

# Transport phenomena in bipolar semiconductors: a new point of view

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## Abstract

In previous work it has been shown that the traditional approach to transport phenomena in bipolar semiconductors is inconsistent. In particular, the effect of non-equilibrium charge carriers and appropriate boundary conditions are not considered in the literature. We have proposed an alternative for linear transport but some effects due to the relationship between the fluctuations in the densities of charge carriers and the temperature gradients were not discussed. Here, we continue our criticism to the conventional treatment and extend the previous model to discuss transport phenomena in a linear approximation and boundary conditions as applied to plane interfaces. By the first time charge carriers out of equilibrium, temperature fields, surface and bulk recombination processes, space charge distribution, etc. are undertaken self-consistently. Our model is contrasted with recent experimental results on the Seebeck coefficient of  $Cd_{1-x}Zn_xTe$ .

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## 1. Introduction

It is well known that Peltier effect, discovered in 1831, is the basis for solid thermoelectric cooling. It arises from the fact that heat extraction or absorption occurs at the contact between two different conducting media if dc electric current flows through this contact. The counterpart to Peltier effect is the Seebeck effect, presented to the physics community by Oersted in 1823. It is the basis for thermoelectric or current generation when there exists a temperature field [1]. Common to both effects is the simultaneous flow of heat and charge and the presence of contacts between different conducting media, since the material cannot be homogeneous. These effects remained without much interest until Ioffe underlined the importance of semiconductors as thermoelectrics. After more than 150 years since the essence of both phenomena has been rather well understood [2], and 50 since Ioffe remarkable work [1], there is a lack of proper models to take into account many aspects that are of paramount importance for new applications in thermoelectric generation and refrigeration [3].

Our effort is intended to provide a new approach to the generally accepted theory of solid-state thermoelectricity within a constructive criticism [4]. Heat flow was the interest in a recent paper [5]. Thermoelectric generation and electric transport were reviewed somewhere else [6,7]. Boundary conditions in an electric current contact has been discussed in another report [8]. Both, heat flow and current generation involving different kind of charge and heat carriers (electrons, holes, phonons, pairs, etc.) out of equilibrium in electric and temperature fields are the subject of the theory under current development: *a new point of view in transport phenomena* [4–10]. The main objective of this contribution is to give a summary of the work above, to further develop the new theory as applied to bipolar and intrinsic semiconductors and to illustrate its use in some specific situations [11,12]. The increasing search for new compounds that exhibit superior thermoelectric properties merits for a careful exam of usual oversimplifications that are not well justified in current models.

## 2. Shortcomings of previous approaches

Thermoelectricity, including thermomagnetic effects, is the study of the interrelated phenomena associated to charge and heat (energy) carriers. We begin by pointing out some

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internal inconsistencies present in the conventional description of these transport phenomena in solids. It will be useful to the purpose of introducing some nomenclature as well. To start with, the effects of the simplest boundary between any two materials have been studied only for open circuits [13]. Practically all textbooks begin by imposing additional conditions to the standard continuity equations (for simplicity we write them in their one-dimensional form):

$$\frac{dj_n}{dx} = eR_n, \quad \frac{dj_p}{dx} = -eR_p, \quad (1)$$

where  $n, p, j_{n,p}$  and  $R_{n,p}$  are the electron and hole concentrations, current densities and bulk recombination rates, respectively. We assume for simplicity that there is not any external source of carriers by light and other means. Hence non-equilibrium carriers will arise only from injection or accumulation of carriers near potential barriers at interfaces and as a consequence of inhomogeneous thermal generation in the sample. Let us apply the continuity equation to the total current, with  $\rho$  the total density of charge,  $\partial\rho/\partial t = -\text{div}\mathbf{J}$ ; in the stationary case we obtain

$$\text{div}\mathbf{J}_0 = \text{div}(\mathbf{j}_n + \mathbf{j}_p) = 0. \quad (2)$$

