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Semiconductor-Electrolyte Interface: Basic Notions and Definitions

A CHARACTERISTIC FEATURE of a SE system in equilibrium is the presence of exchange currents of electrochemical origin. These arise due to charge transfer across the electrochemical barrier that exists at the SE interface. The charge exchange arises as a result of chemical dissolution of the semiconductor (ionic exchange), as well as that between the electrons of the semiconductor and the ions of the electrolyte [30–32, 46–48].

It is well known that covalent-type semiconductors like Ge and Si do not dissolve in oxidizer-free aqueous electrolytes [49]. Charge exchange in this case occurs due to the exchange between the electrons of the c and v bands of the semiconductor and the ions of the electrolyte. In accordance with the Franck-Condon principle, this exchange is accomplished by electron tunneling and becomes possible in the case when the electron energy level in the "ionic" state in the electrolyte coincides with that in the semiconductor. In this case, it is assumed that the conditions allowing the electron exchange are attained as a result of thermal fluctuations in the polar electrolyte which change the energy of electrons in the "ionic" states. It is also assumed that the probability of electron transfer as such is about unity (when the Franck-Condon principle, in the conditions typical of oxidoreduction processes, holds true [21, 22, 46]). So the electron transfer is regarded as a process that is realized by means of electron exchange between states with coinciding energy levels. Thus the exchange rate between occupied and unoccupied electronic states is a function of their relative energy-level positions.

In the general case, one should expect that both electron as well as hole currents will cross the interface. The current values are proportional to the concentrations of ions in the electrolyte capable of exchanging with the electrons of the semiconductor, to the concentration of free carriers in the semiconductor at the SE interface, and to the probability of their transition across the barrier. The relevant contributions of c and v bands depend on which of those dominates

the electron exchange. The relation between the corresponding currents in equilibrium is given by the following expression:

$$j_n^0/j_p^0 \approx \exp(qV_s^0/k_0T), \qquad (1.1)$$

where V_s^0 is the equilibrium value of the potential drop in the semiconductor SCL which defines the near-surface band bending and is a function of the oxidoreduction potential of the system. In strong oxidizer solutions the energy bands are bent upward ($V_s^0 < 0$); hence, the v band plays the major role. In the opposite case ($V_s^0 > 0$), the exchange is primarily with the c band [3, 9, 11, 21]. The occurrence of intense exchange currents governing thermodynamic equilibrium accounts for the high degree of stability of semiconductor surfaces in an electrolyte.

As a result of charge exchange a double layer will be built up. On the semiconductor side this is due to the charge in the SCL and surface states, whereas on the electrolyte side an equal charge of opposite sign will be set. The latter is due to electrolyte ions at the semiconductor surface as well as those in a thin diffuse near-surface layer in the immediate vicinity of the surface (the Goui layer) [50–52]. The potential drop in the electric double layer, referred to as the Galvani potential [9, 52], occurs mainly within the SCL of the semiconductor, whereas in the electrolyte (in the Goui layer) it can be neglected.[1]

The value of the Galvani potential can be represented as a sum of different potentials corresponding to the Fermi level position in a semiconductor, the oxidoreduction potential of the electrode reaction, and an arbitrary additive constant [9, 16]. This value is incorporated into the electrode potential (φ) which represents the potential difference between the two identical metal ends of the electrochemical circuit, the semiconductor being one of its components.[2] The electrochemical circuit also includes the reference electrode, the potential at which is considered to be zero (see Fig. 1.1). It is commonly supposed that a positive shift of φ corresponds to the transport of positive charges from the semiconductor to the electrolyte [17]. Hence, the more positive the charge and the more

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[1] The ion concentrations in the electrolyte are assumed to be large ($N > 0, 1$ mol), with the density of surface states on the semiconductor not so great.

[2] If there are no special reservations all values of the electrode potential presented within this book were measured relative to the normal hydrogen electrode.

