Fabrication of Thermoelectric Bi_2Te_3 Microwires by softening glass drag spinning method and its Characterization

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1. Introduction

Works on obtaining of microwires by the Ulitovsky method with the core of thermoelectric materials such as Bi_2Te_3 have not led to success. This is due to the fact that it is hard to overcome difficulties connected with instability of temperature in the process of the microwire casting and superheating of the thermoelectric material, volatile components and impurities evaporate and as a result the obtained microwire has low thermoelectric characteristics and high inhomogeneity lengthwise.

In order to decrease the influence of these factors on thermoelectric microwire quality another variant of glass-coated melt spinning (GCMS) has been developed. Some aspects of thermoelectric microwire (bismuth telluride and solid solutions based on it) GCMS technology and several results of obtained microwires are presented in this paper.

2. SGDSM Fabrication of microwires of bismuth telluride

For microwire fabrication on the basis of semiconductor materials with many components and volatile impurities at high temperatures another variant of Taylor–Ulitovsky GCMS method with thermal furnace heating has been developed. The main element of a new GCMS method was to use as a heater in the Taylor–Ulitovsky installation a furnace with resistive heating and stable temperature regime, which is ensured by a temperature regulator of the type VRT-3 with approximation of ±0,5°C.

Before the microwire casting the volatile materials were crushed in the small pieces of polycrystal material obtained by the above described method with the mass of about 0,3÷0,5 g and they were introduced into an ampule of glass of the molybdenum type provisory cleaned. After vacuuming up to $P=10^{-4}\div10^{-5}$ torr, the ampule is soldered and welded to a little glass stick which is used as a holder and is introduced into the mechanism of the installation shift, which coiled it on a winding drum.

After the furnace heating up to the temperature of the glass ampule softening by slow *fall*, the ampule is introduced into the heated furnace zone. As a result of the glass ampule softening the material introduced into the ampule melts too and as a result by the capillary stretching a microwire in glass isolation is formed.

3. Structural and mechanical microwire properties

The X-ray studies have shown that the microwire is monophase lengthwise. The structural investigations have demonstrated that the microwire core is in general polycrystal consisting of big disoriented single crystal blocks. There are big enough pieces of single crystal wire.

As the investigations have shown, crystals in the form of microwire of Bi_2Te_3 are characterized by the same slipping elements as those in bulk crystals. On the obtained surfaces *traces* of diamond prism were put.

The form of traces confirms the fact that wires of Bi_2Te_3 consist in principle of blocks being disoriented enough between them. At a constant orientation of the puncheon the form of put traces in different points of the surface is different. Hence, disorientation of the blocks where the puncheon traces is rather big, that means that samples are polycrystal. The polycrystal construction of crystals in the form of microwires of bismuth telluride with bigger diameters is explained by the fact that in both perpendicular and longitudinal splines the traces in parts of approximation are formless.

Investigations carried out in wires with rather small diameter (~5 µm) have shown that in these samples tendency to twinning decreases with the sample diameter decreasing, and simultaneously the microwire homogeneity structure grows.

Experiments on measurement of breaking durability were performed on the installation for testing material strength. In this case the sample for testing represents a roller of 10 microwires of similar diameter and length of 20 mm. All the measurements were carried out on several samples with the same diameters.

The calculation of breaking tension was carried out by the formula $\sigma_P = P/N \bullet S$, where P is the maximal mean load to which the sample resists, N is the number of wire in the sample, S is the total surface of the transverse cross-section together with glass isolation.

Determination of microhardness of the wires was performed by tracing microhardnessmeter PMT-3 traces to transverse and longitudinal cross-sections of the wires. As a puncheon a standard Vickers diamond pyramid was used. Calculation of microhardness was carried out by the usual formula.

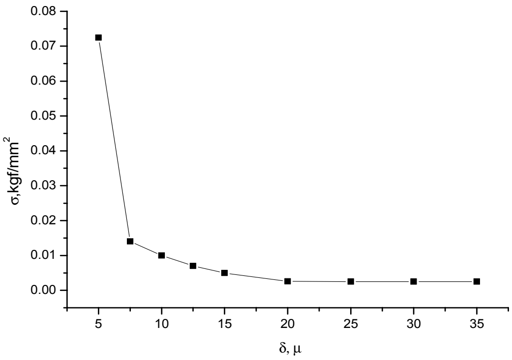

Fig. 2. The dependence of the wire tension on the diameter.

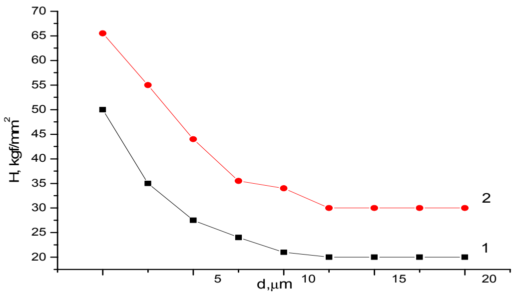

Fig. 3. The dependence of the microhardness on the microwire diameter.

