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A new approach for investigation of photo-induced electromotive force in semiconductors

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Abstract

A new method for photo-induced electromotive force theoretical study of bipolar semiconductors accounting for the distortion of energy bands near the semiconductor surface is presented. This method is based on the exact solution of the continuity equations and the Poisson equation and on the boundary conditions derived for the real metal–semiconductor junction. It is shown that photo-induced electromotive force essentially depends on the surface potential for certain surface parameters.

1. Introduction

Conventional theories [1, 2] of the photo-induced (PI) electromotive force (emf) assume local electroneutrality in the bulk of a semiconductor (the so-called quasi-neutrality approximation). The bulk charge influence on the Dember effect was considered in [3]. It has been shown in [3] that a positive non-equilibrium space charge layer (SCL) arises near the illuminated sample surface and thus decreases the Dember emf value. The results of [3] are obtained under simplified assumptions: the illuminated sample surface is in contact with a dielectric (gas or vacuum), semiconductor energy bands are flat and the surface recombination rate is negligible. However, the PI emf is measured across the metallic contacts placed on illuminated and dark semiconductor surfaces. Firstly, this results in modification of boundary conditions in the real metal–semiconductor junction because of the PI electron's ability to move from semiconductor into metal and the PI hole's ability to accumulate near the illuminated surface [4, 5]. Therefore the charge value in the SCL increases as compared with that of [3]. Secondly, a distortion of semiconductor energy bands [6] creates the equilibrium SCL [7] and the built-in electric field, which also affects the PI carrier density. The charge density in the SCL can increase even more when the built-in electric field is directed from the bulk into the surface of a sample. In this case the voltage difference across the SCL can exceed the Dember emf value. Lastly, in this approach the boundary conditions must be formulated in the SCL because the real metal–semiconductor junction thickness is significantly less than the Debye length [6]. Therefore, the surface recombination parameters in our case do not coincide with the same parameters in the quasi-neutrality approximation [7]. It is clear from the above-mentioned factors that calculation of the PI emf requires the exact solution of the continuity equations and the Poisson equation.

This paper is aimed at the development of the PI emf theory in bipolar semiconductors.

2. Theory

Let us consider a bipolar semiconductor plate $0 \leqslant x \leqslant L$ with the surface at $x = 0$ illuminated by strongly absorbed light. The thickness of the sample L essentially exceeds the diffusion length (see below). A semitransparent metallic contact is placed on the surface $x = 0$ of the sample and the grounded metallic contact is placed on the surface $x = L$. We suppose that the light wavelength corresponds to the region of fundamental absorption and that photo-excitation is weak.

The non-equilibrium densities of electrons δn and holes δp, as well as the non-equilibrium electric potential $\delta\varphi$, are obtained from solution of the continuity equations [3, 8] and the Poisson equation

$$\frac{1}{e}\frac{\mathrm{d}j_n}{\mathrm{d}x} - \frac{\delta n}{\tau_n} - \frac{\delta p}{\tau_p} = 0, \tag{1}$$

$$\frac{1}{e}\frac{\mathrm{d}j_p}{\mathrm{d}x} + \frac{\delta n}{\tau_n} + \frac{\delta p}{\tau_p} = 0, \tag{2}$$

$$\frac{\partial^2\delta\varphi}{\partial x^2} = \frac{e}{\varepsilon\varepsilon_0}(\delta n - \delta p), \tag{3}$$

where $-e$ is the electron charge, j_n, j_p are the electron and hole current densities, τ_n (τ_p) is the parameter characterizing the electron (hole) bulk recombination rate [8], ε is the semiconductor electrical permittivity, ε_0 is the vacuum permittivity.

The expressions for partial currents in the linear approximation with small parameters $\delta n/n_0 \ll 1$, $\delta p/p_0 \ll 1$, $e|\delta\varphi|/kT \ll 1$ take the form [4, 6]

$$\begin{aligned} j_n &= -\sigma_n \frac{\mathrm{d}\delta\tilde{\varphi}_n}{\mathrm{d}x}, \\ j_p &= -\sigma_p \frac{\mathrm{d}\delta\tilde{\varphi}_p}{\mathrm{d}x}, \end{aligned} \tag{4}$$

