

Semiconductor 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 to 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 photoeffects and 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 distributions 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 coulombic 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 coulombic 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

$$E_s = Q/\epsilon_0\epsilon_r \quad [1]$$

where ϵ_0 is the permittivity of free space, $8.85 \times 10^{-12} f m^{-1}$, and ϵ_r 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_s . 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

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holes and electrons, f_+ and f_- , respectively (with positive flux taken as toward the electrode surface), being governed by Eq. [2] and [3]

$$f_+ = (e/kT)E(x)D_p p + D_p \partial p / \partial x \quad [2]$$

$$f_- = -(e/kT)E(x)D_n n + D_n \partial n / \partial x \quad [3]$$

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 E_b is the field in the bulk semiconductor

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

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 surface potential rises 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 during the relaxation [as also observed in solution diffuse double layer formation (10)]. The relaxation processes occur in times 10^4 – 10^5 smaller than for those in solution because of the higher D values of the carriers in the semiconductor (e.g., $95 \text{ cm}^2/\text{sec}$ for electrons and $45 \text{ cm}^2/\text{sec}$ for holes in Ge) compared to those of ions in solution (ca. $10^{-5} \text{ cm}^2/\text{sec}$). 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 donors 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 $2.5 \times 10^{16} \text{ cm}^{-3}$ is given in Fig. 2. The transport of the 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

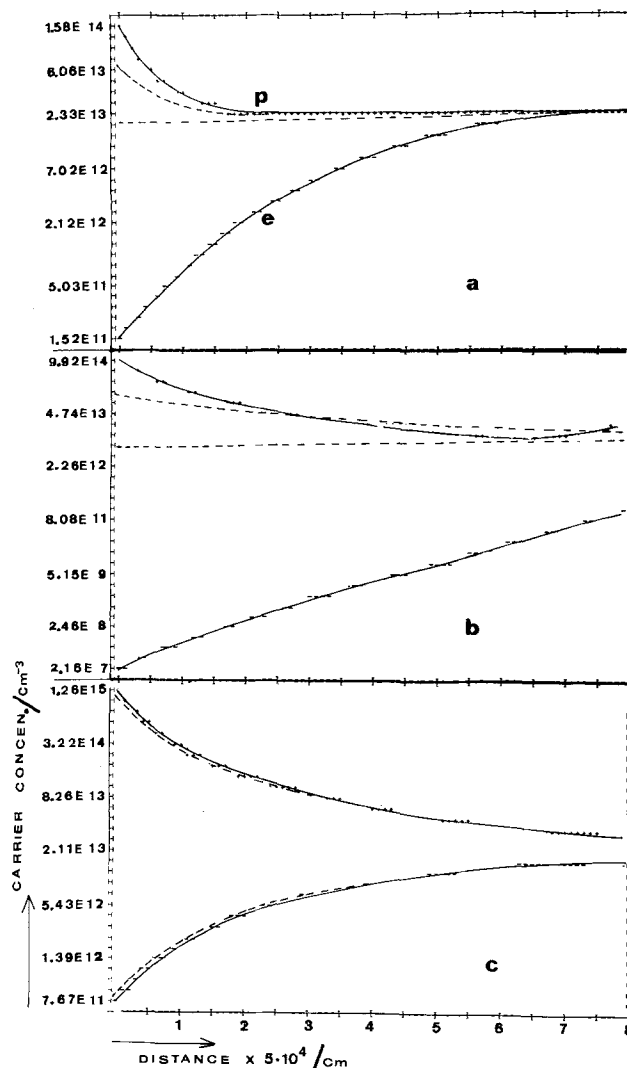
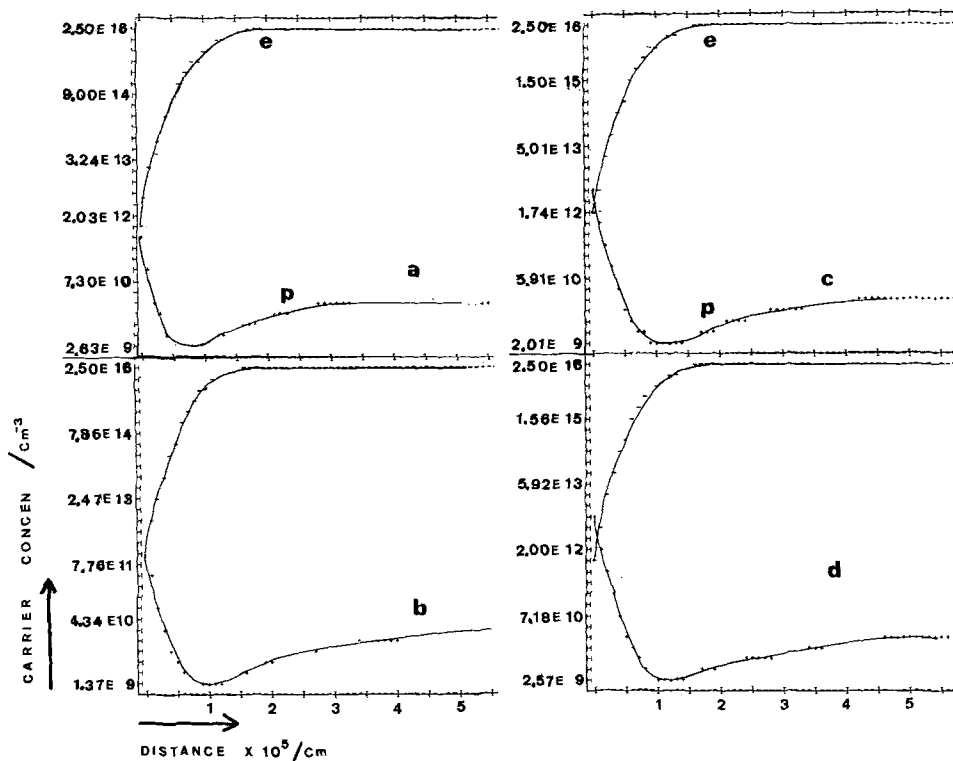


