
**SEMICONDUCTOR STRUCTURES, INTERFACES,
AND SURFACES**

Nonlinear Thermopower in Bipolar Semiconductor Samples

A. Konin

Semiconductor Physics Institute, A. Gostauto g. 11, LT-01108 Vilnius, Lithuania

e-mail: konin@pfi.lt

Submitted June 16, 2008; accepted for publication October 2, 2008

Abstract—The theory of the thermopower in bipolar semiconductor samples is developed taking into account the bending of the energy band near the semiconductor surface. The boundary conditions at the real metal–semiconductor junction and the nonequilibrium space charge appearing near the sample surface are taken into consideration. The model is constructed in the linear approximation in the temperature gradient, i.e., at a small deviation of the carrier density from equilibrium in the sample bulk. It is shown that the dependence of the thermopower on the temperature difference between the heater and cooler can become nonlinear at certain surface parameters and thicknesses of the semiconductor.

PACS numbers: 73.50.Lw

DOI: 10.1134/S1063782609050121

1. INTRODUCTION

Until recently, the approximation of local electrical neutrality was used in most studies devoted to the theory of thermopower in the bipolar semiconductor [1]. In this case, boundary conditions were formulated on the virtual surface arranged at a distance of several Debye lengths from the real metal–semiconductor junction [2, 3]. As follows from the results of [4–7], the approximation of local electrical neutrality is insufficient to study many problems associated with the effect of the bending of the energy band on nonequilibrium charge formation near the sample surface. In [4–7], it was shown that nonequilibrium electron and hole densities are redistributed in the space-charge region (SCR) [3] due to the built-in electric field [4], i.e., the nonequilibrium charge appears. This charge forms the so-called surface-barrier emf [3] which can significantly change the Hall voltage at certain bendings of the energy band and a low surface recombination velocity. The semiconductor–metal junction plays an important role in this process, which leads to asymmetry of boundary conditions for nonequilibrium carriers [4–8], since nonequilibrium electrons can freely cross the semiconductor–metal interface, while holes cannot. In [6], the thermopower was calculated at small deviations of electron and hole densities from equilibrium in both the semiconductor bulk and SCR (linear approximation). This condition imposes a severe limitation on the lattice temperature gradient, especially in the case of an SCR depleted of equilibrium electrons. Under the commonly used condition of a small temperature gradient (a small deviation of the carrier density from equilibrium in the sample bulk), the problem for nonequilibrium electrons and holes becomes nonlinear. In [9], it was shown that the dependence of the surface-barrier photovoltage on the absorbed light intensity becomes

nonlinear at a low photoexcitation level and certain sample surface parameters. By analogy of the effects, it is clear that the nonlinear dependence of the surface-barrier thermopower on the temperature gradient can be expected in the case of an SCR depleted of equilibrium electrons.

This study is devoted to the development of the theory of thermopower in bipolar semiconductors, which takes into account the bending of the near-surface energy band.

2. THEORY

Let us consider a bipolar semiconductor wafer whose surface $x = a$ has an electrical contact, and an ideal thermal contact with a thermostat with temperature T_+ ; the surface $x = -a$ has the same contact with a thermostat with temperature T_- . Let us assume that the sample thickness is much larger than the electron and hole cooling length. Then temperatures T of all quasiparticles are identical and

$$T(x) = T_0 - \Delta T \frac{x}{2a}, \quad (1)$$

where $T_0 = (T_+ + T_-)/2$ is the average sample temperature, $\Delta T = T_- - T_+$ is the temperature difference between semiconductor surfaces, and $2a$ is the sample thickness. For definiteness, we set $T_- > T_+$. Moreover, we consider the semiconductor as nondegenerate at any x .

In what follows, we consider the case of a low temperature gradient ($\Delta T \ll T_0$) and a corresponding small deviation of the nonequilibrium carrier density from equilibrium values in the sample bulk.

