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Assesment of nonlinear phonon drag contribution in the thermopower for a heated conductive nanoparticle on the surface of a semiconductor

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We propose a simple model for estimating the nonlinear phonon drag contribution to thermopower generated by a heat flux propagating from a conductive nanoparticle into a semiconductor. The results of the study confirm that thermoelectric effect in nanostructured electron emitters can produce electric „patch field"patterns with magnitudes sufficient to significantly stimulate emission. The phenomenon predicted by the model can possibly be used to develop thermoelectric converters with unique parameters.

Keywords: thermoelectric effect, phonon drag, field electron emission, nanostructures, thin films.

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Electron field emitters based on nanostructured materials are considered promising for application in vacuum microelectronics devices and a number of other applications [1,2]. At the same time, they often generate considerable interest in terms of physics: for many of their types, operating in relatively weak electric fields (units of V/μm) [3–5], the emission mechanism remains unclear [6]. A sp^2 nano-island film of carbon or metal on a silicon substrate can be considered a „model" type of such an emitter, the one most convenient for experimental study and model construction. The ability of island carbon films to produce low-voltage electron emission was described in [7,8]. It was found that there were no spicules on their surface, as well as areas with low work function or significant variations, which could also explain the observed emissive ability („of spot fields"). A similar emissive ability was also observed for refractory metal films [9]. The insensitivity of the effect to the coating material indicates that the key processes for the emission mechanism may develop not in the islands themselves, but in the adjacent regions of the substrate. In [6,9–11] it was suggested that such a process may be thermoelectric: heating of emission centers creates electric „spot" fields that facilitate emission, but disappear after current take-off ceases. In this paper, we consider the simplest model for estimating the possible value of the thermo-emf generated near the emission center of a nano-island film, taking into account dimensional effects.

It is known from literature that if the characteristic size of the problem is smaller than the path length of heat carriers, the description of heat transfer and thermoelectric effect requires special approaches [12,13]. The phonon L_{ph} path length in silicon at room temperature can exceed 100 nm, whereas the emitting coatings in [7–9] contained nano-islands of d size on the order of 10 nm. At temperatures of the order of room temperature and higher, the main contribution to the thermoelectric coefficient of bulk semiconductors is made by the temperature dependence of the mobility and concentration of free charge carriers, whereas the component associated with phonon entrainment dominates only at cryogenic temperatures, when the phonon path length is comparable to the size of macroscopic samples. However, for the thermoelectric effect in the nanoscale region, the ratio of the contributions of the different mechanisms may be different. In$< L_{ph}$ wide layer, the local distributions differ from the equilibrium distributions and cannot be described by the concept of a single temperature, even as functions of coordinates. Therefore, in evaluating the contribution of phonon drag to the thermo-emf in the region of the heated nanoisland we will be guided only by the most general principles — the laws of conservation of particle energy and momentum. The phonons in the problem with a characteristic scale of the order of 10 nm can still be considered as particles, since at temperatures from 300 K more than 90 % of the heat flux is carried by lattice vibrations with wavelengths of the order of nanometer units [13].

Let us consider the conditions of mechanical equilibrium of „the average" conduction electron in the n-type semiconductor near the heated flat boundary under the action of the electric field and phonon drag force. At this stage we shall neglect the presence of the velocity distribution of electrons. At equality of forces „the average" electron rests, there is no current from the boundary into the semiconductor volume, and the potential difference between them is equal to the thermo–emf. The problem is considered to be one-dimensional, the coordinate x is counted from the boundary into the semiconductor.

Let the field $E(x)$ is created only by the charge of electrons (their concentration is denoted by $n(x)$) and donor impurity (n_D) as well as „reflection" of these charges in the boundary. According to Gauss's theorem

$$E(x) = \frac{e}{\varepsilon\varepsilon_0}\int_x^{\infty}(n(\xi) - n_D)d\xi. \qquad (1)$$

To take into account the ballistic (at least partially) character of heat transfer near the boundary with a nonequilibrium and non-isotropic distribution of phonons by quasi-momentum, let us represent the phonon population as a two-component one. Let one of its components have an equilibrium distribution corresponding to the volume temperature. The other component — the ballistic phonon flux propagating from the boundary into the volume (we shall denote a set of properties that distinguish this component of the phononic population from its equilibrium part, in particular, a different frequency distribution and anisotropy of the wave vector distribution using the term „ballistic flux" which is not quite correct). We will assume that at each act of scattering the phonon of the ballistic flux completely loses the transferred mean momentum and is excluded from consideration. The flux power density at the boundary is equal to q_0 and is further described by a decreasing function $q(x)$.

