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CONTACT RESISTANCE DUE TO POTENTIAL BARRIER AT THERMOELECTRIC MATERIAL–METAL BOUNDARY

The theoretical aspects of estimating the resistance due to carriers passing through a potential barrier at the boundary between thermoelectric material and metal are considered. The temperature dependences of boundary resistivity were calculated for thermoelectric legs of Bi_2Te_3 based materials with the deposited anti-diffusion nickel layers. It was established that the value of boundary resistance in such legs varies with temperature from $0.5\cdot10^{-7}$ to $2.5\cdot10^{-7}$ $Ohm\cdot cm^2$. It was shown that boundary resistance can be reduced by increasing carrier concentration in the ultra-thin nickel contact layer of thermoelectric material due to doping. It was established that increasing the concentration of doping impurities in the near-contact zone by one order of magnitude with respect to its optimal value results in decreasing electrical boundary resistance by two orders. Under these conditions, the resistance value approaches minimum possible value and is 10^{-9} $Ohm\cdot cm^2$. Bibl. 35, Fig. 6, Tabl. 1.

Key words: thermoelectric material-metal contact, potential barrier, electrical boundary resistance.

Introduction

The efficiency of thermoelectric modules is mainly determined by the figure of merit of semiconductor materials of which the thermoelement legs are made. However, the efficiency of a real thermoelement essentially depends on the electrical resistance of a contact between semiconductor material and metal interconnect layers [1 – 3] connecting the thermoelectric legs of module. The Joule heat released in the contact zone reduces the energy efficiency of thermoelectric converters and leads to its dependence on the height of the thermoelement legs [4]. The negative influence of contact resistance on the characteristics of thermoelectric devices is especially perceptible in the conditions of miniaturization of the thermoelement legs, when the thickness of the transient contact layer between thermoelectric material (TEM) and metal becomes commensurate with the height of the thermoelement leg, and the contact resistance commensurate with the resistance of the leg itself [5,6].

The miniaturization of thermoelectric energy converters is a modern direction of their improvement, aimed primarily at reducing the cost of thermoelectric materials and cheapening due to this of thermoelectric modules [6-12]. Therefore, reducing the value of contact resistance to increase the energy efficiency of thermoelectric converters in miniaturization is an urgent task.

In [13], a model of TEM-metal contact structure was considered. It was shown that the contact resistance is formed by its two main components. This is, first, the electrical resistance of the transient layer at the boundary between semiconductor material and metal. This resistance depends on such factors as mutual diffusion of atoms or molecules of contacting materials, their chemical interaction, which results in the formation of new phase [14,15] and even multilayer [16,17] microstructures. Also, some action is exerted by the non-ideality of TEM-metal boundary which is due to roughness, chemical contamination of leg surface prior to deposition of metal thereupon, and other factors [18-20]. Modern technologies of manufacturing TEM-metal contacts, in particular in micromodules, by spraying, chemical deposition of anti-diffusion metal layers on the cleaned, polished and specially treated ends of thermoelectric legs allow minimizing the height of the transient layer and, therefore, its electrical resistance, and to obtain actually "ideal" (without transient layer) TEM-metal boundary. However, the sharp difference between the energy band structures of the semiconductor and the metal leads to the formation of a potential barrier at the TEM-metal boundary [21]. A potential barrier impedes the movement of current carriers across the boundary and is the cause of the second component of contact resistance, commonly called the electrical boundary resistance [22,23].

The purpose of this work is to consider theoretical methods for estimating the TEM-metal boundary resistance and the factors affecting this resistance, to calculate the potential barrier resistance for thermocouples from traditional Bi_2Te_3-based materials and to identify ways to reduce the boundary resistance to a minimum possible value.

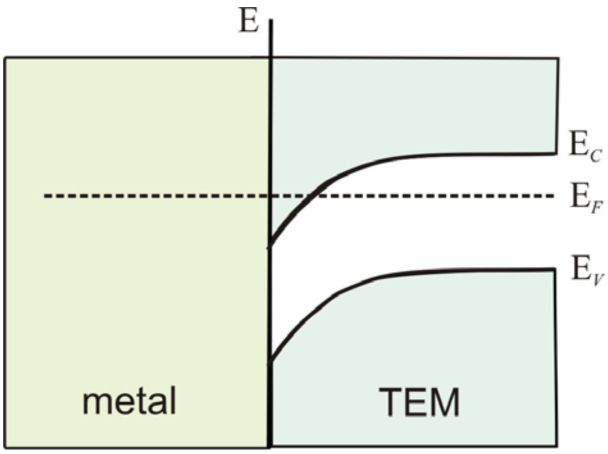
Methods for calculating the electrical resistance of TEM-metal boundary

Methods for calculating the electrical resistance due to carriers passing through semiconductor-metal boundary are described in [21-27]. We consider the main results of these works and apply them to calculate the specific, that is, related to unit area, resistance of TEM-metal boundary.

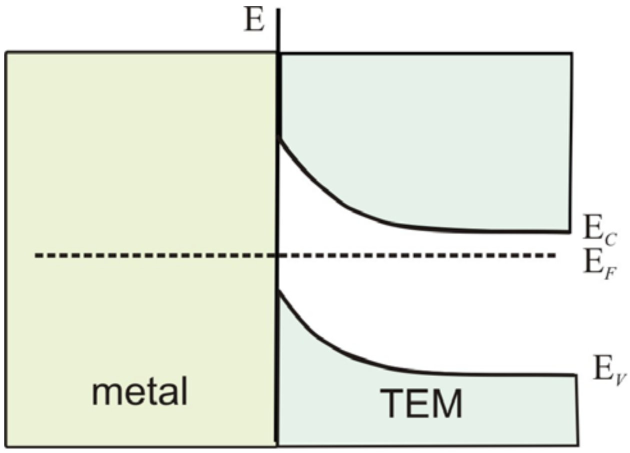
For example, consider the contact of a metal with an *n*-type semiconductor for the case of such current polarity when electrons move from metal to semiconductor. When a metal collides with a semiconductor, due to the difference between their Fermi levels, a contact potential difference arises that distorts the energy bands of the semiconductor [26]. If the difference between the Fermi levels is such that part of the electrons from metal pass to semiconductor, then the so-called anti-locking layer is created in semiconductor near the boundary and the bands are bent down (Fig.1a). It is obvious that such contact will not interfere with the movement of electrons. If, however, the difference between the Fermi levels is such that part of the electrons at the boundary will pass from semiconductor to metal, a locking layer is formed, the bands bend upwards (Fig. 1b) and a potential barrier [27] is created for electrons moving from metal to semiconductor. As noted, this barrier is the cause of the electrical boundary resistance.

