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PHYSICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROCHEMISTRY*

TERMINOLOGY IN SEMICONDUCTOR ELECTROCHEMISTRY AND PHOTOELECTROCHEMICAL ENERGY CONVERSION

(Recommendations 1991)

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Terminology in semiconductor electrochemistry and photoelectrochemical energy conversion (Recommendations 1991)

SYNOPSIS

In this document recommendations for the usage of symbols and terminology in semiconductor electrochemistry are given. Such a supplement to conventional electrochemical usage is necessary because of the additional terminology based on solid state physics and chemistry. Since different symbols are conventionally used in electrochemistry and semiconductor physics for the same quantities, one has had to compromise with symbols in the present document which differ from those originally recommended by the Commission on Electrochemistry. In the present document energy levels in the bulk of the solid and the electrolyte including their interface are introduced and kinetic parameters defined. In addition a terminology on photoelectrochemical cells is recommended. In the latter case, it is distinguished between two modes of operation in these cells, i.e. photovoltaic cells in which radiant energy is converted into electrical energy and photoelectrolysis cells in which radiant chemistry causes a net chemical conversion.

INTRODUCTION

A *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (ref. 1) was prepared by the Commission on Symbols, Terminology and Units in 1969. A few years later the Commission on Electrochemistry published recommendations for usage of symbols and terminology in Electrochemistry (ref. 2) in an Appendix to that Manual (prepared by R. Parsons).

In the present document recommendations for the usage of symbols and terminology in semiconductor electrochemistry are given. Such a supplement to conventional electrochemical usage is necessary because of the additional terminology based on solid state physics and chemistry. Symbols, units and nomenclature in physics recommended by the S.U.N. Commission of the IUPAP [document UJP 11 (SUN 65-3), 1965] are incorporated. SI units are presumed. Since different symbols are conventionally used in electrochemistry and semiconductor physics for the same quantities, we have had to compromise with symbols in the present document which differ from those originally recommended by the Commission on Electrochemistry.

1. ENERGY LEVELS IN THE BULK AND AT THE SURFACE

1.0. A semiconductor is characterized by electron *energy levels* which are described by *energy bands.* Many electrochemical processes at semiconductor electrodes are interpreted in terms of energy models. Therefore a symbol for electron energy has to be introduced. The symbol E was selected because it is commonly used in solid state physics. This is in conflict with electrochemical terminology where E is a potential. Yielding to accepted solid state physics practice, we selected a symbol for potential different from E (see 1.2.).

1.1. The energy bands we consider here are the lowest *conduction band* and the highest *valence band*; for convenience these will be referred to throughout as "the conduction band" and "the valence band".

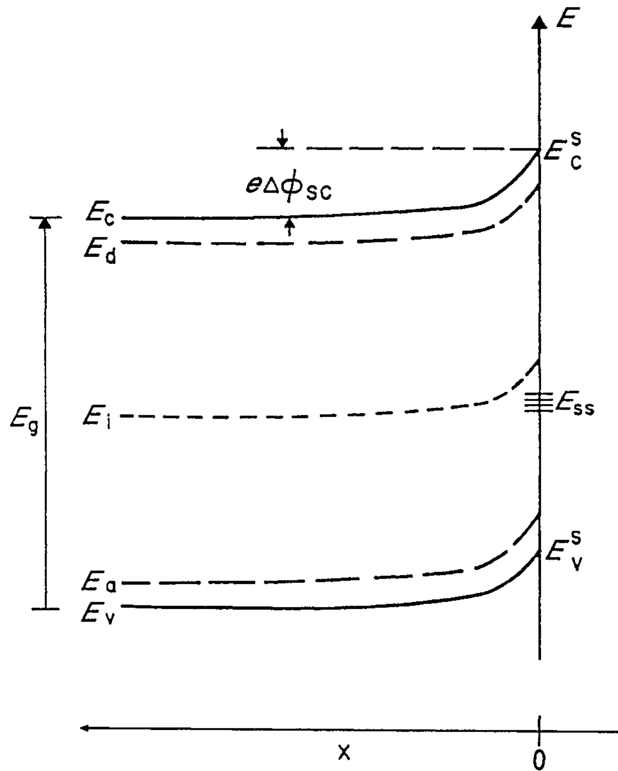

Fig 1: energy scheme of space charge region

The conduction band is nearly empty, or only partly filled with electrons (non-degenerate semiconductor). The lower edge of the conduction band has the

1.1.1. energy E_c in the bulk. The valence band is completely, or nearly filled with electrons. E_c

1.1.2. Its upper edge has the energy E_v in the bulk. The bands are illustrated in Fig. 1 in which x is the distance from the surface. E_v

1.1.3. The energy difference between the two band edges is the *bandgap*, E_g, which is equal to $E_c - E_v$. E_g

1.1.4. The *intrinsic energy level*, E_i, is located near the middle of the bandgap and is defined by E_i

$$E_i = \frac{1}{2} E_g + \frac{3}{4} kT \ln \left[\frac{m_h^*}{m_e^*} \right] + E_v$$

Note: The subscript and superscript symbols in this document (e.g. E_C, E_g, E_C^S) should, according to IUPAC recommendations (cf. ref. 1), have been printed in roman (upright) as in this note. However, because the text is no longer available on the computer memory and resetting cannot be justified on this account alone, necessary changes have not been made.

1.1.5. m_h^* and m_e^* are the *effective masses* of holes and electrons, respectively. — m_h^*, m_e^*

A semiconductor can be doped by introducing *electron donors* or *acceptors* which correspondingly

1.1.6. give rise to states of energy E_d and — E_d

1.1.7. E_a. Energy states located within the bandgap at the surface are *surface states* of — E_a

1.1.8. energy, E_{ss}. — E_{ss}

Energies and potentials at the interface

1.2 If a semiconductor is brought in contact with an electrolyte, a Helmholtz double layer having a potential

1.2.1. drop of $\Delta\phi_H$ (see Note a) is formed. At low ion concentrations — $\Delta\phi_H$

1.2.2. there is a further potential drop ($\Delta\phi_G$) that occurs within the electrolyte (*Gouy layer*). Since the carrier density (electrons or holes) in a semiconductor is usually small, and the Debye length (vide 6.1.12) is substantial, *a space charge region* is formed below the semiconductor surface leading to a corresponding — $\Delta\phi_G$

1.2.3. potential drop, $\Delta\phi_{sc}$, across this region. We will call $\Delta\phi_{sc}$ positive for upward band bending, which is the sense shown in Fig. 1. It is negative for downward band bending. (see Note b) — $\Delta\phi_{sc}$

1.2.4. Then the sum of all potentials is determined by the *Galvani potential*

$$\Delta\phi = \Delta\phi_{sc} + \Delta\phi_H + \Delta\phi_G.$$ — $\Delta\phi$

1.2.5. For a given semiconductor, the Galvani potential is related to the electrode potential U by

1.2.6. $$U = \Delta\phi + \text{const} = \Delta\phi_{sc} + \Delta\phi_H + \Delta\phi_G + \text{const}$$ — U

in which const is determined by the choice of reference electrode, as shown in Fig. 2. The potential across the space charge layer below

Note a : According to *Quantities, Units and Symbols in Physical Chemistry* (Blackwell Scientific Publications, Oxford, 1988), the symbols V and ϕ can be used for potentials and U, ΔV and $\Delta\phi$ for potential differences. We chose U and $\Delta\phi$ for electrode potential and local potential difference, respectively.