In the Debye approximation, all phonons move at the same speed υ_a. This allows summing up the contributions of different scattering processes to the inverse length of their travel time $(-q'(x)/q(x))$ (rather than to the inverse free travel time). The scattering of ballistic phonons on phonons of the equilibrium population, defects and impurities can be estimated by the known value of the run length in the bulk material L_{ph}. It is more difficult to estimate the contribution of the interaction between phonons of the ballistic flux itself, which will obviously depend on the coordinate, decreasing with the flux intensity. In the following equations, the contribution of this scattering channel is not taken into account: subsequent evaluations have shown that it is small compared to the contribution of „dimensional" suppression of heat transfer and drag [12,14,15]. The dimensional effect can be interpreted as a consequence of phonon scattering on the „aperture" d of the contact of the emission center with the semiconductor, and its contribution can be considered as the second term in the ratio $L^{-1} = L_{ph}^{-1} + d^{-1}$.

We will represent the electron contribution to the inverse phonon path length as the product $\sigma n(x)$, where $n(x)$ — is electron concentration. The proportionality coefficient σ has the meaning of the averaged interaction cross section. Its estimate can be obtained from the classical theory of electron-phonon interaction (see, for example, [16]). Continuing the analysis presented in [10], it is easy to arrive at an estimate (very approximate) of $\sigma = 16\pi\hbar/(Mm^2 a\upsilon_a^3)$, where M, a and m — the mass of the atom, the lattice parameter, and the effective mass of the electron. Thus, the attenuation of the ballistic phonon flux can be described by a law

$$q'(x) = -q(x)(L^{-1} + \sigma n(x)). \tag{2}$$

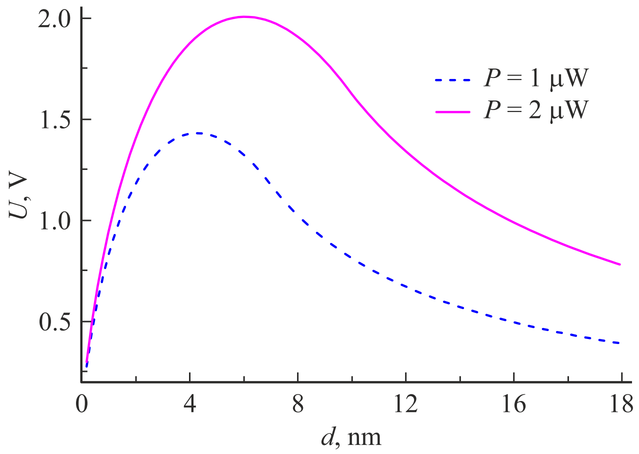
Phonon drag is caused by the transfer of the mechanical momentum of the phonons of the directional flux to the electrons. The momentum transferred to a resting electron per unit time determines the nonpotential thermoelectric force — the source of thermal-emf. Its value can be expressed as $\sigma q(x)/\upsilon_a$, in the Debye approximation ($\upsilon_a = \text{const}$) it is independent of the phonon spectrum. Consequently, the electron equilibrium condition (no current) is written as $\sigma q(x)/\upsilon_a = eE(x)$. If we introduce the notation for „critical" value of the heat flux density $q_c = \upsilon_a e^2/(\sigma^2\varepsilon\varepsilon_0)$ and consider (1), the equilibrium condition can be rewritten as $q(x) = \sigma q_c \int_x^\infty (n(\xi) - n_D)d\xi$. Its differentiation gives $q'(x) = -\sigma q_c(n(x) - n_D)$. By comparing this relationship with (2), passing to the dimensionless function $\eta(x) = q(x)/q_c$ and expressing $n(x)$, we obtain $n(x) = [n_D + \eta(x)/(\sigma L)]/(1 - \eta(x))$. Substituting this expression into (2), we obtain the differential equation for the dimensionless phonon flux density

$$\eta'(x) = -\eta(x)(L^{-1} + \sigma n_D)/(1 - \eta(x)). \tag{3}$$

Its solution with the boundary condition $\eta(0) \equiv \eta_0 = q_0/q_c$ at first sight always allows calculating the function $\eta(x)$, then the distributions $n(x)$ and $E(x)$ and thermo-emf. However, the simplest analysis shows that at $q_0 > q_c$ (i. e. at $\eta_0 > 1$) the equations obtained for $\eta(x)$ and $n(x)$ do not give physically reasonable solutions for the coordinate values $x < x_c$, where x_c — the root of the equation $\eta(x_c) = 1$. The denominators of the right-hand sides are negative, which would mean that the heat flux increases with distance from the boundary and the concentration of electrons is negative (this is not equivalent to the appearance of holes: holes, like electrons, must be pushed out by the phonon drag force into the volume similar to the way charges of both signs are pushed out by the ponderomotive force from the concentration region of the high-frequency electromagnetic field). This result means that at $x < x_c$ the charge carriers cannot be in equilibrium, and the absence of current here can only be ensured by the absence of $n(x) = 0$ at $x < x_c$. Accordingly, equation (2) here has the form $\eta'(x) = -\eta(x)/L$. Its solution, taking into account the boundary condition $\eta(0) = \eta_0$ will be: $\eta(x) = \eta_0 \exp(-x/L)$. At $x = x_c$ this relation must be satisfied simultaneously with the condition $\eta(x_c) = 1$. Hence we obtain the width of the depletion layer $x_c = L\ln\eta_0$. According to (1), inside this layer the electric field varies as $E(x) = E_m - en_D(x_c - x)/(\varepsilon\varepsilon_0)$, and outside it (at $x > x_c$) — as $E(x) = E_m\eta(x)$, where E_m — the maximum field strength, $E_m = e/(\sigma\varepsilon\varepsilon_0)$. Function $\eta(x)$ at $x > x_c$ is calculated by solving equation (3) with the boundary condition $\eta(x_c) = 1$. By integrating the distribution $E(x)$ from 0 to ∞ we obtain an expression for the thermo-emf.

