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\textbf{Galvanic Interconnects for Thermoelectric Cooling Modules}

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The paper studies the use of galvanic technologies in thermoelectricity. The technological features of applying anti-diffusion coatings on bismuth telluride based thermoelectric material (TEM) by electroplating method are considered. The advantages and disadvantages of the properties of anti-diffusion structures obtained by the electrochemical method are determined.

\textbf{Key words:} thermoelectric material, thermoelement legs, anti-diffusion layers, galvanic interconnects.

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\section*{Introduction}

Thermoelectric materials on the basis of p-type Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} and n-type Bi\textsubscript{2}Te\textsubscript{2.7}Se\textsubscript{0.3} solid solutions have been widely used in the manufacture of thermoelectric energy converters [1], especially thermoelectric coolers and thermoelectric generators [2].

Recently, the need for thermoelectric cooling modules with a working temperature of at least 200 °C is significantly increasing. Taking into account this aspect, the current issue is the creation of high-performance technologies for the application of effective anti-diffusion structures, which will ensure the reliable functioning of cooling modules at elevated temperatures.

One of important steps in the manufacture of thermoelectric modules is creation of reliable anti-diffusion and interconnect structures. Interconnection is a complex technological process, which involves creation of physically and chemically compatible contact joints between the p- and n-type legs of thermoelectric material (TEM) with minimum losses on electric and heat spreaders, with high stability, sufficient mechanical strength and resistance to thermal changes (Fig. 1) [3].

Creation of efficient interconnects requires solving a variety of material research and technological problems. Of top priority is the choice of materials intended for direct contact with semiconductor legs. The best for interconnection of legs are metals with high thermal and electrical conductivity, such as copper and silver. Using copper interconnects, it is necessary to coat TEM legs with anti-diffusion layers which contribute to reduction of copper diffusion to thermoelectric material.

The anti-diffusion layer must be inert with respect to thermoelectric material, be characterized by high adhesion, must not create additional mechanical stresses in the interconnect zone, have low contact resistance, high values of thermal and electrical conductivity, thermal expansion coefficient close to that of TEM.

Therefore, in order to create a contact with a minimum transient resistance, it is necessary to choose close values between the work output of metal and semiconductor. Such metals are nickel, cobalt, iron, as well as molybdenum and tungsten, because they are chemically inert with respect to the semiconductor material, have good anti-diffusion properties, are well wetted with solder, their coefficients of linear expansion are close to the coefficient of linear expansion of the thermoelectric material.

\section*{I. Technological methods of interconnects thermoelement legs}

There are various methods of creating an anti-diffusion barrier, for example, soldering, joint hot pressing of thermoelectric legs and interconnect material, tinning with low-melting solders, chemical deposition of metals from salt solutions, electroplating, arc deposition method [4].

The soldering method involves many operations and stages, requiring a detailed selection of fluxes, solders, and complete removal of flux traces after soldering. Tinning method causes a sharp thermal effect on thermoelectric samples, which worsens their properties; high thermal and electrical solder resistances, penetration of aggressive fluxes into the thermoelement, diffusion of impurities from solders to a semiconductor.
A well-known method for interconnection of thermoelement legs [5] includes the following operations. A layer of bismuth is applied to the semiconductor plates with a soldering iron, a layer of POS-type solder is applied onto it, then they are pressed to the interconnect buses through a lead plate 0.5-1.0 mm thick. The disadvantage of this method is low manufacturability and low quality due to the large number of manual operations and relatively high contact resistance.

A method for interconnection of thermoelements based on manganese and cobalt silicides [6], which includes brazing thermoelements with silver, is characterized in that in order to increase the reliability of contact on the surface of silicides, an anti-diffusion barrier is created from carbon silicide solid solution, and thermoelements are soldered in air using protective fluxes to interconnect plate made of iron-nickel-chromium alloy.

There are thermoelements which contain anti-diffusion nickel layers on their end faces that are applied by vacuum deposition, electrolysis or chemical deposition with preliminary surface treatment by laser radiation, or by processing thermoelectric plates with layers in magnetic and electric fields during their further temperature annealing [7]. Such layers are characterized by low adhesive tearing strength, which does not provide the necessary level of mechanical strength and reliability of the thermoelement.

Along with this, thermoelements are also known that contain p- and n-type legs from corresponding thermoelectric materials, the end surfaces of which through anti-diffusion layers are connected to the interconnect layers by electroplating, located on the plates of high-temperature ceramics. Such thermoelements are widely used to solve specific technical problems and are characterized by rather high thermoelectric parameters, with insufficient reliability [8]. In the thermoelement, which consists of electrically interconnect layers and p- and n-type legs, anti-diffusion layers alongside with the end surfaces are also located on part of the lateral surfaces of legs adjacent along the perimeter to the end faces; between the surfaces of anti-diffusion and interconnect layers, solder layers are contained; the end faces of the legs contain grooves [9].

