EFFECT OF CONTACT SURFACE CONDITION ON THE ADHESION STRENGTH OF INTERCONNECT LAYERS OF THERMOELEMENTS BASED ON EXTRUDED BISMUTH TELLURIDE

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• *In this paper, we study the effect of contact surface condition (surface morphology, the match between the elemental composition of the surface and that in the bulk of material) formed during electroerosion cutting on the adhesion strength of "thermoelectric material (based on bismuth telluride) – interconnect coating (molybdenum sub-interconnect layer and aluminium conductor layer)" system. To change the properties of contact surface, different cutting wires were used (brass wire of diameter 0.25 mm, molybdenum wire of diameter 0.3 mm and molybdenum wire of diameter 0.1 mm). It was established that the best adhesion properties are achieved with a molybdenum wire of diameter 0.1 mm. It is due to the fact that using this wire enables to form a contact surface with a damaged layer of minimum thickness, with a maximum developed surface, and the elemental composition of the surface is closest to that in the bulk of thermoelectric material.*

Introduction

Essential effect on the thermoelectric figure of merit of thermoelements is produced by the value of contact resistance at interconnection of semiconductor legs [1-3]. Sufficiently durable contacts with a low transient resistance can be obtained by spraying on the contact surfaces of legs of a molybdenum layer that has a good adhesion to thermoelectric material and prevents from diffusion of contact layer materials into thermoelectric material. The processes of deposition of a molybdenum sub-interconnect layer and an aluminum conductor layer are attended by physico-chemical phenomena at the interfaces, among them diffusion of coating components into the sample, their chemical interaction with formation of intermediate phases, etc. What is more, the mechanical properties of transient region at the semiconductor-interconnection interface are governed both by the depth of damaged layer on the surface of thermoelement legs in machining, and by the adhesion properties of materials [2].

To achieve a reliable interconnection of legs in generator thermopiles, electroerosion cutting offers promise as a technique which enables to obtain high quality contact surfaces with a damaged layer of minimum thickness (not more than several micrometers) and requires no additional mechanical or chemical processing of contact surfaces of legs prior to deposition of interconnect layers [4]. Varying the technological conditions of electroerosion cutting, one can assure formation of a contact surface with a roughness necessary for subsequent flame spraying of interconnect layers with a high adhesion strength.

Our purpose in this work was to study the effect of contact surface condition on the adhesion strength of "thermoelectric material (based on bismuth telluride) – interconnect coating (molybdenum sub-interconnect layer and aluminium conductor layer)" system. Contact surfaces with different properties were formed during electroerosion cutting of thermoelectric material with the use of different cutting wires.

Experimental procedure and samples

To cut into legs the thermoelectric material based on *n*-$(Bi_2Te_3\text{-}Bi_2Se_3)$ and *p*-$(Sb_2Te_3\text{-}Bi_2Te_3)$ solid solutions shaped as rods of square section 5 × 5 mm, we employed an electroerosion cutting technique. The choice of this technique is determined by the fact that electroerosion cutting is most sparing relative to surface condition and structure (in cutting, there are minor damaged layers and no changes in material phase composition [2]). Besides, this technique is universal, rather productive, simple and flexible in readjustment.

The electroerosion cutting technique consists in that pulse electric voltage is fed in water to metal (commonly brass, molybdenum or tungsten) wire. A spark gap is formed between the wire and the sample being cut, and, as a result of sparking, at the moment of voltage pulse the material being cut is damaged, and erosion products are removed by a flush.

In the present work, electroerosion cutting of rods into legs was performed with the use of three types of cutting machines differing in material and/or thickness of cutting wire:

– Sodick AQ 300L, Japan (brass wire of diameter 0.25 mm);

– P&G Industrial DK7732, China (molybdenum wire of diameter 0.3 mm);

– retrofitted machine LF96F3, Russia (molybdenum wire of diameter 0.1 mm).

The following cutting parameters were used: cutting speed 8 mm/min, generator source voltage 1 V, spark gap voltage 25 V. Cutting modes were maintained automatically. As a liquid, all three machines employed water circulating through a filter system forming part of machines.

Upon cutting and drying of samples, the interconnect layers were deposited by flame spraying on UPU-3D plant under conditions determined in [4] (plasma treatment mode: voltage within 30 to 40 V, current within 250 to 300 A; the distance from plasmatron to legs surface is from 120 to 150 mm; linear speed of plasmatron is from 20 to 40 mm/s; spraying angle is 90 degrees to the surface).

