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Typical mechanisms of degradation of thermoelectric materials and ways to reduce their impact on the reliability of thermoelectric modules

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The review considers a number of typical mechanisms of degradation of thermoelectric materials in the process of their functioning as a part of thermoelectric generator modules. Among them are diffusion and self-diffusion in thermoelectric materials and contact structures, loss of dopants by thermoelectric materials due to sublimation, formation of intermetallic compounds in contact structures, accumulation of structural defects under the influence of thermal and mechanical loads, mechanical destruction of thermoelectric legs, contact structures and other structural members of modules, chemical interaction of thermoelectric materials with other structural members. The main design and technological ways and methods of reducing the negative impact of these mechanisms on the reliability of thermoelectric materials and modules are also considered.

Keywords: diffusion, self-diffusion, sublimation, contact intermetallic compounds, accumulation of structural defects, mechanical strength, chemical interaction, constructive and technological ways and factors of increasing reliability.

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Introduction

The reliability of thermoelectric generator and cooling modules is even more important than their consumer performance. Considerable attention to the reliability of thermoelectric generator and cooling modules is due to their use as part of such products and objects and in such conditions when replacement of failed modules is impossible or significantly difficult. These are spacecraft, military equipment, some medical devices, in particular, pacemakers, etc. This forces the developers of generator and cooling modules to study and investigate the degradation mechanisms of thermoelectric materials and modules and take special design and technological measures to reduce their negative impact on reliability.

The main mechanisms of degradation of thermoelectric materials and modules include diffusion and self-diffusion in thermoelectric materials and contact structures, loss of dopants by thermoelectric materials due to sublimation, formation of intermetallic compounds in contact structures, solid phase electrolysis, accumulation of structural defects under the influence of thermal and mechanical loads, mechanical destruction of thermoelectric legs, contact structures and other structural elements of modules, chemical interaction of constituent thermoelectric materials with the environment or other elements of module construction.

Therefore, the purpose of this article is to provide a brief overview and analysis of the main degradation mechanisms of thermoelectric materials and modules, design and technological ways and methods to reduce their impact on the reliability of modules.

I. Changes in the characteristics of thermoelectric materials and modules due to the sublimation of volatile dopants and components and the interaction of the leg material with the environment

In many semiconductor thermoelectric materials, dopants or components of starting materials have the ability to sublimate [1, 2], especially at high temperatures. Sublimation creates a certain shortage of dopant atoms. As a result of diffusion, impurities from the depth of the crystal come to the evaporation surface and also evaporate. As a result, there is either a change in the composition of the base material, or its depletion in dopant, which can not only change the thermoelectric characteristics of the material, but sometimes even the type of its conductivity. Such components or impurities include tellurium and selenium in alloys of the *Bi(Sb) -Te(Se)* system, tellurides and selenides of lead and tin, halogens as dopants, cadmium in alloys of the *Cd-Sb* system, silicon in the *Ge-Si* system, etc. Let us consider this mechanism in more detail.

We begin with alloys of the *Bi(Sb) -Te(Se)* system. In [3] it was found that stoichiometric Bi_2Te_3 always possesses *p*-type conductivity and only tellurium content above 63% at.% gives *n*-type conductivity, which means a relative tellurium excess of about 5%. It is this excess tellurium that can partially sublimate if thermoelectric legs of *n*-type conductivity function as part of thermoelectric generator modules. Stoichiometric tellurium in the range of application of the alloys of this system does not sublimate, since it is firmly bound in the tellurium layers. To obtain *p*-type legs, Bi_2Te is doped with an excess of non-sublimating bismuth. Also, to obtain *n*-type legs, tellurium is partially replaced by selenium, so that part of the telluric layers in quintets is replaced by selenium layers [2]. Thus, for example, *n*-type materials are obtained with the compositions $Bi_2Te_{2.4}Se_{0.6}$, $Bi_2Te_{2.7}Se_{0.3}$, $Bi_2Te_{2.4}Se_{0.6}$, $Bi_2Te_{2.4}Se_{0.9}$. But since all these materials are low-temperature, special coatings of the lateral surface of the legs made of such materials are not used precisely to prevent sublimation. Nevertheless, polymer coatings of the lateral surface of such legs are used, for example, to prevent damage to semiconductor thermoelectric materials in the process of manufacturing thermoelectric modules. So, for example, in the Author's certificate [4] in order to improve the technology of manufacturing thermopile, the following is proposed. On the surface of each leg, which is not subjected to processing and joining immediately after cutting the thermoelectric material into legs, apply a protective coating containing epoxy resin and a catalyst and characterized in that it additionally contains polynaphthol with such a ratio of ingredients in mass percent: epoxy resin - 62.9, polynaphthol - 35.2, caustic potassium - 1.9. With a similar purpose, the patent [5] proposes to cover the lateral surface of thermoelectric legs with a special electrodeposited paint-and-lacquer coating with fluoroelastomer, hardening at a high temperature.

In this case, the reliability of thermoelectric module is increased due reducing the rate of its thermal degradation and increasing resistance to cyclic temperature effects; increasing the resistance of semiconductor thermoelectric legs to chemical, thermal and mechanical influences during the manufacture and operation of modules increasing the adhesion and elasticity of the polymer coating of thermoelectric legs and excluding its peel-off in the temperature cycling mode. This is achieved by the fact that the rods are made of thermoelectric material by hot extrusion, after which the lateral surface of the rods is prepared and a water-based paint-and-lacquer composition with fluoroelastomer is applied to it by the method of cathodic or anodic deposition to obtain a protective polymer coating. Next, the rods are washed and heat treated in order to solidify the coating, then the rods are cut in order to obtain semiconductor thermoelectric legs of a given length, following which, anti-diffusion layers are applied to the end surfaces of thermoelectric legs so that their edges are in contact with the protective coating, but do not cross it.