Fig. 1. Free carrier concentration for intrinsic Ge, with and without surface states. $n^0 = p^0 = 2.5 \times 10^{13} \text{ cm}^{-3}$; $\epsilon_r = 16$ esu, u_n and u_p are 3800 and $1800 \text{ cm}^2/\text{V}\cdot\text{sec}$, respectively; charge injected = $3.91 \times 10^{-7} \text{ C}/\text{cm}^2$. Solid lines, without surface states; times after charge injection: (a) $9.474 \times 10^{-12} \text{ sec}$ ($V_s = 0.015 \text{ V}$, $E_b = 2.37 \times 10^3 \text{ V}/\text{cm}$); (b) $1.895 \times 10^{-10} \text{ sec}$ ($V_s = 0.106 \text{ V}$, $E_b = 7.03 \times 10^2 \text{ V}/\text{cm}$); (c) $1.895 \times 10^{-9} \text{ sec}$ ($V_s = 0.096 \text{ V}$, $E_b = 2.8 \times 10^1 \text{ V}/\text{cm}$), V_s at equilibrium = 96 mV , $E_s = 2.76 \times 10^3 \text{ V}/\text{cm}$ at all times. Dashed lines, with surface states for which $N_t = 2.0 \times 10^{11} \text{ cm}^{-2}$, $E_t = E_F^0$, $k_e = 0.53 \times 10^{10} \text{ sec}^{-1}$; $k_v = 2.63 \times 10^{-5} \text{ cm}^3 \cdot \text{sec}^{-1}$. For the same times as in the absence of surface states, the results are: (a) $V_s = 0.006 \text{ V}$, $E_s = 2.757 \times 10^3 \text{ V}/\text{cm}$, $\Delta Q_{ss} = 3.77 \times 10^{-10} \text{ C}$, $E_b = 2.62 \times 10^3 \text{ V}/\text{cm}$; (b) $V_s = 0.067 \text{ V}$, $E_s = 2.71 \times 10^3 \text{ V}/\text{cm}$, $\Delta Q_{ss} = 6.77 \times 10^{-7} \text{ C}$, $E_b = 2.14 \times 10^3 \text{ V}/\text{cm}$; (c) $V_s = 0.094 \text{ V}$, $E_s = 2.65 \times 10^3 \text{ V}/\text{cm}$, $\Delta Q_{ss} = 1.533 \times 10^{-8} \text{ C}$, $E_b = 31 \text{ V}/\text{cm}$.

