Violation of Quasineutrality in Semiconductor Transport: The Deember Effect

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Exact solution of the linearized equations for steady-state transport in semiconductors yields two modes that vary exponentially in space, one involving screening (without entropy production) and one involving diusion and recombination (with entropy production). Neither mode is quasineutral. For constant surface photoexcitation with generation of electrons and holes, the steady-state response is a linear combination of these modes, subject to global electroneutrality. The resultant charge separation produces a voltage di erence across the sample (the Deember effect).

The Deember effect is the voltage di erence that develops across the bulk of a material that steadily absorbs light at one surface. [3] It has been observed in insulators, [3] high resistivity semiconductors, [6] and C[60] thin  ms. [4] An extensive discussion of photovoltages, both at surfaces and in the bulk, is given in Ref. [4].

A n intuitive physical picture of the Deember effect is as follows. [3] Incident light produces equal numbers of electrons and holes at the surface. The higher mobility electrons travel further than the lower mobility holes. The resultant charge separation am ously moves to a dipole layer. As a consequence the illuminated surface is at the higher voltage, in agreement with experiment. However, conventional theories of the Deember effect, [3] which assume quasineutrality (local electroneutrality), yield no dipole layer; moreover, they yield a non-zero net charge.

The present work obtains exact solutions for the surface modes of the linearized macroscopic transport equations. It di ers from previous analytic work in that: (1) It explicitly satis es the principles of irreversible thermodynamics, which constrain the form for the charge-carrier uxes and recombination rates by the condition that the rate of entropy production be non-negative; (2) In solving the transport equations, it employs both electron and hole densities n and p as variables, rather than assuming deviations from equilibrium satisfy quasineutrality (n = p); (3) Using the resultant two steady-state surface modes, it explicitly enforces overall electroneutrality.

One surface mode corresponds to ordinary screening by a multi-charge-carrier system (e.g. Debye-Huckel screening), without uxes or entropy production: the screening mode. The other surface mode has both electron and hole uxes as well as entropy production: the diusion-recombination mode. The characteristic length l of the screening mode is typically shorter than the characteristic length L for the diusion-recombination mode. Neither mode is locally electroneutral. Applied to the Deember effect, the light generates a diusion-recombination mode with a relatively extended negative charge and a screening mode with a relatively concentrated positive charge, in agreement with the physical picture given above.

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 the energy density, T the temperature, s the entropy density, and ~e and ~h the electron and hole electrochemical potentials, the fundamental thermodynamic di erential for this system is

\[ du = T \frac{ds}{dN} + \frac{\gamma_e}{h} dn + \frac{\gamma_h}{h} dp \]

where ~e and ~h the chemical potentials (to be distinguished from the densities n and p),

\[ \frac{\gamma_e}{h} = e \hspace{1cm} \frac{\gamma_h}{h} = h + e \]

Here the electrical potential satis es Poisson’s equation

\[ \frac{\gamma_e}{h} = e \hspace{1cm} \frac{\gamma_h}{h} = h + e \]

where s is the semiconductor dielectric constant, 0 is the permittivity of free space, and the charge density e(n + N^+ - N^-) = N^+ and N^- are the respective densities of ionized donors and acceptors, and ~e and ~h are often called quasi-Fermi energies.

The conservation laws for this system are

\[ 0 = \frac{\gamma_e}{h} = e \hspace{1cm} \frac{\gamma_h}{h} = h + e \]

where \( \gamma_e \) and \( \gamma_h \) are the entropy xes of the system. The xes, r, and P are to be determined.

The time-derivatives of (1) and (2) lead to

\[ 0 = \frac{\gamma_e}{h} + T \frac{\gamma_e}{h} \hspace{1cm} \frac{\gamma_h}{h} \]

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Expressing P as a non-negative quadratic form requires that \( \frac{\gamma_e}{h} = T \frac{\gamma_e}{h} + \frac{\gamma_e}{h} \hspace{1cm} \frac{\gamma_h}{h} \hspace{1cm} \frac{\gamma_h}{h} \); that

\[ \frac{\gamma_e}{h} = T \frac{\gamma_e}{h} \hspace{1cm} \frac{\gamma_h}{h} \]

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\[ \frac{\gamma_e}{h} = T \frac{\gamma_e}{h} \hspace{1cm} \frac{\gamma_h}{h} \]

