ISOTHERMAL ANNEALING INFLUENCE ON STRUCTURAL DEFECTS AND SOME CHARACTERISTICS OF BISMUTH TELLURIDE WIRE CRYSTALS

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Possibilities to control microdefect formation in bismuth telluride wire crystals by choice of optimal modes of isothermal annealing are discussed. It is found that a decrease of density of structural defects, such as microcracks, dislocations, and twins after isothermal annealing leads to improvement of both mechanical and electric parameters.

Optimal performance characteristics of high sensitive transducers require homogeneous in composition and structurally perfect materials. It is known that bismuth telluride and its solutions are semiconductor materials with the highest thermoelectric properties in the low temperature range [1]. This is the reason for comprehensive studying of their heat-physical and electric parameters. Investigation of bismuth telluride wire crystals in glass isolation is of a special interest for finding a possibility to design various miniature inertialess low-powered transducers of physical quantities into electric signals on their basis.

In the present work, on the basis of literature and experimental data [2, 3], results of investigation of isothermal annealing influence on structural defects and some mechanical characteristics of bismuth telluride wire crystals in glass isolation are given.

The bismuth telluride wire crystals in glass isolation were obtained by the liquid phase casting by modified Ulitovsky method [4].

The crystal structure perfection was studied by optic and scanning microscopy and by the method of selective etching. Efficient compositions of polishing solution and etching conditions on the basis of bromine and icy acetic acid were found. A layer of thickness 1-5 μm was removed for 10-30 sec. In order to prevent oxidation, the crystal polishing was carried out at constant mixing of the solution at room temperature. Dislocation density was determined by selective chemical etching in a saturated solution of iodine in ethyl alcohol, followed by washing in 10% aqueous solution of hydrochloric acid for prevention of an oxide film formation. The etching time was 1-2 min. The experiment on determination of breaking strength was carried out by the loading method on the installation of wire crystal breaking.

Microhardness on longitudinal and transverse ground ends of wire crystals was measured by virtue of device ПМТ-3. The indentor was a Vickers diamond pyramid, microhardness was calculated by the usual formula.

Earlier it has been found that wire crystals are mainly polycrystal, consisting of disoriented single crystal blocks. Number of blocks and disorientation degree decrease at the transition from thick wires to thin ones. Typical structural defects are microcracks, twins and growth dislocations, their density being of the order of $N=10^4\div10^7$ cm^{-2}. The sidewalls of the conducting core are sufficiently smooth, flat, they tightly adjoin the glass coating, the glass does not put any pressure upon the conducting core, and they do not chemically interact. It is known that Bi_2Te_3 single crystals are intermetallic compounds with hexagonal unit cell. Bulk crystals possess layered structure, and they easily spall by planes (111). Plane (111) is also a glide plane, while plane (110) is a twinning plane of the given crystals. As it was shown by the investigations, bismuth telluride wire crystals are characterized by the same elements of gliding and twinning. Therefore, peculiarities of plastic deformation of wire crystals and bulk samples appeared to be analogous. This was found while studying the form of indentations and relief of the surface around them on the transverse and longitudinal ground ends of wire crystals of different diameters. The indentor indentation on transverse and longitudinal ground ends of wire crystals is accompanied by spalling, brittle failure and intensive twinning.

There were experimentally determined optimal modes of annealing resulting in improvement of structural characteristics of wire crystals. It was found that after the annealing, large-block oriented single crystal pieces of wire crystals are formed, and sometimes large sections without blocks with the length up to (20-50) mm can be found. On longitudinal and transverse cuts of wire crystals a decreased number of microcracks and twins is observed. The density of growth dislocations decreases appreciably down to $N=10^3\div10^4$ cm^{-2}, and there are many low-dislocation sections $N<5\cdot10^2$ cm^2 and almost dislocation-free sections. After the isothermal annealing a more uniform distribution of the dislocation density on longitudinal and transverse sections of the samples is also observed. Besides, a decrease of the distortion degree and twin number around the indentations as well as microcrack healing were observed.

It was found that annealing leads not only to improvement and healing of structural defects, but also to a significant change of mechanical parameters of wire crystals (see the Table).