where $\sigma_n = e\mu_n n_{\mathrm{eq}}$ is the electron conductivity, $\sigma_p = e\mu_p p_{\mathrm{eq}}$ is the hole conductivity, $\delta\tilde{\varphi}_n = \delta\varphi - \delta F_n/e$ is the non-equilibrium electron electrochemical potential, $\delta\tilde{\varphi}_p = \delta\varphi + \delta F_p/e$ is the non-equilibrium hole electrochemical potential, $\delta F_n = kT\delta n/n_{\mathrm{eq}}$ is the non-equilibrium electron chemical potential, $\delta F_p = kT\delta p/p_{\mathrm{eq}}$ is the non-equilibrium hole chemical potential, μ_n (μ_p) is the electron (hole) mobility, k is the Boltzmann constant, T is the temperature of the semiconductor and $n_{\mathrm{eq}}(x)$, $p_{\mathrm{eq}}(x)$ are the equilibrium densities of electrons and holes. The equilibrium values $n_{\mathrm{eq}}(x)$, $p_{\mathrm{eq}}(x)$ for special cases are obtained in [6].

Let us formulate the boundary conditions (BCs) in the real metal–semiconductor junction (MSJ), which lies at the surface $x = 0$ (a detailed BC derivation is presented in [4]).

Henceforth we should take into account that the MSJ thickness is significantly less than the Debye length [6]. We suppose also that the Debye length significantly exceeds the electron mean free path.

Let us integrate the Poisson equation (3) with x from $-\xi$ to α and with α from $-\xi$ to ξ and take the limit $\xi \to 0$. Taking into account the absence of an electric field in the metal and the finite value of the non-equilibrium charge density near the surface $x = 0$ one obtains

$$\delta\varphi(+0) = \delta\varphi_{\mathrm{M}}, \tag{5}$$

where $\delta\varphi_{\mathrm{M}}$ is the variation of the electric potential of the metallic contact.

Let us integrate equation (1) with x from α to ξ and with α from $-\xi$ to ξ and take the limit $\xi \to 0$. Taking into account the electron–hole pair (EHP) surface generation rate G and the absence of surface recombination and generation in metal, one obtains

$$j_n(+0) = \sigma_{n\mathrm{S}}[\delta\tilde{\varphi}_n(-0) - \delta\tilde{\varphi}_n(+0)] + e(v_n\delta n(+0) + v\delta p(+0) - G), \tag{6}$$

where $\sigma_{n\mathrm{S}}^{-1} = \lim_{\xi\to 0}\int_{-\xi}^{\xi}\sigma_n^{-1}\,\mathrm{d}x$, $\sigma_{n\mathrm{S}}$ is the electron surface conductivity, $v_n = \lim_{\xi\to 0}\int_0^{\xi}\tau_n^{-1}\,\mathrm{d}x$, $v = \lim_{\xi\to 0}\int_0^{\xi}\tau_p^{-1}\,\mathrm{d}x$. By analogy we derive from equation (2)

$$j_p(+0) = \sigma_{p\mathrm{S}}[\delta\tilde{\varphi}_p(-0) - \delta\tilde{\varphi}_p(+0)] - e(v_n\delta n(+0) + v\delta p(+0) - G), \tag{7}$$

where $\sigma_{p\mathrm{S}}^{-1} = \lim_{\xi\to 0}\int_{-\xi}^{\xi}\sigma_p^{-1}\,\mathrm{d}x$, $\sigma_{p\mathrm{S}}$ is the hole surface conductivity.

Integrating equations (1), (2) with x from $-\xi$ to α and with α from $-\xi$ to ξ and taking the limit $\xi \to 0$, one obtains for the left of $x = 0$:

$$j_n(-0) = \sigma_{n\mathrm{S}}[\delta\tilde{\varphi}_n(-0) - \delta\tilde{\varphi}_n(+0)], \tag{8}$$

$$j_p(-0) = \sigma_{p\mathrm{S}}\,[\delta\tilde{\varphi}_p(-0) - \delta\tilde{\varphi}_p(+0)]. \tag{9}$$

From condition $j_p(-0) = 0$ (there are no holes in the metal) and equation (9) we derive that $\sigma_{p\mathrm{S}} = 0$. It follows from equation (8), condition $j_n(-0) = 0$ (the external electric circuit is open) and condition $\sigma_{n\mathrm{S}} \neq 0$ (electrons can move from semiconductor into metal) that

$$\delta\tilde{\varphi}_{\mathrm{M}} = \delta\varphi(+0) - \frac{1}{e}\delta F_n(+0). \tag{10}$$

Taking into account the constancy of the metal chemical potential we derive from equations (5) and (10) that

$$\delta F_n(+0) = 0. \tag{11}$$

It follows from equations (5)–(7) and (11) that the BCs for values δn, δp, $\delta\varphi$ take the form

$$\frac{1}{e}j_n(+0) = v\delta p(+0) - G, \tag{12}$$

$$\frac{1}{e}j_p(+0) = -v\delta p(+0) + G, \tag{13}$$

$$\delta n(+0) = 0, \tag{14}$$

$$\delta\varphi_{\mathrm{M}} = \delta\varphi(+0), \tag{15}$$

where v is the surface recombination rate (SRR). On account of the relation $j_n + j_p = 0$ only one of the BCs (12), (13) is sufficient for calculations. Thus the BCs are presented by equations (13)–(15).

