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IMPROVED RELIABILITY CONTACT CONNECTING STRUCTURES FOR BISMUTH TELLURIDE BASED THERMOELECTRIC MATERIALS

A method for preparation of thin multilayer contact structures based on generator thermoelectric material is developed and their antidiffusion properties are studied. It is shown that maximum dynamic stability of thermoelectric devices is observed in the case when alloys of iron subgroup metals with phosphorous and tungsten having amorphous structure are used as antidiffusion layers.

It is established that contact structures proposed here allow minimization of the negative effect of inconsistency between thermal expansion coefficients of thermoelectric material and antidiffusion films which increases considerably the service life of thermoelectric devices.

Key words: thermoelectric material, bismuth telluride, anti-diffusion layers, multi-layer films, nickel-tungsten alloy.

Introduction

Solid-state thermoelectric energy converters offer a number of essential advantages over traditional electric generators and are finding ever widening application. So far, however, conversion efficiency provided by thermoelectric plants is lower compared to generators of traditional design. Moreover, current status of thermoelectric converters production is characterized by unjustifiably high consumption of thermoelectric material (TEM) and the resulting high cost [1].

One of the factors restricting wide application of thermoelectric converters is insufficient reliability of contact and connecting structures of thermoelements. In the field, thermoelectric and connecting materials must have mutual physical and chemical stability, which, on the one hand, assures their long-term operation, and, on the other hand, creates a reserve for increasing conversion efficiency due to operating temperature rise.

There are various methods of thermoelements connection: soldering, melt loading, joint pressing of thermoelectric legs and connecting material, thermal, magnetron, ion cluster sputtering of connecting materials in vacuum or inert gas, galvanic or chemical deposition of connecting material.

Of primary importance is selection of connecting materials that are in direct contact to semiconductor legs. The elements of iron subgroup, *Ni*, *Co*, *Fe,* are chemically inert to semiconductor material, have satisfactory anti-diffusion properties, good solder wettability, their linear expansion coefficients are close to that of thermoelectric material [2].

The methods of chemical and galvanic deposition of metals on semiconductors enables one to avoid the difficulties related to thermal processing of thermoelements in soldering, pressing, plasma deposition, melt loading, as long as galvanic processes proceed at low temperatures, are easy to operate, do not require costly equipment and make possible efficient control of the thickness of deposited layers.

A promising way of solving this problem is to create contact and connecting layers with preassigned properties and technologies of their connection to thermoelectric materials with attainment of ultimately low values of contact resistances [3].

Of critical importance for the technological properties of electrolytic coatings with metals and alloys is deposit structure. The structure of some or other electrolytic coating can be estimated no only during X-ray and metallographic studies, but also by the results of polarization measurements.

The galvanic method of alloys preparation is not new. However, systematic studies of general properties of electrolytic deposition of alloys began comparatively recently. Practical significance of these works lies in the fact that they expand considerably the range of galvanic coatings, and in many cases coatings based on alloys posses valuable properties, not typical of the metals of which this alloy is composed. Galvanic coating with alloys is related to a series of specific difficulties. Thus, there must be more precise control of such process parameters as current density on electrodes, concentration of ions in case of deposited metals. In many cases alloy deposition is done by galvanothermic method, which lies in alternate deposition of thin layers of each metal and subsequent thermal processing of products during which metals mutually diffuse, forming an alloy of variable composition. This method has not become as popular as galvanic one [4].

Experimental

Experimental works were carried out for the deposition of anti-diffusion layers on bismuth telluride based TEM samples prepared by consecutive application of thin (1.5 – 3 μm) layers of nickel subgroup metals and their alloys with other metals.

On the discs of thermoelectric material synthesized at Institute of Thermoelectricity after their surface prefinishing by the method adopted at ITE the following coatings were deposited:

1. TEM | *SnNi*(10 μm) | *SnBi*(4 μm) – for *n*- and *p*-type discs;
2. TEM | *NiW*(3 μm) | *SnNi*(10 μm) | *SnBi*(4 μm) – for *n*-type discs;
3. TEM |*Fe*(3 μm) | *NiW*(3 μm) | *SnNi*(10 μm) | *SnBi*(4 μm) – for *p*-type discs;
4. TEM | $Co_{chem.}$(3 μm) | *SnNi*(10 μm) | *SnBi*(4 μm) – for *n*- and *p*-type discs

The coatings were deposited from electrolytes under conditions described in [5 – 7].