The nonequilibrium densities of electrons δn , holes δp , and the nonequilibrium electric potential $\delta \phi$

are found by solving the continuity equations [4, 10] and the Poisson equation,

$$\frac{1}{e} \frac{dj_n}{dx} - \frac{\delta n}{\tau_n} - \frac{\delta p}{\tau_p} = 0, \quad (2)$$

$$\frac{1}{e} \frac{dj_p}{dx} + \frac{\delta n}{\tau_n} + \frac{\delta p}{\tau_p} = 0, \quad (3)$$

$$\frac{d^2 \delta \varphi}{dx^2} = \frac{e}{\epsilon \epsilon_0} (\delta n - \delta p), \quad (4)$$

where $(-e)$ is the electron charge, j_n and j_p are the electron and hole current densities, τ_n and τ_p are the semiconductor bulk parameters with the dimension of time (but not being electron and hole lifetimes), ϵ is the semiconductor permittivity, and ϵ_0 is the permittivity of free space. Expressions for recombination rates were derived in [10] based on the Shockley–Read model and the charge conservation law, and in [11] based on irreversible thermodynamics.

The expressions for the electron and hole current densities in the general case are written as [2]

$$\begin{aligned} j_n &= -en\mu_n \frac{d\varphi}{dx} + \mu_n kT_0 \frac{dn}{dx} + en\mu_n \alpha_n \frac{\Delta T}{2a}, \\ j_p &= -ep\mu_p \frac{d\varphi}{dx} - \mu_p kT_0 \frac{dp}{dx} + ep\mu_p \alpha_p \frac{\Delta T}{2a}, \end{aligned} \quad (5)$$

where φ is the electrostatic potential, n and p are the total electron and hole densities, μ_n and μ_p are the electron and hole mobilities, k is the Boltzmann constant, and $\alpha_{n(p)}$ is the electron (hole) thermopower coefficient. All kinetic coefficients in (5) were calculated at the temperature T_0 . We note that $dT/dx = -\Delta T/2a$, which dictates the signs of the last terms in (5). The boundary conditions were obtained in [4, 8] as

$$j_n(\pm a) = \mp e v_p \delta p(\pm a), \quad (6)$$

$$\delta n(\pm a) = 0, \quad (7)$$

$$\delta \varphi_M(\pm a) = \delta \varphi(\pm a), \quad (8)$$

where v_p is the surface recombination velocity (SRV) and $\delta \varphi_M$ is the change in the electric potential of the metal contact.

Boundary conditions (6) and (7) can be interpreted as follows. Nonequilibrium holes cannot cross the metal–semiconductor interface (metal does not contain holes); hence, they accumulate and recombine on the surfaces $x = \pm a$. Nonequilibrium electrons can cross the metal–semiconductor interface (the surface conductivity of electrons is sufficiently high [4]); therefore, they do not accumulate on the surfaces $x = \pm a$, since metal does not contain nonequilibrium electrons. We also note that the thickness of the transition layer, which is the interface itself in the case at hand (see [4]), is much smaller than the Debye length. Therefore, v_p is the actual SRV on the semiconductor surface, in contrast to

theoretical models based on the quasi-neutrality condition [2, 3].

The diffusion length λ significantly exceeds the Debye length r_D in most semiconductors. Under this condition, the solution to (1)–(3) may be sought in the form of the sums of three modes, i.e., the classical (C) spatial, diffusion–recombination (DR), and screening (S) modes (subscripts C, R, and S, respectively),

$$\begin{aligned} \delta n &= \delta n_R + \delta n_S, & \delta p &= \delta p_R + \delta p_S, \\ \delta \varphi &= \varphi_C + \delta \varphi_R + \delta \varphi_S. \end{aligned} \quad (9)$$

The characteristic length of the variation of the DR mode is the diffusion length λ , the characteristic length of the variation of the S mode is the Debye length r_D , and the potential φ_C linearly depends on the coordinate x .

Let the temperature gradient be small if the nonequilibrium carrier density in the sample bulk is significantly lower than equilibrium, i.e., the inequality $\delta n_R \ll \min\{n_0, p_0\}$ is satisfied, where $n_0(p_0)$ is the density of the equilibrium electron (hole) in the sample bulk.

We find the DR mode by solving Eqs. (2), (3), and (5), taking into account the condition $\lambda \gg r_D$. Therefore, in calculating the DR mode, we can set $n = n_0 + \delta n_R$, $p = p_0 + \delta p_R$, and $\varphi = \varphi_C + \delta \varphi_R$. From (2) and (3), we obtain

$$j_n + j_p = 0. \quad (10)$$

From (5) and (10), we find

$$\varphi_C = \frac{(\sigma_n \alpha_n + \sigma_p \alpha_p) \Delta T}{\sigma} \frac{x}{2a}, \quad (11)$$

