Exact surface solutions for semiconductors: The Dember effect and partial currents

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Exact solution of the correct linearized equations for steady-state transport in semiconductors yields two modes that vary exponentially in space. One involves screening (without entropy production) and one involves diffusion and recombination (with entropy production), neither being quasineutral. They are applied to surface photoexcitation (the Dember effect) and to the adjustment of partial electron and hole currents from surface to bulk. Other transport situations are briefly discussed.

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INTRODUCTION

Electrical screening is an equilibrium phenomenon unrelated to transport or recombination. At a metal surface, an external field is screened by a distribution of induced charge that extends inward from the surface by a finite distance (i.e., a surface mode). At the surface of a semiconductor with electron and hole densities n and p, the steady-state linearized transport equations can be expected to lead to two surface modes, one of which should corresponds to dissipation-free electrical screening. However, in the familiar relaxation-time approximation for recombination, where $(\partial n/\partial t)|_{rec} = -\delta n/\tau_n'$ and $(\partial p/\partial t)|_{rec} = -\delta p/\tau_p'$,[1–3] straightforward computation shows that both surface modes involve transport coefficients and recombination times. This puts in doubt not merely the screening mode, but the second mode as well. Any study of electrical screening, or of carrier flux across surfaces, must ensure that it is dissipation-free where appropriate, and gives the correct rate of energy dissipation when dissipation does occur.

To ensure that dissipation occurs properly in the recombination terms, we apply the principles of irreversible thermodynamics; these constrain the form of the charge-carrier fluxes and recombination rates by requiring that the rate of entropy production be non-negative. To study transport across interfaces, for the resulting transport equations (including recombination) we obtain the surface solutions, which are obtained more easily using electrochemical potentials, rather than densities, as the primary variables. This approach generalizes to three (and more) carrier systems, and other two carrier systems.

The surface solutions provide a powerful and general tool for the study of surface transport, as we show explicitly for (1) the Dember effect, wherein light steadily absorbed at a surface causes a voltage difference between the surface and the bulk, with electron and hole partial currents;[4–6] (2) the adjustment of the electron and hole partial currents from surface to bulk. When applied to the Dember effect, having two surface modes makes it possible to explicitly enforce global electroneutrality without having to make the incorrect and restrictive assumption of quasineutrality $(\partial_i n \approx \partial_i p)$. To our knowledge, all previous analytic theories of the Dember effect violate global charge conservation.

As expected, one surface mode corresponds to ordinary screening by a multicharge-carrier system (i.e., Debye-Hückel screening), without fluxes or entropy production. This screening mode alone, thus, can be generated on the application of an electric field. The other surface mode has both electron and hole flux, or transport, as well as entropy production: the *diffusion-recombination mode.* The characteristic length l of the screening mode typically is shorter than the characteristic length L for the diffusion-recombination mode. Both modes possess charge. In the Dember effect, light generates a diffusion-recombination mode with a relatively extended negative charge and a screening mode with a relatively compact positive charge. The resultant charge separation is consistent with, but more complex than, a physical picture wherein incident light produces equal numbers of electrons and holes at the surface, the higher mobility electrons extending further than the lower mobility holes.[5,6]

IRREVERSIBLE THERMODYNAMICS

Consider a uniform semiconductor with an ideal surface having no extrinsic surface states and no charged intrinsic states. The recombination rate r is the same for both electrons and holes. With u the energy density, T the temperature, s the entropy density, and $\tilde{\mu}_e$ and $\tilde{\mu}_h$ the electron and hole electrochemical potentials, the fundamental thermodynamic differential for this system is

$$du = Tds + \tilde{\mu}_e dn + \tilde{\mu}_h dp. \tag{1}$$

With μ_e and μ_h the chemical potentials (to be distinguished from the diffusivities μ_n and μ_p),

$$\tilde{\mu}_e \equiv \mu_e - e\phi, \quad \tilde{\mu}_h \equiv \mu_h + e\phi. \tag{2}$$

Here the electrical potential ϕ satisfies Poisson's equation

$$\nabla^2\phi = -\frac{\rho}{\epsilon_0\epsilon} = -\frac{e}{\epsilon_0\epsilon}(p - n + N_d^+ - N_a^-), \tag{3}$$

where ϵ is the semiconductor dielectric constant, ϵ_0 is the permittivity of free space, and the charge density $\rho = e(p - n + N_d^+ - N_a^-)$. N_d^+ and N_a^- are the respective densities of ionized donors and acceptors, and $\tilde{\mu}_e$ and $\tilde{\mu}_h$ are often called quasi-Fermi energies.

