Theoretical Estimation of Characteristics of Thermoelectric Materials Made of Nanopowders

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Abstract

The results of theoretical estimations of characteristics of thermoelectric materials composed of nanometer particles that are connected with each other through point contacts are presented in this paper. The goal of conducted calculations is the verification of possibility of the increasing of thermoelectric material efficiency $Z = \alpha^2 \cdot \sigma/(\kappa el + \kappa ph)$, where α – Seebeck coefficient, σ – electric conductivity, κel – heat conductivity associated with electrons and κph – heat conductivity associated with phonons. Possibility of Z increase is based on very simple idea of drastic κph decrease caused by the presence of nanometer gaps between separate thermoelectric particles that stop free photon propagation in the sample and the conservation of α and σ thanks to the tunneling of electrons through these gaps. Results of calculations are discussed.

Introduction

One of the first attempts to estimate possibility of increasing the figure of merit of the flat thermoelectric vacuum structures (TVS), i.e. the structures composed of semiconductor layers separated by very thin vacuum gaps was made in 1969 [1]. Term "vacuum" can be used here so as the nanometer gap width is much less than the free path of molecules in gases. The thermoelectric figure of merit is determined as $Z = \alpha^2 \cdot \sigma/(\kappa_{el} + \kappa_{ph})$, where α is the Seebeck coefficient, σ is the electrical conductivity, and κ_{el} and κ_{ph} are the electron and phonon thermal conductivities. Possibility of Z increase is based on very simple idea of drastic κ_{ph} decrease caused by the presence of nanometer gaps between separate thermoelectric layers that stop free photon propagation in the sample and with the conservation of α and σ thanks to the tunneling of electrons through these gaps. It was shown that the Seebeck coefficient in such structure could be more than in the bulk thermoelectric in definite range of Fermi level that should lead to Z increase too. However there were not taken into account the thermoelectric material characteristics as functions of Fermi energy and influence the transmission coefficient of electron tunneling through vacuum potential barrier.

Now in connection with rapid development of nanotechnologies the idea of TVS creation should be raised up and discussed once more. One of the stimulative reasons for conducting present theoretical estimations was the appearance of high efficient installation for producing inexpensive nonopowders in Scientific and Research Institute of Vacuum Technique. We can anticipate that TVSs made of nanopowders should have better basic thermoelectric characteristics than ones in bulk thermoelectric materials.

Estimation of vacuum gap characteristics

Here we consider the model of the thermoelectric vacuum structure (TVS) composed of two flat thermoelectric plates of thickness D separated by vacuum gap of width d. We assume that thermoelectric material in plates have simple parabolic band structure, electron energy is counted off from the bottom of the conduction band, electrons can pass through the gap thanks to tunneling effect and phonon thermal conductivity in vacuum gap is absent.

The electric and energy flux densities of electrons through vacuum gap between two semi-infinite thermoelectric layers ere given by

$$js = \frac{-2qe}{hp^3} \cdot \int_0^{\infty} vx \cdot (fc - fh) \cdot T(Ex)\, dp^3, \qquad (1)$$

$$qs = \frac{2 \cdot qe}{hp^3} \cdot \int_0^{\infty} vx \cdot (Ex + Et) \cdot (fc - fh) \cdot T(Ex)\, dp^3, \qquad (2)$$

where V_x – x-component of electron velocity in direction perpendicular to thermoelectric surface, f_c and f_h – Fermi-Dirac distribution functions in cold left and hot right plates respectively, q_e – electron charge, m – effective electron mass, h_p – Plank constant, $T(E_x)$ – transmission coefficient through potential barrier, $dp^3 = dp_x dp_y dp_z$, p_x, p_y and p_z - components of electron momentum, $V_x = p_x/m$, $E = p_x^2/2m$, $E_t = (p_x^2 + p_z^2)/2m$ and $E = E_x + E_t$.

Fermi-Dirac distribution functions in thermoelectric plates are given by

$$fc = \frac{1}{\exp\left[\frac{(Ex + Et - Ef)}{Kb \cdot T}\right] + 1}, \qquad fh = \frac{1}{\exp\left[\frac{(Ex + Et - Ef - q \cdot U)}{Kb \cdot (T + \Delta T)}\right] + 1} \qquad (3)$$

where E_f – Fermi level, T and T+ΔT – absolute temperature at cold and hot plates respectively, U – potential difference between plates, K_b – Boltzmann constant.

