Semi conductor Electrodes

VII. Digital Simulation of Charge Injection and the Establishment of the Space Charge Region in the Absence and Presence of Surface States

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ABSTRACT

Transport of free carriers following charge injection to a semiconductor electrode is simulated. The relaxation of the free carrier results in the buildup of the space charge region whose properties are calculated. For an intrinsic semiconductor, the relaxation resembles that of the cations and anions in the diffuse double layer at a metal/electrolyte interface following charge injection into the metal. For an extrinsic semiconductor, some additional specific effects arise, which are discussed. The effect of surface states is considered and the interaction of a surface level with the semiconductor bands is simulated. This interaction results in trapping of charge from the space charge region and delivery of it to the surface. The properties of the space charge region in the presence of surface states are calculated, and their effect on the relaxation process demonstrated.

There has been much interest recently in semiconductor electrodes, and especially in photoelectrochemical experiments which may lead to devices of practical use, such as for solar energy utilization [see (1-3) and references therein]. Although the basic principles of the semiconductor electrode/electrolyte interface were formulated some time ago and have been reviewed extensively (4-8), the quantitative treatment of the behavior of semiconductor electrodes is quite complicated involving carrier diffusion and migration, thermal- and photogeneration, and recombination in the semiconductor itself in addition to the usual mass transfer and kinetic processes in the electrolyte phase and interphase charge transfer steps. Digital simulation methods (9, 10) have been very valuable in the treatment of complex kinetic or mass transfer problems in electrochemical systems. It is the aim of this paper and following ones in this series to apply digital simulation techniques to electrochemistry at semiconductor electrodes and the behavior of the semiconductor/electrolyte interface under illumination. In this paper we discuss the basic concepts of simulation of a semiconductor and the sequence of events following charge injection to a semiconductor electrode and leading to the formation of a space charge region. Following papers will describe the establishment of a photovoltage at an ideally polarized semiconductor electrode under steady illumination and the production of a photocurrent when charge transfer across the electrode/solution interface occurs.

Digital Simulation Model of Formation of Space Charge Region

Although the carrier distribution and field in a semiconductor electrode can frequently be calculated by direct analytical methods (6-8), a digital simulation of it is convenient since these calculations provide the starting point for simulations of the photoeffects of interest. Moreover, simulations allow the investigation of the effect of surface states on the field and are useful in testing the digital model under conditions where some rigorous solutions are known. Consider a semiconductor electrode in contact with an electrolyte solution and at the flatband potential, i.e., the point of zero charge. We now consider the events that occur following the coulostatic injection of charge into the semiconductor. As a dielectric the semiconductor electrode can sustain a charge and an electric field within its volume; however, because of the existence of mobile carriers in the semiconductor, this charge is subject to redistribution and will ultimately accumulate at the semiconductor/electrolyte boundary in a region called the space charge region. Usually the charge distribution in a semiconductor electrode will be found somewhere between the two extreme cases of a metal electrode, where all the charge is essentially located at the surface, and a dilute electrolytic solution in contact with a charged metal electrode, in which the charge (ionic) distribution is very diffuse. The space charge region is of fundamental importance in describing the electrochemical properties of the semiconductor and it is the equilibrium distribution, rather than its mode of formation, that is usually of interest (5). The response of the semiconductor to charge injection is very similar to the relaxation of the diffuse double layer in solution following coulostatic charge injection to a metal electrode recently considered by Feldberg (10). The situation in a semiconductor differs from that for the usual electrolytic solution because of the much higher mobility of the carriers (holes and electrons) the presence of fixed charges (from acceptors or donors) in an extrinsic semiconductor, and the possible importance of dissociation and recombination processes in the semiconductor. The utilization of the basic concepts of electrostatics and mass transfer is very similar to that employed by Feldberg (10), however, so that only a brief outline of the simulation method will be given here. For those interested in utilizing this approach, the computer program is described briefly in the Appendix.