The conservation laws for this system are

$$\partial_t u + \partial_i j_i^u = 0, \quad \partial_t s + \partial_i j_i^s = \frac{\mathcal{P}}{T} \geq 0, \tag{4}$$

$$\partial_t n + \partial_i j_i^n = r, \quad \partial_t p + \partial_i j_i^p = r. \tag{5}$$

Here j_i^u is the energy flux density, j_i^s is the entropy flux density, $\mathcal{P}$ is the local rate of heat production ($\mathcal{P}/T$ is local rate of entropy production), j_i^n is the electron number flux density, and j_i^p is the hole number flux density. The fluxes, r, and $\mathcal{P}$ are to be determined.

The time derivatives of Eqs. (1), (4), and (5) lead to

$$\begin{aligned} 0 \leqslant \mathcal{P} &= -\partial_i j_i^u + T\partial_i j_i^s - \tilde{\mu}_e(r - \partial_i j_i^n) - \tilde{\mu}_h(r - \partial_i j_i^p), \\ &= -\partial_i(j_i^u - T j_i^s - \tilde{\mu}_e j_i^n - \tilde{\mu}_h j_i^p) - j_i^s \partial_i T - j_i^n \partial_i \tilde{\mu}_e \\ &\quad - j_i^p \partial_i \tilde{\mu}_h - r(\tilde{\mu}_e + \tilde{\mu}_h). \end{aligned} \tag{6}$$

Expressing $\mathcal{P}$ as a non-negative quadratic form uniquely requires that $j_i^u = T j_i^s + \tilde{\mu}_e j_i^n + \tilde{\mu}_h j_i^p$; that

$$j_i^s = -\frac{\kappa}{T}\partial_i T - \alpha_{sn}\partial_i j_i^n - \alpha_{sp}\partial_i j_i^p, \tag{7}$$

where $\kappa \geqslant 0$ is the thermal conductivity: that

$$\begin{aligned} j_i^n &= -\alpha_{nn}\partial_i \tilde{\mu}_e - \alpha_{np}\partial_i \tilde{\mu}_h - \alpha_{ns}\partial_i T, \\ j_i^p &= -\alpha_{pn}\partial_i \tilde{\mu}_e - \alpha_{pp}\partial_i \tilde{\mu}_h - \alpha_{ps}\partial_i T, \end{aligned} \tag{8}$$

where $\alpha_{nn} \geqslant 0$ and $\alpha_{pp} \geqslant 0$, $(\kappa/T)\alpha_{nn} \geqslant \alpha_{ns}^2$, $(\kappa/T)\alpha_{pp} \geqslant \alpha_{ps}^2$, and $\alpha_{nn}\alpha_{pp} \geqslant \alpha_{np}^2$ (by the Onsager symmetry principle,[7] $\alpha_{sn} = \alpha_{ns}$, $\alpha_{sp} = \alpha_{ps}$, and $\alpha_{np} = \alpha_{pn}$); and

$$r = -\lambda(\tilde{\mu}_e + \tilde{\mu}_h) = -\lambda(\mu_e + \mu_h). \tag{9}$$

where $\lambda \geqslant 0$ is related to the electron and hole lifetimes τ_n and τ_p. In equilibrium $r = 0$, so Eq. (9) implies that $\tilde{\mu}_e = -\tilde{\mu}_h$ and $\mu_e = -\mu_h$ in equilibrium, as expected.

We now express r, j_i^n, and j_i^p in a more conventional form. Linearizing Eq. (9) about equilibrium with $\delta\mu_e = (\partial\mu_e/\partial n)\delta n$ and $\delta\mu_h = (\partial\mu_h/\partial p)\delta p$ yields

$$r = -\frac{\delta n}{\tau_n} - \frac{\delta p}{\tau_p}, \quad \tau_n^{-1} \equiv \lambda\frac{\partial\mu_e}{\partial n}, \quad \tau_p^{-1} \equiv \lambda\frac{\partial\mu_h}{\partial p}. \tag{10}$$

