Contact Systems for Thermoelements with Operating Temperatures up to 1200 K

Maxim Shtern Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia m.y.shtern@gmail.com

Alexander Kozlov Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia alex_kozlov@yahoo.com Maxim Rogachev Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia rmaks1988@yahoo.com

Alexey Sherchenkov Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia aa_sherchenkov@rambler.ru

Abstract— To increase the efficiency of thermoelectric devices, nanostructured thermoelectric materials for operation in the temperature range from 170 to 1200 K having high values of thermoelectric figure of merit were obtained. Thermoelectric materials have the following maximum values of ZT: Bi₂Te_{2.8}Se_{0.2} – 1.15; Bi_{0.5}Sb_{1.5}Te₃ – 1.17; Bi₂Te_{2.4}Se_{0.6} – 1.16; Bi_{0.4}Sb_{1.6}Te₃ - 1.18; PbTe – 1.31; GeTe – 1.41; SiGe – 1.23 for n-type and 1.21 for p-type. Parameter ZT is determined for the operating temperature range of each material. Increase of the figure of merit for nanostructured TEMs in comparison with the usual structure is determined by the decrease of thermal conductivity by 10–15% due to the phonon heat transfer.

In order to increase the efficiency of thermoelectric generators by increasing the temperature difference between hot and cold thermoelement junctions, multisection thermoelements are used. For such a thermoelement with operating temperatures up to 1200 K, the structures and technology of contact systems obtained by vacuum deposition of thin films have been proposed and justified. The influence of the preparation of thermoelectric material surface and the structure of contact systems on their thermal stability, contact resistance and mechanical strength has been established. Effective contact systems are proposed for the temperature range from 300 to 1200 K: Ni; Mo/Ni and Mo/Ta-W-N/Ni, having an adhesive strength of at least 16.0 MPa and a contact resistance of not more than $4.9 \cdot 10^{-9}$ Ohm·m².

Keywords— thermoelectricity; thermoelements; nanostructured materials; multisectional thermoelements; contact systems; thermal stability, contact resistance.

I. INTRODUCTION

Thermoelectric devices (TD) belong to semiconductor energy converters operating on the Peltier and Seebeck effects. Devices operating on the Peltier effect are used to convert electrical energy into heat. These are devices for cooling and temperature controlling in the range from 170 to 450 K. The Seebeck effect is used to convert thermal energy into electrical in thermoelectric generators (TEG), temperature and heat flow sensors.

It is important to note that TDs are alternative energy sources:

Yury Shtern Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia hptt@miee.ru

Egor Korchagin Institute of Advanced Materials and Technologies National Research University of Electronic Technology Zelenograd, Moscow, Russia eg.ad2013@yandex.ru

- thermal for Peltier devices in the case of conversion of low-potential thermal energy of the earth, water, air using thermoelectric heat pumps for heating and hot water supply of buildings;

- electrical for TEGs, which realize direct conversion of thermal energy from various sources into electrical energy.

The main advantages of thermoelectric energy conversion are following: direct energy conversion, reliability, long service life, low thermal inertia, autonomy, a large number of uncontested applications. It is also necessary to note the wide scope of application of thermoelectricity: from household appliances to high-tech products, spacecraft, special and military applications. Thermoelectric cooling and temperature controlling, including precision, in many cases has no alternative, for example, for electronic technology. TEGs hold great perspectives for the use of waste heat. Spacecraft use maintenance-free radioisotope TEGs, which are also advisable to use in the development of the Arctic, Antarctic, hard-to-reach regions, for example, the Far North. In these cases, TEGs have no alternative in generating electrical energy.

The widespread use of TD is restrained by their low efficiency, which is determined first of all by the thermoelectric figure of merit (Z) of semiconductor materials used for the manufacture of thermoelements - the main structural elements of all TD. The most effective thermoelectric materials for the manufacture of TD with operating temperatures from 170 to 1200 K are solid solutions based on tellurides of bismuth, antimony, lead and germanium, and solid solutions of silicon and germanium. The dimensionless parameter of thermoelectric figure of merit (ZT) of these materials is, at best, 1 [1-4]. However, recent advances in nanotechnology have opened up new opportunities in the creation of efficient nanostructured thermoelectric materials. In such materials, it is possible to significantly increase Z by reducing the phonon component of thermal conductivity [2–5].