The results of tension measurements in the diameter range 5÷35 μm are shown in Fig.2. As it is seen from the figure, when the wire diameter decreases σ_P grows, at the same time it becomes more obvious at the diameters less than 15 μm. Beginning with diameters >20 μm the dependence becomes weaker and the curve transverses almost parallel to the abscissa axis. It should be specified that in the region of small diameters a certain scattering of experimental points is observed. This is due to structural noncompleteness of the wires. However, the dependence behavior is shown rather convincing, and at passing from the diameters d=35 μm to d=5 μm the tension changes correspondingly from 0,002 kgf/mm^2 to 0,07 kgf/mm^2.

The influence of the size effect is also shown while measuring microhardness (Fig.3). Indeed, when the diameter decreases from 20 μm to 6 μm the wire microhardness grows from 39 kgf/mm^2 to 60 kgf/mm^2. Microhardness of the wires with bigger diameter (25÷30) μm has the value of hardness of bulk samples. Comparing the curves of behavior of microhardness and microdurability one can see that growth of the size effect of breaking durability is connected with properties of microwires as a whole and glass isolation and core of the microwire. When the core diameter decreases its role in determination of mechanical properties decreases, and the isolation role increases. However, it should be mentioned here the inverse tendency in the wire core structure – with the diameter decreasing the degree of systematization in its structure and as a result in effects of durability increases. This is demonstrated by the debyegram showing that when the diameter decreases there takes place transition from the polycrystal state into the monocrystal one. The breaking durability is estimated by the value of load P during the microwire breaking, or by the relative values – the breaking tension $\sigma = P/S$, where S is the perpendicular sector of the microwirws.

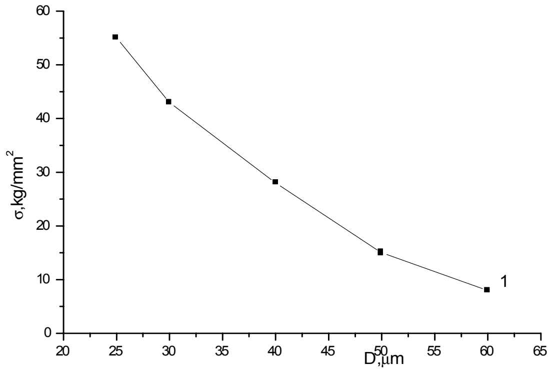

Fig.4. The dependence of the microwire durability on the cover diameter for nontreated samples (1) and the ones treated by annealing (2).

It was determined that in durability characteristics the basic role belongs to the glass cover because the microwire core of bismuth telluride is very fragile and practically does not make contribution to the microwire breaking durability. This is confirmed by the measurement of the breaking durability in bare capillary and microwire possessing the same characteristics of the breaking durability. For the diameters 15÷30 µm the breaking durability changes in the limits of 70÷9 kg/mm^2 correspondingly. Hence, when the microwire diameter decreases the value of breaking durability increases (Fig.4). The dependence is well approximated with the following empirical formula $\sigma /s = 4A/(\pi D^2)$, where A=32500 kgµm^2/mm^2, D is the isolation diameter in µm.

4. Electrophysical and thermoelectric microwire properties

As a result of studying of the electrophysical and thermoelectric microwire properties, the dependence of the parameter value on the microwire growth conditions it was found that the thermopower for the samples with hole (p) or electron (n) conductivity at the temperature T=300 K is correspondingly the following: α_p=+150÷+300 µV/K; α_n=-100÷-140 µV/K; while the resistivity has the values $\rho_p=(1\div7)\bullet10^{-3}$ Ohm•cm; $\rho_n=(1\div3)\bullet10^{-3}$ Ohm•cm.

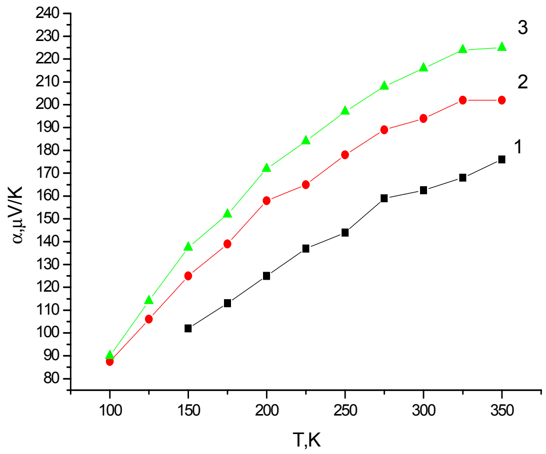

Fig.5. The temperature dependence of the thermopower of the samples of type p: 1 – before annealing, 2 - after annealing at the temperature 473 K, 3 - at the temperature 520 K. Time of annealing is 24 hours.