Another situation, however, is with medium-temperature thermoelectric materials, such as lead and tin tellurides and selenides. Due to the higher temperatures of their use, the prevention of sublimation of tellurium and selenium, and, moreover, their sublimation in general is of fundamental importance. For example, in the case of a change in the temperature of lead telluride from 780 to 960 K, the elasticity of its vapor increases from $9.8 \cdot 10^{-5}$ to $4.8 \cdot 10^{-2}$ mm Hg. This forces to take special measures to prevent sublimation of such thermoelectric materials in general and their components. This factor is even more important for the Ge-Si system, which operates at higher temperatures. It should be noted that the strongest ability of semiconductor materials to sublimate is manifested in the case of their presence in vacuum. Subliming components condense on other structural members of thermoelectric modules and energy converters in general, which have a lower temperature, including in open areas of electrical insulation. In particular, in [6] it is noted that in the course of bench tests of the converter reactor of the "Romashka" installation, a significant decrease in the insulation resistance was found due to an increase in surface conductivity. It was possible to significantly restore the insulation by letting air into the heated chamber for a short time, the oxygen of which oxidized the condensate and reduced the surface conductivity of the electrical insulating assemblies. And in the process of bench resource tests of thermopiles made of silicon-germanium alloy of RTG "Orion" in the temperature difference ~ 440°C (with maintenance of hot junction temperature not higher than 1000°C with the average about 970°C) after 11407 hours as a result of interaction with alloy vapors the molybdenum heater failed. After installing a new heater and replacing all thermocouples, the test was continued. It was found that the resistance in the steady state increases almost linearly by about 1% over 1000 hours. If there is an increase in thermoEMF, it is an order of magnitude less than the increase in resistance. Glassy enamels are usually used as protection against sublimation; in particular, a borosilicate glass coating is used to protect legs made of *p*-type alloys based on germanium telluride. Despite the fact that the saturated vapor pressure of lead telluride is two orders of magnitude lower than germanium telluride, the legs of the *n*-type thermoelement are also covered with borosilicate enamel.

Analysis of the causes of failure of RTG thermopiles containing thermoelement legs made of lead telluride and an alloy based on germanium telluride has shown that the cause is the destruction of silver or copper connecting buses. Destruction of the buses was caused by interaction with the vapors of tellurium sublimated from *p*-type legs based on germanium telluride due to defects in the enamel coating found near the failed connecting buses. Violation of the enamel coating can occur under the action of thermal stresses. Molecules of oxygen, water and carbon dioxide adsorbed by thermoelectric material play a significant role in their appearance. To prevent the detrimental effects of enamel coating defects, additional layers of enamel, including organosilicon ones, are applied to it. Inter-element porous thermal insulation is also effective, which prevents the passage of vapors of subliming elements to connecting buses and open areas of electrical insulation.

From the silicon-germanium alloy at high temperatures, the dopant phosphorus and silicon are primarily sublimated, which, condensing, reduce the electrical insulation resistance. The presence of oxygen, adsorbed or present in the environment, accelerates the sublimation process. During the oxidation of the alloy, volatile molecules of silicon and germanium monoxides (Si, Ge) are formed [6, 7]. Monoxides in the condensate decompose ($2SiO \rightarrow Si_2 + O_2$), forming an electrically conductive layer. At high temperatures, the reverse process is possible, so the anti-sublimation coating of glass on a silicon-germanium alloy is short-lived. As a result of the interaction of dioxide with silicon and germanium under the coating, the pressure of subliming monoxides increases, which contributes to the destruction and delamination of the glass coating.

Silicon nitride (Si_3N_4) is used as antisublimation protection of the silicon-germanium alloy. As in any coating, it may have defects in the form of cracks and pores. In this regard, it is successively applied in the form of thin layers, increasing to an optimal thickness of about 1 μm. In the presence of such a coating on silicon, its weight loss is reduced by an order of magnitude. The service life of the coating depends on the environment and impurities in the material. Oxygen and moisture adsorbed in the material interact with the components of the material, increasing the pressure of the sublimating elements under the coating and destroying it. Also, destructive effect on the coating has the impurity in the environment of carbon monoxide (CO).

In [8], it was reported about the successful ceramic coating of thermoelectric manganese silicide legs. The effect of the composition of glass ceramics on the change in the thermoelectric properties of coated materials compared to uncoated materials was investigated in the process of thermal cycling between room temperature and a temperature of 600^0C. The composition of glass ceramics in mass percent is as follows: SiO_2 – 66.3, Al_2O_3 – 1.8, Li_2O – 2.3, Na_2O – 2.7, K_2O – 9.8, B_2O_3 – 1.2, BaO – 15.9. The coating was prepared by mixing the powder of this glass-ceramic with ethanol. 10 cycles were carried out between room temperature and a temperature of 600^0 C at a heating (cooling) rate of 1000 deg/hour with an interval of 1 hour. It is shown that the thermoelectric characteristics of the coated material after thermal cycling are practically equal to the characteristics of the original uncoated material, whereas in the absence of a coating, the characteristics of the material are significantly reduced.

There is also a patent [9], the essence of which is to cover part of the surface of a leg based on skutterudite with a metal foil in order to prevent sublimation from thermoelectric material, which, as it is believed, can lead to a drop in the power and efficiency of a thermoelectric generator with such legs.

The creation of an environment of pure inert gases also suppresses the sublimation phenomena of degradation, and the better the higher their pressure.

II. Diffusion of main components and dopants in the materials of thermoelectric legs

The degradation of the parameters of thermoelectric materials and modules is significantly affected by the diffusion of dopants and the main components of semiconductor materials of thermoelectric legs. The most significant factor influencing this degradation mechanism of thermoelectric materials and modules is temperature and its gradient, because the temperature dependence of diffusion coefficients of both dopants and the main components of semiconductor materials of thermoelectric legs is subject to the law of Arrhenius. In this case, the nature of the change in the parameters of thermoelectric materials can be significantly influenced by the anisotropy of the diffusion coefficient, which occurs, in particular, in single crystals of bismuth telluride and alloys based on it, having a layered structure composed of hexagonal layers. Thus, studies performed by the author [10] showed that for such impurities in bismuth telluride as copper, gold and cadmium significant anisotropy is inherent in both the preexponential multiplier and the diffusion activation energy, and for silver preexponential multipliers in the perpendicular directions almost do not differ, and activation energies differ by about 2.5 times. Table 1 gives an approximate idea of the depth to which certain impurities in bismuth telluride could diffuse over 20 years if this depth were not limited to, say, the length of thermoelectric legs in a real module.

