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New Problems and Prospects in the Electrochemistry of Semiconductors

Yu.Ya.Gurevich and Yu.V.Pleskov

This review gives a unified discussion of current theoretical ideas in semiconductor electrochemistry and in the interpretation of physicochemical processes at the semiconductor/electrolyte interface (mainly, the electrochemical phenomena associated with the photo-excitation of the electron-hole ensemble of the semiconductor and used in practical devices for solar energy conversion, laser etching of semiconductors, photo-corrosion protection, etc.). New problems and likely future developments in the electrochemistry of semiconductors are discussed. 90 references.

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I. INTRODUCTION

The electrochemistry of semiconductors, identified as a new branch of science over a quarter of a century ago, has been developed intensively as a part of electrochemical physics† since the 1960's. Its scientific foundations were laid, and new methods of treating semiconductor surfaces were developed and adopted in the technology of semiconductor devices[1]. The results stimulated a reconsideration of the most general electrochemical concepts, such as the zero-charge potential, the exchange current, the transfer coefficient of an electrochemical reaction, etc. This was followed by a period of decreasing interest in semiconductor electrochemistry, mainly because the practical applications were found to be more limited than had been expected.

The resurgence of research activities in this area, which is still in progress, arose from the discovery (in the 1970's) of solar energy conversion by the photo-electrolysis of water with semiconductor electrodes to give hydrogen. Partly because of the increasing concern with the danger of exhausting natural resources, and partly with the aim of minimising the contamination of the environment, substantial effort has been directed[2] towards the development of ecologically "clean" liquid solar cells which exploit renewable sources of energy. Practical developments in "solar semiconductors" gave a new impetus to the study of semiconductor electrochemistry (mainly, the photo-electrochemistry of semiconductors). In their turn, advances in semiconductor electrochemistry stimulated new developments in conventional electrochemistry. For example, the study of semiconductor electrodes has led to a critical reappraisal of general concepts such as the electrochemical potential of electrons in solution, the relationship between the "physical" energy scale and the "electrochemical" scale of electrode potentials, etc. These problems will be examined in the first part of the present review.

In the later Sections we shall discuss some new problems in the electrochemistry (and photo-electrochemistry) of the semiconductors themselves, such as the "clamping of the Fermi level" on the surface of a semiconductor electrode (as an alternative to the more usual "clamping of the band edges"), the quasi-thermodynamic description of electrode reactions (in particular, the concept of the quasi-Fermi level, and its limitations), etc. We shall also briefly outline the principles of some very recent practical developments in the electrochemistry of semiconductors.

For information on the physics of semiconductors and semiconductor surfaces the reader is referred to Bonch-Bruevich and Kalashnikov's monograph[3]; general problems in semiconductor electrochemistry are discussed in Refs.1, 4, and 5. A more detailed and comprehensive discussion of some of the problems mentioned in this review is given in our textbook[6].

II. CHARACTERISTIC ENERGY LEVELS IN THE ELECTRODE–ELECTROLYTE SOLUTION SYSTEM

The description of the energy characteristics of electrons in electrochemical systems is of the greatest importance both in method development and in practical terms. The concept of the electrochemical potential of electrons in a solution containing an oxidation–reduction system is valuable when applied to electrochemical and photo-electrochemical processes. Also, the reorganisation energy of the solvent can substantially affect the kinetics of the reactions which accompany the charge transfer act. Lastly, the electronic energy levels, directly related to the oxidation or reduction state of the components, determine the quantitative aspects of the related electron flows.

1. The Electrochemical Potential of Electrons in a Solution

Consider an electron in a solution which contains an oxidation–reduction system taking part in a reversible electron transfer reaction:

$$\mathrm{Ox} + n\,\mathrm{e}^- \rightleftarrows \mathrm{Red}\,. \qquad (1)$$

In this expression Ox and Red denote the oxidised and the reduced form of the substance in the solvated state, and n is the number of electrons involved in the electrode reaction. Under conditions of thermodynamic equilibrium we must have

$$\tilde{\mu}_{ox} + n\tilde{\mu}_e = \tilde{\mu}_{red} \qquad (2)$$

where $\tilde{\mu}_{\mathrm{ox}}$ and $\tilde{\mu}_{\mathrm{red}}$ are the electrochemical potentials of the components of the oxidation–reduction system in the solution

†The term "electrochemical physics" was officially adopted by the International Electrochemical Society to denote all the aspects of electrochemistry which have strong associations with physics.

(referred to one mole of substance), and $\tilde{\mu}_e$ is the electrochemical potential of the electrons in the solution. We can define the quantity $\tilde{\mu}_{ox,red}$ as

$$\tilde{\mu}_{ox,red} = RT \ln c_{ox,red} + z_{ox,red}\mathcal{F}\emptyset + \mu^0_{ox,red} \qquad (3)$$

where R is the gas constant, T is the absolute temperature, $c_{ox,red}$ is the concentration (more generally, the activity) of the reactants Ox and Red in solution, $z_{ox,red}$ are their charges, $\mathcal{F}$ is the Faraday, $\emptyset$ is the electrical potential, and $\mu^0_{ox,red}$ are constants independent of $c_{ox,red}$ and of $\emptyset$.

From (2) and (3) we can calculate the equilibrium electrode potential ϕ^0 of an electrode on which reaction (1) is taking place:

$$\varphi^0 = \varphi^0_0 + \frac{RT}{n\mathcal{F}} \ln \frac{c_{ox}}{c_{red}} \qquad (4)$$

where ϕ^0_0 is the standard electrode potential for the given solution. This quantity depends on the difference $\mu^0_{ox} - \mu^0_{red}$, and therefore also on the nature of the electrode reaction and on the choice of reference electrode.

At the same time, when thermodynamic equilibrium according to reaction (1) has been established we can introduce the concept of the electrochemical potential of electrons in the electrolyte solution, $\tilde{\mu}^{el}_e$, which is quite unrelated to the presence (or absence) of the electrode. This possibility follows from the general thermodynamic principle that the detailed mechanism by which an equilibrium is established is immaterial. Thus we can, for example, assume that the electron transfer reaction between the Ox and the Red component does not in general involve the participation of the electrode. Under these conditions the quantity $\tilde{\mu}^{el}_e$ for reaction (1) is given by the expression

$$\tilde{\mu}^{el}_e = \frac{1}{n}(\tilde{\mu}_{red} - \tilde{\mu}_{ox}) \qquad (5)$$

where $\tilde{\mu}_{red}$ and $\tilde{\mu}_{ox}$ are defined for the potential $\emptyset$(el) in the bulk of the electrolyte solution. Since the parameters $\tilde{\mu}_{red,ox}$ are a function only of the properties of the reactants Ox and Red and of the solvent, it follows that $\tilde{\mu}^{el}_e$ also is independent of the nature of the electrode and of the structure of the phase boundary. Furthermore, it is the quantity $\tilde{\mu}^{el}_e$ which defines the electrochemical potential of the electrons in the given electrode at equilibrium. In particular, this electrochemical potential must be the same for any electrode in equilibrium with the given Ox/Red system.

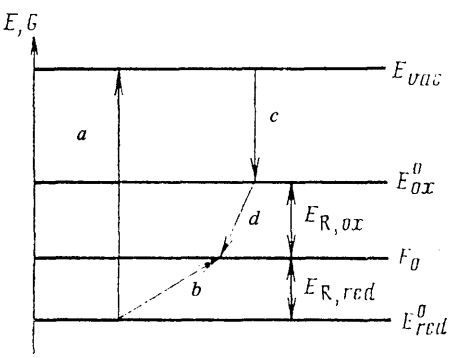


Figure 1. Position of the energy levels of an electron in a solution containing an oxidation–reduction system: E is the internal energy, G is the free energy.

To establish the relationship between μ^{el}_e and the characteristic parameters of the oxidation–reduction system we shall consider a solution containing only one particle of Red. We shall denote the most probable (thermodynamic) electronic energy level of the Red particle as E^0_{red}, and that of an Ox particle as E^0_{ox}, and the potential energy of an electron in vacuum (or, more exactly, in the vapour phase) at a point close to the surface of the solution but outside the region of influence of the surface forces will be termed E_{vac}. If the surface is uncharged the parameter E_{vac} is the same as the energy of an electron at rest at infinity. Putting $n = 1$ in Eqn.(1) to simplify the argument, we can now examine the following thermodynamic cycle[7,8] (see Fig.1).

a) An electron is transferred in a single jump from a solvated Red particle (energy level E^0_{red}) to the level E_{vac}.

b) The state of the solvent near the oxidised Red particle (now an Ox particle) is changed to bring the Ox particle into thermodynamic equilibrium with the solution.

c) The electron from the level E_{vac} is suddenly transferred to the resulting Ox particle (level E^0_{ox}) without changing the state of the solvent.

d) The necessary rearrangement of the solvent near the resulting Red particle is carried out, and as a result the system as a whole returns to its initial equilibrium state.

In this cycle the changes in internal energy of the system corresponding to steps (a) and (c) are a measure of the position in energy of the levels E^0_{red} and E^0_{ox} relative to E_{vac}: they are equal to the ionisation energy of the Red particle and to the electron affinity of the Ox particle in the solution respectively. The energy characteristics of steps (b) and (d) are the reorganisation energies of the solvent $E_{R,red}$ and $E_{R,ox}$ for the particles Red and Ox respectively.

In this process $E_{R,red} > 0$ and $E_{R,ox} > 0$ are the absolute measures of the energy (or, more accurately, of the free energy) needed to change the equilibrium state of the medium (solvent) from its initial state to the final state for a unit change in the charge on the particle[9,10].

Thus according to the above analysis we can write

$$E^0_{red} + E_{R,red} - E^0_{ox} + E_{R,ox} = 0. \qquad (6)$$

The quantity F_0, defined according to Eqn.(6) by the expression

$$F_0 = E^0_{red} + E_{R,red} = E^0_{ox} - E_{R,ox} \qquad (7)$$

is a measure of the change in free energy of the system accompanying the removal (at equilibrium) of an electron from a Red particle from the solution into the vacuum (or the equilibrium transfer of an electron from the vacuum to an Ox particle). From (6) and (7) we obtain

$$F_0 = \tfrac{1}{2}(E^0_{ox} + E^0_{red}) + \tfrac{1}{2}\Delta E_R \qquad (8)$$

where

$$\Delta E_R = E_{R,red} - E_{R,ox}$$

and

$$E^0_{ox} - E^0_{red} = E_{R,ox} + E_{R,red}. \qquad (9)$$

We note that Eqn.(9) can be obtained also by considering the equilibrium transfer of an electron directly from the reactant Red to the reactant Ox within the solution.

In polar liquids like water (especially in the case of outer-sphere reactions[11]) we can assume that $E_{R,ox} = R_{R,red} = E_R$. From Eqns.(8) and (9) we then obtain

$$F_0 = \tfrac{1}{2}(E^0_{ox} + E^0_{red}), \quad E^0_{ox} - E^0_{red} = 2E_R. \qquad (10)$$

It follows therefore that in the simplest case (which we are now considering) the characteristic level E_0 lies half-way between E^0_{ox} and E^0_{red} in energy, and the distance in energy between E^0_{ox} and E^0_{red} is twice E_R.

Thus, starting from (3) and (5), and noting that the parameter F_0 as defined above relates to one particle, we obtain the following expression for the electrochemical potential $\tilde{\mu}_e^{el}$:

$$\tilde{\mu}_e^{el} = N_A F_0 - RT \ln (c_{ox}/c_{red}) \qquad (11)$$

where N_A is Avogadro's number. Eqn.(11) can be obtained also by statistical mechanics[6,8] without using Eqn.(5) and without carrying out the thermodynamic cycle. In other words, the concept of the electrochemical potential of electrons in a solution can be introduced strictly and logically in both the thermodynamic and the statistical mechanics approach.

By analogy with the Fermi level of the electron in solids, which refers to a single electron, we can define the quantity $F_{redox} = \tilde{\mu}_e^{el}/N_A$ as the electrochemical potential of the electrons in solution referred to a single particle (sometimes loosely called the Fermi level of the electrons in solution).

