MODEL OF THERMOELECTRIC MATERIAL COMPOSED OF NANOPARTICLES WITH QUANTUM-POINT CONTACTS

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Abstract

The model of thermoelectric material composed of nanoparticles with point contacts was considered. Theoretical estimation of the material basic characteristics was made. Calculations showed that the thermoelectric figure of merit ZT of nanocomposite material could exceed ZT of the same bulk thermoelectric material at definite conditions. It can be explained by the increase of total electric conductivity of material thanks to tunneling electrons through area adjacent to point contact and by conservation of thermopower and thermal conductivity of point contact. Results of calculations are discussed.

Introduction

The quantum-point contact (QPC) may play a central role in development of high efficiency thermoelectric materials. Possibility of increasing the thermoelectric figure of merit $ZT = T \cdot \alpha^2 \cdot \sigma / (\kappa_{el} + \kappa_{ph})$, where α - the Seebeck coefficient, σ - the electrical conductivity, and κ_{el} and κ_{ph} - the electron and phonon thermal conductivities, is connected with increasing of the effective area contact for electrons thanks to tunneling electrons through vacuum gap surrounding the physical area of QPC [1]. In this paper we proposed the simple model for calculations of characteristics of material composed of spherical nanoparticles with point contacts.

Model of material

The model of material is presented on Fig. 1 a).

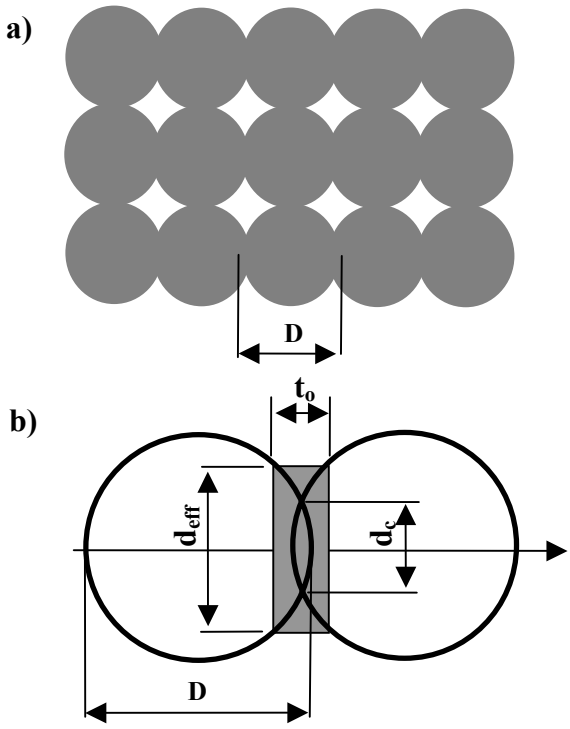

Fig. 1. a) Model of thermoelectric material composed of spherical nanoparticles (balls) and point contacts. b) Unit cell of material consisted of semiconductor ball and QPC.

Material can be regarded as the regular structure composed of spherical semiconductor particles (balls) with quantum-point contacts. Ball diameter and physical diameter of QPC are denoted as D and dc respectively. These values lay in range of 1-300 nm. So as $dc < D << \lambda e$, where λe – the mean free path of electrons, we can regard the material as combination of long one-dimension nanowires (1D nanowires) with variable diameter from dc to D in direction of electric current flow. Also we can divide each nanowire into a number of unit cells consisted of one ball

and one QPC (dashed area on Fig. 2 b)) connected in series. Calculations can be performed only for one unit cell. It is justified by the next reasons: the probability of electron propagation through QPC is very small and most electrons inside each ball are in thermal equilibrium. Propagation of electrons through QPC can be described in ballistic regime. Electric conductance of one ball is proportional to quantum conductance $2q^2/h$. In calculations of electron transport through QPD we must use effective diameter of contact deff > dc thanks to tunneling electrons through vacuum gap surrounding the physical point contact. The value of deff may be found from Fig. 1 b), where to ≈ 0.6-0.7 nm is maximal distance that electron can pass by tunneling with the probability more than 0.95 [1].

