THE IMPEDANCE RESPONSE OF SEMICONDUCTORS
An Electrochemical Engineering Perspective

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CHEMICAL ENGINEERS working in the field of electronic materials are not normally concerned with processes taking place within the semiconductor. Most direct application of chemical engineering principle is seen in the analysis of the growth of semiconductors in the gas phase (CVD or MOCVD) or in the liquid phase (crystallization, Czochralski crystal growth, and Bridgman growth). Application of chemical engineering principles to these processes is not easy but is direct because the species of concern are not electrically charged. In contrast, the species within the semiconductor (e.g., electrons, holes, ionized electron donors or acceptors) are charged, and proper analysis of processes taking place within the semiconductor requires that this electrical charge be treated.

Since ions in electrolytic solutions are also charged, the principles learned in the application of transport phenomena, reaction engineering, and thermodynamics to electrochemical systems can be applied almost directly to the study of semiconductor devices. Here, these principles are applied to interpret the impedance response of semiconducting electrodes.

BACKGROUND

Impedance techniques can be applied to semiconductors to identify the electronic structure, i.e., the distribution of states within the semiconductor bandgap. A simplified schematic representation of the band structure is shown in Figure 1. Electrons can be excited from the valence or bonding orbitals to the conduction band by receiving thermal or electromagnetic (illumination) energy. The species formed by this excitation are electrons (in the conduction band) and holes (absence of an electron in the valence band). Both species are charged (electrons have a negative charge and holes have a positive charge) and can move in response to concentration or potential gradients.

The minimum energy required to excite an electron from the valence band to the conduction band is the bandgap energy. In the ideal semiconductor, electrons cannot exist at energy levels between the valence and conduction energies. In real materials, electronic states within the band gap can exist due to the presence of impurities (carbon, oxygen, and chromium are examples) or of dislocations, vacancies, or other lattice defects. These states can be electron donors or electron acceptors. Donor species are those which become positively charged when an electron is released, while acceptors become negatively charged when an electron is added. Because these species are charged, the distribution of electrical potential can be affected. Inter-band electronic states can be undesirable since they facilitate electronic transitions which can reduce the efficiency of electronic devices. In some cases, inter-band states are intentionally added when the added reaction pathways for electrons result in desired effects. Electroluminescent devices, for example, rely on emission of photons which takes place when electrons are transferred from the conduction band to an inter-band state in a large-bandgap semiconductor. The energy level of the states caused by introduction of the impurity determines the color of the emitted light. The impact of these states can be significant, even in concentrations that would seem to be very low by normal chemical engineering standards. There is, therefore, a need for developing new ways to evaluate the concentration, energy, and distribution of such electronic states.

A variety of techniques have been developed to study semiconductors which are based on impedance spectroscopy. We wish to focus here on a variant of electrochemical photocapacitance spectroscopy [1-5] in which the capacity of a reverse-biased electrode is measured as a function of the wavelength of incident sub-bandgap light. Let us note here that we really do not measure a capacity. Instead, we measure a periodic cell potential in response to a periodic current (or vice-versa) from which we calculate an impedance which has real and imaginary components. If we assume that this system behaves like an electrical circuit consisting of a capacitor and a resistor in series, we can, through regression techniques, obtain a value for a capacity and a resistance. The capacity obtained in this way is usually emphasized in this type of work since it can be easily related to the charge held in the semiconductor.

Since light of energy sufficient to cause an electronic transition will change the amount of charge held in a given...
state, changes in capacity at a given photon energy indicate the presence of states that allow transitions requiring that amount of energy. From this type of data we can obtain the energy levels of electronic states. The problem in this is that the largest contribution to the capacity is due to shallow level electronic states that are usually intentionally introduced as dopants. In fact, the change in capacity seen under illumination is (at best) proportional to the square root of the ratio of the defect concentration to the dopant concentration. This means that the technique of Haas and Teich [1-4] can be applied to semiconductors with a large defect concentration as compared to dopant concentration, but provides an unacceptable low signal to noise ratio when the dopant concentration is moderately large. On the other hand, the real part of the impedance, normally ignored since it is so difficult to relate to physical parameters, is very sensitive to these defects as low frequencies. We wish to focus here on the application of electrochemical principles to the problem of identifying the relationship between the real part of the impedance response and the energy, concentration, and distribution of defects. We can do this through development of a mathematical model based on the principles used in analysis of electrochemical systems. The treatment presented here follows a qualitative description of the experimental technique and the methods usually used in its analysis.

