

Photoelectrochemistry: Introductory Concepts

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Photoelectrochemistry is based principally on the semiconductor electrode. It is the semiconductor's ability to absorb light and convert it to electrical and/or chemical energy that forms the basis for the semiconductor liquid-junction solar cell. To understand how this occurs, we must discuss some simple concepts of solid state physics.^{1,2}

Energy Bands

The solids of interest are the so-called *network solids*. These are formed from an essentially infinite array of atoms covalently bonded together. A consequence of the extended bonding network is that electrons in the solid occupy *energy bands* rather than energy levels. Consider the energy level diagram of an atom, A, shown in Figure 1. The atomic energy levels are represented by lines, and occupancy by a pair of electrons is indicated by the paired arrows. If two A atoms are bonded together, simple molecular orbital theory dictates that each atomic level is split into two molecular energy levels, grouped as shown in Figure 1. There are as many molecular energy levels as there are atomic energy levels in the isolated atoms. When a very large number of atoms are bonded into a solid (e.g., Avogadro's number, a quantity typical of a macroscopic solid), each atomic energy level now splits into Avogadro's number of energy levels. The energy levels are grouped into energy bands. Within each band the energy separation between two energy levels becomes so minute that the energy band can be regarded as a continuum of energy levels. Each energy band also has a definite upper and lower limit, called the *band edges*.

Of particular interest are the highest occupied and the lowest empty energy bands. If, for a given solid, these two bands are separated by a gap devoid of energy levels, called the *bandgap*, then the solid is either a semiconductor or an insulator. On the other hand, if the highest occupied and lowest empty energy bands overlap, then the solid is a metal. A second situation giving rise to metallic properties occurs when an energy band is partially filled with electrons. The juxtaposition of occupied and empty energy levels (i.e., no bandgap) is a necessary condition for the electrical conductivity of metals (see below).

From now on we shall consider just these two energy bands. In the language of solid state physics, the highest occupied energy band is called the *valence band* and the lowest empty energy band the *conduction band* (Fig. 2A). The upper edge

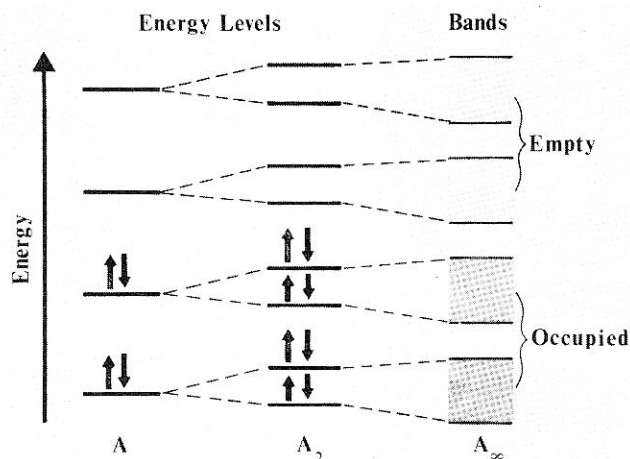


Figure 1. Energy bands of solids. A represents the atom of an element.

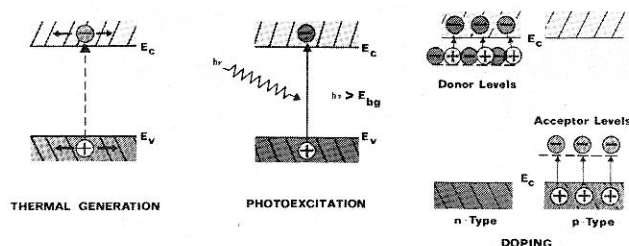


Figure 2. Mechanisms of charge carrier generation. (A) Thermal generation; (B) Photo-excitation; (C) Doping, n-type; (D) Doping, p-type.

of the valence band is marked by E_v , and the lower edge of the conduction band by E_c . An extremely important parameter is the *bandgap energy*, E_{bg} , defined as the separation between the conduction and valence band edges. It is usually expressed in the energy units *electron volts* (eV). The bandgap energy distinguishes semiconductors from insulators. In general, solids with bandgap energies less than 3 eV are considered to be semiconductors, while insulators have bandgap energies larger than 3 eV. An illustration can be given with just the group IV elements. Carbon (diamond), silicon, germanium, and α -tin all have the same crystal structure and similar bonding (both factors affect the bandgap energy). Diamond has a bandgap of 5.4 eV and would make an excellent insulating material if it were cheap. Si ($E_{bg} = 1.1$ eV) and Ge ($E_{bg} = 0.7$ eV) are both widely used semiconductors. α -Sn has a bandgap energy sufficiently small (0.09 eV) that it is considered a metal.