Note b : In solid state physics, opposite signs are used for $\Delta\phi_{sc}$.

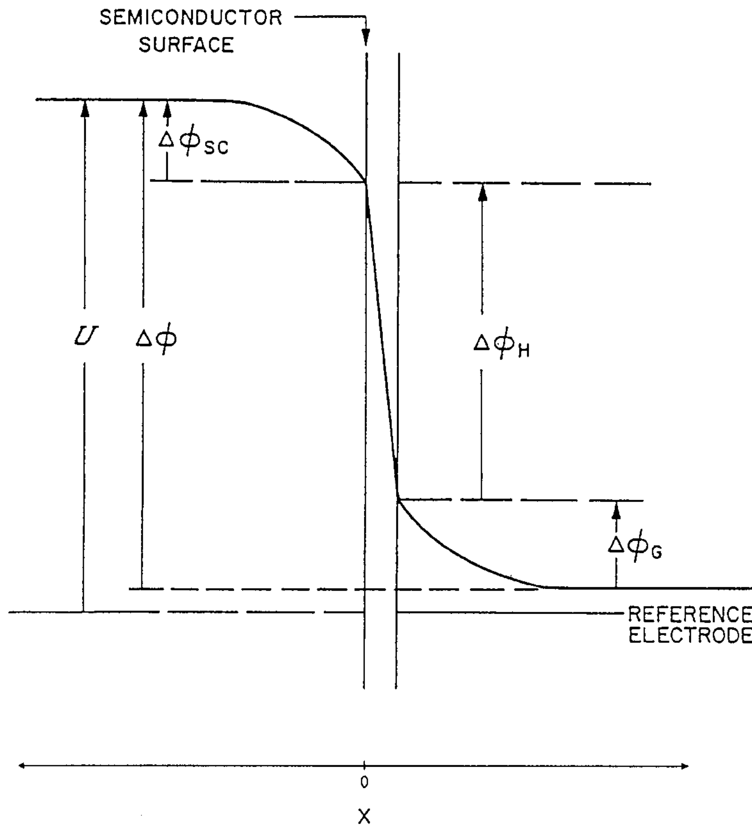

Fig 2: Potential distribution across the semiconductor-electrolyte interface

the semiconductor surface leads to a corresponding bending $e\Delta\phi_{sc}$ of the energy bands as shown in Fig. 1, e being the absolute value of the elementary charge.

1.2.7. At the surface (s) the lower edge of the conduction band, E_c^s, and E_c^s

1.2.8. the upper edge of the valence band, E_v^s, differ from the bulk values, E_c and E_v, by $e\Delta\phi_{sc}$, so that E_v^s

$$e\Delta\phi_{sc} = E_c^s - E_c = E_v^s - E_v$$

The *electrode potential*, U, can be varied by application of an external voltage to a value where the energy bands are flat ($\Delta\phi_{sc} = 0$). This defines

1.2.9. the *flat band potential*,

$$U = U_{fb}$$ U_{fb}

which can be deduced from capacity measurements under appropriate conditions (see section 6, especially 6.1.11.).

1.3. In solid state physics the vacuum level of an electron just outside the surface is taken as a reference point. With respect to this vacuum level all other energies are taken as negative values. In an electrode/solution two phase system, the reference point is in a vacuum just outside the solution surface. This energy scale can be correlated to the standard electrochemical scale by

1.3.1.

$$E_{(vac)} = E_{(SHE)} - eU$$

$E_{(vac)}$

$E_{(SHE)}$

in which $E_{(SHE)}$ is the energy of an electron at the potential of the standard hydrogen electrode in the absolute energy scale. The energy scales are illustrated (Figure 3) in an energy diagram taken from Trasatti (ref. 3) with $E_{(SHE)} = -4.44 \pm 0.02$ eV, based on the standard hydrogen electrode in water.

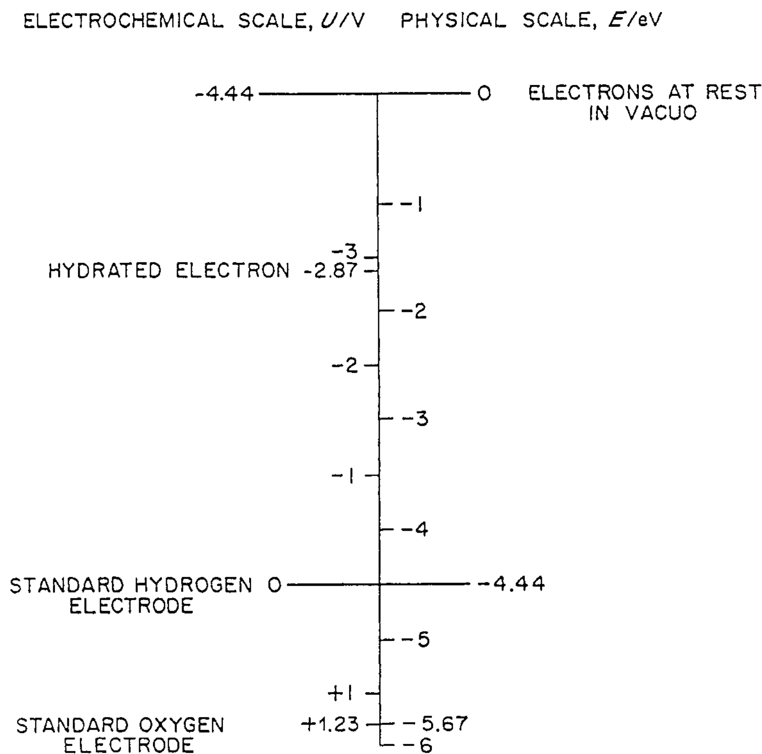

Fig 3: energy scale

2. CONCENTRATIONS OF CHARGE CARRIERS

2.1. In n-type semiconductors the mobile electrons in the conduction band are the majority charge carriers.

2.1.1. Their density, n_o, in the bulk semiconductor is higher than the — n_o

2.1.2. corresponding *hole* (minority carriers) *density*, p_o, in the bulk semiconductor, $n_o > p_o$. — p_o

In a p-type semiconductor the holes are the majority carriers and $p_o > n_o$. At equilibrium one has

2.1.3. $$n_o p_o = n_i^2$$ — n_i

in which n_i is the intrinsic electron density in the conduction band for an intrinsic semiconductor. If the energy bands are bent upwards or downwards the electron and hole densities differ from those in the bulk. If a Boltzmann distribution is assumed,

2.1.4. the *surface electron density* n_s is given by — n_s

$$n_s = n_o \exp\frac{-e\Delta\phi_{sc}}{kT}$$

2.1.5. and the *surface hole density* p_s by — p_s

$$p_s = p_o \exp\frac{e\Delta\phi_{sc}}{kT}$$

The electron and hole densities in the bulk of a semiconductor having shallow donors and acceptors, i.e. one with $|E_a - E_v| \leq kT$ and $|E_d - E_c| \leq kT$, depend, respectively, on

2.1.6. the *donor density*, N_d — N_d

2.1.7. and the *acceptor density*, N_a, as well as on the density — N_a

2.1.8. of energy states in the band, N_c. The latter is given by — N_c

$$N_c = 2\left\{\frac{2\pi m_e^* kT}{h^2}\right\}^{3/2}$$

This is the volume density of states within 1 kT of the lower edge of the conduction band.