We should stress that the position of F_{redox} is quite unrelated to the concentration of "free" electrons in solution, and is determined by the properties of the oxidation–reduction Ox/Red system (which contains only "bound" electrons). The quantity F_{redox} does not describe the energy of any one particle, since in general there are no electrons of energy F_{redox} in the solution (in contrast to metal systems, say, where the Fermi level F_{met} coincides with the energy of the conduction electrons on the Fermi surface). Therefore during an electrochemical reaction the electrons are not transferred from the level F_{redox} to the electrode or from the electrode to F_{redox}: all the electron transfers take place through the levels E_{red}^0 and E_{ox}^0. Nevertheless it is the position of the level F_{redox} which defines the thermodynamic properties of the oxidation–reduction system, and also the properties of the interface between the electrode and the solution which contains the system. For example, using the condition of thermodynamic equilibrium in the semiconductor–solution system in the form of

$$F = F_{redox} \qquad (12)$$

where F is the Fermi level of the electrons in the semiconductor, the conditions which determine the course of the electrochemical reaction can be defined as

$$F > F_{redox} \quad \text{(cathodic reaction)}, \qquad (13a)$$

$$F < F_{redox} \quad \text{(anodic reaction)}. \qquad (13b)$$

The electrochemical potentials of oxidation–reduction systems in solution can be calculated by standard methods from the thermodynamic characteristics of the components. For many reactions in which the material of the semiconductor electrode takes part (for example, anodic or cathodic dissolution) the F_{redox} values can be found in Refs.12–14.

2. Relationship Between the Energy Scale and the Electrode Potential Scale

The position of the levels E_{ox}^0, E_{red}^0, and F_{redox} with respect to E_{vac} can be defined by establishing a quantitative correspondence between the "physical" energy scale, in which the zero value is identified with E_{vac}, and the electrochemical scale of electrode potentials, which are measured from the potential of some arbitrarily chosen reference electrode. The general form of this correspondence is

$$F_{redox} = -e\varphi^0 + \text{const} \qquad (14)$$

where $e > 0$ is the absolute value of the electronic charge.

Let us choose an Ox/Red system for which the equilibrium potential ϕ^0 is arbitrarily taken to be zero. A solution of this system in contact with an inert electrode [i.e. one which does not take part in reaction (1)] is by definition the reference electrode. In this case the constant in Eqn.(14) is equal to F_{redox}, and describes the change in free energy attending the reaction

$$Ox + e_{vac}^- \rightleftarrows Red. \qquad (15)$$

In other words, the term "const" in Eqn.(14) is the change in free energy resulting from the transfer of an electron from a point in the vacuum close to the solution surface to the Fermi level of the metal of the reference electrode (which is equal to F_0 when $c_{ox} = c_{red}$). The quantity F_0/e is sometimes called the "absolute potential" of the electrode[15]. The first attempt to determine this quantity was described by Kanevskii[15]; Lohmann also calculated it by analysing a fairly complex thermodynamic cycle[16].

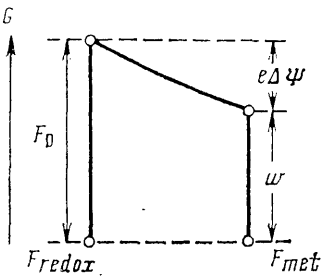


Figure 2. Relationship between the "physical" and the "electrochemical" energy scale.

A simple and accurate method of comparing energy and potential scales[17] relies on a calculation of the electronic work function for the metal in a solution of electrolyte at the potential of the reference electrode. The metal in equilibrium with the Ox-Red system in solution (so that their electrochemical potentials are equal, $F_{redox} = F_{met}$) is shown diagrammatically in Fig.2. The change in free energy for the reaction (15) is the sum of the energies for the steps (c) and (d) of our cycle (Fig.1), i.e. the quantity F_{redox}. We see from the cycle in Fig.2 that

$$-F_{redox} = w + e\Delta\psi \qquad (16)$$

where w is the thermodynamic work function for the emission of an electron from the uncharged metal into a vacuum and $\Delta\psi$ is the Volta potential difference in the metal–solution system produced by the mutual charging of the "free" metal and solution surfaces when brought into contact.

A calculation for a specific case (for example, the normal hydrogen electrode) is easily made by using data[18] for the difference in Volta potentials in the mercury–aqueous solution system: $\Delta\psi = -0.07$ V at the potential of the normal hydrogen electrode. Taking $w = 4.50 \pm 0.03$ eV for the work function of an electron from mercury into a vacuum[19] we obtain from formula (16)

$$-F_{redox}\,(\text{NHE}),\,\text{eV} \quad = 4.50 - 0.07 = 4.43 \simeq 4.4\,.$$

Thus the electrochemical potential of the normal hydrogen electrode F_{redox}(NHE) lies 4.4 eV below the level E_{vac}.[6]

We also note that w (the thermodynamic work function of the electron in the semiconductor) is given by the expression $w = \chi + |F - E_c|$, where χ is the electron affinity of the semiconductor. The position of the level F with respect to the bottom of the conduction band in the bulk of the semiconductor (E_c) is given by the expressions

$$F - E_c = -E_g/2 + kT \ln (N_v/N_c)^{1/2}, \quad n_0 = p_0 \qquad (17a)$$
(intrinsic semiconductor)

$$F - E_c = -kT \ln (N_c/n_0), \quad n_0 \gg p_0 \qquad (17b)$$
(n-type semiconductor)

$$F - E_c = -E_g + kT \ln (N_c/p_0), \quad p_0 \gg n_0 . \qquad (17c)$$
(p-type semiconductor)

In these expressions E_g is the width of the forbidden gap, N_c and N_v are the effective densities of states in the conduction band and in the valence band, and n_0 and p_0 are the concentrations of electrons and holes in thermodynamic equilibrium in the bulk of the semiconductor.

3. Calculation of the Reorganisation Energy of the Solvent

By using these results we can calculate the reorganisation energy of the solvent from data on the photo-emission of electrons from solutions into the vapour phase (see our recent review[20]). When a solution containing "Red" species is illuminated with light of sufficiently short wavelength electrons are emitted into the vapour phase. Since photo-ionisation is a relatively fast process, the photo-electric work function w_{ph} is equal to $-E^0_{red}$ if $E_{vac} = 0$. It follows from (7) and (11) that for $c_{ox} = c_{red}$ this quantity differs from the thermodynamic work function (which is equal to F_0) by the amount $E_{R,red}$. Thus $E_{R,red}$ is calculable as the difference between the photo-electric work function $w_{ph} = -E^0_{red}$ and the parameter $-F_{redox}$. (A similar method of determining E_R was used previously[21] for solutions in which the "emitters" were solvated electrons.)

The work function $w_{ph} = 5.95$ eV has been obtained[22] for photo-emission from aqueous solutions of $Fe(CN)_6^{4-}$. Using the above value of $F_{redox} = -4.4$ eV, and also a value of +0.36 V (against the normal hydrogen electrode) for the standard potential of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system, we obtain 5.95 - 4.4 - 0.36 ≅ 1.2 eV for the reorganisation energy of the water surrounding the ferrocyanide and ferricyanide ions. Since in this case the electron transfer reaction takes place in the outer sphere we can assume that $E_{R,ox} = E_{R,red} = E_R$.

Few reliable experimental data on E_R are available at present[9]. According to Memming[23] the $E_{R,ox}$ and $E_{R,red}$ values for aqueous solutions at room temperature lie between 0.5 and 2 eV. We should also note that the "homogeneous" values of E_R (determined, for example, by photo-electron emission from solutions) are substantially higher than the "heterogeneous" values (which can be obtained from measurements of tunnelling currents from semiconductor electrodes into solutions[23]). In the simplest model the "homogeneous" reorganisation energy of the solvent is approximately double the "heterogeneous" value[9,11].

As regards the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system, the "homogeneous" value $E_R = 1.24$ eV obtained by a model calculation[23] agrees very well with the value given above. However, the same workers[23] obtained a much lower value for the "heterogeneous" reorganisation energy of the solvent ($E_R = 0.4$ eV) from experimental measurements of tunnelling currents from heavily doped SnO_2 electrodes.

III. STRUCTURE OF THE SEMICONDUCTOR/ELECTROLYTE INTERFACE

At the interface between a semiconductor electrode and a solution of electrolyte an electrical double layer is produced (as at the metal/solution interface). The double layer consists of regions carrying charges of opposite sign, and located in the two contacting phases. In the semiconductor the charge in the surface layer is produced by a redistribution of the electrons and holes present in this region, and in the solution by a redistribution of the ions. At equilibrium the absolute values of these charges are equal.

1. Model of the Electrical Double Layer

The fundamental reasons for the formation of an electrical double layer are quite general. They include the overflow of charges through the interface during the establishment of thermodynamic equilibrium between the phases, and charging processes which are independent of the transfer of electrons through the interface (for example, the charging of surface states, some types of adsorption, etc.).

According to the generally accepted model[1,24] we can define three regions within the electrical double layer: a region of space charge in the solution, an intermediate region (usually called the Helmholtz layer), and a region of space charge in the semiconductor.

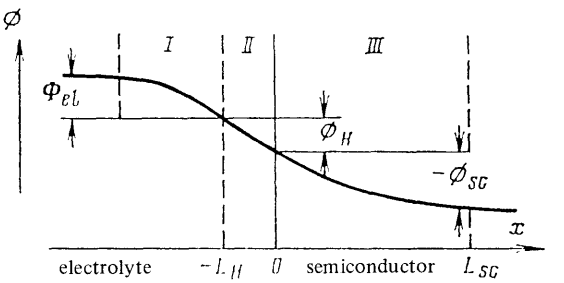


Figure 3. Composition of the potential step at the semiconductor–electrolyte interface: *I*) Gouy layer, *II*) Helmholtz layer, *III*) space-charge layer.

The distribution in space of the potential difference at the interface (Galvani potential) between a semiconductor and an electrolyte, Ø(el/sc), is shown in Fig.3. The semiconductor occupies the space to the right of the vertical full line which defines the interface ($x = 0$). To the left of this line we find the Helmholtz layer, consisting of ions attracted towards the electrode surface and of solvent molecules: the thickness of this layer (L_H) is of the order of the diameter of the ions. Beyond the Helmholtz layer we find, on the solution side, the space-charge region of the solution (the Gouy–Chapman layer).

We shall denote the electrical potential in the bulk of the semiconductor (at $x \to \infty$) as Ø(sc), and in the bulk of the solution (at $x \to -\infty$) as Ø(el), as before. The overall potential drop at the interface, Ø(el/sc) = Ø(sc) - Ø(el), is therefore given by

$$Ø(el/sc) = [Ø(L_H) - Ø(-\infty)] + [Ø(0) - Ø(L_H)] + [Ø(\infty) - Ø(0)], \qquad (18)$$

In this expression $\emptyset(L_H) - \emptyset(-\infty) \equiv \emptyset(el)$ is the potential drop in the space-charge region of the electrolyte solution, i.e. between the bulk of the solution and the outer Helmholtz plane: this quantity is usually called ψ' (the "psi-dash" potential). The second term $\emptyset(0) - \emptyset(L_H) \equiv \emptyset_H$ is the potential drop in the Helmholtz layer. Lastly, the third term $\emptyset(\infty) - \emptyset(0) \equiv -\emptyset_{sc}$ is the potential drop in the space charge region of the semiconductor.

We must lay special stress on the following consideration. In electrochemistry an electrode potential is traditionally taken as positive if it increases the amount of positive charge on the electrode. On the other hand in semiconductor physics a positive surface potential [conventionally measured from $\emptyset(\infty)$] corresponds to electron enrichment of the space charge region, i.e. to the formation of negative space charge. In other words, the potential axes adopted in electrochemistry and in semiconductor physics point in opposite directions. The result is that the potential step in the semiconductor with respect to the bulk potential $\emptyset(sc)$, defined as $\emptyset(sc) = \emptyset(0) - \emptyset(\infty)$, has a sign opposite to that of the last term in the expression for the Galvani potential [Eqn.(18)].