Silicon and germanium comprise the only two important monatomic semiconductors, but many useful binary compounds exist. They may be broadly classified according to group number combinations. Of interest to photoelectro-

¹ These concepts are presented in part in several of current general chemistry texts. See, for example: (a) Dickerson, R. E., Gray, H. B., and Haight, Jr., G. P., "Chemical Principles," Benjamin, Inc., New York, 1970, pp. 539–547. (b) Sisler, H. H., Dresdner, R. D., and Mooney, Jr., W. T., "Chemistry: A Systematic Approach," Oxford University Press, New York, 1980, pp. 300–306. (c) Nebergall, W. H., Holtzclaw, N. F., Jr., and Robinson, W. R., "General Chemistry," Heath and Co., Lexington, MA, 1980, pp. 789–793. (d) Mortimer, C. E., "Introduction to Chemistry," Van Nostrand Co., New York, 1977, pp. 552–557.

² Mickey, C. D., J. CHEM. EDUC., 58, 418 (1981).

chemists are the III–V (Al, Ga, In + As, P, Sb), the II–VI (Zn, Cd + O, S, Se, Te), and the VI–VI (Mo, W + S, Se, Te) semiconductors. Several metal oxides also behave as semiconductors; typical examples include TiO_2 , ZnO , SnO_2 , Fe_2O_3 , and Cu_2O . Ternary combinations are known but are less commonly used.

Conduction and Charge Carrier Generations

In order for electrons to be mobile in a solid (the essence of electrical conductivity), they must be able to occupy a partially empty energy level within an energy band. In metals, empty levels are available immediately above the filled ones, and at room temperature it is easy for electrons to hop up to the empty levels and move under the impetus of an applied voltage. However, in semiconductors and insulators, the filled energy levels are separated from the empty ones by the bandgap. In this simple description, conduction is not possible.

Semiconductors can be made conductive either by putting extra electrons into the conduction band or by removing electrons from the valence band. Consequently, there are two modes of conduction in a semiconductor. The first is the movement of electrons through the (mostly empty) conduction band (Fig. 2A). The second mode is electron flow in the valence band, but its description differs in solid state physics. Removal of an electron from the valence band creates a positively charged vacancy called a *hole* (Fig. 2A). The hole can be regarded as the mobile entity because annihilation of a hole by a nearby electron effectively moves the hole over in space. So electrical current can be carried by either electrons in the conduction band or holes in the valence band, or by both types of charge carriers.

Mobile charge carriers can be generated by three different mechanisms: thermal excitation, photo-excitation, and doping. If the bandgap energy is sufficiently small, thermal excitation can promote an electron from the valence band to the conduction band (Fig. 2A). Both the electron and the accompanying hole are mobile. As the average thermal energy at room temperature is 0.026 eV ($=kT$), this mechanism is important only for narrow bandgap semiconductors ($E_{\text{bg}} < 0.5 \text{ eV}$).

In a similar manner, an electron can be promoted from the valence band to the conduction band upon the absorption of a photon of light (Fig. 2B). A necessary condition is that the photon energy exceeds the bandgap energy ($h\nu > E_{\text{bg}}$). This is the primary event in the conversion of sunlight to usable forms of energy. The bandgap energy therefore sets the condition for photon absorption. Defining λ_{bg} according to eqn. (1), wavelengths greater than λ_{bg}

$$\lambda_{\text{bg}}(\text{nm}) = 1240/E_{\text{bg}}(\text{eV}) \quad (1)$$

are not absorbed by the semiconductor; it is transparent at those wavelengths. At wavelengths shorter than λ_{bg} , photons are adsorbed within a short distance of the semiconductor surface. The semiconductor thus exhibits a *threshold response* to light. The table lists values of E_{bg} and λ_{bg} for several semiconductors important in photoelectrochemistry. One consideration in choosing a useful semiconductor is the range of solar wavelengths which are absorbed by the semiconductor. Theoretical calculations of the wavelength-intensity distribution of sunlight combined with the maximum power output by the solar cell have led to the prediction that maximum solar energy conversion efficiency will be obtained for $E_{\text{bg}} = 1.5 \pm 0.5 \text{ eV}$ ($600 \text{ nm} < \lambda_{\text{bg}} < 1100 \text{ nm}$).

The third mechanism of generating mobile charge carriers is *doping*. Doping is the process of introducing new energy levels into the bandgap. Doping can be effected by either disturbing the stoichiometry of the semiconductor (such as partially reducing a metal oxide) or by substituting a foreign element into the semiconductor lattice. The classic example of the latter method is the introduction of group III or group

Bandgap Energy and λ_{bg} for Semiconductors Important to Photoelectrochemistry

Semiconductor	Bandgap Energy (eV)	λ_{bg} (nm)
SnO_2	3.5	350
ZnO	3.2	390
SrTiO_3	3.2	390
TiO_2	3.0	410
CdS	2.4	520
GaP	2.3	540
Fe_2O_3	2.1	590
CdSe	1.7	730
CdTe	1.4	890
GaAs	1.4	890
InP	1.3	950
Si	1.1	1130

V elements into group IV semiconductors. Two types of doping can be distinguished. For *n-type* doping, occupied donor levels are created very near the conduction band edge (Fig. 2C). Electrons from the donor levels are readily promoted to the conduction band by thermal excitation. Electrons in the conduction band outnumber the few thermally-generated holes in the valence band; hence, current is carried mainly by negative charge carriers. Likewise, *p-type* doping corresponds to the formation of empty acceptor levels near the valence band edge (Fig. 2D). The acceptor levels trap electrons from the valence band, creating positive charge carriers. The donor and acceptor levels become charged due to loss or gain of electrons, but they are not charge carriers because they are fixed within the crystal lattice. Semiconductors are commonly described as *n-type* or *p-type* to indicate the dominant charge carrier; undoped semiconductors are referred to as *intrinsic* semiconductors.