2.1.9. The *volume density of energy states* N_v within 1 kT of the upper edge of the valence band is given by N_v

$$N_v = 2\left[\frac{2\pi m_h^* kT}{h^2}\right]^{3/2}$$

The correlations between n and N_c, or p and N_v, are given by 3.2.3. and 3.2.4.

Electron and holes can also be trapped in surface states.

2.1.10. The density of surface states is expressed as N_{ss} per unit surface area. N_{ss}

3. CHEMICAL POTENTIALS AND FERMI LEVELS

In accordance with the definition of the

3.1. chemical potential of a species B in phase β, μ_B^β, the electrochemical potential of electrons in a μ_B^β

3.1.1. semiconductor (sc) is given by $\tilde{\mu}_e^{sc}$ $\tilde{\mu}_e^{sc}$

3.1.2. and that of holes by $\tilde{\mu}_h^{sc}$. Considering only the bulk of the semiconductor, the $\tilde{\mu}_h^{sc}$

3.2. electrochemical potentials of electrons and holes are identical

3.2.1. to the *Fermi levels* of electrons, $E_{F(e)}$, $E_{F(e)}$

3.2.2. and holes, $E_{F(h)}$, respectively. The Fermi levels are related to the electron and hole densities by $E_{F(h)}$

3.2.3.

$$E_{F(e)} = E_c + kT \ln \frac{n_o}{N_c}$$

and

3.2.4.

$$E_{F(h)} = E_v - kT \ln \frac{p_o}{N_v}.$$

If equilibrium exists between electrons and holes, then

3.2.5.

$$E_{F(e)} = E_{F(h)} = E_F$$

Similarly the electrochemical potential, $\tilde{\mu}_e^s$, of electrons $\tilde{\mu}_e^s$

3.3. in an electrolytic solution containing a redox system is defined in terms of the difference between the electrochemical potentials of the reduced and oxidized forms, i.e.

3.3.1.

$$\tilde{\mu}_e^s = \tilde{\mu}_{red} - \tilde{\mu}_{ox}$$

The corresponding concentration dependence is given by

3.3.2. $$\tilde{\mu}_e^s = \tilde{\mu}_e^{so} + kT \ln \frac{c_{ox}}{c_{red}}$$ $\tilde{\mu}_e^{so}$

3.3.3. The standard electrochemical potential $\tilde{\mu}_e^{so}$ is related to the standard redox potential by

3.3.4. $$\tilde{\mu}_e^{so} = E_{(SHE)} - eU_{redox}^o$$

If the two phases in contact, semiconductor and electrolyte, are at equilibrium, then the electrochemical potential of the electron must be equal on both sides of the interface, or

3.3.5. $$E_F = \tilde{\mu}_e^s$$

This leads to a corresponding charging of the interface and a certain potential distribution. This situation is illustrated for an n-type semiconductor in Fig. 4a.

3.4. If the electrode potential is varied by an external source, the deviation from equilibrium η

3.4.1. is defined as the *overpotential*, η. This overpotential occurs as the difference between the electrochemical potential of electrons on the two sides of the interface, provided that electrons and holes are in equilibrium in the whole electrode. If no equilibrium exists, the Fermi energies of electrons and holes are different. By analogy with 3.2.3. and 3.2.4. we define *quasi-Fermi levels* for electrons and holes in terms of carrier densities,

3.4.2. $$E_{F(e)}(x) = E_c + kT \ln \frac{n(x)}{N_c}$$

and

3.4.3. $$E_{F(h)}(x) = E_v - kT \ln \frac{p(x)}{N_v}$$

The carrier densities $n(x)$ and $p(x)$ vary with the distance x from the surface so that, under non-equilibrium conditions, the quasi-Fermi levels depend on x. The majority carrier density is usually so little affected that its Fermi level remains constant over whole electrode, as shown for an n-type semiconductor in Fig. 4b. Here the overpotential

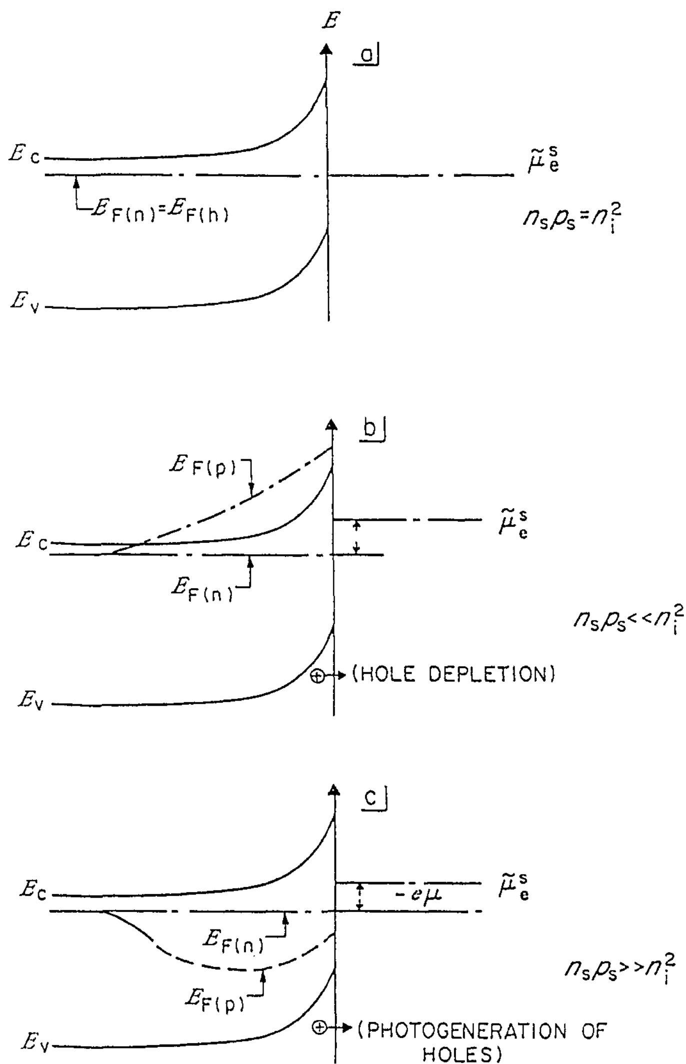

Fig 4: variation of band bending and Fermi level during polarisation of a n-type electrode
a) at equilibrium
b) under anodic polarization
c) under cathodic polarization

occurs as the difference between the Fermi level in the electrolyte and the quasi-Fermi level of the majority carriers.

3.4.4. Electrons and holes are not in equilibrium, for instance, when minority carriers (holes in n-type) are consumed in an anodic process, $np \ll n_i^2$. According to 3.4.4. the quasi-Fermi level of holes is then located far above the Fermi level of electrons (Fig. 4b). The deviations occur over a distance from the surface corresponding to the diffusion length of the minority carriers (see also 5.2.).

