L.N.Vikhor

L.N. Vikhor, P.V. Gorsky

Institute of Thermoelectricity of the NAS and MES of Ukraine, 1, Nauky Str.,
Chernivtsi, 58000, Ukraine

P.V.Gorsky

ELECTRICAL RESISTANCE OF THERMOELECTRIC MATERIAL-METAL CONTACT

In the framework of percolation theory in the model of the Anderson chart of random links calculated is the bulk resistance and thermoEMF of transient contact layer "thermoelectric material (TEM)-metal" as a semiconductor material with diffused metal particles. Optimal diffusion profile of metal particles in transient layer is determined from considerations of maximum power factor. Following this, the electrical contact resistance is calculated both for a perfect collection and with regard to different from unity collection coefficient of metal connecting electrode. With a perfect collection it turns out that the value of contact resistance of soldered contacts for the most common solders in thermoelectricity does not exceed $9\cdot10^{-7}$ Ohm·cm^2. With regard to collection coefficient of metal electrode it turns out that for the considered solders and TEM the electrical contact resistance does not exceed $2.0\cdot10^{-4}$Ohm·cm^2. The main reason for a drastic reduction of this resistance value in the framework of existing theoretical approaches is neglect of the fact of smallness of connecting electrode collection coefficient.

Key words: contact, soldering, contact resistance, transient layer, percolation theory, diffusion profile, screening length, density of conducting dislocations, collection coefficient

Introduction

Thermal and electrical contact resistances are essential parameters of thermoelectric devices producing a dramatic effect on their final characteristics, such as generated power, efficiency, etc. At the same time, theory of thermoelectricity lacks approaches that would reliably estimate these resistances and experimental methods of their measurement often suffer from too many errors. Owing to this fact, designers of thermoelectric devices are forced to “assign” certain “guess” values of these resistances to ensure a satisfactory agreement between the predicted output parameters of devices and the experimentally observed ones.

In the framework of existing theoretical approaches [1, 2] the electrical contact resistances for the most part considered as “emission” ones, are often drastically underrated as compared to these “guess” or “experimental” values. Eventually, these resistances are calculated by rather simple formula:

$$\rho_c = \rho_b d\,, \tag{1}$$

where ρ_b is the bulk resistance of transient layer, d – its thickness. However, this formula is valid only in the case when connecting electrode ideally collects charge carriers, i.e. its entire area is active. In fact, this is by no means always the case, so formula (1) must be modified, i.e. written in the form:

$$\rho_c = \frac{\rho_b d}{K_c}\,. \tag{2}$$

In this formula, K_c is coefficient of charge carrier collection which, as it will be clear from the subsequent, is considerably lower than unity. Thus, the purpose of this paper is to estimate TEM-metal contact resistance with and without consideration of collection coefficient.

Analysis of a physical model of transient layer

A physical model of transient layer is shown in Fig.1.

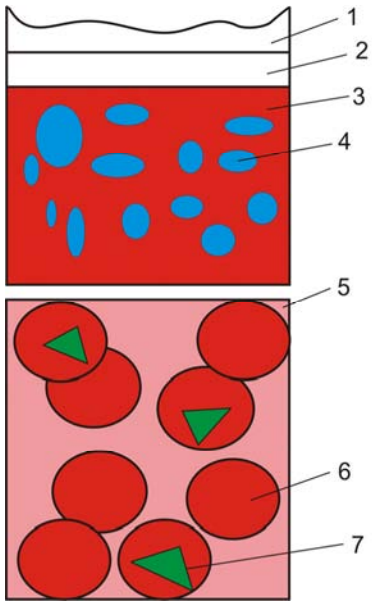

Fig.1. A physical model of transient layer:1-connecting electrode;2-barrier layer, 3-TEM;4-diffused metal particles;5-interface plane; 6-Debye sphere; 7-conducting dislocation perpendicular to interface.