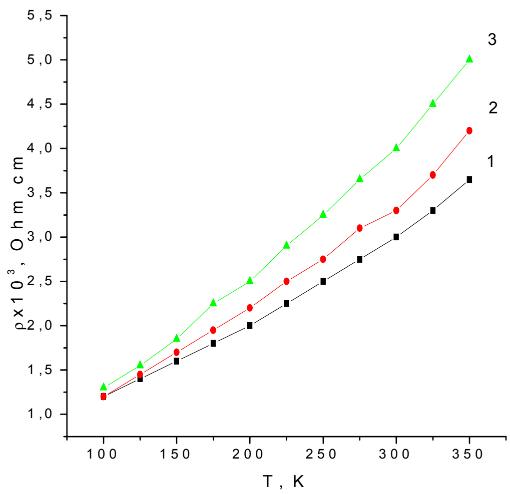

Fig.6. The temperature dependence of the resistivity of the sample of type p. Assignations as in Fig.5.

For improvement of the microwire characteristic ther performed work on treatment of microwires at different temperatures and time interval. The results of investigation of the treated samples are given in Fig.5-8

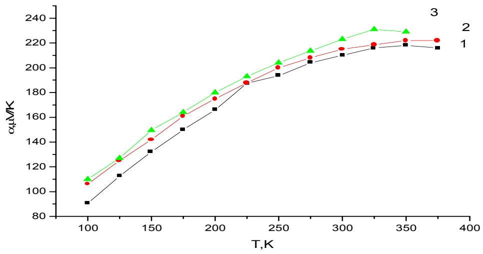

Fig.7. The temperature dependence of the thermopower of the samples of type p treated at the temperature 450 K in the time interval: 1 - 48 hours, 2 - 96 hours, 3 - 72 hours.

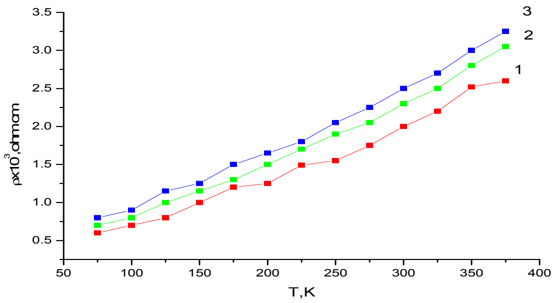

Fig. 8. The temperature dependence of the resistivity of the samples of type p treated at the temperature 450 K in the time interval: 1 - 1 hour, 2 - 72 hours, 3

5.Conclusions

In order to fabricate microwire on the basis of semiconductor materials with many components and volatile impurities at high temperatures by glass-coated melt spinning technology the Taylor–Ulitovsky method was developed. The main aspect of the developed technology is to use as a heater in the Taylor–Ulitovsky installation a furnace with resistive heating and stable temperature regime.

The elaborated technology has been used for preparation of glass coated microwires of semiconductor thermoelectric materials based on bismuth antimony telluride. The X-ray studies have shown that the microwire is monophase lengthwise. The structural investigations have demonstrated that the microwire core is composed in principle of a set of systematized unidirectional single crystals. Investigations carried out on the microwires with relatively small diameters (~5 μm) have shown that tendency to twinning decreases with the diameter decreasing and at the same time the microwire homogeneity structure grows.

It was determined that in durability characteristics the basic role belongs to the glass cover because the microwire core of bismuth telluride is very fragile and practically does not make contribution to the microwire breaking durability. It was established that when the microwire diameter decreases the breaking tension increases. The influence of the size effect is shown to appear in the tension and microhardness dependences on the microwire core diameter. Comparing the curves of behavior of microhardness and microdurability it was established that increasing role of the size effect of breaking durability is connected with properties of microwires as a whole - glass isolation and core of the microwire. When the core diameter decreases from 20 μm to 6 μm the wire microhardness grows from 39 kgf/mm^2 to 60 kgf/mm^2.

The Bi_2Te_3 microwires which have been used in the design of different thermoelectric microdevices are characterized by the following optimal electrophysical and thermoelectric parameters at the temperature of 300 K: α_p=+(180÷200) μV/K; ρ_p=(4÷6)•10^{-3} Ohm•cm; α_n=-(130÷140) μV/K; ρ_n=(1÷3)•10^{-3} Ohm•cm.

For improvement of the microwire characteristics there were performed works. A thermal treatment of the microwires at different temperatures and time intervals was performed for improvement of the microwire characteristics. Isothermal annealing of the microwires increases both the thermopower and the resistivity in the samples of type p, and the larger the temperature and annealing time the higher obtained physical parameters. In contrast to the samples of type p, in the samples of type n the thermopower after annealing grows and the resistivity decreases. The study of characteristic evolution in time show that the ones of treated microwires are more stable. Therefore it is recommended that before being used in different transducers thermoelectric Bi_2Te_3 microwires must be treated at necessary temperatures.

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