During light excitation the *minority carrier density* is strongly increased compared to its equilibrium value. In this case we have

3.4.5. $$np \gg n_i^2$$

and the quasi-Fermi level of the minority carriers is closer to its corresponding band (valence band in the case of holes). The distance dependence of the quasi-Fermi level is complicated. It is determined by the *diffusion length* and the penetration depth of light (see 8.1.), as illustrated in Fig. 4c.

In most situations except those in which intense light creates a significant number of carriers, the Fermi level of the majority carriers remains constant because their population increase is relatively small.

4. ENERGY STATES AND THEIR DENSITIES IN ELECTROLYTES CONTAINING REDOX SYSTEMS

A number of theories concerning electron transfer processes at electrodes have been developed. In semiconductor electrochemistry the model and formalism derived by Gerischer (ref. 4) is sometimes applied. This model has the advantage that energy levels of localized electron states in an electrolyte can be introduced. Although it is not the purpose of this document to evaluate a theory, certain terminology is introduced here because the model is utilized, at least for a qualitative description. In this model redox systems are characterized by a set

of *occupied energy states*

4.1.1. with members at values E_{red} and a set of *empty energy states* — E_{red}

4.1.2. with members at values E_{ox} — E_{ox}

Usually a gaussian distribution is used to describe the density of states per unit energy with D_{red} — D_{red}

4.1.3. describing occupied states and D_{ox} — D_{ox}

describing empty states.

The *density of the occupied states*, at any energy, N_{red} — N_{red}

4.1.4. is related to the concentration of the reduced form c_{red}, by — c_{red}

$$N_{red} = D_{red}\, c_{red}$$

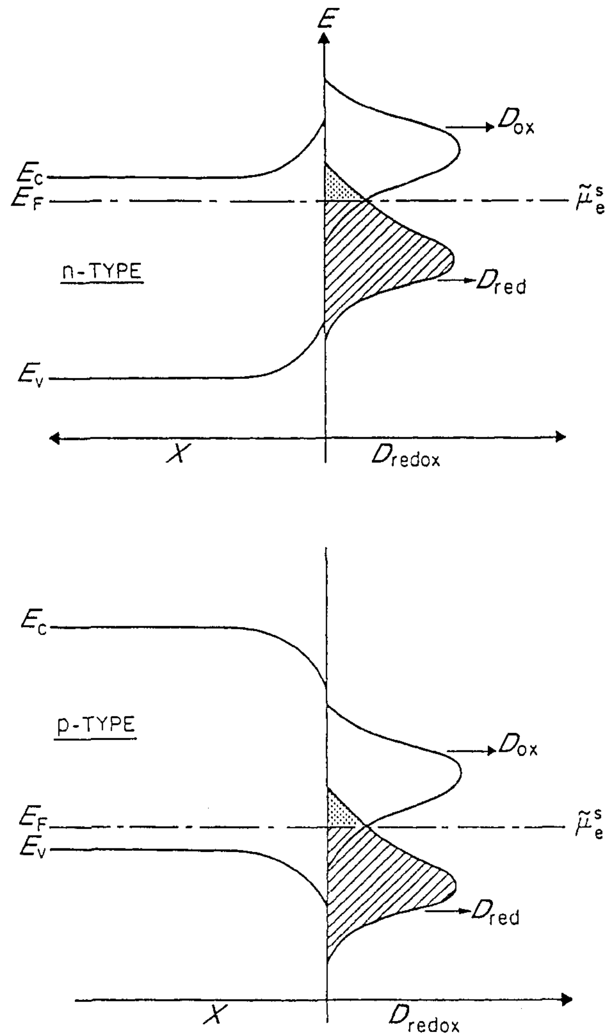

Fig 5: energy states at the semiconductor-electrolyte interface

4.1.5. The *density of empty states* N_{ox} is given by N_{ox}

$$N_{ox} = D_{ox}\ c_{ox}$$

4.1.6. in which c_{ox} is the concentration of the oxidized form. c_{ox}

The distribution functions have equal values at the equilibrium value of the electrochemical potential of the electrons, i.e., at this energy one has equal densities of occupied and empty states. The energy scheme given in Fig. 5 may be useful for the interpretation of the kinetics (see Section 7).

5. DIFFUSION LENGTH AND MOBILITY OF ELECTRONS AND HOLES IN THE SEMICONDUCTOR

5.1.1. The *diffusion coefficient of electrons*, D_e, D_e

5.1.2. is related to the *electron mobility*, μ_e (see Note c) by the Einstein equation μ_e

5.1.3.

$$D_e = \frac{kT}{e}\,\mu_e$$

In the same way the diffusion coefficient

5.1.4. for holes, D_h D_h

5.1.5. is related to the hole mobility μ_h μ_h

5.1.6. by

$$D_h = \frac{kT}{e}\,\mu_h$$

In charge transfer reactions (see Section 7) the minority carrier density can be a determining factor of the transfer rate.

5.2.1. The corresponding diffusion length, L_e of electrons, the minority carriers in p-type material, is defined by L_e

$$L_e = (D_e \tau)^{1/2}$$

5.2.2. and of holes, L_h, in n-type material by L_h

$$L_h = (D_h \tau)^{1/2}\,.$$

τ is the lifetime of the minority carriers generated, for instance, by thermal or light excitation (see also 8.5.2.).

6. CHARGES AND CAPACITIES AT THE INTERFACE

6.1. The potential and charge distribution within the space charge region below the semiconductor surface is determined by the Poisson equation

6.1.1.

$$-\frac{d^2\phi_{sc}}{dx^2} = \frac{\rho(x)}{\varepsilon_r \varepsilon_o}$$

in which $\varepsilon = \varepsilon_r \cdot \varepsilon_o$ is the permittivity with ε_r being the relative permittivity (dielectric constant) of the semiconductor and ε_o being the permittivity of vacuum.

Note c : Although this symbol is also used for the chemical potential we prefer to take it as well for mobility of electrons because such usage is common in solid state physics and the chemical potential and mobility of electrons commonly do not occur in one equation.

6.1.2. The charge, ρ, depends on the distance x from the surface and is given by

6.1.3. $$\rho(x) = e[N_d^+ - N_a^- - n(x) + p(x)]$$

N_d^+

N_a^-

in which N_d^+ and N_a^- are the total densities of the charged donor and acceptor states, respectively (see also Section 2). The *field strength* $\mathbf{E}_s$

$\mathbf{E}_s$

6.1.4. at the surface is given by

$$-\mathbf{E}_s = \frac{d\phi_{sc}}{dx} |_{x=0}$$

which can be obtained by integration of the Poisson equation.

6.1.5. 6.1.1. The *space charge*, σ_{sc}, which produces this field strength is given by

σ_{sc}

$$\sigma_{sc} = \varepsilon_r \varepsilon_o \mathbf{E}_s$$

σ_{sc} is positive for upward and negative for downward band bending (see 1.2.3).

