Energy Diagram of Semiconductor/Electrolyte Junctions

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# Energy Diagram of Semiconductor/Electrolyte Junctions

In electrochemistry and photoelectrochemistry, it is most common to refer the voltage to a reference electrode (RE) or in a two-electrode cell with respect to a counterelectrode (CE).[1,2] However, in a semiconductor film that is composed of several junctions, as in semiconductor nanoheterostructures including catalytic layers, it is convenient to use the energy scale with reference to the vacuum level (VL).[3] This type of reference in the energy diagram allows one to track the local variations of energy, electrostatic potential, and Fermi energy inside the solid, and it is the standard representation in solid-state electronics as well as in materials characterization involving ultraviolet photoelectron spectroscopy (UPS) measurements.[4,5] In contrast, the measurement with respect to RE only takes the voltage at a point on the surface of the solid. Therefore, the relationship between the two pictures can lead to some confusion. In this Guest Commentary, we provide a consistent set of definitions and a diagram that allow one to combine both types of conventions. It is far from the scope of this paper to define the physical meaning of all quantities involved, but we do provide a set of mathematical relationships that allow us to relate the different expressions of voltage and energies such as the flatband potential and the energy (or potential) of the semiconductor conduction band at the surface.

The energy diagram of an n-type semiconductor electrode in contact with electrolyte is shown in Figure 1a. In the scheme, the vertical direction indicates increasing electron energy. The arrow indicates the convention of sign for a given quantity. The arrow for A, joining levels B (base of the arrow) and C (tip of the arrow), means that the defined quantity is $A = C - B$. We consider the general definitions (see also Table 1):

(a) V is a voltage in volt units (V). In the diagram, it is given in energy units as $-qV$, q being the positive elementary charge. A voltage in the diagram is positive if the arrow in the diagram points downward. V_r is measured with respect to the RE. V_{app} is measured with respect to an equilibrium situation (as $E_{Fn} = E_{redox}$). The sign for V_{sc}, V_H, and other internal voltage drops is specified by the arrow as noted above.

(b) ϕ is an electrostatic potential (volts) that is given (in energy units as $-q\phi$) as the local vacuum level (LVL) with respect to the reference level at which $\phi = 0$.

(c) E is an energy level, or electrochemical potential level, in units of electronvolts (eV). It is measured with respect to the LVL. Note that a usual reference for the absolute electron energies is the energy of the electron at rest in vacuum just outside of the surface of interest.[4] In Figure 1a, the VL in the electrolyte, E_{vac}^{el}, is taken as the reference of absolute energies scale. The dipole at the electrolyte/vacuum interface[6] is not represented in Figure 1a. Because a change of local ϕ moves the LVL, all energies in the semiconductor shift accordingly. Material properties such as χ and ζ_{nb} are defined positive. An arrow pointing downward in the diagram indicates a negative energy difference.
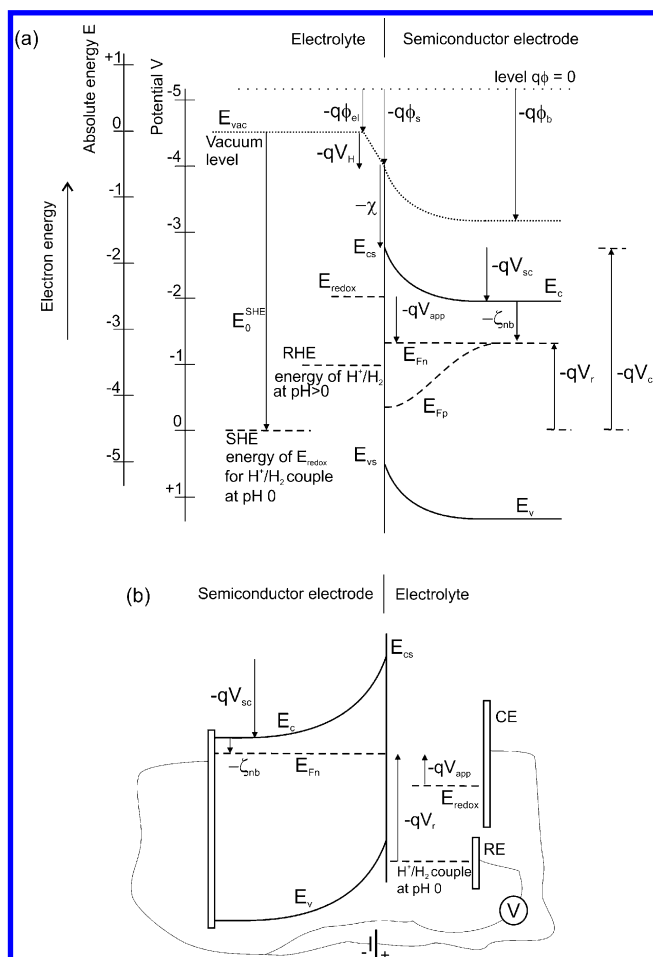
Figure 1. (a) Scheme of an n-type semiconductor electrode, indicating energies in the absolute energy scale (with respect to the VL), and potentials in the electrochemical scale, with respect to the standard hydrogen electrode energy (SHE). The reversible hydrogen electrode (RHE) potential is also indicated. (b) Scheme of a photoelectrochemical cell. The semiconductor is polarized against the electrolyte forming a Schottky barrier. The back contact is an ohmic contact.