In addition, the efficiency of the TEG can be increased by increasing the temperature difference between the hot and cold junctions of thermoelements and, accordingly, by expanding the operating temperature range. This idea can be realized by using multisection legs in the thermoelement. Each section operates in a certain temperature range and is made of thermoelectric material having maximum Z at these temperatures [6–10]. One of the main problems in the creation of multisection thermoelements is providing efficient commutation of n- and p-type legs in the thermoelement with each other, and sections in the legs of a multisection thermoelement. This commutation is carried out using contact systems (CS). There are several methods for the formation of contact layers of which consist CS. It is promising to obtain them by the method of vacuum deposition [11–17], which provides a minimum value of contact resistance and can be used in combination with other methods, for example, chemical and electrochemical deposition of contact layers.

Great attention is paid to the creation of contacts in the structure of thermoelements. The most promising are the developments presented by the authors [12, 18-20]. However, the disadvantages of the proposed contacts are low adhesion and high contact resistance in some cases and insufficient temporal thermal stability in others. This is caused by unsatisfactory preparation of the surface of thermoelectric materials, on which the contacts are deposited. In addition, such metals as Cu, Ag, Au, Co, Ni, which are often used in the manufacture of contacts cannot be used at elevated temperatures for direct contact with semiconductor materials without a diffusion barrier layer. At low temperatures, these metals, interacting with the semiconducting materials of the thermoelement, form insignificantly thick boundary layer consisting of intermetallic compounds, which increases the adhesive strength of the contact. However, at elevated temperatures, this layer becomes significant, increasing the contact resistance. The adhesion of the contact also decreases due to the lower mechanical strength of intermetallic compounds in comparison with that of thermoelectric materials.

The best parameters possess contact systems presented in the work [6]. At the same time, as shown by our studies at temperatures above 500 K, during prolonged thermal annealing diffusion of the elements of the contact layers into the thermoelectric material is observed, leading to its degradation. The adhesion of the contacts also decreases while the contact resistance increases. The reason is the poor preparation of the contact surface of thermoelectric materials and the absence or insufficient reliability of the diffusionbarrier layer, which will be shown below.

In this work, in order to increase the efficiency, the thermoelectric materials developed by us earlier [6] were manufactured in the form of bulk nanostructured samples with an increased Z value. The obtained thermoelectric materials were used to make sections of multisection thermoelements, on which the structure and technology of contact systems were tested. The purpose of the research was to eliminate the interaction between the materials of the contact system and thermoelectric materials in the thermoelements, to ensure thermal stability, high adhesion, and low contact resistance of contact systems at elevated temperatures. Thus, the temporal thermal stability of the thermoelements, high mechanical strength and reliability of the contacts and, as a consequence, the efficiency of the thermoelements with operating temperatures up to 1200 K are achieved.

II. THERMOELECTRIC MATERIALS

For fabricating sections of a multisection thermoelement with operating temperatures up to 1200 K (Fig. 1), nanostructured thermoelectric materials were used. The following compositions were applied as low-temperature materials with operating temperatures up to 400 K: $Bi_2Te_{2.8}Se_{0.2}$ (doped by 0.14 wt. % CdCl₂) for n-type leg and $Bi_{0.5}Sb_{1.5}Te_3$ (doped by 2 wt % Te and 0.14 wt % TeI₄) for ptype leg. After the synthesis of materials with the above compositions, zone melting was performed to obtain the required structure, which in addition to the composition provide high values of thermoelectric parameters and, accordingly, Z. These materials were used to manufacture low-temperature sections No. 1 of the n- and p-type thermoelement legs (Fig. 1).



Fig. 1. Multisection thermoelement: 1 - Ni, 2 - Mo, 3 - Ta-W-N

The second sections (sections No. 2), operating at temperatures up to 600 K, have the following compositions: $Bi_2Te_{2.4}Se_{0.6}$ (doped by 0.18 wt % CuBr) for n-type and $Bi_{0.4}Sb_{1.6}Te_3$ (doped by 0.12 wt % PbCl₂ and 1.50 wt % Te) for p-type thermoelement legs. The structure of these materials was formed by extrusion.

Sections of thermoelement legs operating at temperatures up to 900 K (sections No. 3) are synthesized with the following composition: n-type PbTe material (doped by 0.2 wt % PbI₂ and 0.3 wt % Ni) and p-type GeTe material (doped by 7.4 wt % Bi). The structure of these materials was formed by hot pressing.

High-temperature fourth sections (section No. 4) of thermoelement with operating temperatures up to 1200 K was made of n-type $Si_{0.8}Ge_{0.2}$ (doped by 2.2% P) and p-type $Si_{0.8}Ge_{0.2}$ (doped by 1.8 % B).