The BCs (13), (14) can be explained as follows: the non-equilibrium electrons can cross the MSJ (because $\sigma_{n\mathrm{S}} \neq 0$) and therefore do not accumulate on the surface $x = 0$. In the model considered the MSJ thickness is significantly less than the Debye length. Therefore, the parameter v characterizes the SRR in the real MSJ. Note that in the quasi-neutrality approximation the BCs have been formulated at a virtual surface, which is disposed at a distance of several Debye lengths from the real MSJ.

It should be stressed that $\delta n \neq \delta p$ because of the non-equilibrium SCL arising at a several Debye length distance near the surface $x = 0$ [3]. Therefore, the quasi-neutrality approximation is insufficient and the exact solution of the continuity equations and the Poisson equation must be obtained. We shall derive this solution below.

In most semiconductors the diffusion length significantly exceeds the Debye length. Under this condition the solution of equations (1)–(4) could be obtained as a sum of two modes: the diffusion–recombination (DR) mode and the screening (S) mode [3, 5]. These modes are denoted by subscripts R and S accordingly;

$$\delta n = \delta n_{\mathrm{R}} + \delta n_{\mathrm{S}}, \qquad \delta p = \delta p_{\mathrm{R}} + \delta p_{\mathrm{S}}, \qquad \delta\varphi = \delta\varphi_{\mathrm{R}} + \delta\varphi_{\mathrm{S}}. \tag{16}$$

The characteristic S mode decay length is the Debye length r_{D} and the characteristic DR mode decay length is the diffusion length λ. On account of the inequality $r_{\mathrm{D}} \ll \lambda$ we can

neglect the bulk recombination deriving S mode. Therefore the continuity equations (1) and (2) for the S mode (as in the case of flat energy bands [3]) take the form

$$\frac{\mathrm{d}j_{n\mathrm{S}}}{\mathrm{d}x} = 0, \qquad \frac{\mathrm{d}j_{p\mathrm{S}}}{\mathrm{d}x} = 0. \tag{17}$$

The solution of equation (17) is

$$j_{n\mathrm{S}} = \mathrm{const} = 0, \qquad j_{p\mathrm{S}} = \mathrm{const} = 0 \tag{18}$$

because the S mode is not equal to zero in a layer of several r_D distance from the surface $x = 0$. From equations (18) and (4) we obtain

$$\delta n_\mathrm{S} = \frac{en_\mathrm{eq}}{kT}\delta\varphi_\mathrm{S}, \qquad \delta p_\mathrm{S} = -\frac{ep_\mathrm{eq}}{kT}\delta\varphi_\mathrm{S}. \tag{19}$$

It follows from equation (19) that $\delta p_\mathrm{S} = -\delta n_\mathrm{S}\, p_\mathrm{eq}/n_\mathrm{eq}$, i.e. the electron and hole densities of the S mode do not coincide (which is as it should be). Substituting equation (19) into equation (3) one gets for the S mode

$$\frac{\mathrm{d}^2\delta\varphi_\mathrm{S}}{\mathrm{d}x^2} = \frac{e^2}{\varepsilon\varepsilon_0 kT}(n_\mathrm{eq} + p_\mathrm{eq})\delta\varphi_\mathrm{S}. \tag{20}$$

The DR mode is obtained from the solution of equations (1)–(4) taking into account that λ is the characteristic DR mode decay length and the inequality $\lambda \gg r_\mathrm{D}$ is valid. Therefore, deducing the DR mode we can assume that $n_\mathrm{eq} = n_0$, $p_\mathrm{eq} = p_0$ and $\varphi_\mathrm{eq} = 0$.