The main advantages of flame spraying technique as a method for deposition of anti-diffusion and interconnect layers on semiconductor elements are as follows: high temperature of plasma stream (plasma temperature 7000 – 20000°C is commonly employed), which allows using any refractory materials for spraying; oxygen-free plasma-supporting gas that protects sprayed materials from oxidation; high speed and temperature of sprayed particles enabling to get high density of coatings and their better adhesion to substrate surface; the surface of processed material is generally not heated higher than 100 – 200°C.

In the course of flame spraying, on the contact surfaces of investigated samples during one spraying cycle there was deposited a sub-interconnect *Mo* layer 40 – 60 μm thick followed by a conductor *Al* layer ~ 1 mm thick. To minimize thermoelectric material heating in the process, gas mixture $Ar_2 + H_2$ was used as a plasma-supporting gas.

The adhesion of deposited coatings to thermoelectric material was determined by means of tearing machine Instron 5882. Contact surfaces of legs of both conductivity types both immediately after cutting on different types of electroerosion cutting machines and after testing on tearing machine were studied by means of scanning electron microscopy (SEM) with the use of Quanta 600 FEG microscope. *X*-ray spectral microanalysis through use of energy-dispersive detector of the same microscope was carried out to determine the elemental composition of surfaces after electroerosion cutting. The surface roughness and the thickness of damaged layers in the near-contact area were determined by means of SURTRONIC 25 profilometer or OLYMPUS GX51 optical microscope.

Results and discussion

It is known [5] that good adhesion properties of interconnect layers on semiconductor legs largely determine the quality of contact on "metal-semiconductor" interface and, accordingly, the thermoelectric properties of generator thermopiles. In turn, the adhesion strength of interconnect layers depends on the condition of contact surface, in particular, the presence of a damaged layer on it, its thickness, composition, structure and properties. In case of a low adhesion strength, the interconnect layers on the generator thermopile while in operation can separate with a catastrophic increase of thermopile resistivity.

As an example, Fig. 1 represents a typical pattern of interconnect layers separation on *p*-type legs that appeared during cyclic test of generator thermopile along the "thermoelectric material (based on bismuth telluride) – interconnect coating (molybdenum sub-interconnect layer and aluminum conductor layer)" interface. As shown by test on tearing machine, the overwhelming portion of molybdenum coating is separated from the thermoelectric material and is left on the aluminum layer, i.e. it is the case of a low adhesion of molybdenum layer to thermoelectric material, whereas the adhesion properties on the "molybdenum sub-interconnect layer – aluminium conductor layer" contact are satisfactory enough.

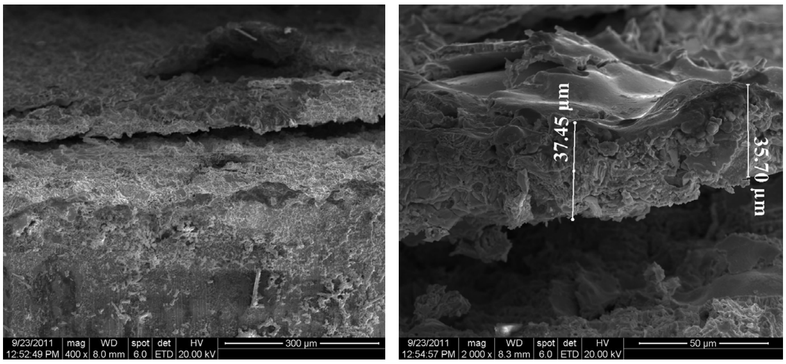


Fig.1. SEM-image of partially intact molybdenum coating on p-type leg. Below (base) is a semiconductor, above – separated molybdenum coating. Coating thickness is indicated by markers.

It is reasonable to assume that a low adhesion of molybdenum layer to thermoelectric material will be determined by the condition of thermoelectric material contact surface formed immediately after electroerosion cutting of semiconductor legs prior to flame spraying of interconnect layers.

The results of adhesion test of "thermoelectric material – interconnect coating" system have shown that adhesion strength depends on such factors as thermoelectric material properties (conductivity type – electron or hole), as well as material type and thickness of wire used for electroerosion cutting (Table 1). It is evident that these factors also affect the condition of contact surface of legs and, accordingly, the adhesion strength.

