GLASS-COATED MELT SPINNING FABRICATION TECHNOLOGY AND SOME PHYSICAL PROPERTIES OF Bi_2Te_3 MICROWIRES

D.F.Meglei , V.G.Kantser and M.Dantu
LISES Institute of Applied Physics, Academy of Sciences of Moldova
Academiei str. 5, MD2028, Chisinau, Moldova

Both the results of fabrication technology development of thermoelectric Bi_2Te_3 microwires and some aspects of its physical characterization are presented. A variant of Taylor–Ulitovsky method with thermal furnace heating was developed for obtaining of microwires in glass isolation on the basis of semiconductor materials with many components and volatile impurities at high temperatures like Bi_2Te_3.The technology rout of Bi_2Te_3 microwire fabrication as well as of Bi_2Te_3 alloys by Taylor–Ulitovsky glass-coated melt spinning method with thermal heating is described. The correlation between the diameter of the core and of the glass isolation has been established in dependence on the technological fabrication conditions. The mechanical properties (flexion and breaking durability, microhardness, torsion) of Bi_2Te_3 microwires have been investigated in dependence on fabrication conditions and wire diameters. The microwire mechanical characteristics is shown to increase considerably with the core diameter reducing and in the increasing of the ratio of isolation diameter to core diameter. When the core diameter decreases its role in determination of mechanical properties decreases, and the isolation role increases and microwires represent a whole coaxial composite system of glass isolation and semiconductor core. Due to increasing of microwire elasticity the tensosensitivity is shown to attain high values. As a result of studying of the electrophysical and thermoelectric microwire properties the dependences of the resistivity and Seebeck parameters on the microwire growth conditions (thermal treatment, annealing temperature etc.) have been obtained. It was shown that isothermal annealing of the samples increases both the thermopower and resistivity in the samples of hole type conductivity, 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.

1. INTRODUCTION

Physics and technology of micro- and nanostructure are a broad area of worldwide research and development activity. In particular, the investigations of thin wire structures were significantly extended and at present the physics of quasi-one dimensional quantum structures became one of the dominant directions of low dimensional physics. The development in low-dimensional fabrication techniques has recently reopened the field of thermoelectricity. Nanowire arrays based on Bi are the most promising systems for reengineering the transport properties through the quantum confinement effect of the anisotropic carriers and size induced semimetal-semiconductor phase transitions, which are expected to result in good parameters for thermoelectric applications [1]. On the basis of theoretical investigation the thermoelectric figure of merit $Z_{LD}T$ of Bi nanowires is expected to increase significantly [1,2]. However the measurements of thermoelectric properties (such as the Seebeck coefficient and the thermal conductivity) as well as a quantitative explanation of these measurements (and even of existing results on electrophysical investigations) are more challenging. Only recently, the first results of the Seebeck coefficient measurements in submicron glass-coated and template Bi-wires have been obtained [3,4]. The thermoelectric power was found to be positive for glass coated wires with diameters less than 800 nm and it increases with the decreasing of wire diameters. Therefore, the possibility of reengineering of the thermoelectric properties of Bi, PbTe and Bi_2Te_3 (the best bulk thermoelectric materials) microwires is one of more promising. Although the wires with diameters more than 1 μ are far from the characteristic dimensions of quantum size effects they present a considerable interest. In particular glass coated-type single crystals microwires are of significant importance due to the following reasons: (1) the one-dimensional shape of microwire should be favorable for some synthetic textures, and (2) microwires may be convenient for some tiny-dimensional applications such as natural “thermoelectric wires” taking advantage of their

characteristic shape. Moreover, microwire are known to be high quality single crystals with low defect densities.

The study of these microwire systems offer the solution for a set of problems concerning their accurate miniaturization and stabilization of parameters, broadening of the functional range depending on action of climate and mechanical conditions. Small diameter of the microwire (up to 1 μm) ensures essential decrease of its mass and dimensions, and therefore decrease of the thermal and electric inertia. Continuous glass isolation of the microwire protects the material from interaction with the surroundings, due to this stability, solidity and other parameters of sensors prepared on the basis of the microwires increase.

A method of obtaining of a microwire in glass isolation was proposed in 1948 by professor A.V.Ulitovsky [5]. The essence of this method consists in the following [6]: the material sample is introduced into a glass ampule and then is introduced into a high-frequency inductor, as a result the material sample melts and is suspended under action of the electromagnetic field force. Regulating the temperature of the sample, the velocity of the capillary stretching out of the sample and the velocity of the ampule fall it is possible to obtain a rather long piece of the microwire of different sizes.

In connection with rapid development of production of microwires with glass isolation of different metals and metal alloys and their use on large scale in microelectronics there appeared a necessity to work out a technology of obtaining of microwires on the basis of new materials and especially on the basis of semimetals and semiconductors, which are characterized by stronger functional dependences of physical parameters on external actions than metals.