For the injection of positive charge with a charge density, \( Q \) (C/m^2), the field at the semiconductor surface (i.e., the semiconductor/solution interphase), \( E_s \) (V/m), assuming planar geometry so that lines of force of the field are normal to the electrode surface, will be given by

\[
E_s = \frac{Q}{\epsilon f_e f_r} \tag{1}
\]

where \( \epsilon_f \) is the permittivity of free space, \( 8.85 \times 10^{-12} \) F/m, and \( f_e \) is the dielectric constant of the semiconductor relative to vacuum; for a positive charge, \( E_s \) is taken as positive pointing toward the solution. If charge is conserved in the semiconductor, the field at the surface \( (x = 0) \) will always be given by Eq. [1]. In the interior of the semiconductor, \( E(x) \) will depend upon the charge distribution. At the instant of charge injection, the field everywhere in the semiconductor will be \( E_0 \). This field will cause holes \( (h^+) \) to migrate toward the surface and electrons \( (e^-) \) to migrate in the opposite direction. This migration is opposed by the diffusion of holes and electrons with the net flux of...
holes and electrons, $f_+$ and $f_-$, respectively (with positive flux taken as toward the electrode surface), being governed by Eq. [2] and [3]

$$f_+ = (e/kT)E(x)D_pp + D_{pp}/\partial x$$  \[2\]

$$f_- = -(e/kT)E(x)D_nn + D_{nn}/\partial x$$  \[3\]

where $D_p$ and $D_n$ are the diffusion coefficients and $p$ and $n$ are the concentrations of holes and electrons, respectively. The net effect of this mass transfer is the transfer of positive charge to the electrode surface. This new charge distribution will modify $E(x)$. At equilibrium the space charge region is established with no charge remaining in the bulk semiconductor, so that the field there is zero, and with constant concentration profiles for holes and electrons maintained by the counterbalancing of the migrational flux caused by the equilibrium field distribution and the diffusional one. The surface potential, $V_s$, at all stages is given by Eq. [4], where $B_0$ is the field in the bulk semiconductor

$$V_s = \int_0^\infty [E(x) - E_0] dx$$  \[4\]

Results

Intrinsic semiconductor in the absence of surface states.—For an intrinsic semiconductor (e.g., intrinsic Ge), the response to charge injection and relaxation is quite analogous to diffuse double layer relaxation in solution given by Feldberg (10), with the holes replaced by cations and the electrons by anions (Fig. 1). The time for the potential to rise from zero to some maximum value and then relaxes to its new equilibrium value. The carriers which are attracted to the surface (e.g., holes) and which at equilibrium show a continuous drop in concentration with distance from surface towards the bulk, show a minimum in their concentration profile. The drift of the carriers in the semiconductor (e.g., 95 cm²/sec for electrons and 45 cm²/sec for holes in Ge) compared to those of ions in solution (ca. 10⁻⁵ cm²/sec). The space charge is essentially established within 10⁻⁹ sec, a period during which double layer formation in solution will not yet have started. Thus space charge region effects probably can be differentiated from solution double layer ones according to the time window of the experiment.