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-

Fig. 2. Free carrier concentration following charge injection to n-type Ge. $n^0 = 2.5 \times 10^{16} \text{ cm}^{-3}$, $p^0 = 2.5 \times 10^{10} \text{ cm}^{-3}$; $\epsilon_r = 16 \text{ esu}$; $u_n = 3800 \text{ cm}^2/\text{V-sec}$, $u_p = 1800 \text{ cm}^2/\text{V-sec}$; injected charge $= 4.96 \times 10^{-6} \text{ C/cm}^2$. Time after charge injection: (a) $2.37 \times 10^{-12} \text{ sec}$ ($V_s = 250.5 \text{ mV}$); (b) $4.74 \times 10^{-11} \text{ sec}$ ($V_s = 251 \text{ mV}$); (c) $2.37 \times 10^{-10} \text{ sec}$ ($V_s = 251 \text{ mV}$); (d) $4.74 \times 10^{-10} \text{ sec}$ ($V_s = 251 \text{ mV}$). $E_s = 3.50 \times 10^4 \text{ V/cm}$ and $E_b < 2 \times 10^{-3} \text{ V/cm}$ for all times shown.



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^{-9} sec) the number of holes generated thermally is negligibly small. For the n-type Ge ($p^0 = 2.5 \times 10^{10} \text{ cm}^{-3}$) the value for the zero-th order generation rate constant is about $10^{15} \text{ cm}^{-3} \text{ sec}^{-1}$. 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 diffusion layer for the holes and arbitrarily assigning 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 double layer relaxation effects. Some other technique, 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 (8, 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 N_t , located at an energy E_t with respect to the Fermi energy, E_F^0 , and having an occupancy or filling function, f_t (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)

$$R_e = k_e N_t f_t \quad [5]$$

$$R_c = k_c (1 - f_t) N_t n_s \quad [6]$$

$$R_v = k_v N_t f_t p_s \quad [7]$$

$$R_h = k_h N_t (1 - f_t) \quad [8]$$

The k 's are the corresponding rate constants for interaction of the surface level with the conduction and valence band, respectively; n_s and p_s are the surface concentrations of electrons and holes. Since the ratios k_e/k_c and k_h/k_v do not depend on the surface potential, their values determined at the flatband potential, V_{fb} , apply at other potentials, as well. At equilibrium at V_{fb} , $p_s = p^0$, $n_s = n^0$, $f_t = f_t^0$, $R_e = R_c$, and $R_h = R_v$. Then from Eq. [5]-[8]

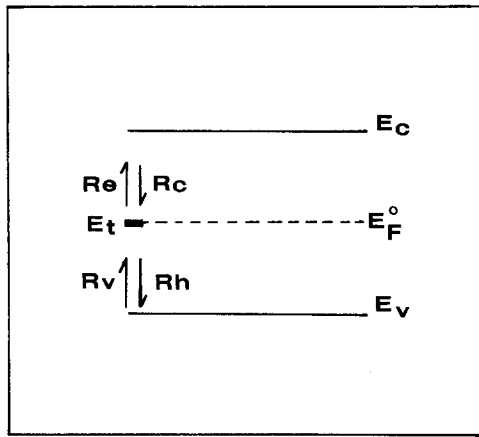


Fig. 3. Schematic model for interaction of a surface level with the semiconductor bands. R_e and R_c are the rates for exchange of electrons with conduction band; R_v and R_h are the rates for exchange of holes with the valence band.