These equations are independent, and therefore the electron and hole bulk recombination rates have to be the same [14,15]:  $R_n = R_p$ . They are widely written in the form  $R_n = \delta n/\tau_n$ ,  $R_p = \delta p/\tau_p$ , where  $\delta n = n - n_0$  and  $\delta p = p - p_0$  denote the non-equilibrium concentrations of electrons and holes, respectively, and  $\tau_n$  and  $\tau_p$  are their lifetimes. ( $n, p$  and  $n_0, p_0$  are the full concentrations and the corresponding equilibrium values.) This condition, leading to  $\delta n/\tau_n = \delta p/\tau_p$ , is unphysical, and has to be modified [15]. Notice that  $\delta n$  and  $\delta p$  in current literature do not contain all contributions to fluctuations in the charge carriers densities.

A similar difficulty results when considering the traditional theory to calculate the thermoelectromotive force (t.e.m.f.) in bipolar semiconductors under open circuit conditions [4]. Since not only  $\mathbf{J}_0$  but also  $j_n$  and  $j_p$  will be equal to zero, the chemical potentials of electrons  $\mu_n$  and holes  $\mu_p$  cannot be related by the general relationship  $\mu_n + \mu_p = -\varepsilon_g$ , where  $\varepsilon_g$  is the energy gap. The electrochemical potentials  $\varphi - \frac{u_n}{e}$  and  $\varphi + \frac{u_p}{e}$ , is the electron charge, are thus different and there will be ambiguity in the definition of the t.e.m.f. One obtains, e.g., that electron and hole power coefficients have to be identical, which certainly cannot be correct. Another baseless idea commonly found is to assume that interband recombination is a sufficient condition for  $\delta n = \delta p$  to be fulfilled. There is no proof of this conclusion and we illustrate situations where it is not valid [15].

In a simple case, that of a homogeneous bipolar semiconductor electrically neutral and in thermodynamic equilibrium, one has that the equilibrium electron and hole concentrations  $n_0$  and  $p_0$  are not equal and that the law of mass action is not necessarily valid. Notice, however, that a *built-in electric field* will not appear, the temperature is uniform and the chemical potentials do not change in space

( $\mu_{n,p}^0 = \text{constant}$ ): the electrochemical potential level, constant in space, is common to all particle subsystems.

To examine more complex situations, it is convenient to introduce a characteristic screening length also called the Debye radius  $r_d$ , defined by  $r_d^2 = k_B T_0 / 4\pi e^2 (n_0 + p_0)$  (the dielectric constant has been taken equal to 1 for simplicity). Beyond  $r_d$  a charge just sees a cloud of charge. Imagine for simplicity that the semiconductor is a finite sample of length  $2a$  limited by ideal metallic junctions, i.e. any redistribution of charge in the metal will reside in its surface. In the semiconductor, it depends on its length compared to  $r_d$ . When  $r_d^2 \ll a^2$ , one has quasi-neutrality [16]. In this case, one can assume that  $\delta n = \delta p = 0$  and the concept of contact potential is a useful one.

When  $r_d^2 \geq a^2$ , quasi-neutrality is not satisfied and the concept of contact potential loses its meaning. Both regimes are illustrated in Fig. 1. In the latter case there will be a space charge distribution whose width is of the order of  $r_d$ . In this case, even under equilibrium conditions, we have a non-uniform distribution of chemical potentials,  $\mu_{n,p}(x) = \mu_{n,p}^0(T_0) + \delta\mu_{n,p}(x)$ , and it will appear a *built-in electric field*. After applying a temperature gradient, there will appear charge carriers concentration gradients, because at different points we have different rates of thermal generation. As a result, the chemical potentials will change,  $\mu_{n,p}(x) = \mu_{n,p}^0(x) + \delta\mu_{n,p}(x)$ , but the situation is of local equilibrium and there will not be space charge distribution.

