SEMICONDUCTOR ELECTROCHEMISTRY

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Summary

This chapter begins with a brief overview of aspects of solid state physics that are relevant to semiconductor electrochemistry. Topics and concepts reviewed include Fermi Dirac statistics, Fermi levels, contact formation and band bending. The basic principles of semiconductor/electrolyte junctions are then outlined along with their application in different photoelectrochemical devices, including solar cells. The special properties of nanostructured semiconductor/electrolyte systems are contrasted with those of bulk analogues, and applications of mesoporous semiconductor films in dye-sensitized solar cells and water splitting systems are described. The chapter concludes with a short survey of a range of experimental methods used in semiconductor electrochemistry.

1. Introduction

Widespread interest in the potential applications of semiconductor electrochemistry was sparked by the oil crisis in the early 1970s, when the search for renewable energy sources suddenly became an urgent priority. Although the foundations of the subject had already been laid a decade earlier by the seminal work of Gerischer and others, it was a 1972 paper in Nature by Fujishima and Honda reporting the photoelectrochemical splitting of water using a titanium dioxide electrode that caught the world's attention. The promise of generating hydrogen using sunlight encouraged scientists world wide to turn their attention to semiconductor photoelectrochemistry. Although further progress on water splitting was slow, the following decade saw the rapid development of highly efficient regenerative solar cells based on single crystal and polycrystalline semiconductors in contact with redox electrolytes. Unfortunately, one of the main

problems with these cells is that they rely on rapid electron transfer to or from the solution redox species to prevent parasitic corrosion reactions involving photogenerated minority carriers (e.g. holes in the case of *n*-type semiconductors). In practice, these side reactions limit the lifetime of photoelectrochemical solar cells to such an extent that they are unable to compete with conventional solid state devices. However, the field of semiconductor photoelectrochemistry saw a remarkable resurgence of activity following another Nature paper, this time in 1992, by O'Regan and Grätzel, who demonstrated that efficient and stable regenerative photoelectrochemical cells could be made using a thin porous layer of nanocrystalline titanium dioxide coated with a ruthenium-based sensitizing dye. These dye-sensitized solar cells (DSC) have now achieved efficiencies that are comparable with other low cost thin film photovoltaic devices. Interestingly, the way that the DSC operates differs substantially from its solid state predecessors, since band to band excitation of electrons is not involved. Instead, sunlight is absorbed by the sensitizer dye, and the photoexcited dye molecules inject electrons into the conduction band of the nanocrystalline TiO_2. The injected electrons are collected at the contact by trap-limited diffusion, and the oxidized dye is regenerated rapidly by electron transfer from solution redox species. Since no holes are generated in the TiO_2 by the illumination, it is generally the stability of the dye and electrolyte that determines the solar cell lifetime.

Semiconductor electrochemistry is also important in other areas besides solar energy conversion. For example, the processing of silicon for electronic devices involves etching processes that can be understood in terms of a combination of chemical and electrochemical reaction steps. Electro- chemical etching of silicon is also used to prepare porous silicon layers, which exhibit unusual optical and electronic properties arising from quantum confinement of electrons and holes within the nanostructured material. Electrochemical processes are also involved in the deposition of metal contacts during fabrication of electronic devices. Electrochemistry has also been used to grow semiconductor layers for thin film solar cells: the best known example is the BP Solar Apollo® process for the growth of CdTe films for CdS|CdTe cells. More recently, electrodeposition has been used to fabricate layers of Cu(In|Ga)Se$_2$ (CIGS) for thin film solar cells. Finally the area of photocatalysis using semiconductor colloids is closely related to semiconductor electrochemistry.

The development in applied aspects of semiconductor electrochemistry has been paralleled by a steady growth in our understanding of the basic physical and chemical processes taking place at semiconductor/electrolyte interfaces. At the same time, a range of experimental methods has been developed to deal with the need to understand the mechanisms and kinetics of electrode reactions taking place at illuminated semiconductor electrodes. These involve measuring not only time- and frequency-resolved currents and voltage responses to illumination but also corresponding changes in properties such as microwave reflectivity or visible/infrared transmission. Methods developed for bulk semiconductor electrodes have been applied successfully to investigate nanostructured semiconductor electrodes. The objective of this chapter is to give a reasonably comprehensive and balanced overview of the present state of the art. For further details, the interested reader is directed to the books and publications listed in the various sections.