**IMPEDANCE TECHNIQUES**

Impedance techniques involve perturbation of a steady-state condition by a sinusoidal current or applied potential of low magnitude. A typical amplitude for an applied potential perturbation might be 10 mV, and the resulting sinusoidal current should have the same frequency, but may be shifted in phase. Thus the impedance, obtained by dividing potential by current, can be described as having real and imaginary components, i.e.,

\[ Z = Z_R + jZ_I \]  (1)

A typical way to analyze impedance experiments is to compare the results to the impedance of simplified "equivalent" electrical circuits.

**Equivalent Circuit Representations of Simple Systems**

Electrochemists commonly present the resulting data in the form of an impedance plane plot (Z, as a function of Zr, with frequency as a parameter). An impedance plane plot is given in Figure 2 for an electrical circuit consisting of a resistor. This is, of course, a very simple case. A Bode plot for this system (see Figure 2b) shows that the real part of the impedance is constant for all frequencies, and since there is no phase shift, the imaginary part of the impedance is equal to zero. Thus, Zr = R, and ZI = 0.

The impedance data for a resistor and capacitor in series are given in Figure 3. The real part of the impedance is independent of potential, and the magnitude of the imaginary part is inversely proportional to frequency, i.e., the highest values are seen at low frequencies. For this case, Zr = R, and ZI = 1/ωC.

**Equivalent Circuit Representations for Electrochemical Systems**

Simple electrochemical reactions at an electrode surface are often modeled in terms of the circuit shown in Figure 4. The resistance R is associated with the Ohmic resistance of the cell, the capacity is associated with the double layer capacitance, and the resistance R is related to the rate constant for the surface reaction. The impedance plane plot for this case is in the shape of a semicircle with the high frequency asymptote shifted from the origin by an amount equal to the solution resistance. Additional elements can be added to account for reactions proceeding in parallel or in series. A perfect semicircle is usually not observed experimentally, and a number of factors have been used to explain the observed deviation of the semicircle. Roughening of the surface or growth of films during the course of an experiment can, in some cases, account for these observations. Mass transfer effects are also often important. These are treated by adding a Warburg element (see Figure 5). The impedance response of a Warburg element is a function of frequency and is derived by solving the convective diffusion equation for a given geometry to obtain the frequency dependence of the concentration of reactants at the electrode surface. See reference 6 and chapter 9 in reference 7 for more discussion on the application of impedance techniques to typical electrochemical systems.

**An Equivalent Circuit Representation for Defects in Semiconductors**

The fifth case considered here is that of a second resistor and capacitor in series added in parallel to the capacitor of Figure 3. The resulting impedance data are shown in Figure 6. The magnitude of the imaginary part of the impedance is largest at lower frequencies, and the real part of the added circuit components is seen at lower frequencies. The real and imaginary components of impedance, based on the equivalent circuit given in Figure 6, are

\[ Z_r = R + \frac{R_s - R}{1 + R_s R_C} \]  (2)

\[ Z_I = \frac{1}{\omega C} \left( \frac{R_s - R}{1 + R_s R_C} \right) \]  (3)

respectively.

If the experimental system behaves like a given electrical circuit, nonlinear regression techniques could be used to obtain values for the resistor and capacitor components in that circuit. If the electrical circuit chosen does not account for all aspects of the data, e.g., if the circuit of Figure 3 is used to model the data shown in Figure 4, the circuit components will be functions of frequency. Note that the circuits given in Figures 3 and 6 do not allow passage of direct cur-

FIGURE 2. Impedance data for a system consisting of a resistor (with no capacitive component) a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

FIGURE 3. Impedance data for a system consisting of a resistor and a capacitor in series a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

FIGURE 4. Impedance data for a system consisting of a resistor in series with the parallel combination of a capacitor and a resistor: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.