The chemical method of creating an anti-diffusion barrier is accompanied by gas evolution, which degrades the quality of the contact of the barrier layer with the semiconductor [10]. Nickel interconnect layers with a thickness of 0.1-0.2% and a protective coating from a nickel-copper alloy with a thickness of 0.3-0.5% of the length of the legs are applied by chemical methods from aqueous solutions, while nickel and nickel-copper alloy are precipitated from alkaline, ammonia solutions at a temperature of 97-99 °C and a pH of 8.5-9.5, and the process of nickel plating is initiated by contacting the block with aluminum or a metal of the iron subgroup for 20-30 s, which is ruptured after 4-5 s after the start of the process, fixing by the rapid release of gas bubbles [11].

II. Application of galvanic interconnects methods for the creation of thermoelectric cooling modules

The application of metal interconnect layers on the clean surface of semiconductors and the fabrication of thermoelements can be accomplished using an electrochemical method [12, 13, 14]. The electrolytic method has several advantages over other methods: easy process control (controlling the thickness and properties of the metal coating by changing the current density and direction, composition and concentration of the electrolyte, temperature) high purity and uniformity of the coating, good adhesion, no heating and does not require expensive equipment. The method provides a clear metal-semiconductor boundary, high electrical conductivity of the deposited metal layers, possibility of deposition of metals with a high melting point at 20-60 °C. Contact resistance when using this method does not exceed 10-5 Ohm × cm².

A method of creating an anti-diffusion barrier on bismuth telluride plates by electrochemical deposition of metals, including nickel, involves pre-treating the surface of the plates with solutions of nitric and hydrochloric acids, after which nickel is applied by electrolytic method [15].

The method includes chemical processing of plates, electrochemical etching and electrochemical nickel plating. The combination of parameters of
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electrochemical etching and electrolytic deposition of nickel allows creating an anti-diffusion barrier in the form of a coating with an adhesive strength of at least 100 kg / cm² for p-type materials and up to 150 kg / cm² for n-type materials [16].

A galvanically deposited nickel-iron-tungsten alloy was proposed as an anti-diffusion barrier [17], which had not been studied before, and the adhesive strength of the coating and its anti-diffusion properties had not been measured accordingly. The electrolyte, in addition to nickel salts, contains sodium tungstate and ferrous sulfate, which significantly improves the anti-diffusion properties of the coating and the operating temperature of the anti-diffusion barrier. The use of a galvanically deposited nickel-iron-tungsten alloy makes it possible to create an anti-diffusion barrier on the surface of a thermoelectric material with an adhesive strength of 200-215 kg/cm², which exceeds the cohesive strength of the material itself.

In the monograph [18], methods of obtaining, mechanisms of formation and growth, structure and properties of nanostructured films of galvanically deposited nickel-tungsten alloy were studied in detail. Electron microscopy methods have shown that electrolytically deposited films based on the metals of iron subgroup with tungsten additions have an X-ray-amorphous structure, which opens up new prospects for their use in many industries.

The electrolyte for the galvanic deposition of antimony films is characterized by the fact that an OC-20 surfactant is added to the potassium antimonide based electrolyte in order to improve the sediment structure and intensify the deposition process on the surface of thermoelectric material. The described properties of antimony films obtained from the proposed electrolyte allow them to be used to create an anti-diffusion barrier on the surface of p-type TEM samples [19].

The author [20] investigates the possibility of obtaining anti-diffusion coatings on copper contact plates and thermoelements by the method based on carrying out a heterogeneous reaction in an organic solvent [21]. The thus realized metallization of thermoelements provides good wetting of material by tin-bismuth soldering.

It is expedient to apply multilayer contact structures on the TEM. Results [22] showed that the maximum dynamic stability of thermoelectric devices is observed when metal alloys of iron subgroup with phosphorus and tungsten having amorphous structure are used as anti-diffusion layers. Experimental works were carried out on the deposition of anti-diffusion layers on TEM samples based on bismuth telluride, obtained by successive application of thin (1.5-3 μm) metal layers (SnNi (10 μm) | SnBi (4 μm) - for n- and p-type discs, NiW (3 μm) | SnNi (10 μm) | SnBi (4 μm) - for n-type discs; Fe (3 μm) | NiW (3 μm) | SnNi (10 μm) | SnBi (4 μm) - for p-type discs; Co(3 μm) | SnNi (10 μm) | SnBi (4 μm) - for n- and p-type discs;) subgroups of nickel and their alloys with other metals. The introduction of tungsten in the coating in the form of galvanic alloys with different metals can significantly improve the anti-diffusion properties of the resulting contact layers.