This model takes into account diffusion of metal particles in TEM, and the lower part of the figure serves to explain the physical meaning of collection coefficient (see below). Their electric resistivity will be assumed to be equal to the electric resistivity of metal. Thus, transient layer can be regarded as TEM with metal particles distributed in the depth. Collection coefficient K_c is determined by the possibility of reaching the connecting electrode by charge carriers owing to their motion along conducting dislocations perpendicular to interface. But due to shielding of electrostatic attraction between the dislocation and charge carriers, only those carriers can arrive at it that are at a distance from the dislocation line which does not exceed the Debye shielding length. Thus, if each Debye sphere within the area of connecting electrode has one or more dislocations, collection is perfect. As to the figure, it corresponds to imperfect collection, i.e. to the case of $K_c < 1$. Owing to this, we first determine contact resistance at $K_c = 1$, and then correct it on the basis of the results of calculation of K_c.

Calculation of contact resistance with a perfect collection

To calculate contact resistance, we must first determine the electric resistivity of transient layer. For this purpose we will need the ratio determining the distribution of metal particles in the depth of the layer. It can be rigorously found only from diffusion equation, however, to write, the more so to solve this equation for the real process of creating a contact, for instance, by soldering method, is rather difficult. Therefore, we will use a simplified simulation approach and write the distribution $p(x)$ of a relative volumetric share of metal particles in a transient layer as follows:

$$p(x) = 1 - (x/d)^{\delta}. \tag{3}$$

"Shape parameter" δ characterizes "blurring" of transient layer. The value $\delta = 0$ corresponds to the absence of transient layer, i.e. to a perfect flat TEM-metal contact with a sharp boundary, and the value $\delta \to \infty$ corresponds to full substitution of transient layer by metal. The value $\delta = 1$ corresponds to the case of steady-state diffusion of metal in TEM with a constant diffusion factor.

With this distribution, the bulk kinetic coefficients of transient layer, namely electrical conductivity σ, thermal conductivity κ and thermoEMF α in the framework of percolation theory [3, 4] can be determined as:

$$\begin{pmatrix} \sigma \\ \kappa \end{pmatrix} \Big/ \begin{pmatrix} \sigma_M \\ \kappa_M \end{pmatrix} = \int_0^1 0.25\left(R - 3p^{\delta} - n_{\sigma,\kappa} + 3n_{\sigma,\kappa}p^{\delta} + 2\right)dp, \tag{4}$$

$$\alpha = \int_0^1 \frac{\left(1-p^{\delta}\right)\sigma_M\alpha_M\left(2\sigma+\sigma_{TE}\right)\left(2\kappa+\kappa_{TE}\right) + p^{\delta}\sigma_{TE}\alpha_{TE}\left(2\sigma+\sigma_M\right)\left(2\kappa+\kappa_M\right)}{\left(1-p^{\delta}\right)\sigma_M\left(2\sigma+\sigma_{TE}\right)\left(2\kappa+\kappa_{TE}\right) + p^{\delta}\sigma_{TE}\left(2\sigma+\sigma_M\right)\left(2\kappa+\kappa_M\right)}dp. \tag{5}$$

where:

$$R = \sqrt{9n_{\sigma,\kappa}^2 p^{2\delta} - 6n_{\sigma,\kappa}^2 p^{\delta} + n_{\sigma,\kappa}^2 - 18n_{\sigma,\kappa}p^{2\delta} + 18n_{\sigma,\kappa}p^{\delta} + 4n_{\sigma,\kappa} + 9p^{2\delta} - 12p^{\delta} + 4}, \tag{6}$$

In formulae (4) – (6), $\sigma_M, \sigma_{TE}, \kappa_M, \kappa_{TE}, \alpha_M, \alpha_{TE}$ are electrical conductivities, thermal conductivities and thermoEMF of metal and thermoelectric material, respectively, $n_{\sigma} = \sigma_{TE}/\sigma_M$, $n_{\kappa} = \kappa_{TE}/\kappa_M$.