(d) Subindex s is for a surface quantity, and subindex b is for a bulk semiconductor quantity.

The doped n-type semiconductor has a uniform distribution of donor ions N_D that are balanced by the same quantity of free electrons $n_0 = N_D$ in the neutral region, where the band edge is flat. The following quantity indicates the amount of doping

$$\zeta_{nb} = E_{cb} - E_{Fn,b} \qquad (1)$$

and we can write

Table 1. Energies and Potentials for a Semiconductor−Electrolyte System

V_r	the *measured voltage* with respect to the RE; it is the difference between the Fermi level of electrons in the semiconductor back contact, $E_{Fn,b}$, and the Fermi level of the metallic part of the RE (the SHE in Figure 1).
V_{app}	the *applied voltage*, the voltage applied to the semiconductor with respect to the equilibrium (unbiased) situation in the dark
ϕ	local electrostatic potential
E_{vac}	energy of the LVL
$q\phi = 0$ reference level	reference for the electrostatic potential; normally, it is taken as the VL outside of the surface;[7] however, in Figure 1a, the reference level is displaced from E_{vac}^{el} for the sake of clarity.
E_{Fn}	Fermi level of electrons; in general, it is a function of the position.
E_{Fp}	Fermi level of holes
$E_{Fn,b}$	Fermi level of electrons at the back contact (in Figure 1a, $E_{Fn,b} = E_{Fp,b}$)
E_0^{SHE}	energy of SHE with respect to VL of the electron (standard value −4.44 eV)
E_{redox}	Fermi level of electrolyte species (redox level)
E_c	energy of the edge of the conduction band
E_v	energy of the edge of the valence band
χ	electron affinity (a positive energy)
ζ_{nb}	difference between the semiconductor conduction band energy and the electron Fermi level (a positive energy for nondegenerate semiconductors); $\chi + \zeta_{nb}$ is the chemical potential of electrons (reverse sign).[8]
V_{sc}	semiconductor barrier height at the depletion layer (voltage)
V_H	potential drop across the Helmholtz layer
V_{cs}	potential of the conduction band at the semiconductor surface
V_{fb}	flatband potential
V_{VL}	potential of the VL
V_{bi}	built-in potential

$$\zeta_{nb} = k_B T \ln\left(\frac{N_c}{n_0}\right) \tag{2}$$

where N_c is the effective density of states in the conduction band, and $k_B T$, the thermal energy.

The potential in the Helmholtz layer is

$$V_H = \phi_s - \phi_{el} \tag{3}$$

It is positive in Figure 1a. A change of V_H produces the same effect as a modification of the surface dipole on top of a semiconductor, that is, a modification of the position of the band edge E_{cs} with respect to the VL in the electrolyte.

The potential V_{sc} is related to the height of the barrier in the semiconductor

$$V_{sc} = \phi_b - \phi_s \tag{4}$$

Here, ϕ_b is the electrostatic potential in the semiconductor neutral region, and ϕ_s is the potential at the semiconductor surface. V_{sc} is positive in Figure 1a.

The measured voltage of the semiconductor electrode with respect to a RE is

$$V_r = -\frac{E_{Fn,b} - E_0^{SHE}}{q} \tag{5}$$

The measured voltage has the following expression in terms of the semiconductor parameters, the barrier height, and the Helmholtz potential

$$V_r = \frac{E_0^{SHE} + \chi + \zeta_{nb}}{q} + V_{sc} + V_H \tag{6}$$

The potential of the VL is $V_{VL} = E_0^{SHE}/q = -4.44$ V.

