron–hole pair and the absorbed photon, we have:

$$k_e + k_h = k_{\rm ph} \approx 0 \tag{11.17}$$

since the wavevector for a phonon with an energy of the order of a few electron volt is negligible. Thus $k_h = -k_e$, and in a band-structure plot $E(k)$ the transition is vertical. This is the typical case when the maximum of the valence band and the minimum of the conduction band coincide, and one speaks of a *direct transition* – see Fig. 11.7. The threshold for direct transitions is given by $\hbar\nu = E_g$.

When the maximum of the valence band and the minimum of the conduction band do not lie at the same wavevector k, *indirect transitions* involving a phonon may occur. The principle is depicted on the right hand side of Fig. 11.7. A phonon is needed to conserve the total momentum. The adsorption threshold for indirect transitions between the band edges is:

$$h\nu = E_g + \hbar\Omega \tag{11.18}$$

where the last term accounts for the energy of the participating phonon.

The absorption coefficient α near the band edge depends on the photon energy according to:

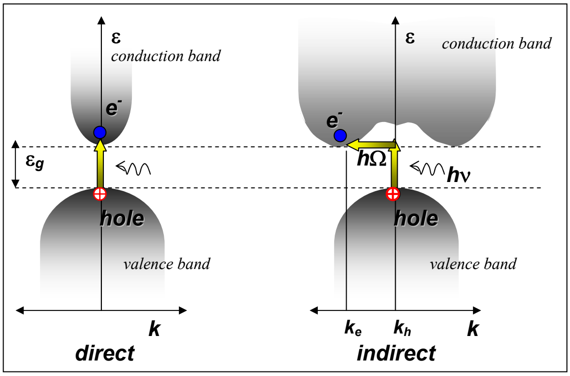

Fig. 11.7. Direct and indirect transitions

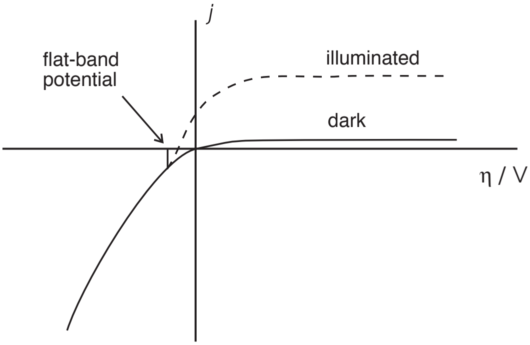

Fig. 11.8. Current-potential characteristics for an n-type semiconductor in the *dark* and *under illumination*. The difference between the two curves is the photocurrent.

$$\alpha = A\,\frac{(h\nu - E_g)^{n/2}}{h\nu} \tag{11.19}$$

We will not give the details of the derivation of this equation, which is complicated and depends on selection rules and the band structure. A is a constant and n depends on whether the transition is direct $(n = 1)$ or indirect $(n = 4)$.

The potential dependence of this photocurrent is shown in Fig. 11.8. It sets in at the flat-band potential and continues to rise until the band bending is so large that all the holes generated by the incident light reach the electrode surface, where they react with a suitable partner. If the reaction with the redox system is sufficiently fast, the generation of charge carriers is the rate-determining step, and the current is constant in this region.

In a real system the photocurrent can depend on a number of effects:

1. The generation of the carriers in the semiconductor.

2. The migration of the carriers in the space-charge region.
3. Diffusion of carriers that are generated outside the space-charge region.
4. Loss of carriers either by electron-hole recombination or by trapping at localized states in the band gap or at the surface.
5. The rate of the electrochemical reaction that consumes the carriers.

When all these factors contribute, the situation becomes almost hopelessly complicated. The simplest realistic case is that in which the photocarriers are generated in the space-charge region and migrate to the surface, where they are immediately consumed by an electrochemical reaction. We consider this case in greater detail. Suppose that light of frequency ν, with $h\nu > E_g$, is incident on a semiconducting electrode with unit surface area under depletion conditions (see Fig. 11.6). Let I_0 be the incident photon flux, and α the absorption coefficient of the semiconductor at frequency ν. At a distance x from the surface, the photon flux has decreased to $I_0 \ \exp(-\alpha x)$, of which a fraction α is absorbed. So the rate of carrier generation is:

$$g(x) = I_0 \alpha \ \exp(-\alpha x) \tag{11.20}$$

This equation presumes that each photon absorbed creates an electron-hole pair; if there are other absorption mechanisms, the right-hand side must be multiplied by a quantum efficiency. The total rate of minority carrier generation is obtained by integrating over the space-charge region:

$$\int_0^{L_{\rm sc}} I_0 \alpha \exp\left(-\alpha x\right) \ dx = I_0 \left[1 - \exp\left(-\alpha L_{\rm sc}\right)\right] \tag{11.21}$$

where the width L_{sc} of the space charge region is (see appendix):

$$L_{\rm sc} = L_0 (\phi - \phi_{\rm fb})^{1/2}, \quad \text{with} \quad L_0 = \left(\frac{\epsilon \epsilon_0}{e_0 n_{\rm b}} \right)^{1/2} \tag{11.22}$$

so that the the photocurrent generated in the space-charge layer is:

$$j_p = e_0 I_0 \left(1 - \exp\left[-\alpha L_0 (\phi - \phi_{\rm fb})^{1/2}\right]\right) \tag{11.23}$$