Analysis shows that for given parameters of TEM and metal there is such a value of diffusion profile "shape parameter" δ_0 whereby maximum power factor $P = \alpha^2\sigma$ is achieved. In so doing, maximum thermoelectric figure of merit need not be achieved, since the ratio of electrical conductivity to thermal conductivity is weakly dependent on δ, and thermoEMF value with increase in δ is decreased, as long as replacement of semiconductor by metal should reduce it. Therefore, the resistivity of "optimized in power factor" contact layer is:

$$\rho_{b0} = \left[\sigma_M \int_0^1 0.25\left(R_0 - 3p^{\delta_0} - n_{\sigma} + 3n_{\sigma}p^{\delta_0} + 2\right)dp\right]^{-1}, \tag{7}$$

where:

$$R_0 = \sqrt{9n_{\sigma}^2 p^{2\delta_0} - 6n_{\sigma}^2 p^{\delta_0} + n_{\sigma}^2 - 18n_{\sigma}p^{2\delta_0} + 18n_{\sigma}p^{\delta_0} + 4n_{\sigma} + 9p^{2\delta_0} - 12p^{\delta_0} + 4}. \tag{8}$$

Hence, with a perfect collection contact resistance is equal to $\rho_{b0}d$.

Correction of contact resistance with regard to collection coefficient

Traditionally [5, 6], collection coefficient is determined by the formula:

$$K_c = \pi L_D^2 N_D. \tag{9}$$

In this formula, L_D is the Debye shielding length of electric potential, N_D is the density of conducting dislocations perpendicular to interface. This formula for collection coefficient has a simple physical meaning. Namely, collection coefficient is nothing but the averaged number of conducting dislocations in the electrode area perpendicular to interface and nevertheless getting into the Debye sphere of electrical potential shielding, which quite fits the above analyzed physical model. From the solution of the Poisson equation for a system of major charge carriers in TEM in the approximation linear in desired potential with regard to degeneracy degree follows the expression for L_D:

$$L_D^2 = \frac{\varepsilon\varepsilon_0 h^3}{8\pi\sqrt{2kT}e^2 m^{*3/2}}\left[\int_0^\infty \frac{\sqrt{x}\exp(x-\eta)}{\exp(x-\eta)+1}dx\right]^{-1}, \quad (10)$$

Parameter η characterizing chemical potential of free charge carrier system is found from the equation:

$$n_0 = \frac{8\pi\sqrt{2}\left(m^* kT\right)^{3/2}}{h^3}\int_0^\infty \frac{\sqrt{x}}{\exp(x-\eta)+1}dx\,. \quad (11)$$

In formulae (10) – (11), ε is dielectric constant of TEM, T is absolute temperature, n_0 is the bulk concentration of charge carriers in TEM, m^* is density-of-state effective mass, the rest of notations are generally accepted.

Calculation of contact resistance value

Let us apply the obtained general results to evaluation of the electrical resistance of TEM-metal contact created by soldering method. We will take into account the fact that at present soldering for creation of contacts in the manufacture of thermoelectric modules is done by such solders as eutectic alloys of bismuth with tin (melting temperature 135°C) or lead with tin (181°C), as well as pure tin (230°C), or tin with small additions of silver (217°C) or antimony (240°C). Let us determine the expected electric resistances of contacts obtained at soldering with these solders. In so doing, the influence of anti-diffusion sublayer will be ignored. Solder parameters which are necessary for the calculation, namely electric conductivity, thermal conductivity and thermoEMF also will be determined in the framework of percolation theory, based on their composition and known parameters of their constituent elements. We have to do it, since the reliable values of *all* kinetic coefficients of solders are unknown.

The plots of dependences of power factor on diffusion profile shape parameter and optimal diffusion profiles of transient layers for different TEM-solder pairs with regard to TEM parameters [7] and calculated parameters of solders are shown in Fig. 2-6.

The expected values of contact resistances for the above contact pairs at thicknesses of "optimized layers" equal to 25μm are given in Table 1.