Extrinsic semiconductor in the absence of surface states.—For a highly doped semiconductor (e.g., n-type Ge) the picture is different. Here, unless strong inversion prevails (e.g., at very positive potentials), the electrical state of the electrode will be mainly determined by the majority carrier distribution (electrons) and the dopant level (the donor atoms), while the minority carriers (holes) will adjust themselves to the field established by the donor and majority carriers. One must also consider the origin of the minority carriers (holes) arriving at the surface during relaxation, because positive charge injection at the metal/semiconductor ohmic contact of the n-type semiconductor occurs largely through electron extraction, rather than hole injection, and the total number of minority carriers originally existing in the bulk semiconductor may be insufficient to populate the space charge layer. A similar problem may apply to an intrinsic semiconductor as well. A typical simulation for n-Ge with a donor level, $N_D$, of 2.5 × 10¹⁰ cm⁻³ is given in Fig. 2. The transport of majority carriers is very fast and they are extracted nearly instantaneously from the surface (and arrive at the metallic contact to compensate for the electrons which were extracted from there by the charge injection). Because most of the charge distribution is associated with the electron distribution, the electric field and surface potential also quickly achieve their equilibrium value. Minority carriers show a relatively slow relaxation to their equilibrium value, because their low bulk concentrations can provide only small fluxes toward the surface. The holes are supplied to the surface and enter the space charge region (taken arbitrarily as the point where the electric field drops to 10⁻⁴ times its surface value) mainly by diffusion. Thus, adjacent to the space charge region, which is the region of primary interest, a relatively wide diffusion layer [known as the “quasi-neutral region” (11)] will be formed. There the electrical field is nearly zero and minority carriers are transported across it by diffusion in a manner analogous to the diffusion of ions toward an electrode in solution in the presence of an excess of supporting electrolyte. In the experiment under consideration here, the quasi-neutral region will eventually disappear. In other kinds of experiments, however, e.g., those connected with a con-
tinuous withdrawal of minority carriers from the electrode surface in a faradaic reaction, a steady-state quasi-neutral region will remain in which the gradient of minority carriers determines the limiting current. The diffusion layer width of the minority carriers is governed by the spontaneous thermal generation of carriers, which is not taken account of explicitly in the simulation. Within the time domain of the simulation (ca. 10⁻⁸ sec) the number of holes generated thermally is negligibly small. For the n-type Ge (p⁺ = 2.5 x 10¹⁰ cm⁻³) the value for the zero-th order generation rate constant is about 10¹⁸ cm⁻³ sec⁻¹. This generation will terminate the diffusion layer of holes at some point when, at a given time, the flux divergence of holes will equal their net generation rate. For the sample under discussion, a wide and essentially linear diffusion layer for holes results, which in this relaxation mode gradually collapses. We cannot extend the simulation, which is concerned primarily with the thin space charge region, to such a distance from the electrode surface. Instead the thermal generation of minority carriers was considered indirectly by terminating the simulation when the transport of holes is arbitrarily assigned the hole concentration as the bulk value at some suitably large distance from the space charge region. Hence the simulated transport of holes to the electrode surface may be larger than the rate found for a more rigorous simulation, where the final relaxation of minority carriers would be determined by the thermal generation rate. Experimentally, it seems unlikely that the relaxation of minority carriers can be observed by purely electrochemical methods, since its influence on the electrode potential is negligibly small. Moreover, a current transient attributable to minority carrier relaxation which might probe their surface concentration would be complicated by the solution diffusion layer. Some other techniques, such as internal reflection spectroscopy at wavelengths which correspond to the absorption spectrum of holes and which is sensitive to their surface concentration (12, 13), might be useful.

Effect of surface states.—Surface states and their relevance to the electrochemistry of semiconductor electrodes have been widely discussed (6, 14). We shall confine ourselves here to a simple model and simulate the interaction of a discrete surface level with the semiconductor bands at the surface in a charge injection experiment. In this case, charge is trapped by the surface level causing a simultaneous change in its occupancy. After relaxation, new surface concentrations and surface-state level occupancies will exist, such that the interaction between the level and the band again does not produce a net effect. The total injected charge will be distributed between the semiconductor surface and space charge region lowering the surface field and surface potential of the semiconductor compared to a situation without the surface states. The simulation assumes very fast (perhaps hypothetically fast) surface states which respond immediately to any perturbation in the equilibrium concentration of free carriers, thus modifying their surface concentrations during their relaxation. The final results should be valid for slower surface states as well. For slow surface states, the relaxation of free carriers can be considered complete before interaction between the space charge region and the surface level begins. Assume the existence of a discrete surface level with a concentration density of states Nₓ located at an energy Eₓ with respect to the Fermi energy, E_F, and having an occupancy or filling function, fₓ (representing the fraction of traps occupied by electrons). Figure 3 represents schematically this situation and the following expressions will be written for exchanging holes and electrons with the bands (6, 15):

\[ \text{Rate of holes to surface: } \frac{\text{Rate}}{\text{Rate}} = k_h N_h f_h \]  

\[ \text{Rate of electrons to surface: } \frac{\text{Rate}}{\text{Rate}} = k_e N_e f_e \]  

\[ \text{Rate of holes to band: } \frac{\text{Rate}}{\text{Rate}} = k_v N_v f_v \]  

\[ \text{Rate of electrons to band: } \frac{\text{Rate}}{\text{Rate}} = k_e N_e f_e \]