The Fermi Level

A discussion of the Fermi level (alternatively called the Fermi energy) is crucial in photoelectrochemistry because of the following key point: *changes in the electrode potential correspond to changes in the position of the Fermi level with respect to a reference energy*. The reference energy can be the energy of an electron in a vacuum, or it can be the Fermi level of a reference electrode. To keep the discussion qualitative, we will use the probability definition of the Fermi level. *The Fermi level is the energy (E_f) at which the probability of an energy level being occupied by an electron is exactly $1/2$.*³ In metals, the Fermi level can be considered to be the tidemark of electrons in the energy band. Above the Fermi level the probability of occupancy drops to zero, and the energy levels are empty, while below E_f the energy levels are filled (probability $\rightarrow 1$). However, in a semiconductor the Fermi level occurs in the bandgap (the definition does not require an energy level at E_f ; it merely depends on a probability if an energy level were present). For an intrinsic (undoped) semiconductor, E_f occurs approximately midway between the conduction and valence band edges (Fig. 3).

A second key point is that doping shifts the Fermi level with respect to the band edges. N-type doping results in a shift of E_f toward E_c (Fig. 3). The shift is consistent with the fact that the probability of occupancy of energy levels at E_c has increased; there are more electrons in the conduction band. Thus, the energy at which the probability equals $1/2$ must be closer to E_c . Likewise, p-type doping shifts E_f nearer to E_v (Fig. 3).

As the doping level increases (as measured by the number of mobile charge carriers per cm^3), E_f shifts closer and closer to the band edges. A very high doping level causes E_f to move

³ More generally, the probability that an energy level at energy E will contain an electron is given by the Fermi-Dirac distribution: $f = \text{probability} = \{1 + \exp[(E - E_f)/kT]\}^{-1}$. When $E = E_f$, $f = 1/2$.

into the conduction or valence band; at this point the semiconductor becomes a metal.

For a given semiconductor with a fixed doping level, the Fermi level can be manipulated by the applied potential. Consider a semiconductor electrode connected externally to a reference electrode; both electrodes are immersed in the same electrolyte. In such a situation, $E_i^{sc} = E_i^{reference}$, i.e., the Fermi levels of the two electrodes match in energy. Now if the semiconductor electrode is biased (by means of a battery or a potentiostat) at a potential one volt positive with respect to the reference electrode, the Fermi level of the semiconductor shifts *down* in energy with respect to the reference Fermi level. The downward shift arises from the lower energy of electrons in a region of more positive (less negative) potential. Furthermore, the energy difference between the two Fermi levels ($E_i^{sc} - E_i^{reference}$) is exactly one electron-volt (by definition). Biasing the semiconductor negative raises the semiconductor Fermi level above the reference Fermi level. Thus, it is possible to control the semiconductor Fermi level with respect to solution energy levels by means of the applied potential. In the bulk of the semiconductor, the Fermi level remains fixed relative to E_c and E_v , but the situation is different near the electrolyte interface. The difference is the subject of the next article.

We have developed here some simple concepts of solid state physics that apply to a particular class of solids. The reader should note that although the terminology is foreign to chemistry, the concepts are not. These concepts will be useful in explaining how a semiconductor electrode responds to perturbations of light and potential, as described in the succeeding articles.

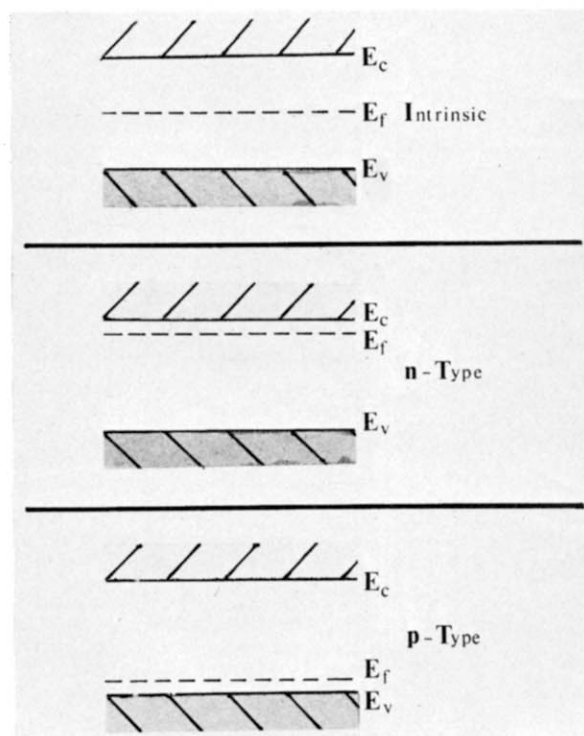


Figure 3. The Fermi level and the effects of doping.