We see that the obtained estimates of contact resistance with a perfect collection are more than an order higher than those proposed, for instance, in [1, 2]. Therefore, it seems reasonable to compare them to certain experimental data. For instance, in [8] it is shown that by doping of a near-contact layer in materials of $(Bi, Sb)_2(Se,Te)_3$ system donor impurities of iodine or acceptor impurities of silver one can obtain for *p* and *n*-type materials the electrical contact resistances of the order of $2.7\cdot10^{-7}$ and $4.5\cdot10^{-7}$ Ohm·cm^2, respectively. Thus, in this case a transient layer is close to optimal, and collection coefficient – to unity. On the other hand, the values of contact resistance obtained with regard to difference of collection coefficient from unity are approximately in the limits given in [1], where it is mentioned that soldered contacts have resistances of the order of 10^{-4} Ohm·cm^2 or less.

In this case the resistance of "metal" part of the contacts, i.e. solder-copper pairs, can be ignored. As regards comparison of the results to some other experimental data, note that the reference book [9] for soldered contacts of similar thermoelectric material with copper indicates electrical contact resistance of the order of 10^{-5} Ohm·cm^2 or less. On the other hand, contact resistance measurements by "block" method in thermoelectric cooling mode [10] show that with the aid of improved processes of soldered contacts creation this resistance can be reduced at 300 K to $1.3\cdot10^{-6}$ Ohm·cm^2 for *p*-type Bi_2Te_3 and

$1.12\cdot10^{-6}$ Ohm·cm^2 for *n*-type Bi_2Te_3, which is close to "perfect" calculated contact resistance of $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-*Bi-Sn* pair corresponding to $K_c = 1$.

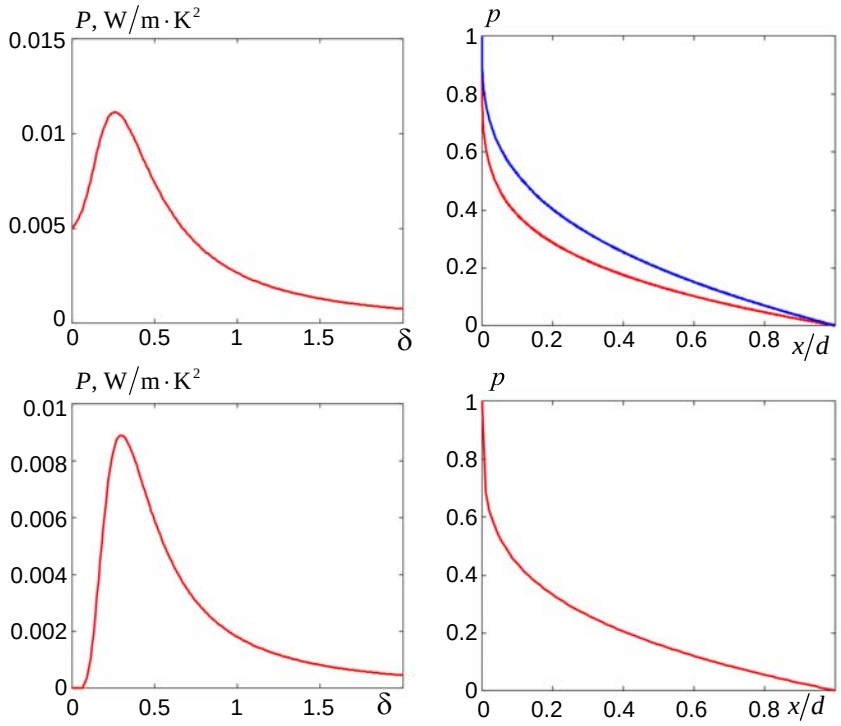

Fig. 2. Dependence of power factor on shape parameter (a) and optimal diffusion profile (b) for contact pair $Bi_{0.5}Sb_{1.5}Te_3$-Sn; c, d- the same dependences for contact pair $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Sn. Two curves in Fig.2b and subsequent similar figures denote that optimum is attained not at one δ value, but in a certain interval wherein power factor changes slowly.