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. SYNTHESIS OF BULK THERMOELECTRIC MATERIALS

Since the standard bulk thermoelectric materials of Bi_2Te_3 and their solid solutions prepared for thermoelectric coolers or generators cannot be used as an initial material for GCMS due to the reasons mentioned above, let us dwell briefly on synthesis of the initial thermoelectric material for microwire fabrication by GCMS. As thermoelectric materials in the temperature range T=250-300 K semiconducting alloys of the compounds Bi_2Te_3, Bi_2Se_3, Sb_2Te_3, Sb_2Se_3 are used [7-9]. As materials of conductivity n alloys $Bi_2Te_{3-x}Se_x$ (x=0,1÷0,6) are used. Most frequently the alloy $Bi_2Te_{2.7}Se_{0.3}$ is utilized. As thermoelectric materials of conductivity p the alloy $(Bi_2Te_3)_{25}(Sb_2Te_3)_{75}$ is used. The authors of work [8] recommend more complex alloys $(Bi_2Te_3)_{90}(Sb_2Te_3)_5(Sb_2Se_3)_5$ as a thermoelectric material of conductivity n and $(Bi_2Te_3)_{25}(Sb_2Te_3)_{72}(Sb_2Se_3)_3$ as a material of conductivity p.

Use of the alloys as thermoelectric materials is conditioned by the necessity of maximal reduction of thermal conductivity of the crystal lattice x_r, having values $(8\div12)\bullet10^{-3}$ W/cm•K. The thermal conductivity of the crystal lattice is influenced by the type of doping impurities, which in dependence on the technological conditions and physical-chemical peculiarities in principle may be substitutive, interstitial and even antistructural as well as of the size of crystalline granules.

It should be noted that secondary components and dopants of thermoelectric materials often precipitate in the basic crystalline intruder form between surfaces of breaking plane (111), in places of intersection of the surfaces of binary and bisector planes. By virtue of the mentioned reasons these materials may be considered to be structurally sensible.

As initial components materials with a high degree of purity are used: Bi-000, Sb-000, Te-000, Se-000. Dopants are taken of the purity not less than that of the basic components. Usually as

dopants there are used halogens of the mentioned elements - SeJ_3, $SbBr_3$, $BiCl_3$, BiJ_3, InTe, $TeBr_3$. Dopants being not hydrophilicare preferable, since it is more convenient to work during weighing grave errors may be excluded.

Such components as Bi, Te, Sb, Se (if they were not purified by the method of zone melting) are filtrated for clearing of oxides and gases. Filtration is performed at the temperature being higher by 20-50 degrees than the melting temperature of the component under conditions of continuous evacuation. Filtration may be performed by capillaries with diameter 0,5÷1,5 mm or by a layer of filler, beads of quartz or glass "Pirex". The thickness of the layer is selected in dependence on the diameter of glass beads. It should be emphasized that filtration by capillary despite small productivity is preferable because in filtration by beans a danger of contamination is not excluded. Filtrated components usually are kept in evacuated ampules and are used when it is necessary.

Alloys of the thermoelectric materials in the liquid state are relatively volatile. So for keeping of ratio between the basic compounds and conservation of dopants after air evacuation from ampules a pressure of 0.6÷0.8 atm. of dry argon or nitrogen is created.

Let us note that even taking into account the mentioned measures of precaution, loss of materials (including dopants) after growth reaches 0,15% mass from the weight of synthesized mass of the materials of conductivity n and up to 0,25% mass of the materials of conductivity p.

In order to avoid breaking of ampules in the growth process due to thermal broadening or interaction of materials with walls of the ampules they are covered with a layer of carbon by the method of thermal gaseous pyrolysis of vapours of acetone or methane at the temperature 800÷1000°C during 20-40 min. As a gas carrier dry argon or nitrogen is used. Apparatus and technology of carbonizing for these purposes are described in [10].

Synthesis is performed at the temperature of 700÷720°C in cylindrical furnace supplied with a crank gear, which balances at an angle of 30° relatively the horizontal plane. Mixing lasts about 3 hours. After this the ampule rapidly cools in a bath with water or a solution saturated with sodium chloride.

Synthesized (optimized) alloys of conductivity p have the Seebeck coefficient α_p=+(260±10) μV /K, and the electric conductivity σ_p=(500±100) Sm/cm. Those of conductivity n are α_n=-(130±10) μV/K and σ_n=(1300:100) Sm/cm.

For the synthesis there was used a method of simultaneous melting of elementary components, and it is possible to use the method of simultaneous melting of compounds Bi_2Te_3, Sb_2Te_3, Bi_2Se_3, Sb_2Se_3. This method is better when it is necessary to purify additionally materials - filtration, purification by the zone melting method, etc.

While preparation of ampules, if the growth is performed vertically, it is necessary to use calibrated quartz tubes. If they are not available, quartz of double melting is used, then the ampule bottom is made in narrower part of the quartz tube in order to avoid the effect of float between the ingot and walls of the ampule when the melting zone is in the lower part.