To obtain a nanostructure, the above mentioned thermoelectric materials before using for fabrication of the thermoelement sections were preliminarily ground in a crusher and knife mill to obtain a powder with an average particle size of not more than 500 microns. The grinding was then carried out in a planetary high-energy ball mill. Thus, powders with a particle size of 10–50 nm were obtained. Bulk nanostructured materials were produced using spark plasma sintering.

2021 International Seminar on Electron Devices Design and Production (SED)

After the manufacture of bulk nanostructured samples, the temperature dependences of their thermoelectric parameters were studied using the methods presented in the work [21]. Based on the data obtained, the temperature dependences of the thermoelectric figure of merit of materials were calculated according to the formula below and the parameter ZT:

$$Z = s^2 \cdot \sigma / \kappa.$$
 (1)

where: s – Seebeck coefficient, σ – electrical conductivity, κ – thermal conductivity.

As can be expected, the maximum values of ZT for nanostructured samples exceed this parameter for materials with a usual structure. The maximum values of ZT for thermoelectric materials were as following: $Bi_2Te_{2.8}Se_{0.2} - 1.15$; $Bi_{0.5}Sb_{1.5}Te_3 - 1.17$; $Bi_2Te_{2.4}Se_{0.6} - 1.16$; $Bi_{0.4}Sb_{1.6}Te_3 - 1.18$; PbTe - 1.31; GeTe - 1.41; SiGe - 1.23 for n-type and 1.21 for p-type.

Parameter ZT is presented for the operating temperature range of each material. It has been established that increase of the figure of merit for nanostructured TEM in comparison with the materials with usual structure is determined by the decrease of the thermal conductivity by 10–15% due to the phonon heat transfer.

III. STRUCTURE AND TECHNOLOGY OF CONTACT SYSTEMS FOR THERMOELEMENTS WITH OPERATING TEMPERATURES UP TO 1200 K

As mentioned above, one of the main tasks in the creation of thermoelements and, moreover, multisection thermoelements is to provide thermal stability, high adhesion, low contact resistance of contact systems formed on the surface of thermoelectric materials. This is especially important at elevated temperatures, when diffusion processes intensify, mechanical stresses in contact systems increase.

As will be shown below, the absence of the necessary mechanical treatment of the surface of thermoelectric materials and its high roughness leads to the deformation of the films of the contact layers, as a result of which diffusion of the components of thermoelectric materials occurs through the contact layers, mainly tellurium in one direction and components of the contact layers in the other. This leads to the degradation of the semiconductor material and increases the contact resistance.

At elevated temperatures, these processes intensify, which are observed even when the surface roughness of thermoelectric materials is optimized, if Ni is used as a contact layer directly deposited to the surface of the thermoelectric material.

In this work, to eliminate this negative fact, the following was done. When preparing the surfaces of thermoelectric materials, a surface roughness was achieved that did not exceed the thickness of the first contact layer formed directly on the surface of the semiconductor material. At low temperatures up to 400 K, Ni was used as a contact layer, which performed all the necessary functions of contacts. At elevated temperatures, Mo was deposited directly onto the thermoelectric material, which has a low resistivity and low diffusion ability. It provides ohmic contact and adhesive strength with thermoelectric material, and also plays role of a

diffusion barrier layer. To ensure the temporal thermal stability of contact systems at high temperatures, an additional diffusion-barrier layer of amorphous material (Ta-W-N) was used. The amorphous state is characterized by ideal atomic-structural homogeneity, and the absence of crystal structure defects (dislocations, vacancies, grain boundaries, etc.) predetermines the exceptionally high chemical inertness of amorphous films, their low diffusion permeability and, accordingly, high thermal stability. The last layer of the contact system was formed from Ni, which served as a commutation layer for connection with the next thermoelement section or a commutation bus.

The surface preparation of the thermoelectric material before the formation of contact systems was carried out as follows. The required surface roughness was achieved by mechanical treatment using an ugly polishing method on lapping plates. This is due to the fact that in the case of soft materials, the abrasive is embedded in the material, changing its properties. All considered thermoelectric materials, except for SiGe, have low microhardness values from 25 to 70 kg/mm². After mechanical treatment, the samples were cleaned in Nefras C2-80/120 solvent and then in deionized water to remove the remains of the residual waste semiconductor material and vaseline oil used for polishing. Before loading into the chamber of the sputtering system, the samples were cleaned in isopropyl alcohol (Kontakt IPA) followed by drying with nitrogen.

Two types of samples of thermoelectric materials for studying influence of the roughness on the characteristics of contacts were prepared: with the roughness of the surface on which the contact system was formed 600 nm, which is comparable with the thickness of the diffusion-barrier layers; with the roughness of 200 nm, which is lower than the thickness of the barrier layer.