The conduction band edge at position x in the semiconductor is modified by the local electrostatic potential

$$E_c(x) = -\chi - q[\phi(x) - \phi_{el}] \tag{7}$$

The energy of the edge of the conduction band at the surface is

$$E_{cs} = -\chi - qV_H \tag{8}$$

The potential of the conduction band edge (with respect to RE), V_{cs}, is determined by the expression

$$E_{cs} = E_0^{SHE} - qV_{cs} \tag{9}$$

therefore

$$V_{cs} = \frac{E_0^{SHE} + \chi}{q} + V_H \tag{10}$$

The flatband potential is the voltage at which $V_{sc} = 0$

$$V_{fb} = V_r|_{V_{sc}=0} \tag{11}$$

hence, from eq 6[9]

$$V_{fb} = \frac{E_0^{SHE} + \chi + \zeta_{nb}}{q} + V_H^{fb} \tag{12}$$

In the presence of specifically adsorbed ions at the semiconductor surface, V_H^{fb} may not be zero when $V_{sc} = 0$.

The following expression, obtained from eqs 6 and 12, is a useful way of writing the voltage V_r[1]

$$V_r = V_{fb} + V_{sc} + (V_H - V_H^{fb}) \tag{13}$$

Using eqs 10 and 12, we formulate an expression that shows that the flatband potential directly correlates with the position of the edge of the conduction band with respect to the given RE.

$$V_{fb} = V_{cs} - (V_H - V_H^{fb}) + \frac{\zeta_{nb}}{q} \tag{14}$$

In many situations, as in Figure 1b, we may refer the voltage applied to the semiconductor to an equilibrium situation, denoted with subscript 0, in which all Fermi levels

are flat and aligned. The voltage V_{app} so defined is of central interest for the analysis of the photoelectrochemical performance of a semiconductor electrode. Here, we assume that an applied voltage, with respect to such an equilibrium initial situation, only modifies the potential drop in the Helmholtz layer V_H and the semiconductor barrier height V_{sc} (the semiconductor back contact is ohmic). Then, the applied voltage can be stated in the following ways

$$V_{app} = -\frac{1}{q}(E_{Fn,b} - E_{redox}) \tag{15}$$

$$V_{app} = V_r - V_{r0} \tag{16}$$

$$V_{app} = \phi_b - \phi_{b0} \tag{17}$$

In a photoelectrochemical cell, as shown in Figure 1b, the voltage applied across the cell may, in addition, include potential drops in the electrolyte and CE. However, such potential drops often can be discounted from the total voltage using experimental techniques as impedance spectroscopy.[10]

The built-in potential is an equilibrium quantity defined as

$$V_{bi} = \phi_{b0} - \phi_{s0} \tag{18}$$

Note that V_{bi} may be either positive (as in Figure 1a), or negative. However, V_{bi} is generally reported in absolute value in the literature.

The applied voltage can now be stated as

$$V_{app} = V_{sc} - V_{bi} + (V_H - V_{H0}) \tag{19}$$

or alternatively, in terms of the flatband potential (from eqs 13 and 16)

$$V_{app} = V_{sc} + V_{fb} - V_{r0} + (V_H - V_H^{fb}) \tag{20}$$

Note that V_{fb} has been defined above with respect to RE. If we define the applied potential in the special situation in which the band is flat, we have

$$V_{app}^{fb} = V_{fb} - V_{r0} \tag{21}$$

Therefore, we can write

$$V_{app} = V_{sc} + V_{app}^{fb} + (V_H - V_H^{fb}) \tag{22}$$

The applied voltage V_{app} is positive in Figure 1a (reverse polarization) and negative in Figure 1b (forward bias). The relationship of the flatband potential to the built-in potential directly comes from eq 19

$$V_{app}^{fb} = -V_{bi} + V_H^{fb} - V_{H0} \tag{23}$$

In Figure 1a, a negative potential V_{app}^{fb} must be applied to the semiconductor in equilibrium with the electrolyte in order to flatten the bands.

In summary, we have provided a consistent set of relationships and a diagram that allows one to build the energy diagram that is widely used in photoelectrochemistry measurements. While the simple semiconductor/electrolyte junction has been presented, the statement of local band bending with respect to VL easily allows for generalization to electrodes composed of a series of materials that have different energy gaps and several band offsets. Furthermore, the state of the surface can be probed by measurement with respect to a RE employing standard techniques such as the Mott−Schottky plot. For example, changes in the semi-

conductor energetics with pH variations or band unpinning due to surface state charging can be easily incorporated as they cause variation of the Helmholtz potential V_H.

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