Transition of the synthesized materials from the state with the parameters σ_n=1300 Sm/cm, α_n=130 μV /K, σ_p=500 sm/cm, σ_p=+260 μV /K into the state when $\sigma_{n,p}$=1000 Sm/cm, α=±200 μV /K is performed by the method of recrystallization.

Recrystallization may be performed by different methods (Czochralki, zone melting, Bridgman). Let us choose the vertical method of zone melting.

The installation used for this purpose has the following components:

1. system of movement with different velocity of a carriage with an electric furnace;
2. system of rotation of ampules around longitudinal axis. The system permits to impart angular acceleration to the ampule after certain pauses of stay or uniform angular movement. This is essential both in the processes of homogenization of the components or purification and in the processes of growth;
3. system of the temperature stabilization on the basis of electronic complex of the temperature stabilization with high precision VRT-3 ;
4. system of control, which permits the apparatus to function in the following regimes:
   a) zone purification of basic elements or compounds;

b) homogenization of distribution of dopants or components;

c) growth of crystals with automatic switching off the installation when the technological process is over.

All these processes may be performed with different velocities of movement of the electric furnace, different intervals and frequencies of putting in motion or angular acceleration of the ampule. Possible qualities of this system are not overestimated and at present it is clear that it gives us a possibility to maximally exclude porosity of the ingot both in bulk and on the surface.

Velocity of growth of thermoelectric materials varies according to the data of different researchers from 0,1 up to 100 mm/hour. The economic factor gives use of the velocities of 10-100 mm/hour and sometimes higher.

The temperature gradient on the boundary solid-liquid used while growth is also high. This interval is between 10 K/cm and 200 K/cm.

Peculiarities of the technology of thermoelectric materials proceed from set purposes:

1) Total compensation and creation of negative charge carriers (in material of conductivity n) or partial compensation (in materials with conductivity p) of concentration of holes;
2) Optimization of the basic charge carrier concentration in the range $5\bullet10^{18}\div2\bullet10^{19}$ cm^{-3};
3) Possible minimization of thermal conductivity of the lattice, excluding of the bipolar thermal conductivity;
4) Dependence of the coefficient of segregation of components in the solid phase of:
   a) growth velocity;
   b) temperature gradient;
   c) mutual influence of basic components and dopants;

dependence of kinetic properties of macro- and microstructure (plates, twin crystals of penetration, pores, splits, dislocations of all the types).

Another difficult technical moment, very important in our opinion, is creation of a thermal system intended for keeping the temperature gradient constant on the boundary solid-liquid not depending on the velocity of the carriage movement and on the power of the electric furnace. This makes the majority of researchers to work in conditions when there takes place violation of similarity of the crystallization processes. Due to this many results not only coincide but sometimes contradict each other.

It follows from the mentioned above that the final results of the technology of thermoelectric materials are influenced by such peculiarities of the used installation as the geometry of the electric furnaces, degree of the thermal connection between them and ampules, etc. For example, in [9,11] it was stated that a maximal value of the thermoelectric efficiency is found in ingots with diameter 10÷15 mm. In other works they mention that the most effective are materials with the ingot diameter 6÷8 mm. The most probable explanation of the mentioned above is that the same topologies of the thermal field were not realized for different diameters of ingots.

More important is the problem concerning the quantity of supplementary tellurium in materials of conductivity p varying from 1,5 up to 9% mass in different works. Solution of this problem has given a possibility to obtain thermoelectric material intended for obtaining of microwires with necessary electro-thermo-physical parameters.

3. FABRICATION OF MICROWIRES OF BISMUTH TELLURIDE AND OF THEIR SOLID SOLUTIONS

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=$10^4 \div 10^5$ 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.

The obtained microwire is coiled by the winding drum mechanism into bobbins of different diameters. Changing the furnace temperature and the velocity of the ampule fall in the heated zone as well as the velocity of the microwire obtaining it is possible to obtain microwires with different diameters of core and glass isolation with necessary parameters [6].

The diameter of the core and isolation of the microwire is measured by the optical method with the help of microscopes PMT-3, BIOLAM, MII-11 with ocular micrometer with a screw MOV-1-15^x and with the help of set of immersion liquids.

The results of the measurements have shown that in dependence on the heated furnace temperature, velocity of the ampule fall into the heated zone and velocity of the microwire obtaining it is possible to change the diameter of the core d and glass isolation D. The smallest obtained diameter is d= 5 μm, and the biggest 100 μm. The isolation diameter changes within the limits D~(1,5÷3) d.

The investigations carried out on variation of the diameters of the core and isolation lengthwise microwire in the limits of one bobbin have shown that change of these values from the mean value makes up about ±20% length of 100 m (Fig.1, 2).