2. Overview of Basic Semiconductor Physics

2.1. Electrons and Holes in Semiconductors

The concentrations of electrons in the conduction band and holes in the valence band in an intrinsic (undoped) semiconductor are generally very small at room temperature if the bandgap of the material is 1 eV or greater. The thermal equilibrium concentrations of electrons and holes (n and p respectively) in the intrinsic case are determined by the product (see Glossary for definition of symbols)

$$np = n_i^2 = p_i^2 = N_C N_V \exp\!-\!\left(\frac{E_C - E_V}{2k_B T} \right) \tag{1}$$

Consequently, the majority of semiconductors discussed here are essentially insulators in their pure state. The conductivity can be increased by adding either electron donors or electron acceptors to create *n*- and *p*-type extrinsic conductivity. The ionization energy of the dopants is usually sufficiently small that they are fully ionized at room temperature, so that the electron (or hole) density is equal to the doping concentration (usually referred to as the doping density).

The electron occupation of energy levels is determined by Fermi-Dirac statistics. The probability that an energy level of energy E is occupied is given by the Fermi Dirac function:

$$f_{FD}(E) = \frac{1}{1 + \exp\!\left(\dfrac{E - E_F}{k_B T} \right)} \tag{2}$$

Here the Fermi energy (or Fermi level), E_F, is equivalent to the Gibbs free energy or electrochemical potential of electrons in the system. For non-degenerate conditions where $(E - E_F)/k_B T > 1$, the occupation probability reduces to the Boltzmann limit

$$f_{FD}(E) \rightarrow \exp\!-\!\left(\frac{E - E_F}{k_B T} \right) \tag{3}$$

In this limit, the concentrations of electrons and holes can be expressed conveniently in terms of the Fermi energy as follows.

$$n = N_C f_{FD}(E_C) = N_C \exp\!-\!\left(\frac{E_C - E_F}{k_B T} \right) \tag{4a}$$

$$p = N_V \left[1 - f_{FD}(E_V) \right] = N_V \exp\!\left(\frac{E_V - E_F}{k_B T} \right) \tag{4b}$$

It follows that the Fermi energy is close to the conduction band, for *n*-type

semiconductors ($n \gg p$), whereas for p-type semiconductors ($p \gg n$), it is close to the valence band. For intrinsic semiconductors ($n = p = n_i$), the Fermi energy is close to the centre of the bandgap. As an example, consider the case of a moderately doped *n*-type GaAs ($E_g = 1.42 \text{ eV}, N_C = 4.7 \times 10^{23} \text{ m}^{-3}$) with a donor density of 10^{22} m^{-3}. The calculation based on the Boltzmann approximation indicates that the Fermi level is located $3.85 k_B T$ (97 meV at 298 K) below the conduction band energy.