From this table we see that such impurities as copper, gold, silver and cadmium during this time and even earlier are able to penetrate the entire length of the thermoelectric leg. Thus, it is necessary to use special anti-diffusion layers when creating contact structures, which we will discuss below.

The following regularities of diffusion of the above indicated impurities in Bi_2Te_3 single crystals were found:

a) sharp anisotropy of the diffusion coefficient, which increased with decreasing temperature;

b) abnormally high diffusion coefficient in the direction of the cleavage planes (layers), especially for copper and gold, which at 500^0C reached about 10^{-4} cm^2/s;

c) abnormally low diffusion activation energies in the direction of the cleavage planes (layers), especially for copper and gold (about 0.18 eV);

d) there is no correlation between the diffusion rate (activation energy) and the value of the diffusing ion: copper diffuses at the same rate as gold, although their ionic radii differ by almost one and a half times, amounting to 0.096 and 0.137 nm, respectively. On the other hand, the radii of cadmium and silver ions, being 0.097 and 0.126 nm, respectively, differ less, and their diffusion parameters differ more significantly;

e) the distribution of impurities in the depth of the diffusion zone both in the plane of the layers and perpendicular to them is described by Fick's law.

Table 1

Depth of penetration of some impurities into bismuth telluride over 20 years.

Impurity	Depth of diffusion parallel to the layers at 300K,mm	Depth of diffusion parallel to the layers at 500K,mm	Depth of diffusion perpendicular to the layers at 300K,mm	Depth of diffusion perpendicular to the layers at 500K,mm
Cu	$2.325{\cdot}10^3$	$9.347{\cdot}10^3$	0.287	69.433
Ag	21.114	542.57	$1.097{\cdot}10^{-5}$	0.093
Au	$1.04{\cdot}10^3$	$4.18{\cdot}10^3$	0.653	45.839
Cd	9.783	399.712	$1.181{\cdot}10^{-8}$	0.013
Te			$1.302{\cdot}10^{-13}$	$6.846{\cdot}10^{-6}$

The exception was iodine. It turned out that its distribution systematically deviates from the theoretical dependence towards higher concentrations. It has been suggested that this deviation is due to the dependence of the iodine diffusion coefficient on the concentration. The basis for this assumption was the high solubility of iodine in bismuth telluride until the formation of the triple compound BiTeJ, which is structurally isomorphic to Bi_2Te_3. The concentration dependence of the iodine diffusion coefficient in Bi_2Te_3 was calculated by the so-called Matano method. The calculation showed that the iodine diffusion coefficient on the predominant part of the diffusion penetration depth is inversely proportional to the square of the iodine concentration.

The anisotropic nature of the diffusion was explained by the peculiarities of the layered structure of Bi_2Te_3 and the so-called heterodesmic nature of the bond between *Bi* and *Te* atoms.

The high velocity and low activation energy of diffusion along the cleavage planes (layer planes) are due to the significant distances between the layers and the weak bond between the quintets of bismuth and tellurium atoms (Te_{II} - Bi - Te_I - Bi - Te_{II})), as well as the high homogeneity of the crystal field lattice in this direction.

On the other hand, solder components can also penetrate into the material, which are also capable of undesirably changing the thermoelectric characteristics of the semiconductor materials of the thermoelectric legs. This is important for thermoelectric coolers, in which connection, at least from the cold side, is done with an anti-diffusion layer. Therefore, for example, in [9], the diffusion coefficients of silver and antimony in solid solutions Bi_2Te_3-Sb_2Te_3 and Bi_2Te_3-Bi_2Se_3 were investigated. It was found that the corresponding diffusion coefficients in the temperature range 100 – 500^{0}C are subject to the following dependences:

$$D_{Sb\to Bi_2Te_3\to Sb_2Te_3} = 2.5\cdot 10^{-7}\exp\left(-0.51/kT\right), \quad (1)$$

$$D_{Ag\to Bi_2Te_3\to Bi_2Se_3} = 3.9\cdot 10^{-4}\exp\left(-0.36/kT\right). \quad (2)$$

In formulae (1) and (2), the numerical values of the preexponential factors are given in cm^2/s, and the numerical values of the activation energies are in eV. The relatively low values of the diffusion activation energy were explained by the intercrystalline nature of diffusion, since the experiments were carried out on polycrystalline samples. The rediffusion (emergence to the surface) of silver in the Bi_2Te_3-Bi_2Se_3solid solution was also discovered and investigated. During the research, it was found that the cause of rediffusion is the oxidation of the Bi_2Te_3-Bi_2Se_3 alloy and the redistribution of impurity ions between the bulk of the substance and the oxide film. In an inert or reducible medium (argon, vacuum, hydrogen), the rediffusion process is weakened.

From the point of view of the mathematical description of such a physical model of the rediffusion process, the problem of the redistribution of an impurity between the volume of a substance and an oxide film on the surface in the first approximation is reduced to the problem of diffusion from a semi-bounded body with a boundary that moves in the presence of complete binding at this limit of particles that diffuse. In this case, the depth distribution of silver concentration N is described by the equation:

$$N(x,t) = \frac{N_0}{2}\left[\operatorname{erf}\left(\frac{x+vt}{2\sqrt{Dt}}\right) + \exp\left(-\frac{vx}{D}\right)\operatorname{erf}\left(\frac{x-vt}{2\sqrt{Dt}}\right)\right], \quad (3)$$

where N_0 is the initial concentration of silver, evenly distributed in the bulk of the sample, v is the average speed of the binding boundary, x is depth, t is time, D is the diffusion coefficient of the dopant. In this case, for silver in the Bi_2Te_3-Bi_2Se_3 samples annealed in air, the value of the indicated diffusion coefficient at 300^{0}C is $4\cdot 10^{-8}$ cm^2/s. It was also found that preliminary doping of Bi_2Te_3-Bi_2Se_3 solid solutions with iodine significantly reduces rediffusion. It has been suggested that iodine imposes an additional bond on silver ions, preventing them from reaching the surface. This feature of iodine as a doping impurity was proposed to be used to increase the stability of solid solutions based on Bi_2Te_3 doped with metals of the copper subgroup.