For a dilute semiconductor, as considered here, $(\partial\mu_e/\partial n) \approx k_B T/n_0$ and $(\partial\mu_h/\partial p) \approx k_B T/p_0$, so $\tau_n = (n_0/k_B T\lambda)$ and $\tau_p = (p_0/k_B T\lambda)$.[8] Now set $\alpha_{sn} = \alpha_{sp} = \alpha_{np} = 0$, $\alpha_{nn} = D_n(\partial n/\partial\mu_e)$, and $\alpha_{pp} = D_p(\partial p/\partial\mu_h)$, where D_n and D_p are the electron and hole diffusivities. Next, define the electron and hole mobilities μ_n and μ_p, which satisfy the Einstein relations

$$\mu_n = \frac{eD_n}{n}\frac{\partial n}{\partial\mu_e} \approx \frac{eD_n}{k_B T}, \quad \mu_p = \frac{eD_p}{p}\frac{\partial p}{\partial\mu_h} \approx \frac{eD_p}{k_B T}. \tag{11}$$

In one dimension (1D), j_i^n and j_i^p then become, as expected,[2,3]

$$\begin{aligned} j_x^n &= -D_n\partial_x n + \mu_n n\partial_x\phi, \\ j_x^p &= -D_p\partial_x p - \mu_p p\partial_x\phi. \end{aligned} \tag{12}$$

Note that Poisson's equation linearizes to

$$\begin{aligned} \nabla^2\delta\phi &= -\frac{e}{\epsilon_0\epsilon}(\delta p - \delta n) = \frac{e^2}{\epsilon_0\epsilon}\left(\frac{\partial n}{\partial\mu_e} + \frac{\partial p}{\partial\mu_h}\right)\delta\phi \\ &\quad - \frac{e}{\epsilon_0\epsilon}\left(\frac{\partial p}{\partial\mu_h}\delta\tilde{\mu}_h - \frac{\partial n}{\partial\mu_e}\delta\tilde{\mu}_e\right). \end{aligned} \tag{13}$$

SURFACE SOLUTIONS

We work at fixed T. One steady-state solution that automatically satisfies Eqs. (5), (8), and (9) has $\delta\tilde{\mu}_e = \delta\tilde{\mu}_h = 0$ and $j_i^n = j_i^p = 0$. Thus the system is in local equilibrium, with no entropy production. This corresponds to ordinary screening: the *screening mode*, given as subscript S. From Eq. (13), its potential $\delta\phi_S$ satisfies

$$\nabla^2\delta\phi_S = \frac{e^2}{\epsilon_0\epsilon}\left(\frac{\partial p}{\partial\mu_h} + \frac{\partial n}{\partial\mu_e}\right)\delta\phi_S = q_S^2\delta\phi_S, \tag{14}$$

where

$$q_S^2 = q_{Sn}^2 + q_{Sh}^2, \quad q_{Sn}^2 \equiv \frac{e^2}{\epsilon_0\epsilon}\frac{\partial n}{\partial\mu_e}, \quad q_{Sp}^2 \equiv \frac{e^2}{\epsilon_0\epsilon}\frac{\partial p}{\partial\mu_h}. \tag{15}$$

For the present system, $q_{Sn}^2 = (e^2 n_0/\epsilon_0\epsilon k_B T)$, $q_{Sp}^2 = (e^2 p_0/\epsilon_0\epsilon k_B T)$, so $q_S^2 = (e^2/\epsilon_0\epsilon k_B T)(n_0 + p_0)$. The solution to Eq. (14) that goes to zero as $x \to \infty$ is

$$\delta\phi_S = A_S \exp(-q_S x). \tag{16}$$

$l \equiv q_S^{-1}$ is the *screening length*. From Eqs. (16) and (13), the screening mode has charge density

$$\delta\rho_S = -\epsilon_0\epsilon\nabla^2\phi_S = -(\epsilon_0\epsilon)q_S^2 A_S \exp(-q_S x). \tag{17}$$

Here $\delta n_S = (\partial n/\partial\mu_e)\delta\mu_e = (e n_0/k_B T)\delta\phi_S$ and $\delta p_S = (\partial p/\partial\mu_h)\delta\mu_h = -(e n_0/k_B T)\delta\phi_S$, so $\delta n_S/\delta p_S = -n_0/p_0$.

