

TEMPERATURE DEPENDENCES OF THE KINETIC COEFFICIENTS OF A BISMUTH TELLURIDE MICROWAVE PREPARED BY A NOVEL TECHNIQUE

D. Meglei*, A. Nikolaeva, L. Konopko, S. Alekseeva, and P. Bodiul

Gitsu Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Academiei str. 3/3, Chisinau, MD-2028 Republic of Moldova

**E-mail: meglei@nano.asm.md*

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Abstract

An improved technique for preparing glass-insulated microwires of highly volatile materials has been proposed, developed, and tested; owing to the isolation of the material from the environment, this technique provides the formation of a microwire with physical parameters corresponding to those of the starting material. The microwire preparation technique has been tested using a bismuth telluride (Bi_2Te_3) alloy. The thermopower and conductivity of the Bi_2Te_3 microwire have been measured in a temperature range of 10–300 K. The derived data for Bi_2Te_3 in the form of a microwire and a bulk crystal have been compared.

1. Introduction

There are several methods for the production of microwires. Thus, the method of drawing in an inert gas under a pressure of 2–10 atm is commonly used to obtain microwires of various metals and alloys. The drawing process consists in the pulling of the work material through a tapering hole. This method provides high performance and the possibility of obtaining a microwire with a length of a few meters and a diameter of 50–100 μm [1]. However, the preparation of a longer microwire is faced with the technical problem, namely, the necessity to coordinate the drawing speed and the quality of the microwire.

A more efficient technology for preparing a glass-insulated microwire was proposed by Taylor in 1924 [2, 3]. Later, this technology was improved by Prof. Ulitovsky [4]. At present, the Ulitovsky–Taylor method is commonly used for obtaining microwires.

However, a disadvantage of these known techniques for producing microwires of low-melting materials is the difficulty of maintaining the properties of the material along the entire wire length.

The aim of this study was to develop an advanced technique for preparing a glass-insulated microwire of low-melting materials providing the preservation of the initial parameters of the material and to test the proposed technique.

2. Experimental

The Ulitovsky method for preparing microwires is as follows: a few grams of a metal or an alloy is placed in a glass tube and introduced into the field of a high-frequency inductor. Under the action of an electromagnetic field, the metal is heated and undergoes melting; a droplet is formed from the melt. A portion of the glass tube adjacent to the molten metal is softened; a shell enveloping the droplet is formed from the glass. A glass fiber is drawn from softened glass;

it is wound on the coil of a receiving device. Certain glass fiber drawing modes provide conditions for the entrainment of the metal in the resulting glass capillary.

Figure 1 shows a setup for preparing a microwire by the Ulitovsky method.

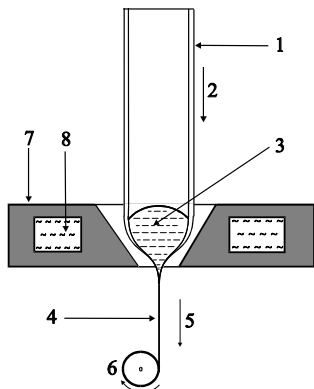


Fig. 1. Diagram of a setup for the production of a glass-insulated semiconductor microwire by the Ulitovsky method: (1) glass tube; (2) tube movement direction; (3) semiconductor material melt; (4) glass-insulated microwire; (5) microwire pulling direction; (6) coil; (7) high-frequency inductor; and (8) water for cooling the inductor.

Certain glass fiber drawing modes provide conditions for flowing of the material into the resulting glass capillary. Thus, a microwire composed of a core material and a continuous glass insulation is formed.

Despite the advantages of the Ulitovsky method for obtaining microwires, it has a disadvantage, namely, the material is heated in the air or an inert gas atmosphere, and the tube through which the microwire is pulled is not isolated from the environment. In this case, the possibility of evaporation of a portion of the material into the environment is not excluded.

If our aim is to prepare a microwire of a material containing volatile components, then this method does not provide the formation of a microwire with the physical parameters of the starting material.

We have improved the technique for preparing microwires of materials containing volatile components so as to provide the preservation of the initial properties of the material.

The key element of the novel method was the use of a resistive heating furnace as a heater. A stable temperature mode with an accuracy of $\pm 0.5^\circ\text{C}$ was provided by a controller. Volatile substances were ground into small pieces of a polycrystalline material with a weight of about 0.3–0.5 g. After that, the substance was placed into a molybdenum-type glass tube (Fig. 2). After evacuation to $P = 10^{-4}$ – 10^{-5} Torr, the tube was soldered and welded to a small glass rod, which was used as a holder for introducing into the setup (Fig. 3). After heating of the furnace to the glass tube softening temperature, the tube was slowly introduced into the heated zone of the furnace. The glass of the tube and the material placed into it underwent melting; the capillary was extended to form a micelle in a glass insulation. After that, the resulting microwire was wound onto a drum in coils of various diameters.

Variations in the furnace temperature, the velocity of motion of the tube in the heating zone, and the rate microwire drawing provide the formation of microwires with different sizes of the core and the glass insulation.