In the general case there may also be a contribution due to the diffusion of carriers from the bulk. This is treated in Problem 12.3, where the concept of a *diffusion length* L_d of the minority carriers is introduced. The sum of both contribution results in:

$$j_t = e_0 I_0 \left(1 - \frac{\exp\left[-\alpha L_0 (\phi - \phi_{\rm fb})^{1/2}\right]}{1 + \alpha L_d}\right) \tag{11.24}$$

For $\alpha L_d \ll 1$ the contribution from the bulk can be neglected. If in addition $\alpha L_{\rm sc} \ll 1$ the exponential can be expanded, and the flat-band potential can be determined by plotting the square of the photocurrent versus the potential:

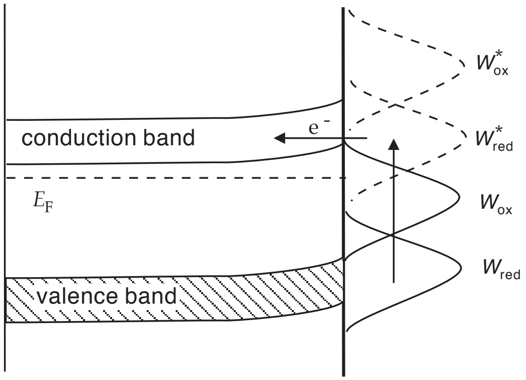

Fig. 11.9. Photoexcitation of a redox couple.

$$j_p^2 = (e_0 I_0 \alpha L_0)^2 (\phi - \phi_{fb}) \tag{11.25}$$

A plot of j_p^2 versus potential should result in a straight line, whose slope depends on the photon energy. The flat-band potential can be obtained from the intercept. We shall consider an example in Chap. 12.

11.4.2 Photoexcitation of a redox species

Another kind of photoeffect occurs if a redox system in its ground state overlaps weakly with the bands of the electrode but has an excited state which overlaps well. As an example, we consider an n-type semiconducting electrode with a depletion layer at the surface, and a reduced species red whose distribution function $W_{red}(\epsilon, \eta)$ lies well below the conduction band (see Fig. 11.9), so that the rate of electron transfer to the conduction band is low. On photoexcitation the excited state red* is produced, whose distribution function $W^*_{red}(\epsilon, \eta)$ overlaps well with the conduction band, so that it can inject electrons into this band. The electric field in the space-charge region pulls the electron into the bulk of the electrode, thus preventing recombination with the oxidized species, and a photocurrent is observed.

11.5 Dissolution of semiconductors

From a chemical point of view a hole at the surface of a semiconductor entails a missing electron and hence a partially broken bond. Consequently semiconductors tend to dissolve when holes accumulate at the surface. In particular this is true for enrichment layers of p-type material. At the depletion layers of n-type materials the holes required for the dissolution can also be produced by photoexcitation.

Such dissolution reactions usually contain several steps and are complicated. An important example is silicon. In aqueous solutions this is generally covered by an oxide film that inhibits currents and hence corrosion. However, in HF solutions it remains oxide free, and *p*-type silicon dissolves readily under accumulation conditions. This reaction involves two holes and two protons, the final product is Si(IV), but the details are not understood. A simpler example is the photodissolution of *n*-type CdS, which follows the overall reaction:

$$\mathrm{CdS} + 2\mathrm{h}^+ \rightarrow \mathrm{Cd}^{2+} + \mathrm{S} \tag{11.26}$$

under depletion conditions.

On polar semiconductors the dissolution may also involve electrons from the conduction band, leading to the production of soluble anions. For example, under accumulation conditions the dissolution of *n*-type CdS takes place according to the reaction scheme:

$$\mathrm{CdS} + 2\mathrm{e}^- \rightarrow \mathrm{Cd} + \mathrm{S}^{2-} \tag{11.27}$$

The dissolution of semiconductors is usually an undesirable process since it diminishes the stability of the electrode and limits their use in devices such as electrochemical photocells. On the other hand, the etching of silicon in HF solutions is a technologically important process.