General equations

We conduct calculations of 1D semiconductor unit cell in ballistic regime (λe >> D) like to Landauer-Buttiker formalism for metal nanowires [2].

Sharvin resistance of ball in ballistic regime is presented equation (1) [3], where the second term is the number of traverse modes of electron propagation in 1D structure:

$$Rs = \left[\frac{2 \cdot q^2}{hp} \cdot \frac{ke^2 \cdot \left(\frac{\pi}{4} \cdot D^2 \right)}{4 \cdot \pi} \right]^{-1} = \left(\frac{\pi^2 \cdot m \cdot E \cdot D^2}{2 \cdot hp^2} \right)^{-1}$$

where hp – Plank constant, q –electron charge, ke – electron wave vector and E – electron energy.

Number of channels in 1D structure can be expressed by staircase function of Nch(D) at mean electron energy E=Kb·T, where Kb – Boltzmann constant and T – absolute temperature:

$$Nch(D) := floor\left(\frac{1}{2} \cdot \frac{\pi^2}{hp^2} \cdot m \cdot Kb \cdot T \cdot D^2 \right).$$

Expressions for electric current and energy flux through 1D structure can be presented as:

$$I = \int_0^\infty q \cdot ve \cdot (fl(E) - fr(E)) \cdot g(E) \cdot Nch(D) \cdot T(E)\, dE$$

$$Q = \int_0^\infty ve \cdot E \cdot (fl(E) - fr(E)) \cdot g(E) \cdot Nch(D) \cdot T(E)\, dE$$

where $ve(E) = (2E/m)^{1/2}$ – electron group velocity, $g(E) = (m/2E)^{1/2}/hp$ – density of states, T(E) – coefficient of electron transmission, fl(E) and fr(E) – Fermi-Dirac function on the left and right sides from QPC respectively at different values of temperature and potential:

$$fl(E) = \frac{1}{e^{\frac{E-Ef}{Kb \cdot T}} + 1}, \quad fr(E) = \frac{1}{e^{\frac{E-Ef-q \cdot \Delta V}{Kb \cdot (T+\Delta T)}} + 1}.$$

In linear response regime electric conductance, heat conductance connected with electron flow and the thermopower coefficient (the Seebeck coefficient) in confined structure are determined by the next equations:

$$\sigma(D,\eta) = \frac{2 \cdot q^2}{hp} \cdot Nch(D) \cdot M0(\eta),$$

$$\kappa e(D,\eta) = \frac{2 \cdot Kb^2 \cdot T \cdot Nch(D)}{hp} \cdot \left(M2(\eta) - \frac{M1(\eta)^2}{M0(\eta)} \right),$$

$$\alpha(\eta) = \frac{Kb}{q} \cdot \left(\frac{M1(\eta)}{M0(\eta)} - \eta \right),$$

where x = E/Kb·T and η = Ef/Kb·T – dimensionless electron energy and Fermi energy respectively

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

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

$$M2(\eta) = \int_0^\infty \frac{T(x) \cdot x^2 \cdot \exp(x-\eta)}{(\exp(x-\eta)+1)^2} dx.$$

Ball characteristics

Ball characteristics σb(D, η), κeb(D, η) and αb(η) were calculated with help of the above equations at T(E) = 1.

Full ball heat conductance is equal to sum of electron and phonon heat

conductance:

$$\kappa b(D,\eta) = \kappa eb(D,\eta) + \kappa ph\_b(D),$$

where κph_b as function of D and mean free path of phonons λph that can be presented as in [4]:

$$\kappa ph\_b(D) = \frac{\kappa o \cdot D}{\left(1 + \frac{\lambda ph}{D}\right)},$$

where κo – heat conductivity of bulk semiconductor material.