Introducing dimensionless variables $x = E_x/K_bT$, $t = E_t/K_bT$ and $\eta = E_f/K_bT$ (reduced Fermi level), equations (1) and (2) can be written as

$$js(\eta) = \frac{-qe \cdot m(Kb \cdot T)^2}{2 \cdot \pi^2 \cdot hp^3} \cdot \int_0^{\infty} \int_0^{\infty} T(x)(fc - fh)\, dt\, dx, \qquad (4)$$

$$qs(\eta) = \frac{m(Kb \cdot T)^3}{2 \cdot \pi^2 \cdot hp^3} \cdot \int_0^\infty \int_0^\infty T(x)(x + y)(fc - fh)\, dy\, dx \cdot \quad (5)$$

We introduce functions M0(η), M1(η) and M2(η) by integrals:

$$M0(\eta) = \int_0^\infty \int_0^\infty \frac{T(x)\exp(x + t - \eta)}{(\exp(x + t - \eta) + 1)^2}\, dt\, dx, \quad (6)$$

$$M1(\eta) = \int_0^\infty \int_0^\infty \frac{T(x)(x + t)\exp(x + t - \eta)}{(\exp(x + t - \eta) + 1)^2}\, dt\, dx, \quad (7)$$

$$M2(\eta) = \int_0^\infty \int_0^\infty \frac{T(x)(x + t)^2\exp(x + t - \eta)}{(\exp(x + t - \eta) + 1)^2}\, dt\, dx \cdot \quad (8)$$

Expanding (fc-fh) in series on small parameters ΔT/T and q_eV_d/K_bT and leaving only the first expansion terms, one can derive equations of the Seebeck coefficient, electric and thermal conductivities. The Seebeck coefficient αs(η) = U/ΔT is derived from (6) at condition $j_s(\eta) = 0$:

$$\alpha s(\eta) = \frac{Kb}{qe} \cdot \left(\frac{M1(\eta)}{M0(\eta)} - \eta \right), \quad (9)$$

electric conductivity of gap unit area $\sigma_s(\eta) = j_s(\eta)/V$ is derived from (6) at conditions ΔT=0 and V→0:

$$\sigma s(\eta) = \frac{qe^2 \cdot m \cdot Kb \cdot T}{2 \cdot \pi^2 \cdot hp^3} \cdot M0(\eta), \quad (10)$$

thermal conductivity of gap unit area $\kappa_s(\eta) = qs(\eta)/\Delta T$ is derived from (6) and (7) at conditions $j_s(\eta) = 0$ and ΔT → 0:

$$\kappa s(\eta) = \frac{m \cdot Kb^3 \cdot T^2}{2 \cdot \pi^2 \cdot hp^3} \cdot \left(M2(\eta) - \frac{M1(\eta)^2}{M0(\eta)} \right). \quad (11)$$

Integrals (8) – (9) drastically depend on the transmission coefficient of electron through vacuum gap T(E,d). In general T(E,d) can be presented as

$$T(E,d) = \frac{1}{\frac{W(d)^2}{4E(W(d) - E)} \cdot \sinh\left[\frac{d}{hp} \sqrt{2m(W(d) - E)} \right]^2 + 1}, \quad (12)$$

$$W(d) = Wo - 1.15 \cdot \frac{q}{\varepsilon o} \cdot \frac{\ln(2)}{2 \cdot \pi \cdot d}, \quad (13)$$

where W(d) – effective barrier height, Wo – barrier height counted off from bottom of conduction band and approximately equal to work function of semiconductor. The second term in (13) takes into account the mirror forces that lower barrier height. T(E,d) decreased very rapidly with increase of d, approximately by 5 orders of value at d increase on 0.5 nm. The integrand functions in equations (6)-(8) have the sharp maximum at electron energy about 0.5-0.8 K_bT. The optimal value of d_{opt} at which the transmission coefficient reaches maximum value is derived from equation (13) at W(d) = 0. So d_{opt}=0.6 nm for Wo=4 eV and d_{opt}=2.4 nm for Wo=1 eV.