FIGURE 5. Impedance data for a system consisting of a resistor in series with the parallel combination of a capacitor and a resistor and a Warburg element: a) impedance plane plots with frequency as a parameter; b) Bode plots for real and imaginary components of impedance.
state, changes in capacity at a given photon energy indicate the presence of states that allow transitions requiring that amount of energy. From this type of data we can obtain the energy levels of electronic states. The problem in this is that the largest contribution to the capacity is due to shallow level electronic states that are usually intentionally introduced as dopants. In fact, the change in capacity seen under illumination is (at best) proportional to the square root of the ratio of the defect concentration to the dopant concentration. This means that the techniques of Hask and Trench [1-4] can be applied to semiconductors with a large defect concentration as compared to dopant concentration, but provides an unacceptable low signal to noise ratio when the dopant concentration is modestly large. On the other hand, the real part of the impedance, normally ignored since it is so difficult to relate to physical parameters, is very sensitive to these defects as low frequencies. We wish to focus here on the application of electrochemical principles to the problem of identifying the relationship between the real part of the impedance response and the energy, concentration, and distribution of defects. We can do this through development of a mathematical model based on the principles used in analysis of electrochemical systems. The treatment presented here is a compact description of the experimental technique and the methods usually used in its analysis.

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\[ Z = Z_r + iZ_i \]  

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**An Equivalent Circuit Representation for Defects in Semiconductors**

The fifth case considered here is that of a second resistor and capacitor in series added in parallel to the capacitor of Figure 2. The resulting impedance data are shown in Figure 6. The magnitude of the imaginary part of the impedance is largest at lower frequencies, and the impact of the added circuit components is seen at lower frequencies. The real and imaginary components of impedance, based on the equivalent circuit given in Figure 4, are

\[ Z_s = R_s + \frac{1}{j \omega C_t} \]  

(2)

and

\[ Z_s = R_s + \frac{1}{j \omega C_t} + \frac{1}{j \omega C_r} \]  

(3)

respectively.

If the experimental system behaves like a given electrical circuit, nonlinear regression techniques could be used to obtain values for the resistor and capacitor components in that circuit. If the electrical circuit chosen does not account for all aspects of the data, e.g., if the circuit of Figure 3 is used to model the data shown in Figure 6, the circuit components will be functions of frequency. Note that the circuits given in Figures 3 and 6 do not allow passage of direct cur-
The imaginary part of the impedance tends toward — while the real part of the impedance is shifted from the bulk resistance by a constant which includes the time constant associated with the defects. The high frequency limit is:

\[ Z = \frac{R}{G + C} \]  

This behavior is more easily seen in a logarithmic impedance plane plot as shown in Figure 7. This type of plot emphasizes the high frequency data at the expense of the low frequency asymptote. The high frequency limit obscures the influence of the defects and yields the same result as would be obtained for a resistor and capacitor in series. For this reason, experimental data are frequently taken at high frequencies (greater than 10 kHz is usually sufficient). The defects, represented by \( C \) and \( R \), have a major influence at low frequencies, i.e.,

\[ Z = \frac{R}{G + C} \]

(6)

\[ Z = \frac{R}{G + C} \]

(7)

\[ Z = \frac{R}{G + C} \]

(8)

\[ Z = \frac{R}{G + C} \]

(9)

\[ Z = \frac{R}{G + C} \]

(10)

\[ Z = \frac{R}{G + C} \]

(11)

\[ Z = \frac{R}{G + C} \]

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\[ Z = \frac{R}{G + C} \]

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\[ Z = \frac{R}{G + C} \]

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\[ Z = \frac{R}{G + C} \]

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\[ Z = \frac{R}{G + C} \]