Table 1

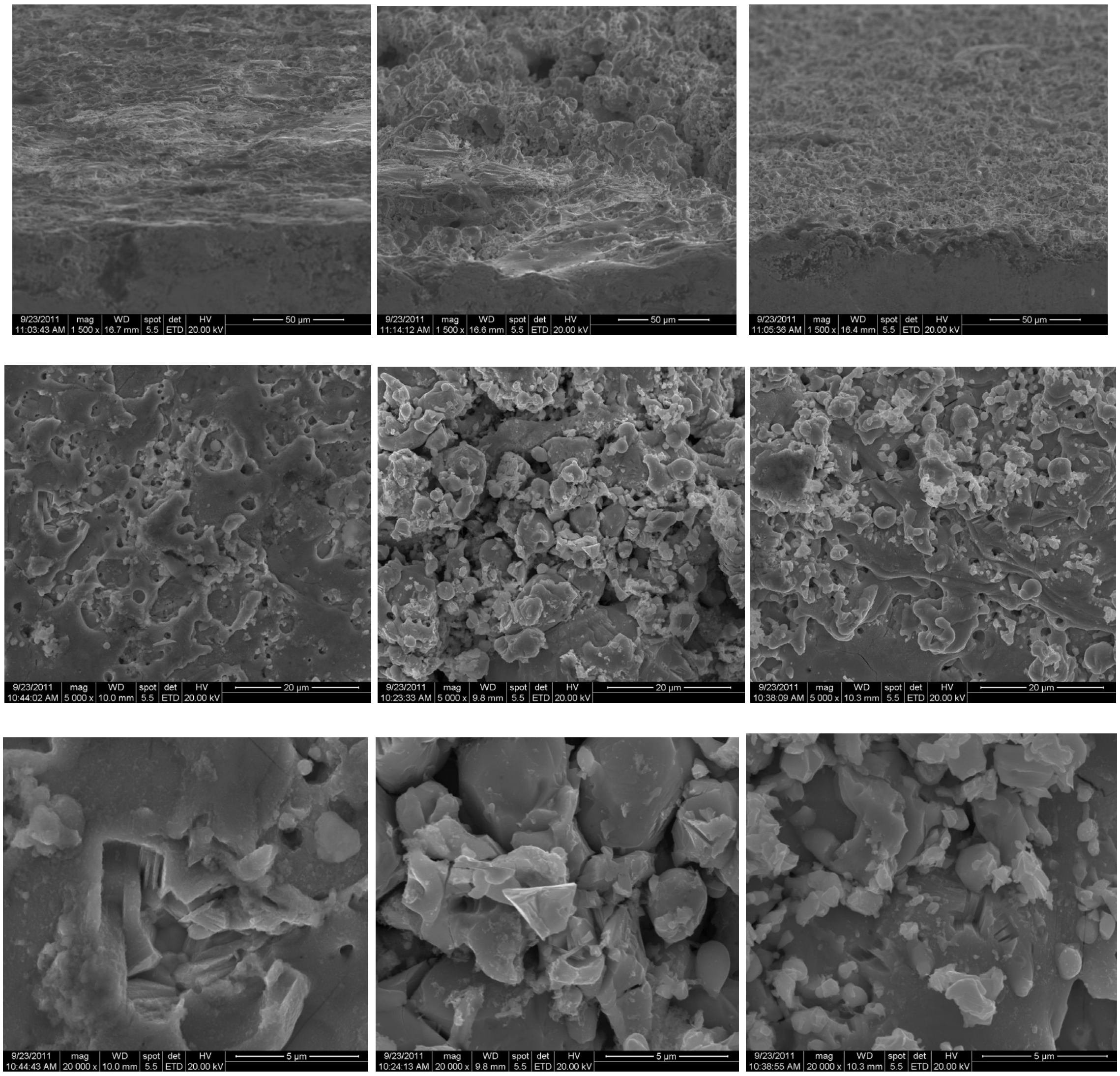
Averaged results of measuring the adhesion strength of "thermoelectric material – interconnect coating" system

Cutting wire material	Adhesion strength, kg/mm^2	
	p-type conductivity	*n*-type conductivity
Brass wire of diameter 0.25 mm (Sodick AQ 300 L machine)	0.56	0.63
Molybdenum wire of diameter 0.3 mm (P&G Industrial DK7732 machine)	0.85	0.93
Molybdenum wire of diameter 0.1 mm (LF96F3 machine)	0.87	0.96

From the table it can be seen that whatever the material and thickness of cutting wire, the adhesion strength is about 7 to 11% higher in case of using *n*-type conductivity thermoelectric material as compared to *p*-type conductivity material. A detailed study of mechanisms of influence of thermoelectric material properties on the adhesion strength is the subject for further research. However, it can be supposed that such influence can be due to the difference in density and mechanical (plastic) properties of *n*- and *p*-type materials caused by their different chemical composition and affecting the surface roughness formed in the process of cutting.