Since the space charge, σ_{sc}, depends on the potential,

6.1.6. $\Delta\phi_{sc}$, across the space charge layer, the *differential capacity*, C_{sc}, *of the space charge* is defined as

C_{sc}

$$C_{sc} = \frac{d\sigma_{sc}}{d(\Delta\phi_{sc})}$$

In an equivalent circuit diagram, C_{sc} is in series

6.1.7. with the *Helmholtz capacity*, C_H (see Note d)

C_H

Three cases are distinguishable for the space charge region, as shown for a n-type semiconductor in fig. 6

6.1.8. (i) *accumulation region*:

The energy bands are bent downward and

$n_s > n_o$ and $p_s < p_o$

Note d : also represented by C^i (see Pure Appl. Chem. 58, 437 (1986)).

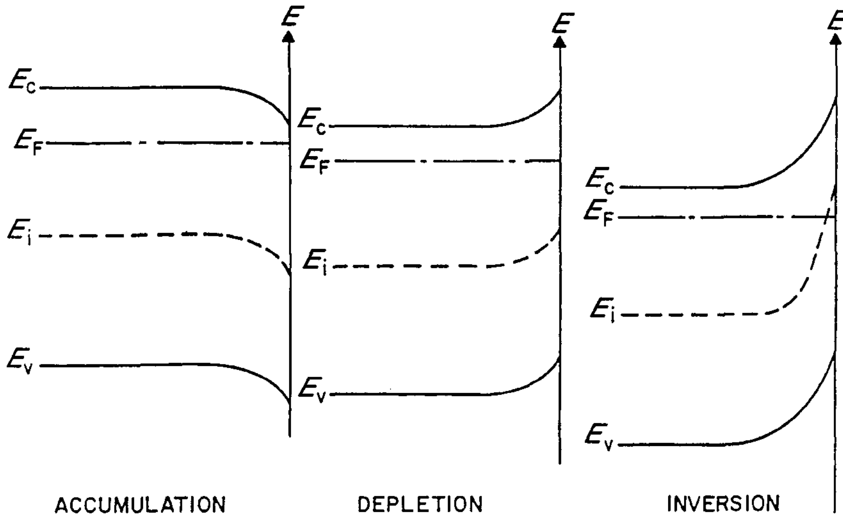

Fig 6: Formation of accumulation, depletion and inversion layer within the space charge region

6.1.9. (ii) *depletion region*:

The energy bands are bent upward and

$n_s < n_o$

If equilibrium between electrons and holes exists at the surface ($n_s p_s = n_i^2$), then

$p_s > p_o$ but $p_s < n_s$

In the latter case depletion occurs only if the Fermi level is still above E_i at the surface.

6.1.10. (iii) *inversion region*

The energy bands are bent upwards and the Fermi level is located below E_i at the surface, i.e.

$$p_s > n_s$$

This condition can only be achieved if electrons and holes are at equilibrium at the surface. If minority carriers (holes) are consumed in a reaction equilibrium may no longer exist and

$$p_s < n_s$$

In this case we have only a depletion of majority carriers (electrons) at the surface although the band bending is high. A quantitative

relation of the space charge capacity, C_{sc}, to $\Delta\phi_{sc}$ can be calculated from 6.1.6, which is valid for all three regions. In the accumulation and inversion region C_{sc} varies exponentially with $\Delta\phi_{sc}$. The majority and minority carriers determine C_{sc} in the accumulation and inversion regions, respectively. In the depletion range the $C_{sc} - \Delta\phi_{sc}$ relation can be approximated by the *Mott-Schottky equation*

6.1.11.

$$\frac{1}{C_{sc}^2} = \left[\frac{2\,L_D}{\varepsilon_r\,\varepsilon_o}\right]^2 \left[\frac{e\Delta\phi_{sc}}{kT} - 1\right]$$

This equation is only valid under certain conditions, e.g. with a homogeneous distribution of shallow donor and acceptor states and their complete ionization. Further, surface states or bulk defects contributing to parallel capacitive components must be negligible (see 6.2.4).

6.1.12. The *Debye length* L_D is given by L_D

$$L_D = \left\{\frac{\varepsilon_r\,\varepsilon_o kT}{2n_o e^2}\right\}^{1/2}$$

By varying $\Delta\phi_{sc}$ by means of the electrode potential, U, the *flat band potential*, U_{fb}, (see Section 1) can be determined (subject to the conditions under which eq. 6.1.11 is valid) by extrapolation ($1/C_{sc}^2 \rightarrow 0 \rightarrow \Delta\phi_{sc} \approx 0$).

6.1.13. The *thickness of the space charge layer under depletion conditions* is defined by d_{sc}

$$d_{sc} = \frac{\varepsilon_r\,\varepsilon_o}{C_{sc}} = 2\,L_D \left\{\frac{e\Delta\phi_{sc}}{kT} - 1\right\}^{1/2}$$

i.e., it varies with carrier density and band bending.

The Mott-Schottky equation is of special importance because it is also valid for very large band bendings (E_F below E_i) if electrons and hole are not in equilibrium ($p_s n_s < n_i^2$); i.e., if no true inversion occurs. This situation may occur in aqueous electrolytes when minority carriers are consumed rapidly in anodic reactions at n-type and in cathodic reactions at p-type electrodes.

The region of potential for accumulation is very small if the Fermi level is close to the respective band in the bulk.

6.2. Charges can also be located in surface states (Figure 1). The

6.2.1. corresponding charge density, σ_{ss}, in surface states of particular energy is related to the *density of surface states*, N_{ss}, by

σ_{ss}

6.2.2.

$$\sigma_{ss} = -efN_{ss}$$

in which the *Fermi distribution function* f is given by

6.2.3.

$$f = \frac{1}{1 + \exp\frac{E_{ss}-E_F}{kT}}$$

If $E_F = E_{ss}$ at the surface then $f = 0.5$. Since $E_{ss} - E_F$ depends on the potential across the space charge layer $\Delta\phi_{sc}$, σ_{ss} varies with $\Delta\phi_{sc}$. Therefore one can define a *differential surface state capacity C_{ss} by*

6.2.4.

$$C_{ss} = \frac{d\sigma_{ss}}{d(\Delta\phi_{sc})} = eN_{ss}\frac{df}{d(\Delta\phi_{sc})}$$

C_{ss}

Since the charges in the surface states are always changed in the same direction as the space charge itself, C_{ss} can be described in an equivalent circuit by a capacitance in parallel to that of the space charge.

In some cases the properties of the semiconductor-electrolyte interface can also be investigated by the surface conductance method. The surface conductivity is given in terms of the mobilities μ_e and μ_h by (see Note e)

$$\Delta\sigma = e(\mu_e\Gamma_e + \mu_h\Gamma_h)$$

$\Delta\sigma$

6.3.3. in which Γ_e and Γ_h are the excess electron and hole densities given by

Γ_e

Γ_h

$$\Gamma_e = \int_o^\infty (n-n_o)dx;\ \Gamma_h = \int_o^\infty (p-p_o)dx$$

n and p depend on the band bending.

Note e : The symbol σ is also used for surface charge; we follow physics usage here.