(47)

\[ Z = \frac{R}{G + C} \]

(48)

\[ Z = \frac{R}{G + C} \]

(49)

\[ Z = \frac{R}{G + C} \]

(50)
The electrical circuit given in Figure 6 is especially relevant to our system because it describes the behavior of an ideally polarized semiconductor electrode that contains a reasonable concentration of inter-band defects. In the high frequency limit,

$$\text{FIGURE 7. Impedance data for the system of Figure 6 consisting of a resistor in series with the parallel combination of a capacitor and a resistor and capacitor in series.}$$

and

$$Z_{eq} = \frac{Z_1 + Z_2}{Z_1 Z_2} + Z_3$$

The imaginary part of the impedance tends toward $-\omega C$ while the real part of the impedance is shifted from the bulk resistance by a constant which includes the time constant associated with the defects. The averaged capacitance is given by

$$C = C_1 + C_2$$

This interpretation of the circuit elements is based, to a large extent, on the results of the mathematical model presented in subsequent sections.

To compare these idealized cases to experimental results, impedance plane plots are presented in Figure 8 with potential as a parameter for an n-GaAs electrode in contact with a mercury pool [8]. The logarithmic plot was used to emphasize the behavior at high frequencies. Linear regression of these data with Eqs. (2) and (3) yields frequency-independent values of circuit components which correspond to the solid line. The component values do vary with applied potential, and, if illumination had been used, the component values would vary with the photon energy of the illumination. The problem we face is how to tie these component values to physical characteristics of the semiconductor. One way to gain this intuition is to develop models for the system based on treatment of transport phenomena and reaction kinetics and to compare the results of these models to those from the equivalent electrical circuits.

**THEORETICAL DEVELOPMENT**

Development of mathematical models for the impedance response of semiconductor systems generally takes place in two steps: development of a steady-state model followed by development of a model treating the time constant perturbation of voltage or current about the steady-state value. Since the species of interest have charge associated with them, we need to include treatment of electrical potential as well as concentrations. Thus, the electrostatic potential and the concentrations of electrons, holes, and ionized defect states become dependent variables for this system. The rate of slow doping species are usually assumed to be completely ionized at room temperatures and thus contribute to a fixed concentration of charge. Parts of the development presented here are given in references 9, 10, 11, and 12. References 13 and 14 provide good background to general aspects of semiconductor physics, and 15 provides a good mathematical foundation for electrochemical engineering.

**Mass Transport Expressions**

The electrochemical potential $\mu_i$ of a given species $i$ can arbitrarily be separated into terms representing a secondary chemical potential, a chemical contribution, and an electrical contribution, i.e.,

$$\mu_i = \mu_i^{(1)} + \mu_i^{(2)} + \phi$$

where $\mu_i^{(1)}$ is the volumetric concentration of species $i$, $f_i$ is the activity coefficient, $x_i$ is the charge number, and $\phi$ is the potential which characterizes the electrochemical state of the system and can be defined in many ways. This treatment is entirely analogous to the definition of chemical potentials as used for electrically neutral systems. In fact, the usual chemical potentials are recovered for the case where $x_i$ is equal to zero.

The flux $N_i$ of species $i$ is governed by the gradient of the electrochemical potential, given in one dimension by

$$N_i = -D_i \frac{d\mu_i}{dx}$$

where $x$ is the mobility of species $i$. If the semiconductor is nondegenerate, the electron and hole activity coefficients $f_i$ can be considered to be constant, and Eq. (8) can be substituted into Eq. (9) to give the dilute solution transport expression

$$J_i = D_i \frac{d\mu_i}{dx}$$

From Eq. (10), the fluxes of electrons and holes are driven by concentration and potential gradients. This distinction is a result of the separation of the chemical and electrical contributions given in Eq. (8). If desired, degenerate semiconductor conditions can be modeled by calculating the value of the activity coefficients $f_i$ for electrons and holes [16, 17] and by the equation of continuity, i.e.,

$$\frac{d}{dt} \int \rho_i \, dV = \frac{d}{dt} \int \rho_i \, dV = 0$$

where $\rho_i$ is the electron or hole density and $V$ is the volume.