To study the relief, determine the surface roughness of the samples of thermoelectric materials and the thickness of the deposited contact layers profilometer KLA-Tencor P-7 was used.

The deposition of contact layers was carried out in a single vacuum cycle on unheated samples of thermoelectric materials with using of URM3.279.026 setup equipped with two magnetron systems. Following deposition regime was applied and film characteristics obtained:

- residual pressure in the vacuum chamber: not higher than $1 \cdot 10^{-3}$ Pa;

- pressure of the working gas Ar in the vacuum chamber: $6 \cdot 10^{-1}$ Pa;

- impurity concentration in the deposited film: no more than 1%;

- the thickness variation of the deposited film over a surface area of 50 cm^2 : not higher than 10%.

Single-layer nickel contact systems were formed for sections of thermoelement legs with low operating temperatures (Fig. 1).

The Mo/Ni contact system was formed by successive sputtering processes: first with a Mo target and then with a Ni target. Deposition of Mo and Ni was carried out at rates of 0.08 and 0.35 nm/s, respectively, the range of deposited film thicknesses was 200–400 nm.

2021 International Seminar on Electron Devices Design and Production (SED)

Three layer Mo/Ta-W-N/Ni contact system was formed by successive sputtering. Firstly, Mo target was sputtered in argon atmosphere, then composite Ta-W target in a mixture of argon and nitrogen gases, and at last Ni target in argon atmosphere. The deposition of Mo and Ni layers was carried out under the conditions indicated above. The reactive deposition of the Ta-W-N layer was carried out under the following conditions:

- residual pressure in the vacuum chamber: not higher than $1 \cdot 10^{-3}$ Pa;

- pressure of the reactive working gas N_2 in the vacuum chamber: $4{\cdot}10^{\text{-2}}\,\text{Pa};$

- pressure of the working gas Ar in the vacuum chamber: $6 \cdot 10^{-1}$ Pa;

- film deposition rate: 0.1 nm/s;

- deposited films thickness: 100-400 nm.

At the last stage of the process, Ni commutation layer was formed by sputtering a Ni target in an argon atmosphere.

Fig. 1 shows a multisection thermoelement with formed contact systems. Contact systems consisting of different contact layers (Ni; Mo/Ni; Mo/Ta-W-N/Ni) were formed on the samples of thermoelectric materials used for the manufacturing sections of thermoelement legs. Samples with formed contact systems (sections of thermoelement legs) were subjected to thermal annealing (annealing in vacuum at temperatures of 400, 600, 900, and 1200 K for 400 hours). After thermal annealing, the following studies were carried out.

To determine the thermal stability of contact systems, the samples were studied by Auger electron spectroscopy (AES) on a Scanning Auger Nanoprobe PHI-670xi (Physical Electronics) with a Schottky field emission thermal cathode. The sample was tilted by 30° relative to the normal position of the primary beam and the analyzer axis "cylindrical mirror", which is necessary for the ion cleaning of the surface with Ar+ beam and profile analysis. The AES method makes it possible to study the elemental composition of a near-surface layer with 2-3 nm thickness, and in addition, in combination with layer-by-layer ion sputtering of the sample surface, makes it possible to carry out a profile analysis of the distribution of elements over the sample depth. AES was used to study the diffusion of materials (components of thermoelectric materials and contact layers) through the contact layers.

The measurement of the adhesive strength of the films deposited on the samples was carried out by the direct tearing with using Force Gauge PCE-FM50 setup. Adhesion strength is measured in terms of the pull-off force per unit area (Pa). The error of measuring the adhesive strength did not exceed 5%.

The specific contact resistance was measured by the TLM method [7, 21-24]. A measuring stand was prepared for this purpose. To eliminate the resistance of the measuring commutation, a four-wire measurement circuit was used. Motech LPS-305 power supply was applied, and 100 mA current was passed through the contact during measurements. The voltage drop across the contact was determined using a Keithley DMM 6500 multimeter. The contact resistance measurement error did not exceed 10%.

IV. RESULTS AND DISCUSSION

The results of studying contact systems are presented in Table 1. For samples $Bi_2Te_{2.8}Se_{0.2}$ and $Bi_{0.5}Sb_{1.5}Te_3$ (section No. 1) with the roughness of 600 nm and formed Ni contacts with the thickness of 500 nm Te diffusion through the contact was observed even without thermal effect (300 K). This is due to the deformation of the contacts at high surface roughness and diffusion of Te through the cracks and discontinuities in the formed film. For this reason, low adhesive strength and high contact resistance was obtained. For samples with the roughness of 200 nm, which is much less than the thickness of the deposited film, no such problems were found.