Estimation of thermoelectric plates characteristics

The basic characteristics of semiconductors with any level of generation are given by following equations [2]:

$$\alpha(\eta, r) = \frac{Kb}{qe} \cdot \alpha o(\eta, r), \quad (14)$$

$$\sigma(\eta, r) = \frac{4 \cdot qe^2 \cdot \sqrt{m} \cdot (Kb \cdot Th)^{\left(r + \frac{3}{2}\right)}}{3hp^3 \cdot (2 \cdot \pi)^{1.5}} \cdot \tau o(r) \cdot \sigma o(\eta, r), \quad (15)$$

$$\kappa e(\eta, r) = \sigma(\eta, r) \cdot Th \cdot \left(\frac{Kb}{q} \right)^2 \cdot L(\eta, r), \quad \kappa(\eta, r) = \kappa e(\eta, r) + \kappa ph(\eta, r), \quad (16)$$

$$Z(\eta, r) = \alpha(\eta, r)^2 \cdot \frac{\sigma(\eta, r)}{\kappa(\eta, r)}, \quad (17)$$

where α(η,r) – the Seebeck coefficient, $\sigma_e(\eta,r)$ – electric conductivity, $\kappa_e(\eta,r)$ – electron component of thermal conductivity, κ_{ph} - phonon component of thermal conductivity, $\kappa(\eta,r) = \kappa_e(\eta,r) + \kappa_{ph}$ – total thermal conductivity, Z(η,r) – the figure of merit, and dimensionless functions $\alpha_o(\eta,r)$, $\sigma_o(\eta,r)$, L(η,r) and F(η,r) are given by:

$$\alpha o(\eta, r) = \frac{\left(r + \frac{5}{2}\right) \cdot F1\left(\eta, r + \frac{3}{2}\right)}{\left(r + \frac{3}{2}\right) \cdot F1\left(\eta, r + \frac{1}{2}\right)} - \eta,$$

$$\sigma o(\eta, r) = \left(r + \frac{3}{2}\right) \cdot \frac{F1\left(\eta, r + \frac{1}{2}\right)}{\Gamma 1\left(\frac{3}{2}\right)},$$

$$L(\eta, r) = \frac{\left(r + \frac{7}{2}\right) F1\left(\eta, r + \frac{5}{2}\right)}{\left(r + \frac{3}{2}\right) F1\left(\eta, r + \frac{1}{2}\right)} - \frac{\left(r + \frac{5}{2}\right)^2 F1\left(\eta, r + \frac{3}{2}\right)^2}{\left(r + \frac{3}{2}\right)^2 F1\left(\eta, r + \frac{1}{2}\right)^2}$$

$$F(\eta, r) = \int_0^\infty \frac{\varepsilon^r}{e^{x - \eta} + 1}\, dx,$$

where Γ(r) – Gamma function, r – exponent of electron energy in the relaxation time $\tau(E) = \tau o(r) \cdot E^r$, τo(r) – constant different for different mechanisms of the scattering of electrons, r = – 1/2 for electron scattering on thermal phonons and r = 3 /2 for electron scattering on ionized atoms of impurities.

Estimation of flat TVSs effective characteristics

It is evident that for calculation of basic characteristics of flat thermoelectric vacuum structure it is enough to consider only two semiconductor plates with vacuum gap between them connected in a series. In this case the effective characteristics of TVSs can be easily derived:

$$\alpha eff(\eta, D, d) = \alpha(\eta) \cdot \left[1 - \frac{\left(1 - \frac{Kb}{qe} \cdot \frac{K(\eta)}{\alpha(\eta)} \right)}{\left(1 + \frac{\kappa s(\eta, d)}{\kappa(\eta)} \cdot D \right)} \right], \quad (18)$$

$$\sigma eff(\eta, D, d) = \frac{(D + d)}{D} \cdot \frac{\sigma e(\eta)}{1 + \frac{\sigma e(\eta)}{\sigma s(\eta, d) \cdot D}}, \quad (19)$$

$$\kappa eff(\eta, D, d) = \frac{(D + d)}{D} \cdot \frac{\kappa(\eta)}{1 + \frac{\kappa(\eta)}{\kappa s(\eta, d) \cdot D}} \quad (20)$$

$$Zeff(\eta, D, d) = \frac{\alpha eff(\eta, D, d)^2 \cdot \sigma eff(\eta, D, d)}{\kappa eff(\eta, D, d)}. \quad (21)$$

For more easy comparison and analysis of results of calculations we introduce dimensionless characteristics that are determined as ratio of TVS effective characteristics to corresponding bulk thermoelectric characteristics by the following equations $\gamma(\eta,D,d)$:

$$\begin{aligned} \gamma\alpha(\eta, D, d) &= \frac{\alpha eff(\eta, D, d)}{\alpha(\eta)}, \\ \gamma\sigma(\eta, D, d) &= \frac{\sigma eff(\eta, D, d)}{\sigma e(\eta)}, \\ \gamma\kappa(\eta, D, d) &= \frac{\kappa eff(\eta, D, d)}{\kappa(\eta)}, \\ \gamma z(\eta, D, d) &= \frac{Zeff(\eta, D, d)}{Z(\eta)}. \end{aligned} \quad (22)$$

where $\gamma\alpha(\eta,D,d)$, $\gamma\sigma(\eta,D,d)$, $\gamma\kappa(\eta,D,d)$ and $\gamma z(\eta,D,d)$ correspond to the Seebeck coefficient, electric and thermal conductivity and the figure of merit respectively.