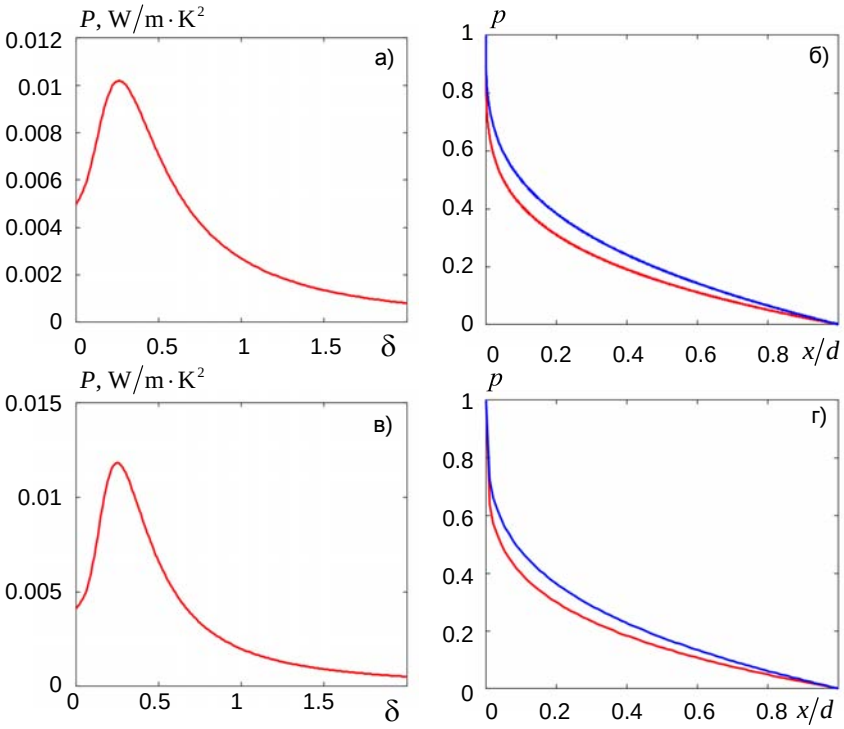

Fig.3. The same dependences as in Fig.2, but for contact pairs $Bi_{0.5}Sb_{1.5}Te_3$-Sn-Pb (a,b) and $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Sn-Pb (c,d).