So far only the case of semiconductors in thermal equilibrium has been considered. Under illumination, electrons can be excited from the valence band to the conduction band, creating electron-hole pairs. The concentrations of electrons and holes therefore deviate from their thermal (dark) equilibrium values. If photogenerated electrons and holes are in thermal equilibrium with the semiconductor lattice, Fermi Dirac statistics can still be applied provided that separate quasi-Fermi energies, $_nE_F$ and $_pE_F$, are defined for each carrier type. In the bulk of a doped semiconductor, the increase in majority carrier concentration under illumination is usually relatively small, so to a good approximation the quasi Fermi level for majority carriers is not changed by illumination. By contrast, the minority carrier concentration increases by orders of magnitude under illumination, so that the quasi Fermi level for minority carriers moves away from the equilibrium Fermi level towards the minority carrier band. In practice the resulting separation of quasi Fermi levels is determined by the rates at which electron hole pairs are generated and recombine (radiatively or non-radiatively). Recombination can take place in the bulk of the semiconductor or at the surface. Surface recombination is enhanced by the presence of surface states with energies that lie in the bandgap. If surface recombination is rapid, then it may become the dominant route, and in this case the electron and hole concentrations near the surface will be close to their equilibrium (dark) values. Figure 1 illustrates this situation for a homogeneously illuminated semiconductor wafer in the absence of space charge effects (i.e. no band bending – see below).
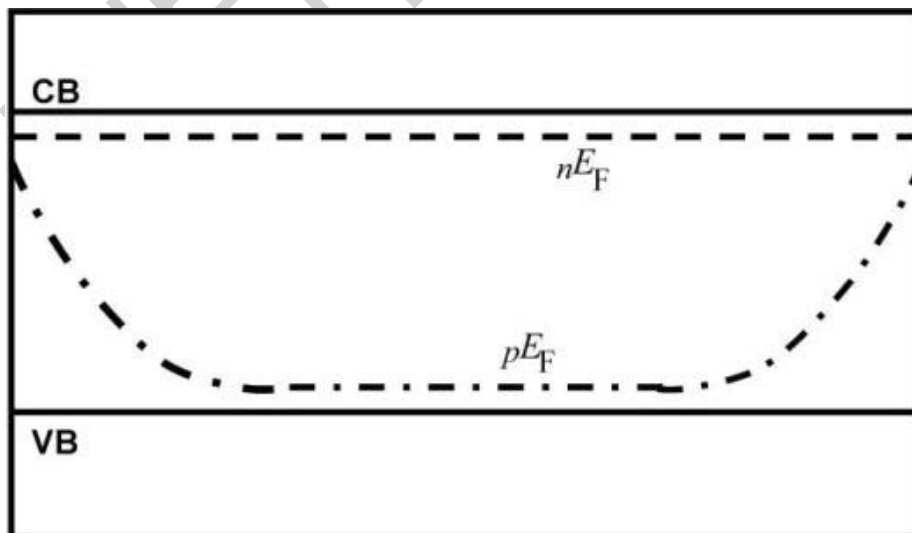

Figure 1. Quasi Fermi levels for electrons and holes ($_nE_F$ and $_pE_F$) in an illuminated *n*-type silicon wafer with recombination taking place at the front and back surfaces (no band bending).

2.2. Metal Contacts and *p-n* Junctions

Solid state devices generally require metallic contacts. The behavior of these contacts is not always predictable due to the presence of intermediate layers, but in principle the type of contact depends on the electronic work functions of the semiconductor and the metal. Formation of the contact involves establishing electronic equilibrium, so that the Fermi levels in the metal and the semiconductor must be equal after contact. During the equilibration process, electrons are transferred across the junction as shown, for example, in Figure 2 for an *n*-type semiconductor in contact with a metal that has a higher work function (lower Fermi level). In this case, the equilibration of the Fermi levels results in formation of a Schottky barrier, giving rise to diode behavior. If the work function of the metal is lower than that of the *n*-type semiconductor, electrons flow in the opposite direction, and an ohmic contact is formed. In the case where a Schottky barrier is formed, the removal of majority carriers (electrons) from the semiconductor gives rise to a region where the ionized donor atoms in the lattice constitute an immobile space charge. The width of this space charge region depends on the doping level, typically ranging from 1 micron to 10 nm for doping densities of 10^{21} to 10^{25} m^{-3} respectively. The space charge generates an electric field that causes the band bending shown in Figure 2.
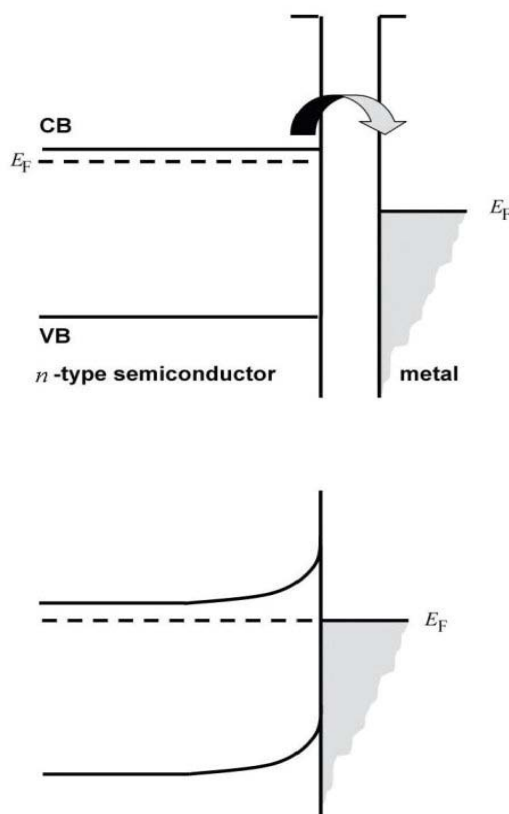