The above and other more general questions can be answered satisfactorily under the new scheme. Before proceeding we mention that to increase the efficiency of thermoelectrics it has been seen valuable to employ multilayered materials and other composites. In those cases, beside fluctuations in the densities of charge carriers and temperature gradients, appropriate boundary conditions [8] are likely to be very important for transport phenomena, particularly since surface effects might be considerably enhanced.

### 3. A new approach

In practice one has situations where there are charge carriers through heterojunctions and there exist

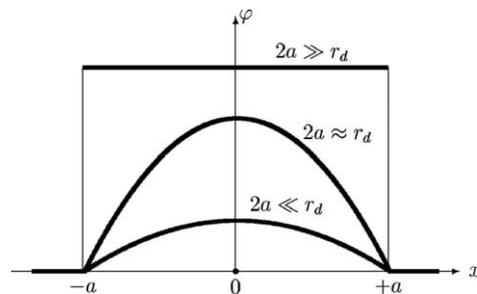


Fig. 1. Electric potential distribution for several lengths when quasi-neutrality condition is not satisfied. Notice that when  $2a \gg r_d, \varphi_0(x) \rightarrow \varphi_0$ .

temperature gradients that cause thermal generation of carriers. This is more complex since redistribution takes place and it competes with the thermal generation process. A direct method consists in solving the dynamic case  $J_0 \neq 0$  without quasi-neutrality, and consider the total non-equilibrium charge carriers concentration. Without loss of generality we limit to a linear change in temperature. We use the following relation for the recombination rates [6,15]:

$$R_n = R_p = R = \frac{1}{\tau} \cdot \frac{1}{n_0 + p_0} \left[ p_0 \delta \tilde{n} + n_0 \delta \tilde{p} - \frac{en_0 p_0}{T_0} (\alpha_p^0 - \alpha_n^0) \frac{\Delta T}{2a} x \right], \quad (3)$$

$\alpha_{n,p}^0$  are defined by [17]

$$\alpha_{n,p}^0 = \mp \frac{1}{e} \left( \frac{\mu_{n,p}^0(T_0)}{T_0} - \frac{3}{2} \right), \quad (4)$$

and  $\tau^{-1} = \alpha(T_0) \times (n_0 + p_0)$ , where  $\alpha(T_0)$  is the capture factor at  $T_0$ .

We underline that  $n_0(x)$  and  $p_0(x)$  refer to the electron and hole concentration after the establishment of thermodynamic equilibrium and that  $\delta \tilde{n}(x)$  and  $\delta \tilde{p}(x)$  include the total variations from diverse mechanisms. In other words,  $n(x) = n_0(x) + \delta \tilde{n}(x)$  and  $p(x) = p_0(x) + \delta \tilde{p}(x)$ . This is a substantial difference with the conventional approach, and we discuss its implications in the rest of this section.

When quasi-neutrality condition is satisfied, the concentrations do not depend on coordinates, i.e.  $n_0(x) = n_0(T_0)$  and  $p_0(x) = p_0(T_0)$ . The same happens to the contact potential  $\varphi_0$ :  $\varphi_0 = [\mu_n^0(T_0) - \mu_m - \Delta \varepsilon_c] / e = \text{constant}$ . In that case, the usual expressions in textbooks are valid. Here  $\mu_m$  is the chemical potential of the metal and  $\Delta \varepsilon_c$  is the energy difference between the bottoms of the conduction bands of the metal and the semiconductor. Within the semiconductor the electric potential is  $\varphi_s^0 = \varphi_0$  while in the metal it is  $\varphi_m^0 = 0$ . Notice that  $\varphi_m^0(x = \mp a) \neq \varphi_s^0(x = \mp a)$ .