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where $\sigma$ is the thermal conductivity; that

$$j^n_p = n n \Theta_n e^{-n} e^{-p \Theta_n e^{-n}};$$
$$j^p_n = n n \Theta_n e^{-n} e^{-p \Theta_n e^{-n}};$$

(8)

where $n_n = 0,$ $p_p = 0,$ and $n_n \neq n_p \neq p_n$ (the $\Theta$'s are related to the di usivities, and $\Theta_n = \Theta_n$ by
the Onsager symmetry principle $\Theta$), and that

$$r = (e + n_n) = (e + h_n);$$

(9)

where $r$ is related to the electron and hole lifetimes $n_n$ and $p_p.$ In equilibrium $r = 0$, so $\Theta$ implies the well-known results that $e = e$ and $h = h$ in equilibrium. We now express $r,$ $j^n,$ and $j^p$ in more conventional form.

Linearizing $\Theta$ about equilibrium with $e = (\Theta_n) n$ and $h = (\Theta_n) p$ yields

$$r = \frac{n}{n} n \Theta_p n + \frac{1}{n} \Theta_n n + \frac{1}{p} \Theta_h p + \frac{1}{p} \Theta_p p;$$

(10)

For a dilute semiconductor, as considered here, $(\Theta_n) n_k T = n_0$ and $(\Theta_p) p_k T = p_0,$ so $n = \frac{n_0}{k_b T}$ and $p = \frac{p_0}{k_b T}.$

Now set $n_n = n_0$ and $p_p = p_0,$ where $n_n$ and $p_p$ are the electron and hole di usivities. Next, we the electron and hole mobilities $n$ and $p,$ which satisfy the Einstein relations:

$$n = \frac{eD_n}{n} \Theta_n e^{-n} e^{-k_b T};$$
$$p = \frac{eD_p}{p} \Theta_p p e^{-k_b T};$$

(11)

Then in one-dimension $j^n$ and $j^p$ become e

$$j^n_p = D_n \Theta_n n + n \Theta_n ;$$
$$j^n_p = D_p \Theta_p p + p \Theta_p :$$

(12)

Note that Poisson's equation linearizes to

$$r^2 = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p;$$

(13)

Static surface solutions in one-dimension. One steady-state solution that automatically satisfies $\Theta$, $\Theta,$ and $\Theta$ has $\gamma = \gamma = 0$ and $j^n = j^p = 0.$ Thus the system is in local equilibrium, with no entropy production. This corresponds to ordinary screening, and thus we call it the screening mode, with subscript $S.$ From $\Theta$, its potential $s$ satisfies

$$r^2 = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p;$$

(14)

where

$$q^n = q^n_n + q^n_h ;$$
$$q^n_n = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_n ;$$
$$q^n_p = \frac{e}{0} \Theta_p p + \frac{e}{0} \Theta_p ;$$

(15)

For the present system, $q^n_n = (e^2 n_0 = k_b T),$ $q^n_p = (e^2 p_0 = k_b T),$ so $q^n = (e^2 = k_b T)(n_0 + p_0).$ The solution to (14) that goes to zero as $r ! 1$ is

$$s = A_S \Theta_n (q x);$$

(16)

1 $q^1$ is the screening length. From $\Theta$ and $\Theta,$ the screening mode has charge density

$$s = 0 \Theta n = 0 \Theta p = 0 \Theta;$$

(17)

Here $n_n = (\Theta_n = \Theta_n = \Theta_n = \Theta_n = \Theta_n) s$ and $p_p = (\Theta_n = \Theta_n = \Theta_n = \Theta_n = \Theta_n) s.$

The second steady-state solution to $\Theta,$ $\Theta,$ and $\Theta$ has $\gamma = \gamma$ and $\gamma = \gamma$ non-zero, so the are non-zero. With $n_n = p_p = 0,$ combining $\Theta,$ $\Theta,$ and $\Theta$ yields

$$n_n \Theta_n n = (e + h_n);$$
$$p_p \Theta_p p = (e + h_p);$$

(18)

Let us denote properties of this di usion-recombination mode by the subscript $D$. Now set

$$q^n_D = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p = \frac{e}{0} \Theta_n n + \frac{e}{0} \Theta_p p;$$

(19)

Then, with

$$\gamma = A_D \Theta_n (q x);$$
$$\gamma = A_D \Theta_p (q x);$$

(20)