$$\delta \varphi_R = (\mu_n - \mu_p) kT_0 \sigma^{-1} \delta n_R, \quad (12)$$

$$j_n = eD \frac{d\delta n_R}{dx} + (\alpha_n - \alpha_p) \frac{\sigma_n \sigma_p \Delta T}{\sigma} \frac{x}{2a}, \quad (13)$$

where $\sigma_n = en_0 \mu_n$ is the conductivity of the equilibrium electron, $\sigma_p = ep_0 \mu_p$ is the conductivity of the equilibrium hole, $\sigma = \sigma_n + \sigma_p$, and $D = (kT_0/e\sigma)(\sigma_n \mu_p + \sigma_p \mu_n)$ is the diffusivity. The continuity equation for the DR mode is given by

$$\frac{d^2 \delta n_R}{dx^2} - \frac{\delta n_R}{\lambda^2} = 0, \quad (14)$$

where $\lambda = \sqrt{D\tau}$ is the diffusion length and $\tau = \tau_n \tau_p / (\tau_n + \tau_p)$ is the lifetime of electron–hole pairs in the sample bulk. Due to the symmetry of boundary conditions (6), the solution to Eq. (14) is given by

$$\delta n_R = \delta n_R^+ \frac{\sinh(x/\lambda)}{\sinh(a/\lambda)}. \quad (15)$$

We note that the hole density of the DR-mode is related to the electron density of this mode as $\delta p_R = (1 - \gamma) \delta n_R$,

where $\gamma \propto r_D^2/\lambda^2 \ll 1$. Therefore, the approximation of local electroneutrality in the sample bulk is satisfied with high accuracy.

In the calculation of the S mode, we can disregard bulk recombination, since this mode decays at a distance of several Debye lengths from the surface $x = \pm a$, and the nonequilibrium carrier density decreases due to recombination (DR mode) at the distance of the diffusion length λ . Therefore, the continuity equation for the S mode [4, 5]

$$\frac{dj_{nS}}{dx} = 0, \quad \frac{dj_{pS}}{dx} = 0 \quad (16)$$

transforms into the following system set:

$$j_{nS} = \text{const} = 0, \quad j_{pS} = \text{const} = 0. \quad (17)$$

Let us denote the S mode near the surface $x = a$ as δn_S^+ , δp_S^+ , and $\delta \varphi_S^+$. Since $\Delta T > 0$, it follows from (6) and (13) that $\delta n_R(a) = \delta n_R^+ > 0$ at $v_p = 0$. Due to the relation $r_D \ll \lambda$, we can consider that the DR mode is unchanged in the region of S-mode existence. Therefore, we can consider the densities $\tilde{n}_+ = n_{\text{eq}} + \delta n_R^+$ and $\tilde{p}_+ = p_{\text{eq}} + \delta n_R^+$ as equilibrium for electrons and holes of the S mode near the surface $x = a$. Here, $n_{\text{eq}}(p_{\text{eq}})$ is the actual density of the equilibrium electron (hole). In other words, the S-mode electron and hole densities are measured from the \tilde{n}_+ and \tilde{p}_+ levels, respectively. Therefore, from (5) and (17), we obtain

$$\begin{aligned} \delta n_S^+ &= (n_{\text{eq}} + \delta n_R^+) \left[\exp\left(\frac{e\delta\varphi_S^+}{kT_0}\right) - 1 \right], \\ \delta p_S^+ &= (p_{\text{eq}} + \delta n_R^+) \left[\exp\left(-\frac{e\delta\varphi_S^+}{kT_0}\right) - 1 \right]. \end{aligned} \quad (18)$$

From (18) and boundary conditions (7), we find

$$\delta p_S^+(a) = [p_{\text{eq}}^+ + \delta n_R^+] \frac{\delta n_R^+}{n_{\text{eq}}^+}, \quad (19)$$

$$\delta \varphi_S^+(a) = -\frac{kT_0}{e} \ln \left[1 + \frac{\delta n_R^+}{n_{\text{eq}}^+} \right], \quad (20)$$

where $n_{\text{eq}}^+ = n_0 \exp(e\varphi^s/kT_0)$, $p_{\text{eq}}^+ = p_0 \exp(-e\varphi^s/kT_0)$, and φ^s is the surface potential [2].