Figure 2. Formation of a Schottky barrier at the junction between a metal and an *n*-type semiconductor. Note that the barrier is formed because the work function of the metal is higher than that of the semiconductor, so that electrons flow out of the semiconductor, creating a space charge region. The band bending in the lower figure arises from the space charge associated with immobile ionized donors in the lattice.

Similar arguments apply to the formation of *p-n* junctions. In the case where the junction is formed in the same material doped *n* and *p*-type (homojunction), equilibration leads to band bending as illustrated in Figure 3.
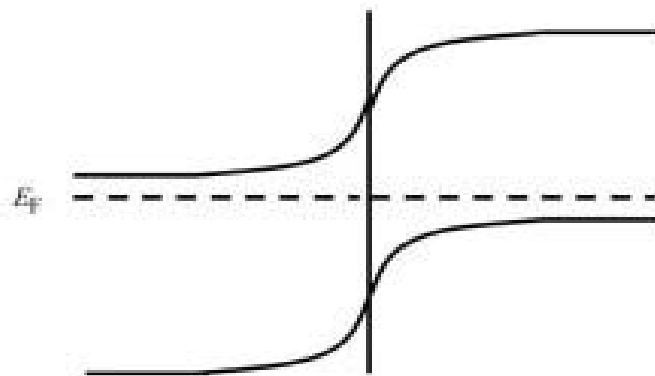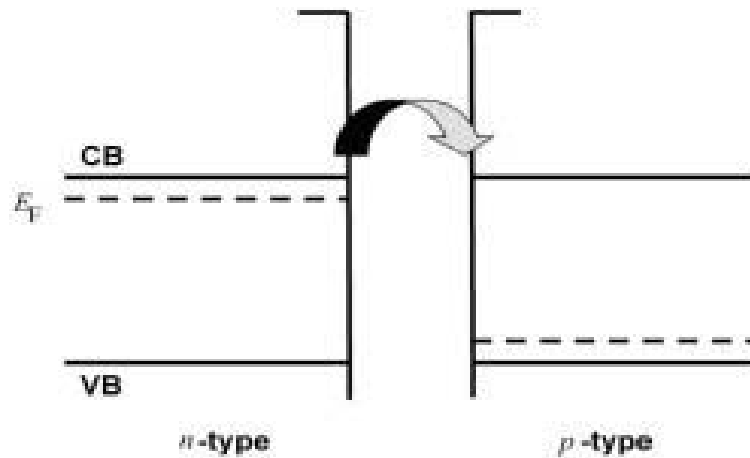

Figure 3. Formation of a *p-n* homojunction. In this case, the semiconductor is the same on both sides of the junction. Only the doping is different (*n*- and *p*-type). Equilibration of the Fermi level creates a space charge and corresponding band bending on both ides of the junction. On the *p*-type side the charge is negative (ionized acceptors – A⁻), and on the *n*-type side it is positive (ionized donors – D⁺).

The rectifying (diode) metal-semiconductor and *p-n* junctions are the basis of photovoltaic solar cells. Illumination of the both types of junction generates electron and holes that are separated and collected at selective contacts to generate electrical power.

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Biographical Sketch

Laurie Peter started his scientific career as an electrochemist, obtaing his PhD from the University of

Southampton in 1969 for studies of electrode processes in aprotic media. His postdoctoral work in the group of Heinz Gerischer in Berlin introduced him to the area of photophysics, and he spent four years investigating energy and charge transfer in organic molecular crystals. Since 1974 he has held positions at Southampton and Bath Universities, where he is currently Professor of Physical Chemistry. His current research interest include dye-sensitized solar cells and thin film inorganic solar cells.