Let us now analyze the influence of cutting wire material and thickness on the condition of damaged layer on the contact surface of thermoelectric material formed during electroerosion cutting of legs.

First of all, it should be noted that measurement of the thickness of damaged layers after cutting with the use of different cutting wires did not reveal any considerable differences. For all wire types the thickness of damaged layer was on the order of several micrometers.



a) b) c)

Fig. 2.SEM-images of p-type legs surface after electroerosion cutting with the use of different cutting wires: a) brass wire of diameter 0.25 mm; b) molybdenum wire of diameter 0.3 mm; c) molybdenum wire of diameter 0.1 mm.

The differences in the properties of contact surfaces after electroerosion cutting with the use of different cutting wires were discovered when studying them by means of scanning electron microscopy. SEM-images of contact surfaces after cutting of *p*-type legs are shown in Fig. 2 (the upper row of images is a side view of contact surface, the rest of images is top view). It is evident that surface morphology essentially depends on the type of cutting wire employed. Thus, with the use of a brass wire the surface which is formed is the smoothest (least developed) with a low roughness; the surface structure (the presence of particles, their clusters, pores) is feebly marked. With the use of molybdenum wires the surface roughness becomes greater, i.e. the degree of surface development is increased. Now on the surface there are clearly visible individual particles forming a damaged layer and assuring high surface roughness. The average size of particles is smaller and their distribution according to size is more uniform in case of using a molybdenum wire of smaller diameter (0.1 mm). It is exactly a molybdenum wire of diameter 0.1 mm used for cutting of legs that later on assures maximum adhesion strength of deposited interconnect layers (Table 1). Note that the specificity of flame spraying of interconnect layers lies in the fact that particles of deposited powder change into flowed drops, are entrained with ionized gas flux and, getting on the substrate, spread, solidify and form a coating [6]. In this case maximum adhesion will be achieved if the surface subject to deposition has a developed roughness comparable to the size of deposited particles. It is obvious that contact surface with the most optimal properties for flame spraying is formed on cutting of thermoelectric material with a molybdenum wire of diameter 0.1 mm.

Besides, it was established that apart from the differences in morphology, the elemental composition of a damaged layer also varies in the course of electroerosion cutting and depends on the type of cutting wire (Table 2). In the same table, the elemental composition in the bulk of thermoelectric material is represented for comparison.

Table 2

Elemental composition of thermoelectric material contact surfaces after electroerosion cutting

Element, weight %	Cutting wire material			Material bulk composition
	Brass wire of diameter 0.25 mm (Sodick AQ 300 L machine)	Molybdenum wire of diameter 0.3 mm (P&G Industrial DK7732 machine)	Molybdenum wire of diameter 0.1 mm (LF96F3 machine)	
Sb	25.79	28.17	27.89	27.14
Te	53.28	53.05	52.97	50.65
Bi	15.40	16.32	17.24	19.97
Se	1.60	1.61	1.62	2.23
Cu	2.14	-	-	-
Zn	1.38	-	-	-
Fe	0.41	0.85	0.27	-

From the data in Table 2 it can be concluded that using a brass wire causes contamination of legs surface with copper (~ 2 weight %) and zinc (~1 weight %). It is logical to suppose that the lowest adhesion strength (Table 1) of interconnect layers on the contact surface formed after cutting with a brass wire can be due to these contaminations. The legs produced on machines with the use of a molybdenum wire lack these contaminations. It should be also noted that in all the samples the elemental composition of a damaged layer includes iron (~ 0.5 weight %). This can be due to using steel toolset for fastening semiconductor rods in cutting machines, as well as to insufficient purification of water used for cutting.

Conclusions

Thus, it was established that the adhesion strength of "thermoelectric material (based on bismuth telluride) – interconnect coating (sub-interconnect molybdenum layer and aluminium conductor layer)" system depends on the condition of thermoelectric material contact surface (surface morphology, the presence of contaminations) formed in the course of electroerosion cutting. The properties of contact surface depend on the type of cutting wire (brass wire of diameter 0.25 mm, molybdenum wire of diameter 0.3 mm and molybdenum wire of diameter 0.1 mm).

The best adhesion properties are achieved with the use of a molybdenum wire of diameter 0.1 mm. It is due to the fact that with the use of this wire a contact surface is formed with a damaged layer of minimum thickness, with maximum roughness, the elemental composition of the surface is closest to that in the bulk of thermoelectric material.

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