Results of calculations of TVSs

The calculations were conducted for two variants of the relaxation time, for scattering electrons on ionized atoms of impurities (r=3/2) and on thermal phonons (r= – 1.2).

We used the following characteristics of thermoelectric material: effective electron mass $m = 0.45m_o$, constants in the relaxation time $\tau o(-1/2) = 5.15 \cdot 10^{-22}$ $s \cdot J^{0.5}$ and $\tau o(3/2) = 2.1 \cdot 10^{17}$ $s \cdot J^{-1.5}$ for ion concentration of $Ni = 10^{23}$ m^{-3}, lattice thermal conductivity $\kappa_{ph} = 1$ W/m·K, work function Wo=4 eV. At the room temperature T=300 K and for scattering electrons on thermal phonons the basic characteristics of thermoelectric material had the following values: the Seebeck coefficient $\alpha = 2 \cdot 10^{-4}$ V/K, electric and thermal conductivity $\sigma_e = 9.8 \cdot 10^4$ 1/Ohm·m and $\kappa = 1.48$ W/m·K, respectively, and the figure of merit $Z = 2.9 \cdot 10^{-3}$ 1/K. These characteristics are very close to characteristics of alloy of bismuth telluride (Bi_2Te_3).

Relative characteristics $\gamma\alpha(\eta,D,d)$, $\gamma\sigma(\eta,D,d)$, $\gamma\kappa(\eta,D,d)$ and $\gamma z(\eta,D,d)$ as functions of reduced Fermi level $\eta = E_f/K_bT$, thickness of thermoelectric layers D in nm and width of vacuum gap d in nm are presented in figures 1-5. Low indexes in expressions $\gamma(\eta,D,d)$ "i" and "p" correspond to scattering electrons on ionized atoms of impurities and thermal phonons respectively.

Calculations show that effective Seebeck coefficient decreases and effective electric and thermal conductivities increase with increase of reduced Fermi level η.

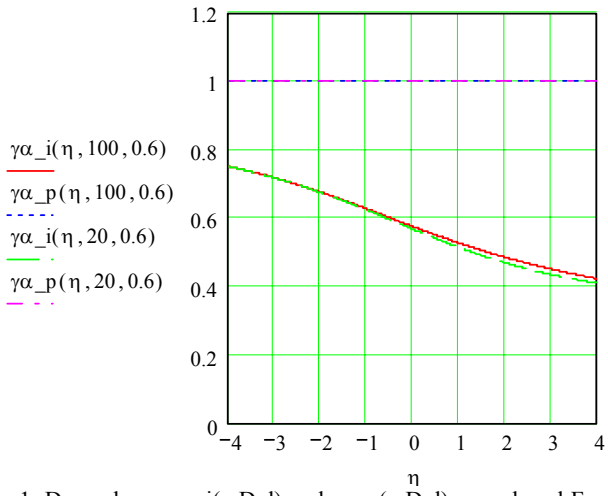

Fig. 1. Dependence $\gamma\alpha\_i(\eta,D,d)$ and $\gamma\alpha\_p(\eta,D,d)$ on reduced Fermi level η for d=0.6 nm and D = 100 and 20 nm.

Fig. 1 shows that the effective Seebeck coefficient is equal to the Seebeck coefficient of bulk material $\gamma\alpha\_p(\eta,D,d)=1$ for scattering electrons on thermal phonons so as coefficients have the same dependence on η. In general, $\alpha_{eff}(\eta)$ is lower $\alpha(\eta)$ for scattering on ions and decreases with increase η.