The diagram of TEM-metal energy bands in the presence of a potential barrier is shown in Fig. 2. In this figure, $E_b = \varphi_m - \chi_n - \Delta\varphi_b$ is the height of potential barrier, φ_m is electronic work function, χ_n is affinity of semiconductor electrons, $\Delta\varphi_b$ is the energy of barrier reduction due to the non-ideal metal-semiconductor contact.

The electrical boundary resistance depends on the mechanism of carriers passing through the potential barrier. Carriers can overcome the potential barrier by thermionic emission over the barrier (TIE) or tunneling through the barrier. There are two types of tunneling: tunneling of carriers with energies close to the Fermi energy in a semiconductor, the so-called field emission (FE) and tunneling of carriers with higher energies, the so-called thermionic field emission (TFE) (Fig.2). [27].



a)



b)

Fig.1. Bending of semiconductor energy bands in the zone of contact with metal.
a) anti-locking layer, b) locking layer.

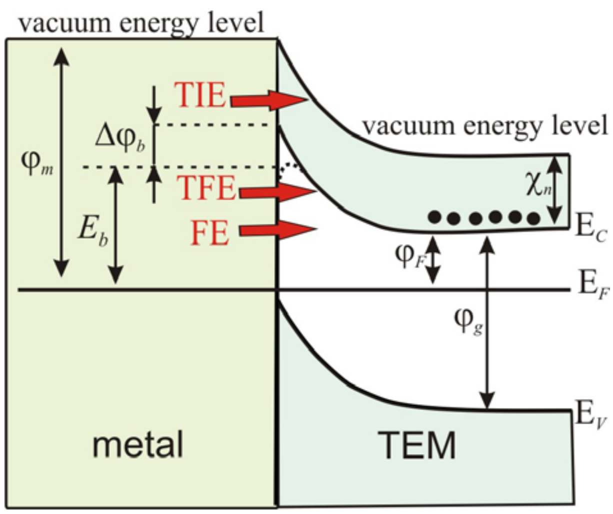


Fig.2. Diagram of energy bands of metal contact with thermoelectric n-type material.
Mechanisms of electrons passing through potential barrier:
FE – field emission, TFE – thermionic field emission,
TIE –thermionic emission.

The criterion of the mechanism for carriers passing is the ratio of thermal energy kT to parameter E_{00}, which was proposed by Padovani and Stratton [28] and is defined as

$$E_{00} = \frac{e\hbar}{2}\sqrt{\frac{N_d}{m^*\varepsilon_s\varepsilon_0}} \tag{1}$$

where e is electron charge, N_d is impurity concentration in semiconductor, m^* is the effective mass of charge carriers, ε_0 is the dielectric constant, ε_s is the relative permeability of semiconductor. Under high temperature conditions in weakly doped semiconductors, when $kT/E_{00} \gg 1$, the thermionic emission mechanism without tunneling prevails. For heavily doped (degenerate) semiconductor at low temperatures $kT/E_{00} \ll 1$, the field emission (FE) is predominant. When $kT/E_{00} \approx 1$, the thermionic field emission (TFE) mechanism is operating.

In case of thermionic emission, the ratio for estimating the boundary resistivity r_b is obtained on the basis of standard equations of thermionic emission and is given by [21,25,27]

$$r_b = \frac{k}{eAT}\exp\left(\frac{E_b}{kT}\right), \tag{2}$$

where $A = \frac{em^*k^2}{2\pi^2\hbar^3}$ is the effective Richardson constant.

In the cases of tunneling of carriers, for the calculation of r_b one can use the approximate analytical expressions [27-29]:

$$r_b = \frac{k\sin(\pi c_1 kT)}{e\pi AT}\exp\left(\frac{E_b}{E_{00}}\right), \quad \text{when } kT/E_{00} \ll 1, \tag{3}$$

$$r_b = \frac{k^2\cosh(E_{00}/kT)\sqrt{\coth(E_{00}/kT)}}{eA\sqrt{\pi(E_b-\varphi_F)E_{00}}}\exp\left(\frac{E_b-\varphi_F}{E_{00}\coth(E_{00}/kT)} + \frac{\varphi_F}{kT}\right), \text{ when } kT/E_{00} \approx 1, \tag{4}$$

where $c_1 = \frac{1}{2E_{00}}\ln\left(\frac{4E_b}{-\varphi_F}\right)$, φ_F are the energies of semiconductor Fermi level (φ_F is counted from the bottom of conduction band and for the degenerate semiconductors is a negative value).

Thus, from the analytical expressions (2) – (4) it is clear that the value of TEM-metal boundary resistivity r_b depends on the temperature, the height of potential barrier E_b and the impurity concentration in TEM N_d. In the mode of thermionic emission the value of r_b is actually independent of the impurity concentration and is determined only by the height of potential barrier: $r_b \sim \exp\left(\frac{E_b}{kT}\right)$. In tunneling mode, the exponential dependence of r_b on barrier height is supplemented by the dependence on impurity concentration. For the mechanism of FE $r_b \sim \exp\left(E_b/\sqrt{N_d}\right)$, and for TFE $r_b \sim \exp\left(E_b\Big/\left(\sqrt{N_d}\coth\frac{E_{00}}{kT}\right)\right)$ [29]. Under the condition of high impurity concentration N_d, when the mechanism of FE is operating, r_b assumes low values. With decreasing impurity concentration, the FE tunneling mechanism is substituted by TFE and goes over to thermionic emission TE, and the resistance r_b in this case increases.