Polarisation of the electrode, i.e. a change by $\Delta\phi$ in the electrode potential, usually affects all three components of the Galvani potential. However, in the not too dilute solution (>0.1 M) which are usually used in electrochemical experiments the quantity $\emptyset_{el} = \psi'$ is negligibly small, and therefore the changes in this quantity are also negligible. We shall assume this to be the case throughout this review. We shall also assume that the ohmic potential drop is negligible, so that we can write

$$\Delta\varphi = \Delta\emptyset_H - \Delta\emptyset_{sc}. \qquad (19)$$

In addition to the charge carriers, dipoles present at the interface can also contribute to the formation of the double layer: these dipoles could be the surface dipoles accompanying bond formation between atoms on the semiconductor surface and atoms adsorbed from the solution, or surface dipoles produced by the oriented adsorption of solvent molecules.

The formation of an array of dipoles does not contribute to the charge on the electrode, but it produces an additional potential step included in the parameter $\emptyset_H$. This step ($\emptyset_{H,dip}$) is usually found experimentally to be relatively insensitive to changes in the electrode potential ϕ, but very sensitive to the previous treatment of the electrode surface and to the composition of the surrounding medium.

A dependence of the potential on the coordinate in the semi-conductor [$\emptyset(x)$] is equivalent, in the band model, to a bending of the energy bands. The bending is downwards if $\emptyset_{sc} > 0$, and upwards of $\emptyset_{sc} < 0$. In the latter case, corresponding to electron depletion in the surface layer, a depletion layer (the Mott–Schottky layer) is formed near the interface of *n*-type semiconductors if the following inequality applies:

$$-\frac{kT}{e}\ln\frac{n_0}{p_0} < \emptyset_{sc} < -\frac{kT}{e} \qquad (20a)$$

The space charge in this case consists mainly of ionised impurity donors, present at a concentration $N_D \cong n_0$. Similarly, on *p*-type semiconductors the charge of the depletion layer produced by downward bending of the bands in the potential region

$$\frac{kT}{e} < \emptyset_{sc} < \frac{kT}{e}\ln\frac{p_0}{n_0} \qquad (20b)$$

consists mainly of acceptor impurities containing trapped electrons (present at a concentration $N_A \cong p_0$).

The formation of a depletion layer is the most important case in practice, since in the wide-band doped semiconductors used in modern semiconductor electrochemistry experiments the potential range defined by the expressions (20) is quite wide.

If $\emptyset_{sc} = 0$ the bands remain "flat" up to the interface. In this case the space charge in the semiconductor is zero. The potential ϕ of the semiconductor electrode measured against some reference electrode and corresponding to the condition $\emptyset_{sc} = 0$ is called the flat band potential $\phi = \phi_{fb}$. The flat band potential in the electrochemistry of semiconductors is equivalent to the zero-charge potential in the electrochemistry of metals (more precisely, to the zero free charge potential[25]), and it plays an important role in the kinetics of electrochemical processes on semiconductor electrodes.

We should note that for $\phi = \phi_{fb}$, though $\emptyset_{sc} = 0$, the parameter $\emptyset_H$ is finite (usually as a reult of the specific adsorption of ions from solution). Thus in the case of oxide semiconductors (TiO_2, ZnO, etc.), or of semiconductors whose surface is oxidised in aqueous solutions (for example, Ge), the concentrations of OH^- and H^+ ions chemisorbed on the surface are not equal, and this effect can made a substantial contribution to $\emptyset_H$. Because of the thermodynamic equilibrium between the ions adsorbed on the surface and those in the bulk of the solution this contribution to $\emptyset_H$ should be a linear function of the pH of the solution. At a pH value depending on the nature of the semiconductor electrode the total charge of the adsorbed ions is zero. This pH value (or the analogous parameter for the adsorption of ions other than hydrogen), called the point of zero zeta-potential or the isoelectric point, is equivalent to a zero total charge potential for the condition $\emptyset_{sc} = 0$ in Rzhanov's terminology[26]. We note that even at the isoelectric point the parameter $\emptyset_H$ is usually different from zero as a result of adsorption of dipolar solvent molecules at the interface, and also (in the case of oxidised semiconductors) because of the polarity of the bond between the semiconductor atom and the oxygen.

Electronic surface states (including interfacial states) play an important role in semiconductor electrode processes. Adsorbed particles and defects are always present at the contact between the semiconductor and the solution. As a result, a real semiconductor surface contains different types of electronic level, characterised by a complex (usually, quasi-continuous) energy spectrum, at concentrations which can be as high as 10^{14} cm^{-2}. For a more detailed discussion of these aspects the reader is referred to Refs.26 and 27.

The existence of electronic surface levels causes two very important effects. Firstly, electrons and holes can be trapped at the surface, forming an electric charge which induces an equal and opposite charge in the bulk. This effect is responsible for the influence of the surface on the equilibrium properties of the semiconductor. Secondly, surface levels can radically influence the kinetics of processes involving electrons and holes, partly by providing additional carrier recombination and generation centres and partly by acting as intermediate energy levels in processes involving charge transport through the phase boundary.

2. Potential Distributions. "Clamping" of the Band Edges and of the Fermi Level at the Surface

Let us now examine the distribution of $\emptyset(el/sc)$, the overall potential step, between its components $\emptyset_H$ and $\emptyset_{sc}$. According to the basic laws of electrostatics, the following expression should apply at the phase boundary:

$$\varepsilon_H\mathscr{E}_H = 4\pi Q_{ss} - \varepsilon_{sc}\mathscr{E}_{sc}. \qquad (21)$$

In this equation $\mathscr{E}_H$ and $\mathscr{E}_{sc}$ are the electric field strengths near the interface on the side of the Helmholtz layer and of the semiconductor respectively, ε_H and ε_{sc} are the corresponding static dielectric constants, Q_{ss} is the density of charge on the surface states (depending on ϕ_{sc}), and the minus sign before the second term of Eqn.(21) allows for the inconsistency in the sign convention mentioned above. For approximate calculations we may put $|\mathscr{E}_H| \approx |\phi_H|/L_H$ and $|\mathscr{E}_{sc}| \approx |\phi_{sc}|/L_{sc}$, where L_H and L_{sc} are the thicknesses of the Helmholtz layer and of the semiconductor space charge layer respectively, related to the corresponding capacities by the expressions $C_H = 4\pi\varepsilon_H/L_H$ and $C_{sc} = 4\pi\varepsilon_{sc}/L_{sc}$. If the charge on surface states is small we conclude from Eqn.(21) that $|\phi_H| \ll |\phi_{sc}|$ if the following inequality applies:

$$\varepsilon_{sc}L_H/\varepsilon_H L_{sc} \ll 1 \qquad (22)$$

For reasonable values of the parameters ε_{sc} and ε_H the condition (22) is usually satisfied, since $L_H \ll L_{sc}$. However, in strongly doped semiconductors (in which the concentrations n_0 or p_0 are very high) or at high values of $|\phi_{sc}|$ the thickness L_{sc} may be so small that the inequality (22) fails to apply.

In order to establish the influence of surface states on the potential distribution we must calculate their capacity $C_{ss} = -dQ_{ss}/d\phi_{sc}$. This can be done very simply in the monenergetic model, which assumes that all the electronic energy levels on the surface have the same energy E_{ss}. We can easily show (see, for example, Ref.6) that if

$$N_{ss} > \varepsilon_H kT/(\pi e^2 L_H) \qquad (23)$$

where N_{ss} is the number of surface states per unit surface area of the interface, we must have $|\Delta\phi_H| > \Delta\phi_{sc}|$. In other words, if the condition (23) is satisfied, a change in the potential of the electrode causes a more substantial change in the potential of the Helmholtz layer than in that of the space-charge layer. The critical value of N_{ss} (for which the inequality (22) reduces to an equality) is of the order of 10^{13}–10^{14} cm^{-2}.

Thus, since in most cases $L_H < L_{sc}$, we also have $|\phi_{sc}| \gg |\phi_H|$, and therefore the parameter ϕ_{sc} in reasonably concentrated solutions of electrolytes probably accounts for the greater part of the potential step at the interface [ϕ(el/sc)]. However, this conclusion does not apply in the following cases:

1) when the electrode is strongly charged, and the Fermi level at the surface is brought close to the edge of the appropriate band ("metallisation" of the surface);

2) at high concentrations of surface states, when a change in occupancy (i.e. in the charging) of the surface states causes a marked redistribution of the potential and can significantly increase the contribution of the component ϕ_H at a fixed value of ϕ(el/sc);

3) in heavily doped semiconductors, when the Fermi level in the bulk of the material is close to the edge of the band of current carriers (or even lies within that band, as it does in metals).

All we have said so far applies equally to the distribution of potential at the interface under equilibrium conditions and with polarisation applied to the electrode from an external source of current.

Let us consider the two most important special cases[28–30].

1. Assume that when the electrode potential is changed $|\Delta\phi_{sc}| \gg |\Delta\phi_H|$. This condition means that the potential jump in the Helmholtz layer is practically unaffected by the polarisation of the electrode ($\Delta\phi = -\Delta\phi_{sc}$). Therefore the energy levels on the surface (and, in particular, those of the band edges $E_{c,s}$ and $E_{v,s}$) remain in a fixed position relative to the energy levels of the solution and of the reference electrode (Figs.4*a* and 4*c*). This situation is described as "clamping" of the band edges at the surface.

The physical explanation of the "clamping" effect is that the parameter ϕ_H is mainly determined by the chemical interactions between the semiconductor and the solution and is not affected by external influences (such as polarisation, or illumination). As a result, the position of the band edges at the surface ($E_{c,s}$ and $E_{v,s}$) are the same for all samples of the given semiconductor material in contact with the given electrolyte solution, whatever the type and magnitude of the conductivity, since the chemical nature of the solid is practically unaffected by the doping. Experimental determinations of $E_{c,s}$ and $E_{v,s}$ for various semiconductors[31] have confirmed this conclusion.

2. Assume, conversely, that the polarisation of the electrode gives $|\Delta\phi_H| \gg |\Delta\phi_{sc}|$, i.e. that the change appears mainly in the potential of the Helmholtz layer. Under these conditions (Fig.4*a* and 4*c*) the energy levels at the surface are shifted relative to the energy levels in solution by an amount $\Delta\phi = \Delta\phi_H$. On the other hand, with respect to the Fermi level in the semiconductor (F) the band edges $E_{c,s}$ and $E_{v,s}$ at the surface keep the same position as before the change in the potential of the electrode, since the parameter ϕ_{sc} is unchanged. In order to stress the difference between this case and the previous case the band edges are said to be "unclamped" from the surface (the same phenomenon is sometimes referred to, less accurately, as "clamping" of the Fermi level with respect to the band edges).

The Fermi level "clamping" effect allows the parameter F to reach the value F_{redox} even in systems with very high positive or negative values of the equilibrium potential, in which the level F_{redox} lies outside the forbidden energy gap of the semiconductor. Thus the "clamping" of the Fermi level on a semiconductor electrode allows the electrochemical reaction to proceed under the conditions (13), which could not be achieved with "clamped" band edges.

In real systems we often observe an intermediate case in which polarisation of the electrode affects both the potential steps ϕ_H and ϕ_{sc}, so that in practice neither the band edges nor the Fermi level are clamped. Some results illustrating the "clamping" effects and a more detailed discussion of their origin are given below (Section IV).

3. Determination of the Flat Band Potential

The flat band potential is one of the most important physicochemical characteristics of the semiconductor electrode. In the electrochemistry of semiconductors this concept has become even more important than the zero-charge potential in the electrochemistry of metallic electrodes. The parameter ϕ_{fb} is used in the quantitative description of the double layer structure and of the kinetics of electrochemical reactions on semiconductor electrodes, especially in the photoelectrochemistry of semiconductors, since photocurrents of reasonable magnitude can flow only if the photo-generated electrons and holes can be efficiently separated in the space-charge region (see p.326). This carrier separation is effective only at electrode potentials more positive (for n-type photoelectrodes) or more negative (for p-type) than the flat band potential of the semiconductor (though this necessary condition for the separation of the photo-carriers is not sufficient to ensure the flow of photocurrent).