A similar result was obtained for samples of the materials of section No. 1 and samples of $Bi_2Te_{2.4}Se_{0.6}$ and $Bi_{0.4}Sb_{1.6}Te_3$ (section No. 2) with Ni contacts after thermal annealing at 400 K (Fig. 1). So, for samples with the roughness of 200 nm, high adhesion and low contact resistance of nickel contacts were obtained.

For samples of $Bi_2Te_{2.4}Se_{0.6}$ and $Bi_{0.4}Sb_{1.6}Te_3$ with Ni contacts (section No. 2) at 600 K, even with the roughness of 200 nm, Te diffusion through the contact was found. Thus, the Ni film does not function as a diffusion barrier at these temperatures. In addition, at this temperature, Ni actively diffuses into the thermoelectric material. This affects the characteristics of the contacts (Table 1).

In this regard, in order to provide barrier functions on the discussed samples (section No. 2) contact systems were formed, consisting of Mo and Ni layers with the thicknesses of 400 and 200 nm, respectively. As can be seen from Table 1, this contact system does not perform its functions at a temperature of 600 K and a roughness of 600 nm, but it has good characteristics at a roughness of 200 nm. In further studies, contact systems were deposited on samples of thermoelectric materials only with the roughness of 200 nm.

For the third sections made of PbTe and GeTe, the Mo(400 nm)/Ni(200 nm) contact system has good results at 600 K. However, at 900 K molybdenum 400 nm thick does not perform barrier functions, which can be seen from the results of studies (Table 1). Therefore, for temperatures of 900 K a double barrier layer of Mo(400 nm)/Ta-W-N(400 nm) was used, which proved itself well at temperatures of 1200 K in sections No. 4 on the basis of SiGe. Thus, with the use of a three-layer contact system Mo(400 nm)/Ta-W-N(400 nm)/Ni(200 nm) for sections No. 3 and No. 4 good results were obtained at temperatures of 900 and 1200 K, which is due to the absence of diffusion, high adhesive strength and low contact resistance.

Analyzing the results of the research carried out, the following should be noted. The roughness of the surface of thermoelectric materials, on which contact systems are formed, should be significantly less than their thickness. Otherwise, deformation of the components of contact layers occurs, leading to the cracks and breaks, through which mutual diffusion of thermoelectric material elements and the material of contact layers occurs. The presence of defects in the contact layers was observed by the study of the surface morphology of the contact systems, carried out using a scanning electron microscope with a focused ion beam FEI Quanta 3D FEG.

Material (section	Surface	Contact system and thickness of each	Annealing	Diffusion of	Adhesion	Contact
No conductivity	roughness,	contact layer, nm	temperature,	materials	strength of	resistivity,
type)	nm		K	through contact	contact system,	Ohm·m ²
				layers	MPa	
$Bi_2Te_{2.8}Se_{0.2} (1-n)$	600	Ni(500 nm)	300	yes	8.36	$3.5 \cdot 10^{-9}$
	200	Ni(500 nm)	300	no	16.82	$0.5 \cdot 10^{-9}$
Bi _{0.5} Sb _{1.5} Te ₃ (1- p)	600	Ni(500 nm)	300	yes	7.24	$4.6 \cdot 10^{-9}$
	200	Ni(500 nm)	300	no	17.12	$0.8 \cdot 10^{-9}$
$Bi_2Te_{2.8}Se_{0.2} (1-n)$	600	Ni(500 nm)	400	yes	6.82	$5.5 \cdot 10^{-8}$
	200	Ni(500 nm)	400	no	16.73	0.6 · 10 ⁻⁹
Bi _{0.5} Sb _{1.5} Te ₃ (1- p)	600	Ni(500 nm)	400	yes	7.12	$7.8 \cdot 10^{-8}$
	200	Ni(500 nm)	400	no	16.94	0.9 · 10 ⁻⁹
Bi ₂ Te _{2.4} Se _{0.6} (2- n)	200	Ni(500 nm)	600	yes	6.61	8.2 · 10 ⁻⁸
	600	Mo(400 nm)/Ni(200 nm)	600	yes	8.41	$8.0 \cdot 10^{-8}$
	200	Mo(400 nm)/Ni(200 nm)	600	no	17.02	$2.5 \cdot 10^{-9}$
Bi _{0.4} Sb _{1.6} Te ₃ (2- p)	200	Ni(500 nm)	600	yes	7.22	$8.0 \cdot 10^{-8}$
	600	Mo(400 nm)/Ni(200 nm)	600	yes	6.43	7.9·10 ⁻⁸
	200	Mo(400 nm)/Ni(200 nm)	600	no	17.22	$2.7 \cdot 10^{-9}$
PTe (3- n)	200	Mo(400 nm)/Ni(200 nm)	600	no	16.11	$2.4 \cdot 10^{-9}$
GeTe (3- p)	200	Mo(400 nm)/Ni(200 nm)	600	no	16.76	2.3 · 10 ⁻⁹
PTe (3- n)	200	Mo(400 nm)/Ni(200 nm)	900	yes	7.81	8.5 · 10 ⁻⁸
GeTe (3- p)	200	Mo(400 nm)/Ni(200 nm)	900	yes	8.36	7.6 · 10 ⁻⁸
PTe (3- n)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	900	no	16.11	3.6 · 10 ⁻⁹
GeTe (3- p)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	900	no	16.46	3.3 · 10 ⁻⁹
SiGe (4- n)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	900	no	17.36	$2.9 \cdot 10^{-9}$
SiGe (4- p)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	900	no	17.28	3.1 · 10 ⁻⁹
SiGe (4- n)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	1200	no	16.81	$4.9 \cdot 10^{-9}$
SiGe (4- p)	200	Mo(400nm)/Ta-W-N(400nm)/Ni(200nm)	1200	no	16.92	4.8 · 10 ⁻⁹