It also follows from (2) – (4) that the values of r_b will be low under conditions of low potential barriers. In [30], it was studied which boundary values can be reached by resistance r_b. The expression for estimating the minimum boundary resistance $r_{b\,\min}$ was obtained which is given by [30]

$$r_{b\min} = \frac{k}{eAT}\frac{1}{\ln\left[1+\exp\left(-\varphi_F/kT\right)\right]}\cdot r_{b\min} = \frac{k}{eAT}\frac{1}{\ln\left[1+\exp\left(-\varphi_F/kT\right)\right]}. \quad (5)$$

For the nondegenerate semiconductors $\varphi_F \gg kT$, the relation (5) is transformed into classical formula for calculating the resistivity of anti-locking contact [25, 30]:

$$r_{b\min} = \frac{k}{eAT}\exp\left(\varphi_F/kT\right) = \frac{k}{eAT}\frac{N_c}{N_d} = \frac{(2\pi m^* kT)^{1/2}}{e^2 N_d}, \quad (6)$$

where $N_c = 2\frac{(2\pi m^* kT)^{3/2}}{h^2}$ is the effective density of energy states in conduction band.

For the case of degenerate semiconductors with $\varphi_F < -kT$ [30] the expression for $r_{b\min}$ is given by

$$r_{b\min} = \frac{k}{eAT\left[1+2\alpha\left(-\varphi_F\right)\right]}\frac{kT}{\left(-\varphi_F\right)}, \quad (7)$$

where α is a nonparabolicity parameter of semiconductor conduction band.

The value of the Fermi energy φ_F, required for estimating r_b by the formulae (3), (4) and $r_{b\min}$ by formula (5), is a solution of electroneutrality equation, which for impurity semiconductor with the impurity concentration N_d on the assumption that all impurity atoms are single ionized, is of the form [30,31]

$$N_c F_{1/2}\left(-\frac{\varphi_F}{kT}\right) = N_d, \quad (8)$$

where $F_{1/2}\left(\eta\right) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}}{1+\exp(x-\eta)}\mathrm{d}x$ is the Fermi integral.

Thus, in order to obtain a low TEM-metal boundary resistivity, the impurity concentration in the near-contact region should be high and the height of potential barrier - low. These are classical requirements for improving the ohmicity of semiconductor-metal contact. It should be borne in mind that the barrier height E_b depends on semiconductor energy gap φ_g (Fig. 2). For wide-gap semiconductors it is difficult to achieve good ohmic contacts. In the majority of metals, the value of work function φ_m is high, which also does not contribute to formation of low TEM-metal potential barriers, and, accordingly, good ohmic contacts. Therefore, to get a low TEM-metal boundary resistivity, one can recommend traditional technologies for improving the ohmicity of contacts [27]. One of the methods is to make heavily doped a narrow layer of thermoelectric material which is in contact to metal.

Consider the results of calculating TEM-metal boundary resistivity for classical thermoelements based on Bi_2Te_3 and analyze the effect of heavier doping of the near-contact layer on this resistivity value.

Results of calculating the resistivity of TEM-metal boundary

The electrical boundary resistivity was estimated for thermoelectric legs of traditional *n*-type materials $Bi_2Te_{2.7}Se_{0.3}$ and *p*-type materials $Bi_{0.5}Sb_{1.5}Te_3$ that are in contact to nickel anti-diffusion layers. The parameters of these TEM required for calculations are given in Table 1.

Table 1

TEM parameters

Parameter	TEM		Reference
	$Bi_2Te_{2.7}Se_{0.3}$ *n*-type	$Bi_{0.5}\ Sb_{1.5}Te_3$ *p*-type	
Optimal impurity concentration in TEM $N_{d\ opt}$, m^{-3}	$3{\cdot}10^{25}$	$2{\cdot}10^{25}$	[32]
Carrier mass m^* (m_0 – electron mass)	$1.25m_0$	$0.6m_0$	[32]
Relative dielectric constant ε	98	62	[23]

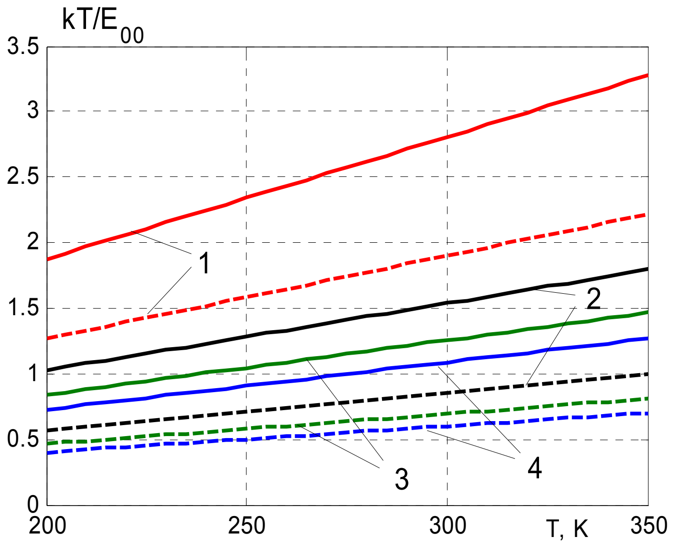
To estimate the effect of heavier doping of near-contact TEM layer, calculations were performed for different values of impurity concentration in this layer, which was increased by the order of magnitude with respect to its optimal value.

To calculate the electrical resistance of TEM-metal boundary r_b, it is primarily necessary to determine the mechanism of carriers passing through the potential barrier. For this purpose, the Padovani-Stratton E_{00} was calculated (1), and the temperature dependence of effective mass m^* and dielectric constant was not taken into account. The temperature dependences of dimensionless criterion kT/E_{00} of the mechanism of passing the barrier for different values of impurity concentration N_d in the near-contact layer of n- and p-type TEM are shown in Fig.3*a*. It follows from the figure that in the temperature range of 200 – 350 K under condition of optimal impurity concentration $N_{d\ opt}$ for *n*-type thermoelectric leg $kT/E_{00} > 1$, and for *p*-type leg – $kT/E_{00} \sim 1$. If the near-contact concentration of impurities, hence of carriers, will be of the order of 10^{26}m^{-3}, then for *n*-type leg $kT/E_{00} \sim 1$, and for *p*-type leg $kT/E_{00} < 1$. Thus, in order to calculate the electrical boundary resistance of *n*-type leg with the optimal impurity concentration, it is expedient to use relation (2), valid for TIE mechanism of passing the barrier, and for the leg with impurity concentration in the near-contact layer of the order of 10^{26} m^{-3} – formula (4) for TFE mechanism. For *p*-type leg with optimal concentration use was made of formula (4), and for high concentrations – formula (3) for FE mechanism to overcome the barrier.