The capacity of the space-charge region of the semiconductor (C_{sc}) is related, in the case of the formation of a depletion layer, to the potential step in the space-charge layer

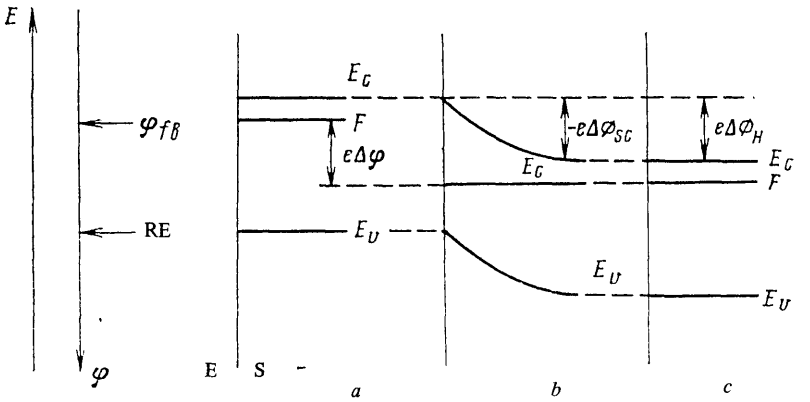


Figure 4. Energy diagram of the interface with an externally applied voltage, showing "clamping" of the band edges (transition from *a* to *b*) and of the Fermi level (transition from *a* to *c*) at the surface of the semiconductor electrode. The initial state *a* is the flat-band case; RE is the reference electrode, E is the electrolyte, S is the semiconductor.

Φ_{sc} by the following expression (written for an *n*-type semiconductor)[1]:

$$C_{sc}^{-2} = \frac{8\pi}{eN_D\varepsilon_{sc}}(|\Phi_{sc}| - kT/e), \qquad (24)$$

According to this equation the plot of C_{sc}^{-2} against Φ_{sc} should be a straight line. Plots in these coordinates are usually called Mott–Schottky graphs (Fig.5). On the assumption that the changes in electrode potential ϕ affect only the component Φ_{sc} and that the capacity C of the contact is equal to C_{sc} we can obtain the concentration of ionised donors from the slope of the straight line, and the flat band potential ϕ_{fb} from its intercept with the potential axis.

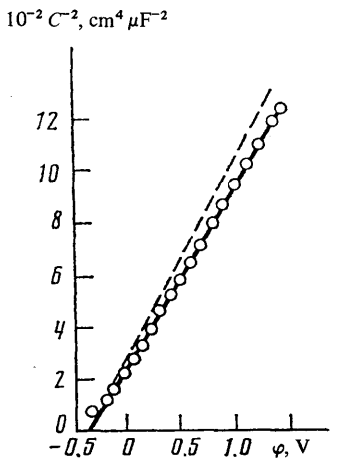


Figure 5. Mott–Schottky plot for a zinc oxide electrode (of conductivity 0.59 Ω^{-1} cm^{-1}) in a 1 *N* KCl solution (pH 8.5).[32] The broken line is calculated by formula (29).

The differential capacity method is widely used in practical electrochemical measurements. We should note, however, that the direct application of formula (24) to the determination of ϕ_{fb} involves a number of assumptions (often not explicitly examined) concerning the properties of the contact between the semiconductor and the electrolyte. The most important of these are:

1. It is assumed that the measured capacity C is not perturbed by the leakage current flowing through the interface, by the finite ohmic resistance of the electrode and of the electrolyte, etc. Accurate corrections for these effects can be calculated (see, for example, Ref.33).

2. It is assumed that the donors (or acceptors) in the semiconductor are fully ionised and uniformly distributed in the space charge region. Deviations from (24) are observed also in the presence of donors (or acceptors) lying deep in the forbidden gap, which are not ionised at room temperature in the bulk of the semiconductor but are partially ionised in the electric field of the space-charge region, thus contributing to the capacity[1].

3. It is assumed that the measured capacity is the capacity of the space-charge region of the semiconductor, and does not include (for example) the capacity of fast surface states, the adsorption capacity, etc. In some cases this condition is satisfied (for example, on the zinc oxide electrode, see below), but often the contribution from the capacity of surface states is substantial.

4. It is assumed that the measured electrode capacity C is unaffected by the Helmholtz layer capacity C_H. Linear plots of the measured capacity C in C^{-2}–ϕ coordinates are usually interpreted (according to formula (24) and to the relationship $C^{-1} = C_H^{-1} + C_{sc}^{-1}$) as evidence that the following conditions are satisfied:

$$C_{sc} \ll C_H, \quad |\Delta\Phi_{sc}| \gg |\Delta\Phi_H|. \qquad (25)$$

However, a detailed study has shown[34] that the possibility of an effect from C_H needs more careful analysis. Thus, if we allow for the change in the potential drop in the Helmholtz layer $\Delta\Phi_H$ caused by the polarisation of the electrode and for the contribution of the capacity C_H to the measured capacity C we obtain [from (24)] the following expression[34] for the

relationship between C and ϕ:

$$C^{-2} = C_H^{-2} + \frac{8\pi}{e\varepsilon_{sc}N_D}(\varphi - \varphi_{fb} - kT/e). \quad (26)$$

We note from (26) that C^{-2} varies linearly with ϕ, i.e. in the same way as C_{sc}^{-2} varies with Φ_{sc} (for C_{sc}^{-2} varies with ϕ on the assumption of Φ_H = const and $\Delta\phi = -\Delta\Phi_{sc}$). Furthermore, the slope of the corresponding straight line in $C^{-2}-\phi$ coordinates is the same, according to (26), as the slope of the $C_{sc}^{-2}-\Phi_{sc}$ straight line (or of the $C_{sc}^{-2}-\phi$ straight line for constant Φ_H). But in this case the intercept of the straight line with the ϕ axis corresponds, according to (26) to the potential

$$\varphi' = \varphi_{fb} + kT/e - e\varepsilon_{sc}N_D/(8\pi C_H^2). \quad (27)$$

As compared to the potential defined by (24) this potential is shifted by an amount $-e\varepsilon_{sc}N_D/(8\pi C_H^2)$. This shift is far from negligible, especially in heavily doped semiconductors.

Thus the linearity of experimental plots of C^{-2} against ϕ does not necessarily prove that the effect of the Helmholtz layer on the measured value of ϕ_{fb} is negligible, i.e. that the inequalities (25) are satisfied. Conversely, non-linearity of the plot of C^{-2} against ϕ is no proof that the conditions (25) are infringed, i.e. that the Helmholtz layer is responsible for the deviation from linearity.

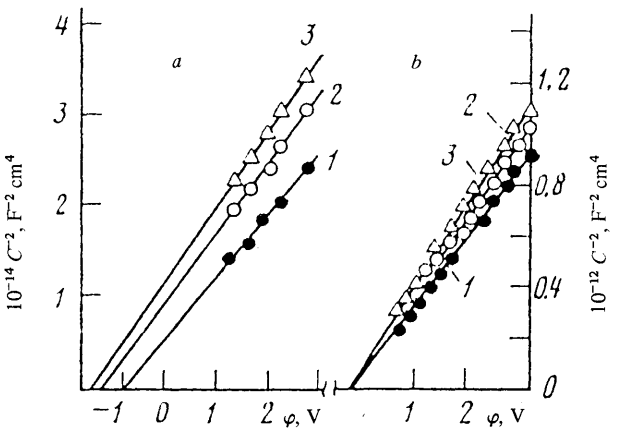


Figure 6. Effect of the frequency of the measuring current on the Mott–Schottky plot[35]: (*a*) CdSe ($N_D = 10^{15}$ cm^{-3}) in a solution of 0.25 M K_2SO_4 + 0.05 M CH_3COOH + 0.05 M CH_3. .COONa, frequency (Hz) 320 (*1*), 2440 (*2*), and 7080 (*3*); (*b*) TiO_2 ($N_D \cong 10^{18}$ cm^{-3}) in a solution of 0.25 M K_2SO_4 + 0.1 M $Na_2B_4O_7$, frequency (Hz) 320 (*1*), 980 (*2*), and 2440 (*3*). Potentials are quoted relative to the normal hydrogen electrode.

Lastly, we should note that ambiguities can arise from the frequency dependence of the Mott–Schottky plots if higher measurement frequencies are adopted in order to minimise the contribution from surface states to the measured capacity. Changes in frequency alter these plots in two ways (see Fig.6). In most cases only the slope changes, and the intercept on the potential axis is unaffected (Fig.6*b*). Sometimes, however, the straight line suffers a shift along the potential axis (as well as a change in slope), and the intercept with the potential axis becomes a function of frequency (Fig.6*a*).

Though a full explanation of these effects has not yet been proposed, plots such as those of Fig.6*b* can be used to measure ϕ_{fb} by extrapolation to the potential axis, though the parameter N_D (or N_A) of course cannot be calculated from the slope. Plots like those of Fig.6*a* are unsuitable even for the determination of ϕ_{fb}.

In addition to the direct experimental determination, a method of calculating the flat band potential ϕ_{fb} from the properties of the semiconductor and those of the solution has been suggested[36].

It follows from (17) and (18) that at thermodynamic equilibrium, and for a high enough concentration of the electrolyte, we can write

$$e(\Phi_H - \Phi_{sc}) = F - F_{redox(ref)} = -\chi + F - E_c - F_{redox(ref)} \quad (28)$$

where $(F - E_c) < 0$ is the difference between the F level and the band edge E_c, and $F_{redox(ref)}$ relates to the reference electrode. The electron affinity of the semiconductor χ which appears in Eqn.(28) can be obtained from semi-empirical formulae relating χ to the first ionisation potential I_1 and the electron affinity A_f of the chemical components of the semiconductor, and also the width of the forbidden gap. Thus, in the simplest case of a binary semiconductor MX we have

$$\chi = {}^1/_2(A_f + I_1 + E_g).$$

The difference $F - E_c$ is given by the expression (17), and the quantity $F_{redox(ref)}$ is assumed to be known (see Section II). Lastly, assuming that at the point of zero zeta-potential (i.e. at the iso-electric point) $\Phi_H = 0$, we can calculate the band bending ($e\Phi_{sc}$) from (28), and hence arrive at the flat band potential.

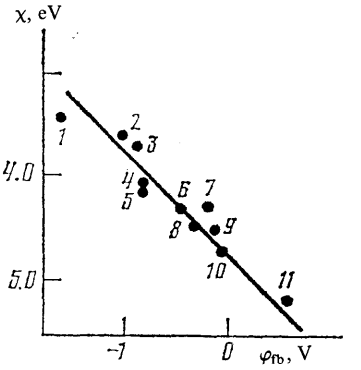


Figure 7. Relationship between the calculated electron affinity and the measured flat band potential (relative to the saturated calomel electrode) for various semiconductors at their isoelectric point[36]: *1*) ZrO_2, *2*) $BaTiO_3$, *3*) $SrTiO_3$, *4*) Ta_2O_5, *5*) ZnO, *6*) TiO_2, *7*) $FeTiO_3$, *8*) SnO_2, *9*) CdO, *10*) Fe_2O_3, *11*) WO_3.

The pH value corresponding to the isoelectric point can be calculated if the standard electrochemical potentials of the reactions involving the adsorbed ions are known, or it can be determined experimentally (as was stated above). This suggests an experimental test of formula (28). In particular, an approximately linear relationship is found between Φ_{sc} and

the pH for a large number of oxide semiconductors. An empirical linear relationship between the calculated χ values and the measured ϕ_{fb} has also been reported (see Fig.7). This plot can be used to estimate the flat band potential of any oxide semiconductor for which the parameter χ can be calculated.

To conclude this Section we should note that a linear relationship between χ and ϕ_{fb} is fully analogous to the well known dependence of the electronic work function w on the zero-charge potential in the electrochemistry of metals[25]. The analogy is particularly clear for wide-gap doped semiconductor, for which $E_c - F$ is quite small ($\lesssim$0.1 eV), so that $\chi \cong w$. Under these conditions, as was pointed out in the previous Section, the deviations from the linear relationship found experimentally in some metals can be ascribed to the differences in the dipole potential step created by the adsorption of solvent on different metals[25]. A similar effect can be expected in semiconductor electrochemistry, though of course it cannot be very marked in the case of a series of semiconductor electrodes of similar chemical type.