QPC characteristics

Effective diameter of QPC deff by simple geometrical reasoning (Fig. 2) is equal to:

$$deff(dc,D) = \sqrt{dc^2 + 2\cdot to\cdot\sqrt{D^2 - dc^2} - to^2}.$$

Coefficient of electron transmission T(E) for plane electron wave falling on point contact of diameter deff can be derived by transformation of formula for Fraunhofer diffraction of light on round aperture. We must replace wave vector of light kphoton on wave vector of electron ke = $2\cdot\pi\cdot(2mE)^{1/2}/hp$ in Fraunhofer formula and complete integration on solid angle in all space behind the point contact. For Tc(E) we have:

$$Tc(dc,D,x) = 2\left(\frac{deff}{D}\right)^2\cdot\int_0^{\frac{\pi}{2}}\frac{J1\left[\frac{deff}{hp}\cdot\sqrt{\frac{m}{2}\cdot(KbT)}\cdot x\cdot\sin(\theta)\right]^2}{\sin(\theta)}\,d\theta \quad (12)$$

QPC characteristics σc(D, η), κec(D, η) and αc(η) were calculated with help of equations.

Full QPC heat conductance is equal to sum of electron and phonon heat conductance:

$$\kappa c(dc,D,\eta) = \kappa ec(dc,D,\eta) + \kappa ph\_c(dc) \quad (13)$$

where

$$\kappa ph\_c(dc) = \frac{\kappa o}{\left(\gamma\left(\frac{\lambda ph}{dc}\right)\cdot\frac{1}{dc} + \frac{16\cdot\lambda ph}{3\cdot\pi\cdot dc^2}\right)}.$$

where γ(λph/dc) is a slowly varying function with γ(0) = 1 and γ(∞) = 0.694. Simple expression for κph_c(dc) was confirmed by molecular dynamic simulation of thermal transport at a nanometer scale constriction [5].

Characteristics of unit cell

Characteristic of unit cell can be simply derived by adding of separate inverse values for circuit of ball and QPC connected in series:

$$\sigma u(dc,D,\eta) = \left(\frac{1}{\sigma c(dc,D,\eta)} + \frac{1}{\sigma b(D,\eta)}\right)^{-1},$$

$$\kappa u(dc,D,\eta) = \left(\frac{1}{\kappa c(dc,D,\eta)} + \frac{1}{\kappa b(D,\eta)}\right)^{-1},$$

$$\alpha u(dc,D,\eta) = \frac{\alpha c(dc,D,\eta)\cdot\kappa b(D,\eta) + \alpha b(\eta)\cdot\kappa c(dc,D,\eta)}{\kappa b(D,\eta) + \kappa c(dc,D,\eta)}$$

Characteristics of material composed of balls with QPC

Bulk material characteristics (electric conductivity σ(dc,D,η), thermal conductivity κ(dc,D,η), thermopower α(dc,D,η) and figure of merit Z(dc,D,η)·T) are presented by the next equations:

$$\sigma(dc,D,\eta) = \frac{\sigma u(dc,D,\eta)}{\sqrt{D^2 - dc^2}},$$

$$\kappa(dc,D,\eta) = \frac{\kappa u(dc,D,\eta)}{\sqrt{D^2 - dc^2}},$$

$$\alpha(dc,D,\eta) = \frac{\alpha c(dc,D,\eta)\cdot\kappa b(D,\eta) + \alpha b(\eta)\cdot\kappa c(dc,D,\eta)}{\kappa b(D,\eta) + \kappa c(dc,D,\eta)},$$

$$Z(dc,D,\eta)\cdot T = T\cdot\frac{\sigma(dc,D,\eta)\cdot\alpha(dc,D,\eta)^2}{\kappa(dc,D,\eta)}.$$

For obtaining σ(dc,D,η) and κ(dc,D,η) we sum up unit cells in parallel and in series with period $(D^2 - dc^2)^{1/2}$.