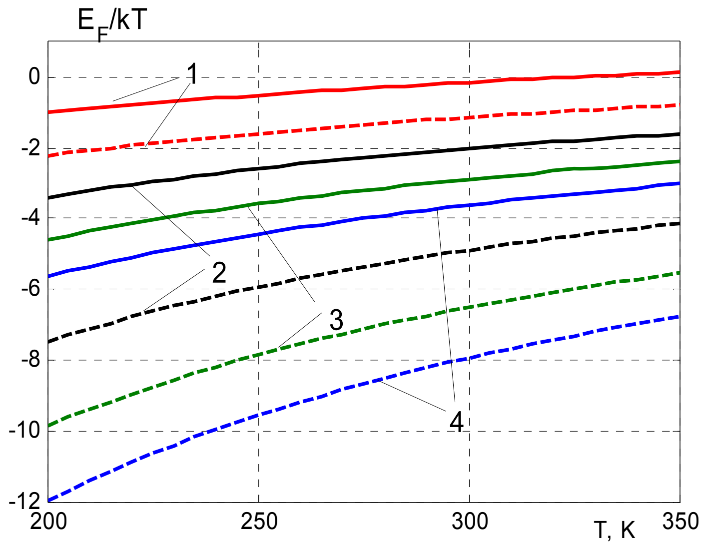
Also, for the calculations one should first of all determine the value of the Fermi energy φ_F in TEM and the height of potential barrier E_b. The temperature dependences of the dimensionless Fermi energy φ_F/kT for Bi_2Te_3-based TEM with different impurity concentrations calculated on the basis of Eq. (8) are shown in Fig. 3*b* and were used to calculate the boundary resistance r_b for these TEM contacts with nickel.

The height of potential barrier can be estimated by simple relations, namely for metal-*n*-type semiconductor boundary $E_b = \varphi_m - \chi_n$, for metal-*p*-type semiconductor boundary $E_b = \varphi_g - (\varphi_m - \chi_p)$ [27]. However, these relations are almost never satisfied [27]. This is due to such major reasons as the presence of a contact gap between metal and semiconductor, the existence of contact energy states, the lowering of the barrier height due to the forces of images, etc.

Therefore, the height of TEM-metal barrier should be determined experimentally. In [33], potential barriers between individual metals and semiconductors are presented. It is shown that the height of barriers $E_b \leq 0.1$ eV, including the boundary between two TEM Bi_2Te_3/Sb_2Te_3 (E_b=0.035 eV). In [22], the barriers between Bi_2Te_3 and Sb_2Te_3 with metal were taken to be E_b=0.1eV. In [34], for the contacts between *Ni* and solid solutions $(Bi,Sb)_2(Se,Te)_3$, the value of barrier height E_b=0.13eV was proposed, which we used to calculate the electrical boundary resistance between nickel and Bi_2Te_3 - based TEM.



a)



b)

Fig.3. Temperature dependences of the dimensionless criterion kT/E_{00} of barrier passing mechanism (a) and the dimensionless Fermi energy φ_F/kT (b) for n-type $Bi_2Te_{2.7}Se_{0.3}$ (solid lines) and p-type $Bi_{0.5}Sb_{1.5}Te_3$ (dashed lines). Impurity concentration N_d in TEM contact layer: 1 – optimal concentration in TEM, 2 – $N_d=10^{26}$ m^{-3}, 3 – $N_d=1.5\cdot10^{26}$ m^{-3}, 4 – $N_d=2\cdot10^{26}$ m^{-3}.

The temperature dependences of the electrical boundary resistance $r_b(T)$, calculated for different concentrations of doping impurities in the near-contact layer, are shown in Fig. 4. As the temperature decreases from 350K to 200 K, under optimal concentration of impurities in TEM, the value of r_b

increases from $0.5{\cdot}10^{-7}$ to $2.5{\cdot}10^{-7}$ Ohm·cm^2. With a rise in impurity concentration, the boundary resistivity drastically decreases and actually is temperature-independent.

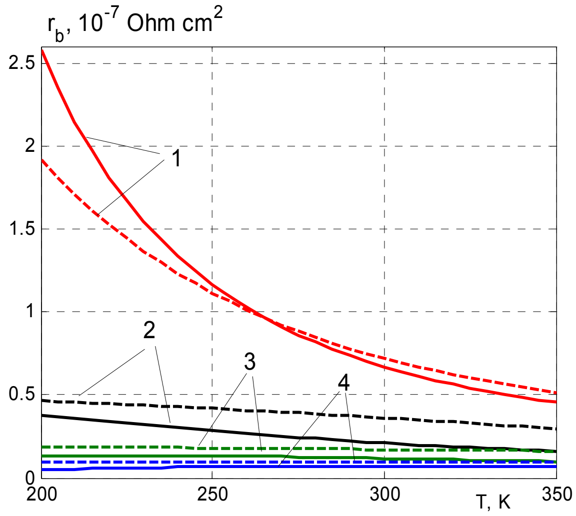


Fig.4. Temperature dependences of boundary resistivity r_b for contacts of nickel with n-type $Bi_2Te_{2.7}Se_{0.3}$ (solid lines) and p-type $Bi_{0.5}Sb_{1.5}Te_3$ (dashed lines), calculated for different concentrations of doping impurities N_d in the near-contact TEM layer: 1 – optimal concentration in TEM, 2 – $N_d=10^{26}$ m^{-3}, 3 – $N_d=1.5{\cdot}10^{26}$ m^{-3}, 4 – $N_d=2{\cdot}10^{26}$ m^{-3}.