IV. QUASI-THERMODYNAMIC DESCRIPTION OF PHOTO-ELECTROCHEMICAL PROCESSES

In this Section we shall examine some of the photo-electrochemical phenomena in semiconductor–electrolyte systems under the influence of light. In addition to their intrinsic scientific interest, these phenomena also have a high relevance to the practical exploitation of electrochemical systems involving semiconductor electrodes. The strongest effects on the electrode processes are obtained by using light of frequency higher than the intrinsic (fundamental) absorption threshold of the semiconductor, so that the energy of the light quanta is sufficient to generate electron–hole pairs. The redistribution of the charge carriers in the semiconductor near the solution boundary caused by the photo-generation can drastically affect not only the rate but also the nature of the electrochemical processes in progress.

1. The Quasi-Fermi Level

Several different methods of describing photo-electrochemical processes have been proposed. For example, the kinetics of photo-electrochemical processes have been studied theoretically by solving the transport equations allowing for the photo-generation of carriers, in conjunction with various boundary conditions[37–40]. This approach offers an exact solution of the problem in a number of simple cases, but if the boundary conditions are relatively complex the method becomes laborious and the resulting equations unwieldy. A qualitative understanding, and often a quantitative treatment, can be achieved more simply, on the other hand, by using a quasi-thermodynamic as opposed to a kinetic approach, based on the quasi-Fermi level concept.

It may be helpful to remind the reader of the significance of the quasi-Fermi level[3]. Assume that illumination of the semiconductor leads to additional generation of current carriers. In a stationary regime under these conditions a dynamic equilibrium is established between the generation and the recombination of electron–hole pairs, resulting in the appearance of steady-state (but not equilibrium!) values of the carrier concentrations n_0^* and p_0^*:

$$n_0^* = n_0 + \Delta n, \quad p_0^* = p_0 + \Delta p, \tag{29}$$

Except in the space-charge region $\Delta n = \Delta p$, since the photo-generation process creates pairs of carriers.

By inserting the concentrations n_0^* and p_0^* into (17) we can calculate the position of the "quasi-Fermi" levels F_n and F_p produced by the splitting of the original Fermi level F. Thus, for an n-type semiconductor in which $\Delta n \ll n_0$ we find from (17b) that $F_n \cong F$. At the same time, since $p_0 \ll n_0$, the condition $\Delta p \gtrsim p_0$ may also apply, and therefore the parameter $F - F_p$ according to Eqn.(17b) becomes

$$F - F_p = kT \ln\left(\frac{p_0 + \Delta p}{p_0}\right); \quad F - F_p \simeq kT \ln\frac{\Delta p}{p}, \quad \Delta p \gg p_0. \tag{30}$$

Similar relationships can be written for p-type semiconductors.

Thus according to Eqn.(30) a significant shift in electrochemical potential can be obtained by photo-generation only for the minority carriers.

2. Description of the Main Types of Photo-electrochemical Reaction

Let us now use the concept of the quasi-Fermi level to describe some qualitative aspects of the development of photo-electrochemical reactions at an illuminated semiconductor–electrolyte interface[12,41].

The basic idea underlying our quasi-thermodynamic approach is that the electrode reaction is accelerated by light as a result of the formation of the quasi-levels F_n and F_p, displaced with respect to the equilibrium position of the Fermi level F. We now need to modify the condition (13). The anodic reaction (with the participation of holes) will take place if

$$F_p > F_{redox} \tag{31a}$$

and the cathodic reaction (with the participation of electrons) will take place if

$$F_n > F_{redox}. \tag{31b}$$

Consider first a semiconductor electrode under open-circuit conditions. An example could be a single particle of a suspension of a semiconductor in a conducting liquid. There will be a region of potential for which no electronic transitions take place at the semiconductor–electrolyte interface in the dark, i.e. for which the semiconductor behaves as an ideally polarisable electrode. The upper and the lower limit of this region of potential are the decomposition potential of the solvent and (or) the decomposition (corrosion) potential of the semiconductor. The stationary potential of the electrode in the ideal polarisability region is determined by chemisorption processes (usually, in aqueous solutions, oxygen chemisorption). The same processes also determine the steady-state band bending.

The energy band diagram of a semiconductor (n-type, in this case) in contact with a solution is shown in Fig.8. In addition to the energy levels of the semiconductor (the bottom of the conduction band E_c and the top of the valence band E_v) the diagram gives the electrochemical potential levels for the anodic dissolution of the semiconductor $E_{dec,p}$ and for the cathodic hydrogen evolution E_{H_2/H_2O} (assuming that the most likely anodic reaction is the decomposition of the semiconductor with the participation of holes and the most likely cathodic reaction the evolution of hydrogen from water with the participation of electrons from the conduction band).

The diagram (Fig.8) assumes the formation of a depletion layer in the surface region of the semiconductor. Electrons and holes generated by light in the electric field of the depletion layer move in opposite directions: in the present case

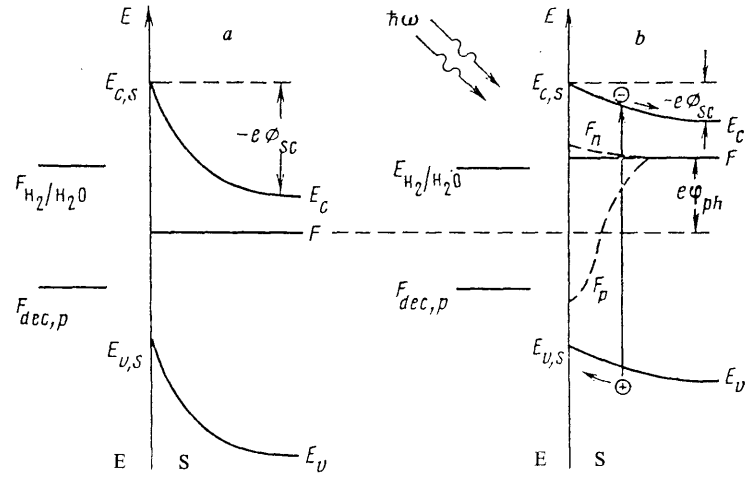


Figure 8. Energy diagram for the contact between a semiconductor and an electrolyte: (*a*) in the dark, (*b*) illuminated; E is the electrolyte, S is the semiconductor.

the holes move towards the interface and the electrons move towards the bulk and away from the interface. The electric field produced by this charge separation partially compensates the field originally present. As a result the bending of the bands ($e\Phi_{sc}$) decreases, i.e. the bands are flattened.

The flattening of the bands produces, in turn, a change in the mutual configuration of other energy levels in the system. We shall assume, to simplify the problem, that the potential step in the Helmholtz layer is unaffected by illumination (Φ_H = const), and hence that the position of the band edges at the surface ($E_{c,s}$ and $E_{v,s}$) is fixed with respect to the reference electrode and therefore also with respect to the energy levels in the solution (band edges "clamped" at the surface, see Section III). At the same time the position of the electrochemical potential F of the semiconductor (Fermi level) is rigidly fixed with respect to the band edges in the bulk of the semiconductor[3]. The result is that under illumination the unbending of the bands "drags" the Fermi level away from the position for the electrode in the dark, as shown in Fig.8. This shift ΔF can be measured by using a reference electrode, and gives rise to the photo-potential $\phi_{ph} = \Delta F/e$.

Consider the effects which accompany the formation of quasi-Fermi levels for electrons and holes. For the majority carriers (electrons) the shift of the level F_n relative to F is very small, as was said above, and can usually be ignored, but for the minority carriers (holes) the quasi-Fermi level F_p can lie relatively far from F in the energy diagram.

At some level of illumination the quasi-Fermi level for holes F_p will reach the level of the anodic reaction on the semiconductor surface (in Fig.8 this is the semiconductor decomposition reaction). Also, because of the shift in the Fermi level F, the quasi-Fermi level for electrons F_n can reach the level of the cathodic reaction (in Fig.8, the evolution of hydrogen from water). The two reactions are induced simultaneously, producing photo-corrosion of the semiconductor. In this way the electrons and holes generated under non-equilibrium conditions in a corrodible semiconductor by illumination are used to accelerate the partial reactions.

In principle the decomposition (dissolution) of the semiconductor could be replaced by another anodic reaction: for example, the oxidation of a dissolved substance or the evolution of hydrogen from water. Obviously, in the latter case the result of the illumination of the semiconductor is the photo-electrolysis of water with formation of hydrogen and oxygen, i.e. the conversion of light (solar) energy into the chemical energy of the products of photo-electrolysis.

When the semiconductor–electrolyte interface is uniformly illuminated the two conjugated reactions proceed at equal rates at each point of the surface. The steady-state potential of the uniformly illuminated semiconductor is a mixed potential. If, on the other hand, the surface of a semiconductor having uniform composition and properties is unevenly illuminated the conditions for the electrochemical reaction are different on the illuminated and on the dark parts of the surface. In this case the conjugated reactions are separated in space, and we can think of local anodes and cathodes. This situation is artificially created, for example, in the selective photo-sensitive etching of semiconductor materials (see below, Section V).

The spatial separation of the anodic and the cathodic reaction on an illuminated semiconductor can be achieved also in other ways: for example, by imparting to specific parts of the semiconductor surface special electrochemical (in particular, electrocatalytic) properties, different from the properties of the rest of the surface. These regions act as local electrodes, and the system as a whole acts as a galvanic couple. An example of this type of micro-heterogeneous system is a suspension of platinised strontium titanate in an aqueous solution. Illumination of this system generates electrons and holes which are separated in the electric field of the depletion layer close to the surface (Fig.9), the holes moving towards the surface of the semiconductor and the electrons towards the bulk, eventually crossing the semiconductor–metal interface into a microscopic inclusion from which they finally enter the solution. In this way hydrogen is generated on the metal surface (in this case, platinum),

and oxygen on the illuminated surface of the strontium titanate. This type of micro-heterogeneous system is currently attracting a great deal of interest for solar energy conversion[42,43].

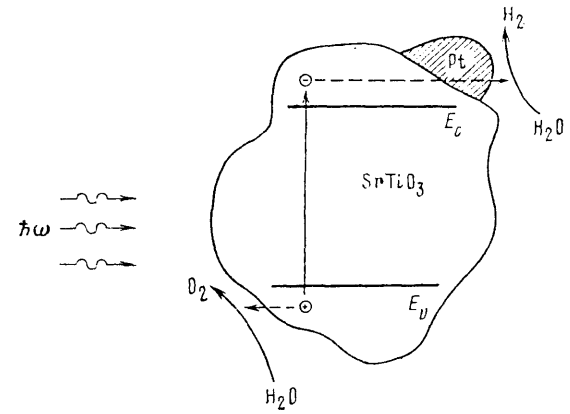


Figure 9. Energy diagram for the photo-electrolysis of water on a particle of a suspension of a semiconductor (platinised $SrTiO_3$) in an aqueous solution.

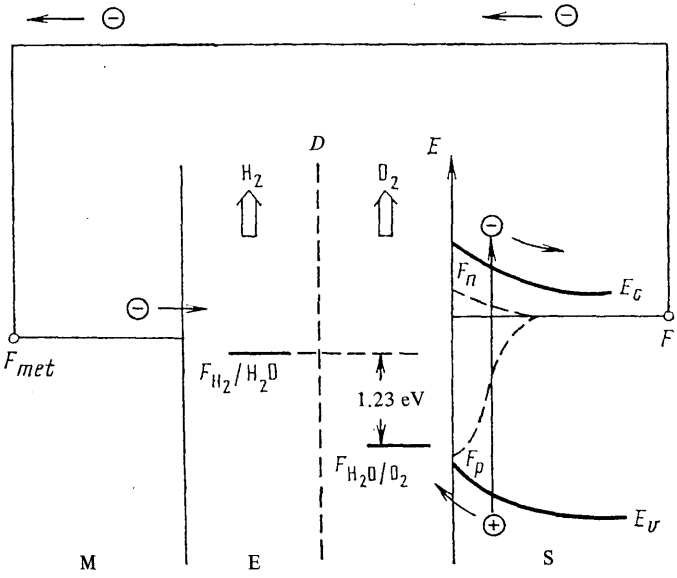


Figure 10. Energy diagram of an illuminated photocell with an *n*-type semiconductor photo-anode for the electrolysis of water: M is the metal, E is the electrolyte, S is the semiconductor, D is the diaphragm.