It is believed that the diffusion of impurities in the plane of the layers is significantly faster than in the perpendicular direction because the diffusing ion interacts with the potential field of the crystal lattice. This process is influenced not only by the Coulomb energy of attraction or repulsion, but also by the energy of repulsion due to the overlap of the electronic shells of converging atoms and the polarization energy of the charged ion by the surrounding dipoles. The movement of an ion in a direction perpendicular to the layers occurs in an inhomogeneous potential field. In this case, the greatest depth of the potential well and, consequently, the most stable position of the ion, takes place in the Bi- Te_{II} interstice (at the edge of the quintet). This result is due to the greatest asymmetry of the forces acting on the impurity ion in this interstice from the side of the surrounding atoms. The study of diffusion, for example, of gold in crystals based on bismuth telluride, showed that upon cooling of the samples after diffusion annealing, an intense decomposition of the solid solution of gold in bismuth telluride (precipitation) occurs. Large clusters of dislocations were detected by electronographic analysis at the sites of precipitation of the precipitate. Therefore, the phenomenon of precipitation is also able to significantly change the thermoelectric characteristics of crystals. In addition, precipitation leads to the appearance of significant plastic stresses, which cause the formation of new dislocations, their accumulation at the sites of precipitation, and the acceleration of the diffusion process. Thus, precipitation significantly affects the mechanical characteristics of crystals and the rate of change in their thermoelectric characteristics due to diffusion processes.

A typical example of the instability of a thermoelectric material is a heavily doped silicon-germanium alloy, the holding of which at different temperatures leads to a change in the concentration of current carriers and a corresponding change in other properties associated with it. This phenomenon, called precipitation, continues to be studied for different compositions. In particular, the study of precipitation in thermoelectric material $Si_{0.68}Ge_{0.32}$ of *p*- and *n*-type, doped with boron and phosphorus, respectively, like other materials, was carried out by changing the concentration of current carriers, the Seebeck coefficient and specific electrical resistance for room temperature after isothermal annealing at different temperatures for up to 5,000 hours. The maximum increase in resistance due to precipitation in the *n*-type material was observed at a temperature of 450° C, and at a temperature above 800°C, the resistance decreases relative to the initial value. In the *p*-type material, only an increase in electrical resistance was observed at temperatures above 700° C with a maximum at a temperature of about 850° C. In *p*- and *n*-type materials maintained in the temperature gradient, the precipitation processes proceeded differently, as a result of which, after endurance of thermoelectric legs in the temperature difference of 400^0C, a different distribution of resistivity along the branch length was obtained. Namely, in the *p*-type material the highest resistivity was observed near the hot junction, and for the *n*-type - near the cold junction.

According to experimental data for some of the compositions used in real products, the dependence of the degradation rate on the content of germanium alloy was established. This dependence was determined on *n*-type silicon-germanium alloy samples with different germanium content, which passed life tests lasting up to one year, by changes in their thermoelectric efficiency during annealing time in the temperature difference of 500-1000 K, including thermoelectric efficiency values, projected for the long term. After annealing for about a year, the thermoelectric efficiency parameter of the samples reached one value. These data indicate that it is not advisable to use germanium-rich alloys for long-life converters. This confirms the opinion expressed in [11,12] that the optimal in terms of thermoelectric efficiency, manufacturability and stability is the alloy $Si_{0.8}Ge_{0.2}$used in RTGs, which are operated in space. Changes in the composition of the alloy, technology and operating conditions of the thermoelectric material in the temperature difference can make adjustments to the change in properties due to precipitation. In particular, studies of samples of silicon-germanium alloy annealed at different temperatures under reactor irradiation indicate the acceleration of precipitation processes. In phosphorus-doped pressed samples of $Si_{0.92}Ge_{0.08}$ alloy obtained using mechanical activation, the achieved maximum electron concentration is in the range $(2.84\div3.26)\cdot10^{26}$ m^{-3} and decreases to values of about $1.0\cdot10^{26}$ m^{-3} after 24 hours of annealing temperature of 700 K due to the transition of part of the phosphorus atoms in the inactive state. Obviously, in samples of silicon-germanium alloy doped with both phosphorus and gallium, a high concentration of electrons is established due to the use of mechanical activation technology. In the process of high-temperature annealing of fine-grained samples of a doped silicon-germanium solid solution, in addition to an undesirable secondary recrystallization process, positive processes occur associated with the homogenization of the material and an increase in the concentration of active phosphorus in it, whereas annealing at low temperatures only causes the transition of phosphorus to an inactive state. For example, in $Si_{0.8}Ge_{0.2}$samples containing 3 mol. % Ga, in which after hot pressing the optimal electron concentration was set by 8-hour annealing at 1500 K, in the annealing process at 873 K, 723 K and even 525 K the electron concentration monotonically decreased to values much lower than optimal [13]. In $Si_{0.8}Ge_{0.2}$ samples with an addition of 2 mol. % Ga, the resistivity and the Seebeck coefficient continuously increased during 4000 hours of annealing at 973 K, and in the case of 1273 K, an increase in these parameters was observed only in the first 600 hours of annealing, and then gave way to a decrease [14]. The stability of a material based on a solid solution of silicon-germanium with the addition of gallium phosphide over time can be assessed by comparing the change in electrical resistivity depending on the temperature of long-term isothermal annealing with similar dependences for "standard" phosphorus-doped material [15,16].

Thermoelectric materials based on solid silicon-germanium solution are designed for stable operation in high temperature regions. For space generators, the temperature difference of 1273–873 K is the most promising [12]. Changes in the concentration of current carriers in the process of holding materials in the working temperature difference for antimony, bismuth and lead tellurides were not observed. Exceptions are solid solutions based on germanium telluride, which can decompose at temperatures below the polymorphic transformation temperature of this material (600 ÷ 650 K). In particular, for copper-alloyed alloys tested in the temperature difference, the concentration of copper in the temperature range of ~ 600 K. It should be noted that this redistribution of copper does not lead to a significant change in the parameters established in the first hours of operation and to reduction of its thermoelectric efficiency at a further exposure.

Thermoelectric materials used to convert heat from radiation sources have been exposed to some degree of radiation. It is known that α-radiation is easily shielded, and the action of β- and γ-radiation has little effect on the material compared to the influence of temperature, so changes in the properties of thermoelectric materials under their influence were not detected. The material is affected by the neutrons of nuclear reactors, which cause nuclear reactions and the formation as a result of a cascade of collisions of radiation defects that can, interacting with the atoms of doping impurities, turn them into an inactive state. This phenomenon was revealed on a doped silicon-germanium alloy during the development and testing of the converter-reactor of the "Romashka" installation.