Results of calculations

We carried out calculations of basic thermoelectric characteristics in the following assumptions: effective electron mass m = 0.5mo, T = 300 K and λph = 10 nm.

The calculated results is valid for 1D structures when its characteristic dimensions lay in the nanometer range

(diameter of spherical particles D = 10 – 300 nm and diameter of point contact dc = (0 – 0.5)·D).

The results of calculations are presented on Fig. 2-6.

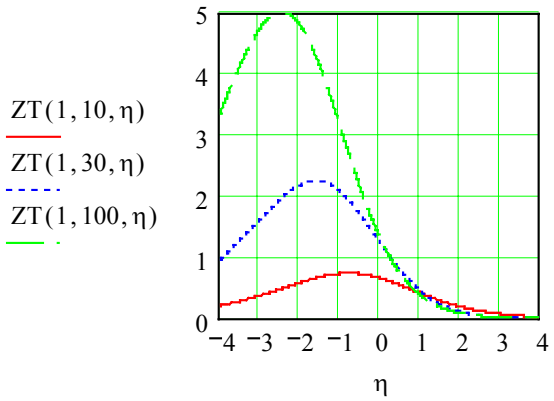

Fig. 2. Dependence of ZT(dc,D,η) on reduced Fermi energy η for diameter of physical point contact dc = 1 nm and particle diameter D = 10, 30 and 100 nm.

With the increase of particle diameter D the maximum of figure of merit increases and move to lower values of Fermi energy.

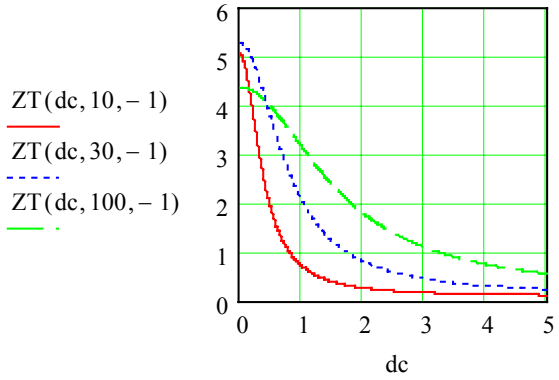

Fig. 3. Dependence of ZT(dc,D,η) on diameter of physical point contact dc in nm for reduced Fermi energy η = 0 and particle diameter D = 10, 30 and 100 nm.

The figure of merit is monotone decreasing function against diameter of point contact dc.

Electric conductivity of material increases with the growth of Fermi Energy and point contact diameter, but remains lower the bulk material conductivity by 2-3 order of magnitude.

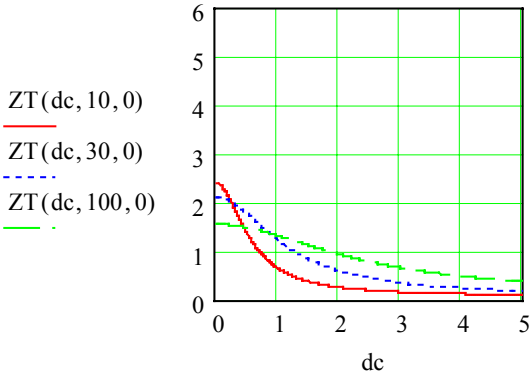

Fig. 4. Dependence of ZT(dc,D,η) on diameter of physical point contact dc in nm for reduced Fermi energy η = 0 and particle diameter D = 10, 30 and 100 nm.

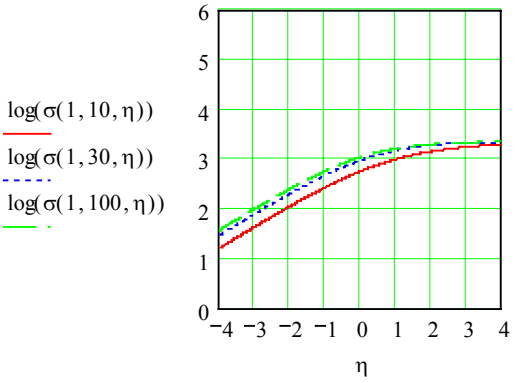

Fig. 5. Dependence of electric conductivity σ(dc,D,η) on reduced Fermi energy η for diameter of physical point contact dc = 1 nm and particle diameter D = 10, 30 and 100 nm.