The k's are the corresponding rate constants for interaction of the surface level with the conduction and valence band, respectively. n_h and p_h are the surface concentrations of electrons and holes. Since the ratios k_h/k_v and k_e/k_v do not depend on the surface potential, their values determined at the flatband potential, V_F, apply at other potentials, as well. At equilibrium at V_F, p_h = p_o, n_h = n_o, f_h = f_o, R_h = R_e, and R_e = R_v. Then from Eq. [5]-[8]
Rp = k_s[SUR − (ns/n₀) (SURMAX − SUR)] [13]

R_p = k_v[p_SUR − p^* (SUR−MAX − SUR)] [14]

Throughout the simulation n_s, p_s, and SUR change. Before charge injection, p_s = p_s^*, n_s = n_s^*, and SUR = SURMAX/2; thus R_p = R_n = 0. Immediately after the charge injection (i.e., of positive charge), n_s becomes smaller than n_s^*, p_s becomes larger than p_s^*, and at this instant SUR still is equal to SURMAX/2. As a result, both R_p and R_n become positive; the magnitude of SUR decreases as electrons are delivered to the edge of the conduction band and holes are collected from the edge of the valence band. As long as this mechanism is operative, concentration profiles in the space charge region will remain much more shallow than in the absence of surface states. This is shown in Fig. 1 for intrinsic Ge, where the charge injected was of such a size that the bands were bent in a way that the surface region was practically depopulated of electrons. At the new position of equilibrium, the value of SUR, p_n, n_s, and SURMAX − SUR will cause the bracketed concentration profile as well as a new surface level occupancy will result. Note that within the simulation negative values of R_p and R_n as calculated in Eq. [13] and [14] are possible. This occurrence results in an oscillatory behavior in which carriers move back and forth from the bands to the surface level. This behavior arose with large values of k_v and k_s resulting in SUR becoming essentially zero within a few simulation steps. In the computer program such effects were prevented by stopping the interaction between the bands and the surface level (i.e., assigning R_p = R_n = 0) whenever R_p and R_n were calculated to have a negative value. Table I summarizes the results of simulations and gives values of quantities of interest in the absence and presence of surface states (which are assumed to be at an energy, E_l = E_F^p) with the initial condition taken as the flatband potential. Note that for the same total amount of charge injected the surface potential will be smaller in the presence of surface states than in their absence. Notice also that the total charge of the surface states and space charge region equals the injected charge and that the occupancy found for the surface level after the charge injection

**Table I. Simulated properties of space charge region of Ge in absence and presence of surface states**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Without surface states</th>
<th>With surface states</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge injected (C/cm^2)</td>
<td>E, (V/cm)</td>
</tr>
<tr>
<td>Intrinsic Ge</td>
<td>n^* = p^* = 2.5 × 10^{10}</td>
<td>2.91 × 10^{-7}</td>
</tr>
<tr>
<td></td>
<td>n^* = p^* = 2.5 × 10^{10}</td>
<td>2.91 × 10^{-7}</td>
</tr>
<tr>
<td>Extrinsic Ge</td>
<td>n^* = 2.5 × 10^{10}</td>
<td>1.45 × 10^{-10}</td>
</tr>
<tr>
<td></td>
<td>p^* = 2.5 × 10^{10}</td>
<td>2.56 × 10^{-10}</td>
</tr>
<tr>
<td></td>
<td>p^* = 2.5 × 10^{10}</td>
<td>4.96 × 10^{-10}</td>
</tr>
</tbody>
</table>

