The protective coatings for the multisectional thermoelements of the generators working at the temperatures up to 1200 K

Yu I Shtern, N V Igumnova, A A Sherchenkov, M S Rogachev and M Yu Shtern
National Research University of Electronic Technology, Russia, Moscow, Zelenograd
E-mail: m.s.rogachev88@gmail.com

Abstract. To increase efficiency structure of multisectional thermoelectric generator working up to the temperature of 1200 K was developed. Compositions were proposed, and thermoelectric materials were obtained for the fabrication of each section of thermoelement. Investigations showed that these materials have high figure of merit. Sublimation of thermoelectric materials in the working temperature of multisectional thermoelement was investigated. To eliminate sublimation of thermoelectric material, Si₃N₄ and SiO₂ protective layers were deposited by plasma-chemical method, which were effective up to the temperature of 1200 K.

1. Introduction
Low efficiency restricts wide application of thermoelectric generators – perspective alternative electric power source. One of the possible ways of increasing efficiency is connected with the increasing of temperature difference (ΔT) between the hot and cold junctions of the thermoelectric element (TE), which can be as high as 900 K. However, existing thermoelectric materials (TM) have high thermoelectric parameters only in narrow temperature range. In this case for the realization of this approach of increasing efficiency it is necessary to fabricate TE with multisectional legs. For this purpose it is required to solve complicated scientific and practical problems. In this work results of the fabrication of a number of semiconductor materials with increased thermoelectric figure of merit in the temperature range from 300 to 1200 K, optimization of geometrical sizes of each section of the TE legs, and development fabrication technology of the protective coverings for the prevention of sublimation of TM section legs at high temperatures.

2. Experimental
A number of TM perspective for the application in the temperature range from 300 to 1200 K were investigated. Taking into account temperature dependencies of thermo- and electrophysical parameters of TM, it is proper to use 4 sections for the TE legs working at the temperatures up to 1200 K (figure 1). Investigations allowed developing 8 TM for the multisectional TE.

For the low temperature sections of TE legs TM with working temperature up to 400 K were prepared by zone melting method:

– n-type leg, section № 1 – Bi₂Te₂.₈Se₀.₂, doped by CdCl₂ (0.14 wt. %);
– p-type leg, section № 1 – Bi₀.₅Sb₁.₅Te₃, doped by Te (2 wt. %) and TeI₄ (0.14 wt. %).

TM for the middle temperature sections of TE legs:
– n-type leg, section № 2 – Bi$_{2.0}$Te$_{2.4}$Se$_{0.6}$, doped by CuBr (0.18 wt. %), prepared by zone melting method, working temperature up to 650 K;
– p-type leg, section № 2 – Bi$_{0.8}$Sb$_{1.6}$Te$_{2.0}$, doped by PbCl$_2$ (0.12 wt. %) + Te (1.50 wt. %), prepared by zone melting method, working temperature up to 650 K;
– n-type leg, section № 3 – PbTe, doped by PbI$_2$ (0.2 wt. %) and Ni (0.3 wt. %), prepared by hot pressing, working temperature up to 900 K;
– p-type leg, section № 3 – (GeTe)$_{0.96}$-(Bi$_2$Te$_3$)$_{0.04}$, prepared by hot pressing, working temperature up to 900 K.

Materials for the high sections of TE legs with working temperature up to 1200 K were prepared by the method of spark plasma sintering:
– n-type leg, section № 4 – Si$_{0.8}$Ge$_{0.2}$, doped by P (2.2 wt. %);
– p-type leg, section № 4 – Si$_{0.8}$Ge$_{0.2}$, doped by B (1.8 wt. %).

Fabricated TM has high values of thermoelectric figure of merit (figure 2, designations: 1 – Bi$_{0.5}$Sb$_{1.5}$Te$_3$; 2 – Bi$_2$Te$_{2.8}$Se$_{0.2}$; 3 – Bi$_{1.2}$Te$_{2.2}$Se$_{0.6}$; 4 – Bi$_{0.8}$Sb$_{1.8}$Te$_{3.0}$; 5 – PbTe; 6 – (GeTe)$_{0.96}$-(Bi$_2$Te$_3$)$_{0.04}$; 7 – Si$_{0.8}$Ge$_{0.2}$ (P 2.2 wt. %); 8 – Si$_{0.8}$Ge$_{0.2}$ (B 1.8 wt. %)), which in the in the working temperature range are not inferior to the best analogues [1].

One of the important problems of the designing of multisectional TE is optimization of the sizes of each section of the TE leg. In addition to the electrical parameters, height of the section (h) for the $\Delta T$ of TE determines the working temperature range of given section. Method and mathematical model for the calculation of sections sizes and software for its realization were developed, which allows optimizing TE structure [2].

Methods of chemical, electrochemical, vacuum deposition were developed and used for the fabrication of contact systems to each TM. Summarizing – structures of contact systems and methods and regimes of contact layers depositions were developed; electrophysical parameters and adhesion strength (adhesion strength was not less than 9.0 MPa) of contact layers were investigated [3, 4].

Application of developed TM and optimized TE structure allowed to create generators with multisectional TE, which demonstrated high efficiency of 10 %.