The concentration of current carriers in doped silicon-germanium alloys decreased with increasing neutron radiation dose, and the electrical resistivity and the Seebeck coefficient increased even in the region of low temperatures, where the precipitation process in the absence of radiation is almost non-existent. Radiation defects are annealed at elevated temperatures, and it has been experimentally established that reactor irradiation of silicon-germanium alloys at temperatures above 820 K does not lead to changes in thermoelectric parameters due to the appearance of radiation defects.

III. Mechanisms of degradation of contact structures

The interconnects of thermoelement legs usually consist of electrically conductive connecting buses and a set of dissimilar layers of materials introduced to match the thermoelectric material with connecting buses, and sometimes formed in the process of keeping the contacts at elevated temperatures. Electrical and thermal resistance of interconnects consists of parameters of connecting buses, all layers available in the contact and transitions between them.

The contact resistance determines the loss of thermoelectric figure of merit, estimated by the parameter of thermoelectric figure of merit of the material in the composition of the converter Z'. The relationship of this parameter with the figure of merit of the material Z is determined by the formula:

$$Z' = \frac{Z}{1+\rho_c/\rho_M l_M}. \tag{4}$$

where ρ_c is electric contact resistivity, ρ_M is thermoelectric material resistivity, l_M is thermoelectric leg length.

Therefore, the degradation of the thermoelectric device as a whole can be significantly due to the degradation of the contact structure, which leads to a significant increase in resistivity, or to the complete destruction of the structure. Contact structures can be created both without and with anti-diffusion layers. Electrical contact resistance consists of two main parts: barrier and bulk. The barrier part is due to a potential barrier at the thermoelectric material - metal interface. The value of this part of the resistance depends on the temperature mode of operation of the thermoelement, which determines the dominant mode of current flow through the contact. If the temperature is low, then a purely tunneling mechanism prevails. If the temperature is high, then the emission mechanism prevails. But the real mode of operation of thermoelements based on low-temperature materials is such that both mechanisms contribute to the total electrical contact resistance. This situation is discussed in detail in [17]. In it, in particular, the barrier component of the electrical contact resistance at the interface of the nickel anti-diffusion layer with *n*-type $Bi_2Te_{2.7}Se_{0.3}$ and *p*-type $Bi_{0.5}Sb_{1.5}Te_3$ materials is determined. It was found that this component decreases with temperature, varying in the range from 200 to 300 K in the range from $2\cdot10^{-7}$ to $2.5\cdot10^{-8}$ Ohm·cm^2. This component sharply decreases if the doping of the near-contact region is carried out in order to significantly increase the concentration of charge carriers of the corresponding type in it. On the other hand, an increase in the contact resistance can be, on the contrary, caused by a decrease in the concentration of charge carriers in the near-contact region and an increase in the potential barrier due to prolonged exposure to high temperatures, which can lead to a redistribution of the dopant both in the bulk of the thermoelectric leg and in the near-contact region. Good results in terms of reducing the initial value of the contact resistance and, consequently, reducing the negative effect of its degradation on the initial parameters of thermoelectric modules can be obtained by creating a superlattice structure in the near-contact region, since such a structure has a lower potential barrier at the interface with the metal. Thus, it is possible to reduce the barrier component of the electrical contact resistance to the so-called detection limit, which is 10^{-9} Ohm·cm^2. For example, iodine or silver can be used as dopants [18, 19]. The possibilities of reducing the barrier component of the electrical contact resistance are also considered in [20, 21].

Let us now consider the volumetric component of the contact resistance. It is due to the purely ohmic resistance of the transient layer between the metal and the thermoelectric material. In the absence of an anti-diffusion layer, this transient layer is due to two factors - the roughness of the semiconductor surface and diffuse penetration of the components of the contact alloy (solder) into the semiconductor with the formation of certain compounds [22]. In the latter case, the volume component of the electrical contact resistance is determined by the product of the thickness of the layer of the formed compound on its resistivity. Another situation is realized in the presence of an anti-diffusion layer. In this case, the volume component of the electrical contact resistance can be determined both by the diffusion of the material of the anti-diffusion layer, for example, nickel, into the thermoelectric material, and by the diffusion of one of the components of the thermoelectric material, for example, tellurium from $Bi_{0.5}Sb_{1.5}Te_3$ or selenium from $Bi_2Te_{2.7}Se_{0.3}$ into nickel with the formation of intermetallic compounds, as well as the roughness of the semiconductor surface.

The effect of nickel diffusion into a thermoelectric material on the electrical contact resistance was considered for two cases: steady-state diffusion from a source of stable intensity [17, 23-25] and unsteady diffusion, including with the formation of intermetallic compounds [26]. The former case is realized, for example, when creating anti-diffusion layers by sputtering [27], the latter is realized directly in the process of functioning of thermoelectric modules. Thus, in [17] it is shown that when the thickness of the transient layer changes in the range of 20–150 μm, the volumetric component of the electrical contact resistance in the temperature range 200–300 K changes from 10^{-7} to $2.2\cdot10^{-6}$ Ohm·cm^2 in the case of $Bi_2Te_{2.7}Se_{0.3}$ and from $2.2\cdot10^{-6}$ Ohm·cm^2 in the case of $Bi_{0.5}Sb_{1.5}Te_3$. As a result, the value of the total electrical contact resistance changes from $4\cdot10^{-7}$ to $2.2\cdot10^{-6}$ Ohm·cm^2 in the case of $Bi_2Te_{2.7}Se_{0.3}$ and from 10^{-7} to $2.4\cdot10^{-6}$ Ohm·cm^2 in the case of $Bi_{0.5}Sb_{1.5}Te_3$. In more detail, namely at an arbitrary intensity of the source of metal supply, the volumetric component of the contact resistance is considered in [21-23].