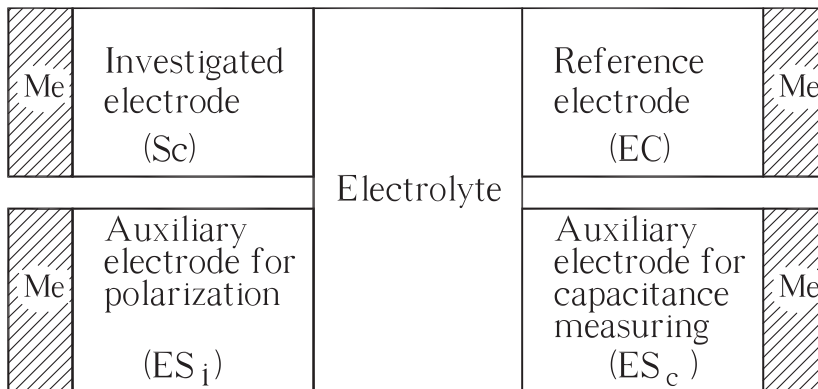| Me	Investigated electrode (Sc)	Electrolyte	Reference electrode (EC)	Me
Me	Auxiliary electrode for polarization (ES$_i$)		Auxiliary electrode for capacitance measuring (ES$_c$)	Me

Figure 1.1 Scheme of the normally broken electrochemical circuit.

negative the electrostatic potential in the SCL of a semiconductor, the more positive is its electrode potential. The value of the equilibrium electrode potential (φ_0) is a function of the chemical potentials of the electrolyte ions. Unlike the Galvani potential, the equilibrium electrode potential does not depend upon the Fermi level position in the semiconductor, because the potential drop at the Ohmic contact required for electrode potential measurements has the opposite dependence on the Fermi level. Thus, the electrode potential for a given semiconductor and electrolyte is constant independent of the incorporated impurities provided the chemical character of the semiconductor and its surface layer are not changed. Hence, measurements of the electrode potential prove to be a convenient method of monitoring the surface conditions of a semiconductor, enabling control of the degree to which the surface is "clean" and reproducible.

One of the most important characteristics useful for the description of electrochemical and physicochemical processes at the SE interface is the energy structure of the latter. To plot the interface energy scheme, assume that the electrolyte contains so-called oxidoreduction pairs, hereafter referred to as redox pairs. These can be represented, in the simplest case, by singly and doubly charged metal ions (M^+ and M^{++}) which can be regarded as occupied and unoccupied electronic states, respectively. In the first approximation, approaches similar to those employed for the treatment of donors and acceptors in semiconductors can be applied in this case as well. The electron energy levels of ions in the electrolyte may be treated as

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the surface state levels in the conventional electron scheme of a semiconductor. Henceforth, their energy positions are referred to as E_{ox}^0 and E_{red}^0 for occupied and unoccupied electronic states, respectively. Note the following peculiarities of these states in which they differ from the usually treated surface electronic states [8, 10, 22, 52] :

1. Ions electrostatically adsorbed on a semiconductor surface have a solvation shell which defines the universal character of the electric double layer. This simplifies consideration of electron exchange processes and enables the controlled alteration of surface band bending under realization of FESE (see Chapter 3).

2. For one and the same adsorbed ion, different charge states correspond to different energy levels of the electron states. This is stipulated by the polarization of the medium and reorientation, with ion charge state modification, of the electrolyte dipole molecules surrounding the ion. This difference is described by the reorganization (rearrangement) energy E_R, which is the energy change of a polar medium due to changes in the polarization accompanying the electron exchange between the semiconductor and electrolyte and satisfies the condition $E_{ox} - E_{red} = 2E_R$.

3. For the electron energy states of ions adsorbed on the semiconductor surface, one should take into account their energy smearing due to thermal fluctuations of ions in the electrolyte. The distribution of the probability of the level to have the energy E is given by the following expression:

$$W(E) = \sqrt{4\pi E_R k_0 T} \cdot \exp\left(-\frac{(E_t - E)^2}{4 E_R k_0 T}\right) \tag{1.2}$$

where E_t is the energy corresponding to the distribution maximum at which the free energy of the whole system is minimized [10]. In this case the level energy exhibits fluctuations around the most probable value, which allows use of notions such as the fluctuation density of electron states in the electrolyte. Note the difference between the concept of fluctuation in the electron distribution due to the electron-phonon coupling at a given energy-level distribution and that of fluctuation of energy levels themselves, relating to electronic states in the electrolyte, which results from the ion-phonon interaction.