The second steady-state solution to Eqs. (5), (8), (9), and (13) has $\delta\tilde{\mu}_e$ and $\delta\tilde{\mu}_h$ nonzero, so the fluxes j_i^n and j_i^p are nonzero. With $\alpha_{np} = \alpha_{pn} = 0$, combining Eqs. (5), (8), and (9) yields

$$\begin{aligned} -\alpha_{nn}\partial_x^2\delta\tilde{\mu}_e &= -\lambda(\delta\tilde{\mu}_e + \delta\tilde{\mu}_h), \\ -\alpha_{pp}\partial_x^2\delta\tilde{\mu}_h &= -\lambda(\delta\tilde{\mu}_e + \delta\tilde{\mu}_h). \end{aligned} \tag{18}$$

Let properties of this *diffusion-recombination mode* be denoted by the subscript D. Now set

$$q_{Dn}^2 \equiv \frac{\lambda}{\alpha_{nn}} = \frac{1}{D_n\tau_n}, \quad q_{Dp}^2 \equiv \frac{\lambda}{\alpha_{pp}} = \frac{1}{D_p\tau_p}. \tag{19}$$

Then, with

$$\delta\tilde{\mu}_e = A_{Dn}\exp(-q_D x), \quad \delta\tilde{\mu}_h = A_{Dp}\exp(-q_D x), \tag{20}$$

Eq. (18) yields

$$q_D^2 = q_{Dn}^2 + q_{Dp}^2 \tag{21}$$

and $A_{Dp}/q_{Dp}^2 = A_{Dn}/q_{Dn}^2$.

The corresponding electrostatic potential $\delta\phi_D$ takes the form

$$\delta\phi_D = A_D \exp(-q_D x), \tag{22}$$

where

$$\frac{A_{Dp}}{q_{Dp}^2} = \frac{A_{Dn}}{q_{Dn}^2} = \frac{q_S^2 - q_D^2}{q_{Sp}^2 q_{Dp}^2 - q_{Sn}^2 q_{Dn}^2} e A_D . \tag{23}$$

$L \equiv q_D^{-1}$ is the *diffusion-recombination length*, normally called the diffusion length. From Eqs. (22) and (3), the diffusion-recombination mode possesses charge density

$$\delta\rho_D = -(\epsilon_0\epsilon) q_D^2 A_D \exp(-q_D x). \tag{24}$$

Moreover, $\delta n_D / \delta p_D = (n_0/p_0)(q_{Sp}^2 - q_{Dn}^2)/(q_{Sn}^2 - q_{Dp}^2)$. This is independent of n_0 for fixed $n_0 p_0 = n_i^2$.

The present multicarrier system, with finite L, can be non-neutral only over a finite distance from the disturbance. On the other hand, a multicarrier system with no recombination (and thus $L \to \infty$) can be non-neutral in the bulk, far from a disturbance.[9]

DEMBER EFFECT

Let light incident at the surface $x=0$ produce equal electron and hole fluxes G, so $j_i^n = j_i^p = G$ at $x=0$. On setting $\alpha_{np} = \alpha_{pn} = 0$, Eqs. (8) and (20) yield the diffusion-recombination mode amplitudes

$$A_{Dn} = \frac{G}{q_D \alpha_{nn}}, \quad A_{Dp} = \frac{G}{q_D \alpha_{pp}}. \tag{25}$$

Overall electroneutrality, or $0 = \int_0^\infty dx[\,\delta\rho_S(x) + \delta\rho_D(x)]$, implies that

$$A_S = -\frac{q_D}{q_S} A_D . \tag{26}$$

(Applying an electric field and light in the appropriate ratio will give $A_S = 0$ but $A_D \neq 0$.)

From Eqs. (17) and (26), and from Eqs. (23)–(25), the total charge density is

$$\delta\rho(x) = \frac{Ge^2}{k_B T} \frac{(\mu_n - \mu_p)}{\mu_n \mu_p} \frac{q_S e^{-q_S x} - q_D e^{-q_D x}}{q_S^2 - q_D^2}, \tag{27}$$

where the mobilities have been employed. Typically $\mu_n > \mu_p$, so $\rho(x=0)$ is positive, as expected if the higher mobility charge-carrier preferentially leaves the vicinity of the surface. Note that $\delta\rho(x)$ changes in sign as x increases, as needed to produce a dipole layer.