**Kinetic Expressions for Electronic Transitions**

Calculation of a rate expression for $G_i$ requires the choice of a kinetic framework. In this work, electrons are allowed to pass between the conduction band (with energy $E_c$), the valence band (with energy $E_v$), and the inter-band species (with energy $E_i$). A general scheme for the various electron transitions associated with this approach are shown in Fig. 9. With these representations, the rates of the electron transitions between the various energy levels can be described by applying mass action principles [e.g., (10)] to give

$$r_i = k_i \rho_{i+}$$

where $k_i$ is the rate constant of reaction $i$, $\rho_{i+}$ is the concentration of positively charged inter-band donor species, $\rho_i$ is the total concentration of inter-band donors, and $\rho$ is the hole concentration. In the absence of inter-band states, generation of electrons and holes occurs through band-to-band mechanisms. The rate of electron generation is given by

$$G_{el} = k_i \rho_i (n - np)$$

where the two right-hand terms represent thermal generation ($\Delta H = kT$) and recombination, respectively, and $n_i$ is termed the "intrinsie concentration" (a physical property equal to the concentration of electrons and holes in the "ideal" undoped semiconductor). The constraint that the rates of generation and recombination are equal provides that $n = np$ under equilibrium conditions. In the presence of inter-band states, the net rate of production for electrons (and holes) is given by

$$\text{FIGURE 8. Impedance plane plot for a semi-insulating n-GaAs electrode in contact with a mercury pool [8].}$$

$$G_{el} = k_i \rho_i (n - np)$$

Usually inter-band defect states are considered to be immobile, the rate of change of the concentration of ionized inter-band states is equal to their (position-dependent) rate of production, $G_i$. For most electrochemical systems, the separation of charge associated with interfacial regions can be treated simply as contributing to rate constants associated with electrode kinetics. This is not appropriate for a semiconductor because the separation of charge is integral to the operation of electronic devices. Poisson's equation,

$$\frac{d^2 \Phi}{dx^2} = -\frac{e}{\varepsilon}$$

can be used to relate the electrostatic potential $\Phi$ to the charge held within the semiconductor. The scaling length for this system, the thickness (measured in dimensions, is given by the Debye length,

$$\lambda_D = \left( \frac{e^2}{\varepsilon} \right)^{1/2}$$

The term $(N_e - N_h)$ includes the charge associated with partially ionized space charge layers (which may be a function of applied potential) as well as the completely ionized dopant species (which may have an arbitrary distribution, but is usually assumed to be independent of operating conditions).
been used to model the impulse response of semiconduc-
tor detectors in the steady state [18, 19, 20] and in the
analysis of electrochemical systems (e.g., [21-24]).
The above expressions are substituted into the governing
equations which are solved sequentially for the steady-
state and the sinusoidal steady-state portions, respectively.
The Impedance can be resolved from the calculated potential quantities over the space charge region into real and imagi-
inary components according to
\[ Z_a = \frac{\Delta V}{\Delta i} \]
and
\[ Z_i = \frac{\Delta V}{\Delta i} \]
respectively.

Steady State Boundary Conditions
The governing equations are initially solved under the steady-state condition, subject to the boundary conditions
\[ \frac{\partial y}{\partial t} = 0, \quad \frac{\partial z}{\partial t} = 0 \]
at the semiconductor-current collector interface (ohmic con-
tact), and
\[ n_{Si} = n_{i}, \quad v = 0, \quad \frac{\partial n_{p}}{\partial x} = 0 \]
at the semiconductor-electrolyte interface (ideally polariz-
able contact). These conditions are appropriate for a semicon-
ductor-mercury contact or for a semiconductor-electrolyte contact where the electrolyte is chosen so that no chemical reaction occurs.