When quasi-neutrality condition is not fulfilled, even for a state of thermodynamic equilibrium there will be inhomogeneities in the concentrations and they will depend on coordinates:

$$n_0(x) = n_0(T_0) + \delta n_0(x) = n_0(T_0) + \frac{n_0(T_0)}{T_0} \delta \mu_n^0(x)$$

and

$$p_0(x) = p_0(T_0) + \delta p_0(x) = p_0(T_0) + \frac{p_0(T_0)}{T_0} \delta \mu_p^0(x).$$

The chemical and electric potentials will change in the same way:  $\varphi^0(x) = \varphi_0 + \delta \varphi^0(x)$ ,  $\mu_n^0(x) = \mu_n^0(T_0) + \delta \mu_n^0(x)$ ,  $\mu_p^0(x) = \mu_p^0(T_0) + \delta \mu_p^0(x)$ , and one has that  $\delta \mu_n^0 + \delta \mu_p^0 = 0$ . There will appear fluctuations in the electric potential that will compensate the fluctuations in the chemical

potential [7]

$$\delta \varphi^0(x) = -\varphi_0 \frac{Ch(x/r_d)}{Ch(a/r_d)} \quad \text{and}$$

$$\delta \mu_n^0(x) = -e\varphi_0 \frac{Ch(x/r_d)}{Ch(a/r_d)},$$

and now one has that  $\varphi_m^0(\pm a) = \varphi_s^0(\pm a)$ .

The continuity equations have to be supplemented with appropriate boundary conditions. This has been done previously [8], with the following results for the metal-semiconductor interface:  $j_p|_{x=\mp a} = \mp eR_S$ ,  $j_n|_{x=\mp a} = J_0 \pm eR_S$ . Here  $R_S$  is the surface recombination rate. In a similar way to the bulk recombination rate, we write for  $R_S$

$$R_S(\pm a) = S \cdot \frac{1}{n_0 + p_0} \left[ p_0 \delta \tilde{n}(\pm a) + n_0 \delta \tilde{p}(\pm a) \mp \frac{en_0 p_0}{T_0} (\alpha_p^0 - \alpha_n^0) \frac{\Delta T}{2} \right], \quad (5)$$

being  $S$  the surface recombination velocity.

For the total current  $J_0$  we obtain the following condition [8]:

$$\frac{j_0}{\pm \sigma_n^S} = \left[ \varphi_s(\pm a) - \frac{\mu_n^S(\pm a)}{e} \right] - \left[ \varphi_m(\pm a) - \frac{\mu_m}{e} \right] + \frac{\Delta \varepsilon_c}{e}. \quad (6)$$

Here  $\sigma_n^S$  is the surface electric conductivity,  $\varphi_s(\pm a)$ ,  $\varphi_m(\pm a)$  are the electric potentials at the semiconductor and metal surfaces, respectively;  $\mu_n^S(\pm a)$  is the electron chemical potential at the semiconductor surface and  $\mu_m$  is the metal chemical potential.

The semiconductor potential  $\varphi_s(\pm a)$  is determined from Poisson equation

$$\frac{d^2 \varphi_s(x)}{dx^2} = -4\pi \rho(x), \quad (7)$$

where  $\rho(x)$  is the charge density;  $\varphi_s(x) = \varphi_0(x) + \delta \varphi(x)$ ;  $\rho(x) = \rho_0(x) + \delta \rho(x)$ , being  $\rho_0$  the equilibrium charge density and  $\delta \rho(x) = -e[\delta \tilde{n}(x) - \delta \tilde{p}(x) + \gamma(\Delta T/2a)x]$ . The continuity of the electric potential in  $x = \pm a$  with  $\varphi(-a) = 0$  and  $\varphi(+a) = V = J_0 L / \sigma_m$  yields [10]

$$\frac{d^2 \delta \varphi}{dx^2} = 4\pi e(\delta \tilde{n} - \delta \tilde{p}) + 4\pi e \gamma \frac{\Delta T}{2a} x. \quad (8)$$