An obvious development of this approach is to create a macro-heterogeneous system, i.e. a short-circuited electrochemical cell consisting of a semiconductor photo-electrode and a non-photosensitive (e.g., metallic) auxiliary electrode (Fig.10). By making the photo-electrode (as before) of strontium titanate in an aqueous solution we can produce photo-electrolysis of water in the illuminated cell, the products (gaseous hydrogen and oxygen) appearing at the separate electrodes of the cell. The reliable and simple separation of the products of the photo-reaction, which is a direct consequence of the spatial separation of the primary photogenerated current carriers (electrons and holes) under the influence of the field in the space-charge region, is the most important advantage offered by semiconductor photo-electrochemical devices for the conversion of light energy into chemical energy.

The spatial separation of anodic and cathodic partial reactions stimulated by illuminating the semiconductor–electrolyte interface can be useful for two reasons. Firstly, by "leading" the current carriers of different sign to different parts of the surface we can greatly reduce the losses due to recombination and raise the quantum yield of the photocurrent and the efficiency of the conversion of solar into electrical energy. Secondly, the efficiency of the photo-electrolysis can be increased very substantially by transferring one of the two conjugated reactions (the one involving majority carriers) to a separate auxiliary electrode. Thus the cathodic partial reaction (hydrogen evolution, say) can be conveniently carried out on a metallic electrode chosen for its favourable electro-catalytic properties towards this reaction.

Let us now consider a system in which equilibrium is established between the semiconductor and the solution in the dark. This is usually the case when the solution contains an easily reversible oxidation–reduction system. Under these conditions the semiconductor acquires the equilibrium potential of the system, i.e. $\phi = \phi^0_{redox}$, or in other words $F = F_{redox}$.

A similar argument shows that illumination of the semiconductor causes a shift in both the Fermi level F and the quasi-Fermi levels for holes and electrons. Both the forward and the reverse reaction described in Eqn.(1) are accelerated. In other words, the most immediate result of the illumination is an effective increase in the exchange current of the Ox/Red system[44]. This is not the only result, however. If the illuminated semiconductor is an electrode in an electrochemical cell, connected to a counter-electrode through a load resistance, spatial separation of the cathodic and the anodic reaction is obtained as in the photo-decomposition of water discussed above (see Fig.10). The reaction involving minority carriers takes place on the auxiliary electrode. As a result, illumination of the semiconductor electrode induces a current in the external circuit, and in conjunction with the load resistor this produces useful power. In other words, light energy has been converted into electrical energy. This is the operating principle of the photo-electrochemical cell which has been called the "liquid solar cell".

Let us examine in detail the operation of such a photocell taking one specific example (Fig.11): the *n*-type CdS|alkaline solution of S^{2-} and S_2^{2-}| metallic cathode system. In the dark the equilibrium in the cell is

$$S_2^{2-} + 2e^- \rightleftarrows 2S^{2-}, \qquad (32)$$

Both electrodes acquire the equilibrium potential of this oxidation–reduction system, because the Fermi levels of the metal and of the CdS and the level $F_{redox} = F_{S^{2-}/S_2^{2-}}$ in the solution are brought to the same level. Since the equilibrium potential of the oxidation–reduction system is more positive than the flat band potential of the semiconductor ($\phi^0_{redox} > \phi_{fb}$) the surface of the semiconductor becomes depleted, thus allowing the spatial separation of the photogenerated electrons and holes. Illumination of the electrode unbends the bands, shifting the Fermi level F of the semiconductor with respect to its dark value F_{dark} (see Fig.11),

and this produces a change in the potential of the electrode (i.e. it produces a photo-potential ϕ_{ph}).

In the simplest case (which is often met in experiments) the potential step in the Helmholtz layer (Φ_H) is unaffected by illumination, and is also independent of ϕ^0_{redox}. In other words the edges of the energy bands are "clamped" at the surface (see Section III). Under these conditions the maximum value of ϕ_{ph} (corresponding to the open-circuit photo-potential for fully straightened bands) is equal to the initial (dark) potential step in the space-charge layer ($-\Phi_{sc}$), i.e. to the difference $|\phi^0_{redox} - \phi_{fb}|$. Efficient energy conversion is achieved by choosing a combination of semiconductor and oxidation–reduction system in solution for which this difference is as large as possible.

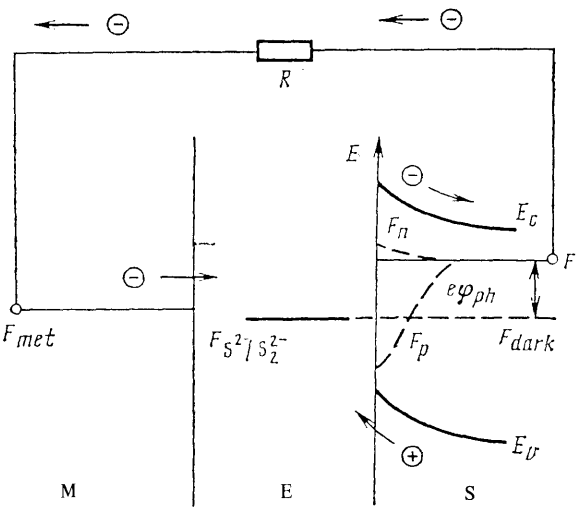


Figure 11. Energy diagram of an illuminated "liquid solar cell" with a CdS photo-anode and an S^{2-}/S_2^{2-} electrolyte; F_{dark} is the Fermi level of the CdS in the dark.

The photo-generation of electron–hole pairs produces quasi-Fermi levels for the minority and the majority carriers, F_p and F_n (see Fig.11). Since on the surface $F_p < F_{S^{2-}/S_2^{2-}}$, and $F_n > F_{S^{2-}/S_2^{2-}}$, both the forward and the reverse reaction are accelerated by illumination in the sulphide–polysulphide system. Closing the circuit through the external load R separates the anodic and the cathodic reaction: the holes flow from the semiconductor photo-anode into the solution, oxidising the S^{2-} ions to S_2^{2-}, and the electrons flow through the external circuit to the metallic counter-electrode (cathode), where they reduce S_2^{2-} to S^{2-}. The potential difference generated across the photo-cell is $I_{ph}R$, where I_{ph} is the photo-current, and the power conversion is $I^2_{ph}R$.

In some cases, however, the potential step in the Helmholtz layer does not stay constant under illumination or after changes in ϕ^0_{redox}. This results in a redistribution of the potential in the double layer, and the photopotential is invariably lower than the difference $|\phi^0_{redox} - \phi_{fb}|$. This occurs, for example, on silicon, gallium arsenide, or molybdenum diselenide electrodes in solutions of various oxidation–reduction systems. In other words, the band edges become "unclamped", and in the limit the Fermi level becomes "clamped" on the semiconductor surface. As a result, a gradual change in the potential ϕ^0 of the oxidation–reduction system causes the open-circuit photo-potential ϕ_{ph} of the cell to increase linearly with ϕ^0 at first ("clamped" band edges), before becoming independent of ϕ^0 ("clamped" Fermi level, see Fig.12).

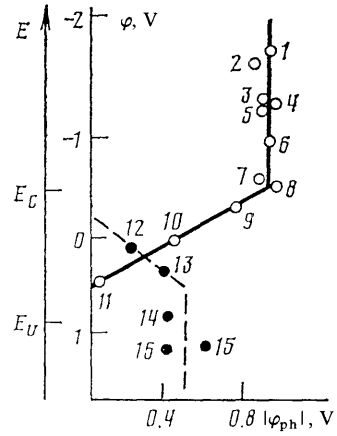


Figure 12. Plot of the absolute value of the open-circuit photo-potential $|\phi_{ph}|$ against the equilibrium potential of the oxidation–reduction system[45]. Photo-electrode of WSe_2, *p*-type (full line) or *n*-type (broken line) in acetonitrile solutions. The oxidation–reduction systems (with charges on the Ox and Red forms shown in brackets) are: *1*) anthracene (0/−1), *2*) phthalonitrile (0/−1), *3*) nitrobenzene (0/−1), *4*) 2,2′-bipyridyl complex of ruthenium (+2/+1), *5*) azobenzene (0/−1), *6*) anthraquinone (0/−1), *7*) benzoquinone (0/−1), *8*) methylviologen (+2/+1), *9*) tetracyanoquinonedimethane (+1/0), *10*) tetramethyl-*p*-phenylenediamine (+1/0), *11*) tetraphenyl-*p*-phenylenediamine (+1/0), *12*) I^-/I_3^-, *13*) Br^-/Br_3^-, *14*) Cl^-/Cl_3^-, *15*) thianthrene (+1/0), *16*) 2,2′-bipyridyl complex of ruthenium (+3/+2). The potentials are quoted against the saturated calomel electrode.

No explanation has yet been put forward for this phenomenon, which seriously limits the application of photo-electrochemical cells to the conversion of solar energy into electrical energy. Possible causes include (see Section III) the strong charging of the semiconductor electrode as the Fermi level approaches the edges of the forbidden gap (for example, during the formation of an inversion layer in the semiconductor[30,46]), a high density of surface states[28,29], or a shift in flat band potential in solutions of oxidation–reduction systems caused by the partial oxidation (or reduction) of the semiconductor surface by the components of this system, making ϕ_{fb} a function of ϕ^0.[47] All these situations could lead to a redistribution of the potential step at the interface between the space charge layer and the Helmholtz layer which could favour the latter layer.

3. Photo-corrosion and Stability

In the field of corrosion and photo-corrosion of semiconductor electrodes the quasi-thermodynamic approach offers useful criteria for determining the propensity of a semiconductor to

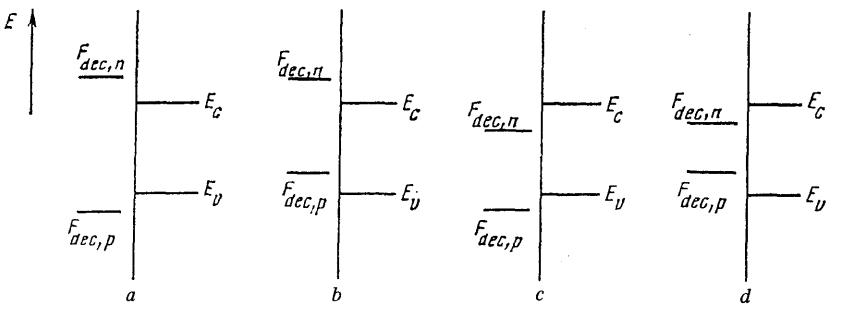


Figure 13. Diagrammatic presentation of the thermodynamic stability of a semiconductor with respect to decomposition in solution: *a*) absolutely stable, *b*) stable towards cathodic decomposition, *c*) stable towards anodic decomposition, *d*) unstable.

photo-corrosion and for identifying means of corrosion protection[12]. For example, in the case of the binary semiconductor MX (where M is the electropositive and X the electronegative component) we can write the following equations for the partial electrochemical reactions: for the cathodic decomposition with the participation of electrons from the conduction band

$$MX + ne^- \rightarrow M + X^{n-} \qquad (33a)$$

and for the anodic decomposition with the participation of holes (h^+)

$$MX + nh^+ \rightarrow M^{n+} + X\,. \qquad (33b)$$

Taking (as a concrete example) the hydrogen electrode as the reference level we can describe the overall reaction in the cell by one of the following equations (with the electrochemical potential of the reaction shown in brackets):

$$MX + \frac{n}{2}H_2 \rightleftarrows M + nH^+ + X^{n-}\,(F_{dec,n})\,, \qquad (34a)$$

$$MX + nH^+ \rightleftarrows M^{n+} + X + \frac{n}{2}H_2\,(F_{dec,p})\,. \qquad (34b)$$

By calculating the free energy change for these reactions we can determine the standard equilibrium potentials for the cathodic ($\phi^0_{dec,n}$) and the anodic ($\phi^0_{dec,p}$) decomposition of the semiconductor.

The thermodynamic condition for an electrode reaction (including a partial corrosion reaction) can be written for the cathodic reaction involving electrons from the conduction band as

$$\varphi < \varphi^0_{dec,n} \quad \text{or} \quad F > F_{dec,n} \qquad (35a)$$

and for the anodic reaction involving holes from the valence band as

$$\varphi > \varphi^0_{dec,p} \quad \text{or} \quad F < F_{dec,p}\,. \qquad (35b)$$

In order to determine the susceptibility of a semiconductor to electrochemical decomposition (or corrosion) in a specific environment we must insert into the energy band diagram the electrochemical potential levels of the electron for reactions (34a) and (34b).