Sinusoidal Steady State Boundary Conditions
The time-dependent equations are solved for the re-
sponse to a superimposed sinusoidal current by introducing
expressions for the dependent variables (such as \( y(t) \)) into the governing equations and linearizing around the steady state solution obtained in the previous step. Approp-
ate boundary conditions for the impedance calculations are given by
\[ \frac{\partial y}{\partial x} = \frac{\partial z}{\partial x} = 0, \quad \text{at the semiconductor-current collector interface, and} \]
\[ n_{Si} = n_{i}, \quad v = 0, \quad \frac{\partial n_{p}}{\partial x} = 0, \quad \text{at the semiconductor-electrolyte interface.} \]
Again, these conditions are consistent with an ideally polarized electrode where the superimposed current acts only as a charging current.

Numerical Method for Solution
The solution of the coupled differential equations is non-
trivial, and a complete solution requires use of a computer.
The results of this type of numerical solution are presented elsewhere (11, 12). The point here is to emphasize that the apparently complex behavior with transport and reaction processes within the semiconductor is response to a sinusoidal perturbation of current or applied potential can be described by a straightforward application of principles learned in the study of electrochemical systems.

Analytic Expressions Used for Analysis of Experimental Data
Analytic solutions to the above equations have been de-
veloped that are valid in the high frequency limit. These
solutions are based on integral of Poisson's equation coupled with assumption of equilibrium concentration distr-
butions. The relationship between the applied potential and the CE series capacitance was derived by Mott and Schottky (see, e.g., Jefferies (19) in the late 1930's to be for (a
n-type semiconductor)
\[ \frac{1}{C} = \frac{y}{z} \]
This is the well-known Mott-Schottky relationship.

Deviations from straight lines in Mott-Schottky plots, are frequently attributed to the influence of potential depen-
dent charging of surface or bulk states. While deviations can also be attributed to non-uniform dopant concentra-
tions, this interpretation is supported by analytic calculations of the contribution of defects to the space charge as a function of applied potential (i.e., 26-27).

CONCLUSIONS
The principles learned in the study of mass transport, thermodynamics, and heterogeneous and homogeneous kinetics with electrochemical systems can be applied directly to the transport and reaction processes that take place within the cell. The theory of dilute solu-
tions is generally appropriate, and values for needed parameters can be obtained through application of statistical thermodynamics.

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electronics and Materials.

NOTATION

Roman Characters

\( q \) concentration of species i, cm\(^{-3} \)
\( C \) space charge capacitance calculated from an RC series circuit, F/cm\(^2 \)
\( \Delta C \) Change in C from a chosen reference level, F/cm\(^2 \)
\( D \) diffusion of species i, cm\(^2\)/s
\( E_a \) inter-band acceptor energy, eV
\( E_c \) conduction band energy, eV
\( E_g \) inter-band donor energy, eV
\( E_F \) Fermi energy, eV
\( E_B \) bandgap energy, eV
\( E_F \) equilibrium constant for reversible reactions i and j
\( E_a \) Energy of generalized inter-band trap species, eV
\( E_B \) valence band edge energy, eV
\( \eta \) activity coefficient for generalized species i
\( \alpha \) Faraday's constant, 96487 Coul.
\( \beta \) deg of inter-band species
\( \gamma \) current density, mA
\( \Delta V \) open circuit voltage, mA

Chemical Engineering Education
Again, at equilibrium, the rates of generation and recombination are equal and \( np = n_i^2 \).

Use of the above stoichiometric expressions requires selection of the six rate constants (or three rate constants and the diffusion (or reaction) constants) associated with these expressions. This apparently arbitrary selection can be approached by looking for mechanisms to relate the rate constants for the reversible, homogeneous reaction pairs (and, the expression for the optical generation of electrons under solar illumination is)

\[
G_{\text{sc}} = \frac{k_1 n_i [a + \frac{k_n a}{k_n + a}]}{k_1 + k_0} \text{exp}(-\frac{n_i}{\text{RT}}) \tag{23}
\]