$$k_c = k_e f_t^0 / (1 - f_t^0) n^0 \quad [9]$$

$$k_h = k_v p^0 f_t^0 / (1 - f_t^0) \quad [10]$$

Hence, for a given semiconductor, k_c/k_e and k_h/k_v depend only on f_t^0 , i.e., on the relative position of E_t to E_F^0 . If for any reason (e.g., because of charge injection) n_s and p_s are perturbed from their equilibrium values which have established a certain occupancy of the surface level, a net exchange of holes and electrons between the surface level and the conduction and valence bands will occur yielding

$$R_n = R_e - R_c = k_e N_t \left[f_t - \left(\frac{f_t^0}{1 - f_t^0} \right) (1 - f_t) \frac{n_s}{n^0} \right] \quad [11]$$

$$R_p = R_v - R_h = k_v N_t \left[p_s f_t - \left(\frac{f_t^0}{1 - f_t^0} \right) (1 - f_t) p^0 \right] \quad [12]$$

R_n is the over-all rate at which electrons are transported from the surface level to the conduction band at the surface and R_p is the over-all rate at which holes from the valence band at the surface are transferred to the level. Both R_n and R_p have units of flux ($\text{cm}^{-2} \text{sec}^{-1}$). The total rate at which the level loses electrons is $R_n + R_p$. This rate, when multiplied by the electronic charge, represents the rate at which the surface level collects positive charge from the space charge region (in $\text{A}\cdot\text{cm}^{-2}$). The rate at which the field in the semiconductor at a point just inside the semiconductor/solution interface (where the surface states are presumably located) drops because of this loss of charge is $e(R_n + R_p)/\epsilon_0 \epsilon_r$. All of these effects were simulated along with the free carrier transport within the semiconductor phase described previously. When a new

position of equilibrium is established, R_p and R_n must vanish. Thus, both rates pass through a maximum when relaxing from one equilibrium situation to another and the values of the rate constants were chosen so that this effect could be observed within the simulation time domain. To obtain this situation we consider Eq. [11] and [12] in a somewhat more operational way. Assume that the semiconductor is initially at the flatband potential and $f_t^0 = 1/2$ (i.e., $E_t = E_F^0$; $f_t^0/(1 - f_t^0) = 1$). We call $N_t f_t^0$ (the number of electrons in the level) SUR and N_t (the maximum number of electrons possible in this level) SURMAX. Then Eq. [11] and [12] can be rewritten as

$$R_n = k_e [\text{SUR} - (n_s/n^0) (\text{SURMAX} - \text{SUR})] \quad [13]$$

$$R_p = k_v [p_s \text{SUR} - p^0 (\text{SURMAX} - \text{SUR})] \quad [14]$$

Throughout the simulation n_s , p_s , and SUR change. Before charge injection, $p_s = p^0$, $n_s = n^0$, and SUR = SURMAX/2; thus $R_p = R_n = 0$. Immediately after the charge injection (e.g., of positive charge), n_s becomes smaller than n^0 , p_s becomes larger than p^0 , 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 level was practically depopulated of electrons. At the new position of equilibrium, the value of SUR, p_s , n_s , and SURMAX - SUR will cause the bracketed portions of Eq. [13] and [14] to be zero. A new 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_e and k_v , 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, $E_t = E_F^0$) 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