Different possible situations are shown in Fig.13. The semiconductor is stable towards cathodic decomposition if the electrochemical potential level for this reaction lies within the conduction band, and it is stable towards anodic decomposition if the appropriate level lies within the valence band. In both cases if the change in potential takes place entirely within the semiconductor ("clamping" of the bands at the surface) the level becomes "inaccessible" to the Fermi level of the semiconductor. Thus in the situation illustrated in Fig.13*a* the semiconductor is absolutely stable, since the levels of both decomposition reactions lie outside the forbidden gap. More often the semiconductor is found to be stable towards only one type of decomposition reaction: the cathodic (Fig.13*b*) or the anodic (Fig.13*c*). Lastly, when both the $F_{dec,n}$ and the $F_{dec,p}$ level lie within the forbidden gap (Fig.13*d*) the semiconductor can decompose, in principle, under both cathodic and anodic polarisation.

The thermodynamic description of photo-corrosion assumes that the electrode reaction causing decomposition of the semiconductor is accelerated (under the influence of light) by the shift in the quasi-Fermi levels for electrons (F_n) and holes (F_p). We must therefore modify the conditions (35). The cathodic photo-decomposition of the semiconductor involving electrons from the conduction band is subject to the necessary condition [see (31)]

$$F_n > F_{dec,n} \qquad (36a)$$

and the anodic photo-decomposition involving holes to the condition

$$F_p > F_{dec,p}\,. \qquad (36b)$$

As soon as either of the conditions (36) is satisfied the corresponding reaction becomes thermodynamically possible.

We should note that the reaction may nevertheless be kinetically hindered. Thus in many cases it is kinetic rather than thermodynamic features of the electrode reaction which determine the corrosion (or photo-corrosion) behaviour of semiconductor electrodes.

In order to identify means of protection against corrosion (or photo-corrosion) we must consider what other reactions can compete with the photo-decomposition process. For example, at the highest levels of illumination the cathodic reaction with the most positive equilibrium potential is the most probable, and the predominant anodic reaction is the one with the most negative equilibrium potential. It follows that the photo-corrosion process can be suppressed by adding suitable oxidisers or reducers to the solution.

Thus anodic photo-corrosion can be prevented by systems whose oxidation–reduction potential is more negative than the decomposition potential: $\phi^0_{redox} < \phi^0_{dec,p}$, i.e. $F_{redox} > F_{dec,p}$ (see Fig.14). The condition for stabilisation towards cathodic photo-decomposition is $\phi^0_{redox} > \phi^0_{dec,n}$, or $F_{redox} < F_{dec,n}$. These protection systems, which stabilise the semiconductor by being thermselves oxidised or reduced,

are used in photo-electrochemical solar energy conversion cells[48-51]. The solvent (for example, water) can act as the protection additive if it is oxidised (or reduced) more readily than the material of the semiconductor electrode. This occurs, for example, in many oxide electrodes (TiO_2, $SrTiO_3$, etc.), for which the most probable anodic photo-reaction is the oxidation of water to oxygen.

Let us examine from this point of view the photo-corrosion behaviour of GaAs and GaP in aqueous solutions. The electrochemical potential levels for the decomposition reactions of these materials are indicated in Fig.15 in relation to the levels E_c and E_v,

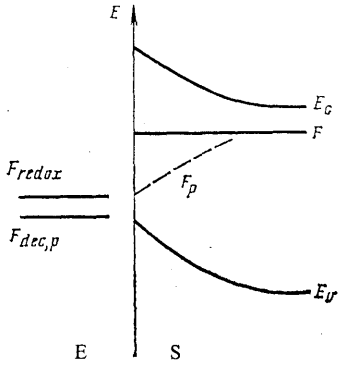


Figure 14. Protection of an n-type semiconductor from anodic photo-decomposition by the addition of an oxidation–reduction system to the solution.

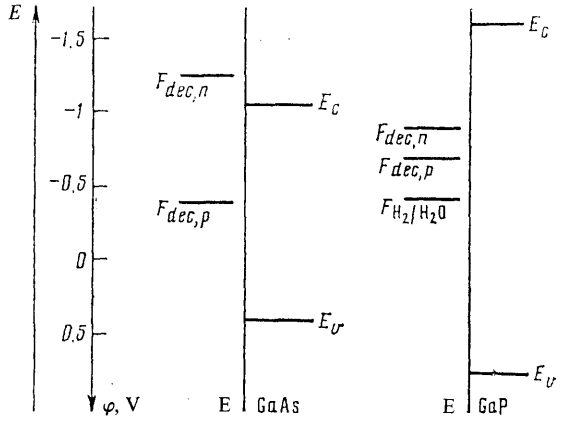


Figure 15. Energy levels at the contact between GaAs or GaP and an aqueous solution at pH 7.[52] The potentials are quoted against the normal hydrogen electrode.

For GaAs the level $F_{dec,n}$ corresponds to the reaction

$$GaAs + 3H^+ + 3e^- \rightleftarrows Ga + AsH_3$$

and $F_{dec,p}$ to the reaction

$$GaAs + 5H_2O + 6h^+ \rightleftarrows Ga(OH)_3 + HAsO_2 + 6H^+.$$

For GaP the level $F_{dec,n}$ corresponds to the reaction

$$GaP + 3H^+ + 3e^- \rightleftarrows Ga + PH_3$$

and $F_{dec,p}$ to the reaction

$$GaP + 6H_2O + 6h^+ \rightleftarrows Ga(OH)_3 + H_3PO_3 + 6H^+.$$

By comparing these diagrams with Fig.13 we note that GaAs is an example of case 13*b*, i.e. it is stable towards cathodic decomposition but potentially unstable towards anodic decomposition, whereas GaP is potentially liable to both cathodic and anodic decomposition, since the levels of both reactions lie within its energy gap (as in Fig.13*d*).

4. Limitations of the Quasi-Fermi Level Concept in Photoelectrochemical Kinetics. Alternative Approaches

As we have shown the quasi-thermodynamic approach based on the concept of quasi-Fermi levels is widely used and, on the whole, effective. It has the undeniable advantages of being physically meaningful and simple. However, it should not be forgotten that the use of the quasi-Fermi level concept is not always justified.

The definition of the quasi-Fermi level within a semiconductor is meaningless unless the following conditions are satisfied:

$$\tau_c, \tau_v < \tau_{cv} \qquad (37)$$

where τ_c and τ_v are the times for the establishment of thermodynamic equilibrium in the electron ensemble of the conduction band and in the hole ensemble of the valence band, and τ_{cv} is the time for the establishment of equilibrium between the electron and the hole ensembles.

The conditions (37) are usually obeyed, but there are additional conditions to be met before this approach can legitimately be applied to the description of electron transfer processes at interfaces. We need to define the times ($\tau_{n,s}$ and $\tau_{p,s}$) elapsed between the photo-excitation of an electron or hole and its capture by the surface (for example, as a result of the electrode reaction). The quasi-Fermi level concept is valid only if these times are greater than τ_c and τ_v, because if the opposite were true insufficient time would be available for the establishment of quasi-equilibrium in the bands, and the "hot" particles would take part directly in the electrode process. On the other hand, the times $\tau_{n,s}$ and $\tau_{p,s}$ must be less than τ_{cv}, because otherwise the electron–hole system would reach full equilibrium and we would revert to $F_n = F_p = F$ close to the surface.

Thus, in addition to (37), the following systems of inequalities must be satisfield:

$$\tau_c < \tau_{n,s} < \tau_{cv}, \quad \tau_v < \tau_{p,s} < \tau_{cv}. \qquad (38)$$

If only one type of carrier is involved in the reaction, only one of these two systems of inequalities has to apply.

If the capture of electrons or holes by the surface is fast, the parameters $\tau_{n,s}$ and $\tau_{p,s}$ are identical to the times of arrival at the interface. If, on the other hand, the surface process cannot be treated as infinitely fast, the times $\tau_{n,s}$ and $\tau_{p,s}$ can be identified with the characteristic times of the process (for example, the time for the elementary act of the electrode reaction). Since the difference between the times τ_c and τ_v (on the one hand) and the time τ_{cv} is fairly large ($\approx 10^{-13}$–10^{-8} s) the conditions (38) are often satisfied, and this explains the success of the quasi-Fermi level concept when applied to various types of heterogeneous process.

Nevertheless, for a quantitative description (see, for example, Ref.53) still further conditions have to be satisfied. In particular, the quasi-levels in the space-charge regions must be reasonably smooth, and the amount of recombination within the space-charge region must be small. Clearly, also, if the carriers are photo-generated near a surface at which a fast electrode reaction is taking place they could be "sucked out" of the semiconductor before coming to equilibrium with the thermalised carriers in the appropriate band. Under these conditions the carrier cannot be described in terms of the quasi-Fermi levels F_n and F_p: it would be more correct to treat the transitions of the carriers from the electrode into the solution not as a quasi-equilibrium but as a dynamic situation, i.e. as separate events[54-56].

The choice between the two approaches to the description of photo-electrochemical reactions (quasi-thermodynamic, or dynamic) in any particular system can be based, in principle, on experimental data[55]. However, the necessary data are scarce and unreliable at present, and this remains a problem for the future.

V. SOME NEW PRACTICAL APPLICATIONS OF SEMICONDUCTOR ELECTRODES

1. Photo-electrochemical Solar Energy Conversion

The photosensitivity of semiconductor electrodes makes the semiconductor–electrolyte interface a potential energy converter for light[57]. A brief description of the mechanism by which photocurrent is induced in a semiconductor electrode was given above (Section IV) for the two most important cases: in the presence of a highly reversible oxidation–reduction system in solution and without such a system (i.e. under conditions which suppress the electrochemical reaction in the dark). In the first case the light energy is converted into electrical energy, in the second into chemical energy. The photo-electrochemical cells corresponding to these two cases are called "liquid solar cells" (or photo-electrochemical cells of the regenerative type) and photo-electrolysis cells respectively. Among the most important photo-electrolysis reactions is the decomposition of water, a possible source of hydrogen as a fuel or as a raw material.

The main advantage of photo-electrochemical cells with semiconductor electrodes (as compared, say, with solid-state semiconductor solar cells) is their relative insensitivity to the crystal lattice perfection and the purity of the semiconductor. Polycrystalline semiconductor electrodes in electrochemical "solar cells" give very effective energy conversion, both in absolute terms and in comparison to monocrystalline electrodes. This offers, at least in principle, the possibility of developing cheap and simple solar energy converters.

The detailed mechanism of the operation of photo-electrochemical converters and the characteristics of specific systems have been discussed in several recent reviews[6,41,48-51,55,58-60], and lie outside the scope of this review. However, it is important at this stage to examine the main problems still to be solved before photo-electrochemical cells can find extensive practical applications.

The main obstacle to the development of "liquid solar batteries" is the photo-corrosion of the semiconductor electrodes, which seriously limits their useful life. In order to eliminate anodic photo-corrosion, for example, a reversible oxidation–reduction system is added to the solution, so that the oxidation of the Red component (a "consumer" of photo-generated holes) competes with the photo-decomposition of the electrode material (see Section IV). In this way it has been possible to eliminate photo-corrosion almost completely in many types of photocell, and to increase the period of continuous operation of the photocell to almost one year. Nevertheless there are other, less obvious mechanisms of degradation of the electrodes[51,61] which prevent photo-electrochemical cells from competing with the useful service life of solid-state solar cells (up to 20 years).

A very real problem in photo-electrolysis is to make the energetics of the electrochemical reaction compatible with the spectrum of solar radiation. The energy distribution of the photons in the solar spectrum is such that the optimum threshold energy of the quantum process chosen for the conversion of the solar energy (i.e. of the semiconductor electrode reaction) lies in the range 1.1–1.4 eV. The free energy for the decomposition of water into hydrogen and oxygen is 1.23 eV, i.e. it lies within the calculated range. However, in practice the reaction requires a large overvoltage. Allowing also for other unavoidable losses, the quantum energy needed for the photo-electrochemical decomposition of water becomes ~2 eV,[58,60] i.e. it is much higher than even the upper limit of the calculated optimum energy range. In other words, in the solar spectrum only a small fraction of very energetic quanta is used directly in the photo-electrolysis of water. (Note that this is far from accidental: indeed, were it not for this condition the relative stability towards solar radiation of a wide variety of living or inanimate systems in nature could not be explained.) This obstacle can be overcome, in principle, in several ways.