$$U = E_m\left(x_c - \frac{n_D\sigma x_c^2}{2} + \int_{x_c}^{\infty} \eta(x)dx\right).$$

At lower heat flux density at the boundary ($q_0 < q_c$ or $\eta_0 < 1$) we obtain the electric field distribution $E(x) = E_m\eta(x)$, where the function $\eta(x)$ is obtained by solving equation (3) with boundary condition $\eta(0) \equiv \eta_0 = q_0/q_c$. The value of the thermo-emf is



View of the thermo-emf dependence on the size of the contact region for two values of thermal power. The $q_0 = P/d^2$ ratio and the approximate analytical approximation $\eta(x)$ were used. The medium parameters correspond to silicon: $\upsilon_a = 6400$ m/s, $\varepsilon = 12$, $n_D = 10^{15}-10^{18}\,\text{cm}^{-3}$, $L_{ph} = 210$ nm, $\sigma = 8.8\,\text{nm}^2$, $E_m = 0.17$ V/nm, $q_c = 2.0 \cdot 10^{-8}\,\text{W/nm}^2$.

calculated as

$$U = E_m \int_0^\infty \eta(x)dx.$$

The physical meaning of the obtained results can be disclosed as follows. Regardless of the heat flux density at the boundary, the excess electronic charge per unit area created by it does not exceed the value of $\varepsilon\varepsilon_0 E_m$. This value is achieved at $q_0 = q_c$. Further increase of q_0 only moves the created charge to the distance x_c away from the boundary. The analysis shows that the dependence of $U(q_0)$ is linear at low q_0 and saturates logarithmically at $q_0 \to \infty$.

In the calculations given in [9,10] in support of the emission model, the total heat power P rather than the heat flux density appeared. The figure shows the results of calculating the dependencies $U(d)$ for the values of $P = 1\,\mu$W(as estimated [10]) and $2\,\mu$W ([9]) according to the formulas obtained in this study. They show the presence of a maximum at values of $d \approx 4$ and 6 nm, shifting to a region of larger values as P increases. This agrees with the results of [7–9], where the emissive ability of the films correlated with the presence of islands on the order of 10 nm in size. The maximum value of the thermo-emf in the plots exceeds 2 V, which may be sufficient to activate the emission by the resulting „patch" field.

It should be recognized that the results of this consideration contradict many ideas [14,15] about the contribution of phonon drag to the thermal emission in nanocontacts. According to them, this contribution decreases as the contact size approaches L_{ph} and beyond, because the boundary scattering of phonons competes with their scattering on electrons, suppressing the momentum transfer to them. However, the object of the presented model was one of the nonlinear effects [17–19], the general theory of which has not yet been provided. In the considered case, the effect of phonon drag leads to the formation of a region with a high concentration $n(x)$ of free charge carriers even in a weakly doped semiconductor, where the probability of phonon scattering on electrons increases. Note that direct experimental observation of the effect predicted by the model may be difficult. The value of the current generated by the described mechanism is limited by the low speed (not more than υ_a) of the generated directional motion of the electron component. If the heat flux density along the boundary is not uniformly distributed, the highest thermoelectric voltage generated by the region with maximum q_0 will be shunted by regions with lower heat flux density. The result will be the formation of stationary eddy currents [18], and a decrease in the observed thermo-emf. A similar effect was discussed in [15]. In case of island films, favorable conditions for the change in their electric potential, according to the considered mechanism, could be implemented only for a few islands, which explains the small number of emission centers observed in [7–9]. Experimental verification of the above estimates can probably be accomplished using an atomic force microscope (see, for example, the [20] experiment, where the absence of „size" suppression of thermo-emf for thermal contacts as small as 4 nm was recorded). Practical use of the predicted phenomenon can be associated with the creation of nanoscale thermoelectric converters with atypical characteristics — high effective thermoelectric coefficient at high internal resistance.

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Conflict of interest

The authors declare that they have no conflict of interest.

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