

Electrochemistry of Semiconductors

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This article is an introduction to the electrochemical properties of semi-conductors. The characterization of semiconductor electrodes using capacitance-potential measurements is also discussed.

The major interest in semiconductor electrodes is due to the photoelectrochemical properties of the semiconductor electrolyte interface; that is, the generation of currents following exposure to electromagnetic radiation (e.g., solar energy conversion). In addition, optically transparent semiconductor electrodes are available for electrochromic displays and spectroelectrochemistry.

The properties of semiconductor electrodes, and their differences from those of metallic electrodes, can be understood by examining the electronic structures of these materials (1). Due to the essentially infinite number of atoms that must be considered, the electronic structure of these solids is typically discussed in terms of energy bands, which are made up of the atomic orbitals of the individual atoms (**F1**) (this is merely an extension of the concept of molecular orbitals). As a result of the large number of orbitals, the difference in energy between adjacent molecular orbitals within a given energy band is so small that the band can be effectively considered a continuum of energy levels. The highest and

lowest energy levels of a band are referred to as the band edges. As with molecular orbitals, the energy bands of interest are the highest occupied (called the valence band) and the lowest unoccupied (called the conduction). It is the energy gap (the band gap) between these bands (i.e., the difference in energy between the upper edge of the valence band and the lower edge of the conduction band) that determines the properties of the material.

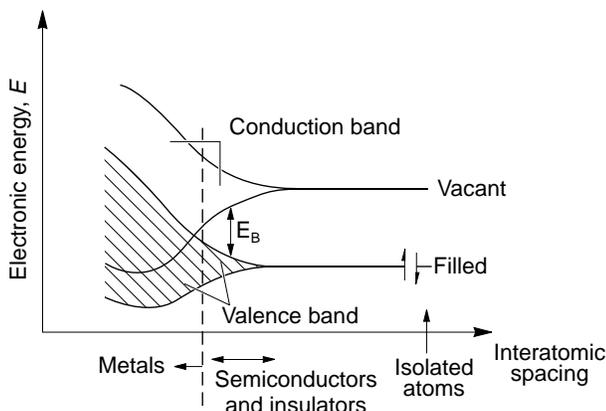
Conductivity of a solid state material (i.e., the movement of electrons through the material) requires that the electrons occupy partially filled orbitals. This is achieved by occupancy of the conduction band. For metals, the conduction and valence bands overlap, so the conduction band can be readily occupied (**F1**). For insulators, the band gap is sufficiently large that electrons cannot be promoted from the valence band to the conduction band. However, for semiconductors, the band gap is not as large, and electrons can be moved into the conduction band. The promotion of electrons leaves a positively charged vacancy in the valence, which is referred to as a hole

(**F2**). These holes can be moved through space by the transfer of an electron to the vacancy; therefore, holes are considered to be mobile.

Electrons can be excited to the conduction band either thermally or photochemically. However, there is another method for generating charge carriers (i.e., electrons or holes) within a semiconductor, referred to as doping. Doping involves the addition of a different element into the semiconductor. The simplest example of this involves the introduction of a group V element (e.g., P) or a group III element (e.g., Al) into a group IV element (e.g., Si). The addition of P into Si introduces occupied energy levels into the band gap close to the lower edge of the conduction band, thereby allowing facile promotion of electrons into the conduction band (**F3a**). The addition of Al introduces vacant energy levels into the band gap close to the upper edge of the valence band, which allows facile promotion of electrons from the valence band (**F3b**). This leads to the formation of holes in the valence band. Undoped semiconductors are referred to as *intrinsic* semiconductors. Doped semiconductors

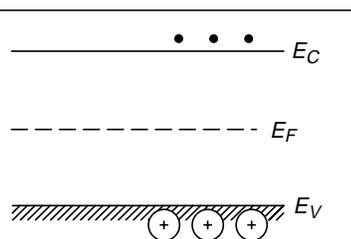
F1

Generation of bands in solids from atomic orbitals of isolated atoms (adapted from ref. 1).