The carried out studies on microcracks lengthwise microwire have shown that in dependence on the velocity of the microwire obtaining, velocity of the core crystallization the quantity of cracks changes. The best results were obtained with a microcrack per 1 m. There are parts with number of cracks up to 16 per length of 1 meter (Fig.3).

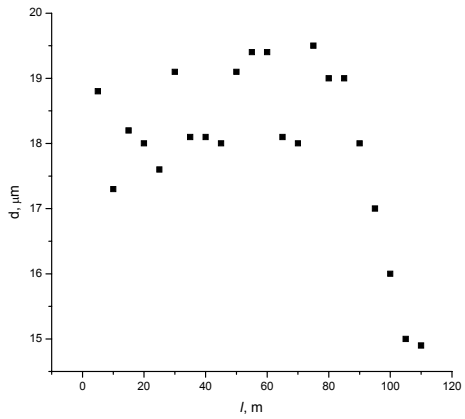

Fig. 1. Dispersion of the core diameter d lengthwise microwire in the limits of one bobbin

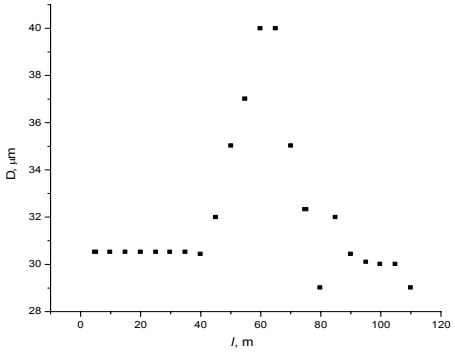

Fig. 2. Dispersion of the isolation diameter D lengthwise microwire in the limits of one bobbin.

For microwire use in sensors the dependence of ratio between the diameter of isolation D and of core d of the microwire is very important (Fig.6). In the range 15÷30 μm the linear dependence between the diameters of the core and isolation of the microwire is practically realized, and the ratio D/d is equal to two. Further decrease of the core diameter leads to considerable growth of coefficient K with the increasing of the microwire isolation thickness. The dependence of the ratio of the isolation diameter on the core diameter may be approximated with formula: K = D/d = 3/lgd,

where d is expressed in μm.

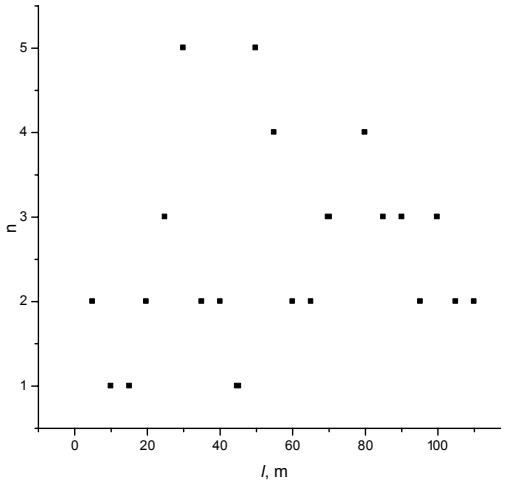

Fig. 3. Number of cracks of the core per 1 m of the microwire in the limits of one bobbin.

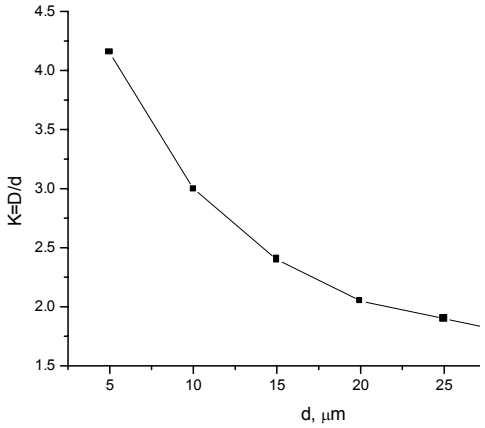

Fig. 6. The dependence of the ratio D/d on the microwire core diameter.

4. 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.

It is known that Bi_2Te_3 single crystals are intermetallic compounds with hexagonal elementary cell. Bulk crystals have a layered structure and are breaking in the planes (111). Plane (111) is also the slipping plane and plane (110) is the twinning plane of these crystals. 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. Due to this, deformation of crystals in the form of microwire and bulk ones is proved to be analogous. This was also found by studying the forms of traces and relief of surfaces around them on longitudinal and transverse cross-sections of different diameters.

The cross-sections were obtained by mechanical polishing of microwires in glass isolation. For obtaining of transverse cross-sections washers of epoxy resin were prepared, wherein the microwires were introduced. Then the surfaces of transverse cross-sections were mechanically polished. The mechanical polishing was carried out on a piece of organic glass using as an abrasive material the diamond paste and the chromium dioxide. For preparation of longitudinal cross-sections of microwires, a fascicle of microwires in glass isolation was glued horizontally with the help of high durability glue to a washer of brass. After this mechanical grinding was produced until approximately half of the microwire diameter was ground. 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.