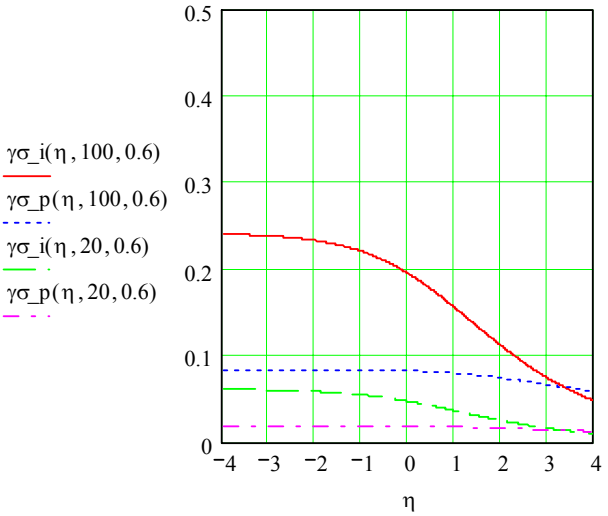

Fig. 2. Dependance $\gamma\sigma\_i(\eta,D,d)$ and $\gamma\sigma\_p(\eta,D,d)$ on reduced Fermi level η for d=0.6 nm and D = 100 and 20 nm.

Fig. 2 shows that the relative electric conductivities $\gamma\sigma\_i(\eta,D,d)$ and $\gamma\sigma\_p(\eta,D,d)$ decrease droningly with η increase.

At the same time the relative thermal conductivities $\gamma\kappa\_i(\eta,D,d)$ and $\gamma\kappa\_p(\eta,D,d)$ increase with η increase, and $\gamma\kappa\_i(\eta,D,d) > \gamma\kappa\_p(\eta,D,d)$ for $\eta<2$ and $\gamma\kappa\_i(\eta,D,d) <$

γκ_p(η,D,d) for η>2. It is interesting that the decrease of relative thermal conductivity is less than the decrease of relative electric conductivity in several times.

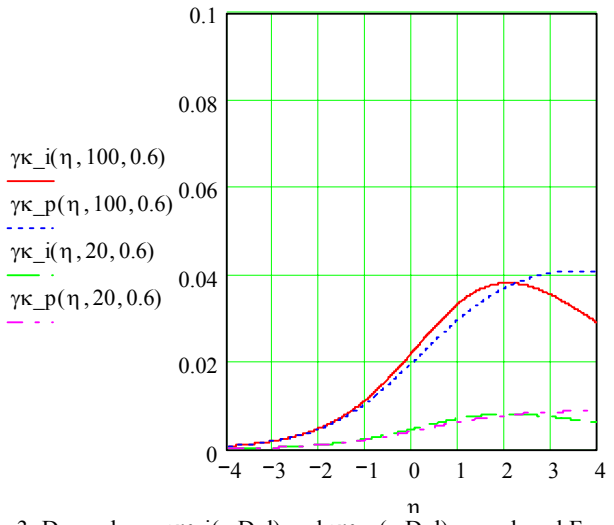

Fig. 3. Dependence γκ_i(η,D,d) and γκ_p(η,D,d) on reduced Fermi level η for d=0.6 nm and D = 100 and 20 nm.

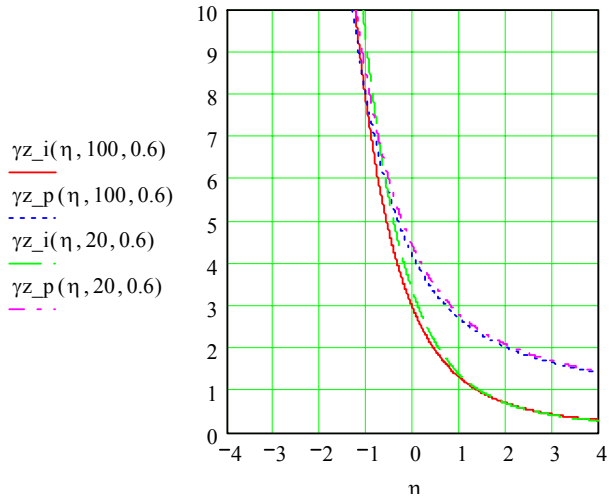

Fig.4. Dependence γz_i(η,D,d) and γz_p(η,D,d) on reduced Fermi level η for d=0.6 nm and D = 100 and 20 nm.