Nickel plating electrolyte for the deposition of thick nickel coatings with low internal stresses, containing saccharin as an inhibitor additive, can be used to increase wear resistance, corrosion resistance and improve the mechanical properties of the surface. The introduction of an insignificant amount of saccharin significantly reduces inherent tensile stresses, and if certain ratios between the current density, temperature and purity of the electrolyte are observed, it even leads to the appearance of inherent compressive stresses of nickel layers [23]. The proposed electrolyte provides a higher deposition rate, makes it possible to obtain thicker coatings (70-100 microns) in a relatively short period of time and reduce the inherent internal stresses of nickel coatings.

The multilayer anti-diffusion structure [24] is made of three layers, with the first layer made of nickel-phosphorus nanolayers, the second layer - of nickel-tungsten alloy, the third layer - of nickel-tin alloy. The first layer is deposited from the electrolyte of chemical nickel plating, the second and third - from electrolytes of galvanic nickel plating.

Illustrative is a method of manufacturing a thermoelectric element containing n-In₃Se₃, including the formation of legs of n- and p-type thermoelectric materials, the application of anti-diffusion and interconnect structures on the ends of the legs of thermoelectric material, the connection of n-type legs with p-type legs. The formation of legs from the n-In₃Se₃ thermoelectric material, the application of anti-diffusion and transition layers is carried out in one stage by the method of vacuum hot pressing of powders of the corresponding materials. Contact layers on the ends of legs with anti-diffusion layers are applied from electrolyte solutions based on Ni and Cu by electroplating. Intermediate layers of Ni and Cu, 2-3 μm and 10-15 μm, respectively, are deposited on the anti-diffusion layer of Fe. These layers are applied in special equipment by electroplating of corresponding electrolytes [25].

In the patent [26] a method of connecting thermoelements is proposed, which consists in applying to the semiconductor plates of interconnect layers with a nickel or cobalt layer and connecting them sequentially by soldering with metal buses. In order to improve the manufacturability of the assembly, semiconductor plates are formed into blocks, pressing the plates together with side surfaces. After fixing the semiconductors in the frame and their corresponding processing (degreasing and etching), a nickel layer or its equivalent cobalt layer with a thickness in the range 0.1-1.05% of the semiconductor thickness, a layer of lead 5-20 % of the thickness of semiconductors, a protective layer of nickel or copper with a thickness of 0.25-1% of the thickness of semiconductors is deposited by galvanic method on the working surfaces of flat block. The last layer - tin-lead solder, for example POS-61, can be applied either galvanically or with a soldering iron.

The authors of [27] proposed a method for producing an anti-diffusion layer on copper interconnect plates, which is characterized in that the protective coating is
applied in 2 stages from different electrolytes and has enhanced anti-diffusion resistance due to the difference in the structure of each layer. The bottom layer is a Ni-P alloy with a thickness of 3-5 μm, the top layer is a Ni coating with a thickness of 40 μm.

The electrolyte tested for connecting low-temperature thermoelectric materials contains 400 kg / m³ NiSO₄ · 7H₂O, 30 kg / m³ H₃BO₃, 15 kg / m³ NiCl₂·6H₂O and 0.03 kg / m³ CdSO₄. The pH value is 3.5-4.0. At an electrical current density of \( j_p = 1.0-1.5 \) kA / m², the deposition of a layer 10 μm thick was carried out in 5-10 minutes in an electrolyte heated to \( T = 330 \) K [28]. Freshly precipitated nickel layers were well wetted and tinned with low-melting solders and without the use of fluxes, which was promoted by hydrogen adsorbed in the sediment. For solder interconnect thermoelements, this quality of electroplating coatings is advisable to use when nickel-plateing metal interconnect buses.

The creation of thermoelectric modules [29] is used, in the manufacture of which a simplified process of connecting with plates of thermal and electrically conductive material of intermediate elements, previously connected to thermoelectric elements, is employed. Solder can be used as the specified connecting material. Such module production allows modules to be manufactured in mass production conditions using conventional materials. Also, galvanically deposited metal can be used as an interconnect material. A layer of nickel is applied between the plate and the semiconductor thermoelectric element, which prevents copper from diffusion into the thermoelectric material.