This consideration was carried out within the framework of the theory of composites. An indispensable condition for its applicability is the assumption that all components (in this case, thermoelectric material and nickel), when incorporated into the composite, retain their inherent thermoelectric characteristics, including their temperature dependences. The influence of the contact resistance on the efficiency of a thermocouple in the mode of generating electrical energy was also considered. It was shown that if the transient contact layer does not contain clusters, then in the temperature range 200 - 400 K and the thicknesses of the transient contact layers, the electrical contact resistance changes from $1.8\cdot10^{-7}$ to $4.8\cdot10^{-6}$ Ohm·cm^2, the thermal contact resistance changes from 0.02 to 0.34 K·cm^2/W. Increasing the intensity of the inflow of metal into the TEM reduces the electrical and thermal resistances. In the presence of clusters in the same range of temperatures and thicknesses of the transient contact layers, the electrical contact resistance varies from $7\cdot10^{-7}$ to almost $2\cdot10^{-5}$ Ohm·cm^2, and the thermal contact resistance varies from 0.05 to 0.95 K·cm^2/W. Thus, the presence of clusters in the transient contact layer significantly increases the electrical and thermal contact resistances. From this point of view, equalization of the concentration of metal particles in the transient layer should significantly reduce the value of electrical and thermal contact resistance, and, therefore, significantly slow down the degradation of contact structures during the operation of thermoelectric modules. However, studies carried out, in particular, in [28] and a number of other works, have shown that, in fact, for example, in the process of holding contact structures with nickel anti-diffusion layers at an elevated temperature, their degradation occurs not so much due to the diffusion of nickel into a thermoelectric material but due to the diffusion of tellurium or selenium, depending on the type of conductivity of the thermoelectric leg, into the thermoelectric material with the formation of nickel tellurides or selenides, or more complex compounds. In so doing, degradation is associated with the growth of layers of these compounds over time. Simplified in the framework of the theory of composites, this situation was considered in [26]. From the obtained results it follows that in the presence of a layer of intermetallic compounds with a thickness of 20 μm the electrical contact resistance in the temperature range from 200 to 400 K varies from $1.1\cdot10^{-6}$ to $3\cdot10^{-6}$ Ohm·cm^2, thermal - from 0.09 to 0.155 K·cm^2/W. If the thickness of the intermetallic layer is 150 μm, the electrical contact resistance will vary from $8.25\cdot10^{-6}$ to $2.48\cdot10^{-5}$ Ohm·cm^2. Thus, the growth of the intermetallic layer at the interface between the thermoelectric material and the metal in the process of functioning of thermoelectric modules can be a significant factor in their degradation. In particular, in [29] it was shown that upon holding the Ni/$(Bi_{0.25}Sb_{0.75})Te_3$ contact pair, in which the initial thickness of the nickel layer was 70 mm, at a temperature of 250^0C for 750 h, the transient contact layer of nickel telluride reached 110 microns. In this case, the electron diffraction study recorded the presence of pores and cracks in this layer, which undoubtedly indicated the beginning of the contact destruction process. A similar diffuse porosity and even the appearance of cracks was observed by direct electron microscopic studies in the layers of compounds formed at the interface between nickel and $Bi_2Te_{2.7}Se_{0.3}$ and $Bi_{0.5}Sb_{1.5}Te_3$ [30].

However, the value of the volumetric components of electrical and thermal resistance can be significantly reduced if the resistivity of the semiconductor in the near-contact region is as close as possible to the resistivity of the metal. And this can be done by creating a superlattice heterocontact layer in the near-contact region, the band spectrum of which is described by the Fivaz model. This possibility is due to the fact that limiting the disordered movement of free charge carriers in the direction perpendicular to the plane of the thermoelectric material layers can effectively block their scattering, which leads to a sharp decrease in the resistivity of the thermoelectric material in the plane of the layers. And in this case, the influence of the specific location of metal particles in the transient layer, and hence the presence of clusters on the electrical and thermal contact resistances is significantly leveled. But the positive effect of the nonparabolicity of the band spectrum of the thermoelectric material described by the Fivaz model on the electrical and thermal contact resistances is the better, the greater the degree of this nonparabolicity. The latter is characterized by the ratio of the Fermi energy of an ideal two-dimensional gas with a parabolic band spectrum to the width of a narrow miniband, which determines the movement of free charge carriers in the direction perpendicular to the layers. In this case, as shown in [31,32], for the thickness of the transient layer equal to 20 μm, the electrical contact resistance in the temperature range from 200 to 400 K varies from $8\cdot10^{-9}$ to $3.7\cdot10^{-8}$ Ohm·cm^2. At the thickness of the transient layer equal to 150 μm, the contact resistance varies from $6\cdot10^{-8}$ to $2.8\cdot10^{-7}$ Ohm·cm^2. And this reduction should also help reduce the impact of degradation of contact structures on the parameters of thermoelements and thermoelectric modules.

In [6], the results of studying the temperature and time dependence of the electrical resistance of tungsten contacts with a thermoelectric silicon-germanium n-type alloy with different mass content of germanium are presented. It was found that as the germanium content increases, the temperature dependence of the contact resistance becomes sharper. It was also found that, for example, the contact resistance of $Si_{0.7}Ge_{0.3}$ pair with tungsten increases the more sharply the higher the holding temperature of the contacts. The increase in contact resistance is to some extent associated with a decrease in the contact region of the concentration of current carriers due to diffusion and sublimation of the phosphorus doping impurity [33]. In addition, in the contact of the silicon-germanium alloy with tungsten at elevated temperatures, the interaction of silicon with tungsten is observed. As a result, a layer of tungsten silicide appears at the boundary, and the adjacent region of the alloy is enriched with germanium and the energy barrier for electrons increases. The tungsten silicide layer performs an anti-diffusion function, but the reaction continues due to the penetration of silicon atoms into tungsten through this layer. It should be noted that the rate of diffusion of silicon through a layer of tungsten silicide is significantly higher than the rate of diffusion of tungsten in the opposite direction. As a result, diffusion porosity is formed in the thermoelectric material near the contact, which leads to an increase in contact resistance, and, ultimately, to the complete destruction of the contact. A similar formation of diffusion porosity is observed in the contact of the *p*-type silicon-germanium alloy with tungsten at elevated temperatures [34].

Contact resistance in the case of high-temperature annealing can also increase due to the appearance of diffusion porosity. After annealing at a temperature of 1070 K for ~ 375 hours, the contact of tungsten with the silicon-germanium alloy is destroyed. The duration of the contact depends on the operating temperature.