In order to use microwires of Bi_2Te_3 in practice it was necessary to carry out a series of measurements for design of different sensors on their basis. In this way it was studied the wire breaking rigidity on uniaxial elongation and measurements of microhardness on the microwire core. It should be mentioned that the method of microhardness is a unique method which can give necessary information on hardness properties directly of crystal core. This is explained by the fact that this compound is very fragile and such means of investigation as determination of breaking hardness may be carried out only on wires being in glass isolation.

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.

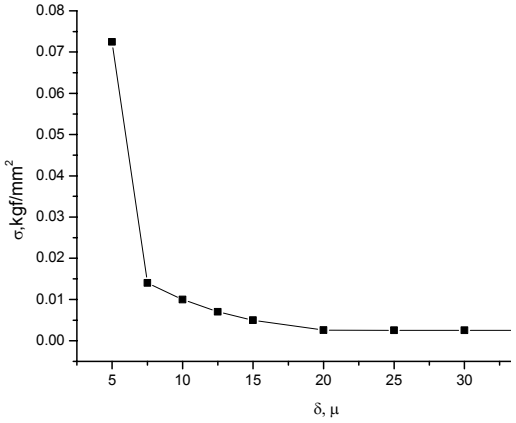

Fig. 4. The dependence of the wire tension on diameter.

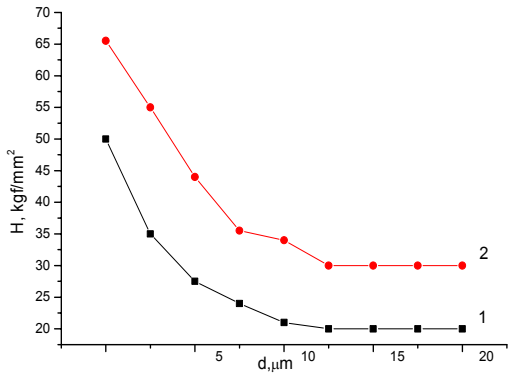

Fig. 5. The dependence of the microhardness on the microwire diameter.

The results of tension measurements in the diameter range 5÷35 μm are shown in Fig.4. 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/m^2 to 0,07 kgf/mm^2.

The influence of the size effect is also shown while measuring microhardness (Fig.5). 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. This process evidently is the result of the size effect.

Investigations of breaking durability of microwires were performed by the method described in [5]. 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 microwire.

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.

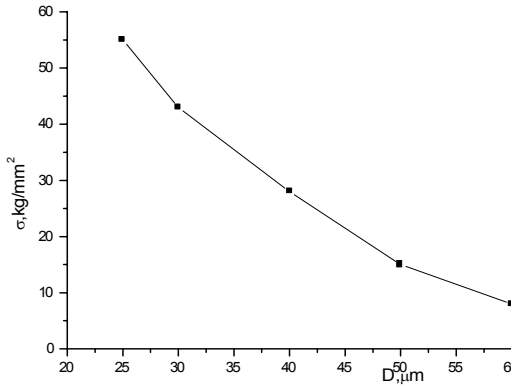

Fig. 7. The dependence of the microwire durability on the cover diameter for nontreated samples (1) and the ones treated by annealing (2).

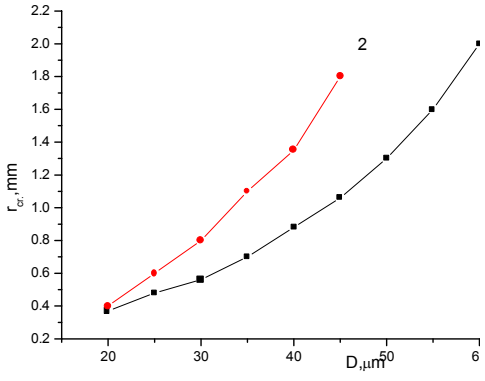

Fig. 8. The dependence of the critical radius of flexion on the cover diameter for nontreated samples (1) and the ones treated by annealing (2).

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.7). The dependence of σ on the microwire transverse cross-section is well approximated with the following empirical formula

$\sigma = A/s = 4A/(\pi D^2)$,

where A=32500 kgμm^2/mm^2, D is the isolation diameter in μm.

Isothermal annealing of microwires leads to some growth of σ in comparison with values of nontreated microwires only in the region of small D.

Flexion durability of the microwire as a unit of measurement of elasticity was determined by the critical radius (r_{cr}) of the microwire spiral where defection of its integrity begins. For diameters 15÷30 μm the value of critical radius of the microwire flexion changes in the limits of 0,4÷2,1 mm. When the diameter decreases the microwire flexion growth is observed.