6.4. The potential distribution across the semiconductor/solution interface is determined by the relative magnitudes of the different capacitances (C_{sc}, C_{ss}, C_H) referred to in 6.1.6, 6.1.7., and 6.2.4. When the differential capacitance of the space charge is much less than the Helmholtz capacity ($C_{sc} \ll C_H$), the externally applied potential occurs almost entirely across the space charge layer (i.e., $\Delta U = \Delta\phi_{sc}$). Operationally, under these conditions U_{fb} is independent of the potential of the redox couple in solution (in the absence of specific adsorption). Consequently the conduction and valence band energies at the surface do not move with respect to electrolyte energy levels at the surface. The Fermi level, however, can move, and can thus be described as "unpinned".

6.4.1. When the semiconductor surface capacitance approaches the order of C_H, (as e.g. from a high density of minority populated surface states), the externally applied potential drop is distributed both across the semiconductor surface and the Helmholtz layer. Thus changes in the redox potential (Fermi level) of the electrolyte will not correspondingly change the band bending. In the limit, variation of the applied potential will result only in a corresponding change of the potential across the Helmholtz layer. Under these conditions, U_{fb} will vary directly with the redox potential and the photopotential (Section 8) will become independent of the nature of the redox couple. This situation has been termed Fermi level "pinning". It is important to note this experimental independence can have other origins; band inversion or accumulation, corrosion reactions, and limitations imposed by bulk recombination processes. Interpretation in terms of Fermi level "pinning" from surface states thus requires exclusion of other phenomena.

7. KINETICS OF ELECTRODE REACTIONS

7.1. An electrochemical oxidation or reduction of a species A dissolved in the electrolyte can occur via *electron transfer* to or from the

conduction band,

7.1.1.

$$A + ne^- \rightleftarrows A^{n-}$$

or via *hole transfer* to or from the valence band,

7.1.2.

$$A + nh^+ \rightleftarrows A^{n+}$$

7.2. A current of positive electricity passing from the electrode into the electrolyte is taken as positive. When a single electrochemical reaction occurs at an electrode then

7.2.1. the *total current density*, j, consists of partial anodic (cathodic) currents, $j_a (j_c)$

$$j = j_a + j_c$$

j j_a j_c

In semiconductor electrochemistry it is useful to split the partial currents into two portions, one representing the charge transfer via the conduction band, the other via the valence band. Then we have

7.2.2. $$j_a = j_{a,c} + j_{a,v} \quad \text{and} \quad j_c = j_{c,c} + j_{c,v}$$

$j_{a,c}$ $j_{a,v}$

in which $j_{a,c}$ and $j_{a,v}$ are the *partial anodic current*

7.2.3. densities via the conduction and valence bands, respectively,

7.2.4. and $j_{c,c}$ and $j_{c,v}$, the corresponding *cathodic current densities*.

$j_{c,c}$ $j_{c,v}$

7.2.5. *Exchange current density*, j_o, is the value of the anodic and cathodic currents when the reaction is at equilibrium ($j = 0$),

j_o

7.2.6. $$j_o = j_{o,a} = -j_{o,c}$$

$j_{o,a}$ $j_{o,c}$

7.3. When the potential across the Helmholtz layer, $\Delta\phi_H$, is independent of the overvoltage, η is identical to $\Delta(\Delta\phi_{sc})$, i.e. $\Delta(\Delta\phi_{sc}) = \Delta\phi_{sc} - \Delta\phi_{sc}^o$ (equilibrium) as indicated in Fig. 7.

$\Delta(\Delta\phi_{sc})$ $\Delta\phi_{sc}^o$

7.4. The current-potential dependences are determined by the partial currents. With this model, when the charge transfer processes occur

very close to the band edges, the partial currents can be defined by

7.4.1. $$j_{a,c} = n\ e\ k_{a,c} c_{red} N_c D_{red}(E_c) = \text{const} = j^o_{a,c}$$ $k_{a,c}$

7.4.2. $$j_{a,v} = n\ e\ k_{a,v} c_{red} p_s D_{red}(E_v) = j^o_{a,v} \exp(\frac{e\eta}{kT})$$ $k_{a,v}$

with

$$j^o_{a,v} = n\ e\ k_{a,v} c_{red} p^o_s D_{red}(E_v)$$

in which n is the charge number of the electrode reaction and $k_{a,c}$ and $k_{a,v}$ the corresponding rate constants. N_c, p_s, D_{ox} and D_{red} are defined in Section 2 and 4. It is assumed here that the electron transfer occurs at E_c or E_v as indicated by corresponding arrows in Fig. 7.

The cathodic currents are given by

7.4.3. $$j_{c,c} = -n\ e\ k_{c,c} c_{ox} n_s D_{ox}(E_c) = -j^o_{c,c} \exp(-\frac{e\eta}{kT})$$ $k_{c,c}$

with

$$j^o_{c,c} = -n\ e\ k_{c,c} c_{ox} n^o_s D_{ox}(E_c)$$

and

$$j_{c,v} = -n\ e\ k_{c,v} c_{ox} N_V D_{ox}(E_v) = \text{const} = j^o_{c,v}$$ $k_{c,v}$

in which the k's are the corresponding rate constants.

7.5. According to 7.4.1.-7.4.3. the anodic current via the valence band ($j_{a,v}$) and the cathodic current via the conduction band ($j_{c,c}$) depend on the overpotential via the potential dependence of p_s and n_s, respectively. A corresponding current rise with increasing potential can only occur if the holes or electrons are the majority carriers. If minority carriers are consumed at the semiconductor surface then these can reach the surface only by diffusion. The corresponding *diffusion currents* are given by

7.5.1. $$j_{e,diff} = e\frac{D_e n_o}{L_e}$$ $j_{e,diff}$

for electrons and

$$j_{h,diff} = e\frac{D_h p_o}{L_h}$$ $j_{h,diff}$

for holes, with D_e, D_h, L_e and L_h described as in 5.1.3-5.2.6.