There is a well-known method of manufacturing semiconductor legs for a thermoelectric module and a thermoelectric module [30]. The method includes the manufacture of rods of thermoelectric material by hot extrusion. Then the lateral surface of the rods is prepared. After that, a paint and varnish aqueous composition with fluororubber is applied to the lateral surface using the method of cathodic or anodic electrodeposition to obtain a protective polymer coating [31]. The rods are cut to obtain semiconductor legs of a given length. An anti-diffusion metal coating is applied to the end surfaces of the legs by a combined method. First, a galvanic layer of Ni 59-71%, Sn 29-41% with a thickness of 2-3 μm is applied, and then a chemical layer of Ni 93-97%, P – 3-7% with a thickness of 2-3 μm. A method is known for manufacturing a thermoelectric module with increased service life [32]. A barrier coating is applied on the surfaces of the legs of the thermoelectric module, which prevents diffusion of the solder material and contact plates into the semiconductor material. The coating is applied by vacuum deposition, and then the adhesive coating, which is characterized in that the preparation of the thermoelectric leg using plasma-chemical etching and the application of the barrier coating is carried out in a single technological cycle without breaking the vacuum in the processing chamber.

There is a method for making Peltier modules [33], in which the Peltier elements during manufacture are connected to the conductive side by means of a sintering layer or welding with a contact surface. The contact surfaces are connected to the conductive side of the corresponding element through an intermediate nickel layer about 1-10 microns thick. The peculiarity of such a connection is that it is created directly between the Peltier element and the contact surface, that is, without the use of a soft solder. Another option is that between the intermediate nickel layer and the Peltier element, another interlayer of gold 0.01 and 1.5 μm thick is provided. There is another connection that differs from the previous one by providing a sintering layer of metal sintering material between the intermediate nickel layer and the conductive side of the element. This layer is made in such a way that has a thickness of 10-20 microns. For this sintering layer, metal materials are suitable, such as copper, silver, alloys of copper and silver.

Flexible aluminum electrodes that were introduced into the module using the process of thermal spraying were proposed to improve the operational characteristics of thermoelectric modules. To further increase the anti-diffusion efficiency of Ni transition layers, the thickness of Ni layers was increased to 8-10 μm on the cold side. Ni was applied on p-type Bi₂Te₃ plates (Sb doped) and n-type (Se doped) by electroplating. Interphase reactions between Sn and Bi₂Te₃ plates with Ni coating were also investigated. A higher growth rate of coating is observed when Ni is applied on the n-type Bi₂Te₃ plate, due to the lower recovery activation energy due to the higher density of free electrons in the n-type Bi₂Te₃ material. The general phase of Ni₂Sn₃ is formed on the interface between Sn/Ni on the p-type and n-type Bi₂Te₃ plates, while the NiTe phase is formed at a high speed at the interface between Ni and Bi₂Te₃ n-type plates [34, 35]. In the study of the diffusion of nickel and tin in a thermoelectric material of p-type (Bi,Sb)₂Te₃ and n-type Bi₃(Te,Se)₂ by electron microscopy [36], it was found that nickel is a suitable diffusion barrier material for tin as in the case of (Bi,Sb)₂Te₃, and Bi₃(Te,Se)₂. However, in spite of the fact that this is not a problem in (Bi,Sb)₂Te₃, in Bi₃(Te,Se)₂, in the process of soldering, nickel diffuses by a few microns and impairs its performance.

The author [37] proposed a thermoelectric module of increased reliability, in which the conductive layer is formed in the form of a multilayer galvanic coating containing anti-diffusion and metallic layers.

Conclusions

Thus, the main requirement for obtaining permanent joints of semiconductor material with a copper interconnect plate in the manufacture of thermoelements is a need to apply on the legs of the module thick anti-diffusion layers that prevent the diffusion of copper into the thermoelectric material. Electroplating is the most common and affordable method of creating anti-diffusion interconnect layers. This method has several advantages over other methods, namely: easy process control, high purity and uniformity of the coating, good adhesion to the substrate, the lack of high operating temperatures and expensive equipment during application.
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Гальванічні комутації для термоелектричних модулів охолодження

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У роботі досліджено використання гальванічних технологій у термоелектриці. Розглянуто технологічні особливості нанесення антидифузійних покриттів на термоелектричний матеріал (ТЕМ) на основі телуріду вісмуту гальванічним способом. Визначено переваги та недоліки властивостей антидифузійних структур отриманих електрохімічним методом.

Ключові слова: термоелектричний матеріал, вітки термоелементів, антидифузійні шари, гальванічні комутації.