Fig.5 shows the temperature dependences of minimum resistivity $r_{b\ min}(T)$ of TEM-*Ni* barrier, calculated by relation (5) for different values of N_d. $r_{b\ min}$ weakly depends on temperature, and the order of magnitude of this resistance is 10^{-9} – 10^{-10} Ohm·cm^2. $r_{b\ min}$ is a boundary value to which the value of TEM-*Ni* boundary resistance tends under condition of lowering the height of potential barrier.

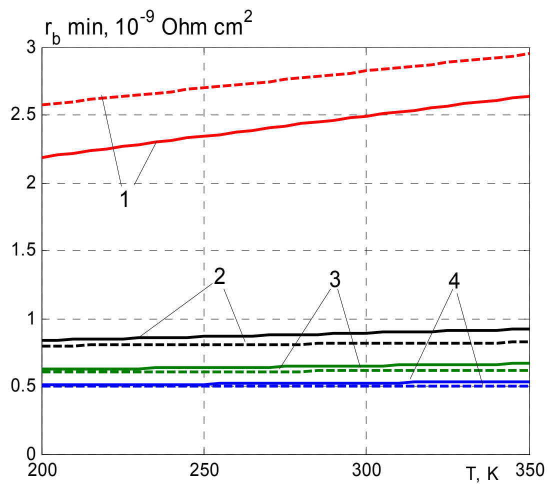


Fig.5. Temperature dependences of minimum boundary resistivity $r_{b\ min}$ for contacts of nickel with n-type $Bi_2Te_{2.7}Se_{0.3}$ (solid lines) and p-type $Bi_{0.5}Sb_{1.5}Te_3$ (dashed lines), calculated for different concentrations of doping impurities N_d in the near-contact TEM layer: 1 – optimal concentration in TEM, 2 – $N_d=10^{26}$ m^{-3}, 3 – $N_d=1.5{\cdot}10^{26}$ m^{-3}, 4 – $N_d=2{\cdot}10^{26}$ m^{-3}.

Fig.6 shows the dependences of boundary resistivity on impurity concentration N_d under conditions of heavier doping of near-contact layer. The same figure shows a similar dependence of minimum boundary resistance. If we increase the concentration of doping impurities in the near-contact TEM layer by one order with respect to its optimal value, the electrical boundary resistance is actually decreased by two orders. Under these conditions, its value r_b approaches minimum value of $r_{b\ min}$, and its order will make 10^{-9} Ohm·cm^2.

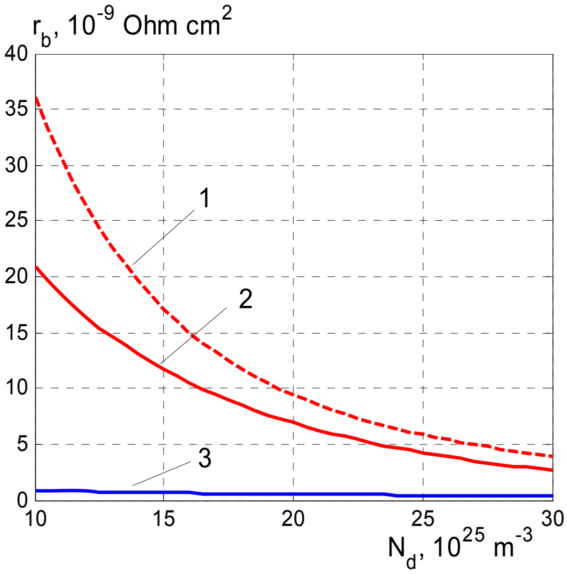


Fig.6. Dependences of boundary resistivity r_b on impurity concentration N_d in the nickel contact layer of p-type $Bi_{0.5}Sb_{1.5}Te_3$ (1) and n-type $Bi_2Te_{2.7}Se_{0.3}$ (2) under condition of T=300 K. 3 – dependences of minimum resistivity $r_{b\ min}(N_d)$ practically coincide for p- and n-type TEM.

Thus, the creation at the boundary between the Bi_2Te_3-based material and the nickel of a thin contact layer with a high concentration of charge carriers neutralizes the effect of the potential barrier and reduces the electrical boundary resistance and the contact resistance as a whole. This is confirmed, in particular, by the experimental results described in [34]. To obtain such heavily doped near-contact layers, special technologies are used, for example, ion implantation of impurities [34].

In [35], the results of theoretical and experimental studies of contact resistance in Bi_2Te_3 -based thermoelectric legs with anti-diffusion nickel layers were analyzed. It was shown that the value of contact resistance does not exceed $5\cdot10^{-6}$ Ohm·cm^2. Creating "ideal" contacts allows reducing this value to 10^{-9} Ohm·cm^2. Using the Comsol Multiphysics thermoelectric software package, we estimated the effect of contact resistance on the efficiency of a Bi_2Te_3-based thermoelectric converter with miniature legs 0.5 mm high. It was concluded that improving the contact technology which would reduce the contact resistance from $5\cdot10^{-6}$ Ohm·cm^2 to the minimum possible 10^{-9} Ohm·cm^2, helps to increase the converter efficiency by 20 %.

Conclusions

1. Methods for calculating the electrical resistance of TEM-metal boundary arising due to formation of potential barrier in the zone of contact between thermoelectric material and metal are proposed. The temperature dependences of the boundary resistance for thermoelectric legs made of Bi_2Te_3-based materials with the deposited anti-diffusion nickel layers are calculated.
2. It is established that boundary resistance in such structures under optimal impurity concentration in TEM reaches the value from $0.5\cdot10^{-7}$ to $2.5\cdot10^{-7}$ Ohm·cm^2 and is a function of temperature.

3. It is shown that the impact of potential barrier at the TEM-metal boundary can be effectively neutralized by creating a thin near-contact layer with a high concentration of carriers due to doping. This requires special technologies, such as ion implantation technique.
4. It is established that increasing the concentration of doping impurities in the nickel contact zone of TEM by one order of magnitude with respect to its optimal value results in decreasing the electrical boundary resistance actually by two orders of magnitude. Under these conditions, its value approaches the minimum possible value, and its order is 10^{-9} Ohm·cm^2, which helps to increase the efficiency of thermoelectric energy conversion by 20 %.