Let us denote the S mode near the surface $x = -a$ as δn_S^- , δp_S^- , and $\delta \varphi_S^-$. Since $\delta n_R(-a) = -\delta n_R^+ < 0$, the S-mode electron and hole densities are measured from

the levels $\tilde{n}_- = -(n_{\text{eq}} + \delta n_R^+)$ and $\tilde{p}_- = -(p_{\text{eq}} + \delta n_R^+)$, respectively. Therefore, from (5) and (17), we obtain

$$\delta n_S^- = -(n_{\text{eq}} + \delta n_R^+) \left[\exp\left(-\frac{e\delta\varphi_S^-}{kT_0}\right) - 1 \right], \quad (21)$$

$$\delta p_S^- = -(p_{\text{eq}} + \delta n_R^+) \left[\exp\left(\frac{e\delta\varphi_S^-}{kT_0}\right) - 1 \right].$$

From (21) and boundary conditions (7), we find

$$\begin{aligned} \delta p_S^-(-a) &= -\delta p_S^+(a), \\ \delta \varphi_S^-(-a) &= -\delta \varphi_S^+(a). \end{aligned} \quad (22)$$

As follows from (20) and (22), the dependence of the S mode potential $\delta \varphi_S^\pm(\pm a)$ on the injection level is nonlinear at the negative surface potential. Therefore, at $\varphi^s < 0$, from (6), (13), (15), and (19), we obtain

$$\delta n_R^+ = \frac{\lambda(\alpha_p - \alpha_n)}{2a(n_0 + p_0)kT_0} \frac{e n_0 p_0 \tanh(a/\lambda) \Delta T}{[1 + S_{\text{eff}} \tanh(a/\lambda)]}, \quad (23)$$

where $S_{\text{eff}} = (v_p \tau / \lambda) [1 + p_0 \exp(-2e\varphi^s/kT_0)/n_0]$ is the effective normalized SRV.

The thermopower U_T measured between metal contacts is

$$U_T = \delta \varphi_M(-a) - \delta \varphi_M(a) = -2\delta \varphi(a). \quad (24)$$

Finally, from (11), (12), and (20), we find

$$U_T = \Delta \varphi_C + \Delta \varphi_R + \Delta \varphi_S, \quad (25)$$

where

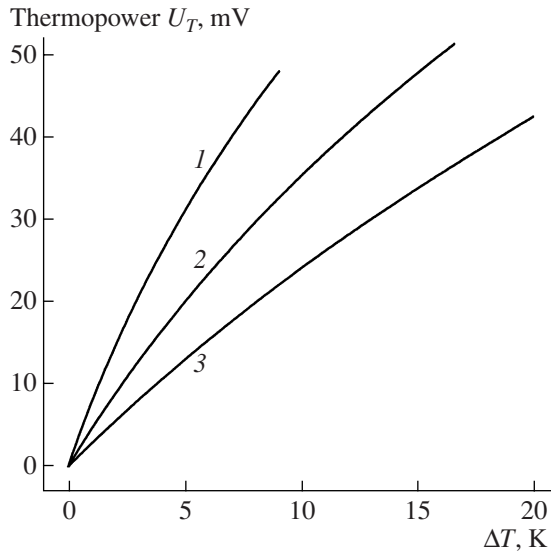
$$\Delta \varphi_C = -\frac{(\alpha_n \sigma_n + \alpha_p \sigma_p)}{\sigma} \Delta T,$$

$$\Delta \varphi_R = -\frac{2kT_0}{\sigma} (\mu_n - \mu_p) \delta n_R^+,$$

$$\Delta \varphi_S = \frac{2kT_0}{e} \ln \left[1 + \frac{\delta n_R^+}{n_0} \exp\left(-\frac{e\varphi^s}{kT_0}\right) \right].$$

3. RESULTS AND DISCUSSION

We can see from (25) that the thermopower consists of three parts: the classical thermopower $\Delta \varphi_C$, the emf $\Delta \varphi_R$ caused by the nonequilibrium charge distribution in the sample bulk (DR mode), and the surface-barrier thermopower $\Delta \varphi_S$ caused by the nonequilibrium charge distribution near the sample surface (S mode). The latter two modes are formed as follows. The heat flow carries away nonequilibrium carriers from the surface $x = -a$ to the surface $x = a$, since $T_- > T_+$. Since SRVs on the surface $x = \pm a$ are identical and the electron mobility is larger than the hole mobility, the density of the space charge of the DR mode is negative at $0 < x \leq a$.



Dependence of the thermopower U_T on the temperature difference ΔT between the heater and cooler for $2a$ sample thicknesses of (1) 0.04, (2) 0.1, and (3) 0.2 cm.