* Charge trapped in surface states plus charge equivalent to surface field; this total should equal charge injected.
** Simulated surface level occupancy, f_s, at equilibrium after charge injection.
*** Surface level occupancy calculated using the function f_s = 1/[1 + exp(V_s/kT)].
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APPENDIX

The desired region of interest is divided into space elements of width $\Delta X$ (e.g., 25-100 A) which are assigned an index $K$ from $K = 1$ (the surface element) to $K = K_{\text{MAX}}$. The concentration of holes and electrons within each element ($p_K$, $n_K$) is assumed constant and the electrical field between element $K$ and $K-1$ is called $E_K$. The concentration at this boundary is assumed to have a concentration equal to the average value for the two elements on both sides of this boundary. Thus, e.g., for holes,

$$p_K = \frac{1}{2} (p_{K-1} + p_K) \quad [A-1]$$

According to the simulation technique, the change of carrier concentration in element $K$, due to the fluxes written in Eq. [2] and [3], within a time interval $\Delta t$ can be expressed (e.g., for holes) as

$$\Delta p_K = DMP (p_{K-1} - 2p_K + p_{K+1}) + 0.5 UMP \quad [A-2]$$

where $DMP$ and $UMP$ are simulation constants to be discussed later. Such an expression is written for all $K$'s, for holes as well as for electrons. The resulting changes in concentration are then added to the present one. As a result a new concentration profile is established which is used to calculate the concentration changes for the next time interval. Changes in the electric field due to the concentration change will be written as

$$E_{K} = E_{K-1} - (e \Delta q_{\text{stat}} / \varepsilon \varepsilon_0) (p_{K} - n_{K} + N_D - N_A) \quad [A-3]$$

where $N_D$ and $N_A$ are donor and acceptor concentrations, respectively. The initial conditions which follow the injection of charge $q_{\text{inj}}$ are

$$p_K = p^0, \quad n_K = n^0, \quad E_{K=1} = q_{\text{inj}} / \varepsilon \varepsilon_0 \quad [A-4]$$

The boundary conditions are

$$p_{K_{\text{MAX}}} = p^0, \quad n_{K_{\text{MAX}}} = n^0, \quad E_{K=1} = (q_{\text{inj}} - \Delta q_{\text{stat}}) / \varepsilon \varepsilon_0 \quad [A-5]$$

where $\Delta q_{\text{stat}}$ is the charge trapped by the surface level. $K_{\text{MAX}}$ should be the value of $K$ within the bulk of the electrode. However, unless a nonlinear space grid is employed, this $K_{\text{MAX}}$ is too large and $\Delta X$ is too small. Thus a smaller value of $K_{\text{MAX}}$ is used (which was still far outside the space charge region); this results in a somewhat steeper concentration profile for holes so that the electric field toward the surface is slightly overestimated. The simulation constants are $DMN$, $DMP$, $UMN$, and $UMP$. They are defined (e.g., for electrons) as

$$DMN = D \Delta t / (\Delta X)^2 \quad [A-6]$$

$$UMN = U_n \cdot (\Delta t / \Delta X) = (e / k T) DMN \cdot \Delta X \quad [A-7]$$

with similar expressions for holes. As usual for simulations (9), both $DMN$ and $DMP$ must be less than 0.5. Similarly, the effect of migration requires that $UMN \cdot E_{K=1}$ and $UMP \cdot E_{K=1}$ both be smaller than 1 (where $E_{K=1}$ is the maximum value of the electric field, at the surface). These conditions impose the following restriction on $\Delta t$ and $\Delta X$

$$\Delta t / \Delta X < 1 / E_{K=1} U_N \quad [A-8]$$

Typical values which satisfy this requirement are $U_n = 2000 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$, $\Delta X = 5 \times 10^{-7} \text{ cm}$, $DMN = 0.45$, and $E_{K=1} = 10^9 - 10^4 \text{ V/cm}$.

REFERENCES