Chapter 10
Semiconductors and Mott-Schottky Plots

10.1 Semiconductors in Solution

When a conductive electrode (e.g., metallic or glassy carbon) is in contact with an electrolytic solution, the excess electronic charge is accumulated at the electrode surface and charge distribution occurs in the solution only. This is related to the fact that as the number of charged species increases, the space in which the redistribution of charges occurs shrinks. At a metallic electrode–solution interface, the charge redistribution in solution depends on the applied potential and is described by the Guy-Chapman-Stern theory. The characteristic thickness of the diffuse layer in nonadsorbing electrolytes varies from 0.3 nm in 1 M to 3 nm in 0.01 M aqueous electrolyte, while the thickness of the Helmholtz layer is much smaller [17].

In the case of semiconductor electrodes, the concentration of conductive species (electrons or holes) is much smaller than that in solution. This creates a redistribution of the space charge in the semiconductor electrode at distances much larger than that in solutions, 10–100 nm [462, 463]. This leads to much smaller capacitances of the semiconductor electrodes. Passive films formed on metallic surfaces behave as semiconductors, and their properties are important in studies of corrosion protection.

Because of the charge redistribution in the conduction and valence band, potential bending appears at the surface. This effect is illustrated in Fig. 10.1. For the *n*-type semiconductor electrode at an open circuit, the Fermi level is usually higher than the redox potential of the electrolyte, and the electrons are transferred from the electrode to the solution, producing a positive charge associated with the space charge region, causing an upward bending of the band edges. The opposite effect, that is, a downward bending of the band edges, is observed for *p*-type semiconductors [3, 17, 462, 463]. The magnitude and direction of bending depends on the applied potential, as seen in Fig. 10.1. At a certain applied potential, no bending is observed, and this potential is called a flatband potential, E_{fb}. The value of this potential may be determined electrochemically using Mott-Schottky plots [464–466].

A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*,
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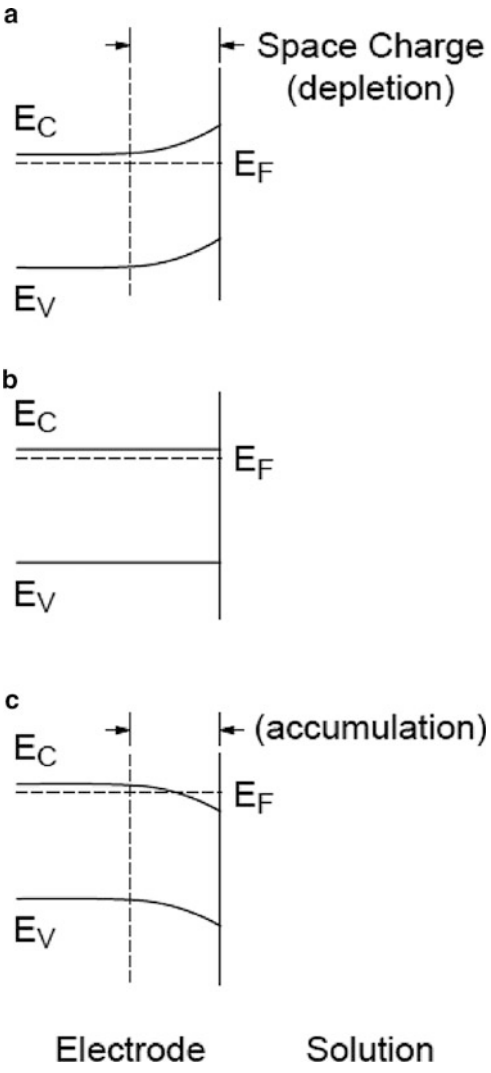

Fig. 10.1 Effect of applied potential, E, on band edges in interior of n-type semiconductor; (**a**) $E > E_{fb}$, (**b**) $E = E_{fb}$, (**c**) $E < E_{fb}$

Under depletion conditions there is a relation between $1/C_{SC}^2$ and the potential, where C_{SC} is the semiconductor electrode capacitance. For n-type semiconductors the following relation is found:

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(E - E_{fb} - \frac{kT}{e}\right), \tag{10.1}$$

where ε is the dielectric constant of the semiconductor, ε_0 is the dielectric permittivity of the vacuum, e is the elementary electric charge, k is the

Boltzmann constant, N_D is the donor density, and $kT/e = 0.0257$ V 25 25 °C. A similar expression exists for *p*-type semiconductors:

$$\frac{1}{c_{sc}^2} = \frac{-2}{\varepsilon\varepsilon_0 e N_A}\left(E - E_{fb} + \frac{kT}{e}\right), \tag{10.2}$$

where N_A is the acceptor density.