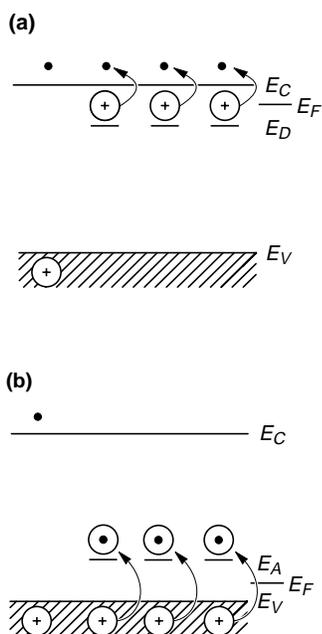
F2

Schematic diagram of the energy levels of an intrinsic semiconductor.



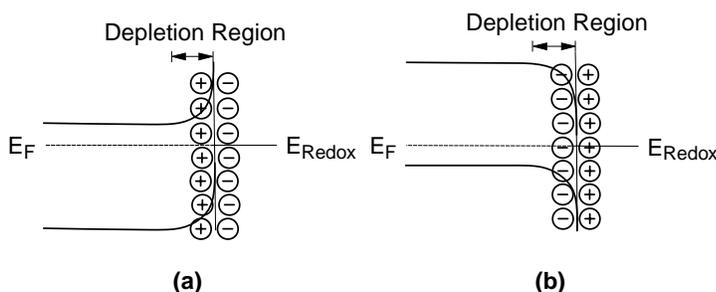
F3

Schematic diagram of the energy levels of an n-type semiconductor (a) and a p-type semiconductor (b).



F4

Band bending for an n-type semiconductor (a) and a p-type semiconductor (b) in equilibrium with an electrolyte.



in which the dominant (or majority) charge carriers are electrons are referred to as *n-type semiconductors*, whereas those in which holes are the majority charge carriers are referred to as *p-type semiconductors*.

Another important concept in discussion of solid state materials is the Fermi level. This is defined as the energy level at which the probability of occupation by an electron is 1/2; for example, for an intrinsic semiconductor the Fermi level lies at the mid-point of the band gap (**F2**). Doping changes the distribution of electrons within the solid, and hence changes the Fermi level. For a *n-type* semiconductor, the Fermi level lies just below the conduction band, whereas for a *p-type* semiconductor it lies just above the valence band (**F3**). In addition, as with metal electrodes, the Fermi level of a semiconductor electrode varies with the applied potential; for example, moving to more negative potentials will raise the Fermi level.

We now need to consider what happens at the (idealized) interface between a semiconductor electrode and an electrolyte solution. In order for the two phases to be in equilibrium, their electrochemical potential must be the same. The electrochemical potential of the solution is determined by the redox potential of the electrolyte solution, and the redox potential of the semiconductor is de-

termined by the Fermi level. If the redox potential of the solution and the Fermi level do not lie at the same energy, a movement of charge between the semiconductor and the solution is required in order to equilibrate the two phases. The excess charge that is now located on the semiconductor does not lie at the surface, as it would for a metallic electrode, but extends into the electrolyte for a significant distance (100-10,000 Å). This region is referred to as the *space charge region*, and has an associated electrical field. Hence, there are two double layers to consider: the interfacial (electrode/electrolyte) double layer, and the space charge double layer.

For an *n-type* semiconductor electrode at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electrons will be transferred from the electrode into the solution. Therefore, there is a positive charge associated with the space charge region, and this is reflected in an upward bending of the band edges (**F4a, F5a**). Since the majority charge carrier of the semiconductor has been removed from this region, this region is also referred to as a *depletion* layer. For a *p-type* semiconductor, the Fermi level is generally lower than the redox potential, and hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region, which causes a downward bending in the band edges (**F4b, F6c**). Since the holes in the space charge region are removed by this process, this region is again a depletion layer.