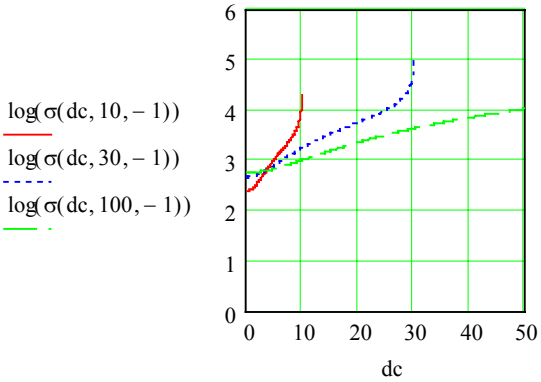

Fig. 5. Dependence of electric conductivity σ(dc,D,η) in 1/Ω.m on diameter of physical point contact dc in nm for reduced Fermi energy η = – 1 and particle diameter D = 10, 30 and 100 nm.

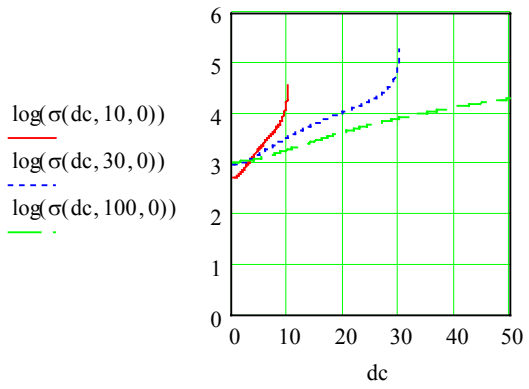

Fig. 6. Dependence of electric conductivity σ(dc,D,η) in 1/Ω.m on diameter of physical point contact dc in nm for reduced Fermi energy η = 0 and particle diameter D = 10, 30 and 100 nm.

Conclusions

In comparison with bulk thermoelectric material the figure of merit Z·T of material made of nanopowders in definite range of variables is greater by 1.5-5.2 times, but electric conductivity is lower by 2-3 orders of magnitude. High value of Z·T is connected with the excess of QPC effective diameter over the diameter of physical contact and consequently domination of electron flow over phonon flow.

The figure of merit reaches maximum values in flat structures in which layers of thermoelectric material are separated by thin (<0.6-0.7 nm) vacuum gaps [1]. In such structures the component of phonon conductivity is fully eliminated. From practical point of view creation of such structures is impossible. The best way of approach to flat structures is the manufacturing of structures with point contacts. Maximum reliability and reproducibility of point contacts can be realized in technology with application of nanopowders.

Proposed model allows optimize characteristics of thermoelectric materials composed of spherical nanoparticles with quantum point contacts in dependence on particle diameter, physical point contact diameter and value of Fermi energy.

References

1. A.I, Holopkin, V.N. Abrutin, V.A. Romanko, P.V. Miroevskiy at al., “Theoretical estimation of characteristics of thermoelectric materials made of nanopowders”, Proceeding of The 5-th European Conference on Thermoelectrics (ECT 2007), Odessa, Ukraine, September 10-12, 2007, pp. 229-233.
2. T. Dittrich, P. Hangii at al., Quantum Transport and Dissipation (Wiley-VCH, Weinhein, 1998).
3. Yu.V. Sharvin, Zh. Eksp. Teor. Fiz 48, 984.
4. G. Wexler, Proc. Phys. Soc., London, 89, 927 (1966).
5. Sanjoy K. Saha and Li Shi, Journal of Applied Physics, 101, 074304 (2007).