References

1. Aswal D.K., Basu R., Singh A. (2016). Key issues in development of thermoelectric power generators: high figure-of-merit materials and their highly conducting interfaces with metallic interconnects. *Energy Convers. Manag*, 114, 50-67.
2. Anatychuk L.I., Kuz R.V. (2012). The energy and economic parameters of Bi-Te based thermoelectric generator modules for waste heat recovery. *J.Thermoelectricity*, 4, 75-82.
3. Drabkin I.A., Osvensky V.B., Sorokin A.I., Panchenko V.P., Narozhnaia O.E. (2017). Kontaktnoie soprotivleniie v sostavnykh termoelektricheskikh vetviakh [Contact resistance in composite thermoelectric legs]. *Fizika i tekhnika poluprovodnikov – Semiconductors*, 51 (8), 1038-1040.
4. Anatychuk L.I. (2003). *Termoelektrichestvo. Tom 2. Termoelektricheskiie preobrazovateli energii [Thermoelectricity. Vol.2. Thermoelectric power converters].* Kyiv, Chernivtsi: Institute of Thermoelectricity [in Russian].
5. Semenyuk V.A. (2006). Thermoelectric cooling of electro-optic components. *Thermoelectrics Handbook: Macro to Nano.* D.M. Rowe (Ed.). London, New York: CRC Taylor&Francis.
6. Semenyuk V. (2019). Effect of electrical contact resistance on the performance of cascade thermoelectric coolers. *J. Electron. Mater*, 48(4), 1870-1876.
7. H. Bottner, J. Nurnus, A. Schubert. (2006). Miniaturized thermoelectric converters, in: *Thermoelectrics Handbook, Macro to Nano.* D.M. Rowe (Ed.). London, New York: CRC Taylor&Francis.
8. Crane N.B., Mishra P., Murray J. L., Nolas G.S. (2009). Self-assembly for integration of microscale thermoelectric coolers. *J. of Electron. Mater*, 38(7), 1252-1256.
9. Huang I-Yu, Linb Jr-Ching, She Kun-Dian, et al. (2008). Development of low-cost micro-thermoelectric coolers utilizing MEMS technology. *Sensors and Actuators*, A 148, 176-185.
10. Navone C., Soulier M., Plissonnier M., Seiler A.L. (2010). Development of $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric modules by a screen-printing process. *J. of Electron. Mater*, 39(9), 1755-1759.
11. Goncalves L.M., Couto C., Alpuim P., Correia J.H. (2008).Thermoelectric micro converters for cooling and energy-scavenging systems. *J. Micromech. Microeng*, 18, 064008-1 - 064008-5.
12. Y. Y. Zhou, J. L. Yu. (2012). Design optimization of thermoelectric cooling systems for applications in electronic devices. *Int. J. Refrig*, 35, 1139-1144.
13. Vikhor L.M., Anatychuk L.I., Gorskyi P.V. (2019). Electrical resistance of metal contact to Bi_2Te_3 based thermoelectric legs. *J. of Appl. Phys*, 126, 164503-1 – 164503-8.
14. Jing H., Li Y., Xu L., et al. (2015). Interfacial reaction and shear strength of SnAgCu/Ni/Bi_2Te_3-based TE materials during aging. *Mater. Eng. and Perform*, 24(12), 4844-4852.
15. Chen L., Mei D., Wang Y., Li Y. (2019). Ni barrier in Bi_2Te_3-based thermoelectric modules for reduced contact resistance and enhanced power generation properties. *J. Alloys and Comp*, 796, 314-320.

16. Chuang C.-H.mailto:please_login, Lin Y.-C., Lin C.-W. (2016). Intermetallic reactions during the solid-liquid interdiffusion bonding of $Bi_2Te_{2.55}Se_{0.45}$ thermoelectric material with Cu electrodes using a Sn interlayer. *Metals*, 6(4), 92-97.
17. Iyore O. D., Lee T. H., Gupta R. P., et al. (2009). Interface characterization of nickel contacts to bulk bismuth tellurium selenide. *Surf. Interface Anal*, 41, 440-444.
18. Gupta R.P., McCarty R., Sharp J. (2014). Practical contact resistance measurement method for bulk Bi_2Te_3 based thermoelectric devices. *J. of Electron. Mater*, 43(6), 1608-1612.
19. Joshi G., Mitchell D., Ruedin J., et al. (2019). Pulsed-light surface annealing for low contact resistance interfaces between metal electrodes and bismuth telluride thermoelectric materials. *J. Mater. Chem. C*, 7**,** 479-484.
20. Gupta R. P., Xiong K., White J. B., Cho K., Alshareef H.N., Gnade B.E.(2010). Low resistance ohmic contacts to Bi_2Te_3 using Ni and Co metallization. *J. of Electrochem. Soc*, 157(6), H666-H670.
21. Bartkowiak M., Mahan G.D. (2001). Heat and electricity transport through interfaces, in: *Recent Trends in Thermoelectric Materials, vol. II, Semiconductors and Semimetals*, vol. 70. New York: Academic Press.
22. Da Silva L. W., Kaviany M. (2004). Microthermoelectric cooler: interfacial effects on thermal and electrical transport. *Int. J. of Heat and Mass Transfer*, 47(10-11), 2417–2435.
23. Vikhor L.M., Gorskyi P.V. (2015). Heat and charge transport at thermoelectric material-metal boundary. *J. Thermoelectricity*, 6, 5-15.
24. Bartkowiak M., Mahan G.D. (1999). Boundary effects in thin-film thermoelctrics. *Proc. of Mat. Res. Soc. Symp*, 545, 265-272.
25. Rhoderick E.H. (1978). *Metal-semiconductor contacts*.Oxford: Clarendon Press.
26. Goldberg Yu.A. (1994). Omicheskii kontakt metall-poluprovodnik AIIIBV: metody sozdaniia i svoistva [Ohmic contact metal- AIIIBV semiconductor: methods of creation and properties]. *Fizika i tekhnika poluprovodnikov - Semiconductors*, 28(10), 1681-1698.
27. Sze S.M., Ng, Kwok K. (2007). *Physics of Semiconductor Devices.* (3rd Ed.). *Hoboken:* John Wiley & Sons, Inc.
28. Padovani F.A., Stratton R. (1966). Field and thermionic-field emission in Schottky barriers. *Sol. St. Electron*, 9, 695-707.
29. Yu. A. Y. C. (1970). Electron tunneling and contact resistance metal-silicon contact barriers. *Sol. St. Electron*.13, 239-247.
30. Kupka R.K., Anderson W.A. (1991). Minimal ohmic contact resistance limits to n-type semiconductors. *J. Appl. Phys*., 69 (6), 3623-3632.
31. Askerov B.M. (1970). *Kineticheskiie effekty v poluprovodnikakh [Kinetic effects in semiconductors].* Leningrad: Nauka.
32. Okhotin A.S., Yefremov A.A., Okhotin V.S., Pushkarskiy A.S. (1971). *Termoelektricheskiie genetatory [Thermoelectric generators].A.R.Regel (Ed.)* Moscow: Atomizdat, 1971.
33. Mahan G.D., Woods L.M. (1998). Multilayer thermionic refrigeration. *Phys. Rev. Lett*, 80(18), 4016-4019.
34. Taylor P.J., Maddux G.R., Meissner G., Venkatasubramanian R., et al. (2013). Controlled improvement in specific contact resistivity for thermoelectric materials by ion implantation. *Appl. Phys. Lett,* 103, 043902-1 - 043902-4.
35. Vikhor L.M., Anatychuk L.I., Gorskyi P.V. (2019). Electrical resistance of metal contact to Bi_2Te_3 based thermoelectric legs. *J. Appl. Phys*, 126, 64503-1 – 164503-8.