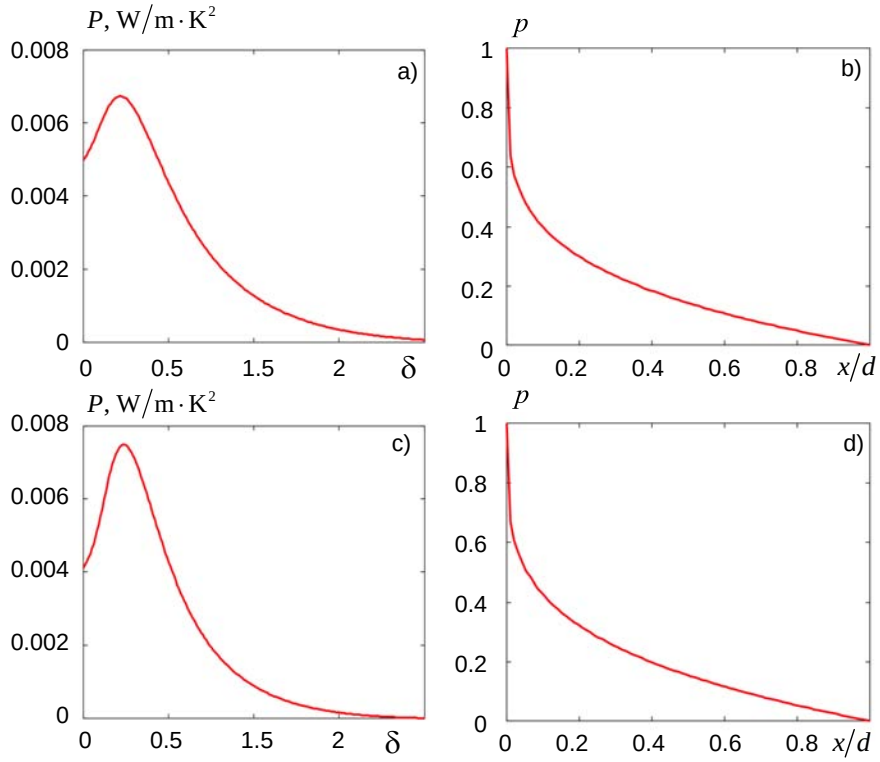

Fig. 4. The same dependences as in Fig. 2, but for contact pairs $Bi_{0.5}Sb_{1.5}Te_3$ -Bi-Sn (a, b) and $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Bi-Sn (c, d).

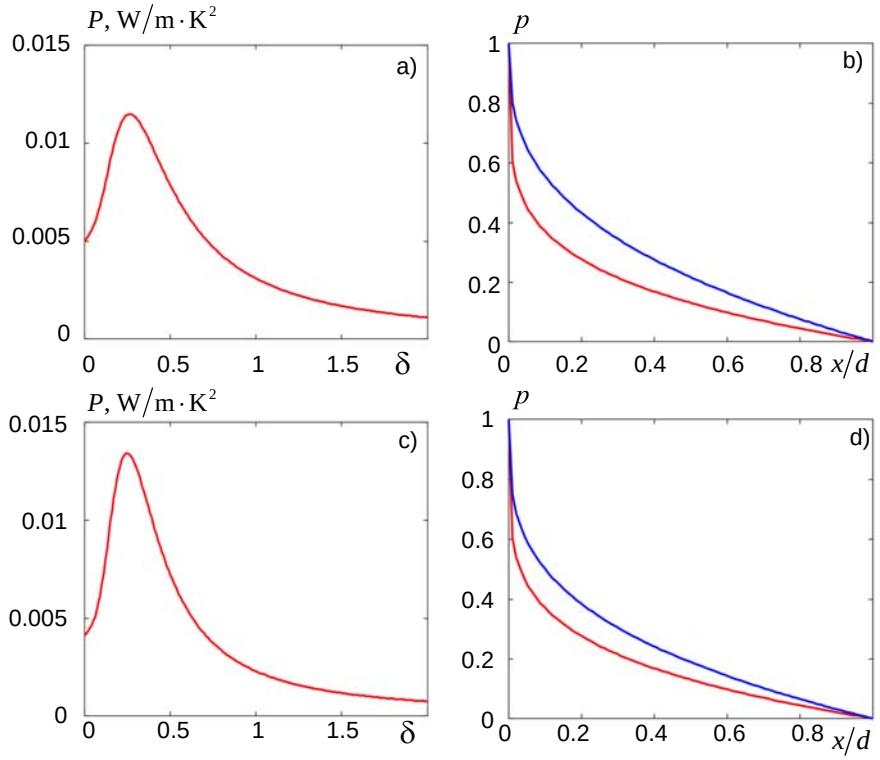

Fig. 5. The same dependences as in Fig. 2, but for contact pairs $Bi_{0.5}Sb_{1.5}Te_3$ –(Sn+Ag) (a, b) and $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-(Sn+Ag) (c, d).