TABLE I. RESULTS OF THE INVESTIGATION OF CONTACT SYSTEMS FORMED ON THE SECTIONS OF THERMOELEMENT LEGS AND ANNEALED FOR 400 HOURS

Nickel acts as a contact material at temperatures up to 400 K. At temperatures in the region of 600 K, Ni cannot be used as a contact layer directly on a thermoelectric material. At elevated temperatures, its interaction with elements of thermoelectric material leading to the formation of intermetallic compounds (antimonide and nickel telluride) in the boundary region reduces adhesion and increases contact resistance. In addition, intensive diffusion of Ni can lead to the degradation of thermoelectric material.

Up to the temperature of 900 K good contact characteristics were obtained using the Mo(400 nm)/Ni(200 nm) contact system. At temperatures above 900 K, it is necessary to enhance the functions of the barrier layer by using the amorphous Ta-W-N system. Thus, at high temperatures, it is advisable to use the Mo(400nm)/Ta-W-N(400nm)/Ni(200nm) contact system, in which Mo provides low contact resistance and high adhesive strength. In this case, along with Ta-W-N, it plays the role of a diffusion barrier layer. Nickel in this contact system is required for commutation of multisection thermoelement.

V. CONCLUSION

Ways of increasing the efficiency of TEG are considered. Compositions and methods of obtaining thermoelectric materials with increased values of thermoelectric figure of merit, which are designed for manufacturing of thermoelements and thermoelement sections operating in the temperature range 170–1200 K. The nanostructured thermoelectric materials are obtained with the following maximum values of the parameter ZT: $Bi_{2}Te_{2.8}Se_{0.2} - 1.15$; $Bi_{0.5}Sb_{1.5}Te_3 - 1.17$; $Bi_{2}Te_{2.4}Se_{0.6} - 1.16$; $Bi_{0.4}Sb_{1.6}Te_3 - 1.18$; PbTe - 1.31; GeTe - 1.41; SiGe - 1.23 for n-type and 1.21 for p-type. The ZT parameter is presented for the operating temperature range of each material. It has been established

that an increase in the figure of merit in nanostructured TEMs, in comparison with the materials with the usual structure, is determined by the decrease of the thermal conductivity by 10-15% due to phonon heat transfer.

The efficiency of TEG can be improved by increasing the temperature difference between the hot and cold junctions of thermoelements and, accordingly, by expanding the operating temperature range. This idea can be realized by using multisection legs in the thermoelement. Each section operates within a certain temperature range and is made of thermoelectric material having a maximum Z in these temperature ranges. The most important elements of the multisection thermoelement design are contact systems, the role of which is to ensure thermal stability and mechanical strength of the thermoelement, minimum contact resistance and resistance of commutation sections and thermoelement legs.

The main problems of creating effective contact systems for high-temperature thermoelements are determined. The influence of the surface roughness of a thermoelectric material on the quality of contacts formed on it was determined. It has been established that the surface roughness should be less than the thickness of the contact layers. A method for mechanical processing of the surface of thermoelectric materials was proposed, which provides the required roughness.

The structure and technology for obtaining effective contact systems for each thermoelectric material have been developed, from which leg sections are fabricated in multisection thermoelements with operating temperatures up to 1200 K.