The constant  $\gamma$  is given by:

$$\gamma = \frac{1}{T_0} \left[ (n_0 + p_0) \left( \frac{\partial \mu_n}{\partial T} \right)_{T=T_0} - \frac{n_0 \mu_n^0 - p_0 \mu_p^0}{T_0} + \frac{3}{2} (n_0 - p_0) \right]. \quad (9)$$

#### 4. Further comments and conclusions

We have summarized a new approach to transport phenomena in bipolar semiconductors that is under

current development. Once one has an equation for the electric potential that includes the effects mentioned above and the appropriate boundary conditions, one can proceed to evaluate many quantities that are required for applications in thermoelectricity: charge and heat currents, electric and field temperatures and more directly measurable quantities like t.e.m.f. One finds that they depend on surface and bulk recombination rates and on lifetimes of quasiparticles in an intricate way. Those effects have to be taken into account for instance to predict correctly the figure of merit of thermoelectric devices.

Experimental work have appeared based on our model [12,18]. They show that the effects are measurable and significant. A more detailed application where simulation of the experimental results on  $Cd_{1-x}Zn_xTe$  builds a bridge between theory and practice will be published elsewhere.

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### References

- [1] A.F. Ioffe, *Physics of Semiconductors*, Academic Press, New York, 1957.
- [2] L.I. Anatyckuck, *Physics of thermoelectricity* Institute of Thermoelectricity, Kyliiv, Chernivtsi, 1998.
- [3] G.D. Mahan, Heat and electricity transport through interfaces, *Semicond Semimetals* 70 (2001) 245.
- [4] Yu.G. Gurevich, *J. Thermoelectr.* 2 (1997) 5.
- [5] Yu.G. Gurevich, G.N. Logvinov, O.Yu. Titov, J. Giraldo, *Surf. Rev. Lett.* 9 (2002) 1703.
- [6] Yu.G. Gurevich, G.N. Logvinov, G. Espejo, O.Yu. Titov, A. Meriuts, *Semiconductors* 34 (7) (2000) 755.
- [7] Yu.G. Gurevich, G.N. Logvinov, I.N. Volovichev, G. Espejo, O.Yu. Titov, A. Meriuts, *Phys. Stat. Sol. (b)* 231 (2002) 278.
- [8] O.Yu. Titov, J. Giraldo, Yu.G. Gurevich, *Appl. Phys. Lett.* 80 (2002) 3108.
- [9] Yu.G. Gurevich, O.Yu. Titov, G.N. Logvinov, O.I. Lyubimov, *Phys. Rev. B* 51 (1995) 6999.
- [10] Yu.G. Gurevich, A. Ortiz, *Rev. Mex. Fis.* 49 (2003) 115.
- [11] A. Gutiérrez, M. E. Rodríguez, J. Giraldo, Yu. G. Gurevich, *Rev. Mex. Fis.* 50 (2004) 620.
- [12] S. Vackova, K. Zdansky, K. Vacek, L. Scherback, P. Foychuk, M. Ilaschouk, *Phys. Stat. Sol. (a)* 177 (2000) 263.
- [13] S.M. Sze, *Semiconductor devices: Physics and Technology*, Wiley, New York, 1985.
- [14] Yu.G. Gurevich, I.N. Volovichev, *Semiconductors* 35 (2001) 306.
- [15] I.N. Volovichev, G. Espejo, Yu.G. Gurevich, O.Yu. Titov, A. Meriuts, *Jpn. J. Appl. Phys.* 41 (2002) 182.
- [16] V. P. Silin, A. A. Rukhadze (1961). *Electromagnetic Properties of the Plasma and Related Media*, Atomizdat, Moscú 1961 (in Russian).
- [17] Yu.G. Gurevich, O.L. Mashkevich, *Sov. Phys. Semicond.* 24 (1990) 835.
- [18] C. Jácome, M. Flórez, Yu.G. Gurevich, J. Giraldo, G. Gordillo, *J. Phys. D: Appl. Phys.* 34 (2001) 1862.