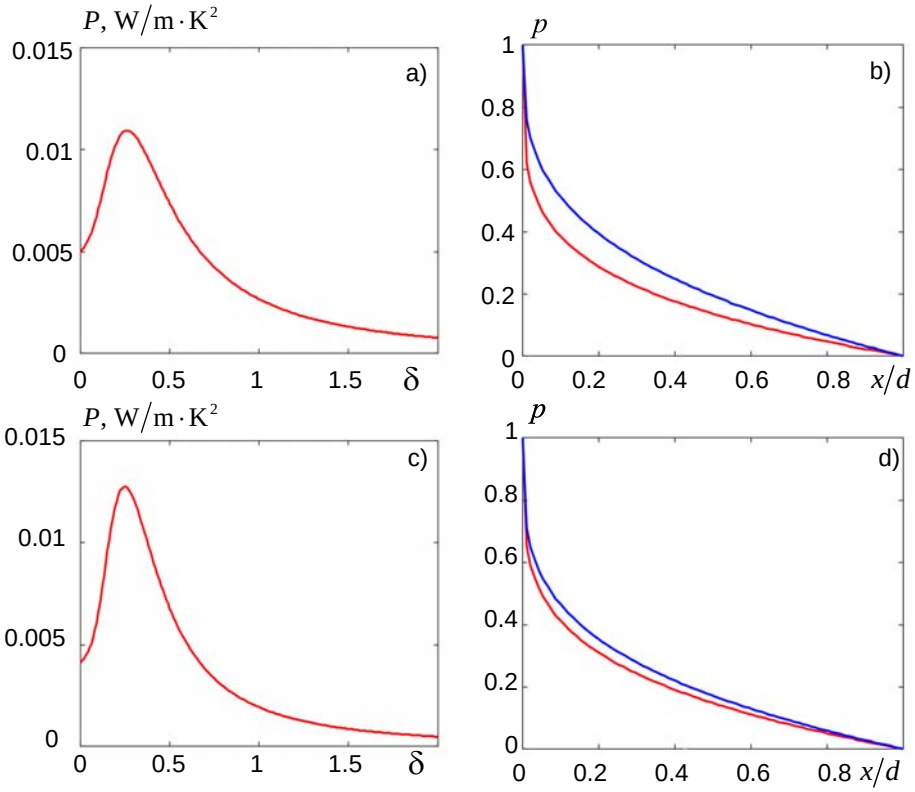

Fig.6. The same dependences as in Fig. 2, but for contact pairs $Bi_{0.5}Sb_{1.5}Te_3$–(Sn+Sb) (a, b) and $(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-(Sn+Sb) (c, d).

Table 1.

Expected values of contact resistances

Contact pair	Contact resistance in Ohm·cm²	
	With a perfect collection	With collection coefficient lower than 1
$Bi_{0.5}Sb_{1.5}Te_3$-Sn	$(2.70\text{-}4.63)\cdot10^{-7}$	$8.45\cdot10^{-5}\text{-}1.45\cdot10^{-4}$
$(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Sn	$3.64\cdot10^{-7}$	$4.74\cdot10^{-5}$
$Bi_{0.5}Sb_{1.5}Te_3$-Sn-Pb	$(3.26\text{-}4.48)\cdot10^{-7}$	$(1.02\text{-}1.40)\cdot10^{-4}$
$(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Sn-Pb	$(4.58\text{-}6.67)\cdot10^{-7}$	$(5.96\text{-}8.69)\cdot10^{-5}$
$Bi_{0.5}Sb_{1.5}Te_3$-Bi-Sn	$6.53\cdot10^{-7}$	$2.04\cdot10^{-4}$
$(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-Bi-Sn	$9.04\cdot10^{-7}$	$1.18\cdot10^{-4}$
$Bi_{0.5}Sb_{1.5}Te_3$-(Sn+Ag)	$(2.35\text{-}4.81)\cdot10^{-7}$	$7.33\cdot10^{-5}\text{-}1.50\cdot10^{-4}$
$(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-(Sn+Ag)	$(3.53\text{-}6.90)\cdot10^{-7}$	$(4.60\text{-}8.99)\cdot10^{-5}$
$Bi_{0.5}Sb_{1.5}Te_3$-(Sn+Sb)	$(2.89\text{-}4.70)\cdot10^{-7}$	$9.02\cdot10^{-5}\text{-}1.47\cdot10^{-4}$
$(Bi_2Se_3)_{0.04}(Bi_{0.5}Sb_{1.5}Te_3)_{0.96}$-(Sn+Sb)	$(4.43\text{-}5.75)\cdot10^{-7}$	$(5.78\text{-}7.49)\cdot10^{-5}$

Remarks: 1) For contact pairs for which optimum is attained in a certain range of values δ, the indicated contact resistance values correspond to the ends of this range. 2) In the calculation of collection coefficients, the density of conducting dislocations perpendicular to interface was taken to be equal to $10^{11}cm^{-2}$.