When silicon or tungsten carbides are used as an anti-diffusion layer, the service life of the silicon-germanium alloy with tungsten for a given temperature is increased due to the fact that the diffusion rate of silicon and tungsten in carbides is significantly lower than in silicides.

It should be noted that in high-temperature interconnect junctions to the silicon-germanium alloy, where graphite is used as an electrode, and silicon carbide or titanium carbosilicide is used as an anti-diffusion layer, at a temperature exceeding the temperature of the onset of interaction of silicon with carbon, contact destruction is also possible due to the formation of diffuse porosity in graphite, since the rate of diffusion of carbon in carbides is higher than the rate of counter-diffusion of silicon atoms.

IV. Mechanical degradation of thermoelectric materials and modules

Mechanical degradation of thermoelectric materials and modules is due to two main factors: thermal expansion of thermoelectric legs, contact materials and other materials from which the thermoelectric module as a whole is made and external mechanical loads to which the module is subjected during operation. These loads include linear acceleration, vibration and shock. Mechanical loads accompany cyclic temperature effect, which creates deformations, and, consequently, the corresponding mechanical stresses of a time variable sign and magnitude. And dynamic stresses, as a rule, significantly exceed static [35]. In addition, deformations and mechanical stresses in unevenly heated bodies are different than in the case of their uniform heating [36]. And this creates additional loads and mechanical stresses mainly in thermoelectric legs. If all of the above stresses are not even accompanied by direct destruction of thermoelectric legs and other elements of the module structure, the deformations caused by them lead to the appearance of active structural defects in the thermoelectric material, in particular dislocations [37], which can unpredictably change both the characteristics of these materials and their degradation rate. Therefore, the improvement of the designs of thermoelectric modules from this point of view is carried out as follows. Coordination of coefficients of linear expansion and elastic characteristics of materials that are in direct contact with each other and special selection of parameters of thermoelectric materials; increasing the strength of thermoelectric materials and adhesive strength of contact joints; selection of such a geometry of the module, which, given the initial characteristics of the module, made it possible to minimize mechanical stresses in thermoelectric legs; the use of damping devices that reduce the mechanical load on the structural elements of the module. Cyclic stability is a fundamental performance parameter for both cooling modules and generator modules. Recently, the attention of researchers has been focused, in particular, on the increased requirements for cyclic stability in connection with the creation of equipment that uses multiple cooling, as well as positional temperature control. The results of numerous tests have shown that conventional single-stage Peltier modules with dimensions of 40 × 40 × 4 mm are destroyed after several hundred cycles under cyclic effects of temperatures in the range of 0÷100°C. From this point of view, increasing the cyclic stability of thermoelectric cooling modules, and generator modules, is undoubtedly relevant [38]. Therefore, the question arises about ways to increase this stability without significant loss of the initial parameters of the modules. From the results of studies of the elastic properties of Bi_2Te_3 single crystals performed in [39-41], it follows that doping them with isovalent impurities in order to reduce thermal conductivity leads to a decrease in their mechanical strength.

Similarly, [42] describes a method of controlling the thermal conductivity of nanostructured thermoelectric material in order to reduce it to such an extent that it is still possible to prevent a decrease in the reliability of the thermoelectric generator module due to thermomechanical degradation of the material. In particular, the relationship between the minimum height of the thermoelectric leg and the thermal conductivity of the material has been established. The lower limit of thermal conductivity of the material is also established, at which the reliability of the thermoelectric generator module can be ensured. Moreover, for static mode, this limit is higher than for dynamic. Establishing the lower limit of thermal conductivity according to the authors of this work will make it possible to create thermoelectric generator modules that would combine high mechanical strength with high efficiency. The need to establish the lower limit of thermal conductivity is due to the fact that, other things being equal, the deformations and mechanical stresses in unevenly heated bodies are significantly greater than in uniformly heated. Therefore, the limitation of the lower limit of thermal conductivity is equivalent to the reduction of the upper limit of the temperature gradient along the thermoelectric legs at a given thermal power consumed by the thermoelectric generator module.

Along with this, there are other ways to reduce mechanical stresses in thermoelectric legs and contact structures by limiting the temperature gradient or reducing its negative impact. Thus, in patent [43] it is proposed to thermally connect a set of thermoelectric legs of the module with heat pipes in order to form a special, so-called cascade structure, which is able to work efficiently and reliably at large temperature gradients. Due to heat pipes, these gradients are somewhat reduced, as a result of which such a cascade structure acts as a kind of "insulator" from mechanical stresses.

In patent [44], a design of a thermoelectric energy source for satellites is proposed, in which a decrease in thermal stresses in thermoelectric legs along their length is achieved by coupling the hot side with specially bent cooling pipes, and a decrease in these stresses in perpendicular directions is achieved due to the presence of free space between legs. This also achieves the compactness of the device required for space applications.

In patent [45], in order to compensate for the negative effect of the temperature gradient on the mechanical strength, and, consequently, the reliability of the thermoelectric cooler, it is proposed to control it using trapezoidal signals.

In [46], in order to reduce the amount of waste of thermoelectric material when cutting single-crystal ingots into legs, it was proposed to grow thermoelectric materials in containers with flat slots by the Bridgman method, as a result of which single-crystal ingots are obtained in the form of flat plates of a certain thickness, rather than cylinders. In order to increase the mechanical strength of such thermoelectric legs, the crystallization rate is specially selected. However, when growing by the Bridgman method, a larger spread of thermoelectric parameters along the length of the ingot is obtained than when growing by the zone melting method.