Table. Dependence of breaking strength (σ) and microhardness (H) of bismuth telluride wire crystals on sample diameter before (σ_1, H_1) and after (σ_2, H_2) isothermal annealing.

d, μm	D, μm	σ_1, kgf/mm^2	σ_2, kgf/mm^2	H_1, kgf/mm^2	H_2, kgf/mm^2
5,4	36,2	48,6	70,2	45,2	76,8
8,9	38,1	381,	58,6	43,4	71,9
10,3	35,2	36,2	48,2	40,3	70,6
12,6	37,4	32m,3	46,0	36,2	62,0
15,3	40,2	29,2	36,2	34,8	50,6
20,2	40,8	21,4	30,6	34,3	46,8
24,8	48,6	16,1	13,9	33,8	42,3
30,6	43,9	14,8	22,3	30,2	41,2
35,8	57,6	15,2	20,3	29,3	37,0
40,9	66,8	13,3	21,3	30,2	36,9
50,3	75,4	10,9	18,9	27,8	36,3

As it is seen from the Table, the breaking strength for unannealed wires with diameters (5÷50) μm changes within the limits of (48-10) kgf/mm^2, and for the annealed wires it increases and achieves (70-20) kgf/mm^2. When the wire diameter is less than 15 μm the strength increases especially sharply. The microhardness (1,3-1,5) times increases for thick wires, and almost twice for the wires with d<15 μm.

It should be noted that the given data are averaged by a large number of measurements due to the fact that the structure of bismuth telluride wire crystals changes depending on both dimensions and various uncontrollable parameters of casting. Hence, at the strength measurement the spread in certain values is 10-15%.

Investigations of the surface of breaking of wire crystals have shown that at small diameters the breaking takes place mainly by the cleavage plane (111) and the spalls have relatively smooth surface. Spalls of the samples of diameter d>15 μm are accompanied by formation of steps, microcracks, step-like structure and twins.

Measurements of bending strength as a measure of its elasticity, determined by the critical radius of the wire bending [5, 6] whereat violation of its integrity takes place, have shown a decrease of elasticity of the annealed wires with respect to the unannealed ones.

Conditions and solution for electrolytic deposition of contacts to wire crystals giving high uniformity of the coating were experimentally chosen. It should be noted that for improvement of mechanical and electric properties of the deposited contacts, the isothermal annealing was carried out for 20-30 min at the temperature 60°C. The thermal annealing improves adhesion of the deposited metal microcontact. This was verified by immersion of the sample into liquid nitrogen. The resistance of the unannealed samples began to increase appreciably after 4-5 immersions, whereas for the annealed samples - after 25-30 immersions.

In the present work a correlation between structural defects and mechanical parameters of bismuth telluride wire crystals as well as electrophysical parameters such as resistivity and thermopower is discussed.

It is found that decrease of density of structural defects after isothermal annealing is favourable for mechanical characteristics of bismuth telluride wire crystals and it gives a possibility to influence electrophysical parameters.

References

[1] B.M. Goltsman, B.A. Kudinov and I.A. Smirnov, Poluprovodnikovye termoelektricheskie materialy na osnove Bi_2Te_3, M. Nauka, 1972.

[2] V. Kantser, D. Meglei and M. Dantu, Electric Field Effect in Cylindrical Capacitor Configuration of Bi and Bi_2Te_3 Microwires, 12th National Conference "Trends in Physics", Romania, Targu Mures, 66, (2002).

[3] V.G. Kantser, D.F. Meglei and M.P. Dantu, Softening Glass Grad Spinning Method of Fabrication of Thermoelectric Bi_2Te_3 Microwires, The 4th National Conference "New Research. Trends in Material Science" ARM-4, Romania, Constanta, 169, (2005).

[4] F.Ia. Badinter, N.R. Berman et al., Litoi mikroprovod i ego svoistva., Chisinau, Stiinta, 1973.

[5] N.R. Berman, M.V. Givelberg and V.G. Ceban, Prochnostnye svoistva mikroprovoda pri izgibe, Izv. AN MSSR, 3, 1969.

[6] Iu.A. Kontsevoi, Iu.M. Litvinov and E.A. Fattakhov, Plastichnoti i prochnosti poluprovodnikovykh struktur, Moscow, "Radio i svyaz'", 1982.