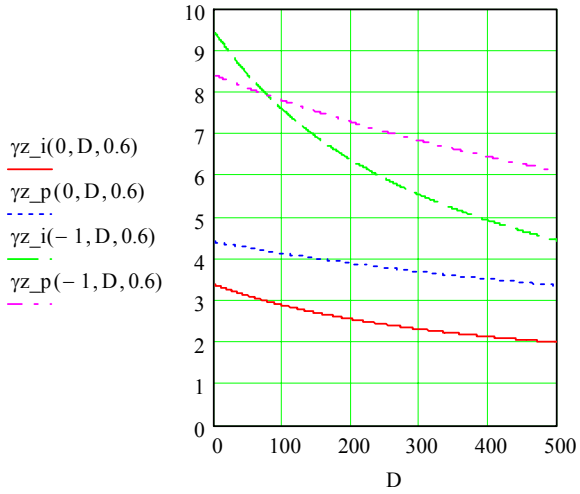

Fig. 5. Dependence γz_i(η,D,d) and γz_p(η,D,d) on thermoelectric plate thickness for d=0.6 nm and η = 0 и – 1.

The relative figure of merit γz_i(η,D,d) and γz_p(η,D,d) decrease droningly with η increase. But if the γz_p(η,D,d)>1 in all range of variable η , then γz_i(η,D,d)>1 for η<1.3 and γz_i(η,D,d)<1 for η>1.3, i.e. Zeff_i of TVS is lower than Z of bulk thermoelectric material for η>1.3.

Fig. 5 shows that the relative figure of merit γz_i(η,D,d) and γz_p(η,D,d) increase with the decrease of thickness of thermoelectric layers D.

The TVS characteristics strongly depend on width of vacuum gap d. Zeff(η,D,d) increases and σ_{eff}(η,D,d) drastically decreases with d increase. In order to have TVS with electric conductivity comparable with electric conductivity of bulk material and Zeff>Z, d should have value close to d_{opt}. The gap width d_{opt} is inversely proportional to the work function W_o. Therefore it is very important to use TE material or coating materials with low work function.

Flat TVS is a good model for calculations of basic characteristics of other similar structures. Real materials with thermoelectric vacuum structure can be produced from powders of different semiconductors. As a first approximation we can imagine powder thermoelectric material as closed-packed particles of spherical form that have a point contacts with each other. Then effective contact area for tunneling current can be evaluated as

$$Sc(D, dopt) = \frac{\pi}{4} \cdot \left[D^2 - (D - dopt)^2 \right], \qquad (23)$$

and effective unit area of sample for tunneling current can be presented as

$$\gamma s(D, dopt) = \frac{\pi}{4} \cdot \left[1 - \frac{(D - dopt)^2}{D^2} \right]. \qquad (24)$$

Taking γ_s=0.1, we have maximum particle diameter D_{max}=9 nm for d_{opt}=0.6 nm (W_o=4 eV) and D_{max}=36 nm for d_{opt}=2.4 nm (W_o=1 eV).

It is evident that energy structure of semiconductor particles drastically changes with decrease of its diameter, besides particle surface conditions begin to play very important role in processes of electron tunneling. Estimation of influence of energy structure change and particle surface conditions on properties of nanopowder thermoelectric materials should be made in the nearest future.

Conducted calculations show that thermoelectric nanopowder materials made of weakly degenerated semiconductor materials (η = –2÷0) should have the electric conductivity on 1-2 order of value lower and the figure of merit in several times higher than ones in bulk materials and that these materials are promising in broad range of applications.

Conclusions

Flat thermoelectric vacuum structures (TVSs) have the following characteristics:

- the figure of merit exceeds by 3-7 times and effective electric conductivity is on 1-2 orders of value less than the same characteristics of bulk material in practically interesting range of Fermi level (η= –2÷0),
- the figure of merit increases and electric conductivity

decreases with decrease of thermoelectric plate thickness,
- optimum width of vacuum gap at which figure of merit and electric conductivity reach its maximums increases from 0.6 to 2.4 nm for decrease of electron work function from 4 to 1 eV.

For materials made of nanopowders there exists the maximum particle diameter in range of 10-30 nm at which the figure of merit and electric conductivity are close to the same characteristics of flat TVSs.

The figure of merit of laminated, powder and porous thermoelectric materials can be significantly higher than the same characteristics of bulk materials.

Made estimations show the necessity of carrying out new calculations of characteristics of nanopowder materials taking into account the change of energy structure and influence of surface state in nanoparticles, as well as conduction of new experiments with thermoelectric nanopowders.

From the practical point of view the increase of figure of merit in 2-4 times signifies the broad expansion of TE device and system applications, lets them to compete with and replace the existing compressor coolers, freezers and air conditioners as well as gives unique opportunities to develop high efficiency solid-state power generators using the waste heat of diesel engines, metallurgical works and thermal power stations in temperature range of 400-900 K.

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