As for metallic electrodes, changing the potential applied to the electrode shifts the Fermi level. The band edges in the interior of the semiconductor (i.e., away from the depletion region) also vary with the applied potential in the same way as the Fermi level. However, the energies of the band edges at the interface are not affected by changes in the applied potential. Therefore, the

change in the energies of the band edges on going from the interior of the semiconductor to the interface, and hence the magnitude and direction of band bending, varies with the

applied potential. There are three different situations to be considered:

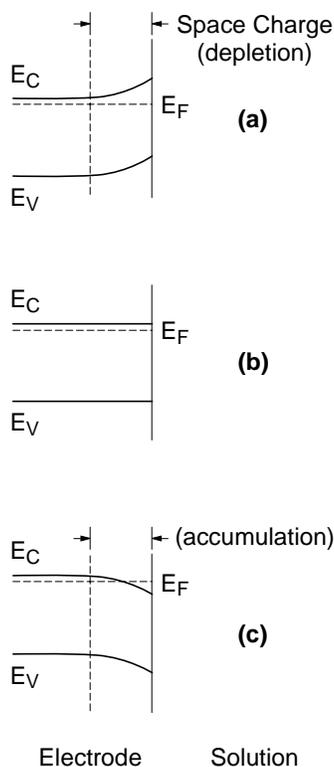
- At a certain potential, the Fermi energy lies at the same energy as the solution redox potential (**F5b**, **F6b**). There is no net transfer of charge, and hence there is no band bending. This potential is therefore referred to as the *flatband potential*, E_{fb} .
- Depletion regions arise at potentials positive of the flatband potential for an *n*-type semiconductor and at potentials negative of the flatband potential for a *p*-type semiconductor (**F5a**, **F6c**).
- At potentials negative of the flatband potential for an *n*-type semiconductor, there is now an excess of the majority charge carrier (electrons) in this space charge region, which is referred to as an *accumulation* region (**F5c**). An accumulation region arises in a *p*-type semiconductor at potentials more positive than the flatband potential (**F6a**).

the separation of the charge. For example, for an *n*-type semiconductor at positive potentials, the band edges curve upwards, and hence the hole moves towards the interface, and the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a solution species; that is, the *n*-type semiconductor electrode acts as a photoanode. Ideal behavior for an *n*-type semiconductor electrode in the dark and under irradiation is shown in **F7**. At the flatband potential for an *n*-type semiconductor and at potentials negative of the flatband potential (Region II), since there is no electric field to separate any generated charge carriers. At potentials negative of the flatband potential (Region I), an accumulation layer exists, and the electrode can act as a cathode, both in the dark and upon irradiation (the electrode is referred to as a dark cathode under these conditions). At potentials positive of the flatband potential (Region III), a depletion layer exists, so there can be no oxidative current in the dark. However, upon irradiation, a photocurrent can be observed at potentials negative of the redox potential of the analyte (which lies at E^0), since some of the energy required for the oxidation is provided by the radiation (via the high energy hole). Using similar reasoning, it can be shown that *p*-type semiconductor electrodes are dark anodes and photocathodes.

There are a number of experiments used to measure the various parameters discussed above. The flatband potential can be determined by measuring the photopotential as a function of radiation intensity, the onset of the photocurrent, or the capacitance of the space charge region. The simplest method is to measure the open-circuit potential (photopotential) of the electrochemical cell under radiation of varying intensity. For a system under equilibrium, the photopotential is the change in the Fermi level due to the promotion of electrons to the conduction band, and it reaches a maximum at the flatband potential.

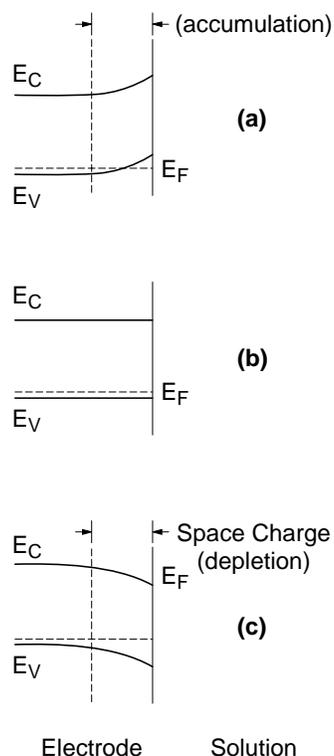
F5

Effect of varying the applied potential (E) on the band edges in the interior of an *n*-type semiconductor.
a) $E > E_{fb}$, b) $E = E_{fb}$,
c) $E < E_{fb}$.