where \( G_{\text{sc}} \) is the fraction of incident photons with energy greater than the bandgap, \( k_0 \) is the bond-band absorption coefficient, and \( n_i \) is the solar flux. Similar expressions apply for sub-bandgap illumination; however, treatment of optical excitation by light with photon energies smaller than the bandgap requires expressing the effective absorption coefficient. Such expressions can be found in the literature (e.g., [18]) for the bandgap for corresponding to the transition of electrons from inter-band acceptor states to the conduction band. This absorption coefficient is a function of the inter-band state energy, the photon energy, and the concentration of ionized states. Absorption of sub-bandgap illumination is negligible for the usual values of semiconductor thickness, inter-band species density, and absorption coefficients. This allows the effects of sub-bandgap illumination to be included as a modification of the rate constants in the expressions for \( r_1 \) and \( r_0 \).

**Impedance Modeling**

A system whose time response \( y(t) \) to a perturbation \( x(t) \) can be described by the expression

\[
b_i y_i(t) = d_i y_i(t) + k_i y_i(t) - y_i(t) + \sum_j b_j y_j(t)
\]

is defined as a linear system. One characteristic of such a system is that a perturbation of the form \( x(0) = \text{const} \) will result in a response of the form \( y(t) = \text{const} \cdot e^{-K_0 t} \).

Parameter variation studies can be further simplified by the fact that the rate constants are interrelated such that, given energy levels for the electronic states, all rate constants can be obtained from a single rate constant. For example, the relationship

\[
k_1 = k_0 \frac{P_b}{P_a}
\]

was obtained by assuming that changes in the free energy of reaction associated with varying the energy of an electronic state are distributed equally between the activation energies for the forward and the reverse directions. This is similar to the mathematical techniques used to separate the free energy of an electrolythetical reaction into chemical and electrical terms. The symmetry factor in this application is assumed to have the form

\[
k_1 = k_0 \frac{P_b}{P_a}
\]

Similar expressions can be developed for band-to-band recombination, i.e.,

\[
k_1 = k_0 \frac{P_b}{P_a}
\]

The use of Eq. (27) to relate the homogeneous, band-to-band rate constant \( k_0 \) to the corresponding inter-band constants \( k_1 \) and \( k_2 \) is equivalent to assuming that the reaction cross section is the same for recombination through trap sites as it is for direct transition. This assumption could easily be relaxed to account for enhanced rates of recombination through traps.

In the case where solar illumination is applied to the semiconductor to the optical generation of electrons under solar illumination is

\[
G_{\text{sc}} = \frac{k_1 n_i [a + \frac{k_n a}{k_n + a}]}{k_1 + k_0} \text{exp}(-\frac{n_i}{\text{RT}}) \tag{23}
\]

and

\[
G_{\text{sc}} = \frac{k_1 n_i [a + \frac{k_n a}{k_n + a}]}{k_1 + k_0} \text{exp}(-\frac{n_i}{\text{RT}}) \tag{24}
\]

were \( k_0 \) is the equilibrium constant for reaction pair \( i, g \) is the degeneracy associated with the inter-band state, \( n_s \) is the conduction band density of states, and \( N_i \) is the valence band density of states. These expressions were derived by assuming thermal equilibrium and substituting standard statistical expressions for electron, hole, and defect concentration in terms of energy level. The numerical value for \( g \) is determined by the acceptor character of the state, e.g., \( g = 4 \) for electron acceptors and \( g = 2 \) for electron donors [14].

Steady State Boundary Conditions

The governing equations are initially solved under the steady-state condition, subject to the boundary conditions

\[
N_s = 0, \quad \frac{dN_s}{dy} = 0, \quad \text{and} \quad d \quad \text{at the semiconductor-collector interface (ohmic contact),}
\]

\[
R_s, \quad N_s, \quad \text{and} \quad \frac{dN_s}{dy} = 0
\]

at the semiconductor-electrode interface (ideally polarizable contact). These conditions are appropriate for a semiconductor-destroyer contact or for a semiconductor-electrode contact where the electrode is chosen so that no chemical reaction occurs.