The dependence of the critical radius of the flexion of the microwire on its diameter is shown in Fig.8. The analytical dependence of the flexion radius is approximated with the empirical formula $r_{cr} = BD^2$,
where $B=6,7\bullet10^2$ μm^{-1}, D is the microwire diameter in μm.

The investigations of microwires treated at different temperatures show elasticity decrease relative to the nontreated samples.

Used in devices, microwires with diameters of 15÷30 μm ration r_{cr}/l as a unit of measurement of elasticity changes in the limits from 28 to 7 in microwires with diameters of 15÷30 μm correspondingly, where l is the sample length.

Study of number of limit of the microwire torsion per a unit of length of the sample under test was accompanied by a stretch of $5\bullet10^{-3}$ N with the torsion velocity of the order of 24 revolution/minute. For the practice diameters 15÷30 μm the value of number of limit of torsion per a unit of length changes in the limits of (0,34÷0,1) rev/min, correspondingly.

Besides, temperature treatment of wires leads to increase of number of torsions per a unit of length in the range of small diameters (Fi.g.9).

5. ELECTROPHYSICAL AND THERMOELECTRIC MICROWIRE PROPERTIES

Measurement of electric and thermoelectric properties was carried out by the usual admitted method [12] on the samples with the length of 5-7 mm taken from different parts lengthwise microwire.

For characterization of quantitative change of the electric resistance of a conductor at its deformation it is used so called coefficient of tensosensitivity

$$S = \frac{\Delta R / r}{\Delta \ell / \ell},$$

where R and ℓ are the electric resistance and length of the samples, ΔR and $\Delta\ell$ are changes of the resistance and length under action of the force applied to the sample.

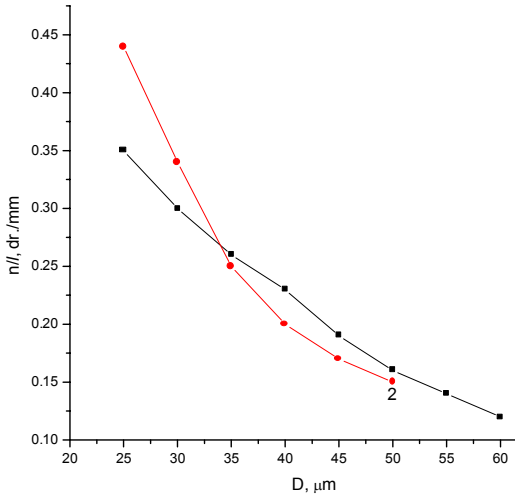

Fig.9. The dependence of number of limit of torsion per a unit of length of the microwire on the cover diameter for nontreated samples (1) and the ones treated by annealing (2).

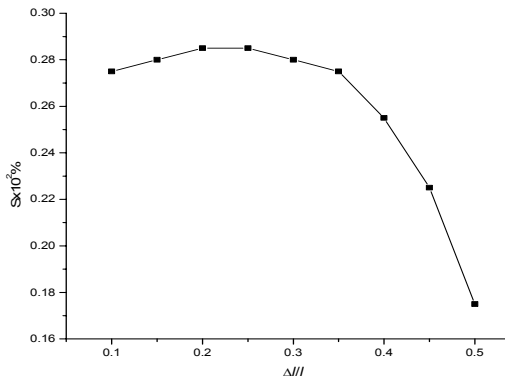

Fig.10. Change of tensosensitivity of the microwire core at its relative deformation.

The results of determination of tensosensitivity of microwires of Bi_2Te_3 have shown that in a number of cases at deformation a deviation in the elasticity behaviour takes place. As such this was observed on the big lengths of microwire samples (~100 mm). At further tension (stretch) of the microwire in these cases tensosensitivity has other values. Differential tensosensitivity in microwires depends on the relative stretch and changes in value in the limits from 9 to 28. In the region of elastic deformation the differential tensosensitivity is relatively stable (ℓ ~50 mm) and attains values of the order of 24-28.

This region may be extended up to the relative stretch of 0,4%, i.e. up to the microwire breaking. Fig.10 shows the dependence of the microwire core tensosensitivity on relative deformation. As it is seen from the figure, in the regions of small deformations tensosensitivity remains constant, and at higher deformations it begins to decrease.

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 Seebeck coefficient or 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 [11, 13].