Appendix: the Mott–Schottky capacity

We consider the depletion layer of an *n*-type semiconductor, assuming that the concentration of holes is negligible throughout. The situation is depicted in Fig. 11.10, which also defines the coordinate system employed. Starting from Eq. (11.1):

$$\frac{d^2\phi}{dx^2} = -\frac{e_0 n_\mathrm{b}}{\epsilon\epsilon_0}\left(1 - \exp\frac{e_0\phi}{kT}\right) \tag{11.28}$$

we again multiply both sides by $2d\phi/dx$, and integrate from zero to infinity, and obtain:

$$-E(0)^2 = \frac{2e_0 n_\mathrm{b}}{\epsilon\epsilon_0}\left(\phi_\mathrm{s} + \frac{kT}{e_0}\right) \tag{11.29}$$

where $\phi_s = \phi_\mathrm{s}$, and a term of the order $\exp[e_0\phi_s/kT]$ has been neglected. Noting that the potential $\phi(x)$ is negative throughout the space-charge region, we obtain:

$$\frac{\sigma}{\epsilon\epsilon_0} = \sqrt{\frac{2e_0 n_\mathrm{b}}{\epsilon\epsilon_0}}\sqrt{|\phi_\mathrm{s}| - \frac{kT}{e_0}} \tag{11.30}$$

Differentiation gives:

$$C = \frac{dq}{d\phi_\mathrm{s}} = \left(\frac{e_0 n_\mathrm{b}\epsilon\epsilon_0}{2[|\phi_\mathrm{s}| - kT/e_0]}\right)^{1/2} \tag{11.31}$$

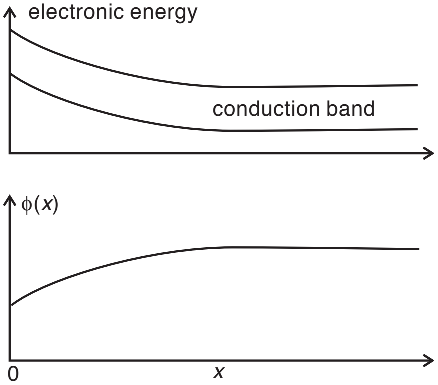

Fig. 11.10. Depletion layer at the surface of an n-type semiconductor; the surface is at $x = 0$.

which on rearranging gives Eq. (11.2).

The total width of the space-charge region can be estimated from the following consideration. Throughout the major part of the depletion region we have: $-e_0\phi \gg kT$, and the concentration of the electrons is negligible. In this region the exponential term on the right-hand side of Eq. (11.28) can be neglected, and the space charge is determined by the concentration of the donors – each donor carries a positive charge since it has given one electron to the conduction band. The band has a parabolic shape, but only the left half of the parabola has a physical meaning. The potential can be written in the form:

$$\phi(x) = -\frac{e_0 n_\mathrm{b}}{2\epsilon\epsilon_0}x^2 + ax + \phi_s \tag{11.32}$$

where:

$$a = \left.\frac{\partial\phi}{\partial x}\right|_{x=0} = -E(0) \tag{11.33}$$

The width L_sc of the space charge region is given by the position where the potential is minimal. Differentiation gives:

$$L_\mathrm{sc} = -\frac{\epsilon\epsilon_0}{e_0 n_\mathrm{b}}E(0) = \sqrt{\frac{2\epsilon\epsilon_0}{e_0 n_\mathrm{b}}|\phi_s|} \tag{11.34}$$

where terms of the order of kT/e_0 have been neglected. For practical purposes it is convenient to express ϕ_s through the flat-band potential:

$$L_\mathrm{sc} = \sqrt{\frac{2\epsilon\epsilon_0}{e_0 n_\mathrm{b}}|(\phi - \phi_\mathrm{fb})|} \tag{11.35}$$

Problems

1. Consider the case of small band bending, in which $|e_0\phi(x)| \ll kT$ everywhere. Expand the exponential in Eq. (11.1), keeping terms up to first order, and calculate the distribution of the potential.
2. (a) Prove that $n_c p_v = N_c N_v \exp(-E_g/kT)$. (b) The effective densities of states N_c and N_v are typically of the order of 10^{19} cm^{-3}. Estimate the carrier concentrations in an intrinsic semiconductor with a band gap of $E_g = 1$ eV, assuming that the Fermi level lies at midgap.
3. Consider the interface between a semiconductor and an aqueous electrolyte containing a redox system. Let the flat-band potential of the electrode be $E_{\mathrm{fb}} = 0.2$ V and the equilibrium potential of the redox system $\phi_0 = 0.5$ V, both versus SHE. Sketch the band bending when the interface is at equilibrium. Estimate the Fermi level of the semiconductor on the vacuum scale, ignoring the effect of dipole potentials at the interface.

References

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