From Eqs. (17) and (24) the total electrostatic potential is

$$\delta\phi(x) = \frac{Ge^2}{\epsilon_0 \epsilon k_B T} \frac{(\mu_n - \mu_p)}{\mu_n \mu_p} \frac{q_D^{-1} e^{-q_D x} - q_S^{-1} e^{-q_S x}}{q_S^2 - q_D^2}. \tag{28}$$

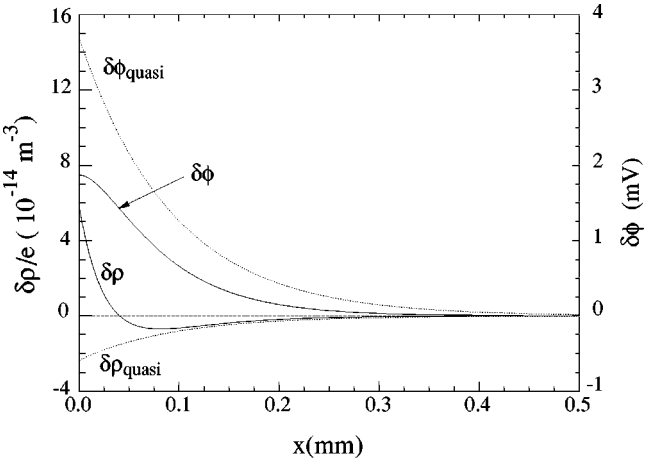

FIG. 1. Solid lines give photoinduced electrical potential $\delta\phi$ from Eq. (28) and charge density $\delta\rho$ from Eq. (27). Dotted lines give corresponding curves from linearized quasineutrality theory.

To compare with experiment, Eq. (28) gives the Dember voltage $\phi_{Dem} \equiv \delta\phi(x=0)$ as

$$\phi_{Dem} = \frac{Ge^2}{\epsilon_0 \epsilon k_B T} \frac{(\mu_n - \mu_p)}{\mu_n \mu_p} \frac{1}{q_S q_D} \frac{1}{q_S + q_D}. \tag{29}$$

Equation (29) makes numerous predictions. First, since typically $\mu_n > \mu_p$, ϕ_{Dem} is positive, as expected for a dipole layer with positive charge closer to the surface. Further, since typically $q_D \ll q_S$, the term $q_S q_D (q_S + q_D) \approx q_S^2 q_D$. The dependences of q_S on n and ϵ and of q_D on μ and τ show that ϕ_{Dem} varies inversely with carrier density n, as the square root of the characteristic recombination time τ and as the inverse square root of the characteristic mobility μ, respectively, and is independent of ϵ.

Figures 1–4 are for an intrinsic semiconductor with equilibrium carrier number density $n_0 = p_0 = n_i = 10^{16}$ m^{-3}, recombination time $\tau = 10^{-5}$ s, electron mobility $\mu_n = 1000$ cm^2/(V s), hole mobility $\mu_p = 200$ cm^2/(V s), room temperature $k_B T = 0.0253$ eV, and dielectric constant $\epsilon = 10$. These values give $l = 26.4$ μm and $L = 64.8$ μm.

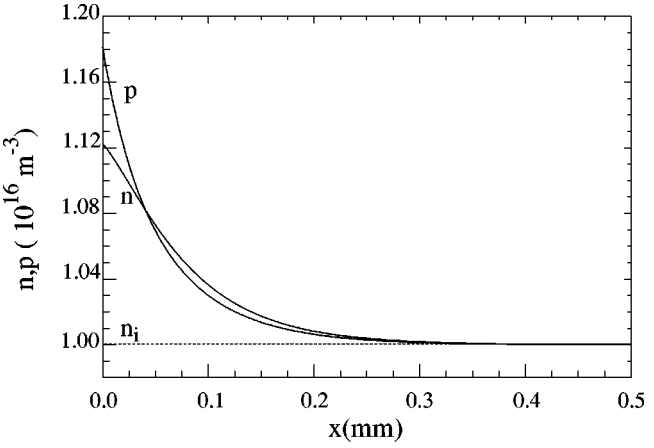

FIG. 2. Electron and hole number densities n and p corresponding to Fig. 1.

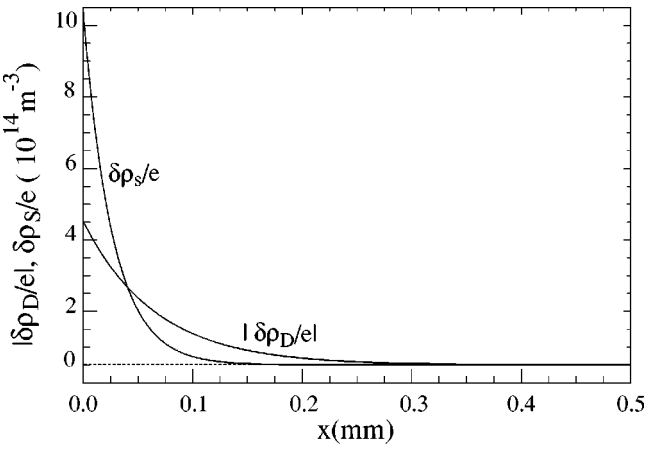

FIG. 3. Charge densities for the screening and diffusion modes from Eqs. (17) and (24).