F6

Effect of varying the applied potential (E) on the band edges in the interior of a *p*-type semiconductor.
a) $E > E_{fb}$, b) $E = E_{fb}$,
c) $E < E_{fb}$.

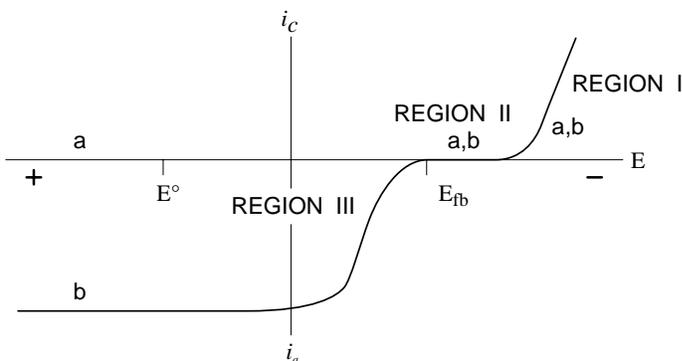


The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation layer or a depletion layer. If there is an accumulation layer, the behavior of a semiconductor electrode is similar to that of a metallic electrode, since there is an excess of the majority of charge carrier available for charge transfer. In contrast, if there is a depletion layer, then there are few charge carriers available for charge transfer, and electron transfer reactions occur slowly, if at all.

However, if the electrode is exposed to radiation of sufficient energy, electrons can now be promoted to the conduction band. If this process occurs in the interior of the semiconductor, recombination of the promoted electron and the resulting hole typically occurs, together with the production of heat. However, if it occurs in the space charge region, the electric field in this region will cause

F7

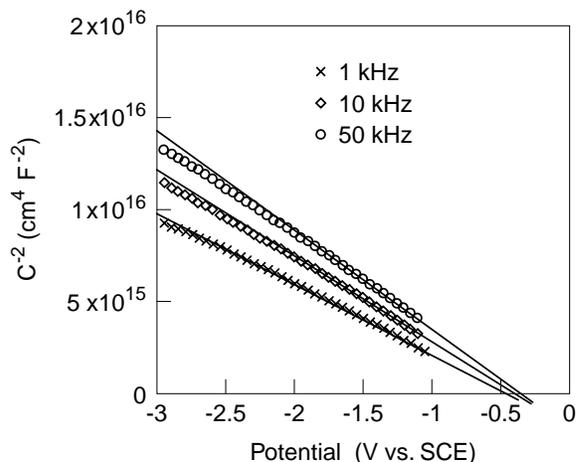
Ideal behavior for an *n*-type semiconductor in the dark (a) and under irradiation.



- C_{sc} = capacitance of the space charge region
- ϵ = dielectric constant of the semiconductor
- ϵ_0 = permittivity of free space
- N = donor density (electron donor concentration for an *n*-type semiconductor or hole acceptor concentration for a *p*-type semiconductor)
- E = applied potential
- E_{fb} = flatband potential

F8

Mott-Schottky plot for a *p*-type semiconductor (figure adapted from ref. 2).