3. Results and Discussion

Measurement results showed that, by varying the temperature of the heated furnace, the rate of introduction of the tube into the heated zone, and the microwire winding speed, it is possible to control the values of core diameter d and glass insulation size D . The smallest and largest core diameter d was 5 and 100 μm , respectively. In a range of $d \sim 15\text{--}30 \mu\text{m}$, the relationship between the core diameter and the microwire insulation size was almost linear; the D/d ratio was 2. The dependence of the ratio between the insulation diameter and the core diameter can be approximated by the following formula: $D/d = 3/\lg(d)$. To improve the microwire characteristics, the resulting microwires were subjected to a heat treatment at various temperatures (450–520 K) and time intervals (24–72 h).

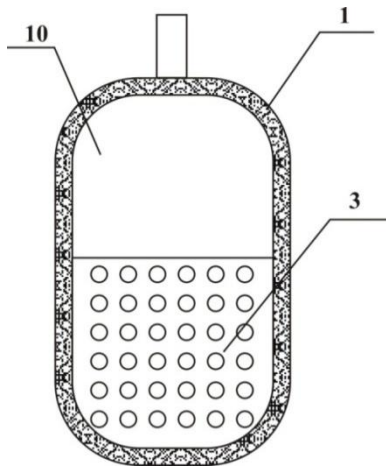


Fig. 2. Molybdenum-type glass tube: (1) tube; (3) material for microwire; and (10) vacuum.

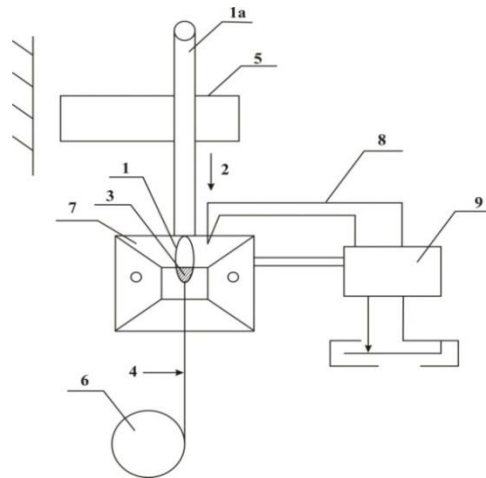


Fig. 3. Diagram of a setup for the production of microwires of low-melting materials: (1) tube; (1a) tube holder; (2) tube movement direction; (3) material for microwire; (4) resulting microwire; (5) tube holder; (6) coil; (7) resistive heating furnace; (8) thermocouple; and (9) VRT-3 heat stabilizer.

The studies show that the isothermal annealing of microwires leads to an increase in both the thermopower and resistivity of the p -type samples; the higher the temperature and treatment time, the more perfect the physical parameters of the microwire. Unlike the p -type samples, in the n -type samples, the thermopower increases and the resistivity decreases after annealing.

The protection of the material from oxidation during the preparation of microwires by this technique is provided by the complete isolation of the material from the environment. The crystallization of the microwire core is stimulated by cooling (cooling rate of $10^5\text{--}10^6 \text{ deg/s}$). Depending on the amount of the material in the tube, the microwire length can vary from 10 to 200 m [5–9].

The developed technique was tested using a bismuth telluride (Bi_2Te_3) alloy. In this case, the volatile component is tellurium (Te).

The Bi_2Te_3 semiconductor compound and solid solutions based on it are among the best low-temperature thermoelectric materials [10, 11].

A Bi_2Te_3 bismuth telluride alloy prepared in accordance with this chemical formula and atomic masses of Bi (208.98 amu) and Te (127.6 amu) [4] was used as a starting material for obtaining a Bi_2Te_3 microwire.

The thermopower and conductivity of the resulting Bi_2Te_3 microwires were measured. The derived parameters were compared with analogous data for bulk crystals. The results are shown in the table.

Conductivity and thermopower of the Bi_2Te_3 microwire (diameter of 10–20 μm) at 300 K in comparison with bulk Bi_2Te_3 crystals

Conductivity type	Conductivity σ , $\Omega^{-1}\text{cm}^{-1}$	Thermopower α , $\mu\text{V/K}$
Hole conductivity, p , microwire	140–1000	150–300
Hole conductivity, p , bulk crystal [12]	1000	200
Hole conductivity, p , bulk crystal [13]	1400	160
Electronic conductivity, n	300–1000	–(100–140)
Electronic conductivity, n , bulk crystal [13]	1655	170
Electronic conductivity, n , bulk crystal [14]		–(120–200)

The data in the table clearly show that the thermopower of the microwire is significantly higher than that of the bulk crystals, while the conductivity is lower.

In addition, in a temperature range of 10–300 K, the thermopower and conductivity of the Bi_2Te_3 microwire were measured (Figs. 4, 5).

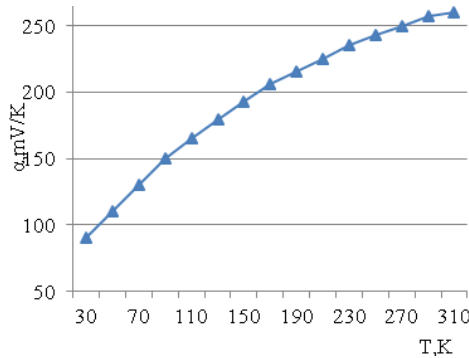


Fig. 4. Temperature dependence of the thermopower of the p -type Bi_2Te_3 microwire.