Sinusoidal Steady State Boundary Conditions

The time-dependent equations are solved for the response to a superimposed sinusoidal current by introducing expressions for the dependent variables (such as Eq. (28)) into the governing equations and linearizing around the steady state solution obtained in the previous step. Appropriate boundary conditions for the impedance calculations are given by

\[
\sigma_N - \sigma_N^0, \quad \sigma_N^0, \quad \text{and} \quad \frac{dN_s}{dy} = 0
\]

at the semiconductor-collector interface, and by

\[
\sigma_N - \sigma_N^0, \quad \sigma_N^0, \quad \text{and} \quad \frac{dN_s}{dy} = 0
\]

at the semiconductor-electrode interface. Again, these conditions are consistent with an ideally polarizable electrode where the superimposed current acts only as a charging current.

Numerical Method for Solution

The solution of the coupled differential equations is non-trivial, and a complete solution requires the use of a computer. The results of this type of numerical solution are presented elsewhere (11, 12). The point here is to emphasize that the apparently complex behavior associated with transport and recombination within the semiconductor in response to a sinusoidal perturbation of current or applied potential can be described by a straightforward application of principles learned in the study of electrochemical systems.

Analytic Expressions Used for Analysis of Experimental Data

Analytic solutions to the above equations have been developed that are valid in the high frequency limit. These solutions are based on integration of Poisson's equation coupled with assumption of equilibrium concentration distribution. The use of the applied potential and the \( E_s \) region capacitance was derived by Mott and Schottky (see, e.g., Jaffe [11]) in the late 1920s to be (for a non-type semiconductor)

\[
\sqrt{\frac{V}{R_T}} = \frac{1}{C} \left( \frac{N_i - N_s}{N_i} \right)
\]

This is the well-known Mott-Schottky relationship.

Deviations from straight lines in Mott-Schottky plots, are frequently attributed to the influence of potential dependent charging of surface or bulk states. While deviations can also be attributed to non-uniform dopant concentrations, this interpretation is supported by analytic calculations of the contribution of defects to the space charge as a function of applied potential (i.e., [22-27]).

**Conclusions**

The principles learned in the study of mass transport, thermodynamics, and heterogeneous and homogeneous kinetics associated with electrochemical systems can be applied directly to the transport and reaction processes that take place within a semiconductor device. This suggests that the theory of electrochemical systems is generally appropriate, and that parameters for the steady state solutions can be obtained through application of statistical thermodynamics.

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**Note**

<table>
<thead>
<tr>
<th>Roman Characters</th>
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<tbody>
<tr>
<td>( c_1 ) concentration of species ( i ), ( 1 \text{ cm}^{-3} )</td>
</tr>
<tr>
<td>( C ) space charge capacitance calculated from an ( E_C - E_s ) curve, ( \text{F cm}^2 )</td>
</tr>
<tr>
<td>( D_k ) diffusivity of species ( i ), ( \text{cm}^2 \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k ) inter-band acceptor density, ( \text{eV}^{-1} )</td>
</tr>
<tr>
<td>( E_s ) conduction band energy, ( \text{eV} )</td>
</tr>
<tr>
<td>( E_a ) inter-band donor energy, ( \text{eV} )</td>
</tr>
<tr>
<td>( F ) Fermi energy, ( \text{eV} )</td>
</tr>
<tr>
<td>( G ) bandgap energy, ( E_G ) = ( E_a - E_v )</td>
</tr>
<tr>
<td>( \epsilon_0 ) equilibrium constant for reversible reactions ( j ) and ( k )</td>
</tr>
<tr>
<td>( E_v ) energy of generalized inter-band trap species, ( \text{eV} )</td>
</tr>
<tr>
<td>( j ) degeneracy of inter-band species</td>
</tr>
<tr>
<td>( k ) current density, ( \text{mA} )</td>
</tr>
</tbody>
</table>

\[ \frac{d}{dy} \text{exp}(-\frac{n_i}{\text{RT}}) \]