With the use of the relations [6] $n_\mathrm{eq}(0) = n_0 \exp(\frac{e\varphi^\mathrm{S}}{kT})$, $p_\mathrm{eq}(0) = p_0 \exp(-\frac{e\varphi^\mathrm{S}}{kT})$, $j_p = -eD\frac{\mathrm{d}\delta p_\mathrm{R}}{\mathrm{d}x}$ we derive from equations (1)–(4) and BCs (13), (14) the DR mode value:

$$\begin{aligned}
\delta n_\mathrm{R} &= \frac{G\lambda}{DF_v}\exp\left(-\frac{x}{\lambda}\right),\\
\delta p_\mathrm{R} &= \frac{G\lambda}{DF_v}(1-\gamma)\exp\left(-\frac{x}{\lambda}\right),
\end{aligned} \tag{21}$$

$$\delta\varphi_\mathrm{R} = \frac{G\lambda}{DF_v}\frac{kT}{e}\frac{(\mu_n - \mu_p)}{(n_0\mu_n + p_0\mu_p)}\exp\left(-\frac{x}{\lambda}\right). \tag{22}$$

Here $\lambda = \sqrt{D\tau}$ is the diffusion length, $D = \frac{kT}{e}\frac{(n_0+p_0)\mu_n\mu_p}{(n_0\mu_n+p_0\mu_p)}$ is the bipolar diffusion coefficient, $\tau = \frac{\tau_n\tau_p}{\tau_n+\tau_p}$ is the lifetime of the EHP in the bulk of the sample, $F_v = [1+S_\mathrm{eff}]$, $S_\mathrm{eff} = \frac{v\tau}{\lambda}[1+\frac{p_0}{n_0}\exp(-\frac{2e\varphi^\mathrm{S}}{kT})]$ is the normalized effective SRR, φ^S is the surface potential (SP), n_0 (p_0) is the electron (hole) equilibrium density in the bulk of the sample and $\gamma = \frac{(\mu_n-\mu_p)}{(n_0\mu_n+p_0\mu_p)}\frac{\varepsilon\varepsilon_0 kT}{\lambda^2 e^2}$. The quasi-neutrality condition is fulfilled for the DR mode because $\gamma \sim r_\mathrm{D}^2/\lambda^2 \ll 1$. Note that the normalized effective SRR value essentially depends on the SP provided that $\varphi^\mathrm{S} < -kT/e$.

The solution for the S mode at small SP ($|\varphi^\mathrm{S}| \ll kT/e$) has the form

$$\begin{aligned}
\delta n_\mathrm{S} &= -\frac{G\lambda}{DF_v}\left[1-\beta+\beta\exp\left(-\frac{x}{r_\mathrm{D}}\right)\right]\exp\left(-\frac{x}{r_\mathrm{D}}\right),\\
\delta p_\mathrm{S} &= \frac{G\lambda}{DF_v}\frac{p_0}{n_0}\left[1-\beta+\left(\beta-\frac{2e\varphi^\mathrm{S}}{kT}\right)\exp\left(-\frac{x}{r_\mathrm{D}}\right)\right]\exp\left(-\frac{x}{r_\mathrm{D}}\right),
\end{aligned} \tag{23}$$

$$\delta\varphi_\mathrm{S} = -\frac{G\lambda}{Dn_0}\frac{kT}{eF_v}\left[1-\beta+\left(\beta-\frac{e\varphi^\mathrm{S}}{kT}\right)\exp\left(-\frac{x}{r_\mathrm{D}}\right)\right]\exp\left(-\frac{x}{r_\mathrm{D}}\right), \tag{24}$$

where $r_\mathrm{D} = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{e^2(n_0+p_0)}}$ is the Debye length and $\beta = \frac{(4n_0+2p_0)}{3(n_0+p_0)}\frac{e\varphi^\mathrm{S}}{kT}$.