The papers [47, 48] emphasized the importance of matching certain parameters of thermoelectric material with each other in order to achieve the required mechanical stability of thermoelectric materials and modules. The so-called thermal resistance parameter R_{Therm} was chosen as a criterion for mechanical stability. This parameter is defined as follows:

$$R_{Therm} = \frac{\sigma_{Tens}\left(1-\nu\right)\kappa}{\alpha_T E}, \tag{5}$$

where $\sigma_{Tens}, \nu, \kappa, \alpha_T, E$ are tensile strength, Poisson's ratio, thermal conductivity, coefficient of linear thermal expansion and Young's modulus of thermoelectric material, respectively. Mechanical stability is considered to be greater the greater this criterion. This means that a material with less tensile strength must have greater thermal conductivity. Therefore, when applying certain methods of reducing the lattice component of the thermal conductivity of thermoelectric material, it is necessary to take into account their effect on the strength of the material. Metals are known to have high strength, but their thermal conductivity is also high. Therefore, in the development of efficient and at the same time reliable thermoelectric materials, and, consequently, modules, there is a need to develop certain tradeoff design and technological solutions. The contradiction inherent in condition (5) puts a certain limit on increasing the thermoelectric figure of merit and efficiency of semiconductor materials of thermoelectric legs. Considering that the main mechanism of mechanical destruction of thermoelectric materials and contact structures is their gradual cracking, the mechanical strength of materials is determined using the so-called Griffiths criterion, i.e.

$$\sigma_{Tens} = \frac{K_{Ic}}{Y\sqrt{c}}, \tag{6}$$

where K_{Ic}, Y, c are the strength of material, the crack shape factor and the crack size according to Griffiths, respectively. Therefore, the challenge is to reduce the size of possible cracks.

In [49], optimized versions of the design of a thermoelectric module are presented, in which mechanical stresses in thermoelectric legs are minimized without reducing the output parameters and characteristics of the module. This is achieved by choosing the optimal shape of the cross-section of thermoelectric legs and their optimal placement in the module.

In [50], to increase the overall strength of the thermoelectric module, it was proposed to use a special frame, the elements of which, located between the legs, limit their movement and deformation under the action of loads, simultaneously performing the functions of a protective coating. In order to minimize heat flow shunting of the legs, the frame elements are made of polyimide.

Conclusions

1. A number of mechanisms of degradation of thermoelectric materials and contact structures are analyzed, namely: sublimation of volatile dopants and components, diffusion mechanisms of degradation of thermoelectric materials, mechanisms of degradation of contact structures and mechanical degradation of thermoelectric materials and contact structures.
2. According to the literature, it is established that the sublimation of volatile alloying impurities and components occurs most intensively in vacuum and the greater the higher the temperature. The most common protection against sublimation is to fill the free space of thermoelectric modules with inert gas or to completely or partially cover the side surface of thermoelectric legs with a material that sharply weakens sublimation, creating a barrier to volatile impurities and components from thermoelectric legs. Such materials may be polymers, glass enamels, borosilicate glass, ceramics or metal foil.
3. The main mechanisms of diffuse degradation of thermoelectric materials due to diffusion processes are the rediffusion of dopants, the formation of precipitates, as well as the formation of structural defects, in particular dislocations. Diffuse degradation leads to an unpredictable change in the thermoelectric characteristics of materials and a decrease in their mechanical strength. The main means of preventing rediffusion is carrying out the processes of growing crystals in a vacuum or inert medium, a special selection of the growth rate, as well as limiting the release of volatile impurities and components from the crystal.

4. Degradation of contact structures is mainly associated with interfacial reactions at the interface between the contact material or materials with semiconductor materials of thermoelectric legs. Intermetallic compounds formed as a result of these reactions significantly increase the electrical resistivity of the contacts. Being brittle, these intermetallic compounds acquire a porous structure over time under the action of a temperature gradient; moreover, they become capable of cracking. This leads not only to an increase in electrical contact resistances, but also to the complete destruction of contact structures. If there is no anti-diffusion layer, then in the case of creating contacts by soldering, the solder components can penetrate into the thermoelectric material, unpredictably changing its thermoelectric properties. This can be prevented by a special choice of modes of pretreatment of the semiconductor surface with the provision of optimal roughness of its surface, the creation of an anti-diffusion layer, the application of a sublayer that enhances the adhesion of the contact structure with the thermoelectric material and pre-doping of the near-contact region or the creation in it of a superlattice heterostructure described by the Fivaz model with a high degree of nonparabolicity of the band spectrum.

5. Mechanical degradation and destruction of thermoelectric materials and modules is associated with the formation in them under the action of accelerations, shock loads, vibration and cyclic temperature effects of structural defects, such as dislocations, pores, cavities and cracks, leading to an unpredictable change in thermoelectric parameters and characteristics of materials and contact structures, and their destruction. The presence of a temperature gradient, which is a necessary condition for the operation of thermoelectric devices, creates special conditions for deformation of thermoelectric legs and other elements of thermoelectric modules, which are not typical for the case of uniform heating. This forces such parameters as mechanical strength of thermoelectric material, temperature coefficient of linear expansion, Poisson's ratio, Young's modulus and thermal conductivity to be matched in a special way. This matching is necessary to limit the harmful effects of large temperature gradients on the strength of thermoelectric materials and modules. In particular, it is important to ensure a safe lower limit of the thermal conductivity of the thermoelectric material, which, while providing the necessary values of the initial characteristics of the module, at the same time limited the temperature gradients in it to values that are safe from the point of view of mechanical strength. Other ways to reduce the rate of mechanical degradation of thermoelectric materials and modules can be a special choice of the geometry of thermoelectric legs and the method of arrangement in the module, the use of special frames that restrict the movement of thermoelectric legs under the action of mechanical and thermal loads, as well as the use of damping devices and devices that limit temperature gradients to safe values.

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Типові механізми деградації термоелектричних матеріалів і шляхи зниження їх впливу на надійність модулів

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У огляді розглянуто ряд типових механізмів деградації термоелектричних матеріалів у процесі їх функціонування у складі термоелектричних генераторних модулів. Серед них дифузія та самодифузія у термоелектричних матеріалах та контактних структурах, втрата легуючих домішок термоелектричними матеріалами внаслідок сублімації, утворення інтерметалічних сполук у контактних структурах, накопичення структурних дефектів під впливом теплових та механічних навантажень, механічне руйнування термоелектричних гілок, контактних структур та інших елементів конструкції модулів, хімічна взаємодія складових термоелектричних матеріалів з іншими елементами конструкції модулів. Також розглянуто основні конструктивні та технологічні шляхи і методи зниження негативного впливу цих механізмів на надійність термоелектричних матеріалів і модулів.

Ключові слова: дифузія, самодифузія, сублімація**,** контактні інтерметаліди, накопичення структурних дефектів, механічна міцність, хімічна взаємодія, конструктивно-технологічні шляхи і фактори підвищення надійності.