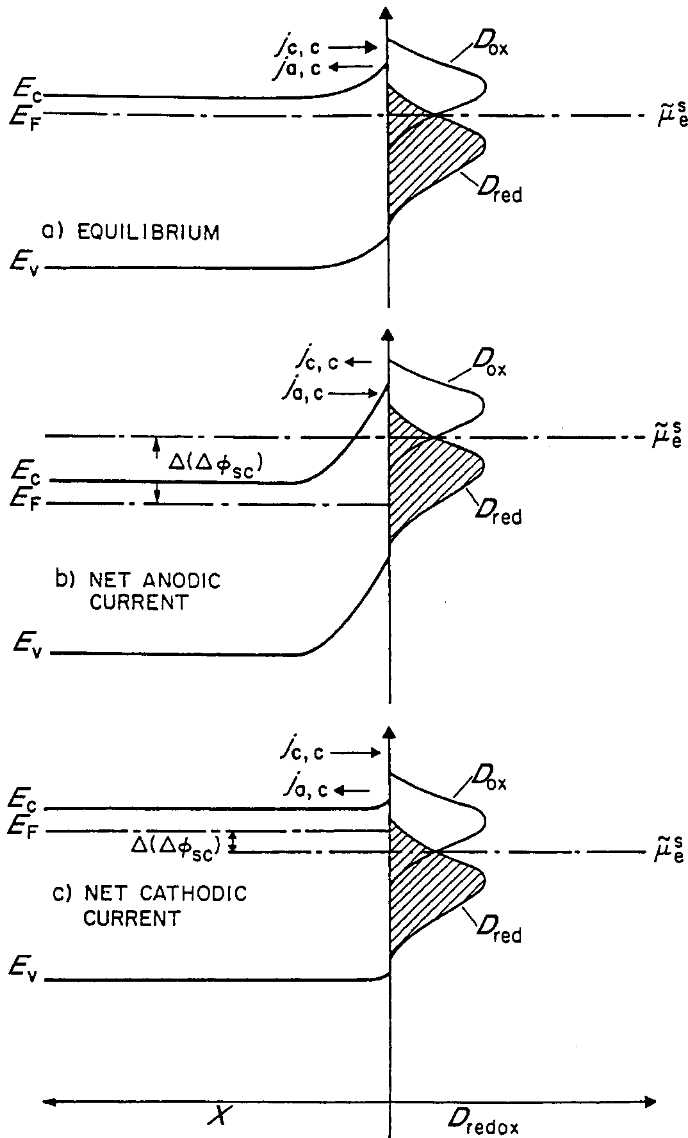

Fig 7: Partial currents (arrows) across the semiconductor (n-type) - electrolyte interface

Accordingly, we have

7.5.2. $j_{a,v} = j_{h,diff}$ for n–type electrodes

and

7.5.3. $j_{c,c} = j_{e,diff}$ for p–type electrodes

These currents are independent of potential and are entirely determined by the generation/recombination behavior of minority carriers in the semiconductor.

7.6. Electron transfer can also occur via surface states. The corresponding anodic and cathodic currents are defined as

7.6.1. $$j_{a,s} = n\ e\ k_{a,s} c_{red} (1-f) N_{ss} D_{red}$$ $j_{a,s}$

and

7.6.2. $$j_{c,s} = -n\ e\ k_{a,s} c_{ox} f N_{ss} D_{ox}$$ $j_{c,s}$

in which $k_{a,s}$ and $k_{c,s}$ $k_{a,s}$ $k_{c,s}$

7.6.3. represent the corresponding rate constants.

8. PHOTOEFFECTS

When light is absorbed by a uniform medium the

8.1. corresponding *absorption coefficient*, α, is defined by α

8.1.1. $$\alpha = \frac{1}{d} \ln \frac{I^o}{I}$$ I^o

8.1.2. I^o is the *incident light intensity*, I the *transmitted intensity*, and d the *thickness of the sample*. It is useful also to define the reciprocal value of α as the *penetration depth of light*, i.e.

8.1.3. $$L_\lambda = \frac{1}{\alpha}$$ L_λ

L_λ depends on the wavelength of the incident light. In the dark the semiconductor electrode attains a certain electrode potential, U_d, vs. a reference electrode under open circuit conditions. U_d
This electrode potential is correlated to a certain band bending, $\Delta\phi_{sc}$. When a semiconductor-electrolyte interface is illuminated under *open circuit conditions* (i.e. at zero current) and light is absorbed by the semiconductor, the band bending, and consequently the potential, $\Delta\phi_{sc}$, across the space charge layer decreases. Under illumination this leads to a corresponding shift of the electrode potential vs. a reference electrode to a new value, U_{ph}. U_{ph}

8.2. The photopotential developed during light excitation is given by

8.2.1. $$\Delta U_{ph} = | U_{ph} - U_d |$$ ΔU_{ph}

The magnitude of the photopotential is taken in absolute values

because the electrode potential is shifted in opposite directions for n- and p-type electrodes (negative vs. a reference electrode for n-, positive for p-).

8.2.2. The electrode potential under illumination, U_{ph}, depends on light intensity and the bands flatten until a final value, U_{ph}^{max}, is approached at higher light intensities. U_{ph}^{max}

This value may reach, but cannot exceed the flatband potential, U_{fb}, because open circuit imposes only the condition that the sum of the anodic and cathodic currents is zero. Several sources such as leakage or recombination of electrons and holes via surface states, bulk defects, and impurities may limit the photopotential in practice. When an n-type semiconductor at equilibrium is illuminated at low intensity, the photopotential is related to the carrier density, p_o, and the additional carrier density, Δp, generated by light, through

8.2.3.
$$\Delta U_{ph} = \frac{kT}{e} \ln \left(1 + \frac{\Delta p}{p_o}\right)$$

This equation is valid for small intensities in n-type semiconductors under the conditions for which the quasi-Fermi levels in 3.4.3 and 3.4.4 can be defined. For p-type materials the relationship

8.2.4.
$$\Delta U_{ph} = \frac{kT}{e} \ln \left(1 + \frac{\Delta n}{n_o}\right)$$

obtains.

At *short circuit*, or under potentiostatic conditions,

8.3. an *anodic photocurrent density* (Δj_{ph}) at n-type electrodes, and a *cathodic photocurrent density* (Δj_{ph}) at p-type electrodes, is generated. This *photocurrent density* is defined as the difference Δj_{ph}

8.3.1. between the total *current density under illumination*, j_{ph}, and j_{ph}

8.3.2. the *dark current density*, j_d j_d

8.3.3.
$$\Delta j_{ph} = j_{ph} - j_d$$

When the band bending imposed by external potential is sufficiently large, the photocurrent density, Δj_{ph}, is usually independent of the

electrode potential and proportional to the incident light intensity, i.e.

8.3.4. $$\Delta j_{ph} \propto I_o$$

8.3.5. The *quantum yield*, Φ, of the photocurrent is defined by

Φ

$$\Phi = \frac{\Delta j_{ph}}{N_{ph} \quad e}$$

8.3.6. in which N_{ph} is *the number of absorbed photons divided by area and time*. For monochromatic light of intensity I_o, divided by area and time and frequency ν, totally absorbed by the electrode,

N_{ph}

8.3.7. $$N_{ph} = \frac{I_o}{h\nu}$$

8.4. In measurements of the photocurrent, Δj_{ph}, vs. the electrode potential, U, the potential at which the photocurrent starts to rise is defined as the

8.4.1. *onset potential*, U_{on}. In practice this value may be difficult to evaluate. Moreover, it may differ strongly from the flatband potential, U_{fb}, even at higher light intensities, as a result of recombination via surface states or of trapping of minority carriers in these states.

U_{on}

8.5. Electron-hole-pairs created by light excitation in the bulk of the electrode may recombine in the bulk or diffuse towards the surface as indicated in Fig. 8.

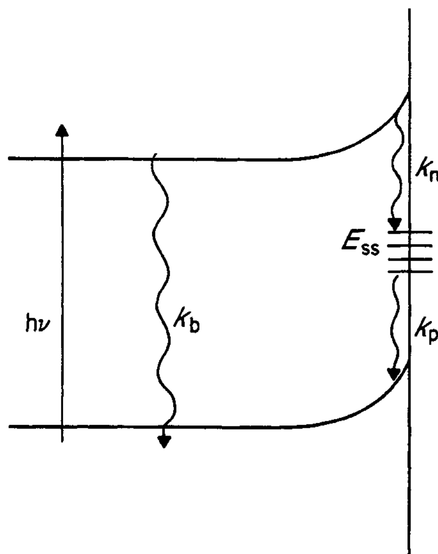

Fig 8: Excitation and recombination of electrons and holes

The *recombination* process in the bulk is characterized

8.5.1. by a pseudo-first order rate constant k_b, provided that the k_b

8.5.2. density of majority carriers created by light, Δn in n-type and Δp in p-type, is small compared to the equilibrium concentration, i.e.

$$\Delta n \text{ (or } \Delta p) \ll n_o \text{ (or } p_o)$$

The reciprocal of k_b is the *lifetime* τ of the τ

8.5.3. minority carriers.