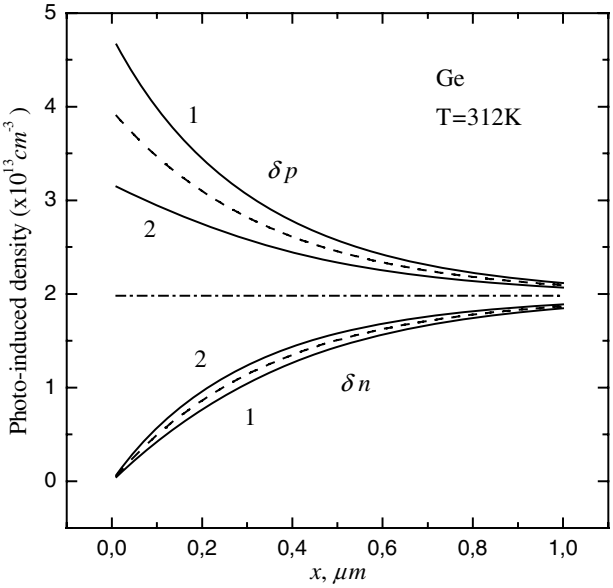

Figure 1. The non-equilibrium carrier density distribution in Ge for some SP values: 1—$\varphi^{\mathrm{S}} = -5.4$ mV, 2—$\varphi^{\mathrm{S}} = 5.4$ mV. The dashed lines give $\delta n(x)$ and $\delta p(x)$ values for flat energy bands. The dot-and-dash line represents the $\delta n_{\mathrm{R}}(x)$ distribution.

It follows from equations (21)–(24) that the S mode depends on the SP and the DR mode does not (which is as it should be).

Let us calculate the PI emf for any SP value. The measured PI emf φ_{P} is equal to the variation of the electric potential of the illuminated metallic contact (the dark metallic contact is grounded). It follows from equations (15) and (16) that

$$\varphi_{\mathrm{P}} = \delta\varphi_{\mathrm{M}} = \delta\varphi_{\mathrm{R}}(0) + \delta\varphi_{\mathrm{S}}(0). \tag{25}$$

We derive from equations (14), (19), and (21)

$$\delta\varphi_{\mathrm{S}}(0) = \frac{kT}{en_{\mathrm{eq}}(0)}\delta n_{\mathrm{S}}(0) = -\frac{kT}{en_{\mathrm{eq}}(0)}\delta n_{\mathrm{R}}(0) = -\frac{G\lambda}{DF_v}\frac{kT}{en_0}\exp\left(-\frac{e\varphi^{\mathrm{S}}}{kT}\right). \tag{26}$$

Finally, we obtain from equations (22), (25), and (26)

$$\varphi_{\mathrm{P}} = \frac{\varphi_{\mathrm{D0}}}{F_v} - \frac{G\lambda}{Dn_0}\frac{kT}{eF_v}\exp\left(-\frac{e\varphi^{\mathrm{S}}}{kT}\right), \tag{27}$$

where $\varphi_{\mathrm{D0}} = \frac{G\lambda}{D}\frac{kT}{e}\frac{(\mu_n-\mu_p)}{(n_0\mu_n+p_0\mu_p)}$ is the classical Dember voltage [6] at negligible SRR value.

3. Discussion of results

It follows from equation (27) that in the case of flat energy bands the PI emf is equal to

$$\varphi_{\mathrm{P}} = -\frac{G\lambda}{Dn_0}\frac{kT}{e}\frac{\mu_p(n_0+p_0)}{(n_0\mu_n+p_0\mu_p)}. \tag{28}$$

The non-equilibrium carrier density distribution in pure Ge ($T = 312$ K, $\lambda = 0.1$ cm, $\mu_n = 3800\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$, $\mu_p = 1800\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$, $r_{\mathrm{D}} = 3.5\times10^{-5}$ cm, $G = 1.3\times10^{16}\ \mathrm{cm^{-2}\ s^{-1}}$) near the surface $x = 0$ is shown in figure 1. It follows from figure 1 and equation (23) that the part of the PI electrons ($-\delta n_{\mathrm{S}}$) is moved from the semiconductor into the metal. This PI electron

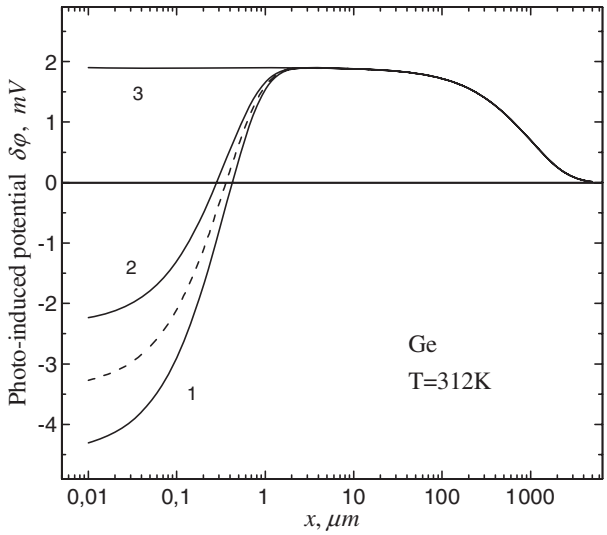

Figure 2. Photo-induced electric potential $\delta\varphi$ distribution in Ge for some SP values: 1—$\varphi^{S} = -5.4$ mV, 2—$\varphi^{S} = 5.4$ mV. Line 3 gives the $\delta\varphi$ distribution from [3]. The dashed line gives the $\delta\varphi(x)$ value for flat energy bands.