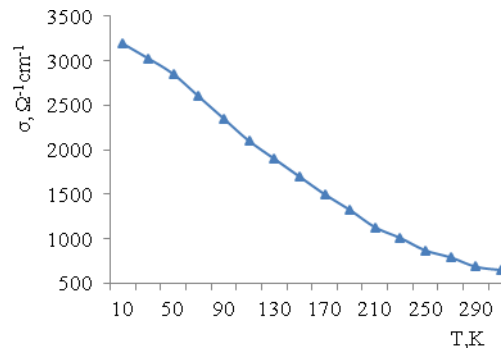


Fig. 5. Temperature dependence of the conductivity of the p -type Bi_2Te_3 microwire.

Figures 6 and 7 show the temperature dependences of the thermopower and conductivity of a bulk Bi_2Te_3 crystal according to the literature [15].

The results of measurements of the electric conductivity (σ) and thermopower (α) of the Bi_2Te_3 bulk sample and the Bi_2Te_3 microwire were used to calculate the power factor (P.f.) using the following formula: $\text{P.f.} = \alpha^2 \times \sigma$ (Figs. 8, 9).

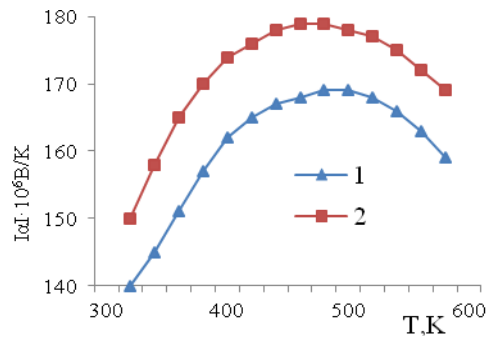


Fig. 6. Temperature dependence of thermopower α of Bi_2Te_3 of (1) n - and (2) p -type [15].

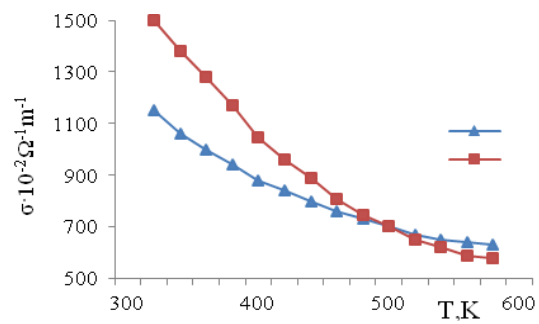


Fig. 7. Temperature dependence of conductivity σ of Bi_2Te_3 of (1) n - and (2) p -type [15].

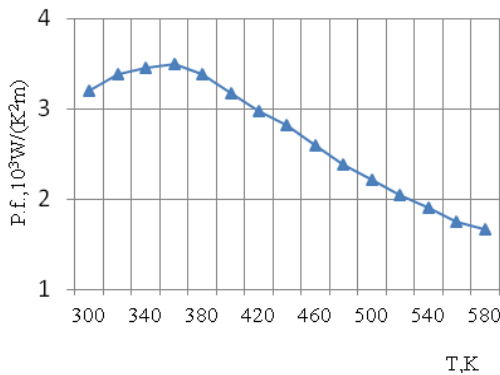


Fig. 8. Temperature dependence of the power factor of p -type Bi_2Te_3 calculated according to the data of [15].

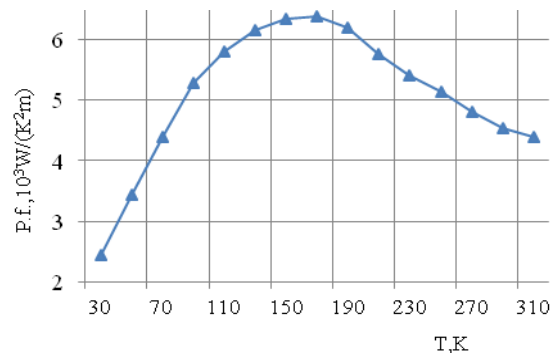


Fig. 9. Temperature dependence of the power factor of the p -type Bi_2Te_3 microwire.

It is evident from Figs. 8 and 9 that the maximum power factor of the microwire is 1.8 times higher than the power factor of the bulk Bi_2Te_3 crystal.

4. Conclusions

The improved technique for preparing a glass-insulated microwire of highly volatile materials provides the formation of a high-quality microwire.

The developed technique has been tested using a bismuth telluride (Bi_2Te_3) alloy. In this case, the volatile component is tellurium (Te).

According to the results of measurements of the electric conductivity (σ) and thermopower (α) of the Bi_2Te_3 bulk sample and the Bi_2Te_3 microwire, the power factor (P.f.) has been calculated as $\text{P.f.} = \alpha^2 \times \sigma$. The maximum power factor of the microwire is 1.8 times higher than the power factor of the bulk Bi_2Te_3 crystal.

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