It has been established that nickel acts as a contact material at temperatures up to 400 K. At higher temperatures,

2021 International Seminar on Electron Devices Design and Production (SED)

Ni is not recommended to be used as the first contact layer formed directly on a thermoelectric material. At elevated temperatures, its interaction with elements of thermoelectric material with the formation of intermetallic compounds (antimonide and nickel telluride) in the boundary region reduces adhesion and increases contact resistance. In addition, intense diffusion of Ni can lead to the degradation of the thermoelectric material.

Up to the temperatures of 900 K, good contact characteristics were obtained using the Mo(400 nm)/Ni(200 nm) contact system. At temperatures above 900 K, it is necessary to enhance the barrier layer characteristics by using the amorphous Ta-W-N system. Thus, at high temperatures, it is advisable to use the Mo(400nm)/Ta-W-N(400nm)/Ni(200nm) contact system, in which Mo provides low contact resistance and high adhesive strength. In this case, along with Ta-W-N, it plays the role of a diffusion barrier layer. Nickel in this contact system is required for commutation of multisection thermoelement.

Thus, the studies carried out have shown that effective contact systems have been developed for multisection thermoelements with operating temperatures from 300 to 1200 K, which have a high adhesive strength not lower than 16.0 MPa and a low contact resistance of not more than $4.9 \cdot 10^{-9}$ Ohm·m². As a result, temporal thermal stability of the thermoelement, high mechanical strength and reliability of contacts and, as a consequence, the efficiency of the thermoelement with operating temperatures up to 1200 K are achieved.

ACKNOWLEDGMENT

This work was supported by the Russian Science Foundation (grant number 20-19-00494).

REFERENCES

- A.A. Sherchenkov, Yu.I. Shtern, R.E. Mironov, M.Yu. Shtern, M.S. Rogachev, "Current State of Thermoelectric Material Science and the Search for New Effective Materials," Nanotechnologies in Russia, vol. 10, pp. 827-840, November 2015.
- [2] Z. Ma, Jiangtao W., P. Song, M. Zhang, L. Yang, J. Ma, W. Liu, F. Yang, X. Wang, "Review of experimental approaches for improving zT of thermoelectric materials," Materials Science in Semiconductor Processing, vol. 121, pp. 105303-1–105303-20, January 2021.
- [3] M.N. Hasan, H. Wahid, N. Nayan, M.S. Mohamed Ali, "Inorganic thermoelectric materials: A review," International Journal of Energy Research, vol. 44, pp. 6170-6222, June 2020.
- [4] Y. Lan, A.J. Minnich, G. Chen, Z. Ren, "Enhancement of Thermoelectric Figure-of-Merit by a Bulk Nanostructuring Approach," Advanced Functional Materials, vol. 20, pp. 357-376, February 2010.
- [5] A.A. Sherchenkov, Y.I. Shtern, M.Y. Shtern, M.S. Rogachev, "Prospects of creating efficient thermoelectric materials based on the achievements of nanotechnology," Nanotechnologies in Russia, vol. 11, pp. 387-400, July 2016.
- [6] M.Y. Shtern, M.S. Rogachev, Y.I. Shtern, A.A. Sherchenkov, A.O. Kozlov, "Creation of multisectional thermoelements for increasing of the efficiency of thermoelectric devices," 2019 International Seminar on Electron Devices Design and Production, SED 2019 – Proceedings, IEEE, 2019. pp. 8798432-1–8798432-6.
- [7] M. Shtern, M. Rogachev, Y. Shtern, D. Gromov, A. Kozlov, I. Karavaev, "Thin-film contact systems for thermocouples operating in a wide temperature range," Journal of Alloys and Compounds, vol. 852, pp. 156889-1–156889-10, January 2021.
- [8] S. Twaha, J. Zhu, Y. Yan, B. Li, "A comprehensive review of thermoelectric technology: materials, applications, modelling and performance improvement," Renew. Sustain. Energy Rev., vol. 65, pp. 698-726, November 2016.