Therefore, the DR mode potential in this range is positive, i.e., it decreases the thermopower (see (24)). Since nonequilibrium electrons freely flow from semiconductor to metal, while nonequilibrium holes accumulate near the surface $x = a$ (see above), the density of the space charge of the S mode is positive near this surface. Therefore, the S mode potential near the surface $x = a$ is negative, i.e., increases the thermopower. We can see from (23) and (25) that the dependence of the thermopower U_T on the temperature difference ΔT can become nonlinear in the region of the negative surface potential at small SRVs ($v_p \ll \lambda\tau$) and in samples that are not bulk samples ($a < \lambda$). Under the condition $n_R^+ \ll n_{eq}^+$, the thermopower is identical to that obtained using the expression derived in the linear approximation [6].

Let us introduce the nonlinearity coefficient β_N of the functional dependence $U_T(\Delta T)$ as

$$\beta_N = \frac{U_T}{F(0)\Delta T} - 1,$$

where $F(\Delta T) = dU_T/d(\Delta T)$. An analysis of (23) and (25) shows that $|\beta_N|$ is at a maximum, when the surface potential is given by $\varphi^s = \varphi_m^s \approx (kT/2e)\ln[v_p\tau p_0 \tanh(a/\lambda)/n_0\lambda]$.

The figure shows the dependence of the thermopower U_T on the temperature difference ΔT between

heater and cooler for a sample with the Ge parameters ($T_0 = 320$ K, $\lambda = 0.1$ cm, $\mu_n = 3800$ cm²/(V s), $\mu_p = 1800$ cm²/(V s), $\varphi^s = -70$ mV, and $v_p = 20$ cm/s) at several half-thicknesses of the sample. Curves 1 and 2 were calculated to such ΔT , at which the condition $\delta n_R^+ \leq 0.1n_0$ is satisfied. We can see that the nonlinearity of the curves $U_T(\Delta T)$ decreases with the sample thickness. For example, for $\Delta T = 9$ K, $\beta_N = -0.35$ at $a = 0.02$ cm, $\beta_N = -0.23$ at $a = 0.05$ cm, and $\beta_N = -0.14$ at $a = 0.01$ cm. Thus, the thermopower nonlinearity effect is pronounced in thin samples at small SRVs in the surface potential range $(\varphi_m^s - kT/e) < \varphi^s < (\varphi_m^s + kT/e)$.

4. CONCLUSIONS

Based on the exact solution of the continuity equations and boundary conditions at the real metal–semiconductor interface, the theory of the thermopower in bipolar semiconductors was developed taking into account the bending of the energy band on the sample surfaces. It was shown that the dependence of the thermopower on the temperature difference between the heater and cooler can become nonlinear at low surface recombination velocities in thin samples and in a certain range of the surface potential. The method developed in this study can also be efficiently applied to calculate other emfs (photomagnetic, Hall, and photovoltage).

REFERENCES

1. Yu. G. Gurevich, G. N. Logvinov, I. N. Volovichev, G. Espejo, O. Yu. Titov, and A. Meriuts, *Phys. Stat. Solidi B* **231**, 278 (2002).
2. V. L. Bonch-Bruevich and S. G. Kalashnikov, *Semiconductor Physics* (Vyssh. Shkola, Moscow, 1975) [in Russian].
3. G. P. Peka, *Physical Phenomena on Semiconductor Surface* (Vishcha Shkola, Kiev, 1984) [in Russian].
4. A. Konin, *J. Phys.: Condens. Matter* **19**, 016214 (2007).
5. A. Konin, *Lithuan. J. Phys.* **45**, 373 (2005).
6. A. Konin, *Fiz. Tekh. Poluprovodn.* **41**, 282 (2007) [*Semiconductors* **41**, 272 (2007)].
7. A. Konin, *Lithuan. J. Phys.* **46**, 307 (2006).
8. A. Konin, *Lithuan. J. Phys.* **46**, 233 (2006).
9. A. Konin, *J. Phys.: Condens. Matter* **20**, 055225 (2008).
10. I. N. Volovichev and Yu. G. Gurevich, *Fiz. Tekh. Poluprovodn.* **35**, 321 (2001) [*Semiconductors* **35**, 306 (2001)].
11. M. Krčmar and W. M. Saslow, *Phys. Rev. B* **65**, 233313 (2002).

Translated by A. Kazantsev