10.2 Determination of Flatband Potential

Capacitance measurements are usually carried out at one frequency, and the measured capacitance is determined as

$$c = \frac{-1}{\omega Z''}, \tag{10.3}$$

where C is the measured electrode capacitance. In general, it consists of the connection between the space charge capacitance, C_{sc}, and the double-layer capacitance, C_{dl}, in series:

$$\frac{1}{C} = \frac{1}{C_{SC}} + \frac{1}{C_{dl}}, \tag{10.4}$$

but usually $C_{SC} \ll C_{dl}$ and $C \approx C_{SC}$. Examples of Mott-Schottky plots are presented in Fig. 10.2.

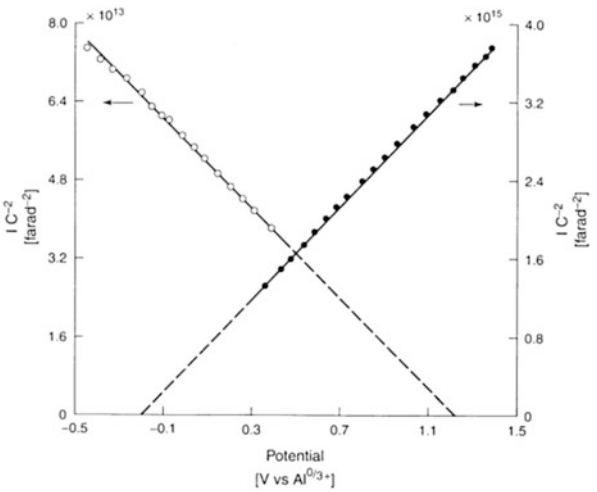

Fig. 10.2 Mott-Schottky plots obtained on *n*-GaAs (*filled circles*) and *p*-GaAs (*open circles*) electrodes in 2:1 $AlC1_3$ – n-butylpyridinium chloride molten salt electrolyte; the frequency was 2 kHz (From Ref. [467], copyright (1983), with permission from Elsevier)

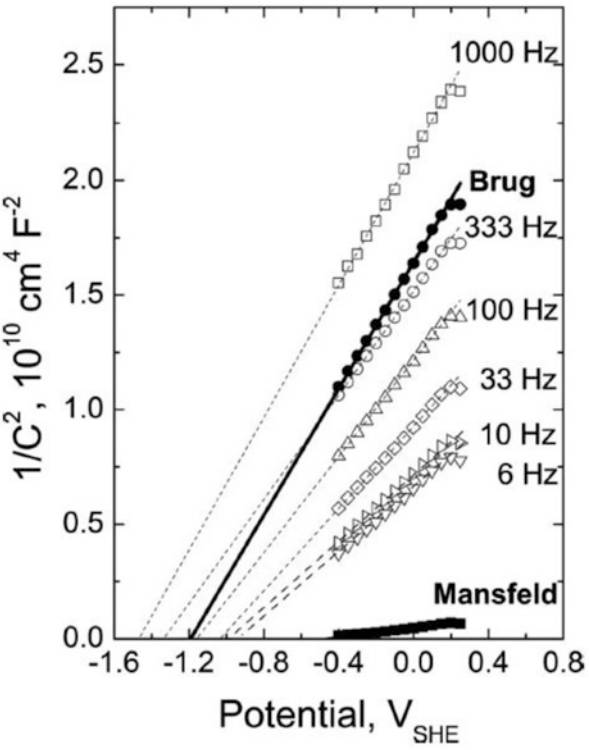

Fig. 10.3 Mott-Schottky plots at Cr electrode using capacitance measured at one frequency (indicated), Eq. (10.3), and using Brug et al. [305] and Hsu and Mansfeld [306] models (From Ref. [468]. Reproduced with permission of Electrochemical Society)

The intercept of these plots provides the value of the flatband potential, E_{fb}, and the slope gives the donor or acceptor density. In agreement with Eqs. (10.1) and (10.2), the slope for *n*-type semiconductor is positive and that for *p*-type semiconductors is negative.

The use of Eq. (10.3) assumes that the semiconductor-electrolyte interface is ideally capacitive and can be represented by the solution resistance, $R_{s,}$ and the interface capacitance, C, in series. However, such an interface is almost never purely capacitive and must be represented by the CPE. This leads to different slopes at different frequencies and sometimes different values of the flatband potential. An example of such a behavior is shown in Fig. 10.3. It is evident that measurements at different frequencies display different intercepts and slopes, and, as a consequence, different E_{fb} and N_D.

In general, behavior described by R_s *CPE* or $R_s(R_p$ *CPE)* circuits is observed, that is, displaying impedances as in Figs. 8.3 and 8.4. Harrington and Devine [468] and Rodriguez and Carranza [469] proposed to determine the average double-layer capacitance from the CPE model using Brug et al. [305] and Hsu and Mansfeld [306] models (Sect. 8.1). They found that the Hsu and Mansfeld model leads to incorrect data, while that of Brug et al. gives correct results.

A comparison of the results obtained from these two models is shown in Fig. 10.3. Of course, in such cases, at each potential the complete impedance spectrum must be obtained, which leads to longer experiments and possible changes in the surface layer with time.

Impedance of semiconductors in the presence of electron transfer through surface states is much more complex; see, e.g., Ref. [470–472].