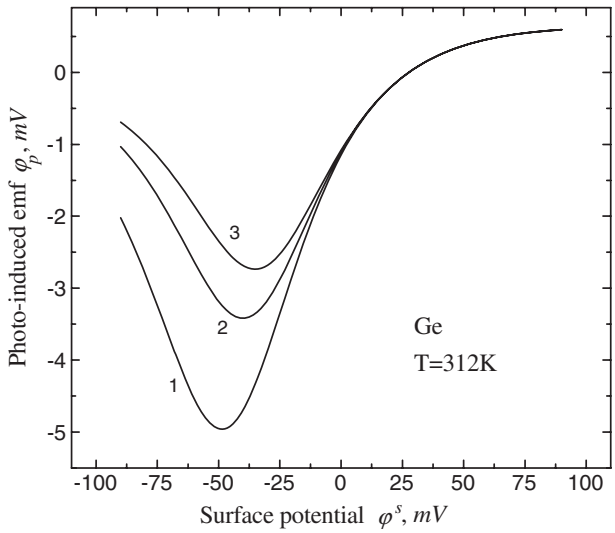

Figure 3. The PI emf dependence on SP φ^{S} for some SRR values: 1—$v = 20$ cm s^{-1}, 2—$v = 40$ cm s^{-1}, 3—$v = 60$ cm s^{-1} ($\varphi_{D0} = 0.66$ mV).

transport results in non-equilibrium potential $\delta\varphi_{S}$ formation and causes the accumulation of photo-induced holes in the SCL near the surface $x = 0$ (see equations (19), (23) and figure 1). So the PI emf value decreases as compared with that of [3] and becomes negative.

The built-in electric field $E_{eq} = -d\varphi_{eq}/dx$ occurs in the semiconductor when the SP is not equal to zero. It is obvious that the electric field E_{eq} has an influence on the non-equilibrium carrier density and thus changes the potential $\delta\varphi(x)$ distribution. The distribution of the PI electric potential in pure Ge ($T = 312$ K, $\lambda = 0.1$ cm, $\mu_n = 3800$ cm^2 V^{-1} s^{-1}, $\mu_p = 1800$ cm^2 V^{-1} s^{-1}, $r_D = 3.5 \times 10^{-5}$ cm, $G = 1.3 \times 10^{16}$ cm^{-2} s^{-1}) for the SRR

$v = 20$ cm s^{-1} is shown in figure 2. It is seen from figures 1 and 2 that the field $E_{eq} > 0$ ($\varphi^S > 0$) decreases the S mode charge density which results in the PI emf value increase (see curves 2). The negative field $E_{eq} < 0$ ($\varphi^S < 0$) increases the S mode charge density which results in the PI emf value decrease (see curve 1).

The PI emf dependence on the SP in pure Ge ($G = 4.5 \times 10^{15}$ cm^{-2} s^{-1} and the other parameters are the same as in figure 2) for some SRR values is shown in figure 3. As is seen from figures 1–3 and equation (27), on decreasing the SP value ($\varphi^S < 0$) the S mode charge density increases. Thus the PI emf value decreases until the normalized effective SRR S_{eff} becomes comparable with unity. The PI emf has a minimum $\varphi_{P.min}$ at the SP value $\varphi_m^S \approx (kT/2e)\ln(v\tau p_0/\lambda n_0)$. The PI emf minimum strongly depends on the SRR value. Further decrease of the SP ($\varphi^S < \varphi_m^S$) results in S_{eff} exponential growth and causes the PI emf value increase. The PI emf tends to the classical Dember voltage ($\varphi_{D0} = 0.66$ mV) when $\varphi^S \gg kT/e$.

Note that the PI emf dependence on the SP can occur in extrinsic semiconductors at strong photo-excitation.

4. Conclusions

The theory of the photo-induced emf accounting for the boundary conditions in a real metal–semiconductor junction as well as the distortion of energy bands near the semiconductor surface has been developed. It is shown that the photo-induced emf essentially depends on the surface potential at a small surface recombination rate. This photo-induced emf calculation method may be used for theoretical study of any kind of emf in bipolar semiconductors [5].

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