Conclusions

1. The main reason for a drastic discrepancy between theoretical and observed electrical resistance values of TEM-metal contacts created by means of soldering is neglect of the fact of smallness of coefficient of charge carrier collection by metal electrode.
2. If charge carrier collection coefficient were equal to 1, the electrical resistance of TEM-metal contact created by soldering with the use of the most common solders would be $(2.35– 9.04)\cdot10^{-7}$ Ohm·cm^2.
3. With regard to collection coefficient smallness, the upper assessed value of the above contact resistance of soldered contact is $2.04\cdot10^{-4}$ Ohm·cm^2.

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References

1. L.W. Da Silva, M. Kaviany, Micro-Thermoelectric Cooler: Interfacial Effects on Thermal and Electrical Transport, *Int. J. Heat and Mass Transfer* **478,** 2417-2435 (2004).
2. L.I. Anatychuk, V.K. Dugaev, V.I. Litvinov, and V.L. Volkov, Contact Resistance between Metal and Thermoelectric Material, *J.Thermoelectricity* **1**, 70-77 (1994).
3. J. Zaiman, *Disorder Models* (Moscow: Mir, 1982), 592 p.
4. A.A. Snarskii, M.I. Zhenirovsky, and I.V. Bezsudnov, On the Wiedemann-Franz Law in Thermoelectric Composites, *J.Thermoelectricity* **3**, 59-65 (2006).
5. A.V. Sachenko, A.E. Belyaev, N.S. Boltovets, V.N. Ivanov, R.V. Konakova, Ya.Ya. Kudrik, L.A. Matveeva, V.V. Milenin, S.V. Novitsky, and V.N. Sheremet, Effect of Microwave Irradiation on the Resistance of Au-TiB_x-Ge-Au-n-n$^+$-n^{++}-GaAs(InP) Ohmic Contacts, *Semiconductors* **46**(4), 558-561 (2012).
6. T.V. Blank, Yu.A. Goldberg, and E.A. Popov, Current Flow along Metal Shunts in Ohmic Contacts to Wide-Gap Semiconductors $A^{III}B^{V}$, *Semiconductors* **43**(9), 1204-1209 (2009).
7. L.D.I vanova, Yu.V. Granatkina, A. Dauscher, B. Lenoir, and H. Sherrer, Influence of the Purity and Perfection of Czochralski-Grown Single Crystals of Bismuth and Antimony Chalcogenides Solid Solution on their Thermoelectric Properties, *Proc. of 5th European Workshop on Thermoelectrics (Pardubice, Czech Republic, 1999), p.175-178.*
8. P.J. Taylor, J.R. Maddux, G. Meissner, R. Venkatasubramanian, G. Bulman, J. Piers, R. Gupta, J. Biershenk, C. Caylor, J. D'Angelo, and Zh. Ren, Controlled Improvement in Specific Contact Resistivity for Thermoelectric Materials by Ion Implantation, *Appl. Phys. Let.* **103** (043902), 1-4 (2013).
9. L.I. Anatychuk, *Thermoelements and Thermoelectric Devices*, *Reference Book* (Kyiv: Naukova Dumka, 1979), 764 p.
10. R.P. Gupta, R. McCarty, and J. Sharp, Practical Contact Resistance Measurement Method for Bulk Bi_2Te_3 Based Thermoelectric Devices, *J. El. Mat.*,Oct.2013, doi 10.1007/s11664-013-2806-6.

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