1. Carry out the reaction in the photo-stimulated electrolysis regime. In this case the main bulk of the quanta in the solar radiation (of energy in the range 1.1–1.4 eV) is used to excite the photo-electrochemical reaction, and additional energy (to the required 2 eV) is provided from an auxiliary source. The most successful use of this procedure is reported in Ref.62.

2. Carry out a process of the "two-quantum" type. By combining within the same photo-electrochemical cell two semiconductor photo-electrodes (an n-type anode and a p-type cathode) we can achieve effective addition of the photopotentials developed on the two electrodes (if their characteristics are suitably chosen) and thus obtain the energy needed for the photo-electrolysis of water[63].

Another approach is to carry out the water decomposition reaction in two separate steps, each in a separate photo-electrochemical cell. The two cells are connected by an intermediate substance which acts as a charge transfer medium and is not consumed by the reaction, but ensures that the chemical potentials developed in the two cells are "connected in series"[6,64]. The analogy between this system and the combination of two photo-systems in natural photosynthesis processes is easy to see.

All these approaches rely on the use of two photo-electrodes, and therefore the overall reaction is formally a two-quantum process, which makes possible the required energy gain.

3. Separate the overall process into two steps: the conversion of the solar energy into electrical energy and the electrolysis of water[65-67]. The single photo-electrochemical cell is replaced by a combination of a solar cell (of the solid-state or of the "liquid" type) and an ordinary electrolysis cell. In this case the two functions (development of an electrical voltage and electrochemical decomposition of water) which were combined in the photo-electrolysis cell are now separately assigned to two specially designed pieces of apparatus. In this way we can generate the required voltage by connecting in series several solar cells; greater flexibility in the choice of the photoelectric and electrocatalytic properties of the electrode materials is also possible.

4. Dehydrogenation of cheap and readily available substances. Since the only wanted product is hydrogen, we can abandon the photo-electrolysis of water and choose an alternative electrochemical reaction with a smaller free energy change: for example, the dehydrogenation of various industrial by-products. Photo-electrochemical processes of this type have been studied intensively in recent years[50,68-71].

Other systems of interest include the use of the invisible (infrared) part of the solar spectrum in addition to visible light[72], and the exploitation of non-traditional reactions such as photo-intercalation into the semiconductor crystal lattice of atoms produced by the electrode reaction[73].

The extensive work currently in progess in this area should result in the development of simple and economically attractive photo-electrochemical processes able to compete with other, non-electrochemical methods of utilising the sun's energy.

2. Laser Etching of Semiconductors

Recent advances in quantum optics have led to the development of a new technology: the laser electrochemistry of semiconductors[74,75]. This field includes several topics related to the stimulation of electrochemical processes on semiconductor electrodes by laser radiation. The most successful of these so far has been the photo-sensitive etching of semiconductors with coherent laser radiation for optical information storage (for example, in holography[76]). Light-sensitive etching in conjunction with polarisation from an external source is called photo-anodic etching, whereas etching in an oxidising solution is called photochemical.

The basis of light-sensitive etching is the influence of illumination on the concentration of minority carriers, which determines the rate of dissolution and corrosion processes in semiconductors.

In laser etching an initially flat semiconductor surface immersed in a solution of electrolyte is exposed (through the solution) to two coherent monochromatic beams of light, incident at equal angles, lying in the same plane, and having the same intensity and wavelength. The interference between these beams produces bands of light and dark regions, and stimulates non-uniform etching of the surface.

The theory of laser etching[74,77] can be used to calculate in simple but practically important cases the characteristics of the etched outline as a function of the parameters of the radiation, of the properties of the semiconductor, and of the special features of the electrode reaction. The profile of the etched pattern is very close to sinusoidal. For the case of "surface-absorbed" light (i.e. light with a very high absorption coefficient) and a fast electrochemical reaction the repetition frequency of the profile (having the dimensions of reciprocal length, d^{-1}) is found to be very high. The physical meaning of this observation is the following: if the holes are generated immediately below the surface, and used in the reaction effectively in the same place, we can ignore the diffusion of photo-generated holes beyond the illuminated regions of the semiconductor.

Thus the spatial resolution of light-sensitive etching, i.e. the maximum achievable value of d^{-1}, is not determined by the diffusion length L_p of the holes, as could have been expected ($d \cong L_p$), but it can have a much higher value ($d^{-1} \gg L_p^{-1}$).

It is now experimentally established that the resolving power of the photo-electrochemical information storage processes d_{max}^{-1} (the maximum number of lines etched in the grating per 1 mm) can be very high: for GaAs and CdS it is greater than 6000 mm^{-1}. We should stress that in materials with a high diffusion length L_p (like silicon and germanium) the resolving power is appreciably higher, as could have been predicted theoretically from the L_p values.

In conclusion we note that the laser electrochemistry of semiconductors is not confined to light-sensitive etching. It includes, for example, the study of threshold electrochemical reactions stimulated by powerful laser pulses. These reactions can occur by new paths, yielding new products, owing to the participation of strongly excited species from the solution and of the non-equilibrium electron–hole plasma of the semiconductor. Therefore they offer new possibilities for the development of unconventional processes in chemical technology.

3. The Ion-selective Field-effect Transistor

The combination in a single device of an ion-selective electrode and a field-effect transitor has yielded a new type of detector of ion concentrations called the ion-selective field-effect transistor. Because of its high sensitivity and selectivity coupled with a small size this device has found wide applications in industry, in medicine and biology, and in scientific research.

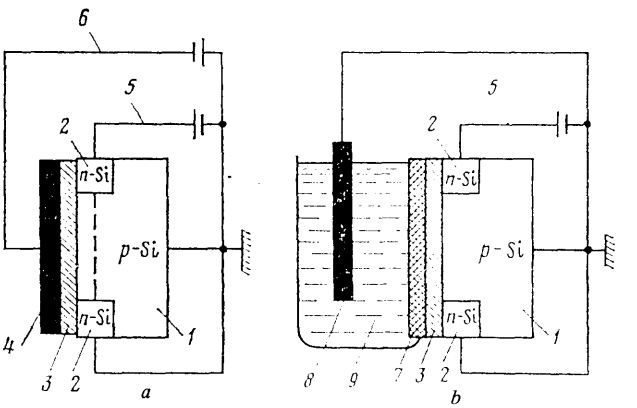


Figure 16. Electrical circuit of a field-effect transistor (*a*) and of an ion-selective field-effect transistor (*b*): *1*) base, *2*) source and drain, *3*) dielectric layer, *4*) gate, *5*) and *6*) low-impedance and high-impedance electric circuits, *7*) ion-selective membrane, *8*) reference electrode, *9*) experimental solution of electrolyte.

The operating principle of the field-effect transistor can be briefly described as follows (see, for example, Ref.78). The transistor (Fig.16*a*) is a metal–dielectric–semiconductor system, i.e. it consists of a semiconductor base on which a dielectric layer and a metallic electrode (the "gate") are deposited. The base is usually a plate of *p*-type silicon, and the dielectric a layer of SiO_2 or Si_3N_4 100–200 nm thick and having a resistance of ~10^{13} Ω. Two regions in which the conductivity type of the silicon is inverted are prepared in the base by localised doping: these *n*-type regions are called the "source" and the "drain" respectively. By inserting voltage sources into the gate–base and source–drain circuits (Fig.16*a*) we can induce a field effect in the transistor. In the absence of a gate voltage the current in the

source–drain circuit is almost zero, because one of the two p–n junctions in this circuit is always reverse-biassed. We now apply to the gate a voltage of sign and magnitude such that an inversion layer is formed near the silicon–dielectric interface (i.e. a layer in which the concentration of minority carriers is greatly increased). In the case shown in Fig.16*a* the gate bias has to be positive with respect to the base. The resulting n-type "channel" short-circuits the source and the drain, allowing current to flow in this circuit (whose resistance is now of the order of 10 Ω). Thus a change in voltage in the high-impedance gate–base circuit effectively controls the current in the low-impedance source–drain circuit, i.e. the device offers a high current gain.

This property of the field-effect transitor is exploited in the ion-selective field-effect transitor to achieve a high sensitivity. The dielectric layer is replaced by an ion-selective membrane, permeable to one kind of ion#, and the metallic gate is replaced by a solution of electrolyte in which the reference electrode needed to complete the electrical circuit is immersed (Fig.16*b*). The role of the external gate voltage is now played by the potential generated on the membrane by the presence of ions to which the membrane is selectively permeable. The magnitude of this potential is given by the Nernst equation [see also formula (4)]

$$\varphi = \varphi^0 + RT/z\mathcal{F} \ln a \qquad (39)$$

where a and z are the activity (in the simplest case, the concentration) and the charge of the potential-determining ion, and ϕ^0 is the standard potential (i.e. the value of ϕ when a = 1 mole litre^{-1}).

For a membrane potential produced in this way the current in the measuring circuit is a function of the activity of the ions (a), thus making the ion-selective field-effect transistor a very sensitive ion detector. A great variety of specific types of this device has been produced, covering a wide range of membrane composition, type of reference electrode, operating regime (for example, including a small auxiliary polarising voltage), etc. A list of the most important of these systems, with a statement of their characteristics and of their application regions, can be found in recent review articles[79,80].

VI. CONCLUSIONS

We have not been able to include in this review all the new ideas and approaches now being actively developed in the field of semiconductor electrochemistry. In conclusion, therefore, we shall simply list the directions which we believe to be the most interesting and promising, though in some cases (for various reasons) interest has only been transient and developments only preliminary. A special discussion of these topics is given in Heller's monograph[61].

New systems. Among the most interesting new materials for practical applications in electrochemistry are the semiconductors with a layer crystal structure[81]. Being d-semiconductors they could be more stable towards photo-corrosion than the semiconductors (mainly sp) discussed above; furthermore, semiconductors with a layer crystal structure can be used as hosts to non-tranditional types of photo-electrochemical reaction: for example, the photo-intercalation of atoms from the solution into the crystal lattice of the semiconductor electrode. Semiconductors with d bands are potentially suitable as electrodes in photo-electrochemical cells. The synthesis and study of new materials with a prescribed set of photo-electric and electrochemical properties have grown into a major activity in the "electrochemical materials science" of semiconductor technology (see, for example, Ref.82).

Another promising area is the study of the photo-electrochemical properties of micro-heterogeneous semiconductor systems: porous electrodes, and suspensions of different particle size (down to colloidal dimensions), in which the photosensitivity of semiconductors is combined with the high catalytic activity of systems having a developed surface.

The modification of semiconductor electrode surfaces by "attached" catalysts (charge carriers)[83] is also being intensively studied at present.

New methods of investigation. Important new information can be expected to flow from the new methods of investigation, both those developed independently within the electrochemistry of semiconductors and of metals and those imported from other disciplines (mainly from surface physics), which have been called non-traditional. The latter relate almost invariably to the effect of radiation on a phase boundary. They include photo-temperature spectroscopy, in which the part of the absorbed light energy used in the photo-electrochemical reaction and that dissipated as heat are distinguished by monitoring the temperature of the photo-electrode, thus allowing the "true" quantum yield to be calculated[84,85], high-time-resolution measurements of the photocurrents induced by nanosecond laser pulses[86,87], electro-luminescence studies of recombination processes in electrodes[88], the photo-emission of electrons from semiconductors into solutions of electrolytes[20], and also the electro-reflectance of light at the semiconductor–electrolyte interface[89]. Photo-acoustic spectroscopy also has been used to study the fine details of the absorption of light by semiconductors[90].

Thus the recent advances have given a fairly comprehensive formulation of the electrochemical behaviour of semiconductors. Because of the number and importance of the new problems, semiconductor electrochemistry has become one of the "growth areas" of modern science.

#In some types of device the membrane is placed directly over the dielectric layer, giving a "four-layer" system.

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Institute of Electrochemistry of the
USSR Academy of Sciences, Moscow