Submitted 19.09.2019

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КОНТАКТНИЙ ОПІР ЗУМОВЛЕНИЙ ПОТЕНЦІАЛЬНИМ БАР'ЄРОМ НА ГРАНИЦІ ТЕРМОЕЛЕКТРИЧНОГО МАТЕРІАЛУ З МЕТАЛОМ

Розглянуто теоретичні аспекти оцінювання величини електричного опору, який зумовлений переходом носіїв заряду через потенціальний бар'єр на границі між термоелектричним матеріалом і металом. Розраховані температурні залежності питомого опору границі для термоелектричних віток з матеріалів на основі Bi_2Te_3 з нанесеними антидифузійними шарами нікелю. Встановлено, що величина опору границі в таких вітках змінюється з температурою від $0.5\cdot10^{-7}$ до $2.5\cdot10^{-7}$ Ом·см^2. Показано, що зменшити опір границі можна шляхом підвищення концентрації носіїв заряду в ультратонкому приконтактному з нікелем шарі термоелектричного матеріалу за рахунок легування. Встановлено, що підвищення концентрації легуючих домішок в приконтактній зоні на один порядок відносно її оптимального значення призводить до зменшення електричного опору границі на два порядки. За цих умов величина опору наближається до мінімально можливого значення, і становить 10^{-9} Ом·см^2. Бібл. 35, рис. 6, табл. 1.

Ключові слова: контакт термоелектричний матеріал - метал, потенціальний бар'єр, електричний опір границі.

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КОНТАКТНОЕ СОПРОТИВЛЕНИЕ, ОБУСЛОВЛЕННОЕ ПОТЕНЦИАЛЬНЫМ БАРЬЕРОМ НА ГРАНИЦЕ ТЕРМОЭЛЕКТРИЧЕСКИЙ МАТЕРИАЛ – МЕТАЛЛ

Рассмотрены теоретические аспекты оценки величины сопротивления, обусловленного переходом носителей заряда через потенциальный барьер на границе между *термоэлектрическим материалом и металлом. Рассчитаны температурные зависимости удельного сопротивления границы для термоэлектрических ветвей из материалов на основе Bi_2Te_3 с нанесенными антидиффузионных слоями никеля. Установлено, что величина сопротивления границы в таких ветвях изменяется с температурой от $0.5\cdot10^{-7}$ до $2.5\cdot10^{-7}$ Ом·см^2. Показано, что уменьшить сопротивление границы можно путем повышения концентрации носителей заряда в ультратонком приконтактном слое термоэлектрического материала за счет легирования последнего. Установлено, что повышение концентрации легирующих примесей в приконтактной зоне на один порядок относительно ее оптимального значения в материале в целом приводит к уменьшению электрического сопротивления границы на два порядка. Библ. 35, рис. 6, табл. 1.*

Ключевые слова: контакт термоэлектрический материал – металл, потенциальный барьер, электрическое сопротивление границы.

References

36. Aswal D.K., Basu R., Singh A. (2016). Key issues in development of thermoelectric power generators: high figure-of-merit materials and their highly conducting interfaces with metallic interconnects. *Energy Convers. Manag*, 114, 50-67.
37. Anatychuk L.I., Kuz R.V. (2012). The energy and economic parameters of Bi-Te based thermoelectric generator modules for waste heat recovery. *J.Thermoelectricity*, 4, 75-82.
38. Drabkin I.A., Osvensky V.B., Sorokin A.I., Panchenko V.P., Narozhnaia O.E. (2017). Kontaktnoie soprotivleniie v sostavnykh termoelektricheskikh vetviakh [Contact resistance in composite thermoelectric legs]. *Fizika i tekhnika poluprovodnikov – Semiconductors*, 51 (8), 1038-1040.
39. Anatychuk L.I. (2003). *Termoelektrichestvo. Tom 2. Termoelektricheskiie preobrazovateli energii [Thermoelectricity. Vol.2. Thermoelectric power converters]*. Kyiv, Chernivtsi: Institute of Thermoelectricity [in Russian].
40. Semenyuk V.A. (2006). Thermoelectric cooling of electro-optic components. *Thermoelectrics Handbook: Macro to Nano.* D.M. Rowe (Ed.). London, New York: CRC Taylor&Francis.
41. Semenyuk V. (2019). Effect of electrical contact resistance on the performance of cascade thermoelectric coolers. *J. Electron. Mater*, 48(4), 1870-1876.
42. H. Bottner, J. Nurnus, A. Schubert. (2006). Miniaturized thermoelectric converters, in: *Thermoelectrics Handbook, Macro to Nano.* D.M. Rowe (Ed.). London, New York: CRC Taylor&Francis.
43. Crane N.B., Mishra P., Murray J. L., Nolas G.S. (2009). Self-assembly for integration of microscale thermoelectric coolers. *J. of Electron. Mater*, 38(7), 1252-1256.
44. Huang I-Yu, Linb Jr-Ching, She Kun-Dian, et al. (2008). Development of low-cost micro-thermoelectric coolers utilizing MEMS technology. *Sensors and Actuators*, A 148, 176-185.
45. Navone C., Soulier M., Plissonnier M., Seiler A.L. (2010). Development of $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric modules by a screen-printing process. *J. of Electron. Mater*, 39(9), 1755-1759.
46. Goncalves L.M., Couto C., Alpuim P., Correia J.H. (2008).Thermoelectric micro converters for cooling and energy-scavenging systems. *J. Micromech. Microeng*, 18, 064008-1 - 064008-5.
47. Y. Y. Zhou, J. L. Yu. (2012). Design optimization of thermoelectric cooling systems for applications in electronic devices. *Int. J. Refrig*, 35, 1139-1144.
48. Vikhor L.M., Anatychuk L.I., Gorskyi P.V. (2019). Electrical resistance of metal contact to Bi_2Te_3 based thermoelectric legs. *J. of Appl. Phys*, 126, 164503-1 – 164503-8.