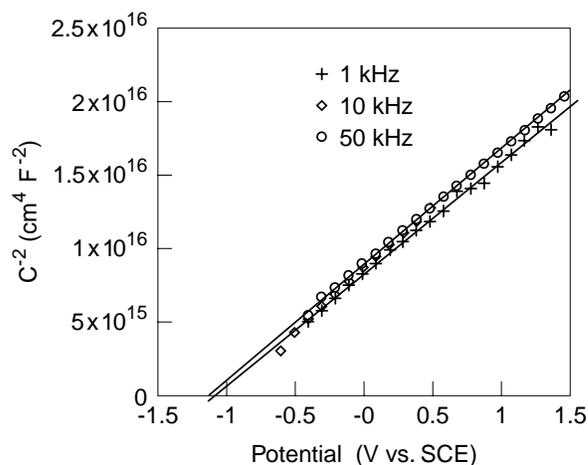


Mott-Schottky plots ($1/C^2$ vs. E) are shown for a *p*-type silicon semiconductor and an *n*-type silicon semiconductor in **F8** and **F9**, respectively (2). The donor density can be calculated from the slope, and the flatband potential can be determined by extrapolation to $C = 0$. The capacitance values are calculated from impedance measurements. The model required for the calculation is based on two assumptions:

- a) There are two capacitances to be considered, that of the space charge region and that of the double layer. Since these capacitances are in series, the total capacitance is the sum of their reciprocals. As the space charge capacitance is much smaller than double layer capacitance (2-3 orders of magnitude), the contribution of the double layer capacitance to the total capacitance is negligible. Therefore, the capacitance value calculated from this model is assumed to be the value of the space charge capacitance.

F9

Mott-Schottky plot for an *n*-type semiconductor (figure adapted from ref. 2).



- b) The equivalent circuit used in this model is a series combination of a resistor and a capacitance (the space charge capacitance). The capacitance is calculated from the imaginary component of the impedance (Z'') using the relationship $Z'' = 1/2\pi fC$. The model is adequate provided the frequency is high enough (on the order of kHz).

Therefore, a plot of photopotential versus light intensity will attain a limiting plateau at the flatband potential. For the second method, although the onset of the photocurrent might be simplistically considered to be the flatband potential, it is actually the potential at which the dark current and photocurrents are equal. Therefore, such measurements should be used with caution.

The third method involves measuring the apparent capacitance as a function of potential under depletion condition and is based on the Mott-Schottky relationship:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 N} \left(E - E_{FB} - \frac{kT}{e} \right)$$

where:

There are a number of different methods for making the measurements required for a Mott-Schottky plot using the BAS-Zahner impedance analyzers. The automatic series function can be used to record impedance spectra over a range of frequencies at different potentials. A given frequency can be selected, and the imaginary component of the impedance can be calculated at this frequency for each potential. Alternatively, a series combination of a resistor and a capacitor can be used as an equivalent circuit to fit the experimental data. This process will automatically generate the capacitance values at the different frequencies. However, in order for the results from this latter approach to be accurate, the equivalent circuit used must be valid over the entire frequency range.

A useful alternative is available as part of the C/E module of the

Thales software. This can be used to run a series of single frequency impedance measurements at different potentials. The data from these measurements can be analyzed using either a series or a parallel combination of a resistor and a capacitor, and plotted as the parameter values vs. the applied potential (3). The Mott-Schottky plot is also available. Again, it should be emphasized that the results from these calculations are only accurate if the equivalent circuit used is valid at the selected frequency.

The behavior discussed above applies only to an idealized semiconductor/electrolyte interface. In real systems, there are a number of factors that can give rise to anomalous behavior. The main cause of non-ideal behavior is photodecomposition of the electrode; that is, oxidation of the electrode itself by holes in the depletion region. This

can be avoided by the addition of an appropriate electroactive species to the solution that competes with the auto-oxidation, or by the stabilization of the electrode surface by chemical modification. Another source of non-ideality is the presence of energy states associated with the surface that are different from those in the interior of the semiconductor. These surface states can act as channels for electron transfer, if they lie at the appropriate energy.

References

1. A.J. Bard and L.R. Faulkner, "Electrochemical Methods," Chap. 14, Wiley, 1980.
2. P. Schmuki, H. Bohni and J.A. Bardwell, *J. Electrochem. Soc.* 142 (1995) 1705.
3. Data from single frequency analysis of series measurements (in the SIM module) can also be exported to the C/E module.