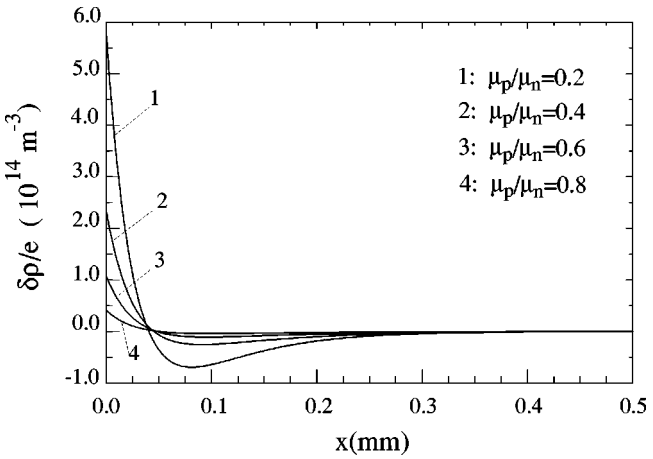

FIG. 4. Charge density $\delta\rho$ from Eq. (27) for different hole mobilities.

(Quasineutrality theory gives $L=93.4$ μm.[5,6]) From Eq. (28), the ratio of the contributions of the diffusion mode and the screening mode to the Dember voltages is $q_D^{-1}/q_S^{-1}=L/l$. Taking $G=2.0\times10^{16}$ m^{-2} s^{-1} gives $\phi_{Dem}=1.844$ mV, 3.11 mV due to the diffusion-recombination mode. (Linearized quasineutrality theory gives 3.63 mV; the nonlinear version gives 3.28 mV.)

Figure 1 presents $\delta\phi$ and $\delta\rho$; $\delta\phi$ is monotonic, whereas $\delta\rho$ changes sign, to make the system overall neutral. Figure 2 presents the associated number densities n and p.

The individual charge densities ρ due to the diffusion-recombination and screening modes are presented in Fig. 3. Note that $\delta n_S/\delta p_S=-1$ and $\delta n_D/\delta p_D=1.306$ for the present parameters. (Increasing both mobilities by a factor of 10 would give $\delta n_D/\delta p_D=1.022$.) Hence quasineutrality is not a good approximation for either mode. $\delta\rho_S$ is positive and concentrated near the surface; $\delta\rho_D$ is negative and more extended. (Quasineutrality theory gives $\delta\rho<0$ for all x.) Not shown is E, which rises from zero at the surface and falls to zero at infinity. (In linearized quasineutrality theory, E is finite at the surface and falls to zero at infinity.) Numerical solutions of the macroscopic transport equations for semiconductors normally do not assume quasineutrality. Hence, with a correct recombination term they retain the full physics[10] although physical interpretation is more difficult.

Figure 4 presents the bulk charge density $\delta\rho$ for μ_n and μ_p as above ($\mu_p/\mu_n=0.2$), and for three additional values of μ_p/μ_n. $\delta\rho$ and ϕ_{Dem} increase with the difference in the electron and hole mobilities.

ADJUSTMENT OF PARTIAL CURRENTS

The electron and hole partial currents are $J^n=-ej^n$ and $J^p=ej^p$. Let the electron-to-hole bulk and surface partial current ratios be $f_B=(J^n/J^p)|_{bulk}$ ($=n_0\mu_n/p_0\mu_p=5$ for Figs. 1–3) and $f_S=(J^n/J^p)|_{surface}$ (e.g., 1). Then the ratio of the surface value of the electron partial current due to the surface solution, $J^n_{surface\ solution}$, to the electron current in the bulk, J^n_{bulk}, is $\alpha=(f_S-f_B)/[(1+f_S)f_B]$. Since this surface partial current is due only to the diffusion-recombination mode, the adjustment takes place over the length L. The screening mode amplitude can be determined only if the materials properties for both sides of the surface are specified.

Surface solutions are present in recent numerical studies showing that spin injection in a semiconductor (e.g., by preferential absorption of polarized light) persists across a $p-n$ junction.[11] Such a system, with up and down electrons and with unpolarized holes, should have three surface modes: one screening mode and two diffusion-recombination modes.

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