Table

Change in the characteristics of thermoelectric devices

Legs coating composition	Annealing time, h	ΔR, Ω	ΔW, W	$\Delta\eta$, %
TEM | *NiW*(3 μm) | *SnNi*(10 μm) | *SnBi* (4 μm) – for *n*-type discs; TEM | *Fe*(3 μm) | *NiW*(3 μm) | *SnNi* (10 μm) | *SnBi*(4 μm) – for *p*-type discs	50	0.003	0.9	0.18
	100	0.014	0.67	0.01
	200	0.026	0.59	- 0.1
	300	0.043	0.39	- 0.25
TEM | $Co_{chem.}$(3 μm) | *SnNi*(10 μm) | *SnBi* (4 μm) – for *n*- and *p*-type discs	50	0.003	- 0.05	- 0.19
	100	0.014	- 0.42	- 0.28
	200	0.107	- 0.58	- 0.56
	300	1.58	- 1.10	- 0.86
TEM | *SnNi*(10 μm) | *SnBi*(4 μm) – for *n*- and *p*-type discs	50	0.05	- 0.33	- 0.24
	100	0.19	- 0.55	- 0.63

Using wire instrument with deposited abrasive, the metalized TEM discs were cut into legs of which thermoelectric devices were assembled and their most important parameters were measured – resistance *R*, power *W*, efficiency η. The devices were annealed at 200 °C, and repeated measurements of parameters were performed at specific time intervals.

Discussion of the results

As is evident from Table 1, the multilayer combined films of iron, nickel-tungsten, nickel-tin and tin-bismuth alloys applied on TEM discs improve considerably the life and reliability of thermoelectric devices.

In the authors' opinion, it is due to the following factors:

1. Both iron and nickel-tungsten alloy are much more passive in the reactions with thermoelectric material components as compared to other coatings under study – cobalt and nickel-tin alloy. In their properties, these alloys belong to heat-resistant alloys due to the content of tungsten and iron. According to the results of investigation of diffusion processes [8], the contact of cobalt to bismuth and antimony telluride is damaged with formation of reactive-diffusion layer of cobalt telluride and cobalt antimonide solid solution. The thickness of this layer is increased with time and operating temperature rise. The specific feature of this layer is low mechanical durability. For given cross-section of legs, attainment by the layer of its critical thickness is accompanied by the damage of contact die to arising thermal stresses, reducing considerably their life stability [9].
2. Nickel-tungsten films, unlike purely nickel or cobalt ones, have X-ray amorphous structure and, accordingly, lower internal stresses. And although nickel-tin alloy deposited under these conditions is also X-ray amorphous, its components at elevated temperatures react much more actively with thermoelectric material components than iron and tungsten. The adhesion strength of coatings under study is 17 – 20 MPa for *n*-type samples and 15 – 17 MPa for *p*-type samples.
3. Forming anti-diffusion coatings of the thin layers of different metals or their alloys, we overlap pores, cracks and other defects that are always available in galvanic films, with a layer of other metal or alloy, which improves considerably the anti-diffusion properties as compared to single metal film.

Conclusions

1 To minimize the negative effect of such factors as inconsistency between linear expansion coefficients of TEM and contact antidiffusion structures, internal stresses of coating itself leading to considerable reduction of the dynamic stability of contact structures, it was proposed to use as antidiffusion layers chemically or electrodeposited thin (up to 3 μm) multilayer films of metals and their alloys.

2 It was established that maximum dynamic stability of composite contact and connecting structures based on chemically or electrodeposited thin multilayer films of metals and their alloys is observed in the case when such coatings employ iron subgroup metals and their galvanic alloys with tungsten.

3 The deposition potential of each metal separately is more negative than the potential whereby alloy is formed (with formation of solid solution the potential energy of its components is reduced). This difference can be so great that metal ions are discharged on the cathode whose

deposition in pure form from aqueous solutions is impossible. This is exemplified by the electrolyte deposition of tungsten alloys with nickel, iron and other metals, whereas purely tungsten coatings can be obtained only from the melts.

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