- [9] C.L. Cramer, H. Wang, K. Ma, "Performance of functionally graded thermoelectric materials and devices: a review," J. Electron. Mater., vol. 47, pp. 5122-5132, September 2018.
- [10] P.H. Ngan, L. Han, D.V. Christensen, "Joining of half-heusler and bismuth tellurides for segmented thermoelectric generators," J. Electron. Mater., vol. 47, pp. 701-710, January 2018.
- [11] M.Yu Shtern, I.S. Karavaev, Y.I. Shtern, A.O. Kozlov, M.S. Rogachev, "The surface preparation of thermoelectric materials for deposition of thin-film contact systems," Semiconductors, vol. 53, pp. 1848-1852, December 2019.
- [12] D.G. Gromov, Yu.I. Shtern, M.S. Rogachev, A.S. Shulyat'ev, E.P. Kirilenko, M.Yu Shtern, V.A. Fedorov, M.S. Mikhailova, "Mo/Ni and Ni/Ta-W-N/Ni thin-film contact layers for (Bi,Sb)₂Te₃-based intermediate-temperature thermoelectric elements," Inorg. Mater., vol. 52, pp. 1132-1136, November 2016.
- [13] R.P. Gupta, K. Xiong, J.B. White, K. Cho, H.N. Alshareef, B.E. Gnade, "Low resistance ohmic contacts to Bi₂Te₃ using Ni and Co metallization," J. Electrochem. Soc., vol. 157, pp. H666-H670, 2010.
- [14] X. Zhu, L. Cao, W. Zhu, Y. Deng, "Enhanced interfacial adhesion and thermal stability in bismuth telluride/nickel/copper multilayer films with low electrical contact resistance," Adv. Mater. Interfaces, vol. 5, pp. 1801279-1–1801279-9, December 2018.
- [15] E.K. Belonogov, V.A. Dybov, A.V. Kostyuchenko, S.B. Kushev, D.V. Serikov, S.A. Soldatenko, "Effect of pulsed photon treatment on the mechanical properties of semiconductor thermoelectric legs, based on Bi₂Te₃-Bi₂Se₃ solid solutions, and the adhesion of switching layers," Journal of Surface Investigation, vol. 13, pp. 371-377, May 2019.
- [16] T. Sakamoto, Y. Taguchi, T. Kutsuwa, K. Ichimi, S. Kasatani, M. Inada, "Investigation of barrier-layer materials for Mg₂Si/Ni interfaces," J. Electron. Mater., vol. 45, pp. 1321-1327, March 2016.
- [17] A. Ferrario, S. Battiston, S. Boldrini, T. Sakamoto, E. Miorin, A. Famengo, A. Miozzo, S. Fiameni, T. Iida, M. Fabrizio, "Mechanical and electrical characterization of low-resistivity contact materials for Mg₂Si," Mater. Today: Proceedings, vol. 2, pp. 573-582, 2015.
- [18] H.-C. Hsieh, C.-H. Wang, W.-C. Lin, S. Chakroborty, T.-H. Lee, H.-S. Chu, A.T. Wu, "Electroless Co-P diffusion barrier for n-PbTe thermoelectric material," Journal of Alloys and Compounds, vol. 728, pp. 1023-1029, 2017.
- [19] C.-H. Chuang, Y.-C. Lin, C.-W. Lin, "Intermetallic Reactions during the Solid-Liquid Interdiffusion Bonding of Bi₂Te_{2.55}Se_{0.45} Thermoelectric Material with Cu Electrodes Using a Sn Interlayer," Metals, vol. 6, pp. 92-1–92-10, April 2016.
- [20] W. Liu, H. Wang, L. Wang, X. Wang, G. Joshi, G. Chen, Z. Ren, "Understanding of the contact of nanostructured thermoelectric n-type Bi₂Te_{2.7}Se_{0.3} legs for power generation applications," Journal of Materials Chemistry A, vol. 1, pp. 13093-13100, November 2013.
- [21] M.Yu. Shtern, "Development and application of a research technique to study thermal and electrophysical parameters of thermoelectric materials at temperatures up to 1200 K," in Proceedings of the 2019 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering, IEEE, 2019. pp. 1920-1926.
- [22] V. Kessler, M. Dehnen, R. Chavez, M. Engenhorst, J. Stoetzel, N. Petermann, K. Hesse, T. Huelser, M. Spree, C. Stiewe, P. Ziolkowski, G. Schierning, R. Schmechel, "Fabrication of high-temperature-stable thermoelectric generator modules based on nanocrystalline silicon," J. Electron. Mater., vol. 43, pp. 1389-1396, May 2014.
- [23] Y. Thimont, Q. Lognone, C. Goupil, F. Gascoin, E. Guilmeau, "Design of apparatus for Ni/Mg₂Si and Ni/MnSi_{1.75} contact resistance determination for thermoelectric legs," J. Electron. Mater., vol. 43, pp. 2023-2028, June 2014.
- [24] G.K. Reeves, H.B. Harrison, "Obtaining the specific contact resistance from transmission line model measurements," IEEE Electron. Device Lett., vol. 3 pp. 111-113, May 1982.