49. Jing H., Li Y., Xu L., et al. (2015). Interfacial reaction and shear strength of SnAgCu/Ni/Bi_2Te_3-based TE materials during aging. *Mater. Eng. and Perform*, 24(12), 4844-4852.
50. Chen L., Mei D., Wang Y., Li Y. (2019). Ni barrier in Bi_2Te_3-based thermoelectric modules for reduced contact resistance and enhanced power generation properties. *J. Alloys and Comp*, 796, 314-320.
51. Chuang C.-H.mailto:please_login, Lin Y.-C., Lin C.-W. (2016). Intermetallic reactions during the solid-liquid interdiffusion bonding of $Bi_2Te_{2.55}Se_{0.45}$ thermoelectric material with Cu electrodes using a Sn interlayer. *Metals*, 6(4), 92-97.
52. Iyore O. D., Lee T. H., Gupta R. P., et al. (2009). Interface characterization of nickel contacts to bulk bismuth tellurium selenide. *Surf. Interface Anal*, 41, 440-444.
53. Gupta R.P., McCarty R., Sharp J. (2014). Practical contact resistance measurement method for bulk Bi_2Te_3 based thermoelectric devices. *J. of Electron. Mater*, 43(6), 1608-1612.
54. Joshi G., Mitchell D., Ruedin J., et al. (2019). Pulsed-light surface annealing for low contact resistance interfaces between metal electrodes and bismuth telluride thermoelectric materials. *J. Mater. Chem. C*, 7, 479-484.
55. Gupta R. P., Xiong K., White J. B., Cho K., Alshareef H.N., Gnade B.E.(2010). Low resistance ohmic contacts to Bi_2Te_3 using Ni and Co metallization. *J. of Electrochem. Soc*, 157(6), H666-H670.
56. Bartkowiak M., Mahan G.D. (2001). Heat and electricity transport through interfaces, in: *Recent Trends in Thermoelectric Materials, vol. II, Semiconductors and Semimetals*, vol. 70. New York: Academic Press.
57. Da Silva L. W., Kaviany M. (2004). Microthermoelectric cooler: interfacial effects on thermal and electrical transport. *Int. J. of Heat and Mass Transfer*, 47(10-11), 2417–2435.
58. Vikhor L.M., Gorskyi P.V. (2015). Heat and charge transport at thermoelectric material-metal boundary. *J. Thermoelectricity*, 6, 5-15.
59. Bartkowiak M., Mahan G.D. (1999). Boundary effects in thin-film thermoelctrics. *Proc. of Mat. Res. Soc. Symp*, 545, 265-272.
60. Rhoderick E.H. (1978). *Metal-semiconductor contacts*.Oxford: Clarendon Press.
61. Goldberg Yu.A. (1994). Omicheskii kontakt metall-poluprovodnik AIIIBV: metody sozdaniia i svoistva [Ohmic contact metal- AIIIBV semiconductor: methods of creation and properties]. *Fizika i tekhnika poluprovodnikov - Semiconductors*, 28(10), 1681-1698.
62. Sze S.M., Ng, Kwok K. (2007). *Physics of Semiconductor Devices.* (3rd Ed.). *Hoboken:* John Wiley & Sons, Inc.
63. Padovani F.A., Stratton R. (1966). Field and thermionic-field emission in Schottky barriers. *Sol. St. Electron*, 9, 695-707.
64. Yu. A. Y. C. (1970). Electron tunneling and contact resistance metal-silicon contact barriers. *Sol. St. Electron*.13, 239-247.
65. Kupka R.K., Anderson W.A. (1991). Minimal ohmic contact resistance limits to n-type semiconductors. *J. Appl. Phys*., 69 (6), 3623-3632.
66. Askerov B.M. (1970). *Kineticheskiie effekty v poluprovodnikakh [Kinetic effects in semiconductors]*. Leningrad: Nauka.
67. Okhotin A.S., Yefremov A.A., Okhotin V.S., Pushkarskiy A.S. (1971). *Termoelektricheskiie genetatory [Thermoelectric generators].A.R.Regel (Ed.)* Moscow: Atomizdat, 1971.

68. Mahan G.D., Woods L.M. (1998). Multilayer thermionic refrigeration. *Phys. Rev. Lett*, 80(18), 4016-4019.
69. Taylor P.J., Maddux G.R., Meissner G., Venkatasubramanian R., et al. (2013). Controlled improvement in specific contact resistivity for thermoelectric materials by ion implantation. *Appl. Phys. Lett,* 103, 043902-1 - 043902-4.
70. Vikhor L.M., Anatychuk L.I., Gorskyi P.V. (2019). Electrical resistance of metal contact to Bi_2Te_3 based thermoelectric legs. *J. Appl. Phys*, 126, 64503-1 – 164503-8.

Submitted 19.09.2019