| Electrode | Without surface states | | | | With surface states | | | | | |
|----------------------------------|--------------------------------------|------------------------------|--------------------------------|---|---|------------------------------|---|-------------------------------------|----------------------|-----------------------|
| | Charge injected (C/cm ²) | E_s , surface field (V/cm) | V_s , surface potential (mV) | N_t ($E_t = E_F^0$) (cm ⁻²) | Charge trapped in ss (C/cm ²) | E_s , surface field (V/cm) | Calculated total charge* (C/cm ²) | V_s^{**} , surface potential (mV) | f_t simulated** | f_t calc*** |
| Intrinsic Ge | | | | | | | | | | |
| $n^0 = p^0 = 2.5 \times 10^{13}$ | 3.91×10^{-7} | 2.76×10^3 | 96 | 2×10^{11} | 1.53×10^{-8} | 2.65×10^3 | 3.91×10^{-7} | 94 | 0.022 | 0.023 |
| $n^0 = p^0 = 2.5 \times 10^{13}$ | 3.91×10^{-7} | 2.76×10^3 | 96 | 4×10^{11} | 3.06×10^{-8} | 2.545×10^3 | 3.91×10^{-7} | 92 | 0.022 | 0.025 |
| Extrinsic Ge | | | | | | | | | | |
| $n^0 = 2.5 \times 10^{16}$ | 1.42×10^{-6} | 1.0×10^4 | 40 | 4×10^{12} | 1.7×10^{-7} | 8.80×10^3 | 1.42×10^{-6} | 33.5 | 0.23 | 0.21 |
| $p^0 = 2.5 \times 10^{10}$ | 2.56×10^{-6} | 1.80×10^4 | 86 | 4×10^{12} | 2.76×10^{-7} | 1.60×10^4 | 2.56×10^{-6} | 73 | 0.068 | 0.051 |
| $p^0 = 2.5 \times 10^{10}$ | 4.96×10^{-6} | 3.50×10^4 | 251 | 4×10^{12} | 3.2×10^{-7} | 3.27×10^4 | 4.96×10^{-6} | 223 | 1.5×10^{-4} | 1.23×10^{-4} |

* Charge trapped in surface states plus charge equivalent to surface field; this total should equal charge injected.

** Simulated surface level occupancy, f_t , at equilibrium after charge injection.

*** Surface level occupancy calculated using the function $f_t = 1/[1 + \exp(eV^{**}/kT)]$.

(initially 0.5 in all cases) agrees reasonably with that obtained from a thermodynamic or statistical expression (6).

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APPENDIX

The desired region of interest is divided into space elements of width ΔX (e.g., 25-100Å) which are assigned an index K , from $K = 1$ (the surface element) to $K = KMAX$. 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,

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

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 Δt can be expressed (e.g., for holes) as

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

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 ones. 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

$$E_K = E_{K-1} - (e\Delta x / \epsilon_0 \epsilon_r) (p_K - n_K + N_D - N_A) \quad [A-3]$$

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

$$p_K = p^0, n_K = n^0, E_K = q_{inj} / \epsilon_0 \epsilon_r \quad (\text{at all } K) \quad [A-4]$$

The boundary conditions are

$$p_{KMAX} = p^0, n_{KMAX} = n^0, E_{K=1} = (q_{inj} - \Delta q_{ss}) / \epsilon_0 \epsilon_r \quad [A-5]$$

where Δq_{ss} is the charge trapped by the surface level. $KMAX$ should be the value of K within the bulk of the electrode. However, unless a nonlinear space grid is employed, this $KMAX$ will have too large a value for practical calculations for $KMAX \cdot \Delta X$ to extend into the bulk semiconductor. Thus a smaller value of $KMAX$ was used (which was still far outside the space charge region); this results in a somewhat steeper concentration profile for holes so that their flux toward the surface is slightly overestimated. The simulation constants are $DMN, DMP, UMN,$ and UMP . They are defined (e.g., for electrons) as

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

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

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 Δt and ΔX

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

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 $E_{K=1} = 10^8\text{-}10^4 \text{ V/cm}.$

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