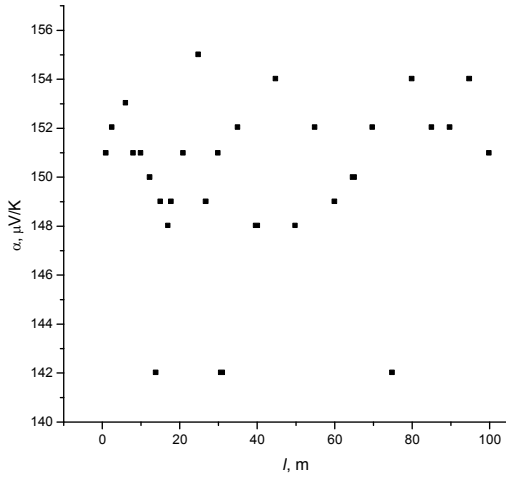

Fig.11. Dispersion of the Seebeck coefficient of the nontreated samples in the limits of one bobbin

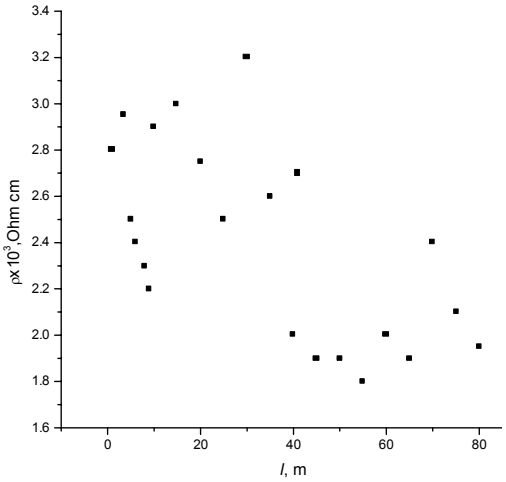

Fig.12. Dispersion of the resistivity of the nontreated samples in the limits of one bobbin.

Fig.11 and 12 show the dependences of the thermopower coefficient α and resistivity ρ of the samples obtained out of a set of microwires, i.e. lengthwise bobbin. As it is seen from the figures, the value of resistivity oscillates mainly from 10^{-3} up to $4\bullet\cdot10^{-3}$ Ohm•cm and dispersion of the Seebeck coefficient represents ±25% mean value. It should be noted that the microwires based on bismuth telluride which are widely used in construction of apparatus have the following parameters at the temperature of 300 K: α_p=+(180÷200) μV/K; $\rho_p=(4\div6)\bullet10^{-3}$ Ohm•cm; α_n=-(130÷140) μV/K; $\rho_n=(1\div3)\bullet10^{-3}$ Ohm•cm.

For improvement of the microwire characteristics there were performed works on treatment of microwires at different temperatures and time intervals. The results of investigation of the treated samples are given in Fig.13-16. It is seen from the figures that isothermal annealing of the samples increases both the thermopower and resistivity in the samples of type p, and the larger the temperature and annealing time the higher obtained physical parameters.

The results obtained for the microwires of type n before and after annealing are shown in Fig.17, 18. As it is seen from the figures, in contrast to the samples of type p, in the samples of type n the thermopower after annealing grows and the resistivity decreases.

Increase of the microwire annealing temperature leads to shift of the maximum in the curves of the temperature dependence of the thermopower into the region of lower temperatures, this most probably being due to the fact that the intrinsic conductivity begins to contribute to the thermopower at lower temperatures.

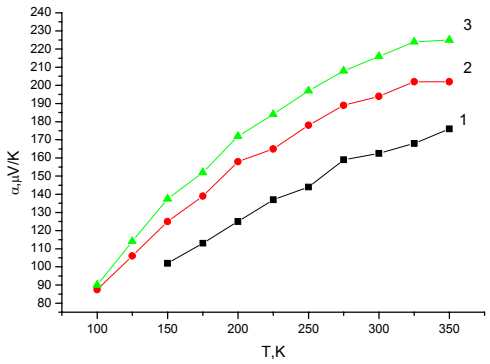

Fig.13. The temperature dependence of the thermopower of the samples of type p: 1 – before annealing, 2 - after annealing at the temperature 473 K, 3 - after annealing at the temperature 520 K. Time of annealing is 24

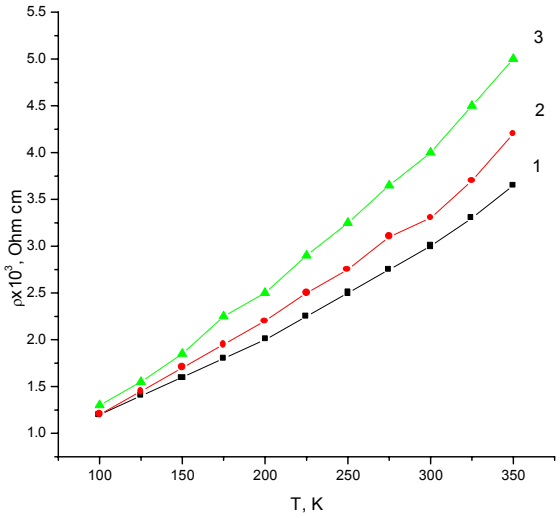

Fig.14. The temperature dependence of the resistivity of the samples of type p. Assignations as in Fig.13.