The electron-hole-pairs that reach the surface by diffusion may also recombine via surface states as indicated in Fig. 8. The corresponding rate constants for

8.5.4. trapping electrons, k_n, or holes, k_p, are second order rate constants. k_n k_p

9. PHOTOELECTROCHEMICAL CELLS

Photoelectrochemical cells consist essentially of two electrodes in contact with an electrolyte, one electrode usually being a light sensitive semiconductor electrode and the other an inert metal or graphite electrode. In principle, both electrodes can consist of semiconducting material of opposite types.

One can further distinguish between two modes of operation in these cells.

1) *Photovoltaic cells* in which radiant energy is converted into electrical energy and

2) *Photoelectrolytic cells* in which radiant energy causes a net chemical conversion in the cell, e.g., so as to produce hydrogen as a useful fuel. These cells can be classified as photosynthetic or photocatalytic. In the former case, radiant energy provides a Gibbs energy to drive a reaction such as $H_2O \rightarrow H_2 + 1/2\,O_2$, and electrical or thermal energy may be later recovered by allowing the reverse, spontaneous reaction to proceed. In a photocatalytic cell the photon absorption promotes a reaction

with $\Delta G < 0$ so there is no net storage of chemical energy, but the radiant energy speeds up a slow reaction.

9.1. Photovoltaic cells

We assume that only one electrode is a semiconductor electrode. The electrolyte contains a redox system. When the semiconductor electrode is illuminated

9.1.1. under a certain load a photovoltage, ΔU_{ph}, between the semiconductor and the counterelectrode and a

9.1.2. corresponding photocurrent density, j_{ph}, are measured. At open circuit conditions ($j_{ph} = 0$), an open circuit photovoltage

ΔU_{ph}^{oc}

9.1.3. ΔU_{ph}^{oc} occurs. At short circuit conditions ($\Delta U_{ph} = 0$) a corresponding

9.1.4. short circuit current density, j_{ph}^{s}, is obtained. Normally the properties of a photovoltaic cells are characterized by a current-voltage plot in which j_{ph} is plotted vs. ΔU_{ph}, as shown in Fig. 9.

j_{ph}^{s}

The product $j_{ph} \times \Delta U_{ph}$ is the *power output per unit area* at any point and is a *maximum*, P_m, for a pair of values given by

P_m

9.1.5. $$P_m = j_{ph}^{m} \cdot \Delta U_{ph}^{m}$$

j_{ph}^{m}

ΔU_{ph}^{m}

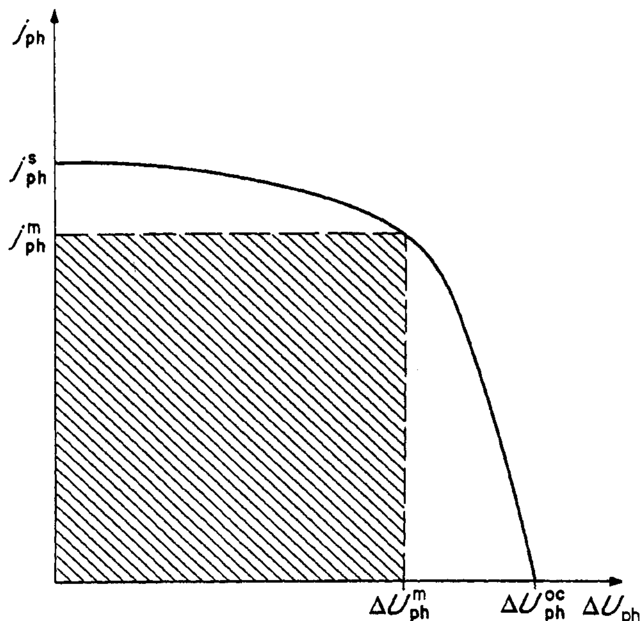

Fig 9: Power plot for a photoelectrochemical cell

9.1.6. The fraction of the limiting power, $U_{ph}^{oc} \times j_{ph}^{s}$, that a photovoltaic cell actually delivers is the *fill factor*, defined as

9.1.7.
$$F_f = \frac{P_m}{j_{ph}^{s} \cdot \Delta U_{ph}^{oc}}$$

9.1.8. The maximum *solar energy conversion efficiency* η_m is defined by

9.1.9.
$$\eta_m = \frac{P_m}{P^o}$$

η_m

9.1.10. in which P^o is the *power per unit area incident* on the electrode from the incident radiation source (sunlight). In certain cases it is also useful to define a monochromatic efficiency, η_λ, where

P^o

η_λ

$$\eta_\lambda = \frac{P_m}{P_\lambda^o}$$

P_λ^o

and P_λ^o is the power per unit area incident on the electrode from the incident monochromatic light of wavelength λ.

In 9.1 the quantities have been defined for current densities with symbol j. If the power is defined as that incident on the electrode area, the total current with symbol i should be used.

It is only useful, however, to define conversion efficiencies if the cell operates regeneratively, i.e., there is no net change of chemical composition with time. This requires that the corresponding electrochemical reactions at the anode and cathode are entirely due to the oxidation and reduction of the redox systems, respectively.

9.2. Photoelectrolysis cells:

In a photoelectrolysis cell the electrolyte and/or solvent are decomposed, e.g., water into hydrogen and oxygen. Such a process can occur in a photoelectrochemical cell in which the two electrodes are short circuited or an external potential difference, U_a, is applied between the two electrodes.

U_a

9.2.1. The *solar conversion efficiency* is defined by

9.2.2.
$$\eta_{sol} = \frac{\text{stored energy} - \text{added electrical energy}}{\text{solar energy input}}$$

η_{sol}

This definition takes into account that photoelectrolysis can often only

be achieved by applying an auxiliary potential difference, U_a. In cases where the photocurrent does not contribute completely to the energy storage because of side reactions, a current efficiency factor β has to be included. One then obtains

9.2.3.
$$\eta_{sol} = \frac{\int (U_o - U_a)\beta I_{ph}\, dt}{\int P^o\, dt}$$

in which U_o is the standard potential of the overall cell reaction.

9.3. Besides photovoltaic and photoelectrolysis cells a third type of cell, the photogalvanic cell, is used for solar energy conversion. Here two inert electrodes are applied and the light is absorbed by the electrolyte, for instance a dye solution. In this case an electron transfer occurs between the excited dye molecules and electron donor or acceptor molecules added to the electrolyte. A photovoltage between the two electrodes is developed if the light is absorbed by the electrolyte near one of the two inert electrodes. Accordingly, the photogalvanic cell is essentially a concentration cell. Since its only function is production of electrical energy, the same terminology and definitions used for photovoltaic cells in this document should be followed.

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