In considering the SE interface energy structure in equilibrium, it is appropriate to introduce the redox potential V_{redox}, which is defined as

$$-qV_{redox} = (E_{ox} + E_{red})/2 + k_0 T \ln(C_{ox}/C_{red}) \tag{1.3}$$
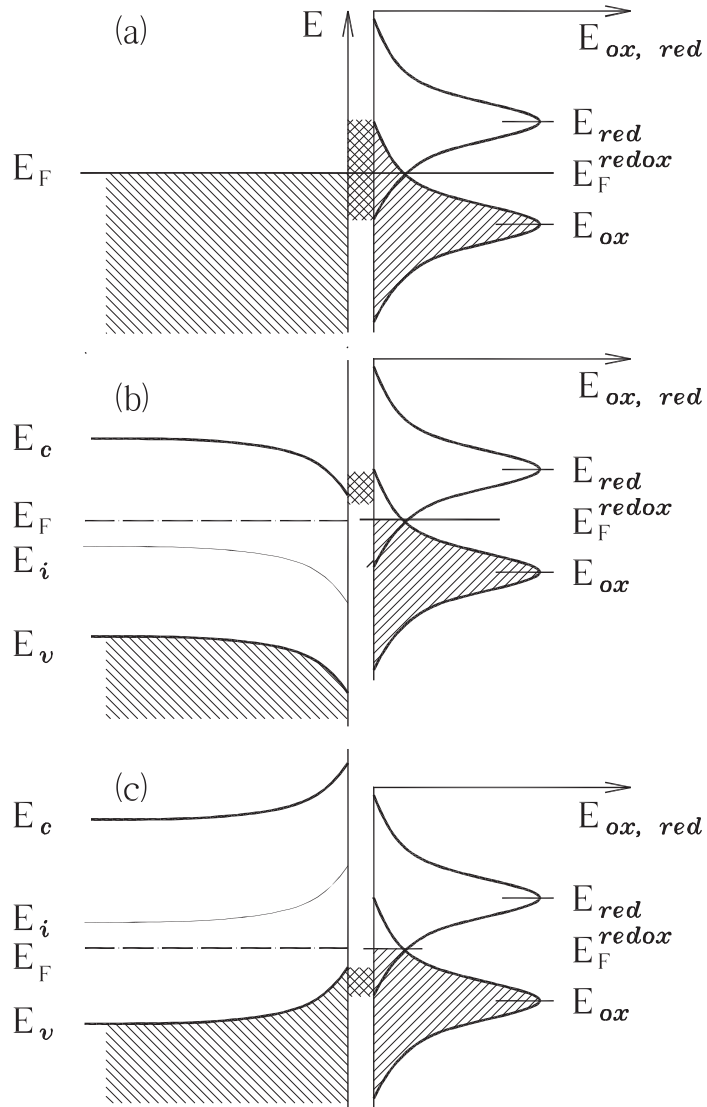
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Figure 1.2 Schematic diagram of electronic energy levels of solid–electrolyte interface in thermodynamical equilibrium state: (a) metal; (b) semiconductor of n type (electron exchange with c band); (c) semiconductor of p type (electron exchange with v band). The energy interval $\sim k_0 T$ the electron exchange between solid and electrolyte occurs is double shaded.

where C_{ox} and C_{red} are the densities (activities in the more general case) of the relevant ions. Here $\ln(C_{ox}/C_{red})$ defines a correction for their concentration (activity) difference. This potential may be treated as the degree to which the redox pairs are capable of giving up or accepting electrons. With $C_{ox} = C_{red}$, the equilibrium corresponds to a coincidence of the $-qV_{redox}$ level with the Fermi level in the semiconductor, that is, $-qV_{redox} = E_F$. So the value of $-qV_{redox}$ itself may be regarded, in relation to the electron exchange, as an analogue to the Fermi level in the electrolyte. It is defined as E_F^{redox}.[3]

Under such assumptions, the energy diagram of the SE boundary can be represented as in Fig. 1.2. From the figure it follows that the major parameter defining the electron state energy distribution at the boundary between a semiconductor and an electrolyte containing a redox pair is the Fermi level position in the redox system (E_F^{redox}) with respect to the semiconductor band edges. If E_F^{redox} lies closer to the c band edge, we have the case when the exchange with the electrons of the c band dominates. When E_F^{redox} lies closer to the v band edge, the electron exchange with the v band plays the dominant role. The positions of the edges of the allowed bands at the surface of a semiconductor that is in contact with the electrolyte can be determined by finding the values of the electrode potential in relation to the reference electrode in the condition of flat bands (φ_{fb}).

Another alternative is measurement of the differential capacitance of the SE interface at electrode potentials corresponding to the degeneracy of the electron (hole) gas in the semiconductor SCL (see chapter 5).

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[3] This analogy proceeds only from the thermodynamical relations defining equilibrium conditions at the SE interface. Strictly speaking, the position of E_F^{redox} in the electrolyte is not connected with free electrons, but is rather defined by the oxidoreduction system, containing only bound electrons [5, 10, 53].