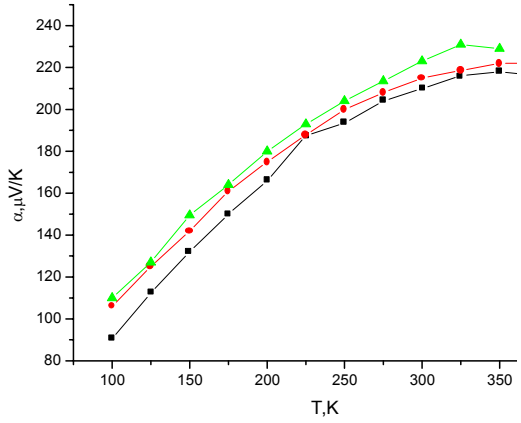

Fig.15. The temperature dependence of the thermopower of the samples of type p treated at the temperature 450 K in the time interval: 1 - 48 hours, 2 - 96 hours, 3 - 72 hours.

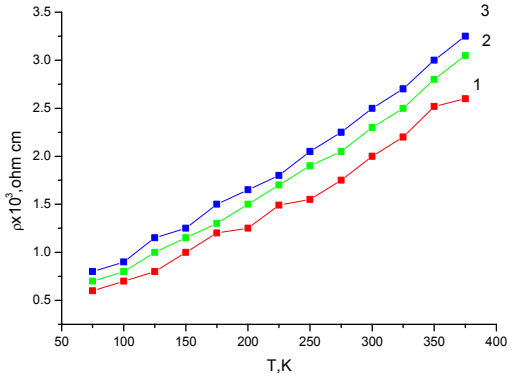

Fig. 16. The temperature dependence of the resistivity of the samples of type p treated at the temperature 450 K in the time interval: 1 - 1 hour, 2 - 72 hours, 3 - 96 hours.

For studying microwires for aging there were used microwires of conductivity of both types being nontreated and treated at different temperatures in different intervals of time. Before treatment preliminarily the thermopower and resistivity of the samples were measured. Afterwards the samples were treated at the temperature of 70°C for 60 hours, then they were kept at room temperature during a

month. After measurement of the parameters for the second time they were treated at the temperature of 100 °C for 40 hours and then kept at room temperature during two months.

The results of the measurements show that in nontreated microwires one can observe some increase of the parameters after annealing for aging and very small changes in the limits of the experimental error (~7%) in the samples thermally treated. Proceeding from this it is recommended that before being used in different transducers microwires must be treated at necessary temperatures.

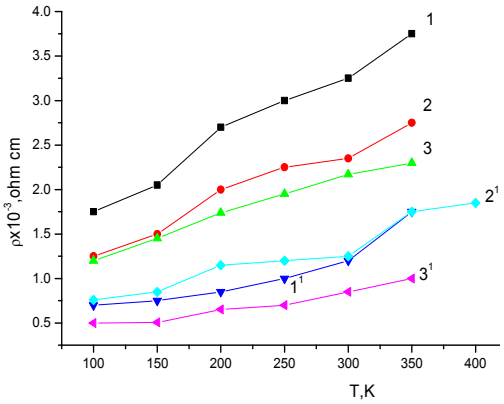

Fig. 17. The temperature dependence of the resistivity of the samples of type n for nontreated wires (1, 2 and 3) and treated ones (1', 2' and 3').

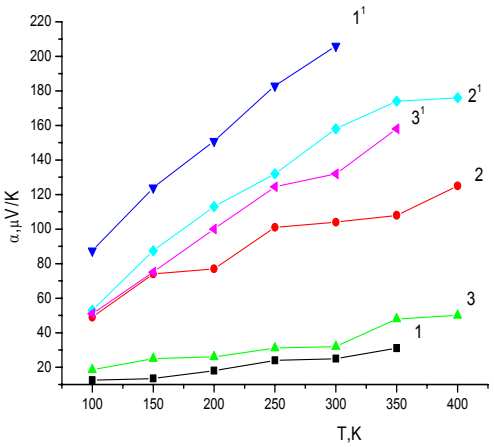

Fig.18. The temperature dependence of the thermopower of the samples of type n for nontreated wires (1, 2 and 3) and treated ones (1', 2' and 3').

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.

A new technological rout of bulk material synthesis as the initial material for microwire fabrication was elaborated to overcome the problems of Bi_2Te_3 semiconductor compound stoichiometry and optimal composition in the microwires.

The elaborated technology has been used for preparation of glass coated microwires of semiconductor thermoelectric materials based on bismuth antimony telluride. The optimal technological conditions of glass-coated melt spinning microwire fabrication on the basis of Bi_2Te_3 and its alloys were established.

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 measurements of tensosensitivity of microwires of Bi_2Te_3 show that in a number of cases under deformation a deviation in the elasticity behavior appears.

The dispersion of the thermopower coefficient α and resistivity ρ on the microwire lengthwise bobbin has been analysed. The value of resistivity oscillates mainly from 10^{-3} up to $4\bullet\cdot10^{-3}$ Ohm•cm and dispersion of the Seebeck coefficient represents ±25% coefficient α mean value. 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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