One of the main problems of the high temperature TE designing is connected with the sufficient sublimation of TM at high temperatures. However, protection methods of TE legs is not developed [5, 6]. At practice for middle temperature materials (working temperature range up to 900 K) heat-resistant enamel KO-818 is used. For high temperature conditions protection options are not presented. In this work ways of protections of the TE legs working at the temperatures up to 1200 K are
proposed. Technologies of protection coverings are developed, and samples with proposed coverings are fabricated. Samples with coverings were investigated.

Investigations of the sublimation of the developed TM for middle and high temperature leg sections were investigated before the formation of the protective coverings in the working temperature ranges characteristic for each section.

Investigations of the samples on the basis of PbTe, GeTe and SiGe by the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out with using of TA Instruments SDT Q600 in the temperature range from 340 to 1200 K, argon flow of 100 ml/min and at the heating rate of 10 K/min.

To prevent TM evaporation of the leg sections following protective coverings were tested: enamel KO-818, Si₃N₄ and SiO₂ layers. Operations of cutting, grinding, polishing and cleaning were performed for all samples before the fabrication of protective covering.

Three layers of enamel KO-818 was manually put on every side of the sample. Draying at the temperature of 470 K during 2 h was carried out after the application of each layer. The total thickness of the layer was 0.1–0.2 mm.

Si₃N₄ and SiO₂ layers were deposited by the plasma chemical method (CORIAL D250) with the thicknesses of 1.0 and 0.25 μm, respectively. During the deposition gas pressure was 133 Pa, and temperature was 520 K. Weight losses of the samples with the protective coverings were controlled after the heat treatment during 1 h. Mettler Toledo XS205DU was used for the measuring of sample weight.

3. Results and discussions

According to the DSC and DTA measurements sufficient changes of the thermal properties and weight losses are observed for TM on the basis of PbTe at the temperatures higher than 950 K (figure 3). Meanwhile the weight losses exceed 15 %. For GeTe (figure 4) intensive endothermic effect was found on the DSC curve with the peak at the temperature of ~968 K, accompanied by the sharp weight losses, which reached ~80 %.

![Figure 3. DSC and TGA curves for PbTe.](image)

According to the DSC and TGA data there is no sufficient heat effects in the temperature range from room temperature to 1200 K for TM on the basis of SiGe. The weight losses are on the order of hundredths of a percent (figure 5).

Then estimation of the weight losses after the heating in the heat chamber of the samples with the protective coverings was carried out. For middle temperature TM on the basis of PbTe and GeTe testing temperature ranges were 670–900 K, while for the high temperature material SiGe-970 – 1200 K (figures 6–8).

4. Conclusions

It was established that enamel KO-818 is cracking already at the temperature of 770 K, and is not suitable for the protection of TM at higher temperatures. Using of Si₃N₄ as protective layer for TM on
the basis of PbTe and GeTe lead to the weight losses of 0.18 and 0.14 %, respectively. For TM on the basis of SiGe weight losses were not found. In the case of using of SiO\textsubscript{2} as protective layer for TM on the basis of PbTe weight losses does not exceed 0.5 %, while for TM on the basis of GeTe and SiGe weight losses were not observed.

**Figure 5.** DSC and TGA curves for SiGe.

**Figure 6.** Temperature dependencies of the weight losses for PbTe sample with the protective coverings: 1 – KO-818; 2 – Si\textsubscript{3}N\textsubscript{4}; 3 – SiO\textsubscript{2}.

**Figure 7.** Temperature dependencies of the weight losses for GeTe sample with the protective coverings: 1 – KO-818; 2 – Si\textsubscript{3}N\textsubscript{4}; 3 – SiO\textsubscript{2}.

**Figure 8.** Temperature dependencies of the weight losses for SiGe sample with the protective coverings: 1 – KO-818; 2 – Si\textsubscript{3}N\textsubscript{4}; 3 – SiO\textsubscript{2}.

The investigations showed that protective covering of enamel KO-818 can be used up to the temperature of 720 K. Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} protective layers fabricated by the plasma chemical method demonstrated effectiveness and stability in all temperature range.

**Acknowledgments**

This work was supported by Russian Science Foundation (project number 16-19-10625).

**References**

[1] Sherchenkov A A, Shtern Y I, Shtern M Y and Rogachev M S 2016 *Nanotechnologies in Russia* **11** 387–400

[2] Shtern I Yu, Gromov D G, Shtern M Yu, Sherchenkov A A and Rogachev M S 2017 *Proc. of the 2017 IEEE Russia Section Young Researchers in Electrical and Electronic Engineering Conf.* (Moscow: MIET) ed. S Lupin pp. 236–9

[3] Shtern Y I, Mironov R E, Shtern M Y, Sherchenkov A A and Rogachev M S 2016 *Acta physica polonica A* **129** 785–7
[4] Gromov D G, Shtern Yu I, Rogachev M S, Shulyat’ev A S, Kirilenko E P, Shtern M Yu, Fedorov V A and Mikhailova M S 2016 Inorganic Materials 52 1132–6
[5] Park S H, Kim Y, Yoo C Y and Yoon G 2016 J. Vac. Sci. Technol. A 34 061101–9
[6] Sadia Y, Ohaion-Raz T, Ben-Yehuda O, Korngold M and Gelbstein Y 2016 J. Solid State Chem. 241 79–85