$\Theta$ yields

$$\gamma = A_D \Theta_n (q x);$$

(22)

where

$$A_D = A_D \Theta_n \Theta_p \Theta_n \Theta_p = A_D ;$$

(23)

$L q^1$ is the di usion-recombination length, usually called the di usion length. By (22) and (3), the di usion-recombination mode possesses charge density

$$D = A_D \Theta_n (q x);$$

(24)

Moreover, $n_n = p_p = (n_0 = p_0).$ This is independent of $n_0$ for fixed $p_0.$

Surface mode amplitudes. Let light incident at the surface $x = 0$ produce equiangle electron and hole uxes $G,$ so $j^n = j^p = G$ at $x = 0.$ On setting $n_n = p_p = 0,$ and $\Theta,$ and $\Theta$ yield the di usion-recombination mode amplitudes
Overall electroneutrality, or $0 = R_i \int_0^x (s(x) + \delta(x))$, implies that

$$A_s = \beta_A A_D.$$  \hfill (26)

From (17) and (24), and from (23-25), the total charge density is

$$\delta(x) = \frac{G e^2}{k_B T} \left( \frac{n}{p} \right) \frac{q_x e^{q_x x}}{q_x^2} \frac{q_x e^{q_x x}}{q_x^2}.$$  \hfill (27)

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

From (17) and (24), the total electrostatic potential is

$$\delta(x) = \frac{G e^2}{k_B T} \left( \frac{n}{p} \right) \frac{q_x e^{q_x x}}{q_x^2} \frac{q_x e^{q_x x}}{q_x^2}.$$  \hfill (28)

To compare with experiment, (28) gives the Demer voltage $\delta_{\text{Dem}} (x = 0)$ as

$$\delta_{\text{Dem}} = \frac{G e^2}{k_B T} \left( \frac{n}{p} \right) \frac{q_x e^{q_x x}}{q_x^2} \frac{q_x e^{q_x x}}{q_x^2};$$  \hfill (29)

Discussion. Eq.(29) makes numerous predictions. First, since typically $n > p$, $\delta_{\text{Dem}}$ is positive, as expected for a dipole layer with positive charge closer to the surface. Further, since typically $q_n - q_p$, the term $q_n q_p (q_n + q_p) / q_p^2$ is negative. The dependence of $q_n$ on $n$ and $p$, and of $q_p$ on $n$ and $p$, show that $\delta_{\text{Dem}}$ varies inversely with carrier density $n$, as the square root of the characteristic recombination time, as the inverse square root of the characteristic mobility, and is independent of $p$.

The dependence on $n$ explains why $\delta_{\text{Dem}}$ is observed in materials with relatively low carrier densities. The dependence on $p$ indicates that $\delta_{\text{Dem}}$ is larger for longer recombination times, the dependence on $n$ indicates that $\delta_{\text{Dem}}$ is larger for lower mobilities.

Figures 1-4 are computed for an intrinsic semiconductor with equilibrium carrier density $n_0 = p_0 = n_i = p_i = 10^{16} \text{ m}^{-3}$, recombination time $\tau = 10^{-5}$ s, electron mobility $\mu = 1000 \text{ cm}^2/(\text{V s})$, hole mobility $\mu = 200 \text{ cm}^2/(\text{V s})$, room temperature $k_B T = 0.0253 \text{ eV}$, and dielectric constant $\varepsilon = 10.7$. These values give $L = 26 \text{ m}$ and $L = 64 \text{ m}$. From (28), the ratio of the contributions of the diffusion mode and the screening mode to the Demer voltage is $q_n \mu \tau / \mu \tau + q_p \mu \tau / \mu \tau = 1$. Taking $G = 10^7 \text{ m}^2/\text{s}$ gives $\delta_{\text{Dem}} = 922 \text{ mV}$, of which the diffusion mode is responsible for 15.56 mV and the screening mode 634 mV. The theory, which is valid for $\gamma_p$ and $\gamma_n$, is all relative to $k_B T$, becomes invalid for significantly larger $G$. 

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**FIG. 1.** Photo-induced electrical potential from (28) and charge density from (27).

**FIG. 2.** Electron and hole number densities $n$ and $p$ corresponding to Figure 1.
Charge densities for the screening and diffusion modes, from (17) and (24).

Fig. 3. Charge densities for the screening and diffusion modes, from (17) and (24).

Fig. 4. Charge density from (27) for different hole mobilities.

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